Universidade do Minho
Escola de Engenharia

Elvira Joana Ferreira Peralta

Study of the Interaction Between Bitumen and Rubber

Junho de 2009

Universidade do Minho
Escola de Engenharia

Elvira Joana Ferreira Peralta

Study of the Interaction Between Bitumen and Rubber

Dissertação de Mestrado em Engenharia Civil
Área de Especialização Engenharia Rodoviária

Trabalho efectuado sob a orientação de
Professor Doutor Hugo Manuel Ribeiro Dias Silva
Professora Doutora Ana Vera Alves Machado Nóbrega

Junho de 2009

ACKNOWLEDGEMENTS

This research was conducted under the supervision of Doctor Hugo Silva, from the Highways Group of the Civil Engineering Department of the University of Minho, to whom I wish to deeply express my gratitude for his guidance, patience, assistance and inspiration throughout my master studies at the University of Minho. I would also like to thank my co-supervisor Doctor Ana Vera Machado, from the Polymer Engineering Department of the University of Minho, for her expert advice and for the time spent on this project. The conclusion of this dissertation was only possible thanks to the collaboration of several persons and entities to whom I would also like to express my gratitude.

I would like to sincerely thank Professor Paulo Pereira, Head of the Highways Group of the Civil Engineering Department of the University of Minho, for his vision and encouraging presence during my research and principally for changing the course of my professional life by believing in me.

I would also like to express my gratitude to Doctor Jorge Pais, from the Highways Group of the Civil Engineering Department of the University of Minho, for the opportunity he gave me to participate in his research project and for his very important support, initial guidance and interest.

I would like to thank Doctor Joel Oliveira and Doctor Elisabete Freitas, from the Highways Group of the Civil Engineering Department of the University of Minho, for their encouragement and Dr. Virginia Fernández for her friendship and assistance.

My special thanks to the technical staff of the Highways Laboratory of the Civil Engineering Department of the University of Minho, Eng. Carlos Palha and Hélder Torres, for their valuable assistance in the preparation of bituminous specimens, experimental works and test samples. I would also like to thank the researchers and the staff from the Chemical and Rheology Laboratories of Polymers Engineering Department of the University of Minho, especially Eng. Filomena and Eng. Jorge, for their guidance in the rheological analysis, Eng. Carla and Eng. Joana, for their help with the chemical analyses and, last but not least, Mauricio, for the microscope observations.

My special recognition to Doctor Loic Hilliou for his availability and valuable guidance on all aspects of the rheological analysis.

I would like to thank all the researchers and friends at the Department of Civil Engineering, in no particular order, Pedro, Glaussia, Rafael, João Paulo and Aline with whom I have had many enjoyable times.

I am also very grateful for the support provided by CEPSA and RECIPAV, for their supply of bitumen and crumb rubber respectively, without which it would not have been possible to carry out the present project.

Finally, I would like to thank my mother Berta and my companion Rui for their constant support, understanding, sacrifice and encouragement during the course of this study and, most of all, for their love and trust in me.

Study of the Interaction between Bitumen and Rubber

ABSTRACT

Approximately 9 to 10 kg of rubber from tyres per inhabitant and year are currently discarded in the industrialized societies. It is a waste material with a highly valuable constituent: vulcanized natural and synthetic rubber. Thus, the introduction of crumb rubber in the production of asphalt rubber (AR) mixes for road pavements should be considered as a sustainable technology which transforms an unwanted residue into a new bituminous mixture highly resistant to fatigue and fracture.

However, the increasing demands in relation to the quality and durability of pavements lead to the need of a profound knowledge in the physicochemical changes of the materials which constitute the AR binders. Thus, the main objective of this research project is to characterize the influence of bitumen and rubber properties and their interaction in the AR binder performance, namely by (i) evaluating the influence of the rubber morphology and physical properties of base bitumen in the physical and rheological properties of AR binder, (ii) assessing the changes that occur, at a molecular scale, in the base bitumen and in the rubber during their mutual interaction, and (iii) analyzing the aging effects during the pavement construction.

In this work several base bitumens interacted with crumb rubber in order to produce AR binders, which were subsequently separated by using a modified “Basket drainage method” to recover the residual bitumen and rubber. The aging effect was studied by using the RTFOT method. Additionally, a new method, the “Sphere AR production simulator”, was developed to reproduce the AR production without the contribution of rubber. CEN standard tests and the dynamic shear rheometer were used to evaluate the changes in the properties of the binders during the production of AR. The rubber changes were studied through microscopic observation, swelling and depolymerization tests.

The laboratory tests demonstrated that the aging of bitumen make it harder due to oxidation and restructuration. Likewise the AR production also contributes to its hardening because of the diffusion of light fractions of bitumen (mainly non volatile molecules) in the rubber particles. The rubber particles swelled 250 to 300% their weight, but the equivalent diameter only increased 2.5%. It was found that the 150/200 bitumen is an excellent alternative to produce AR binders. Minor changes in the loss of weight and in the rheological and physical properties of the AR binder can be observed after aging if compared with the aging effect in the other studied materials (base and residual bitumen). The physical and rheological properties of all tested materials can be related through known mathematical equations.

Study of the Interaction between Bitumen and Rubber

KEYWORDS

Bitumen
Rubber
Asphalt Rubber (AR)
Dynamic Shear Rheometer (DSR)
Molecular Weight Distribution (MWD)
“Sphere AR Production Simulator”
Swelling
Density
Depolymerization
Aging

Estudo da Interacção entre o Betume e a Borracha

RESUMO

Nas sociedades industrializadas actuais são rejeitados aproximadamente 9 a 10 kg de pneus, por habitante por ano, sendo que os materiais desaproveitados do pneu têm um elevado valor intrínseco, nomeadamente o seu constituinte principal: borracha natural e sintética vulcanizada. Assim, a introdução de granulado de borracha na produção de misturas betuminosas com betume de borracha (BB) para pavimentos rodoviários deve ser considerada uma tecnologia sustentável, que transforma um resíduo indesejado numa nova mistura betuminosa com elevada resistência à fadiga e à fractura.

No entanto, a crescente exigência de qualidade e durabilidade dos pavimentos obriga a um conhecimento profundo das alterações físico-químicas que ocorrem nos materiais constituintes do BB. Assim, o principal objectivo deste trabalho é determinar a influência das propriedades do betume e da borracha, e da sua interacção, no desempenho do BB, nomeadamente através da avaliação (i) da influência da morfologia da borracha e das propriedades físicas e reológicas do betume nas características do BB, (ii) das alterações no betume e na borracha, à escala molecular, durante a sua interacção mútua, e (iii) dos efeitos do envelhecimento durante a construção do pavimento.

Neste trabalho, um conjunto de betumes interagiu com granulado de borracha para produzir BB, sendo subsequentemente utilizando um "método do cesto drenante" modificado para separar e recuperar o betume e a borracha residuais. O envelhecimento dos ligantes durante a construção do pavimento foi estudado através do método RTFOT. Foi desenvolvido um "simulador de produção do BB com esferas" para reproduzir o envelhecimento na produção do BB sem a contribuição da borracha. As alterações nas propriedades dos ligantes durante a produção de BB foram avaliadas através de normas CEN e do reómetro dinâmico de corte. As alterações na borracha foram estudadas através de observação microscópica e de ensaios para avaliação da densidade e do grau de inchamento e despolimerização.

Os ensaios laboratoriais demonstraram que o envelhecimento e a produção de BB causam o endurecimento do betume, respectivamente devido à oxidação, crescimento e reestruturação molecular e devido à difusão das fracções leves do betume (principalmente moléculas não voláteis) através da borracha. As partículas de borracha incham cerca de 250 a 300% (em peso), mas o seu diâmetro equivalente aumenta apenas 2.5%. Concluiu-se que o betume 150/200 é uma boa alternativa para produção de BB. As alterações na perda de peso e nas propriedades físicas e reológicas do BB após envelhecimento são inferiores às observadas nos outros ligantes estudados. As propriedades físicas e reológicas dos materiais estudados relacionam-se através de equações matemáticas conhecidas.

Estudo da Interacção entre o Betume e a Borracha

PALAVRAS-CHAVE

Betume
Borracha
Betume Borracha (BB)
Reómetro Dinâmico de Corte (RDC)
Distribuição de Massa Molecular (DMM)
"Simulador da produção de BB com esferas"
Inchamento
Densidade
Despolimerização
Envelhecimento

LIST OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

ρ_{ip} – Density of the isopropyl alcohol

ω – Angular frequency

θ – Angular rotation or deflection angle

ρ_a – Apparent density of the crumb rubber

σ^* – Complex stress

η^* – Complex viscosity

$\eta_{p\infty}$ – Limiting viscosity

m_{ds} – Mass of the dry sample of crumb rubber

m_{ssl} – Mass of the sealed sample of crumb rubber in isopropyl alcohol

m_{sl} – Mass of the sieve in isopropyl alcohol

γ_0 – Maximum strain amplitude

δ – Phase angle

$\dot{\gamma}$ – Shear rate

σ – Shear stress

γ – Strain

η – Viscosity

σ_0 – Yield stress or maximum stress

τ , T – Torque

$BaSO_4$ – Barium sulphate

C – Carbon

$CaCO_3$ – Calcium carbonate

F – Fluorine

De – Deborah Number

dmm – 1/10 mm, decimal of the millimetre

Ea – Activation energy

f – Frequency

Fe – Iron

G* – Complex Shear modulus

$G^*/\sin\delta$ – Rutting parameter

G’ – Elastic or storage modulus

G’’ – Viscous or loss modulus

G_v – Creep stiffness

h – Gap between the parallel plates in the DSR

H – Hydrogen

LN_2 – Liquid nitrogen

Mg – Magnesium

$MgCO_3$ – Magnesium carbonate

MgO – Magnesium oxide

N – Nitrogen

Ø – Diameter

O – Oxygen

$Ø_{eq}$ – Equivalent Diameter

P – Phosphorus

r – Radius

S – Sulphur

Si – Silicon

T – Temperature

t – Time

T_c – Characteristic temperature

Tg – Glass transition temperature

Zn – Zinc

ZnO_2 – Zinc oxide

ZSV or η_0 – Zero shear viscosity

LIST OF ABBREVIATIONS

AC-5 – Asphalt cement (penetration value)

AFM – Atomic force microscopy

AR, ar – Asphalt rubber binder

B, b – Base bitumen

BBR – Bending Beam Rheometer

BS – British Standard

BR – Butadiene rubber

CR – Crumb Rubber

Dens – Density

DMA – Dynamic mechanical analysis

DSR – Dynamic Shear Rheometer

DTT – Direct Tensile Test

DV – Dynamic Viscosity determined in the Brookfield viscosimeter

EN – European standard

ER – Elastic Recovery

ESEM – Environmental scanning electron microscopy

GPC – Gel-Permeation Chromatography

FR, fr – Filtered rubber

FTIR – Fourier Transform Infra-Red Spectroscopy

FTT – Fracture Toughness Test

LTA – Long term aging

IE – Interaction effect

IR – Synthetic Polyisoprene Rubber

LMS – Large molecular size

Micr – Microscopy

MRTFOT – Modified Rolling Thin Film Oven Test

MSD – Molecular size distribution (or LMS)

Mw – Molecular weight

MWD – Molecular weight distribution

NR – Natural Polyisoprene Rubber

PAV – Pressure Aging Vessel

PE – Particle effect

Pen – Penetration at 25 °C

PG – Performance Grade

PI – Penetration Index

PIB – Polyisobutylene or butyl rubber

PMBs – Polymer modified bitumens

R&B – Ring and Ball Softening Point

RCAT – Rotating Cylinder Aging Test

Res, res – Residual Bitumen

RFT – Rotating flask test

rr – Recovered rubber

RTFOT – Rolling Thin Film Oven Test

TFOT – Thin Film Oven Test

TTSP – Time Temperature Superposition Principle

SARA – Bitumen fractions: saturates (S), aromatics (A), resins (R), and asphaltenes (As)

Sb – Sphere Bitumen

SBR – Styrene-Butadiene Rubber

SBS – Poly(styrene-butadiene-styrene)

SP – ASTM (unstirred) softening point

STA – Short term aging

SuperPave – Superior Performing Asphalt Pavement

UK BS – United Kingdom British Standard

WLF – Williams-Landel-Ferry equation

LIST OF ACRONYMS

AASHTO	– American Association of State Highway and Transportation Officials
AG:PT	– Austroads Guides to Pavement Technology (Australian Standards)
ASTM	– American Society of Testing and Materials
CEN	– European Committee for Standardization
EPA	– Environmental Protection Agency (United States of America)
ESIS	– European Structural Integrity Society
FEHRL	– Forum of European National Highway Research Laboratories
FHWA	– Federal Highway Administration (United States of America)
IP	– Institute of Petroleum
NCHRP	– National Cooperative Highway Research Program
SHRP	– Strategic Highway Research Program
TTI	– Texas Transportation Institute
WRI	– Western Research Institute

1. INTRODUCTION

1.1. Background

Healthy economies require an appropriate transportation system, in which roadways are an essential part. Therefore, the construction and maintenance of road pavements should be long lasting and have a significant impact on the economic vitality of a nation. The primary reasons for the deteriorated conditions of roads include the increase in the overall traffic, poor asphalt binder quality coming from high-tech refining processes and climatic changes. Improved construction processes will secure the solution to these challenges. It is necessary to understand the fundamental behaviour and properties of roads before starting to develop advanced construction processes (Glover, 2007).

Every year, approximately 9 to 10 kg of rubber tyres per inhabitant are currently discarded in the industrialized societies. Although tyres are not regarded as a dangerous residue, their hollow shape usually brings sanitary problems and difficulties in their final disposal. When ignited, the resulting fire is impossible to be extinguished, releasing hazardous gases to the atmosphere. Finally, the vulcanized rubber of tyres cannot be recycled or used for the same proposes as the unvulcanized polymer. Furthermore, society is wasting valuable materials from the tyre, namely its main constituent, the vulcanized natural and synthetic rubber.

Thus, the introduction of crumb rubber in the production of asphalt rubber (AR) mixtures for road pavements should be considered as a sustainable technology which will transform an unwanted residue into a new mixture with a high resistance to fatigue and fracture. However, the addition of rubber in a bituminous mixture increases its complexity: the materials that constitute these AR binders and the physicochemical changes in the binder during the production of the AR are not sufficiently characterized. Hence, it is essential to carry out a study to understand the interaction among the AR binder constituents in order to optimize the performance of AR mixes.

The use of bitumen modified with crumb rubber contributes for a sustainable development of road infrastructures through: (i) the definition of an efficient final destination for the used tyres of cars and trucks; (ii) the improved performance of the resulting material used in the pavement.

The Federal Highway Administration (FHWA) describes crumb rubber (CR) as "a scrap tyre rubber which has been processed by ambient grinding or granulating methods, reducing the rubber to particles which generally pass the 4.75 mm (No. 4) sieve" (McDonald, 1966; FHWA, 1993). CR may be obtained from any combination of tyre sources. The FHWA defines asphalt rubber as "asphalt cement modified with crumb rubber" (Jensen and Abdelrahman, 2006).

At present pavement technology and the evaluation of bituminous mixtures are essentially based on empirical-mechanist studies. Frequently, the materials used in asphalt pavements are not sufficiently characterized, more specifically concerning their physicochemical constitution, rheological properties and mutual interaction at a microscopic scale. Therefore, it is essential to develop the knowledge about the interaction between the constituents of bituminous materials used in flexible pavements by carrying out their characterization at a microscopic level, so as to understand their macroscopic structural and physical behaviour. This additional study becomes more significant for modified or unconventional mixtures due to their complexity (e.g. asphalt rubber). Actually, beyond the traditional constituents of the bituminous pavement layers, the use of crumb rubber recycled from used tyres should be studied as a form of environmental protection and as a pavement performance enhancer.

Bitumen is a single-phase homogeneous mixture of many different molecules, which may be differentiated into two broad classes: polar and non-polar. The non-polar molecules serve as a matrix or solvent for the polar molecules, which form weak “networks” of polar-polar associations that give elastic properties to bitumen. The polar materials are uniformly distributed throughout the bitumen, and upon heating the weak interactions are broken to yield a Newtonian fluid. When perturbed, in response to temperature changes and physical stresses, these interactions break and reform up to produce a new combination of interactions (Jones and Kennedy, 1992). The polar molecules interact and primarily give bitumen its elastic characteristics. The non-polar molecules mainly contribute to the viscous behaviour of the bitumen and control the low temperature properties of the bitumen (Youtcheff and Jones, 1994).

During the pavement life cycle, bitumen hardens (aging). The main aging mechanism is irreversible, being characterised by chemical reactions, including oxidation, polymerization and condensation, and by physical processes, which include loss of volatiles and structural morphological changes that in turn have an impact on the rheological properties. However, oxidative hardening has been shown to be the principal responsible factor for a more brittle structure and an increase in the susceptibility to cracking. Oxidative hardening happens at a relatively slow rate and varies seasonally, occurring faster at higher temperatures as diffusion of oxygen increases (Glover, 2007). The second mechanism is a reversible process called physical hardening and may be attributed to molecular structuring, i.e. the reorganisation of bitumen molecules or microstructures to approach an optimum thermodynamic state under a specific set of conditions (Petersen, 1984).

Two of the most fundamental properties of any organic substance are molecular weight and chemical functionality. Theoretically, many physical properties, particularly rheological properties, are a function of molecular weight (Mw) and molecular weight distribution (MWD). The changes in Mw and MWD can be assessed by monitoring the rheological parameters viscosity (η*), and the elastic and viscous stiffness (G' and G''). At reduced frequencies η is largely affected by Mw, but at higher frequencies η reduces, approaching a value independent of the Mw. Another way to assess the changes in Mw and MDW is monitoring the point of interception of G' and G'' curves vs. frequency. The modulus obtained in the interception point is nearly independent of Mw, but it decreases with the increase of MDW. The corresponding frequency is almost independent of MDW, but it increases with Mw (Castro *et al.*, 2001).

There are several available methods to investigate the physical properties of modified asphalts under aging conditions. One of the most used methods is the assessment of the binder rheology with the DSR (Lima *et al.*, 2006). The rheological characteristics of bitumen at a particular temperature are determined by the constitution (chemical composition) and the structure (physical arrangement) of the molecules. Any changes in the constitution, structure or both will result in changes in the rheology. Thus, to understand the changes in the bitumen rheology, it is essential to understand how the structure and constitution of bitumen interact to influence its rheology (Read and Whiteoak, 2003).

When crumb rubber is blended with bitumen at high temperatures (wet process) to produce a modified binder, the two materials interact once the bitumen components migrate into the rubber causing it to swell. Initially, the bitumen-rubber interaction is a non-chemical reaction, where the rubber particles are swollen by the absorption of the aromatic oils of bitumen (Bahia and Davies, 1995). The impact of the crumb rubber modification improves the aging susceptibility, decreasing the binder aging ratio (Martinez *et al.*, 2006). However, the base bitumen should be selected carefully to ensure that the content of light fractions of bitumen is high enough at the end of the curing process (Ould-Henia and Dumont, 2006).

Absorption of bitumen components by the rubber inevitably depletes the bitumen of the absorbed components and, consequently, modifies its properties by making it stiffer and more brittle (Singleton *et al.*, 2000; Artamendi *et al.*, 2002; Airey *et al.*, 2003). Furthermore, the rubber particles may also suffer some form of degradation (mainly devulcanization and depolymerisation) when they are mixed with bitumen at high temperatures for prolonged periods of time (Billiter *et al.*, 1997a; Billiter *et al.*, 1997b; Zanzotto and Kennepohl, 1996). The extent of swelling and degradation depends on the nature of the rubber, the chemical composition of bitumen and the mixing conditions of time, temperature and degree of agitation. In addition, these processes will determine the mechanical properties of the crumb rubber modified binders (Abdelrahman and Carpenter, 1999). The asphalt rubber binders are very asphalt-dependent: lower contents of saturates and asphaltenes improve the asphalt capacity to dissolve rubber (Billiter *et al.*, 1996).

1.2. Research Objectives

The aim of this research project is to characterize the influence of the bitumen properties in the AR binder performance. The programme has been divided into two main phases: (i) an evaluation of the influence of the morphology and physicochemical properties of the AR binder components (base bitumen and rubber) in the physical and rheological characteristics of the AR modified binder; (ii) an investigation on the changes that occur, at a molecular scale, in the base bitumen and in the rubber during their reciprocal interaction in the process of AR binder production and the effect of aging due to the mixing and laying procedures.

In terms of the specific research objectives of this investigation, they can be identified as follows:

- Assess or identify the physicochemical and rheological changes in the properties of the AR binder and of the base bitumen as a consequence of the bitumen-rubber interaction;
- Recognize the morphological alterations on the crumb rubber during AR production and to relate them with the chemical constitution of the bitumen;
- Better understand the influence of aging on the base bitumen and AR binder during the phases of production of the AR binder and mixtures;
- Establish a relationship between the physical and rheological properties of the different studied bitumens and of their resulting AR binders.

1.3. Research Methodology

To achieve the core research objectives listed above, the research methodology was divided into the six tasks described below:

- **Task 1:** Literature Review

  A comprehensive literature review on bitumen and crumb rubber materials, rubber-bitumen interaction and relation between the binder characteristics and the pavement performance was carried out, including literature on the effects of aging in bituminous binders (bitumen and AR).
- **Task 2:** Physical and rheological characterization of the selected bitumens

  The physical properties of various types of bitumen from the same source and obtained in the same distillation column were assessed by using conventional EN standard tests; their rheological behaviour was evaluated with a Dynamic Shear Rheometer (DSR).

- **Task 3:** Monitored production of the ARs; development and application of the “sphere AR production simulator”.

  After being characterized, the bitumen was left to interact with 21.0% of crumb rubber by mass of AR binder. Then, a modified “basket drainage method” was used to separate the residual bitumen from rubber that constitute the AR binder (residual bitumen and depolymerised rubber). The density of the bitumen, rubber and AR binder were monitored during its production. A new “sphere AR production simulator” test was developed during this work to simulate the changes that occur in the base bitumen during the production of AR that are independent from the interaction between bitumen and rubber (such as bitumen aging). Thus, it would be possible to measure the changes in the bitumen caused exclusively by its interaction with crumb rubber.
- **Task 4:** Physical and rheological characterization of the ARs and residual bitumens

  The AR binder and the residual bitumen properties were evaluated by replicating the same tests used for base bitumen characterization, so as to assess the changes in the physical and rheological behaviour of the binder.
- **Task 5:** Analysis of the aging effects on the studied binders

  The aging of AR binders during the mixing and lay-down procedures was studied by using the RTFOT method. The changes in the chemical composition and in the physical and rheological behaviour of the base bitumen, AR binder and residual bitumen, before and after aging, were evaluated by replicating the same tests used for bitumen characterization.
- **Task 6:** Characterization of crumb rubber before and after interacting with bitumen

  The morphology of the crumb rubber particles was assessed by macroscopic and microscopic observation. The rubber apparent and bulk densities (AG:PT/T144) were determined as well as their percentage of devulcanization (ASTM D 6814-02). After interacting with the different bitumens the rubber particles were recovered from the AR binders and filtered from the residual bitumens, being subsequently observed, measured and weighted.

1.4. Thesis Layout

The thesis presents the methodology, results, analysis and discussion resultant from an extensive laboratory investigation. The thesis is divided into six chapters, following the methodology described above. An overview of the execution of the tasks and corresponding thesis chapters is illustrated in the flowchart of Figure 1.1 and a brief description of the contents of each chapter is presented below:

- Chapter Two presents a detailed literature review on the constitution of the materials used to produce asphalt rubber (bitumen, rubber) is presented;

- Chapter Three provides a literature review on the methods and techniques of rheological, physical and morphological characterization of the materials (bitumen, rubber) is compiled;
- Chapter Four presents a literature review on the relations between the composition of the binders and their physical and rheological properties, as well as the changes in the binders characteristics due to the presence and interaction with rubber and due to the aging phenomenon;
- Chapter Five is dedicated to the description of the experimental work and to the discussion of results. The information provided in this chapter was sub-sectioned into five parts. Part 5.1 describes the experimental samples, equipments, materials and methods used, including a detailed explanation of the new "sphere AR production simulator", a method developed in this research. Parts 5.2 to 5.4 present the results and discussion of the physical and rheological characterization of the binders (base bitumen, AR binder and residual bitumen) before and after aging. The changes in the chemical structure of the several binders are also indirectly analysed. The changes in the rubber morphology due to the AR production process using different bitumens are presented and discussed in Part 5.5.
- Conclusions and recommendations for future research are presented in Chapter Six.

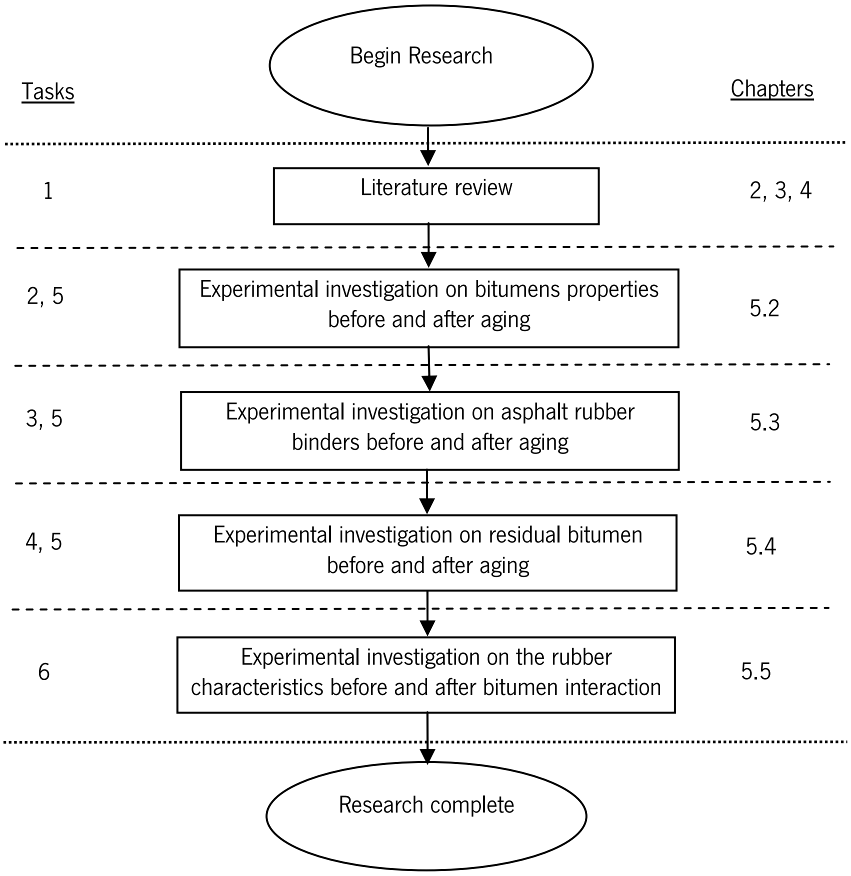


Figure 1.1 – Asphalt rubber binder research methodology and thesis layout

2. CONSTITUTION OF BITUMEN AND RUBBER

2.1. Bitumen Constitution

2.1.1. Bitumen as a construction material

Bitumens have been known since antiquity and they are considered as very technical materials. A great deal of effort has been devoted lately to better understand their physical and chemical properties (Michon *et al.*, 1997). Despite that, knowledge of the structure that controls its properties and its viscoelastic nature in particular, remains incomplete (Masson *et al.*, 2006).

Bitumens are a primary engineering material, often employed as binder in road construction and roofing systems, due to their thermoplastic nature, its water resistance and its adhesion toward most other substances. They possess strong temperature dependent rheological properties, governed by the chemical-physical interactions of their individual constituents (Loeber *et al.*, 1998).

Mixing of mineral aggregate and bitumen produces asphalt mixes, also referred to as asphaltic concrete or bituminous mix (Rodríguez-Valverde *et al.*, 2008). Usually, in order to dry the sandgravel and obtain adequate fluidity (handling) of the bitumen, both must be heated prior to mixing. This is the origin of the term “hot bituminous mix” (Usmani, 1997; Youtcheff, 2006; Rodríguez-Valverde *et al.*, 2008).

2.1.2. Definition of bitumen

Bitumen is a semisolid material, which can be produced by the non-destructive distillation of crude oil during petroleum refining (Abraham, 1960; Rodríguez-Valverde *et al.*, 2008). It can also be found in nature as “natural asphalt” (Redelius, 2004). One of the most important surface deposits of “natural” asphalt is located in Trinidad, the “Trinidad Lake Asphalt” (Read and Whiteoak, 2003).

Bitumen is a complex mixture of hydrocarbons consisting of high molecular weight asphaltenes and resins suspended in lower molecular weight oils (Rozeveld *et al.*, 1997). An elemental analysis of bitumen shows that the composition by weight is approximately 82-86% carbon, 8-11% hydrogen, 0-2% oxygen, and 0-6% sulphur, with traces of nitrogen, vanadium, nickel and iron (Rozeveld *et al.*, 1997).

The chemical composition and mechanical properties of bitumen strongly depend on the origin of the crude oil (Stangl *et al.*, 2007). Furthermore, the method of production greatly influences the structure and the chemical composition of bitumen that determines its rheological properties and the final end uses (Oyekunle, 2006).

Studies carried out indicate that bitumens are complex mixtures of a wide variety of molecules: paraffinics, naphthenics, and aromatics including heteroatoms. This complexity makes the prediction of bitumens properties particularly difficult (Michon *et al.*, 1997).

2.1.3. Bitumen production

The overwhelming majority of producers use atmospheric or vacuum distillation to refine the bitumen. While there is some solvent refining and air blowing utilized, they are clearly of secondary importance (Youtcheff *et al.*, 1994).

Chemically, crude may be predominantly paraffinic, naphthenic or aromatic with combinations of the first two being most common. There are nearly 1500 different crudes produced throughout the world. Based on the yield and quality of the resultant product, only a few of these, presented in Figure 2.1 (compositions are in percentage of weight and represent the +210 °C fraction), are considered suitable for the manufacture of bitumen (Read and Whiteoak, 2003).

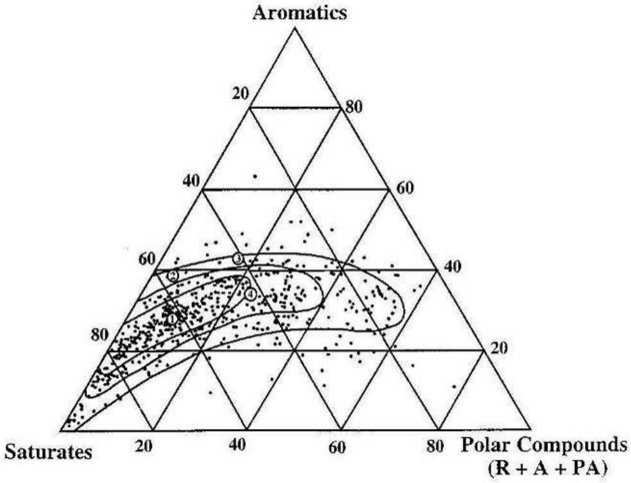


Figure 2.1 – Compositional representation on ternary diagram of 640 different crudes (McLean and Kilpatrick, 1997)

Refining of bituminous and mixed base crude oils produces petroleum bitumens. The process employed depends on the nature of the crude and the grades of the desired bitumen. The oldest and most widely used method is the atmospheric vacuum distillation of suitable crudes that result in the production of straight-run residual bitumens. Upgrading of low-grade bitumens is usually carried out by the airblowing process to give oxidized or semi-blown products (Oyekunle, 2006).

Bitumen is manufactured from crude oil following the next steps, also presented in Figure 2.2 (Read and Whiteoak, 2003):

- Fractional distillation of crude oil at a temperature of 350-380 °C and pressure slightly above atmospheric (in the bottom of the column is taken the heaviest fraction from the crude oil distillation, the long residue);
- Distillation of the long residue in a vacuum (10-100 mmHg) distillation column at a temperature of 350-425 °C (in the bottom of this column is taken the short residue);
- Air blowing of short residues by passing air through the short residue, either in a batch or a continuous basis at temperatures between 240 and 320 °C, producing over 20 different bitumen grades in the range 35 to 300 dmm.

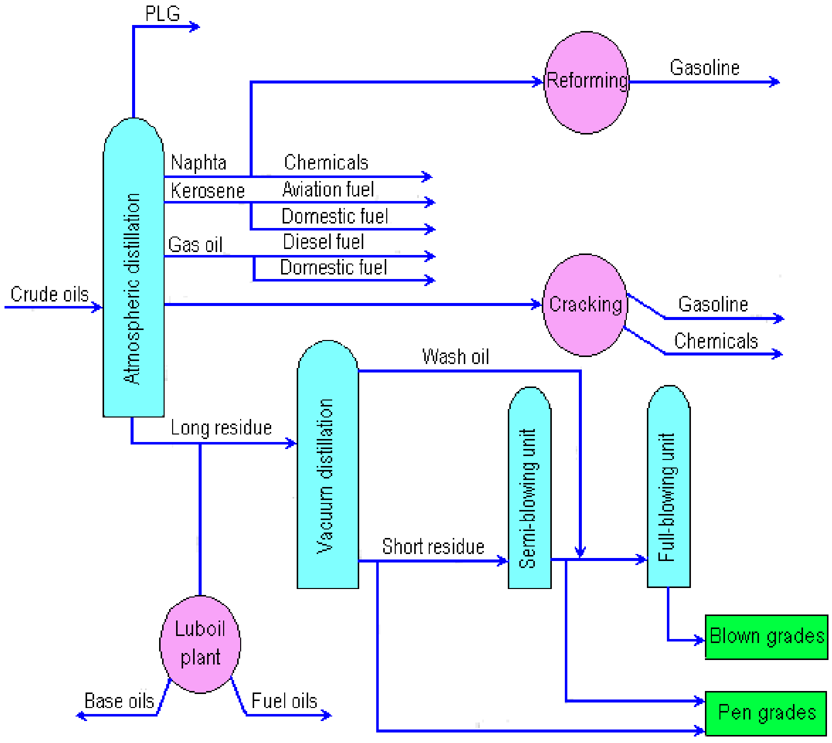


Figure 2.2 – Schematic representation of the crude oil distillation process (Read and Whiteoak, 2003)

Crude heavy fractions (that constitute bitumen) are defined as molecules containing more than 25 carbon atoms (C25), presenting a structural complexity which increases with the boiling point (Figure 2.3) as well as the molecular weight, the density, the viscosity, the refractive index (aromaticity) and the polarity (contents of heteroatoms and metals) (Merdrignac and Espinat, 2007).

These fractions are enriched in highly polar compounds such as resins and asphaltenes. They are composed by various chemical species of different aromaticity, functional heteroatoms and metal contents, when compared to the crude or lighter fractions (Merdrignac and Espinat, 2007).

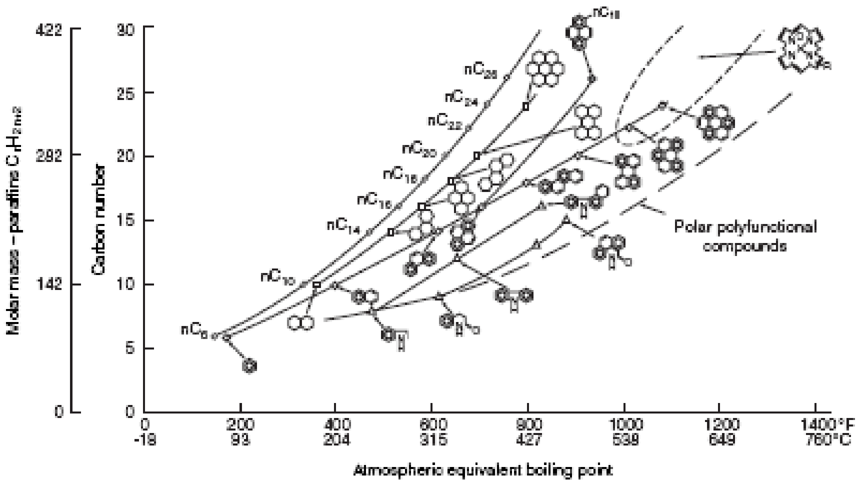


Figure 2.3 – Evolution of molecular weights and structures as a function of the boiling point (Altgelt and Boduszynski, 1994)

Chemical treatment of one cut or a blend of different cuts will produce bitumens with special properties that are not imparted by the distillation process. When several processes are applied to one or more crudes, the resultant bitumen blends have properties clearly superior to those obtained when only one manufacturing process is used (Oyekunle, 2006).

2.1.4. Bitumen models

Bitumen is often regarded as a colloidal system consisting of high molecular asphaltene/resin micelles dispersed in a lower molecular weight oily medium constituted by naphthenic aromatics and saturated compounds. The micelles are considered to be an ensemble of asphaltenes with a sheath of resins which stabilizes the mixture. The asphaltenes and resins may be linked in an open network but may also be dispersed as discrete particles depending on the relative amounts of resin, asphaltene, and oils (Rozeveld *et al.*, 1997). The model is too simple and other structural or composition parameters must be considered to explain the complexity of the bitumen solid-state (Masson *et al.*, 2006).

Resins and asphaltenes are known to constitute the polar fraction of crude oil (Speight *et al.*, 1991). Due to their molecular constitution, asphaltenes and resins have a mutual intrinsic effect on the stability of molecular self-assembling, either in the form of asphaltene-resin micellar association (which promotes re-dispersion) or asphaltene-asphaltene association (which promotes precipitation). Asphaltenes have the greatest affinity to form aggregates and resins clearly show a peptizing behaviour (Ortega-Rodriguez *et al.*, 2003), as illustrated in Figure 2.4 to show the extent of predicted asphaltene aggregation and asphaltene-resin separation (asphaltenes are presented in black and resins are presented in white).

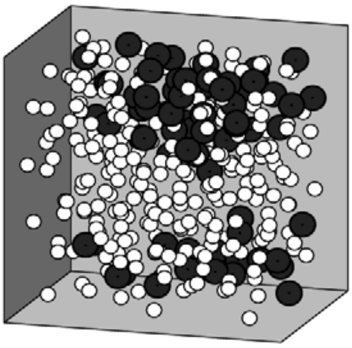
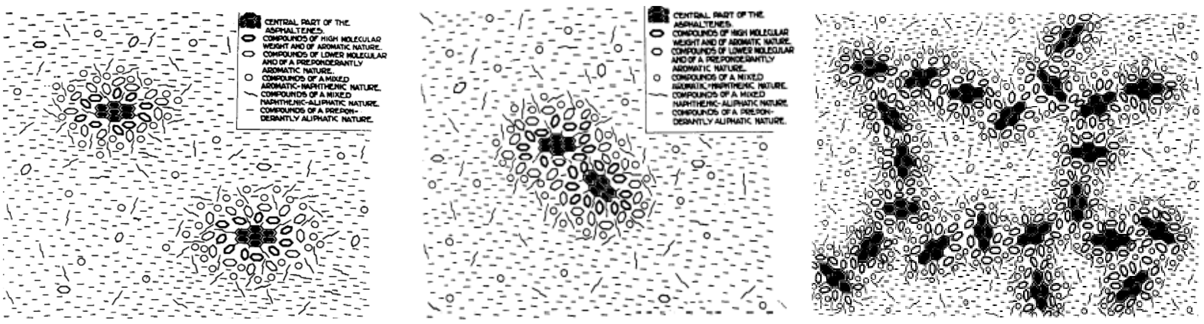


Figure 2.4 – Snapshot of a molecular dynamics simulations-derived system configuration (Ortega-Rodríguez *et al.*, 2004)

Models relied on explaining the chemical structure and performance characteristics of bitumen have been historically defined and limited by the analytical tools applied to its study. The first separation of asphaltenes (Boussingault, 1837) from bitumen (invention of the term asphaltene) set the tone for virtually all other investigations to-date. Without better definition of the constituents of bitumens, researchers were limited in determining the chemical relationships which govern their performance (Youtcheff *et al.*, 1994).

Nellensteyn (1924) introduced the concept that petroleum residua (e.g. bitumens) are colloidal dispersions of asphaltenes in maltenes (which serve as a solvent phase) peptized by polar materials called resins, which may be isolated from maltenes. Mack (1932) studied rheological properties of bitumens and also concluded that bitumens are colloidal.

Pfeiffer and Saal (1940) suggested that bitumen dispersed phases are composed of an aromatic core surrounded by layers of less aromatic molecules and dispersed in a relatively aliphatic solvent phase. They did not claim that there are distinct boundaries between bitumen dispersed and solvent phases, as in soap micelles, but that there is a continuum from low to high aromaticity from the solvent phase to the centers of the entities making up the dispersed phase (Figure 2.5).



Peptized asphaltene micelles (Sol-type bitumens)

Flocculated asphaltene micelles

Gel structure of an asphaltic bitumen of the blown type

Figure 2.5 – Bitumen colloidal model (Pheiffer and Saal, 1940)

Pfeiffer and Saal (1940) observed that asphaltenes, which they considered to be the core constituents of dispersed phases, have a marked tendency to absorb aromatic hydrocarbon solvents, and they assumed that the same tendency would prevail in bitumen systems. That is, the asphaltenes would attract smaller aromatic components of maltenes, which would surround and peptize the asphaltenes. The smaller aromatic molecules would be compatible with naphthenic and aliphatic components of the remainder of the maltene phase. Therefore, there is no contact between materials having greatly different surface tensions anywhere in the system, although differences in surface tension between the aromatic asphaltene cores and the more naphthenic and aliphatic solvent may be fairly large. The same authors considered aromaticity gradients in their model and did not address distributions of heteroatom-containing molecules with polar functional groups. They claimed that bitumen properties are a function of the strength of associations between fundamental components of dispersed phases and the extent to which dispersed phases are peptized by solvent phases (Petersen *et al.*, 1994).

The model of bitumen structure proposed by Pfeiffer and Saal (1940), which is an elaboration of the model suggested by earlier workers, specifically disavows the existence of a sharp boundary between solvent (maltene) and dispersed (asphaltene) phases in bitumens, but proposes an aromaticity gradient instead. Therefore, it may be inappropriate to describe this model as colloidal, because it allows no dispersed-phase surfaces (Petersen *et al.*, 1994).

Labout (1950) proposed that in bitumens having highly aromatic maltene fractions, asphaltenes are well dispersed (peptized) and do not form extensive associations. Such bitumens were designated sol-type bitumens. In bitumens with less aromatic maltene fractions, asphaltenes are not well dispersed and form large agglomeration, which in extreme cases can form a continuous network throughout a bitumen. These bitumens were designated gel-type bitumens (Petersen *et al.*, 1994).

Yen *et al.* (1961), on the basis of X-ray diffraction studies, supported many of the essential features of the colloidal model. They claimed that the predominant interaction in association phenomena in petroleum residua is stacking of condensed aromatic molecules to form larger units. Later, Altgelt and Harle (1975) rationalized bitumen rheological behaviour on the basis of stacking of condensed aromatic structures (Petersen *et al.*, 1994).

Donnet *et al.* (1977) claimed to be able to distinguish between sol-type and gel-type bitumens. Dwiggins (1978) found evidence for what he termed “colloidal particles” in bituminous crude oils. Ravey *et al.* (1988) also investigate the nature of petroleum residua structures. They concluded that asphaltenes from several crudes are fairly similar and consist of polydisperse ensembles of thin (about 1 nm) sheets whose diameters range from 1 to 10 nm. They emphasize that these dimensions are in accordance with those calculated by Dwiggins (1978). More recently, X-ray studies of asphaltenes and petroleum residua have been reported by Herzog *et al.* (1988) and Senglet *et al.* (1990), and both studies found evidence of association of molecules into larger structural units (Petersen *et al.*, 1994).

In the steric colloidal model of Park and Mansoori (1988), asphaltenes are assumed to exist as associations of polar molecules in crude oils, and the associations are not mobilized by addition of solvents such as *n*-heptane. The associations are stabilized by means of resins, some of which are adsorbed by the polar associations and some of which are dissolved in the aliphatic, low molecular weight solvent. Stability of the system requires that the chemical potential of the solvent (including dissolved resins) be equivalent to the chemical potential of the associations (including adsorbed resins). The adsorbed resins tend to repel one another, preventing coagulation of the associations. Adding solvents such as *n*-heptane is believed to cause desorption of resins from the associations, resulting in coalescence of the polar associations and precipitation. The steric colloidal model resembles the colloidal model of Pfeiffer and Saal (1940) in many aspects (Petersen *et al.*, 1994).

Overfield *et al.* (1989) claimed to have verified some aspects of the colloidal nature (in toluene) of asphaltenes, but they also showed that asphaltenes are neither colloids of fixed size nor assemblages of similar small molecules. It was inferred that behaviour of asphaltenes in deuterated toluene reflects behaviour of the molecules composing asphaltenes in petroleum residua (Petersen *et al.*, 1994).

Storm and Sheu (1993) analyzed the rheological data on the mixtures by five independent theories and concluded that asphaltenes are distinguishable in the residues. They claim these results show that asphaltenes are organized into charged spherical particles of widely distributed sizes that are solvated by resins and dispersed in the surrounding fluid (Petersen *et al.*, 1994). Ortega-Rodríguez *et al.* (2003) used this model to represent an asphaltene-resin mixture (Figure 2.6) with $\xi = (N_{Re}:N_{As}) = (8:1)$ in different host media (asphaltene molecules are symbolized by dark dots and resins by light dots).

Jones and Kennedy (1992) refer that bitumen is a single-phase homogeneous mixture of many different molecules, which may be differentiated into two broad classes: polar and non-polar. The non-polar molecules serve as a matrix or solvent for the polar molecules, which form weak “networks” of polar-polar associations that give bitumen its elastic properties (Figure 2.7). The polar materials are uniformly distributed throughout the bitumen, and upon heating the weak interactions are broken to yield a Newtonian fluid. When perturbed these interactions break and reform to produce a new combination of interactions that originates a “new” bitumen.

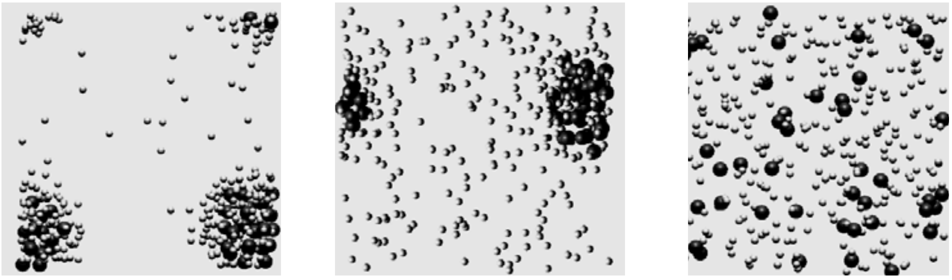
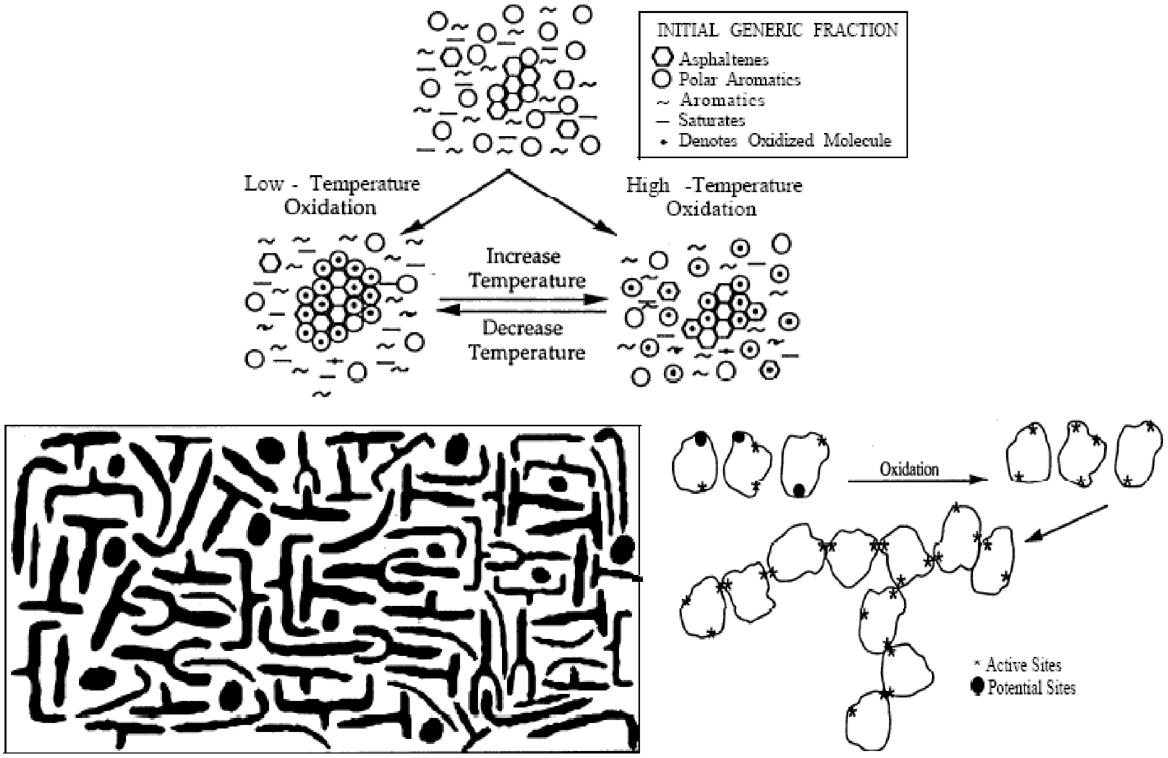

a) b) c)

Figure 2.6 – Snapshots of the final configuration of an asphaltene-resin mixture in (a) n-heptane, (b) toluene, and (c) pyridine host media (Ortega-Rodríguez *et al.*, 2003)



The Bitumen Model

Chain building in bitumens

Figure 2.7 – The bitumen model and the chain building in bitumens (Jones and Kennedy, 1992)

The micellar model was accepted as providing the best available explanation of how bitumens developed the structure that controlled their behaviour. In this model, aromatic asphaltenes exist as a discrete phase in the bitumen and are surrounded by the resins. The resins were intermediates in the bitumen, serving to peptize the otherwise insoluble asphaltenes. The resins and asphaltenes existed as "islands" floating in the final bitumen component – the oils. In many ways the model was not very far from some of Boussingault's (1837) original discussions of the composition of bitumen. While there have been competing molecular structures proposed through the years to explain the viscoelastic behaviour of bitumens, the micellar model had held forth for lack of a definitive proof to the contrary (Youtcheff *et al.*, 1994).

The recent research confirmed the judgement that the micellar model did not adequately explain the behaviour and properties of bitumen. As a result of these investigations the micellar model was gradually replaced with new models which more fully address the chemical-physical property relationships of bitumen. One of the models developed has been named "microstructural" model, and as its name implies, states that bitumen is a single phase mixture of many different polar and non-polar molecules, all of which interact with one another (Youtcheff *et al.*, 1994).

A model based on that suggested by Pfeiffer and Saal (1940), but with modifications, was described to account for bitumen behaviour. It was suggested that bitumens consist of a solvent phase composed of relatively aliphatic, nonpolar molecules that are low in heteroatoms (save perhaps sulfide and thiophenic sulfur and ether and ester oxygen) and that this phase disperses microstructures (structural units formed from molecular associations) consisting of more polar, aromatic, asphaltene-like molecules (Petersen *et al.*, 1994). Localized concentrations of similar molecules can exist in this model. Both the polar and non-polar molecules form loose associations and networks that are dispersed throughout the bitumen. This structure is held together through weak intermolecular forces, which form and break and reform in response to temperature changes and physical stresses. The polar molecules interact and primarily give bitumen its elastic characteristics. The non-polar molecules primarily contribute to the viscous behaviour of the bitumen and control their low temperature properties (Youtcheff *et al.*, 1994).

Modeling bitumen based on a microstructural model and on the thermodynamics of solutions explains many of the relationships between chemical composition and performance (Youtcheff *et al.*, 1994). However, the true nature of bitumen is not completely known. Most books and papers on bitumen chemistry state that bitumen is a colloidal dispersion of asphaltenes in maltenes. The dispersion is stabilized with resins. This statement is based on the well-known fact that when bitumen is diluted with certain hydrocarbon liquids, a precipitate appears. If the hydrocarbon liquid is an n-alkane such as n-heptane or n-pentane, the precipitate is called “asphaltenes”. It has been proposed that the “asphaltenes” are present in the bitumen in the form of micelles. The colloidal model has been criticized from the standpoint that although it appears appropriate, it is difficult to substantiate experimentally (Bukka *et al.*, 1991). Several times, although asphaltenes are the principal viscosity-enhancing component of crude oils, viscosities of heavy residua cannot be accurately predicted from asphaltene contents alone (Hagen *et al.*, 1984). Nevertheless, the colloidal model proposed by Nellensteyn (1924) and modified by Mack (1932), Pfeiffer and Saal (1940), and later investigators enjoys widespread support among petroleum scientists There is a great deal of evidence in favor of its validity (Petersen *et al.*, 1994).

There have also been proposed bitumen models which question the existence of micelles, as Park and Mansoori (1988) model and later as a result of the SHRP research program in the USA (Petersen *et al.*, 1994). Recently it has been shown that the stability of bitumen can be described as a thermodynamic mixture of hydrocarbons which are kept in solution by their mutual solubility (Redelius, 2004).

2.1.5. Bitumen polarity

Polarity is a major contribution to the performance characteristics. Polar materials (Figure 2.8) tend to associate strongly into a matrix (Figure 2.9) which is dispersed in less polar and non-polar materials. The exact nature of the chemical specie is less important than the overall assemblage of a set of polar materials to form a matrix within the non-polar continuous medium. The matrix gives elastic character to the bitumen while the continuous nonpolar phase gives its viscous nature (Robertson, 1991).

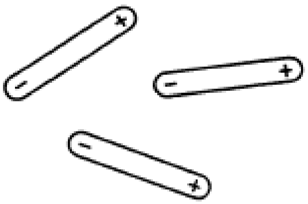


Figure 2.8 – Schematic representation of polar molecules (Robertson, 1991)

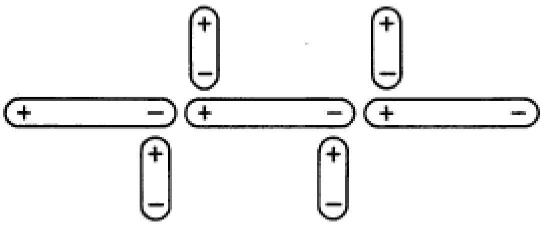


Figure 2.9 – Schematic representation of a multi-molecular structure (Robertson, 1991)

Polarity, which is the separation of charge within a molecule, can be seen by the following example. The dipole moment (separation of charge) of pyridine (C_5H_5N) is 2.19 debyes (in the gas phase) whereas the dipole moment of benzene (C_6H_6) is zero. Benzene is the all carbon analog of pyridine. Polarity also exists in all other heteroatom containing species (Robertson, 1991).

Polarity is important in bitumen because it tends to cause molecules to organize themselves into preferred orientations. All of the naturally occurring heteroatoms, nitrogen, sulfur, oxygen, and metals contribute to polarity within these molecules. Likewise, oxidation products formed upon aging are polar and further contribute to the polarity of the entire system (Robertson, 1991).

The physicochemical properties vary quite significantly from one to another bitumen and each reflects the nature of the crude oil used to prepare it. The most consistent description, or model, of petroleum bitumen polarity is as follows. Bitumen is a collection of polar and non-polar molecules:

- The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the nonpolar materials. Nuclear magnetic resonance and thermodynamic data indicate that the associations are not more than about 40 molecules, but some have smaller assemblies and again it varies from one bitumen to another. Actually, some bitumens show very little association (Robertson, 1991).

- The non-polar phase has the ability to dissociate the organized structure, but again it varies from one bitumen to another. As temperature is raised, the associations of polar molecules decreases and the material becomes more dissociated and therefore less viscous. As temperature is reduced, the opposite occurs (Robertson, 1991).

Recent observations indicate that the non-polar phase also organizes, but at very low temperatures, below 0 °C. Furthermore, bitumen is susceptible to oxidation which increases both the amount of polarity and the number of polar sites present among bitumen molecules. This further contributes to the ability of a bitumen to organize, but again varies from one bitumen to another (Robertson, 1991).

The morphology of bitumens has been studied recently using the present available technology in order to clarify the bitumen structure. Thus, in Figure 2.10 are presented topographic atomic force microscopy (AFM) images of two bitumens showing a flat background in which another phase is dispersed (Masson *et al.*, 2006).

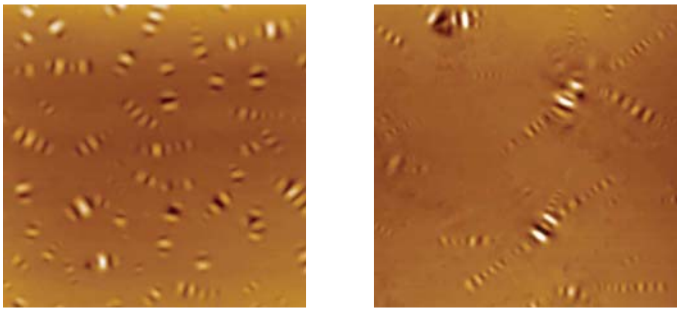


Figure 2.10 – Topographic AFM images of two bitumens (Masson *et al.*, 2006)

In the image of the left side of Figure 2.10 the dispersed phase shows as a succession of pale and dark lines often referred to as “bees” or “bee structures” by contrast to the image of the right side where the bee-like structures are not independent of one another. The bee shape is lost and it is replaced by “multiarm star-shapes” (Masson *et al.*, 2006).

A dispersed phase, with a “bee-like” appearance as shown in Figure 2.10, was attributed to asphaltenes, an assessment that was supported by Pauli *et al.* (2001). However, no correlation was found between the atomic force microscopy morphology and the composition based on asphaltenes, polar aromatics, naphthene aromatics and saturates (Masson *et al.*, 2006).

The morphology and the molecular arrangements in bitumen appear to be partly governed by the molecular planes and the polarity defined by metallic cations (Masson *et al.*, 2006). Thus, the morphology of bitumen was also assessed using the environmental scanning electron microscopy (ESEM). It was observed that the binder surface was modified after the films were exposed for several minutes by the electron beam (Rozeveld *et al.*, 1997).

Before the beam exposure of a bitumen film, the surface appears to be flat and featureless, as shown in Figure 2.11a. However, after the film has been exposed, a network entanglement of strands is visible, as presented in Figure 2.11b. It is hypothesized that the electron beam volatilizes the low molecular weight oils in the bitumen by localized heating and thereby reveals the asphaltenes and resins after the upper surface layer of oil has been removed (Rozeveld *et al.*, 1997).

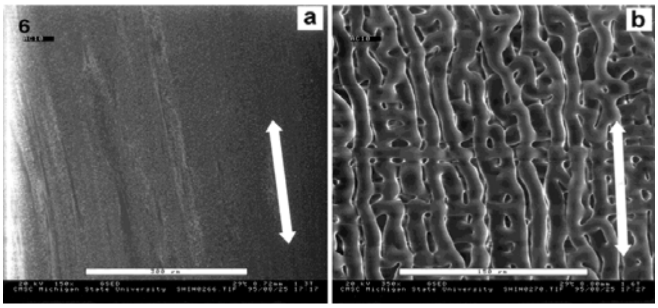


Figure 2.11 – ESEM image of an unmodified AC-5 bitumen binder film (a) before and (b) after beam exposure (Rozeveld *et al.*, 1997)

During the Rozeveld *et al.* (1997) investigations, a three-dimensional, entangled network of arranged fibrils was observed in all asphalt films after several minutes of beam exposure. In the strained sample AC-10 (Figure 2.12), the network structure was much more ordered than the network observed in the unstrained AC-5 bitumen, presented in Figure 2.11b. The fact that network could be modified prior to beam exposure suggests that the network is more than simply a beam-induced artefact and may provide insight into the asphaltene dispersion as a function of the processing. In Figure 2.12 the beam scan direction was 45° to the tensile axis. Figure 2.12c shows that the unexposed regions of the bitumen appear featureless, while Figure 2.12d illustrates that the fibrils in strained bitumens were well aligned and show a ladder type of configuration, with the long segments parallel to the tensile axis. Again, these results confirm that the asphaltene dispersion is modified by the process history of the binder and also suggest that the network is not a beam-induced artefact (Rozeveld *et al.*, 1997). During testing of bitumen with the environmental scanning electron microscope (ESEM), the exposure of the bitumen surface to the electron beam reveals a random string-like network structure also found in the work of Stangl *et al.* (2006).

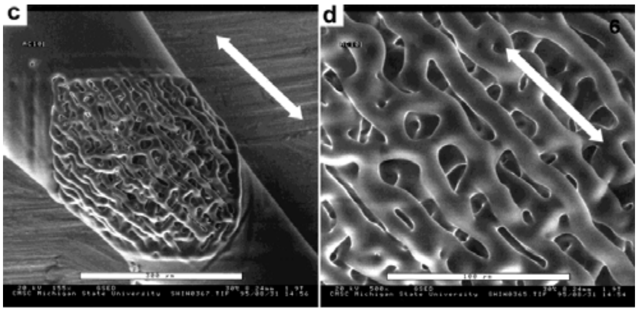


Figure 2.12 – ESEM images of a strained AC-10 film after beam exposure, showing (c) unexposed regions and (d) the network fibrils along the tensile axis, indicated by the white arrow (Rozeveld *et al.*, 1997)

Stangl *et al.* (2007) also theorized that the electron beam volatilizes the low molecular weight fractions of the bitumen by localized heating, whereas the higher molecular weight fractions remain and become visible in the form of string-like structures. ESEM images of the considered types of bitumen after longer beam exposure are shown in Figure 2.13 (Stangl *et al.*, 2007).

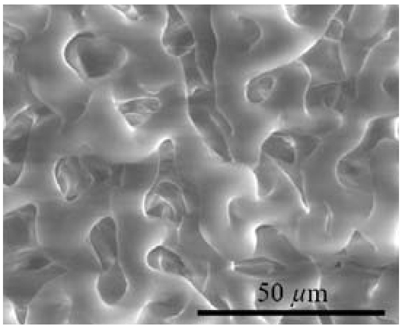


Figure 2.13 – ESEM images of bitumen 50/70 (Stangl *et al.*, 2007)

2.1.6. Chemical constitution of bitumen

Bitumen can be considered to be composed of an infinite number of discrete molecules. These molecules differ in shape, size and chemical composition. The combinations and interactions of these diverse molecules give rise to bitumen's behaviour characteristics through the impact on the free volume of the bitumen (Youtcheff *et al.*, 1994).

It is convenient to divide the chemistry of petroleum bitumen into two parts. The first part is the chemistry at the molecular level and the second part is the chemistry of interaction among all molecular species in bitumen. Much of the physical nature of bitumen can best be described, in terms of composition, as an assembly or matrix of molecular species (building blocks) into large multi-molecular units within the bitumen (Robertson, 1991).

In fact, molecular weight (Mw) wise, bitumen is a mixture of about 300-2000 chemical components, with an average of around 500-700 (Berkers, 2005).

Bitumen is a complex chemical mixture of molecules that are predominantly hydrocarbons of different molecular sizes with a small amount of structurally analogous heterocyclic species (heteroatoms) and functional groups containing sulphur, nitrogen and hydrogen atoms (Redelius, 2004). Bitumen also contains trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides or in porphyrine structures. Elementary analysis of bitumens manufactured from a variety of crude oils shows that most bitumens contain carbon, hydrogen, sulphur, oxygen and nitrogen (Read and Whiteoak, 2003).

This elemental composition results in the formation of a wide range of molecules, which are typically divided into four molecular groups: saturates, aromatics, resins, and asphaltenes (Whiteoak, 1990). Hereby, the molecular mass increases from the saturates (300 to 2000 g/mol) to the asphaltenes (1000 to 10000 g/mol). Moreover, the aromaticity and heteroatom content increase from the saturates to the asphaltenes in the same order. Due to these characteristics in the molecular composition, bitumen is referred to as a “molecular cocktail” (Stangl *et al.*, 2007).

Bitumen is classified as a viscoelastic material. It is composed of several thousand different molecules. The relative distribution of carbon atoms is 30% aromatic and 70% aliphatic. The majority of aromatic carbons are associated with polycondensed heteronuclear aromatic clusters. However, some single phenyl ring compounds with alkane substituents are possible. Structurally, the aliphatic carbons are associated with normal, branched, and cyclic alkanes. These alkane structural units can either be attached to a condensed aromatic cluster or exist independently (e.g., paraffin waxes) (Netzel, 2006).

At the molecular level historical studies have shown that there are at least hundreds of thousands of unique molecular species that exist within any particular bitumen (Robertson, 1991). Because bitumen is a complex mixture of molecules ranging from nonpolar saturated hydrocarbons to polar polynuclear aromatics, after fractionation of the bitumen by specific solvents, its composition is often conveniently reported in weight percent of saturates (S), aromatics (A), resins (R), and asphaltenes (As), collectively called SARA’s (Whiteoak, 1990; Loeber *et al.*, 1998; Raki *et al.*, 2000).

The aromatics and saturates are the lightest molecular weight group in bitumen. Together, the aromatics and saturates (oily phase) constitute the major portion of the total bitumen (40-50%) (Rozeveld *et al.*, 1997).

2.1.7. Bitumen SARA fractions

Over the past five decades, many hydrocarbon separation schemes have been described as starting steps for further characterization (Carbognani *et al.*, 2007). A widely adopted separation methodology came to be known during the 1970s as the SARA method (Figure 2.14), for the hydrocarbon group types that are isolated, namely saturates, aromatics, resins, and asphaltenes (Carbognani *et al.*, 2007).

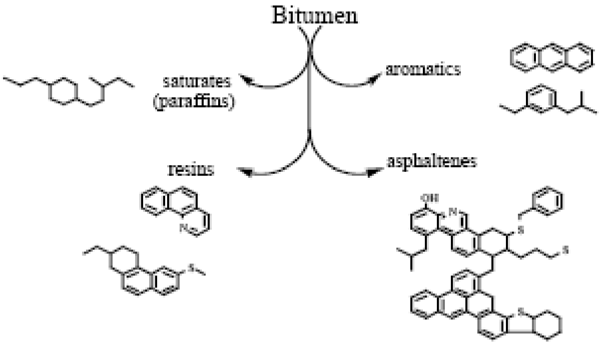


Figure 2.14 – Representative structures for the four bitumen fractions: the saturates, the aromatics, the resins and the asphaltenes (SARA) (Masson *et al.*, 2001)

Maltenes (or petrolenes) are the remaining portion of the bitumen material after the precipitation of asphaltenes with the normal paraffins. They consist of two fractions — heavy oils and resins. These oils are the liquid part of the bitumen and consist of normal-, iso-, and cyclo-paraffins and condensed naphthenes with some alkyl aromatics. The aromatic portion is mostly naphtheno-aromatic hydrocarbons with three or four naphthenic rings per molecule and is nonpolar. The oils have a key feature of dispersing polar agglomerations of asphaltenes and resins. Thus, this component is very important, as it is a colorless liquid, soluble in most solvents and is responsible for viscosity and fluidity of the bitumen (Oyekunle, 2006; Oyekunle, 2007).

- **Asphaltenes**

Geochemists have long contended (Behar *et al.*, 1984) that asphaltenes closely resemble kerogen fragments from source beds of crudes and that asphaltenes actually exist in petroleum and are not artifacts of precipitation. According to current theories, petroleum is derived from algae and bacteria that grew in ancient bodies of water in which oxygen was deficient. In these bodies of water, organic detritus was not recycled but incorporated into sediments. As sediments became deeply buried and lithified, the associated organic matter was converted into a macromolecular, insoluble material called *kerogen*. When the material was buried deep enough to reach temperatures of 350 °C, kerogen cracking reactions began. The products of these cracking reactions were fluids that migrated out of their source rocks (usually shales) and into permeable reservoir rocks. Bandurski (1982) has summarized some of the evidence for the theory that the asphaltenes of a crude oil resemble oil-bearing portions of the source kerogens more than any other component of the crude (Petersen *et al.*, 1994).

Asphaltenes (Figures 2.15 and 2.16) are the fairly high molecular weight (range from 1000 to 100 000) constituent of the four SARA groups and are considered highly polar and complex aromatic materials. Asphaltenes constitute 5-25% of the total bitumen and have a hydrogen/carbon ratio of 1.1. Asphaltenes are believed to be stacks of plate-like sheets of aromatic and naphthenic ring structures held together by hydrogen bonds (Altgen and Harle, 1975). The asphaltene particle size is on the order of 5-30 nm (Rozeveld *et al.*, 1997; Read and Whiteoak, 2003).

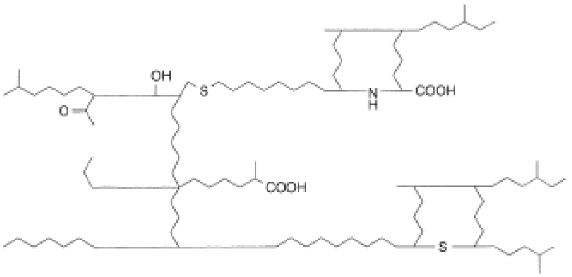


Figure 2.15 – Asphaltene structure (Read and Whiteoak, 2003)

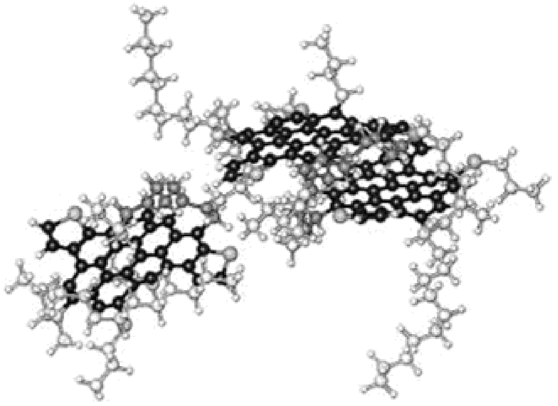


Figure 2.16 – Space filling three-dimensional conformations of lowest energy for the Athabasca bitumen asphaltenes (Zhao *et al.*, 2003)

The complexity of the asphaltene fraction can be defined in solubility terms. Asphaltenes are comprised of those compounds displaying the highest molecular weights, the highest polarities, or both (Speight, 1999). According to the definition, asphaltene types are not soluble in alkane solvents but are soluble in aromatic solvents (Carbognani *et al.*, 2007).

Very early in the study of crude oils, it was observed that mixing oils with several volumes of normal alkane solvents (propane, n-butane, n-pentane, n-hexane, n-heptane) resulted in the precipitation of black, friable solids called asphaltenes. These solids are relatively enriched in heteroatoms (nitrogen, oxygen, sulfur, metals) and are more aromatic than their parent oils. Asphaltenes are involatile, so they become concentrated in residual fractions. Deasphaltened oils (otherwise known as petrolenes or maltenes) differ in properties from whole crude oils; for example, maltenes are much less viscous than whole crudes. Therefore asphaltenes, which normally make up a few mass percentage of crudes, are the principal viscosity-enhancing components, as they are with bitumens (Petersen *et al.*, 1994).

Asphaltenes are defined in standards as the insoluble fraction of crude oil, which drops out after addition of amounts of low-molecular-weight *n*-alkanes (ASTM D 4124).

A common feature in these studies is that asphaltenes are composed of condensed aromatic structures of high molecular weight, having aliphatic side chains and heteroatoms. It has been well established that asphaltenes are stabilized in crude oils by natural resins (surfactantlike agents). The action of these peptizing agents on the asphaltene aggregation and precipitation processes is thought to be of paramount importance (Leontaritis *et al.*, 1989).

Asphaltenes are a collection of polydisperse molecules consisting mostly of polynuclear aromatic units, with varying proportions of aliphatics and alicyclic moieties and small amounts of heteroatoms (Ortega-Rodriguez *et al.*, 2004).

The asphaltene content has a large effect on the rheological characteristics of a bitumen. Increasing the asphaltene content produces a harder, more viscous bitumen with a lower penetration, higher softening point and, consequently, higher viscosity (Read and Whiteoak, 2003).

Asphaltenes are regarded as being formed by the condensation of resins. They are black or brown coloured, hard, non-plastic, non-malleable, and contain predominantly carbon and hydrogen with sulfur, oxygen, nitrogen and other heteroatoms. Asphaltenes are agglomerations of the most highly polar molecules and are responsible for the strength, stiffness and presence of colloidal structure in bitumens. They are insoluble in low molecular weight normal paraffins and are classified by the precipitating solvent (different solvents precipitating different amount of asphaltenes). Asphaltenes are determined by ASTM D327 as the n-heptane insolubles. The size of the asphaltenes particles ranges from 4 to 10 nm (even if their micelles have 15 to 30 nm). Two key parameters that control the stability of asphaltene micelles are the ratio of aromatics to saturates and that of resins to asphaltenes. When these ratios decrease, asphaltene micelles will coalesce and form larger aggregates (Oyekunle, 2006).

An important indicator of bitumen structure is the content of asphaltenes. A large concentration of asphaltenes will bring the bitumens to a “gel” type behavior (non-Newtonian flow characteristics) which is different from bitumens with a few asphaltenes, designated as “sol” type (Newtonian flow). It has been established that asphaltenes are not stable, can form a separate phase and can aggregate as a result of chemical alteration (Glover, 2007).

- **Resines**

Resins (Figures 2.17 and 2.18) are very polar in nature and act as a dispersing agent or peptisers for the asphaltenes (Rozeveld *et al.*, 1997). They are thought to have less condensed structures, acidic endsites, and lower molecular weight than asphaltenes (Speight *et al.*, 1991).

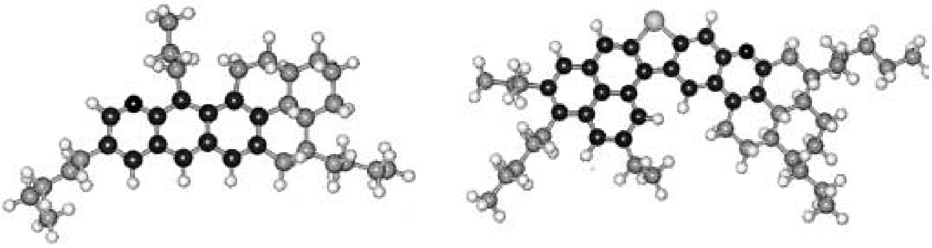


Figure 2.17 – Space filling three-dimensional conformations of lowest energy for the Athabasca bitumen resins (Zhao *et al.*, 2003)

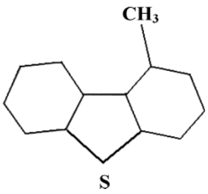


Figure 2.18 – Diagram showing the resin structure $C_{13}H_{10}S_1$ (Murgich, *et al.,* 1999)

Petroleum resins, on the other hand, are a fraction of the deasphalted component of crude oils that adsorbs in silica gel and is extracted with the action of polar solvents (Ortega-Rodriguez *et al.*, 2004).

Like asphaltenes, resins are a largely composed by hydrogen and carbon with small amounts of oxygen, sulphur, nitrogen and other elements including metals, being polar in nature and strongly adhesive. Resins are dispersing agents or peptisers of asphaltenes. Their molecular weights range from 500 to 50 000, particle size of 1 to 5 nm and a hydrogen/carbon ratio of 1.3 to 1.4. The proportion of resin to asphaltenes governs the SOL or GEL type character of bitumen (Read and Whiteoak, 2003).

The resins are semiliquid and sometimes solid materials of dark red color at room temperature. The resins consist of mainly polycylic molecules containing saturated, aromatic and hetero-aromatic rings and heteroatoms in various functional groups. The resins are not as polar as the asphaltenes. These resins provide adhesion, ductility, malleability and plasticity (Oyekunle, 2006). Actually, resins have been found the most responsible for the plasticity of asphalt as well as its adhesion to aggregate (Gawel and Czechowski, 1997).

Resins, which are sometimes called “polars”, are compounds that have chemical functionalities because of the presence of heteroatoms, mainly N, S, and O (Carbognani *et al.*, 2007).

The constituents of the resin fraction play an important role in petroleum. They are responsible for the stability of the system and maintain the asphaltenes and other constituents as a single phase. The absence of the resin fraction (produced by a variety of methods) from the maltenes influences the ability of the de-resined maltenes to accommodate the asphaltenes either in solution or as a stable part of a colloidal system (Andersen and Speight, 2001).

- **Aromatics**

Aromatics (Figures 2.19 and 2.20) comprise the lowest molecular weigh naphthenic aromatic compounds in the bitumen (Rozeveld *et al.*, 1997). They constitute 40 to 65% of the total bitumen. The average molecular weigh of aromatics range from 300 to 20 000. They consist in non-polar carbon chains in which the unsaturated ring systems (aromatics) dominate and they have dissolving ability for other high molecular weight hydrocarbons (Read and Whiteoak, 2003).

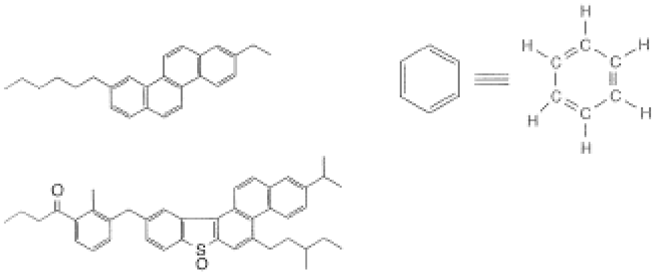


Figure 2.19 – Aromatic structures (Read and Whiteoak, 2003)

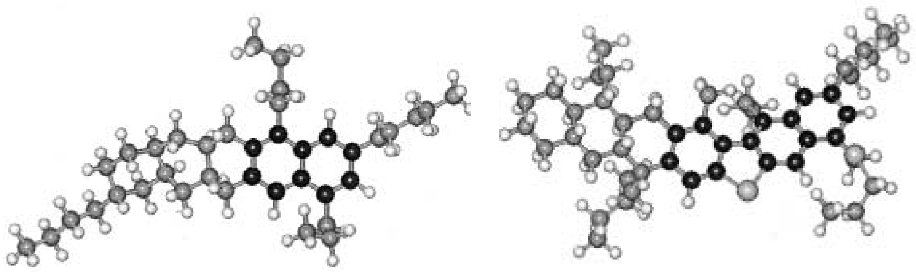


Figure 2.20 – Space filling three-dimensional conformations of lowest energy for the Athabasca bitumen aromatics (Zhao *et al.*, 2003)

- **Saturates**

The saturates (Figures 2.21 and 2.22) consist of straight and branch chain aliphatic hydrocarbons, alkyl-naphthenes and alkyl aromatics (Rozeveld *et al.*, 1997). They are non-polar viscous oils. The average molecular weight range is from 300 to 20 000 and the componets include both waxy and non-waxy saturates (Read and Whiteoak, 2003).

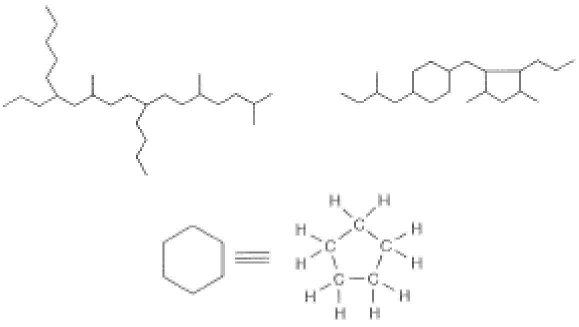


Figure 2.21 – Saturate structures (Read and Whiteoak, 2003)

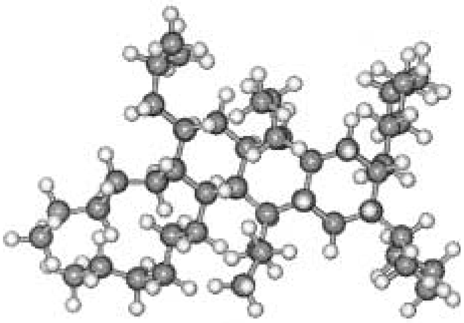


Figure 2.22 – Space filling three-dimensional conformations of lowest energy for the Athabasca bitumen saturates (Zhao *et al.*, 2003)

In ASTM D 2007-03, saturates are defined as the material that, on percolation in a *n*-pentane eluent, is not adsorbed on either the clay or silica gel under the conditions specified, while in accordance with ASTM D 4124-01, saturates are the material that, on percolation in a n-heptane eluant, is not absorbed on calcined CG-20 alumina absorbent under the conditions specified.

The chemical nature of crude oil and the bitumen-producing method influence the content of saturated components in asphalt as well as their chemical constitution. The saturated components in asphalt represent complex mixture of polyalkyl structures in which straight chain paraffins prevail (Gawel and Czechowski, 1997).

Among the saturated components in asphalt, the part that crystallizes at a low temperature, so called wax, was found to have a damaging effect on asphalt performance. The damaging action of wax on asphalt properties was described in detail by Fritsche (1995). However, in asphalts with a high content of polar-aromatic components the wax effect is of a minor importance (Gawel and Czechowski, 1997).

The decisive factor in any adverse effect of waxes is their crystalline structure. Therefore the content of bituminous wax is an optional requirement in the harmonized European Standard for bitumen and bituminous binders, EN 12591 (1999), and has been adopted by certain countries at the limit level of 2.2% when using method EN 12606-1 (a destructive distillation technique) or 4.5% when using method EN 12606-2 (a simulated deasphalting/dewaxing procedure) (Berkers, 2005).

In general, waxes are indissoluble in water, difficult to dissolve in alcohol and can in melted state be mixed with oil (Edwards, 2005).

Paraffin rich crude oil is generally considered not quite suitable for bitumen production, but lack of asphaltene rich crude oils may demand the use of paraffin naphthenic crude oils as base material at the production of bitumen. However, the wax content as a rule does not constitute any criteria of usefulness at bitumen production, as the wax varies with distillation grade and type of crude oil. The choice of base material for bitumen production is therefore judged by the heavy distillate residue rather than by the crude oil wax content. It has been suggested that wax content in bitumen should not be more than 3% (Edwards, 2005).

Wax in bitumen has been for a long time of great interest, particularly the effect on bitumen quality and methods for determining wax content. Opinions about the effect of wax on bitumen quality have varied over the years and sometimes been contradictory. Negative effects of wax in bitumen are linked to crystallizing and melting properties. Different types of wax may affect bitumen performance in different ways (Edwards, 2005).

Often, waxes in bitumen are divided into three general categories: macrocrystalline, microcrystalline and amorphous (non-crystalline) wax. Macrocrystalline waxes in bitumen typically have about 30 carbon atoms and crystallize in larger crystals. At 40 or higher numbers of carbon atoms, smaller crystals are formed. Wax with branched carbon chains, aromatic and alicyclic components or heteroatoms show difficulties in crystallizing and are considered as amorphous, ductile or elastic. A simplified schematic picture of wax in bitumen is shown in Figure 2.23, including some general structural formulas for the main chemical components of macro- and microcrystalline wax in bitumen (Edwards, 2005).

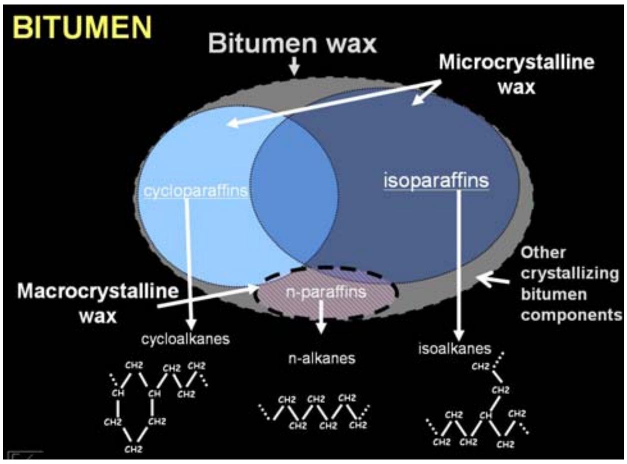


Figure 2.23 – Schematic picture of wax in bitumen (Edwards and Isacsson, 2005)

In the European binder specification EN 12591 (1999), two methods for the determination of wax content are included, the distillation method EN 12606-1 and the extraction method EN 12606-2. In both EN methods, paraffin wax is defined as “mixture of hydrocarbons crystallizing in an ether/ethanol 50% (V/V) mixture at temperatures down to -20 °C, obtained by a specified process and having a range of melting of above 25 °C” (Edwards, 2005).

The term wax generally refers to all waxlike solids and liquids found in nature and to those individual organic substances that crystallize on cooling and melt on heating. It has been demonstrated that, in crude oils, waxes may be paraffin type or microcrystalline type, depending on source of the crude oil. Unlike paraffin waxes, which consist primarily of n-alkanes, microcrystalline waxes are dominated by cycloalkanes and isoalkanes. Waxes from crude oils may also contain small amounts of aromatic carbon, as well as oxygen, present as acid or ketone (Lu and Redelius, 2006).

In bitumen, wax is the generic name given traditionally to straight-chain saturated hydrocarbons and is known as paraffin wax. The crystalline nature and nonsticky character of paraffin waxes was believed to cause negative effects on bitumen quality and on bitumen performance, such as being sensitive to permanent deformation (rutting), prone to low-temperature cracking, and having poor adhesion to aggregates. Accordingly, a limit on wax content has been taken as one of the specification criteria for bituminous materials in some countries (Lu and Redelius, 2006).

In recent work it was shown that bitumen wax, defined as the crystallizing material on the cooling of bitumen, not only consists of n-alkanes but also other types of molecules which were not further analyzed. Waxes differing in chemical composition can lead to different effects on bitumen properties and bitumen performance (Lu and Redelius, 2006).

Waxes of bitumen are found to be complex mixtures of hydrocarbons, such as n-alkanes with carbon number C_{15}-C_{57}, and isoalkanes, cycloalkanes, and aromatics which could be larger than C_{57}. Proportions of these different groups of compounds are strongly dependent on bitumen origins. For most of the bitumens studied, waxes are primarily composed of alkanes but differ greatly in the content and distribution of n-alkanes (Lu and Redelius, 2006).

2.2. Rubber Constitution

According to ASTM D 6814-02, rubber is a natural or synthetic elastomer that can be chemically crosslinked/vulcanized to enhance its useful properties.

There are two types of rubber: natural and synthetic. Natural rubber latex is obtained from the rubber tree called *Hevea braziliensis*. The raw rubber molecule is a long straight-chain isoprene hydrocarbon. The physical appearance of this hydrocarbon is of a spongy, flocculent nature. At temperatures below 100 °C this spongy rubber becomes stiff, hard whereas when warmed above 100 °C, it becomes flexible, soft and transparent (Rahman, 2004).

Crosslinked rubbers or elastomers are three-dimensional molecular networks, with the long molecules held together by chemical bonds. They absorb solvent and swell, but do not dissolve. Furthermore, they cannot be reprocessed simply by heating (Hamed, 1992).

2.2.1. Rubber production

In demanding uses, such as in tyres, engine mounts, and springs, rubbers are used exclusively because of their better elasticity, resistance to set, and durability (Hamed, 1992).

Synthetic rubbers are made from petroleum products and other minerals and produced in two main stages: (i) the production of monomers (small units' molecules), and (ii) the polymerisation to form a rubber. There are various types of synthetic rubber available for different applications. Some of them are: (i) Styrene-Butadiene Rubber (SBR, used in bitumen, tyres, etc); (ii) Silicon rubbers (used in gaskets, seals, etc); (iii) Fluorocarbon rubber (resistant to heat and chemical attack); and (iv) Epichlorohydrin rubber (jackets, hose, cable, packing, etc) (Rahman, 2004).

The properties of the rubber depend on how the molecules are arranged. There are three types of molecular arrangements: (i) linear, (ii) side branched and (iii) cross-linked (Rahman, 2004).

The addition of various chemicals to raw rubber to impart desirable properties is termed rubber compounding or formulation. Typical ingredients include crosslinking agents (curatives), reinforcements, anti-degradants, process aids, extenders, tackifiers, blowing agents, and colorants (Hamed*,* 1992).

The selection of appropriate curatives and fillers is critical to the rubber performance. General purpose elastomers are hydrocarbon polymers. They include styrene-butadiene rubber (SBR), butadiene rubber (BR), and polyisoprene rubber – both natural (NR) and synthetic (IR). These “diene” rubbers contain substantial chemical usaturation in their backbones, causing them to be rather susceptible to attack by oxygen, and especially by ozone. Additionally, they are readily swollen by hydrocarbon fluids. The primary application of these elastomers is in automobile and truck tires (Hamed*,* 1992).

One of the most well known natural polymers is polyisoprene, or natural rubber (NR). Ancient Mayans and Aztecs harvested it from the *Hevea* tree and used it to make waterproof boots and the balls which they used to play a game similar to basketball. It is an elastomer, that is, it recovers its shape after being stretched or deformed (Polymer Science Learning Center, 2005). Nowadays, NR is produced from the latex of the *Hevea brasiliensis* tree. Before coagulation, the latex is stabilized with preservatives (e.g., ammonia, formaldehyde, sodium sulphite) and hydroxylamine may be added to produce technically-specified, constant-viscosity grades of NR. The *Tg* of NR is about -70°C and its structure is thought to be completely *cis*-1,4-polyisoprene (Figure 2.24), except for the chain ends (Hamed*,* 1992).

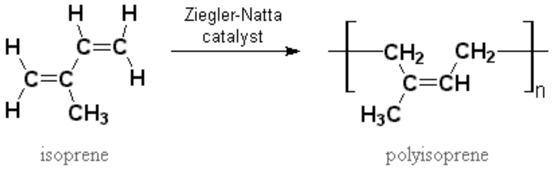


Figure 2.24 – Chemical structure, *cis*-1,4- polyisoprene (Polymer Science Learning Center, 2005)

Polyisoprene is a diene polymer, which is a polymer made from a monomer containing two carbon-carbon double bonds. Like most diene polymers, it has a carbon-carbon double bond in its backbone chain. Polyisoprene can be harvested from the sap of the *Hevea* tree, but it can also be made by Ziegler-Natta polymerization. This is a rare example of a natural polymer that we can make almost as well as nature does (Polymer Science Learning Center, 2005).

Natural rubber (Table 2.1) contains double bonds that promote sulphur vulcanization. Because NR macromolecules are configured identically (stereoregular), they spontaneously pack together as crystallites on standing at low temperature, with a maximum rate at temperatures around -25°C. NR also crystallizes upon straining. In fact, strain-induced crystallization imparts outstanding green strength and tack, and gives vulcanizates with high resistance to cut growth at severe deformations. However, NR macromolecules are susceptible to fracture on shearing. High shearing stresses and oxygen promote the rate of molecular chain scission (Hamed, 1992).

Table 2.1 – Carbon black-filled natural rubber formulation for general purpose engineering use (Hamed, 1992)

Ingredient	Amount (phr*) (*Parts by weight by 100 parts by weight of rubber)
Natural rubber	100
Process oil	5
Stearic acid	2
Zinc oxide	5
N-550 carbon black	25, 50 or 75
Phenylamine antioxidant	1.5
Sulphur	2.5
Cure accelerator: benzothiazyl disulfide	1.0
Cure accelerator: tetramethyl thiuram disulfide	0.1

Cure: 20 minutes at 150 °C

N550 carbon black	25	50	75
Shore A Hardness	51	62	72
300% Modulus (MPa)	7	9	11
Tensile Strength (MPa)	22	24	25
Breaking Elongation (%)	700	600	550

Synthetic polyisoprene rubber (IR) is produced both anionically and by Ziegler-Natta polymerization. The former material has up to 95% *cis*-1,4 microstructure, while the latter may be as much as 98% stereoregular. Even though the difference in stereoregularity is small, Ziegler-Natta IR is substantially more crystallisable. However, both types of IR have less green strength and tack than NR. IR compounds have lower modulus and higher breaking elongation than similarly formulated NR compositions (Hamed, 1992). This is due, at least in part, to less strain-induced crystallization with IR, especially at high rates of deformation (Hamed, 1992).

Butadiene rubber (BR) denotes a copolymer of styrene and butadiene, typically containing about 23% styrene, with a *Tg* of approximately -55°C. It is the most widely used synthetic elastomer, with the largest volume production. It is synthesized via free-radical polymerization as an emulsion in water, or anionically in solution. In emulsion polymerization, the emulsifier is usually a fatty acid or a rosin acid. The former gives a faster curing rubber with less tack and less staining. The molecular weight is controlled (to prevent gelition) by mercaptan chain transfer agents. When polymerization is complete, coagulation of the emulsion is carried out with salt, dilute sulphuric acid, or an alum solution. Alum coagulation results in a rubber with the highest electrical resistivity (Hamed, 1992).

Like isoprene, butadiene rubber (BR) can be synthesized anionically or via Ziegler-Natta catalysis. Cold emulsion BR is also available. Anionic BR, prepared in hydrocarbon solvent, contains about 90% 1,4 structure and 10% 1,2 (i.e., vinyl). The vinyl content can be increased by adding an amine or ether as co-solvent during polymerization. The 1,4 structure is an approximately equal mix of cis and trans. Because it consists of mixed isomers, anionically prepared BR does not crystallize. Emulsion BR has a mostly trans microstructure and also does not crystallize. On the other hand, the Ziegler-Natta product has very high cis content and can crystallize. The *Tg* of low-vinyl BRs is about -100 °C, among the lowest of all rubbers, while that of high-vinyl BRs can reach 0 °C. Low-vinyl BRs are highly resilient and are often blended with SBR, NR, and IR to make tyre treads with good abrasion resistance. Unlike NR, BR is resistant to chain scission during mastication (Hamed*,* 1992).

Polybutadiene (Figure 2.25) was one of the first types of synthetic elastomer, or rubber, to be invented and is very similar to natural rubber, polyisoprene. Tyres treads are often made of polybutadiene copolymers. Belts, hoses, gaskets and other automobile parts are made from polybutadiene, because it stands up to cold temperatures better than other elastomers. A hard rubber called SBS rubber or poly(styrene-butadiene-styrene) is a copolymer containing butadiene. Polybutadiene is a diene polymer or a polymer made from a monomer that contains two carbon-carbon double bonds, specifically butadiene. It is made by Ziegler-Natta polymerization (Polymer Science Learning Center, 2005).

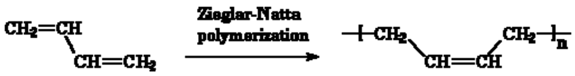


Figure 2.25 – Polymerization process of butadiene

Polyisobutylene (Figure 2.26) is a synthetic rubber developed during the early 1940s. It is the only rubber that is gas impermeable (can hold air for long periods of time). Being able to hold air, it is used to make the inner liner of tyres. Polyisobutylene, sometimes called butyl rubber, and other times PIB, is a vinyl polymer. It is very similar to polyethylene and polypropylene in structure, except that every other carbon is substituted with two methyl groups. It is made from the monomer isobutylene, by cationic vinyl polymerization (Polymer Science Learning Center, 2005).

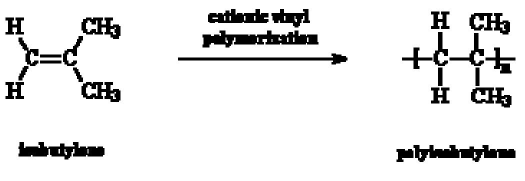


Figure 2.26 – Polymerization of isobutylene monomer (Polymer Science Learning Center, 2005)

Usually, a small amount of isoprene is added to the isobutylene. The polymerization is carried out at a right frosty -100 °C. Polyisobutylene is a copolymer of isobutylene with around one percent of isoprene (Polymer Science Learning Center, 2005).

When emulsion polymerization is carried out at an elevated temperature (superior to 50 °C), the rate of radical generation and chain transfer is high, and the polymer formed is highly branched. To overcome this, polymerization is carried out at low temperature (inferior to 5 °C), producing “cold” emulsion styrene-butadiene rubber (SBR), with less branching, and giving stronger vulcanizates (Hamed, 1992).

About one or two out of every hundred repeat units is an isoprene unit, shown in blue in Figure 2.27. These have double bonds, which mean the polymer can be crosslinked by vulcanization (Polymer Science Learning Center, 2005).

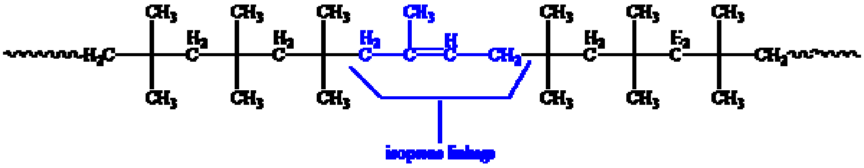


Figure 2.27 – Isoprene polymerization with isobutylene (Polymer Science Learning Center, 2005)

Poly(styrene-butadiene-styrene) or SBS (Figure 2.28) is a hard rubber that is used for the soles of shoes, tyre treads, and other places where durability is important. It is a type of copolymer called a block copolymer. Its backbone chain is made up of three segments. The first is a long chain of polystyrene, the middle is a long chain of polybutadiene, and the last segment is another long section of polystyrene (Polymer Science Learning Center, 2005).

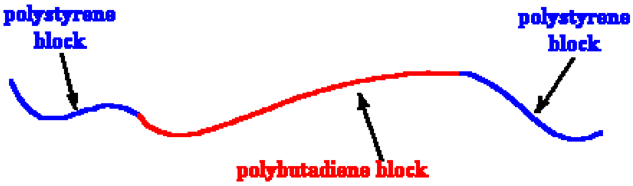


Figure 2.28 – Backbone chain of SBS

Polystyrene is a tough hard plastic, and this gives SBS its durability. Polybutadiene is rubbery, and this gives SBS its rubber-like properties. In addition, the polystyrene chains tend to clump together. When one styrene group of one SBS molecule joins one clump, and the other polystyrene chain of the same SBS molecule joins another clump, the different clumps become tied together with rubbery polybutadiene chains. This gives the material the ability to retain its shape after being stretched (Polymer Science Learning Center, 2005).

SBS is also a type of unusual material called a thermoplastic elastomer. These are materials that behave like elastomeric rubbers at room temperature, but when heated, can be processed like plastics.

Most types of rubber are difficult to process because they are crosslinked. But SBS and other thermoplastic elastomers manage to be rubbery without being crosslinked, making them easy to process into nifty useful shapes (Polymer Science Learning Center, 2005).

The production of SBS rubber starts using a technique called living anionic polymerization. A living polymerization is a polymerization that takes place without any termination reactions. This means that once all the monomer is used up, and has been turned into polymer, the polymer chains are still active. Thus, if more monomer is added, the polymerization reaction continues and makes the polymers bigger (Polymer Science Learning Center, 2005).

2.2.2. Rubber vulcanization

Straight out of the tree, natural rubber latex (polyisoprene) is not good for much. It gets runny and sticky when it is warm, and it gets hard and brittle when it is cold (Polymer Science Learning Center, 2005). However, when sulphur is added to rubber, it forms bridges among the rubber molecules, which tied all the polymer chains in the rubber together. This process is called crosslinking. Bridges made by short chains of sulphur atoms tie one chain of polyisoprene to another, until all the chains are joined into one giant supermolecule (Figure 2.29). An object made of a crosslinked rubber is in fact one single big molecule (Polymer Science Learning Center, 2005).

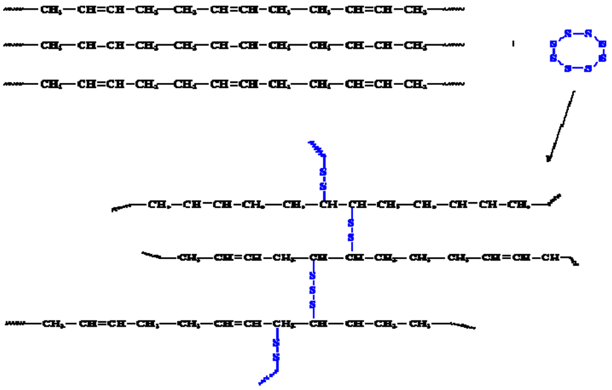


Figure 2.29 – Crosslinking process

Nowadays, two forms of sulphur are used in vulcanization: soluble (rhombic crystals of S_8 rings) and insoluble (amorphous, polymeric sulphur) (Hamed, 1992). Crosslinking with sulphur alone is quite inefficient and requires curing times of several hours. For every crosslink, 40 to 55 sulphur atoms are combined with the rubber. The structure contains polysulfide linkages, dangling sulphur fragments, and cyclic sulphides (Hamed, 1992).

As a result of crosslinking rubbers do not dissolve in solvents and do not flow at high temperatures. Figure 2.30 shows the difference between a single uncrosslinked polymer chains, and a crosslinked network (Polymer Science Learning Center, 2005).

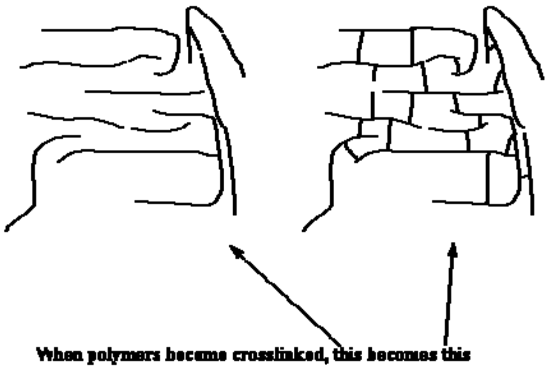


Figure 2.30 – Uncrosslinked and crosslinked rubber

Crosslinked polymers are usually moulded and shaped before they are crosslinked. Once crosslinking has taken place, usually at high temperature, the object can no longer be shaped.

An elastomer, as synthesized, is basically a high molecular weight liquid with low elasticity and strength. Although the molecules are entangled, they can readily disentangle upon stressing, leading to viscous flow. Vulcanization or curing is the process in which the chains are chemically linked together to form a network, thereby transforming the material from a viscous liquid to a tough elastic solid. Strength and modulus increase, while set and hysteresis decrease. Various curing systems are used to vulcanize different types of elastomers. The most widely used vulcanizing agent is sulphur. To be crosslinked with sulphur the elastomer must contain double bonds with *allylic* hydrogens. General purpose diene elastomers such as BR, SBR (Table 2.2), NR, and IR meet this basic requirement (Hamed, 1992).

Table 2.2 – Typical styrene-butadiene rubber (SBR) formulation (Hamed, 1992)

Ingredient	Amount (phr*) (*Parts by weight by 100 parts by weight of rubber)
SBR-1500	100
Process oil	4
Stearic acid	2
Zinc oxide	5
Antioxidant: DPPD	1.5
N-330 carbon black	50
Sulphur	2
Cure accelerator: benzothiazyl disulfide	2
Cure accelerator: tetramethyl thiuram disulfide	0.15

Cure: 25 minutes at 150 °C

	N330 carbon black
Shore A Hardness	65
300% Modulus (MPa)	13.5
Tensile Strength (MPa)	25
Breaking Elongation (%)	500

The mechanical behaviour of an elastomer depends strongly on its crosslink density, which is shown schematically in Figure 2.31 (Hamed, 1992). It shows that the modulus and hardness increase monotonically with crosslink density and the network becomes more elastic. Fracture properties such as tear and tensile strength pass through a maximum as crosslinking increases (Rahman, 2004).

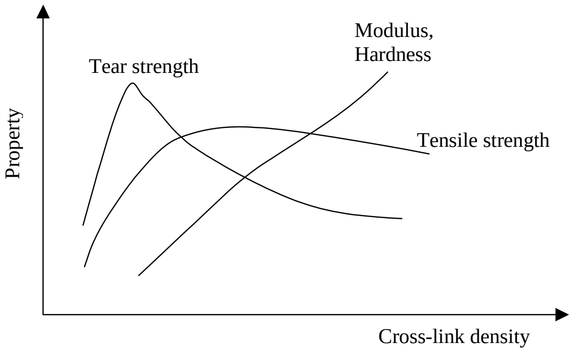


Figure 2.31 – Effect of crosslink density on some mechanical properties of rubber (Rahman, 2004)

Vulcanisation is the curing process of rubber, which transforms the raw rubber into a strong, elastic and rubbery hard state. There are two types of vulcanisation processes: hot (mould cured) and cold (pre-cure system). The hot process is used for the majority of rubber goods, including tyres. Cold vulcanisation is used to produce soft, thin rubber products such as surgical gloves or sheeting. Table 2.3 shows the effect of temperature on rubber (Rahman, 2004).

Table 2.3 – Effect of different temperatures on rubber (Rahman, 2004)

Base structure	Hard transparent and solid
-10 °C	Brittle and opaque
+20 °C	Soft, resilient and translucent
+50 °C	Plastic and sticky
120 °C -160 °C	Vulcanised when agents e.g., sulphur are added
>180 °C	Break down as in the masticator
200 °C	Decomposes

Natural rubber is insoluble with water, alkali and weak acids, but it is soluble in benzene, gasoline, chlorinated hydrocarbons and carbon bisulphate. While it is easily oxidised by chemical oxidising agents, atmospheric oxygen produces a very slow reaction. The most common vulcanisation is through sulphur. The proportion of sulphur agents to rubber varies from a ratio of 1:40 for soft rubber goods, to as much as 1:1 for hard rubber. The sulphur is ground and mixed with the rubber at the same time as the other dry ingredients during the compounding process. When rubber is heated with sulphur to a temperature between 120 °C and 160 °C, it becomes vulcanised by combining the sulphur agents with the rubber molecules and produces a cross-linking network, which makes the rubber stronger and more durable and contributes to improve tyre wear and durability. The reactions of rubber to temperature extremes are an important factor in their applicability that produces improved strength and elasticity as well as greater resistance to changes in temperature, impermeability to gases, resistance to abrasion, chemical action, heat, and electricity. Vulcanised rubber exhibits high frictional resistance on dry surfaces and low frictional resistance on water-wet surfaces, it has good abrasive resistance, flexibility, elasticity and electric resistance. Although vulcanisation converts soft rubber into a hard, usable stage, it is essential to add certain chemicals and additives to make it readily usable in commercial applications. This formulation process is called compounding (Rahman, 2004).

To increase the rate and efficiency of sulphur crosslinking, accelerators are normally added. These are organic bases and can be divided into five major categories: guanidines, thiazoles, dithiocarbonates, xanthates, and thiurams. Of these, the guanidine-type accelerators, such as diphenyl guanidine, give the lowest rate of vulcanization as well as a relatively slow onset of vulcanization. The accelerators that increase the rate of curing the most are the xanthate types. These ultra-accelerators cause crosslinking so readily that they are seldom used in solid rubber because curing would be initiated just from the heat generated while mixing. Rather, xanthates are used mainly for crosslinking rubber as a latex (Hamed, 1992).

The accelerators with the widest application are the thiazoles, a subcategory of which is the delayed-action sulphonamides. Compounds containing sulphonamides may be sheared for long times without premature vulcanization (scorch). This is particularly important in the tyre industry, where a compound may be mixed, repeatedly milled, and then calendared or extruded before being fabricated into a tyre. (Hamed, 1992). Thiurams and dithiocarbonates are considered ultra-accelerators, although they are not as active as the xanthates (Hamed, 1992).

Often, a combination of accelerators is used to obtain the desired scorch resistance and cure rate (Hamed, 1992). Accelerated sulphur curing is more efficient when the activators zinc oxide and steric acid are added. It is thought that these additives combine to create soluble zinc ions that activate intermediate reactions involved in crosslink formation (Hamed, 1992).

When an elastomer is deformed by an external force, part of the input energy is stored, elastically in the chains is available (released upon crack growth) as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat, and in this manner, is made unavailable to break chains. Elastomers have an optimum crosslink density range for practical use. Crosslink levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure (Hamed, 1992). Both the level and type of crosslinking are important. When curing with sulphur, the type of crosslinks depends on (1) sulfur level (2) accelerator type (3) accelerator/sulphur ratio and (4) cure time (Hamed, 1992).

Extenders are added to rubber compositions to reduce cost. Usually, this results in a decrease in physical properties, which limits the amount of extender that can be used. Oil extension of rubber, especially in tyre treads, is widely practiced (Hamed, 1992). Other types of extenders are particulate solids with primary particle sizes greater than about 1 mm. These stiffen rubber compositions, but either have little effect on strength or diminish it. Examples include clay, calcium carbonate, and ground coal (Hamed, 1992).

Tack is the ability of two materials to resist separation after being in contact for a short time under light pressure. Tackifiers are a class of resins added to elastomers to improve tack. Several types are available (Hamed, 1992):

1. Resin derivatives that are chemical mixtures of abietic and related acids are usually esterified by polyhydric alcohols, then hydrogenated, dimerized, or disproportioned to improve aging and heat stability;
2. Coumarone-indene resins consisting of indene, coumarone, styrene, methyl styrene, methyl indene, etc., are obtained from coal coke oven light oils;
3. Aliphatic petroleum resins made from unsaturates obtained while cracking crude oil;
4. Terpene oligomers of alpha- or beta-pinene obtained from pine tree stumps;
5. Alkyl modified phenol-formaldehyde resins.

A tackifier must be compatible with the rubber. This is dependent on chemical composition and molecular weight. For modified phenolics, the para-alkyl group must be large, t-butyl or greater, to improve compatibility with a non-polar hydrocarbon elastomer. When the alkyl group is t-octyl, the most effective tackifying action occurs at a molecular weight of about 2000 (Hamed, 1992).

Peroxides are another type of curing agent for elastomers. Unlike sulphur vulcanization, carbon-carbon double bonds are not required for peroxide curing and thus, peroxides may be used to crosslink saturated elastomers, e.g., ethylene-propylene copolymers, chlorinated polyethylene, chlorosulphonated polyethylene, and silicone rubber. In addition, peroxides readily crosslink diene elastomers. Peroxide curing takes place via a free-radical mechanism and leads to carbon-carbon crosslinks, which are quite stable. The crosslinked materials show good aging resistance and low compression set (Hamed, 1992).

2.2.3. Rubber swelling

Crosslinked materials can absorb solvents. A piece of a crosslinked material that has absorbed a lot of solvent is called a *gel* (Polymer Science Learning Center, 2005).

In practice, rubbers in contact with fluids will swell. The properties of the rubbers under swelling are also subject to dynamic or continuous changes (Kumnuantip and Sombatsompop, 2003). The swelling process is fully reversible and there is no change in composition (such as removal of non-crosslinked or oligomeric components) of the rubber induced by the swelling process (Kariyo and Stapf, 2004).

From the point of view of molecular dynamics, swelling of networks should be fully equivalent to dilution of the uncrosslinked species in a solvent, as long as fast motions are regarded which are not yet affected by the presence of fixed points. The addition of solvent molecules reduces the interchain interactions and lubricates the chain motion, until the concept of a polymer tube loses its meaning and the individual chains move relatively freely in the solvent (Kariyo and Stapf, 2004).

The mechanical response of swollen rubbers changes qualitatively in going from low to high cross-link densities (Douglas and McKenna, 1993).

Frenkel (1940) and Flory and Rehner (1943) introduced some fundamental hypotheses relating to the swelling of rubber and the changes of rubber elasticity associated with this swelling, that is, (1) the free energy of mixing and the elastic free energy in swollen networks are additive and (2) the elastic strain energy density function is “invariant” to swelling (Douglas and McKenna, 1993).

The swelling of dry polymer networks is a rather unique phenomenon. Lightly cross-linked dry networks can absorb large quantities of certain fluids and increase their volume by orders of magnitude without appreciable change of shape. The cross-links give these highly swollen materials a remarkable rigidity (Douglas and McKenna, 1993). Swelling changes the number of cross-links per unit volume and stretches the chains. In this view swelling is like any other kind of deformation (a stretch is a stretch, regardless of its mechanical or thermodynamic origins). The compression experiments of McKenna *et al.* (1988, 1989, 1990) are consistent with this simple picture (Douglas and McKenna, 1993).

Compatibility of the swelling liquid and the rubber may be assessed by comparing the solubility parameters of the components. The solubility parameter for rubber ranges from 17.8 to 20.8 MPa$^{1/2}$ (Gawel *et al.*, 2006).

2.2.4. Tyres production

The tyre manufacturing process is similar to the manufacture other rubber products. The main difference between the two processes is that the building process for manufacturing tyres is generally more complex because there are many rubber components (EPA, 2005). As shown in Figure 2.32, the tyre production process in its most basic form consisting in sequential steps (EPA, 2005).

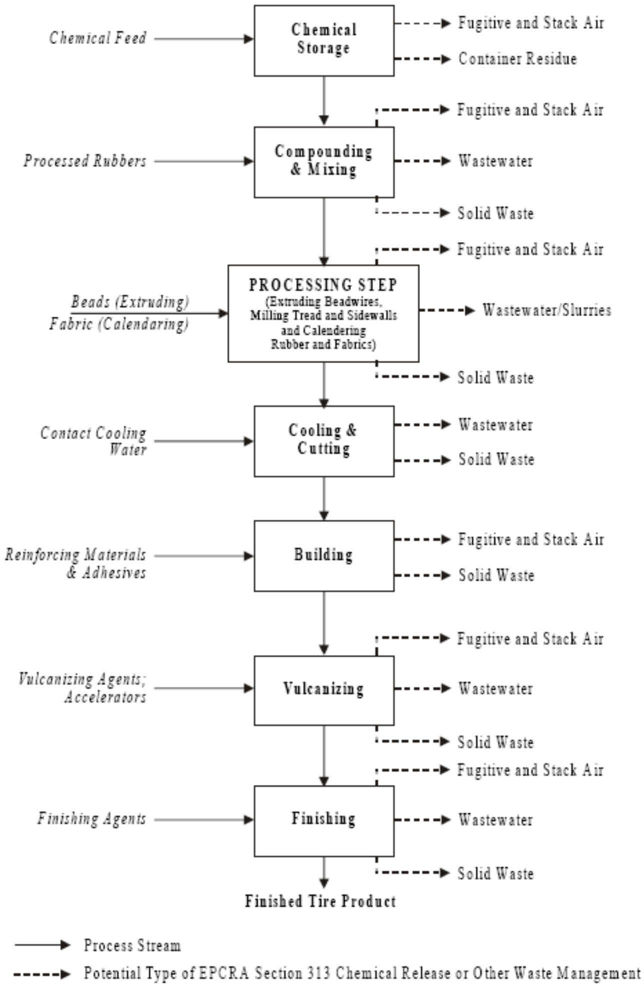


Figure 2.32 – Tyre manufacturing process (EPA, 2005)

The tyre production process begins with compounding and mixing of elastomers, carbon blacks, and pigments. The process begins with mixing basic rubbers with process oils, carbon black, pigments, antioxidants, accelerators and other chemicals such as vulcanizing agents, accelerators, plasticizers, and initiators, each of which contributes to a certain property of the compound. These ingredients are mixed in Banbury mixers operating at high temperature and pressure. The many ingredients are blended into a hot, black gummy compound that will be milled again and again (EPA, 2005).

The cooled rubber takes several forms. Most often it is processed into carefully identified slabs that will be transported to breakdown mills. These mills feed the rubber between massive pairs of rollers, over and over, feeding, mixing, and blending to prepare the different compounds for the feed mills, where they are slit into strips and carried by conveyor belts to become sidewalls, treads or other parts of the tyre (EPA, 2005).

Extruding operations use warming mills and either a hot or cold extruder. The equipment forces the rubber compound through dies that create individual or a continuous sidewall and tyre tread components for future tyre building (EPA, 2005).

Processing fabrics and coating them with rubber is a calendering operation. A specific rubber coats the fabric that is used to make up the tyre's body. The fabrics come in huge rolls, and they are as specialized and critical as the rubber blends. Many kinds of fabrics are used, including polyester, rayon, and nylon (EPA, 2005).

It has high-tensile steel wire forming its backbone, which will fit against the vehicle's wheel rim. The strands are aligned into a ribbon coated with rubber for adhesion, then wound into loops that are then wrapped together to secure them until they are assembled with the rest of the tyre (EPA, 2005).

Tyres are manually built on one or two tyre machines. The tyre starts with a double layer of synthetic gum rubber called an inner liner that will seal in air and make the tyre tubeless. The operator uses the tyre building machine to pre-shape tyres into a form very close to their final dimension to make sure the many components are in proper position before the tyre goes into the mold. The resulting tyre is called a “green” tyre, which is uncured (EPA, 2005).

The lubrication or spraying system provides a coating, primarily silicon, on the green tyre to afford mould release after curing (EPA, 2005).

The curing press is where tyres get their final shape and tread pattern. Hot moulds like giant waffle irons shape and vulcanize the tyre. The moulds are engraved with the tread pattern, the sidewall markings of the manufacturer, and those required by law (EPA, 2005).

The finishing and quality assurance operations include balancing, grinding, and painting and marking the tyre (EPA, 2005). Figure 2.33 also represents in a more clear way the process of tyre production.

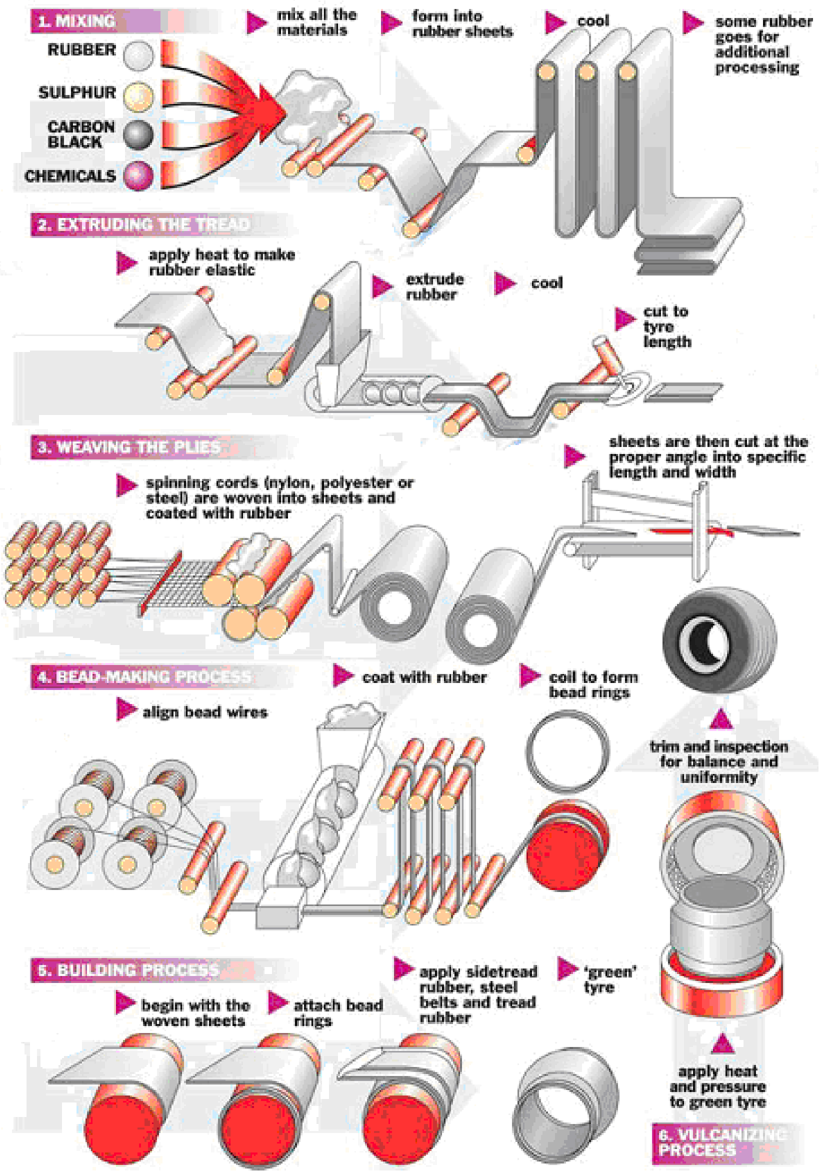


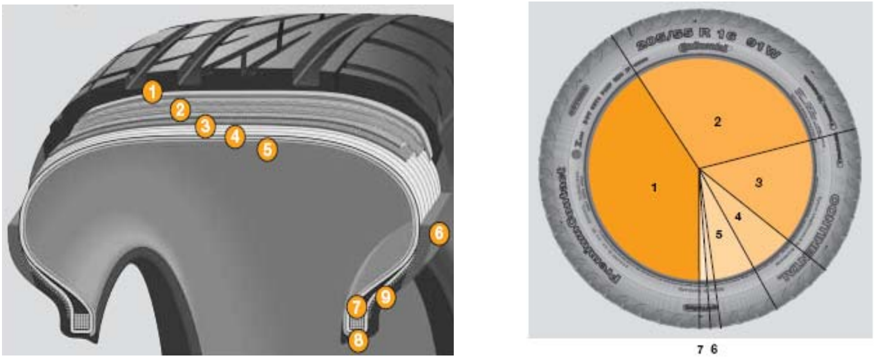
Figure 2.33 – Tyre production (Bridgestone, 2008)

A tyre is made up of three main materials: (i) elastomeric compound, (ii) fabric and (iii) steel. The fabric and steel form the structural skeleton of the tyre with the rubber forming the “flesh” of the tyre in the tread, side wall, apexes, liner and shoulder wedge. The tyre skeleton consists of beads made of steel or fabric depending on the tyre application, which form the “backbone” in the toe of the tyre. The beads are designed to have low extensibility and provide reinforcement for the rubber tyre. The tyre has a series of reinforcing cords or belts that extend from bead to bead transversely over the tyre (Rahman, 2004).

The belts are made of nylon fabric or steel but more commonly both types are used. The rubber treads then cover the belts providing the contact area for the tyre on the pavement. The objective of the skeleton is to reinforce the tyre to allow it to perform well without greatly deforming (Rahman, 2004).

The inherent characteristics of tyres are the same worldwide. They include the resistance to mould, mildew, heat and humidity, retardation of bacterial development, resistance to sunlight, ultra-violet rays, some oils, many solvents, acids and other chemicals. Other physical characteristics include their non-bio-degradability, non-toxicity, weight, shape and elasticity. However, many of the characteristics, which are beneficial during their on-road life as consumer products, are disadvantageous in their post-consumer life and can create problems for collection, storage and/or disposal. Modern tyres have extremely high load bearing capacity up to fifty times of its own weight. The compressed air within the tyre carries 90% of the load. The complex structure of the shell or casing of the tyre is designed to carry the remaining 10% (Rahman, 2004).

Rubber from car tyres (Figure 2.34) is mainly a combination of styrene-butadiene rubber and natural rubber (Gawel *et al.*, 2006).



Tread/belt assembly consisting of	①	Tread – for good road grip and water expulsion
	②	Jointless cap plies – enable high speeds
	③	Steel-cord belt plies – optimise directional stability and rolling resistance
Casing, consisting of	④	Textile cord ply – keeps the tyre in shape even with high inflation pressure
	⑤	Inner liner – makes the tyre airtight
	⑥	Side wall – protects from lateral damage
	⑦	Bead apex – promotes directional stability, steering performance and comfort level
	⑧	Bead core – ensures firm seating on the rim
	⑨	Bead reinforcement – promotes directional stability and precise steering response

1	Rubber (natural and synthetic rubber)	41%
2	Fillers (carbon black, silica, carbon, chalk ...)	30%
3	Reinforcing materials (steel, rayon, nylon)	15%
4	Plasticizers (oils and resins)	6%
5	Chemicals for vulcanisation (sulphur, zinc oxide, various other chemicals)	6%
6	Chemicals as antioxidants (to counter ozone effects and material fatigue)	1%
7	Miscellaneous	1%

Figure 2.34 – Car tyres production (Continental, 2008)

To improve the mechanical and chemical properties of rubber (e.g. tyre) further different compounds and additives are blended into raw rubber, namely activators (e.g. ZnO_2), accelerators (e.g. MgO, fatty acids, amines), ageing retardant (e.g. metal-oxides, polychloroprene), fillers (e.g. $BaSO_4$, $MgCO_3$, $CaCO_3$), and others. Generally metal-oxides, fatty acids, amines and different glycols are used as activators and accelerators (Miskolczi *et al.*, 2008).

As it is well known, the elemental composition of rubbers is very different in the case of each tyre producer, but the widely used tyres always contain Zn, S, Si, Fe, Mg, and occasionally P or F (Miskolczi *et al.*, 2008). In general, truck tyre rubber (Figure 2.35) contains larger percentages of natural rubber compared to that from car tyres (Artamendi and Khalid, 2006).

		Material	Function
1	**Tread strip**	Rubber compound	The tread strip has to provide high wear resistance and good grip under all road conditions. In some instances the tread strip combines two different materials (cap and base); the base is there to minimise the tread tem-perature and the rolling resistance.
2	**Multi-ply steel belt**	Steel cords embedded in rubber compound	Enhances driving stability, reduces rolling resistance and gives the tyre its long service life. Restricts casing growth and increases the tyre's structural strength.
3	**Steel casing**	Steel cord	Gives the tyre its structural strength and its deflection characteristics; substantially determines driving comfort.
4	**Inner lining**	Rubber compound	Major factor in preventing diffusion of air and moisture in tubeless tyres.
5	**Sidewall**	Rubber compound	Protects from lateral scuffing and the effects of the weather.
6	**Bead reinforcement**	Nylon, aramide, steel cord	Securing the end of the steel cord ply on the bead core. Reinforcing the bead against high shear forces.
7	**Bead core**	Steel wire embedded in rubber compound	Ensures the tyre sits firmly on the rim.

1	Natural rubber	19 kg	30%
2	Synthetic rubber	3 kg	5%
3	Halogen butyl rubber	2.5 kg	4%
4	Other chemicals (accessory agents, plasticiser, preservative, vulcanising agents)	24 kg	37%
5	Core wire (electro-plated steel wire)	3.5 kg	6%
6	Nylon fabric	0.5 kg	1%
7	Steel cord (electro-plated stranded steel wire)	11 kg	17%

Figure 2.35 – Truck tyres production (Continental, 2008)

The proportion of natural and synthetic rubber varies according to the size and use of the tyre. The generally accepted rule of thumb is that the larger the tyre and the more rugged its intended use, the greater will be the ratio of natural to synthetic rubber (Rahman, 2004).

The most important component of a tyre is the elastomer (natural and synthetic rubber). The second most important component of a tyre is carbon black. This is not a generic product, which means that wide ranges of specific grades of carbon black are used depending upon the compounding formula used by the individual manufacturer. Carbon black is mainly used to enhance rigidity in tyre treads (to improve traction, control abrasion and reduce aquaplaning) and to add flexibility and reduce heat build up in sidewalls (Shulman, 2000). The particle size of the carbon black, as defined by its specific surface area and structure, impacts upon its integration and utilisation in compounding (Rahman, 2004).

The third largest component is steel, mainly high grade steel. This provides rigidity, and strength as well as flexibility to the casing. New, higher strength metals are being tested by tyre manufacturers, some which are said to resist rusting as well as deterioration, which could impact upon the way that the tyre is recycled (Rahman, 2004).

The most common traditional textiles used in rubber are nylon, rayon and polyester. In recent years, a range of new textiles, primarily amarid, which is an ultra-light weight material, have been substituted for more traditional materials, primarily in the more expensive tyres (Rahman, 2004).

2.2.5. Crumb rubber production

The life cycle of a consumer product is defined as the time span of the product serving the purpose for which it was created. The life span for a tyre is approximately 5-7 years during which time a tyre can be retreaded. It comprises three principal periods: new, continued use (continued chain of utility), and consignment to a waste treatment system (end of tyre life). A post consumer tyre, which may or may not have a structurally sound casing or residual tread depth suitable for further road use, will be discarded and/or consigned to another use, such as scrap tyres in road construction. The brief life cycle of a tyre is shown in Figure 2.36 (Rahman, 2004).

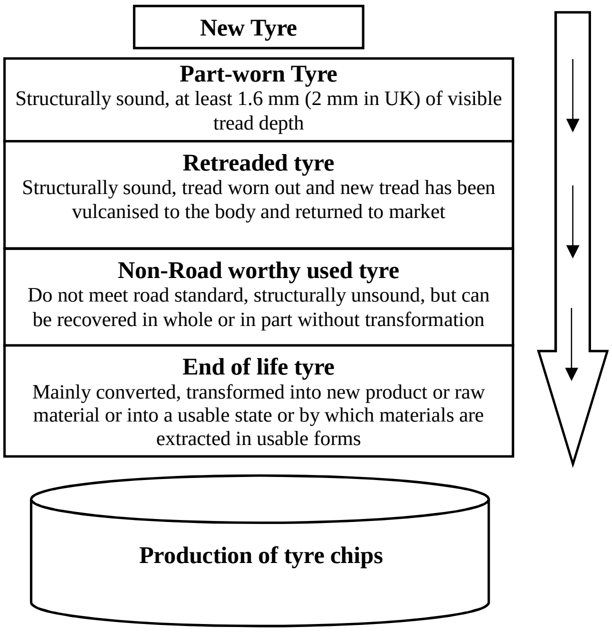


Figure 2.36 – Flow chart of the service life of a tyre (Rahman, 2004)

Once the tyre is permanently removed from a vehicle, it is defined as waste (scrap tyre). A scrap tyre can be useable in different forms, such as a whole tyre, a slit tyre, a shredded or chipped tyre, as ground rubber or as a crumb rubber product. In the following paragraphs a brief description of the use of scrap tyres will be outlined (Rahman, 2004).

Although the majority of truck tyres are steel-belted radial, there are still a number of bias ply truck tyres, which contain either nylon or polyester belt material. Scrap tyres have a heating value ranging from 28000kJ/kg to 35000 kJ/kg, which is the same as coal. Therefore they have been widely used as a cement-making fuel worldwide for the last ten years (Rahman, 2004).

The life span for a tyre is approximately 5-7 years before being defined as waste (scrap tyre). The scrap tyre can be usable in different forms including production of crumb rubber (CR) for asphalt mixtures (Rahman, 2004). Crumb rubber used in hot mix asphalt normally has 100 percent of the particles finer than 4.75 mm. The majority of the particle sizes range within 1.2 mm to 0.42 mm. Some crumb rubber particles may be as fine as 0.075 mm. The specific gravity of the crumb rubber varies from 1.10 to 1.20 (depending on the type of production) and the product must be free from any fabric, wire and/or other contaminants (Rahman, 2004).

The initial step in the production of ground or granulated scrap tyre rubber is shredding. Scrap tyre rubber is delivered to rubber processing plants either as whole tyres, cut tyres (treads or sidewalls), or shredded tyres, with shredded tyres being the preferred alternative. As scrap, the rubber is processed, the particle sizing is reduced, steel belting and fibre reinforcing are separated and removed from the tyre, and further size reduction is then accomplished (Chesner *et al.*, 1998). Crumb rubber can be produced by one of three processes. The granulator process produces cubical, uniformly shaped particles ranging in size from 9.5 mm (3/8 in) down to 0.4 mm (No. 40 sieve), which is called granulated CR. The crackermill process, which is the most commonly used, produces irregularly shaped torn particles sized from 4.75 mm (No. 4 sieve) to 0.42 mm (No. 40 sieve), referred to as ground CR. The micro-mill process produces a very fine ground CR, usually ranging from 0.42 mm (No. 40 sieve) down to as small as 0.075 mm (No. 200 sieve) (Epps, 1994). In the wet process, ground CR is normally used with the McDonald technology and very fine ground CRM is used with the Florida technology (Chesner *et al.*, 1998).

To produce crumb rubber, it is usually necessary to further reduce the size of the tyre shreds or chips. The ambient and cryogenic processes are the two main methods normally used to produce crumb rubber (Rahman, 2004). The preliminary treatment of scrap tyres (debeading, pre-shredding) is pretty much the same in ambient and cryogenic plants.

- **Ambient Scrap Tyre Processing**

Ambient grinding can be classified in two ways: granulation and crackermill. Typically, the material enters the crackermill or granulator at “ambient” or room temperature. The temperatures rise significantly during the grinding process due to the friction generated as the material is being “torn apart”. The granulator reduces the rubber size by means of a cutting and shearing action. A screen within the machine controls product size. Screens can be changed according to end product size. Rubber particles produced in these methods normally have a cut surface shape and are rough in texture, with similar dimensions on the cut edges. Crackermills are low speed machines and the rubber is usually passed through two to three mills to achieve various particle size reductions and further liberate the steel and fibre components. The crumb rubber produced in the crackermill process is typically long and narrow in shape and has high surface area (Rahman, 2004).

The schematic in Figure 2.37 is an example of a typical ambient scrap tyre recycling plant. The process is called ambient, because all size reduction steps take place at or near ambient temperatures, i.e. no cooling is applied to make the rubber brittle (Reschner, 2006).

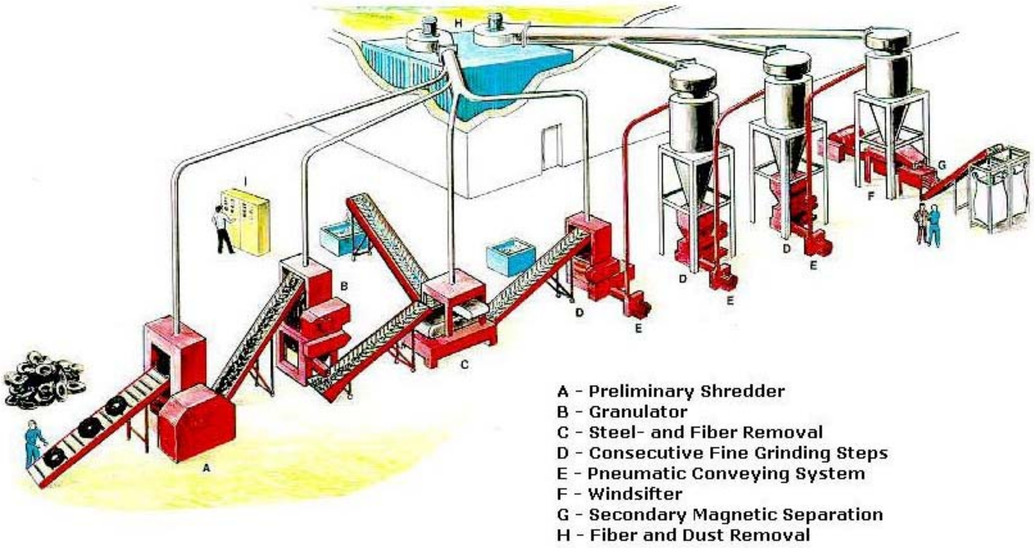


Figure 2.37 – Schematic of an ambient scrap tyre processing plant (Reschner, 2006)

In this plant layout, the tyres are first processed into chips of 2” (50 mm) in size in a preliminary shredder (A). The tyre chips then enter a granulator (B). In this processing step the chips are reduced to a size smaller than 3/8” (10 mm), while liberating most of the steel and fibre from the rubber granules. After exiting the granulator, steel is removed magnetically and the fibre fraction is removed by a combination of shaking screens and wind sifters (C) (Reschner, 2006).

While there is some demand for 3/8” rubber granules, most applications call for finer mesh material, mostly in the range of 10 to 30 mesh. For this reason, most ambient grinding plants have a number of consecutive grinding steps (D). The machines most commonly used for fine grinding in ambient plants are (Reschner, 2006):

- Secondary granulators;
- High speed rotary mills;
- Extruders or screw presses;
- Cracker mills.

Ambient grinding can be operated safely and economically if the bulk of the rubber output needs to be relatively coarse material, i.e., down to approximately 20 mesh material (Reschner, 2006).

- **Cryogenic Tyre Recycling**

This process is called "cryogenic" because whole tyres or tyre chips are cooled down to a temperature of below -80 °C. Below this "glass transition temperature" rubber becomes nearly as brittle as glass and size reduction can be accomplished by crushing and breaking (Reschner, 2006). The use of cryogenic temperatures can be applied at any stage of size reduction of scrap tyre. Typically, the size of the feed material is a nominal 50 mm chip or smaller. The material is cooled in a tunnel-style chamber or immersed in a "bath" of liquid nitrogen to reduce the temperature of the rubber or tyre chip. The cooled rubber is ground in an impact type reduction unit, usually a hammer mill. This process reduces the rubber to particles ranging from 6 mm to less than 0.85 mm. Steel from the scrap tyre is normally separated out of the product by using magnets. The fibre is removed by aspiration and screening. The resulting material appears shiny, clean, with fractured surfaces and low steel and fibre content due to the clean breaks between fibre, steel and rubber (Rahman, 2004).

This type of size reduction requires less energy and fewer pieces of machinery when compared to ambient size reduction. Another advantage of the cryogenic process is that steel and fibre liberation is much easier, leading to a cleaner end product. The drawback, of course, is the cost for liquid nitrogen (LN_2) (Reschner, 2006).

The crumb rubber industrial process takes place in three stages (Recipneu, 2006):

1. Shredding raw material;
2. Cryogenic processing;
3. Bagging and storage.

Shredding raw material consists of fragmenting light and heavy tyres into small, homogeneously cut pieces – the "chips" (Recipneu, 2006).

Cryogenic processing (Figure 2.38) performs the complete and individualized separation of rubber, steel and textiles without noticeable waste or losses in material. This is a continuous, automatically controlled process which takes place under an inert nitrogen atmosphere (Recipneu, 2006).

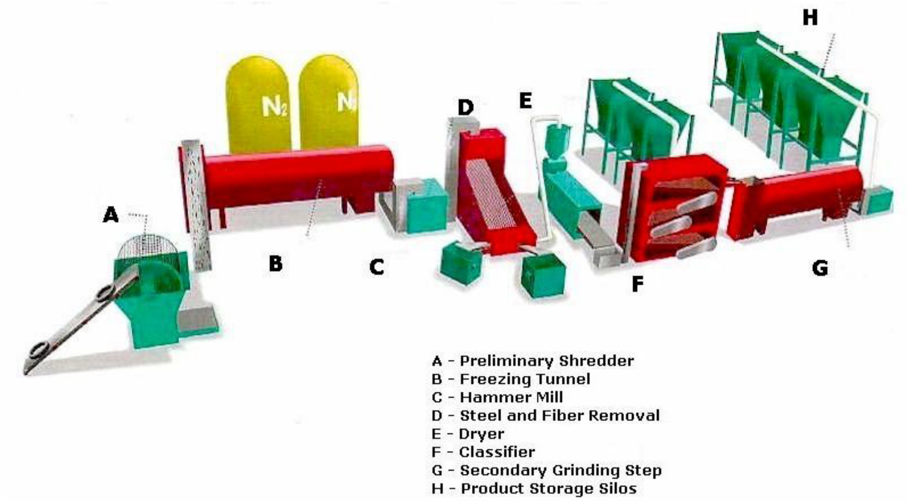


Figure 2.38 – Schematic of a cryogenic scrap tyre processing plant (Reschner, 2006)

In the cryogenic cooling the 2” (50 mm) tyre chips are dropped into a long continuously operating freezing tunnel (B), and are cooled down by the action of liquid nitrogen at around -196 °C, resulting in a cold exchange between the chips at room temperature and the liquid nitrogen. When the chips are cooled to a temperature of -80 °C, the glass transition point (Tg) is reached for all the rubber polymers of the tyre, and then the “rubber” behaves like glass (Recipneu, 2006).

The tyre chips are then dropped into a high RPM hammer mill (C). In the hammer mill, the chips are shattered into a wide range of particle sizes, while, at the same time, liberating fibre and steel. Because the rubber granules may still be very cold upon exiting the hammer mill, the material is dried (E) before classification into different, well defined particle sizes (F) (Reschner, 2006).

The separation, drying, sorting and purifying of the various materials follows the next steps and lead to the completion of the process (Recipneu, 2006):

- Separation of textiles using a shaker screen and different suction profiles;
- Magnetic separation of steel;
- Drying the granulated rubber;
- Sieving the rubber into different standard sizes;
- Elimination of dust and steel contaminations.

From the cryogenic line, the granulate that is obtained moves on to various silos, where it is put into big-bags over palettes, made of synthetic raffia fibre, which can carry up to 1.2 tons. The packaged product is then stored until delivery (Recipneu, 2006).

Generally speaking, cryogenic scrap tyre processing is more economical if clean, fine mesh rubber powder is required (Reschner, 2006). In the cryogrinding process the equipment cost is less, operating costs are lower, productivity is increased, and the product has better flow characteristics than ambient ground rubber (Adhikari *et al.*, 2000).

The cryogenic technology allows the efficient production of rubber powders and very small rubber granules, with negligible steel or textile contaminations, and minimizes the wastes obtained in the recycling operation. The cryogenic products obtained maintain the molecular structures of the initial rubber polymers, which are not degraded in this process by side reactions of oxidation, devulcanization, or scission/reduction of molecular weights (Recipneu, 2006).

Crumb rubber used in hot mix asphalt normally has 100 percent of the particles finer than 4.75 mm. Although the majority of the particles used in the wet process are sized within the 1.2 to 0.42 mm range, some crumb rubber particles may be as fine as 0.075 mm, thus being more adequate to use the cryogenic technology for this utilization of CR. The specific gravity of crumb rubber is approximately 1.15, and the product must be free of fabric, wire, or other contaminants (Chesner *et al.*, 1998).

Crumb rubber is classified as number one, two and so on, depending on quality and size. Table 2.4 presents a summary of CR grades. However, crumb rubbers produced in industry should maintain certain quality requirements with respect to their grades and specifications. ASTM D5603-96 and ASTM D5644-96 are the two most widely used standards for crumb rubber grading (Rahman, 2004).

Table 2.4 – Crumb rubber specification (Rahman, 2004)

Grade	Size	Description
No. 1 and 2 tyre granule (minus 40 grades)	6.35 mm to less than 0.635 mm	Guaranteed metal free. Magnetically separated materials are not acceptable. Fluff from tyre cord removed. Less than 0.635 mm refers to material that has been sized by passing through a screen with 40 holes per centimetre (referred as minus mesh 40 grades).
No. 3 tyre granule (minus 4 grades)	less than 6.35 mm	Magnetically separated materials (these materials cannot be certified as metal free due to residual metal/oxide content. Metal is magnetically separated. Fluff from tyre cord removed. Less than 6.35 mm refers to material that has been sized by passing through a screen with 4 holes per centimetre.
No. 4 tyre granule (minus 80 grades)	6.35 mm to less than 0.3175 mm	Magnetically separated. Fluff from tyre cord removed. Less than 0.3175 mm refers to material that has been sized by passing through a screen with 80 holes per centimetre.

Crumb rubber properties have been reported to affect conventional binder properties. Oliver (1981) found that natural rubber tends to be superior to synthetic rubber for elastic properties and that synthetic rubber is more stable than natural rubber with regard to the interaction conditions of time and temperature. Earlier studies reported that truck tyres are considered rich in natural rubber, while passenger tyres are rich in synthetic rubber. Recent studies and reports show the difference between truck tyre rubber and passenger tyres has been reduced (Jensen and Abdelrahman, 2006).

2.2.6. Devulcanization of tyre rubber

According to ASTM D 6814-02, devulcanization is the process of breaking down chemical crosslinks of cured rubber.

In chemical terms, devulcanization means reverting rubber from its cured, elastic state back into a plastic, mouldable state. This is accomplished by breaking the sulphur bonds of the molecular structure. With the proper devulcanization method (Table 2.5), a much higher percentage of crumb rubber from old tyres can be used as compounding (Reschner, 2006).

Table 2.5 – Important devulcanization methods (Reschner, 2006)

Devulcanization	Process Description
Thermal Reclaim Process	Rubber is exposed to elevated temperatures over an extended period of time in order to break the sulphur bonds as well as the polymer back bone. This process was first patented by H. L. Hall in 1858, but is rarely used today due to environmental concerns and relatively severe degradation of the material.
Mechanical Devulcanization	Vulcanized rubber is exposed to intense mechanical work (mastication) in order to selectively break the sulphur bonds in the polymer matrix. The machines used are two roll mills, high shear mixers and extruders. Mechanical devulcanization method leads to good results and may be economically viable in the near future.
Devulcanization with Ultrasound	Technically speaking, this is a special form of mechanical devulcanization. First research results on this subject are encouraging.
Bacterial Devulcanization	Fine rubber powder is exposed to an aqueous suspension with bacteria that consume sulphur and sulphur compounds, e.g., thiobacillus, rodococcus und sulpholobus. Technically viable, but questionable economics due to the complexity of the process.

3. RHEOLOGICAL AND PHYSICAL CHARACTERIAZATION OF MATERIALS

3.1. Rheological Characterization of Materials

3.1.1. Rheology definition

The science of rheology is only about 70 years of age. It was founded by two scientists meeting in the late 20s having the same need for describing fluid flow properties. The scientists were Professor Marcus Reiner and Professor Eugene Bingham (Alcantara, 2003). The Greek philosopher Heraclitus described rheology as $\pi\alpha\nu\tau\alpha \quad \rho\varepsilon\iota$ – everything flows. Translated into rheological terms by Marcus Reiner this means everything will flow if you just wait long enough (Alcantara, 2003).

Rheology, literally, means the study of flow (from the Greek words $\dot{\rho}\varepsilon\tilde{\omega}$ – to flow, and $\lambda\delta\gamma o\varsigma$ – word, science). This is science concerned with almost all aspects of deformation of real bodies under the influence of external stresses (Ferguson and Kemblowski, 1991). The concepts of rheology can and should be used to define the characteristics of bituminous binders, due to the importance of the time-dependent deformation or creep response that occurs when a the material is subjected to static or dynamic loads or both (Tia and Ruth, 1985).

Deformation and flow of the asphalt binder is important in determining pavement performance. Pavements that deform and flow too much may be susceptible to rutting and bleeding while those that are too stiff may be susceptible to fatigue or thermal cracking. Pavement deformation is closely related to asphalt binder rheology (Glover, 2007).

Fluid rheology is used to describe the consistency of different products, normally by the two components viscosity and elasticity. By viscosity is usually meant resistance to flow or thickness and by elasticity usually stickiness or structure (Alcantara, 2003).

The study of bitumen rheology is an important phenomenon to characterise the dynamic mechanical behaviour of binders. Bitumen is a thermoplastic, viscoelastic material. Viscoelasticity is a rate dependent material characterisation that includes a viscous contribution to the elastic straining. This means, bitumen, as a viscoelastic material, behaves as glass-like elastic solid at low temperature or during high loading frequencies and as viscous fluid at high temperatures or low loading frequencies. The thermal and mechanical deformation of bitumen can be defined by its stress-strain-time and temperature response (Rahman, 2004).

3.1.2. Rheology fundaments

Fluids are usually divided into three different groups according to their flow behaviour (Alcantara, 2003):

- Newtonian fluids;
- Non-Newtonian fluids, time independent;
- Non-newtonian fluids, time dependent.

Flow curves (Figure 3.1) are normally used for the description of flow behaviour (Alcantara, 2003).

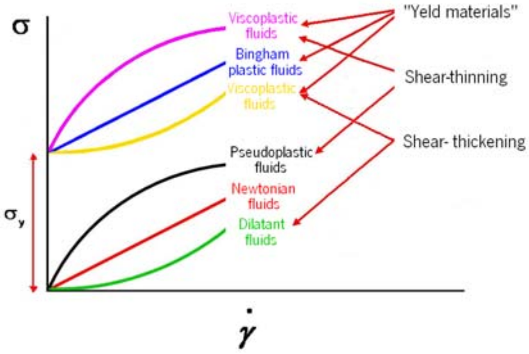


Figure 3.1 – Flow curves of fluids with and without yield stress (Ferguson and Kemblowski, 1991)

Various models for approximation of rheological data have been presented (Table 3.1). One of the most widely spread models is the so-called power law for approximation of viscosity data. The main reason for the power law being so popular is that the shearing rheological behaviour of a fluid is represented simply by a straight line in a log-log shear rate/shear stress graph. Another reason is that the shearing behaviour of most fluids lends itself to a good approximation applying the power law (Alcantara, 2003).

Table 3.1 – Mathematical models for flow behaviour

Newtonian	$\sigma = h\dot{\gamma}$
Shear thinning	$\sigma = K\dot{\gamma}^n \ (n < 1)$
Shear thickening	$\sigma = K\dot{\gamma}^n \ (n > 1)$
Bingham	$\sigma = \sigma_0 + \eta_p\dot{\gamma}$
Herschel-Bulkley	$\sigma = \sigma_0 + K\dot{\gamma}^n$
Casson	$\sigma^{1/2} = \sigma_0^{1/2} + \eta_\infty^{1/2}\dot{\gamma}^{1/2}$

σ = shear stress; $\dot{\gamma}$ = shear rate; σ_0 = yield stress; $\eta_{p,\infty}$ = limiting viscosity

Kinematic viscosity is measured with kinematic instruments, normally different types of cups which mean that the knowledge and control of shear rates is limited or non-existent. Thus, kinematic viscosity values are of little or no use for design of equipment for non-Newtonian fluids (Alcantara, 2003).

Dynamic viscosity takes into account the effect of shear rate and time and is therefore the only type of viscosity relevant for non-Newtonian design purposes. Dynamic viscosity is measured with dynamic instruments, either rotating (shearing) or oscillating (Alcantara, 2003).

An instrument capable of measuring shearing viscosities is called a viscometer and the oscillating type is called a rheometer (Alcantara, 2003).

All materials, from gases to solids, can be divided into three following categories of rheological behaviour (Alcantara, 2003):

- Viscous materials – in a purely viscous material all energy added is dissipated into heat;
- Elastic materials – in a purely elastic material all energy added is stored in the material;
- Viscoelastic materials – a viscoelastic material exhibits viscous as well as elastic behaviour.

Typical examples of viscoelastic materials are bread dough, polymer melts and artificial or natural gels.

In most cases of viscoelastic behaviour the time factor has a significant impact on the flow properties observed (Figure 3.2). A measure of the influence of time is the so-called Deborah Number or De, expressed by Equation 3.1 (Alcantara, 2003):

$$\text{De} = \text{Response time} \ / \ \text{Observation time} \qquad (3.1)$$

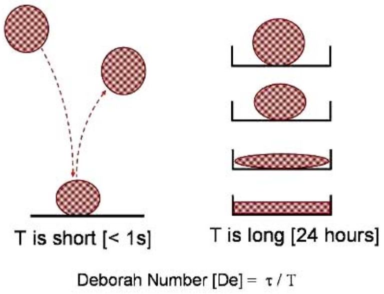


Figure 3.2 – Schematic representation a viscoelastic material behaviour

An example of a system having a large Deborah Number is a normal glass window. If old enough (e.g. an old church window), a difference in thickness at the top and at the bottom can be easily measured. Although the viscosity of glass is high, about 1040 Pa.s, it is still a liquid and consequently it flows. However, the observation time has to be long, perhaps a couple of centuries to observe the movement. When shearing a viscoelastic fluid so-called normal stresses will appear. These normal stresses can result in flow behaviour quite different from that of Newtonian fluids (Alcantara, 2003).

3.1.3. Rheological measurements

Rheological measurements are normally performed in kinematic instruments in order to get quantitative results useful for design and development of products and processing equipment. For design of products (e.g. in the food, cosmetic or paint industry), rheological measurements are often performed to establish the elastic properties, such as gel strength and yield value, both important parameters affecting particle carrying and spreading ability. For design of process equipment the properties during shearing of the product is of prime interest. Those properties are established in a normal viscosity measurement (Alcantara, 2003).

A rheological measurement normally consists of a strain (deformation) or a stress analysis at a constant frequency (normally 1 Hz) combined with a frequency analysis (e.g. between 0.1 and 100 Hz). The strain sweep gives information of the elastic modulus – G', the viscous modulus – G'' and the phase angle – δ. A large value of G' in comparison of G'' indicates pronounced elastic (gel) properties of the product being analysed. For such a product the phase angle is also small (a phase angle of 0° means a perfectly elastic material and a phase angle of 90° means a perfectly viscous material). The frequency sweep gives information about the gel strength where a large slope of the G' curve indicates low strength and a small slope indicates high strength (Alcantara, 2003).

The complex shear modulus (Equations 3.2 and 3.3) is a measure of the overall resistance to deformation (Khalid, 2005).

$$G^* = \sigma^* / \gamma \tag{3.2}$$

$$G^* = G' + i \cdot G'' = \sqrt{G'^2 + G''^2} \tag{3.3}$$

Where:

σ^* – Complex stress (Pa);

γ – Strain;

G* – Complex shear modulus (Pa);

G' – Elastic or storage modulus (Pa);

G'' – Viscous or loss modulus (Pa).

A viscosity measurement normally consists of a shear rate analysis. The shear rate sweep should preferably cover the range applied in the intended equipment (Alcantara, 2003).

Viscoelastic materials have high mechanical damping and mechanical vibrations and do not build up easily at natural frequencies and high temperatures. It is normal practice to use oscillatory type testing for doing dynamic mechanical analysis (DMA) to investigate the rheology of a viscoelastic material, like bitumen. DMA allows the viscous and elastic nature of the bitumen to be determined over a wide range of temperatures and loading times. In the dynamic test (Figure 3.3), the material is subjected to an oscillatory shear strain (Equation 3.4) of angular frequency ω (Rahman, 2004).

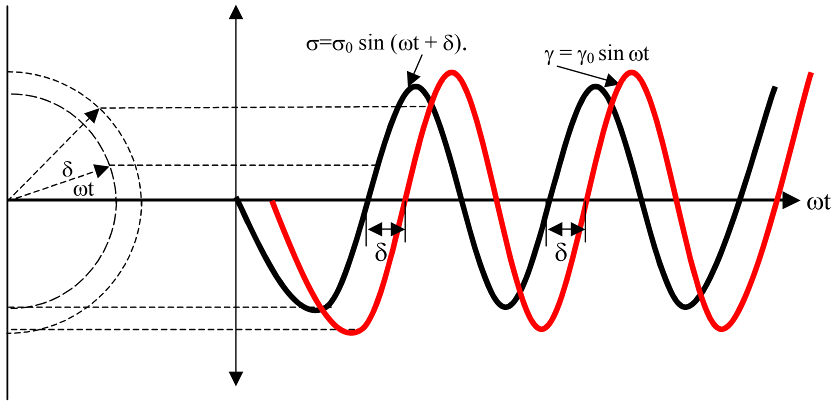


Figure 3.3 – Stress-strain response of a viscoelastic material (Rahman, 2004)

$$\gamma = \gamma_0 \sin \omega t \tag{3.4}$$

Where:

$\omega = 2\pi f$ – the angular frequency of the sinusoidal strain (rad/s);

f – the frequency of the sinusoidal strain (Hz);

γ_0 – maximum strain amplitude.

For linear viscoelastic material the stress response is also sinusoidal, but is out of phase as shown in Equation 3.5 or in the expanded Equation 3.6 (Rahman, 2004).

$$\sigma = \sigma_0 \sin(\omega t + \delta) \tag{3.5}$$

$$\sigma = (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t \tag{3.6}$$

Where:

σ_0 – maximum stress (Pa);

δ – phase angle (°).

The stress equation consists of two components, in phase with the strain ($\sigma_o \cos\delta$) and 90° out of phase ($\sigma_o \sin\delta$). The relationship between stress and strain can be defined by Equation 3.7.

$$\sigma = \gamma\left[G'\sin\omega t + G''\cos\omega t\right] \tag{3.7}$$

The values of G' and G'' (Equations 3.8 and 3.9) is obtained from Equations 3.6 and 3.7.

$$G' = \frac{\sigma_o}{\gamma_o}\cos\delta \tag{3.8}$$

$$G'' = \frac{\sigma_o}{\gamma_o} sen\delta \tag{3.9}$$

Thus the component of the stress $G'\gamma_o$ is in phase with the oscillatory strain and the component $G''\gamma_o$ is 90° out of phase (Rahman, 2004).

The combination of Equations 3.8 and 3.9 gives the phase angle δ (Equation 3.10), which is a measure of the viscoelastic character of a material (Khalid, 2005).

$$tg\delta = \frac{G''}{G'} \tag{3.10}$$

The EN 14770, the European standard for the dynamic shear rheometer (DSR) test (Figure 3.4), describes a procedure for the determination of the complex shear modulus and phase angle using that rheometer. Isotherms of G* (Pa) and δ (°) against frequency (Hz) are the basic test results. The test has been standardised in the USA as AASHTO TP5-97. Penetration has been correlated with DSR measurements (FEHRL, 2006).

The DSR is a dynamic oscillatory test apparatus that can be used to describe the linear viscoelastic properties of bitumen over a range of temperatures and frequencies. It applies a sinusoidal shear strain to a sample of bitumen sandwiched between two parallel disks and is shown schematically in Figure 3.5. The amplitude of the stress is measured by determining the torque transmitted through the sample in response to the applied strain. As the DSR only takes two measurements, namely torque and angular rotation, the remaining mechanical properties are calculated by using these two parameters (Rahman, 2004).

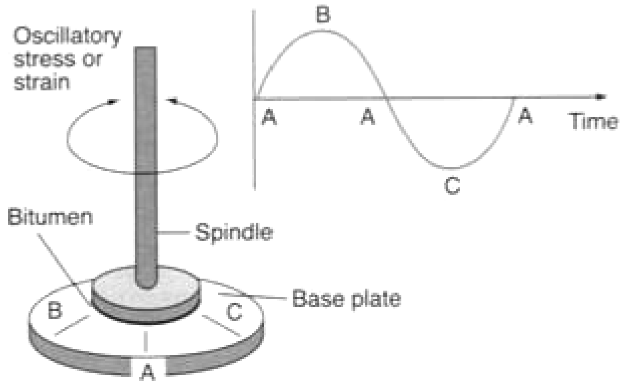


Figure 3.4 – Schematic of DSR mode of test (FEHRL, 2006)

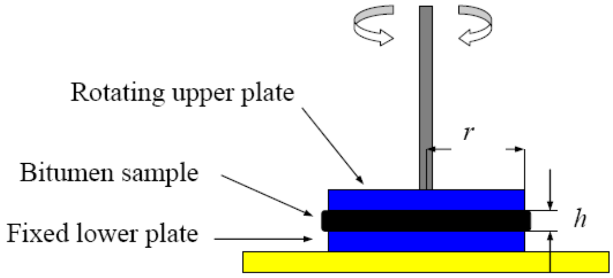


Figure 3.5 – Testing geometry of DSR (Khalid, 2005)

The basic Equations 3.11 and 3.12 are used to calculate the stress and strain parameters.

$$\tau = \frac{2T}{\pi r^3} \tag{3.11}$$

Where:

τ – maximum shear stress (N/mm^2);

T – torque (N.m);

r – radius of the parallel disks (mm) (Figure 3.5).

$$\gamma = \frac{\theta r}{h} \tag{3.12}$$

Where:

γ – shear strain;

θ – deflection angle (radians);

h – gap between parallel disks (mm) (Figure 3.5).

Therefore, from the calculation of strain and stress, the absolute complex modulus (G*) can be calculated according to Equation 3.13.

$$G^* = \frac{\tau_{\max}}{\gamma_{\max}} \tag{3.13}$$

The shear stress and strain in Equations 3.11 and 3.12 are dependent on the radius of the parallel disks and vary in magnitude from the centre to the perimeter of the disk. The shear stress, shear strain and complex modulus are calculated for the maximum value of radius. The phase angle (δ) is measured automatically using the instrument by accurately determining the sinusoidal waveforms of the strain and torque. The edge of the sample should be curved to get better results. Various parallel disk sizes can be used during DSR testing and the size of the disk that should be used to test the bitumen decreases as the expected stiffness of the bitumen increases. In other words, the lower the testing temperature, the smaller the diameter of the disk that needs to be used to accurately determine the dynamic properties of the bitumen (Rahman, 2004).

- **DSR setup and calibration**

The applied strain during DSR testing must be kept small to ensure that the test remains in the linear viscoelastic region. A linear region may be defined at small strains where the shear modulus is relatively independent of shear strain. This region will vary with the magnitude of the complex modulus and, therefore, the strains should be kept small at low temperatures and increased at high temperatures. The linear region can be found by plotting complex modulus versus shear strain from stress or strain sweep tests. According to Strategic Highway Research Program (SHRP), the linear region can be defined as the point where complex modulus decreases to 95% of its maximum value as shown in Figure 3.6 (Rahman, 2004).

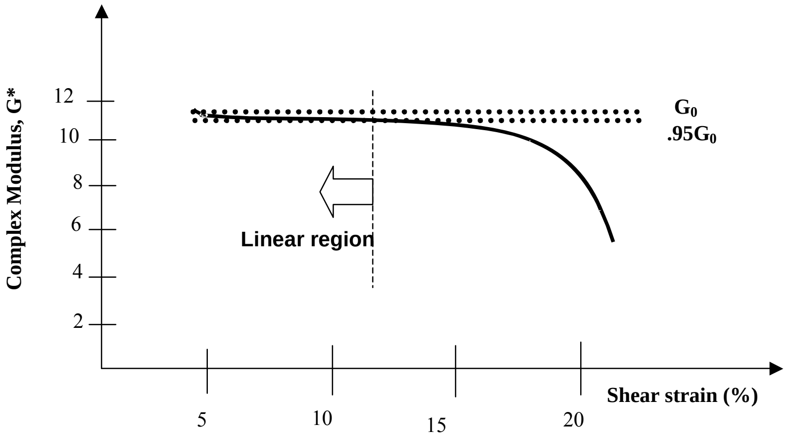


Figure 3.6 – Strain sweep to determine linear region (Rahman, 2004)

The testing configuration of the DSR consists of a number of different parallel plate and cone/plate geometries to measure a wide range of bitumen stiffness. Different disk sizes and suggested testing temperatures have been proposed by various researchers based on different sample types. The most widely used method, presented in Table 3.2 (Rahman, 2004), is suggested by SHRP Project A-002A.

Table 3.2 – SHRP suggestion of disk diameters for DSR rheology testing (Rahman, 2004)

Disk diameter	Test temperature range	Typical G* range
8 mm	0 °C to +40 °C	10^5 Pa to 10^7 Pa
25 mm	+40 °C to +80 °C	10^3 Pa to 10^5 Pa
40 mm	> 80 °C	$<10^3$ Pa

The proper choice of disk (plate) size or specimen should be dictated by the stiffness of the test specimen, rather than temperature. For instance, at low temperatures, large disks measure stresses lower than the true value while in contrast reducing the plate diameter improves the results although it does not appear possible to measure the limiting elastic stiffness of 10^9 Pa using a DSR (Rahman, 2004).

Goodrich (1988) and Collins *et al.* (1991) studied dynamic oscillatory tests on thick bitumen samples, 1 to 2.5 mm and 1.5 mm to 2.2 mm respectively. However, the gap height between the two parallel disks is generally in the range between 0.5 to 1.0 mm and it is also recommended that when the complex shear modulus of the bitumen is greater than approximately 30 MPa, parallel plate geometry should not be used as the compliance of the rheometer can be sufficient to cause errors in the measurements. According to SHRP, the following guidelines should be used (Rahman, 2004).

- Bending beam rheometer (BBR) or torsional bar geometry when G* > 30 MPa;
- 8 mm parallel plates with a 2 mm gap when 0.1 MPa < G* < 30 MPa;
- 25 mm parallel plates with a 1 mm gap when 1 kPa < G* < 100 kPa;
- 40 mm parallel plates with a gap ≤ 1 mm when G* < 1kPa.

Although these recommended guidelines provide a useful indication of plate and gap geometry, care should be taken when using them over wide frequency sweeps and for different binders. This is particularly relevant at the transitions between the different sample geometries and, therefore, it is recommended that there should be an overlap of rheological testing with two disk and gap configurations being used at the transition points (Rahman, 2004).

Regular calibration of temperature and torque is essential to maintain reasonable repeatability and reproducibility of the rheological data. The circulating fluid (water or air) from the temperature control unit should be constant during testing as small variations in temperature significantly change the results. Most DSR manufacturers use standard fluid to carry out calibration to confirm constant temperature, displacement and torque. The problem with using this standard liquid is that it has low viscosity in comparison with bitumen. Therefore, it can be misleading when measuring high bitumen stiffness (Rahman, 2004).

There is no European standard for the binder fatigue test (Figure 3.7). In the test, a fatigue crack is induced by applying continuous oscillatory shear loading with a rheometer. It has been shown that the DSR can only be used to evaluate fatigue properties in a narrow stiffness or temperature region. The fatigue phenomena due to the repeated of traffic loads imposed on binders is reputed to produce large deformations. Therefore, binders have to be tested in the non-linear region in order to accumulate significant damage (FEHRL, 2006).

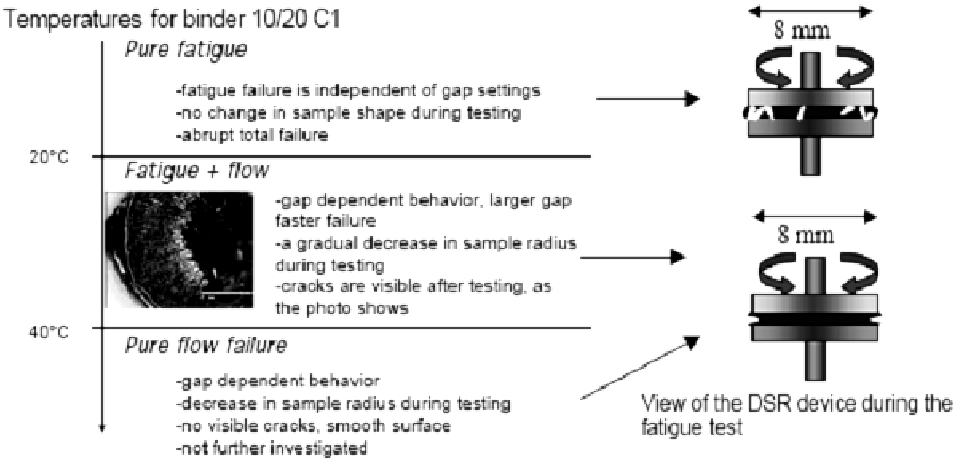


Figure 3.7 – Schematic phenomena taking place in the DSR during fatigue testing (FEHRL, 2006)

- **Rheological Data Representation**

Dynamic shear tests can be performed at different temperatures and frequencies to measure stiffness and phase angle. There are different techniques of data presentation available to represent the results graphically. However, the most commonly used representative methods are discussed below.

An isochronal plot is a curve, which represents the behaviour of a system at a constant frequency or loading period. In the dynamic test, the data can be presented over a range of temperatures at a given frequency. This technique has distinctive advantages as it gives a clear idea of the mechanical properties (complex modulus, phase angle) and temperature susceptibility in a single plot with different temperatures. A typical isochronal plot is presented in Figure 3.8 (Rahman, 2004).

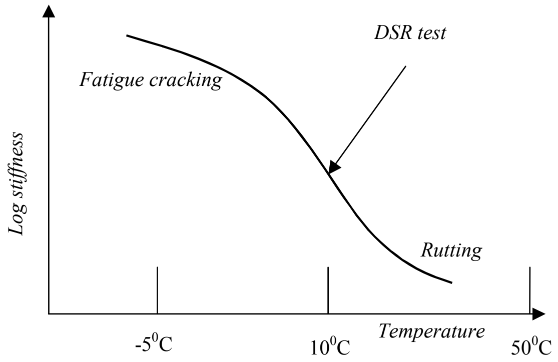


Figure 3.8 – Typical isochronal plot (Rahman, 2004)

An isothermal plot or isotherm is an equation, or a curve on a graph, representing the behaviour of a system at a constant temperature. In this type of plot, data at a given temperature is plotted over a range of frequencies or loading durations. The curve can be used to compare different viscoelastic functions at different loading times at a constant temperature (Figure 3.9). In addition, this type of plot can be used to study the time dependency of the material. As DSR testing is only performed over a limited frequency range, it is impossible to represent a wide range of rheological properties in an isothermal plot. Therefore, master curves are used to extend the data over a wider range of loading times using the time temperature superposition principle (Rahman, 2004).

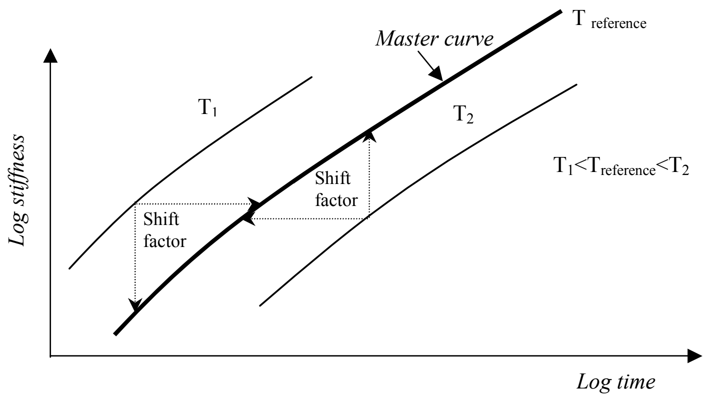


Figure 3.9 – Typical isothermal plot and generated master curve (Rahman, 2004)

Time temperature superposition principle (TTSP) used in analysing dynamic mechanical data involves the construction of master curves. Work done by various researchers, have found that there is an interrelationship between temperature and frequency (or temperature and loading time) which, through shifting factors, can bring measurements done at different temperatures to fit one overall continuous curve at a reduced frequency or time scale. This continuous curve represents the binder behaviour at a given temperature for a large range of frequencies. The principle that is used to relate the equivalency between time and temperature and thereby produce the master curve is known as the time-temperature superposition principle or the method of reduced variables (Rahman, 2004).

Master curves are used to present the extended data (mechanical properties) over a wide range of loading times and frequencies in one graph (several years of loading time). In their simplest form, master curves are produced by manually shifting modulus versus frequency plots (isotherms) at different temperatures along the logarithmic frequency axis to produce a smooth curve. A numerical factor, called the shift factor, is used to shift the data at a specific temperature to the reference temperature (Figure 3.9). Breaks in the smoothness of the master curve indicate the presence of structural changes with temperature within the bitumen, as would be found for waxy bitumen, highly structured "GEL" type bitumen and polymer-modified bitumen (Rahman, 2004).

According to di Benedetto and de La Roche (1998), besides the isochronal, isothermal and master curves, the rheological behaviour of the materials can also be represented in the Cole-Cole plane (i.e. G'' *vs.* G') and in the Black space (i.e. G* *vs.* δ).

3.1.4. Other rheological bitumen tests besides DSR

The bending beam rheometer (BBR) test is a three-point bending-beam test (Figure 3.10), designed to characterise the low-temperature behaviour of bituminous binders. The test determines the flexural creep stiffness of bituminous binders in the range of 30 MPa to 1 GPa by means of the bending beam rheometer. The bending beam rheometer is used to measure the mid-point deflection, in three-point bending, of a beam of bituminous binder (FEHRL, 2006).

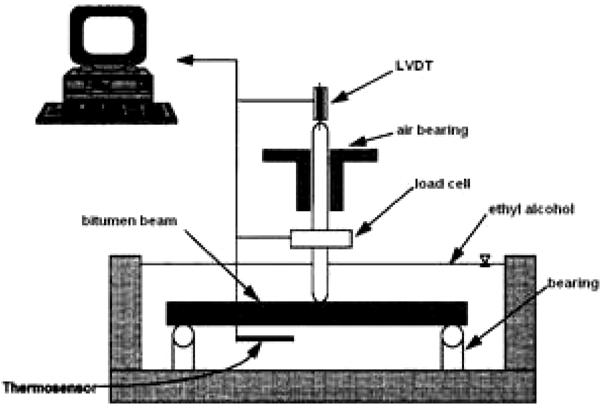


Figure 3.10 – BBR experimental setup (FEHRL, 2006)

The test has been standardised in the USA as ASTM D 6648-01. There is a broad correlation with the Fraass breaking point for paving grade bitumens and also some suggestion with polymer modified bitumens (PMBs) (FEHRL, 2006).

There are two European standard tests for measuring viscosity with capillaries in the capillary viscometer test (FEHRL, 2006):

- EN 12595 (1999) specifies a method for the determination of kinematic viscosity of bituminous binders at 60 °C and 135 °C, in the range from 6 mm^2/s to 300 000 mm^2/s. Results from the method can be used to calculate dynamic viscosity if the density of the material is known or can be assessed. This method is usually used to determine the viscosity of unmodified bitumen at 135 °C;
- Standard EN 12596 (1999) specifies a method for the determination of dynamic viscosity by vacuum capillary of bituminous binders at 60 °C, in the range from 0.0036 Pa.s to 580 000 Pa.s. This method is usually used to determine viscosity of unmodified bitumen at 60 °C.

These methods are not suitable for measuring modified bitumen. EN 12595 has been standardised in the rest of the world as ASTM D 2170-95 and EN 12596 (1999) as ASTM D 2171-94 (FEHRL, 2006).

The coaxial cylinder viscosity test, described in European standard EN 13702-2 (2003) has been developed for modified binders, but it is suitable for all types of bituminous binders (FEHRL, 2006). The cone and plate viscosity test of EN 13702-1 (2003) can be used as an alternative. The coaxial cylinder viscosity test and cone and plate viscosity test are similar tests (FEHRL, 2006).

It has been stated that “originally, the penetration was related to the steady state dynamic viscosity, which is difficult to measure below the ‘Ring and Ball’ temperature. The correlation between the penetration and the dynamic viscosity has been reconfirmed repeatedly” (FEHRL, 2006).

The creep zero shear viscosity test is described in CEN TC 336/WG1/TG1. The test is a binder creep test, designed to measure zero shear viscosity (ZSV or η_0). ZSV is also referred to as the first Newtonian viscosity and is believed to be a suitable indicator to evaluate the partial contribution of the bituminous binder (including polymer modified binders) to the rutting resistance of asphalt (FEHRL, 2006).

The repeated creep test was designed to determine the resistance of the binder to permanent deformation under conditions of repeated loading and unloading cycles. An AASHTO test protocol has been published in NCHRP report 459 (2002) (FEHRL, 2006). This model yields the value of the viscosity η_0 of the serial dashpot of Burger’s model, which is responsible for the permanent deformation component. The creep stiffness G_V, calculated from Equation 3.14, is proposed as an indicator for the resistance to permanent deformation (FEHRL, 2006). The repeated creep test has not yet been standardised in Europe (FEHRL, 2006).

$$G_v(t) = \frac{\eta_0}{t} \qquad (3.14)$$

The direct tensile test (DTT) is a procedure used to measure the strain at failure and stress at failure in an asphalt binder test specimen pulled at a constant rate of elongation. It can be used with unaged or aged material (FEHRL, 2006). Strain at failure is used as the criterion for specifying the low temperature properties of asphalt binders in accordance with the SHRP binder classification in conjunction with the BBR test (FEHRL, 2006).

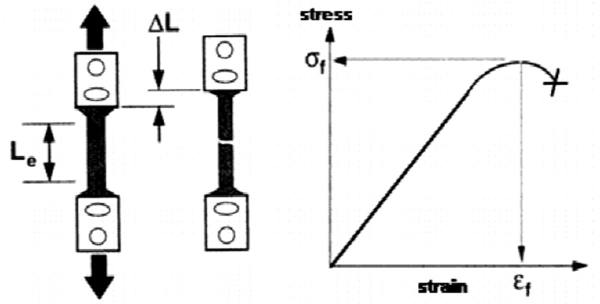


Figure 3.11 – DTT measurement principle (FEHRL, 2006)

The direct tensile test is not yet standardised in Europe. However, the test has been standardised in AASHTO standards TP3-98 and T314. The combination of the BBR and DTT results can be used to determine a critical thermal cracking temperature (FEHRL, 2006).

The method and calculation of the deformation energy using the force ductility test are described in EN 13589 (2003) and EN 13703 (2003) (FEHRL, 2006). The primary use of the force ductility test is to distinguish between modified and unmodified bitumen. Polymer-modified bitumen is specified in EN 14023 (FEHRL, 2006).

The tensile test (EN 13587, 2003) and the Vialit test (EN 13588) are also used for assessing the cohesive properties of bitumen (FEHRL, 2006).

The Fraass breaking point test provides a measure of the brittleness of bitumen and bituminous binders at low temperatures (FEHRL, 2006). The European standard for Fraass breaking point is EN 12593 (1999). There is a broad correlation of the Fraass breaking point test with the BBR for unmodified bitumen and also some suggestion with PMBs (FEHRL, 2006).

The resistance to fracture of a material is known as its fracture toughness (FEHRL, 2006). There are no specific standards for the fracture toughness of bitumen. The fracture toughness test (FTT) used to test bitumens has been developed for fracture toughness testing of metals. Some example of this test are UK BS 7448, ASTM standards (ASTM E1820-01; ASTM E1290-02), and the European Structural Integrity Society (ESIS) procedures (ESIS P1-92, 1992; ESIS P2-92, 1992) (FEHRL, 2006).

The compressional rheometer (Figure 3.12) is able to measure complex shear modulus (G*), storage modulus (G') and loss modulus (G'') without the need for delicate air bearings and motor necessary for a typical controlled stress rheometer (Bell and Claxton, 2000) (FEHRL, 2006).

This oscillatory squeeze flow rheometer is currently not included in any CEN standard test method because it has only recently been introduced (FEHRL, 2006). It has been concluded that, on the basis of both the quality of the data and the speed with which measurements can be made, this instrument combines the measurement of the rheological properties of bitumens, with the ability to rapidly predict traditional properties. The oscillatory squeeze flow rheometer was designed as an alternative to the dynamic shear rheometer (DSR) (FEHRL, 2006).

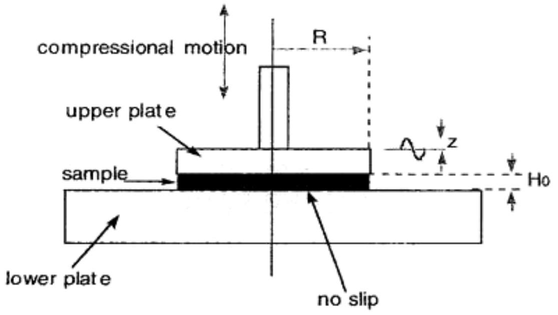


Figure 3.12 – Schematic of operation of compressional rheometer (FEHRL, 2006)

By the application of the oscillation zero shear viscosity test described in CEN TC 336 WG1/TG1, it is possible to perform an oscillation test as an alternative to the creep zero shear viscosity test in order to determine the zero shear viscosity (ZSV, again notated as η_0) (FEHRL, 2006).

3.2. Physical Properties of Binders

There are several conventional physical property tests to evaluate the quality and consistency of manufactured bitumens. These tests are standardised in numerous specifications, (e.g. British specifications, ASTM and European standards). However, all these methods are practically identical with negligible differences. Consistency tests are one of the main types of conventional tests that describe the degree of fluidity of bitumen at any particular temperature (Rahman, 2004).

3.2.1. Penetration

The penetration test is an empirical method to measure the consistency of the bitumen. The test method is described in BS 2000, Part 49, 1983, in the Institute of Petroleum (IP) as IP 49/83 and in ASTM D5. According to BS 2000 Part 49, penetration is defined, as the distance a standard needle loaded with a 100 g weight will penetrate into a bitumen sample for 5 seconds. Usually penetration is measured at 25 °C, which also approximates the average service temperature of the hot mix asphalt (HMA) pavements. However, other temperatures with different needle loads and penetration times may be used as well. In addition, Gershkoff (1991) developed a relationship (Equation 3.15) between empirical penetration tests results and the measured fundamental stiffness of the bitumen tested at the same temperature (25 °C) and loading frequency (2.5 Hz) (Rahman, 2004).

$$Log(Penetration) = 4.55 - 0.52 Log\,|G^*|_{0.4} \qquad (3.15)$$

Where:

$|G^*|_{0.4}$ – Complex modulus at 25 °C with loading frequency 2.5 Hz.

EN 1426 (1999) is the European standard for the penetration test (Figure 3.13), which consists in the measurement of the penetration of a standard needle into a conditioned test sample (FEHRL, 2006).

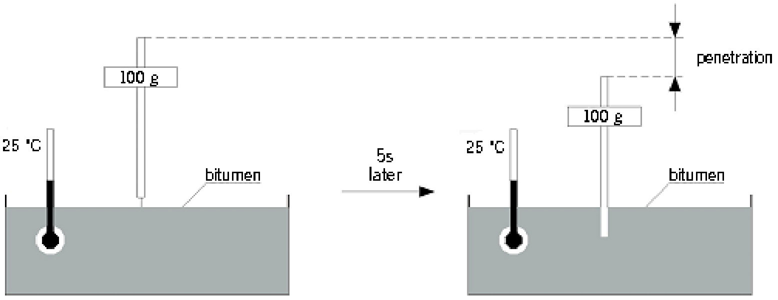


Figure 3.13 – Bitumen penetration test (Branco *et al.*, 2005)

For unmodified bitumens, the penetration test correlates well with the stiffness of the bitumen (FEHRL, 2006).

The penetration index (PI) is a measure for the temperature susceptibility of a bitumen that can be derived mathematically either from the penetration values at two temperatures or from the standard penetration and softening point values, as given in Equations 3.16 and 3.17 respectively (FEHRL, 2006).

$$PI = \frac{\log(pen@T_1) - \log(pen@T_2)}{T_1 - T_2} \quad (3.16)$$

$$PI = \frac{1952 - 500\log(pen) - 20SP}{50\log(pen) - SP - 120} \quad (3.17)$$

For paving grade bitumen used for highways, the PI typical range is -1.5 to +1.0. The calculation of the penetration index has not been standardised (FEHRL, 2006).

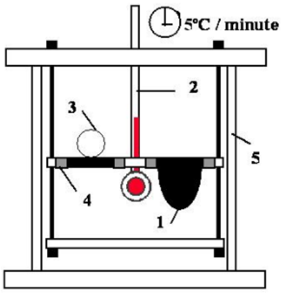
The PI is a property of an asphalt derived from the penetration and softening point as described by Pfeiffer and Van Doormaal (1936) and is a useful means of classifying asphalts according to major rheological characteristics. Asphalts with penetration indices less than -2 are generally Newtonian materials with high viscosity-temperature susceptibility. Asphalts with penetration indices between -2 and +2 are of the normal type (most paving asphalts fall in this category). Asphalts with penetration indices greater than +2 have relatively lower temperature susceptibility of viscosity and include all of the air-blown asphalts used for roofing and other industrial purposes (Simpson *et al.*, 1961).

3.2.2. Softening point

The softening point test is also an empirical method to determine the consistency of a penetration or oxidised bitumen. In this test two steel balls are placed on two discs of bitumen contained within metal rings and these are raised in temperature at a constant rate (5 °C/min) in a water bath (bitumen with softening point 80 °C or below) or in glycerol (bitumen with softening point greater than 80 °C). The softening point is the temperature (°C) at which the bitumen softens enough to allow the balls enveloped in bitumen to fall a distance of 25 mm into the bottom plate. In short, this test method measures a temperature at which the bitumen phase changes from semi-solid to liquid. The test method is described in BS 2000 Part 58, 1983, IP 58/83 and ASTM D36 (Rahman, 2004).

Softening point (ring and ball or R&B) test (Figure 3.14) is a method for the determination of the softening point of bitumen and bituminous binders (FEHRL, 2006).

The European standard for R&B softening point test is EN 1427 (1999). The principal difference was that some standards, including ASTM D36-95, do not include stirring the liquid. It is generally considered that, for paving grade bitumens, the R&B softening point is equivalent to a penetration of 800 × 0.1 mm (FEHRL, 2006).



Legend:

1 - Deformed bitumen sample
2 - Thermometer
3 - Sphere (ball)
4 - Ring with bitumen sample
5 - Beaker (500 mL) with water

Figure 3.14 – Determination of a bitumen softening point, by the ring and ball method (Branco *et al.*, 2005)

3.2.3. Viscosity

Viscosity, or resistance to flow, is a fundamental characteristic of bitumen as it determines how the material will behave at a given temperature and over a range of temperatures. Viscosity (η) is related to stress and strain rate and is determined by Equation 3.18 (Rahman, 2004).

$$\eta = \frac{Stress}{Strain\ rate} \tag{3.18}$$

If a material behaviour is independent of the rate of shear then it is called Newtonian behaviour. Bitumen usually exhibits Newtonian behaviour at high temperature (60 °C) and sometimes at temperatures as low as 25 °C. At these low temperatures, however, many types of bitumen do not exhibit Newtonian flow but show shear-thinning (pseudo plastic) behaviour. Thus for viscosity measurements on bitumens to be meaningful, the rate of strain must be known (Rahman, 2004).

Both absolute and kinematic viscosities are important for specification and comparative purposes. Specifications are based on absolute viscosity ranges at 60 °C and minimum kinematic viscosity at 135 °C. A minimum penetration at 25 °C is also included in most specifications. The absolute viscosity is measured by “pulling” the bitumen through the viscometer with a vacuum, whereas for the kinematic viscosity, the bitumen flows under its own weight. Kinematic viscosity is related to dynamic viscosity of the material and is measured using a capillary tube viscometer (Figure 3.15). The basic principle of a capillary tube viscometer is to measure the time required for a fixed quantity of material to flow through a standard orifice (Rahman, 2004).

In addition, sliding plate and rotational viscometers are used for determining viscosity at temperatures below 60 °C. In this project, a rotational viscometer was used according to ASTM D4402-87. This test measures the apparent viscosity of bitumen from 38 °C to 260 °C and uses a temperature controlled thermal chamber for maintaining the test temperature (Rahman, 2004).

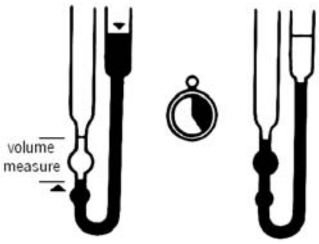


Figura 3.15 – Capilar viscosimeter (Branco *et al.*, 2005)

All the consistency tests described above cannot totally describe the overall behaviour of bitumen and relate it to pavement performance because of their empirical nature. In addition, these test methods do not give an indication of the viscoelastic nature of bitumen at any particular test temperature and do not have the flexibility to be carried out at different loading modes. To overcome these problems more fundamental testing methods were introduced which provide sound representation of the fundamental rheological properties under different temperatures and loading conditions (Rahman, 2004).

Brookfield viscosity test seems to be the most convenient to define the flow properties of binders modified with rubber under high temperatures, since it is impossible to measure asphalt-rubber viscosity with most conventional viscosity apparatus currently available due to presence of particles of rubber. Brookfield viscosity is obtained by applying a torque with a spindle of fixed dimensions, which is immersed in the binder sample at a desired temperature (Figure 3.16). The standard ASTM D6114/97 fixes the specific conditions for Brookfield viscosity tests on asphalt rubber samples (Neto *et al.*, 2006).

Figure 3.16 – Brookfield viscosimeter apparatus

3.2.4. Resilience

The resilience test is described in ASTM D 5329 standard. This test can be used to measure the elastic properties of the asphalt rubber binder and is expressed as percentage of rebound for the binder. This is one of the most important properties in the specifications and is a more reliable measure of elasticity (Ashcroft, 2002).

The resilience test (ASTM D5329) consists of applying a total displacement of 10 mm to a binder sample at a temperature of 25 °C and then releasing the load to obtain the elastic rebound. The sample is compressed at a rate of 1 mm/s by means of a rod that acts on a metallic sphere (17 mm diameter). Then compression is released and the elastic recovery that takes place after 20 s is measured and expressed a percentage of the initial displacement (10 mm). Figure 3.17 illustrates the test sequence from the (a) unloaded stage, then (b) maximum compression and finally the (c) elastic recovery (Neto *et al.*, 2006).

(a) (b) (c)

Figure 3.17 – Resilience test (ASTM D 5329)

3.2.5. Other binder tests

The tensile test is performed at a constant stretching speed and temperature and was originally intended for polymer modified bitumens. Test specimens are elongated until failure or up to a given proportional elongation over their initial length. The European standard for the test is EN 13587 (2003).

The tensile properties measured are useful as indicators for quality assessment of the materials. One of them, the conventional energy (calculated in accordance with EN 13703/2003), has been chosen as the specification criterion to evaluate the cohesion characteristics of polymer modified bitumens. EN 13703 (2003) for deformation energy states two calculation procedures for the conventional energy, depending on the method followed (FEHRL, 2006).

Similarly defined, but not equivalent, tensile properties can be measured through the force ductility test standardized in EN 13589 (2003).

The Vialit pendulum test (Figure 3.18) assesses the degree of cohesion of the bituminous binder and is standardised in EN 13588 (2004).

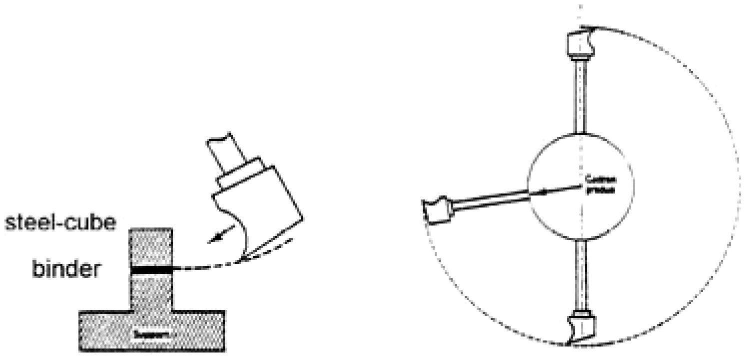


Figure 3.18 – Schematic of the pendulum test (FEHRL, 2006)

This test is of greatest significance in situations where aggregate is placed in direct contact with traffic stresses (for example in surface dressings and the chippings in hot rolled asphalt surface courses). The maximum impact energy is usually increased by polymer modification, as is the overall energy across the entire temperature range (FEHRL, 2006).

In summary, Figure 3.19 presents the several tests that can be used to characterize the behaviour of a bituminous binder, organized by different categories.

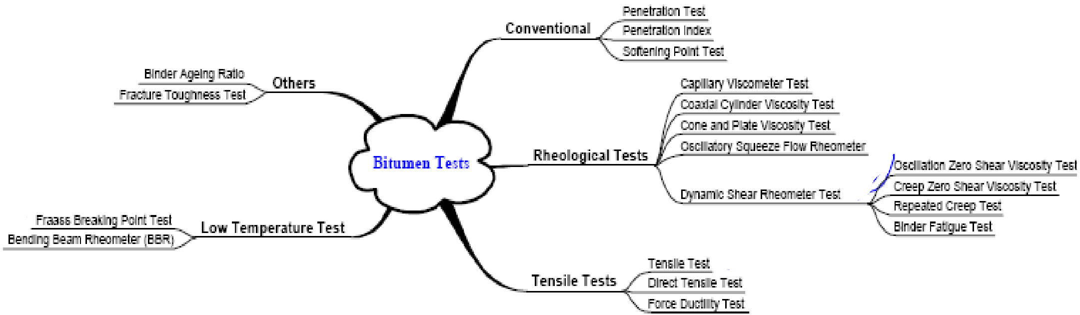


Figure 3.19 – Bitumen test relationships (FEHRL, 2006)

3.2.6. Binder conditioning regimes

The rolling thin film oven test (RTFOT) is one of the most commonly used standardised tests (EN 12607-1, 1999) to simulate the short-term ageing of binders (Figure 3.20). This test is used to measure the combined effects of heat and the air on a thin film of bitumen or bituminous binder in permanent renewal. It simulates the hardening which a bituminous binder undergoes during the mixing, transporting and compacting processes, referred to as short-term ageing (FEHRL, 2006).

The RTFOT test has been standardised in the USA as ASTM D 2872. Two other ageing procedures that used in a similar manner are the thin film oven test (TFOT), EN 12607-2 (1999), and the rotating flask test (RFT), EN 12607-3 (1999) (FEHRL, 2006).

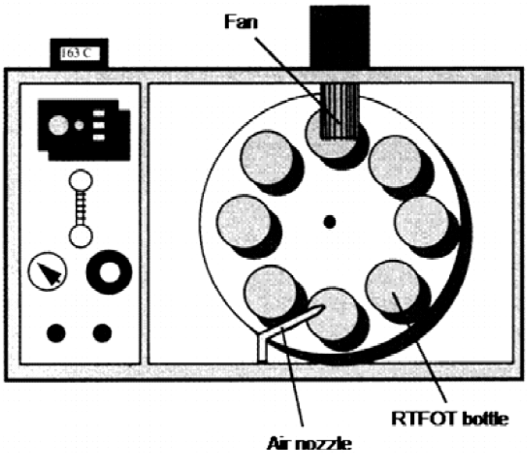


Figure 3.20 – RTFOT schematic drawing (FEHRL, 2006)

The TFOT simulates the short-term ageing of binders. The European standard for the TFOT is EN 12607-2 (1999). The TFOT was adopted by AASHTO in 1959 and by ASTM in 1969 (ASTM D1754, 2002) as a means of evaluating the hardening of bitumen during plant mixing. However, a major criticism of the TFOT is that the thick binder film results in a large volume to the exposed surface area of the binder. There is a concern that ageing (primarily volatile loss) may be limited to the “skin” of the bitumen sample because the bitumen is not agitated or rotated during the test (FEHRL, 2006).

The European standard for the rotating flask test (RFT) method is EN 12607-3 (1999), and it consists of ageing a 100 g sample of bitumen in the flask of the rotary evaporator for a period of 150 min at a temperature of 165 °C preventing the formation of a skin on the surface of the binder (FEHRL, 2006).

One of the main problems with using the RTFOT for modified bitumens is that these binders, because of their high viscosity, will not roll inside the glass bottles during the test. In addition, some binders have a tendency to roll out of the bottles. To overcome these problems, the modified rolling thin film oven test (MRTFOT) was developed. The principle is that the steel rods create shearing forces to spread the binder into thin films, thereby overcoming the problem of ageing high viscosity binders. However, recent research work has indicated that using the metal rods in the MRTFOT does not solve the problem of roll-out of modified binder (FEHRL, 2006).

The pressure ageing vessel (PAV) was developed in the SHRP project to simulate long-term, in-service oxidative ageing of bitumen in the field (Figure 3.21). The method involves hardening of bitumen in the RTFOT or TFOT followed by oxidation of the residue in a pressurised ageing vessel (FEHRL, 2006).

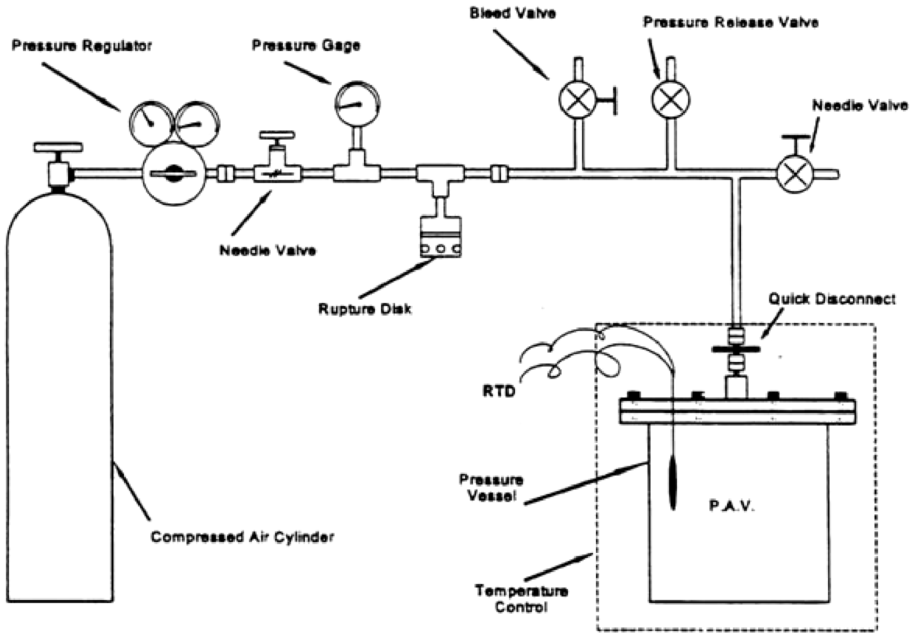


Figure 3.21 – Pressure ageing vessel (FEHRL, 2006)

The European standard for the PAV is still in draft form as prEN 14769. The test has also been standardised in the USA as AASHTO PP1-98 (FEHRL, 2006).

Rotating cylinder ageing test (RCAT) is a device (Figure 3.22) for ageing/conditioning bituminous binders. Tests simulating short-term ageing (STA) and/or long-term ageing (LTA) of paving grade or modified bitumen or of mastics can be performed. At the time of writing, a European standard for the test has been submitted for CEN enquiry as prEN 15323 (2005) (FEHRL, 2006).

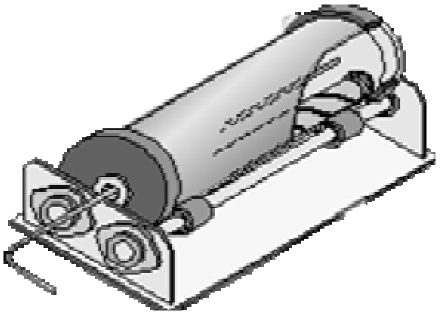


Figure 3.22 – The RCAT device scheme (FEHRL, 2006)

The RCAT method is a conditioning method, but measurement of the characteristics at different time allows a kinetic approach of the ageing phenomenon. This approach is based on the fact that the development of some characteristics of the binder can be described in a linear manner using Equation 3.19 (FEHRL, 2006).

$$S_t = S_0 + \sqrt[n]{K \cdot t} \text{ with } K = k \cdot \left(S_0 - S_f\right)^n \tag{3.19}$$

In Equation 3.19, S_0, S_t and S_f represent the reaction indicator S at time t = 0, t = t and f = time at the end of its functional life (when the binder can no longer fulfil its intended role in the asphalt mixture), K is the overall reaction constant and k is the rate constant. R&B softening point, reciprocal of the logarithm of the penetration, asphaltenes content A7 and rheological characteristics (viscosity, complex modulus, phase angle, and other) can serve as reaction indicators. Some infrared absorption intensities can also be used (FEHRL, 2006).

The two major advantages of RCAT method are the use of the same device to simulate short-term and long-term ageing separately or in combination and the large amount of aged binder or mastic prepared (it is possible to age mastics with a filler content of up to 30% by volume without any major problem). The latter advantage allows a great reduction in the number of handling operations that are useless and/or detrimental to the repeatability of characteristics determination (FEHRL, 2006).

In the case of short-term ageing, RTFOT and RCAT_{163} ageing are approximately equivalent. In the case of long-term ageing, literature gives more details about the advantages and the disadvantages of RCAT method compared to the PAV_{100} conditioning, where the value represents testing temperature (°C) during the PAV conditioning. The most important are (FEHRL, 2006):

- The ageing of the sample is homogeneous because RCAT test is dynamic. With the PAV test, due to the thickness of the binder film and to the static test, the concentration of oxygen will not be distributed homogeneously during the reaction. In spite of the pressure applied, the diffusion phenomenon will lead to differences in ageing between the surface and the bulk of the exposed sample. Furthermore, in the case of the static test (PAV), the ageing of PMBs also presents some scatter because of the migration of certain polymers to the surface;
- The amount of aged binder is sufficient for further tests, and test portions (25 g to 30 g) can easily be taken at various intervals to monitor the development of characteristics and properties with reaction time (kinetic approach);
- The temperature of RCAT_{90} test is more appropriate because 100 °C appears as a transition temperature between ageing mechanisms;
- The pressure condition is safer because of some risks of accident with a pressurised cabinet exposed to a temperature of 100 °C;
- The duration of the RCAT test is its major disadvantage: 240 h for RCAT_{85} and 140 h for RCAT_{90}. These run times exceed largely the 20 h needed for PAV_{100}.

The correlation between PAV_{100} and $RCAT_{90}$ ageing methods was estimated by the comparison of results for the increase in R&B softening point. For eight pairs of values, the correlation factor, R^2, was 0.80 (FEHRL, 2006).

The use of weatherometer test has never been standardised. The weatherometer is an apparatus in which specimen materials can be subjected to artificial and accelerated weathering tests which simulate natural weathering. Controlled cycles of ultraviolet radiation, light, salt, electric arcs, water spray, and heating elements are used to simulate the natural conditions of sun, rain and temperature changes (About.com, 2009).

Figure 3.23 summarizes the several binder conditioning regimes that can be used to simulate the short- and long-term aging of a bituminous binder, organized by different categories of tests.

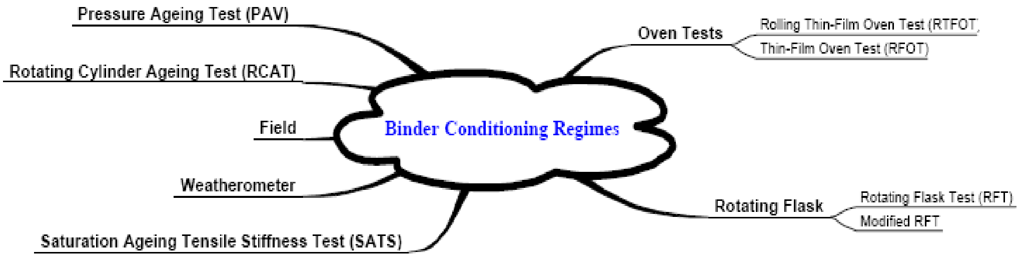


Figure 3.23 – Binder conditioning relationships (FEHRL, 2006)

3.2.7. Binder quality control

Essentially, satisfactory performance of a bitumen on the road can be ensured if four properties are controlled (Read and Whiteoak, 2003): i) rheology; ii) cohesion; iii) adhesion, and iv) durability.

The rheology of the bitumen at service temperatures is adequately characterised by the values of penetration and penetration index (Read and Whiteoak, 2003).

Magnitude and type of effect on bitumen rheology depend on the bitumen itself as well as type and amount of additive. Bitumen composition is of decisive importance (Edwards, 2005).

The cohesive strength of bitumen is characterised by its ductility at low temperature (Read and Whiteoak, 2003).

Durability can be defined as the ability to maintain satisfactory rheology, cohesion and adhesion in long-term service (Read and Whiteoak, 2003).

Many years of experience with the QUALAGON (Figure 3.24) have shown that the set of criteria on which it is based does provide an adequate description of quality in measurable quantities. In its graphical form, the QUALAGON acts as a template and actual product properties can be depicted on it to facilitate quality assessment (Porter, 1991).

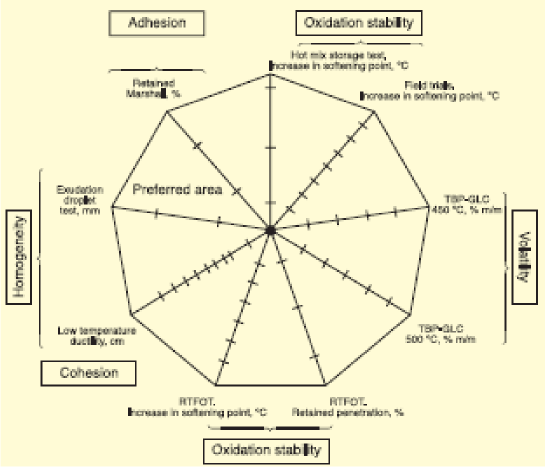


Figure 3.24 – The penetration grade QUALAGON© (Read and Whiteoak, 2003)

Simpson *et al.* (1961) referred that the complex stress-strain modulus or stiffness of an asphalt may be determined from the nomograph with a knowledge of the penetration, softening point, and penetration index of the asphalt or, alternatively, may be determined experimentally by means of the microelastometer described by Labout (1958).

4. CHARACTERISTICS OF BITUMEN AND RUBBER RELATED TO THE PAVEMENT PERFORMANCE

4.1. Relation between the Chemical, Physical and Rheological Properties of Bitumen and the Pavement Performance

The physical, mechanical, and rheological behaviour of bitumen in road and building construction is governed by its structure and chemical composition (Petersen *et al.*, 1994; Rahman, 2004). For this reason, considerable effort goes toward widening the knowledge of this composition and relating it to performance (Raki *et al.*, 2000).

Asphalt can be classified by its chemical composition and physical properties. The pavement industry typically relies on physical properties of asphalt for the characterization of performance (Figure 4.1), although the physical properties of bituminous binders are a direct result of its chemical composition (Glover, 2007).

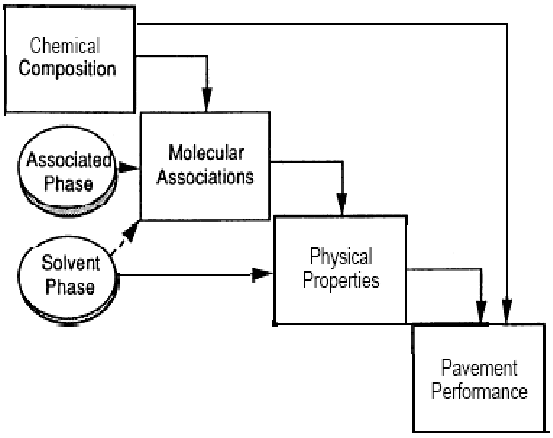


Figure 4.1 – Chemistry physical property – performance relationships (Jones and Kennedy, 1992)

In fact, the principal value of the composition studies is to develop an understanding of what compositional features are needed to produce material with the desired properties. Then this information can be used to select, mix and/or modify asphalts to obtain binders that will perform in a cost-effective manner (Robertson, 1991).

Actually, the production of marketable grades is mostly achieved by blending two or more basic grades (Oyekunle, 2007).

4.1.1. Relation between the chemical and physical properties of bitumens

As indicated in published literature, there exists a fundamental interdependence between composition of asphaltic bitumen and its physical properties. Thus, if we wish to predict or judge the physical response of an asphalt either during handling or in service, it can be an advantage to have knowledge of its composition (Corbett, 1970).

The bitumen chemical composition has influence on penetration, softening point, penetration index (Figure 4.2), viscosity, viscosity-temperature slope, shear susceptibility, and complex stress-strain modulus. Variation of the hydrocarbon-type composition of asphalt can lead to products of widely varying physical properties (Simpson *et al.*, 1961).

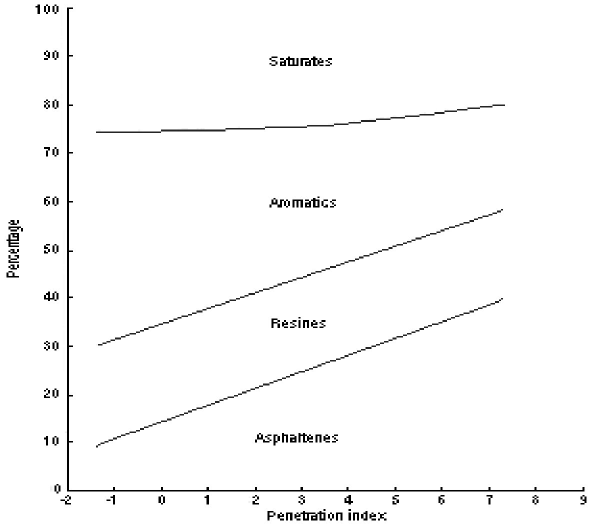


Figure 4.2 – Relationship between broad chemical composition and penetration index (Lubbers, 1985)

Each bitumen fraction or combination of fractions perform separate functions in respect to physical properties, and it is logical to assume that the overall physical properties of an asphalt are thus dependent upon the combined effect of these fractions and the proportions in which they are present (Corbett, 1970). Therefore, by appropriate cross blending, one can, within reason, achieve a wide variety of properties. Viscosities can be pushed up or down at will (Robertson, 1991).

In a general way all bitumens are classified in terms of “grade” by penetration and ring and ball softening point measurements. However, a simple compositional analysis shows that the same grade bitumen does not have the same chemical composition (Figure 4.3) or the same rheological and physicochemical behaviour when mixed with polymers, acids or stones (Loeber *et al.*, 1998).

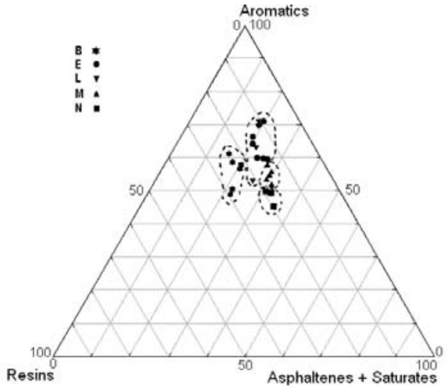


Figure 4.3 – Schematic representation of the different bitumens separated in groups with the same physical properties (Loeber *et al.*, 1998)

Asphalts with high asphaltene content have lower penetration values, while there is a linear relationship between asphaltene content and softening point. There is no observed correlation between ductility and other asphalt properties (Oyekunle, 2007).

Penetration at both 25 °C and 0 °C decrease simultaneously with increasing softening point and with the rise in asphaltene content. The softening point increases with the increase in asphaltene content and decreases with the oil content in a linear fashion (Oyekunle, 2007).

Both the saturates and the naphthene-aromatics have relatively low viscosities and softening points compared with the polar-aromatics and asphaltenes which are quite high (Corbett, 1970).

For most asphalts a plot of log viscosity vs. log shear rate gives a straight line and the slope of this line is defined as the shear susceptibility of viscosity. A large negative slope indicates a highly susceptible asphalt (Simpson *et al.*, 1961).

The most widely varying physical parameter is ductility, whose value is significantly determined by the content of resins present in the particular asphalt. Ductility and resins content show similar trends. It is clearly seen here that the ductility of asphalt increases with an increase in the resins content and decreases with the increase in the contents of both asphaltenes and oils (Oyekunle, 2007).

Ductility appears to be largely dependent upon the polar-aromatics although the penetration consistency at the test temperature may be also a key factor. Saturates and asphaltenes as such do not contribute to ductility, and naphthene-aromatics appear to have only a minor influence (Corbett, 1970).

The two liquid fractions (saturates and aromatics) have relatively good temperature susceptibilities within themselves and are lower in density, as would be expected of compounds that contain a predominance of paraffin type groups. The solid components, on the other hand, are much more aromatic and have poorer temperature susceptibilities and higher densities (Corbett, 1970).

The combination of either the saturates or the naphthene-aromatics with asphaltenes improves the temperature susceptibility, and the combination of polar-aromatics with asphaltenes makes the temperature susceptibility poorer (Corbett, 1970).

4.1.2. Relation between the chemical and rheological properties of bitumens

Some of the most important rheological properties of asphalt depend on chemical constitution (Simpson *et al.*, 1961). The chemical composition of asphalt can be related to its performance as follows (Youtcheff *et al.*, 1994):

- Asphalt consists of two physical families of molecules, polars and non-polars;
- Polar molecules differ according to: strength and number of polar groups, molecular weight, distribution of molecular weights, and degree of aromaticity (a measure of the amount of aromatic versus aliphatic and cyclic molecules);
- Non-polar molecules differ according to molecular weight, distribution of molecular weights, and degree of aromaticity;
- The "compatibility" between polar and non-polar fractions, or the degree to which they can interact with each other, is controlled by the relative aromaticity of the two fractions.

Rheology is the science that deals with the deformation and flow of matter. The rheological characteristics of bitumen at a particular temperature are determined by the constitution (chemical composition) and the structure (physical arrangement) of the molecules. Any changes in the constitution, structure or both will result in rheological changes. Thus, to understand changes in bitumen rheology, it is essential to understand how the structure and constitution of bitumen interact to influence its rheology (Read and Whiteoak, 2003).

Since asphalt is a viscoelastic material, its response to an applied stress consists of both viscous and elastic responses. The relative amounts of each are determined by the temperature and duration of load application and by the rheological characteristics of the asphalt. The complex behaviour of all types of asphalts over wide ranges of loading times and temperatures have been represented by van der Poel (1954) in a single nomograph (Simpson *et al.*, 1961).

It is believed that asphalt is a set of "hardcore" agglomerates (structured units) that consist of polars dispersed in a less polar to nonpolar phase. The result is a material which has an elastic behaviour as a result of the network formed by the polar molecules, but it is also a material with a viscous behaviour that can flow or creep because various parts of the network can move with respect to each other under prolonged stress (Robertson, 1991).

Traxler (1961) discussed the development of the colloidal model of asphalt structure, emphasizing the rationalization of rheological properties of asphalts. The state of dispersion of asphalt should, according to the model, govern physical properties. In asphalts in which the presumably high molecular weight asphaltenes are well dispersed (because of the presence of considerable amounts of aromatic compounds in the solvent phase and sufficient amounts of peptizing resins), high temperature susceptibilities, high ductilities, low values of complex flow, low rates of age hardening, and little thixotropy should be observed. Such asphalts are designated *sol*-type asphalts. In poorly dispersed asphalts, low temperature susceptibilities, low ductilities, significant thixotropic properties and elasticities, and rapid age-hardening rates are observed. Such asphalts are designated *gel-type* asphalts. Many asphalts are between these extremes (Petersen *et al.*, 1994).

The most important structure forming elements of asphalts are the asphaltenes, whose quantity and nature of interaction with resins and oils largely determine the rheological properties (Oyekunle, 2007).

Oxidation changes the structure and composition of binder's molecules, resulting in increased quantity of high-molecular weight molecules, generating the term oxidative hardening. This hardening is reflected, in chromatogram of the asphalt, as change of molecular size distribution. Asphalt binder with large quantities of high-molecular weight molecules tend to exhibit poor low-temperature behaviour, but some good high-temperature behaviour (Yapp, 1991; Jennings, 1980).

The low-temperature rheological behaviour appears to be highly dependent on the aliphatic part of the bitumens, but the aliphatics appear to play very little role in the rheological properties at higher temperature (Michon *et al.*, 1997).

High-molecular weight or large molecular size (LMS) results in higher viscosity and stiffness of a binder (Amirkhanian and Kim, 2004).

According to Glover (2007), two of the most fundamental properties of any organic substance are their molecular weight and chemical functionality. Rheological properties of materials are a function of molecular weight (Mw)[1] and molecular weight distribution (MWD)[2]. Chemical functionality determines the extent of intermolecular association, influencing aging and stripping behaviour. A number of analytical techniques can be applied to study the changes in asphalt materials during the oxidation process.

The changes in Mw and MWD can be assessed by monitoring the rheological parameters η, G' and G''. At low frequencies the viscosity (η) is largely affected by the Mw. It was observed that an increase of 4% in the Mw leads to an increase of more than 12% in the η (Figure 4.4). However, as the frequency augments the η reduces, approaching a value independent of the Mw (Castro *et al.*, 2001).

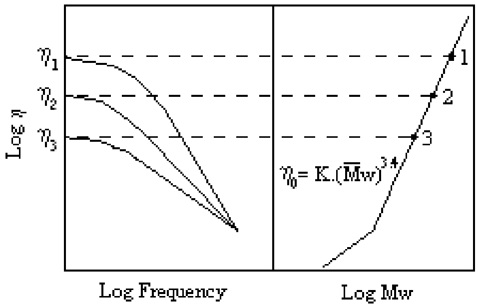


Figure 4.4 – Effect of the Mw on the viscosity

Another way to assess the changes in the Mw and MDW is monitoring the point of interception of the G' and G'' curves vs. frequency. The modulus obtained at the interception point is nearly independent of the Mw, but decreases with the increase of the MDW. The corresponding frequency is almost independent of the MDW, but increases with the Mw (Castro *et al.*, 2001).

4.1.3. Relation between the chemical properties of the bitumen and the pavement performance

The significant failure modes in asphalt pavements that may be related to materials are generally agreed to be (Robertson, 1991): i) Permanent deformation; ii) Rutting; iii) Fatigue cracking; iv) Low temperature cracking; v) Moisture damage, and vi) Total loss of adhesion.

The results of laboratory tests together with observations of performance in practice have identified key links between physical properties and the constitution of the bitumen. Thus, it has been indicated that if

---

[1] Molecular weight (Mw) is the mass of one molecule of that substance, relative to the unified atomic mass unit u (equal to 1/12 the mass of one isotope of carbon-12).

[2] Molecular weight distribution (MWD) is the relative amounts of molecules of different molecular weights that comprise a given specimen of bitumen. It resembles a probability distribution curve were the various average molecular weights are indicated in their expected rank.

the molecular weight distribution and chemical constitution of the bitumen is unbalanced, it can exhibit heterogeneity which may adversely affect both the cohesive and adhesive properties of the bitumen (Read and Whiteoak, 2003).

The relative contributions of the elastic and viscous behaviour vary with composition. The exact nature of the chemical specie is less important than the distribution of charge within the specific molecule. Figure 4.5 shows that excessive structuring leads to brittle cements which tend to crack, while too little structuring leads to materials which deform under stress (Robertson, 1991).

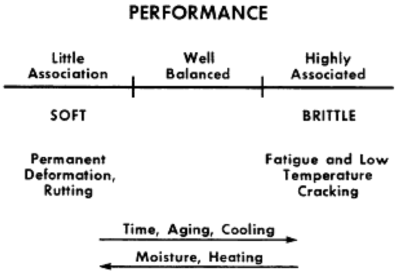


Figure 4.5 – Effects of aging, time, temperature and moisture in pavements (Robertson, 1991)

Cracking can be related to binder composition. If the molecular network (agglomerate, micelle, colloid, or whatever term is preferred) becomes too rigid, the ability of an asphalt to deform elastically will be lost. Instead, the asphalt fractures and likely will be separated to a point that healing cannot occur. The constant working of very rigid matrix will eventually suffer fatigue and crack (Robertson, 1991).

Many researchers have long felt that the polar materials in asphalts played a major role in pavement performance (Jones and Kennedy, 1992). The non-polar “solvent” makes a critical contribution to the low-temperature properties of the pavement. In fact, low-temperature cracking in pavements is virtually independent of any other variable in the pavement system. At low temperatures the non-polar asphalt molecules align and order themselves, and there is a free-volume collapse in the pavement. This collapse takes place without crystallization and will cause thermal cracking if too severe. It is primarily a function of the molecular weight of the non polar fraction, but chain branching in the molecules is also important, hindering collapse and retarding low-temperature cracking (Jones and Kennedy, 1992).

“Good” asphalts have a proper balance of polar and non-polar molecules. The true molecular weight of the non-polar molecules is also important in asphalt performance, especially in low-temperature performance. Asphalts that have too much polar material will be subject to fatigue cracking in thin pavements, brittleness, and thermal cracking. Asphalts that have too much non-polar material, or asphalts in which the non-polars are too low in molecular weight, will suffer from fatigue cracking in thick pavements, moisture sensitivity, and rutting (Jones and Kennedy, 1992).

Increase in asphaltenes content results in higher viscosity and softening point of asphalt. Though it is generally accepted that saturated compounds in asphalt affect its properties to a lesser degree than aromatics and polar-aromatics, the former, however, have a significant effect on the adhesion of asphalt to aggregate, its brittleness at low temperatures and ageing resistance (Gawel and Czechowski, 1997).

Bitumen chemistry may have a significant influence on the low temperature behaviour of asphalt pavements (Isacsson and Zeng, 1997). Cracking at low temperature is expected to be most closely related to the compositional feature of aliphatic/aromatic ratio (Robertson, 1991).

Apparently, the most feared influence of wax in bitumen is the sudden decrease in viscosity due to the melting of crystallized wax, if this phase transition should occur within a temperature range affecting the resistance to permanent deformation of binder and asphalt pavement. Other possible drawbacks are brittleness, physical hardening, poor ductility and poor adhesion (Edwards, 2005).

The use of low penetration grade bitumen in a dry process crumb rubber modified asphalt mixture will reduce the rate and possibly the amount of swelling of the crumb rubber particles. However, any changes in the rheological properties of the binder following rubber-bitumen interaction could result in the binder becoming embrittled with reduced flexibility and ability to resist cracking and fretting (Airey *et al.*, 2003).

The use of high penetration grade bitumen will increase both the rate and possibly the amount of rubber swelling and therefore the shape and rigidity of the rubber. However, the binder should still have enough flexibility after the rubber-bitumen interaction to resist cracking and fretting (Airey *et al.*, 2003).

4.2. Bitumen-Rubber Interaction Mechanisms

When crumb rubber is blended with bitumen at high temperatures to produce a modified binder, i.e. wet process, the two materials interact as bitumen components migrate into the rubber causing it to swell. Initially, the interaction between CR and bitumen is a non-chemical reaction where the rubber particles are swollen by absorption of the bitumen’s aromatic oils (Heitzman, 1992). Absorption of bitumen components by the rubber inevitably depletes the bitumen of the absorbed components and, consequently, modifies its properties making it stiffer and more brittle (Artamendi and Khalid, 2006).

In addition to traditional oxidation of bitumen at high temperatures, the residual bitumens experienced further changes in their chemical constitution as a result of the crumb rubber-bitumen interaction and the absorption, by the rubber, of the lighter, more volatile fractions of the bitumen (Rahman, 2004). Furthermore, the rubber particles may also suffer some form of degradation, mainly devulcanization and depolymerization, when mixed with bitumen at high temperatures for prolonged periods of time (Artamendi and Khalid, 2006).

The extent of these two processes, swelling and degradation, depends on the nature of the rubbers, the bitumen's chemical composition and the mixing conditions, time, temperature and degree of agitation. In addition, these processes will determine the mechanical properties of the crumb rubber modified binders (Artamendi and Khalid, 2006).

Literature reports three stages of interaction that have been evaluated with regard to asphalt rubber binder (Jensen, and Abdelrahman, 2006):

- An early stage that occurs immediately after mixing crumb rubber with asphalt;
- An intermediate storage stage during which the binder is held at elevated temperatures for up to a few hours before mixing with aggregate;
- An extended (storage) stage when asphalt rubber binders are stored for extended periods before mixing with aggregate.

The effects of crumb rubber on asphalt rubber binders can be separated into interaction effect (IE) and particle effect (PE). The IE is the effect of the lighter fractions of the binder diffusing into the crumb rubber particles. The PE is the effect of the crumb rubber particles acting as filler in the binder (Putman and Amirkhanian, 2006):

- The IE is greatly influenced by the crude source of the binder and could potentially be used as an indicator of a binder's compatibility with CR (higher IE would indicate a more compatible binder);
- The PE is most significantly affected by the CR content of the binder. Higher CR contents result in greater PE values;
- The effect of CR size on the PE follows the same trends as either the viscosity or G* of the CRM binders.

4.2.1. Rubber swelling due to interaction with bitumen

There are several factors that play a role in the crumb rubber-bitumen interaction. On the part of the bitumen, the interaction depends on the amount of the aromatic fraction, the temperature, and the viscosity. The properties of the CR that can affect the interaction include production method (ambient or cryogenic grinding), particle size, specific surface area, and chemical composition (i.e., amount of natural rubber) (Putman and Amirkhanian, 2006).

The reaction, according to Heitzman (1992), is not chemical in nature. It involves absorption of aromatic oils from the asphalt cement into the polymer chains, which are the key components of the bitumen. Heitzman (1992) reported that the reaction does not result from melting of the crumb rubber into the asphalt cement. Rather, rubber particles are swollen by absorption of the asphalt's oily phase at high temperatures, 160 to 200 °C, to form a gel-like material (Jensen and Abdelrahman, 2006).

During the interaction process, rubber particles swell in a time and temperature dependent manner, which results in a reduction in the interparticle distance, thereby increasing viscosity. Once the rubber has swelled, if temperature is maintained too high or for too long a period, the rubber begins to disintegrate into the asphalt by partial depolymerization. This depolymerization causes a reduction in viscosity. Change in the viscosity of the asphalt rubber binder has traditionally been used to indicate the progress of the interaction between asphalt and rubber (Jensen and Abdelrahman, 2006).

Equilibrium swelling and diffusion coefficient are related to the grade and source of the binders as well as the type of rubber (Artamendi and Khalid, 2006).

The swelling rate and equilibrium of rubber penetration with the selected asphalt components were found to be dependent on these components and the rubber content in asphalt. At fixed conditions of stirring asphalt with rubber, the equilibrium swell value decreases with the increase in rubber content (Gawel *et al.*, 2006).

The wide variation in asphalt-rubber interactions underscores the importance of considering this fact in choosing an asphalt for use with ground tire rubber (Billiter *et al.*, 1997a).

The kinetics of swelling indicated a faster rate of bitumen absorption by truck-tyre rubber than by car-tyre rubber (Artamendi and Khalid, 2006). Natural rubber is more effective than synthetic rubber, but as the latter is much more prevalent. The two are likely to be mixed in any commercially prepared product and be predominantly synthetic (Glover *et al.*, 2002).

During the curing process, rubber particles absorb light fractions of bitumen and swell with different extent. The measured swelling ratio varies from 200 to 400% and is mainly related to the rubber content and the bitumen composition. The rubber gradation has a limited effect on that swelling ratio (Ould-Henia and Dumont, 2006).

A key element in understanding the interaction process is the effect of temperature on the swelling activity. Green and Tolonen (1977) considered a concept for the change in free energy and concluded that temperature has two effects on the interaction process. The first effect is on the rate of swelling of rubber particles. As the temperature increases, from 160 to 200 °C, the rate of swelling increases. The second effect is on the extent of swelling. As the temperature increases, the extent of swelling decreases as the rubber network becomes stiffer to achieve equivalent change in entropy. They explained that should experimental data show an increase in swelling with temperature, it would indicate that some other reaction is taking place, which they call detachment (Jensen and Abdelrahman, 2006).

The increase of specific surface and consequently of contact area between rubber particles and straight asphalt contribute to the process of absorption of the light fractions of straight binders by the rubber particles (Neto *et al.*, 2006). Additionally, very small particle size crumb rubber will tend to more quickly reduce viscosity during storage due to its quicker and more thorough swelling and subsequent depolymerization (Fontes *et al.*, 2006).

Particle size controls the swelling mechanism over time and affects the binder matrix. The time required for swelling increases with the particle radius squared. Larger particle sizes require much greater times to swell. Finer particle sizes may require almost no time to react. An #80 mesh particle size requires about one minute to react with an AC-30 grade asphalt at 163 °C (Jensen and Abdelrahman, 2006).

The increase in rubber mass through the absorption of the light molecular weight fractions of the binders is independent of the rubber-bitumen ratio provided that there is sufficient bitumen (light fractions) to allow absorption to occur (Airey *et al.*, 2003).

Equilibrium swelling mass uptake depended on bitumen origin and grade, hence, on chemical composition. In general, bitumens with high asphaltene content were less prone to swell the rubbers (Artamendi and Khalid, 2006).

The absorption of the light fractions of asphalt not only increases the effective volume of rubber particles, but also changes the nature of the asphalt liquid phase (Jensen and Abdelrahman, 2006).

Bitumen composition is a major factor affecting the interactions between bitumen and rubber. It is admitted that light fractions of bitumen swell the rubber particles and some authors introduced the concept of compatibility between rubber and bitumen and recommended the use of base bitumen containing highly aromatic oily fractions (Ould-Henia and Dumont, 2006).

Aromatic content is considered to be a factor that affects asphalt-rubber interaction. Bouldin *et al.* (1990) indicated that softer asphalts would be more compatible with rubber polymers and crumb rubber modification would be more effective than with stiffer asphalts. Green and Tolonen (1977) listed asphalt viscosity as a factor that affects the time required for rubber particles to swell (Jensen and Abdelrahman, 2006).

When crumb rubber is added to asphalt binder, the crumb rubber absorbs the maltenes fraction (saturates, aromatics and resins) leaving the asphalt rubber binder with a higher content of asphaltenes (Martinez *et al.*, 2006). The amount of swelling mostly depends on the temperature, particle size, test duration, viscosity and complex chemical nature of the solvent (Rahman, 2004).

The maximum increase in rubber mass (bitumen absorption) after 48 hours at 160 °C appears to be independent of crude source and only marginally related to the penetration grade of the bitumen, with the softer, high penetration grade bitumens generally resulting in a greater amount of absorption compared to the harder, low penetration grade bitumens (Rahman, 2004).

Equilibrium swelling and diffusion coefficient increase when the grade of the binder used is increased. For the same penetration grade, binders with high asphaltene content swell the rubbers markedly less and at lower rate than those with lower asphaltene content (Artamendi and Khalid, 2006).

The initial rate of bitumen absorption is directly related to the viscosity (penetration grade) as well as the chemical composition (crude source) of the binders with the softer (less viscous) and lower asphaltene content binders having the highest rates of absorption (Rahman, 2004).

Gawel *et al.* (2006) concluded that the rate of swell increases as the viscosity of the liquid decreases. The extent of swelling is greater when the rubber content in asphalt is lower. This finding suggests that it is not the whole asphalt material but only some of the components, those occurring in comparatively small amounts, which contribute to the swelling of the rubber. Primarily lighter fractions are involved. The lighter asphalt-vacuum residue blend components penetrate more readily into the internal matrix of the polymer. Asphalt-rubber binder (rubber removed) is richer in higher molecular weight components.

Gawel *et al.* (2006) also found that, of the nonpolar components, the n-alkanes and n-alkylbenzenes possess the highest propensity to penetrate into rubber particles. Preferential absorption of the compounds with linear aliphatic chains into the rubber suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Green and Tolonen (1977) emphasize the importance of controlling the swelling process through controlling the interaction time and temperature. They concluded that rubber particles absorb the lighter fractions of the "maltene phase" of the asphalt, so the viscosity of the "continuous phase" of the binder increases. They also concluded that the swelling process may continue at a reduced rate even at ambient temperature (Jensen and Abdelrahman, 2006).

4.2.2. Bitumen diffusion into rubber

When polymer networks are exposed to low-molecular weight liquids, the liquid molecules diffuse into and are absorbed within the polymer network. The liquid molecules will occupy positions among the polymer molecules forcing them to move apart such that the polymer swells. This process continues until the concentration of the liquid is uniform and equilibrium swelling is reached. Uncrosslinked polymers may be swollen by and dissolve in liquids with suitable interaction parameters. For crosslinked polymers, however, solvents might be absorbed into and swell the network, but the network structure will prevent dissolution. Thus, swelling of rubbers by organic liquids may be considered to be a partial dissolution process in which there is only a limited solubility of the polymer in the solvent (Artamendi and Khalid, 2006).

In general, the best solvents or swelling agents for a given polymer are those whose chemical structure is closely related to that of the polymer. For example, hydrocarbon rubbers, e.g. NR, SBR and polybutadiene, are readily soluble in hydrocarbon liquids, such as gasoline, benzene, etc., but insoluble in polar liquids, such as acetone and alcohol (Artamendi and Khalid, 2006).

Diffusion is defined as the process by which matter is transported from one part of a system of higher concentration to another of lower concentration as a result of random molecular motions (Artamendi and Khalid, 2006). Diffusion is a result of the kinetic properties of particles of matter. The particles will mix until they are evenly distributed.

Diffusion is assumed to follow Fick's law. Therefore, the rate of bitumen fractions transfer into rubber is proportional to their concentration gradient (Khalid, 2005). In the case of rubber and bitumen, as the rubber is, by definition, above its glass transition temperature, the polymer chains have considerable mobility so the system is essentially that of two fluid phases in contact but one phase has a network structure of polymer chains. So, in principle, when rubber and bitumen are placed in contact, low molecular weight components of the bitumen, i.e. aromatic oils, will diffuse into the rubber causing it to swell (Artamendi and Khalid, 2006).

Swelling of rubbers can be regarded as a diffusion process in which the two components are chemically neutral. In the case of a polymer-liquid mixture, for a given polymer swollen in different liquids, the swelling should be a maximum when the enthalpy of dilution is a minimum, thus when the solubility parameter of the liquid is equal to that of the polymer (Artamendi and Khalid, 2006).

The diffusion coefficient depends in a great degree on temperature, as the temperature increases the diffusion coefficient also increase, and to a lesser degree on bitumen chemical composition (Artamendi and Khalid, 2006).

Temperature affects the rate of diffusion. As the temperature increases the diffusion coefficient values for the two rubbers (waste truck and car-tyre rubber) also increase. The increase in the diffusion coefficient values with increasing temperature can be related to the viscosity of the bitumen at different temperatures. As the temperature increases, the viscosity of the bitumen decreases, increasing the rate of diffusion into the rubbers. This was attributed to higher polymer chain flexibility associated with natural rubber in truck-tyre rubber and, to a lesser extent, the greater solubility of bitumens aliphatic components in truck-tyre rubber (Artamendi and Khalid, 2006).

Additionally, as the temperature increases, the amplitude of segmental oscillations of polymer chains also increases. Greater segmental motion results in an increase in the size of free volume and subsequent increase in diffusivity as the temperature is increased (Artamendi and Khalid, 2006).

According to Khalid (2005), there is a linear relationship between initial weight gain of rubber particles and $\sqrt{}$time. However, truck-tyre rubber absorbed more bitumen than car-tyre rubber.

Artamendi and Khalid (2006) affirmed that aromatic solvents markedly swelled car- and truck-tyre rubbers, while aliphatic solvents, swelled truck-tyre rubber far more strongly than car-tyre rubber. It was concluded that the same pattern of solubility applied to absorption of bitumen components by the rubbers.

4.2.3. Rubber devulcanization and depolymerisation by bitumen

Two main types of activities that affect AR binder properties have been reported in the literature: particle swelling and detachment or depolymerization. These processes occur as the binder is subjected to different combinations of time and temperature (Jensen and Abdelrahman, 2006).

The substantial decrease in the fatty acid content of the rubber (the component of the curing system of the polymer) after immersion in hot asphalt-vacuum residue blend gives evidence supporting the movement of these components from the rubber into the asphalt. They are most probably concentrated in the naphthene-aromatic fraction, as it may be inferred from the increased content of this fraction in the residual bitumen (Gawel *et al.*, 2006).

Lower molecular weight, highly aromatic asphalts are better able to devulcanize the rubber during cure. Higher molecular weight asphalt cements, with high content of polar compounds and asphaltenes, are better able to depolymerise the rubber during the curing process (Leite and Soares, 1999).

The viscosity of asphalt rubber binders is also very asphalt dependent. The lower the saturates and asphaltenes content, the better an asphalt dissolves rubber. High shear, high temperature curing conditions and very low particle size, reduce the effect of saturates and asphaltenes content in the rubber dissolution (Leite and Soares, 1999).

Different particle sizes are in different interaction stages at any one time, mainly because fine particles achieve their maximum swelling faster than coarse particles and begin to depolymerise earlier. Modification of the liquid phase is also affected by the size of the particles. Because of their high surface area, fine particles absorb more light asphalt components in a shorter period of time, leaving the liquid phase of the binder stiffer. When rubber particles significantly depolymerise after time at high interaction temperature, the liquid phase of a binder made with fine material will be stiffer than the liquid phase of a binder made with a coarse material. Using high shear rate (or high frequency) mixer reduces the particle size of coarse crumb rubber and allows the interaction process to progress with greater speed (Jensen and Abdelrahman, 2006).

The extension of curing time and increase of curing temperature and rate of mixing reduce the high temperature viscosity, due to the devulcanization and depolymerization of the rubber during the curing process, which allows the asphalt to digest rubber producing a more homogeneous product with better compaction properties and fewer tendencies to settle (Leite and Soares, 1999).

The application of higher temperatures for long periods of time, during asphalt rubber production, results in swelling followed by depolymerization (Khalid, 2005), whereas applying lower temperatures results only in swelling (Leite and Soares, 1999).

The asphalt rubber binder should be homogeneous with the rubber being devulcanized but not depolymerised. However, it is quite possible that rubber depolymerization to a great extent can worse aging characteristics (Leite and Soares, 1999).

Post-vulcanization (Green and Tolonen, 1977) is an interesting phenomenon that sometimes occurs when mixing asphalt cement with rubber. During rubber processing there are sulphur and other agents that have not been entirely chemically bonded during vulcanization of the rubber. When mixing rubber with hot asphalt, the vulcanization process will be reactivated and continue for some time, depending on the interaction temperature. This extra time is longer for lower interaction temperatures than for higher interaction temperatures. This extra time was reported as thirty minutes at 150 °C (Green and Tolonen, 1977). Vulcanization delays the development of modified binder properties. This phenomenon should be suspected when CRM interacts with asphalt for short interaction periods and targeted properties are not achieved (Jensen and Abdelrahman, 2006).

Some authors speak about some breakings in cross-links (devulcanization) due to heating during the curing process (Billiter et al, 1997). This phenomenon induces a progressive decrease in viscosity which is considered in some papers as the initial degradation of the polymer chains. Both swelling and devulcanization are present during the asphalt rubber curing, even for the so-called dry process. The predominance of one of the phenomena relies on the processing parameters and essentially on blending temperature and blending duration (Ould-Henia and Dumont, 2006).

4.3. Effects of Rubber Addition on the Binder Properties

When crumb rubber is mixed and heated with bitumen, the produced modified binder has significantly different properties than the original. Property modification is due to physical and/or compositional changes during the interaction process (Jensen and Abdelrahman, 2006).

A large documentation on asphalt rubber binders permitted the identification of the main parameters affecting the properties of the final blend, enumerated hereafter (Ould-Henia and Dumont, 2006):

- Rubber powder;
  - Chemical composition and the ratio of natural to synthetic rubber;

  - Size distribution;
  - Micro-morphology of particles;
  - Content;
- Curing temperature;
- Mixing shear energy;
- Base bitumen composition (SARA decomposition approach);
- Curing duration.

Adding rubber particles to bitumen binder alters the performance of HMA for paving applications by modifying binder properties. Property modification depends on both material variables and interaction variables. Material variables include bitumen properties and crumb rubber properties. Bitumen properties include stiffness and chemical composition while crumb rubber properties include source and method of processing. Another material factor affecting the binder properties is crumb rubber concentration. Interaction process variables include time and temperature. A material variable, compatibility between bitumen and CR, must also be considered (Jensen and Abdelrahman, 2006).

Hanson and Duncan (1995) concluded that bitumen sources had little or no effect on the way the rubber reacted with bitumen. However, Western Research Institute (WRI) found that bitumen source controlled the asphalt rubber binder properties and had significant effect on the way asphalt-rubber interacted at different temperatures (Jensen and Abdelrahman, 2006).

The properties of asphalt-rubber binders produced by wet process depend basically on the characteristics of both crumb rubber and bitumen used in the process (Neto *et al.*, 2006). The changes in binder properties reflect changes in the gel-like structure developed during the interaction process. Particle swelling stiffens the binder by decreasing the inter-particle distance and by decreasing the liquid phase of the binder (Jensen and Abdelrahman, 2006).

The use of two different base bitumen of the same “commercial” bitumen grade in asphalt rubber production results in two final products with different properties. The base bitumen should be selected carefully to ensure that the content of light fractions of bitumen is large enough at the end of the curing process (Ould-Henia and Dumont, 2006). Since the interaction that occurs with asphalt rubber binders is dependent on the presence of aromatic oils in the bitumen, the source of the base bitumen binder has a significant effect on the performance of asphalt rubber binders (Putman and Amirkhanian, 2006).

Bitumen grades were shown to have more effect on performance related properties of asphalt rubber binders than crumb rubber source. A major factor affecting the product was found to be the rubber content. The interaction conditions of time and temperature were shown to affect the developed properties of asphalt rubber binders. The effect of time is greatly dependent on the temperature (Jensen and Abdelrahman, 2006).

According to ASTM D6114/97, the asphalt-rubber binders are obtained from a combination of bitumen, crumb rubber recycled from used ground tires and others additives, as necessary. These additives are normally extender oils used to improve the workability of asphalt-rubber or the compatibility between the straight binder and the crumb rubber used (Neto *et al.*, 2006).

In general, crumb rubbers can be used within a wide range of contents and sizes to reduce the low temperature stiffness of bitumen binders. However, the optimum crumb rubber content must be determined for each crumb rubber size and bitumen binder (Gopal *et al.*, 2002), because rubber concentration was found to have the largest effect on the final properties of the binder (Jensen and Abdelrahman, 2006).

In 1995, Bahia and Davis concluded that the impact of crumb rubber content (2-20%), on the reduction of stiffness at low temperature (-20 to 0 °C) is a linear function of the rubber content and was independent of the rubber source and that the lower the stiffness of the bitumen the less significant the effect of the rubber (Gopal *et al.*, 2002). Compared to the other factors, rubber source is not found to have an important effect on the change in properties (Bahia and Davies, 1995).

Addition of rubber results in improving high-temperature performance grade of the binder, although rubber type, content, particle size and reaction time are factors affecting the level of improvement. Increasing stiffness brings up an effect of improving high-temperature performance of asphalt-rubber binder (Amirkhanian and Kim, 2004).

Experiments on binders made with finely ground rubber indicate faster property modification than coarser rubber. For the same specific interaction conditions, less fine rubber is required to achieve the same degree of property modification, as compared to coarser CR (Jensen and Abdelrahman, 2006).

The small particle size of elastomer (CR) was a very important factor to achieve good properties in the asphalt-rubber blends. It contributed to reduce time and temperature curing consequently reduced depolymerization and improved aging resistance (Leite and Soares, 1999).

The effect of the interaction conditions on the development of the high temperature properties can be summarized as follows (Jensen and Abdelrahman, 2006):

- The interaction temperature controls the activity of the interaction process. There are two main activities within the interaction process: swelling and depolymerization. Interaction temperature affects the process by controlling the time when swelling is replaced with depolymerization;
- Shearing energy can be very effective in controlling crumb rubber particle sizes during the interaction process. Higher shear turns coarser particles into fine particles and help stabilize CR binder properties.

4.3.1. Rheology of the asphalt rubber binders

Increasing the curing time, curing temperature, and rate of mixing increased the amount of rubber dissolution into the bitumen during the curing process. Increased rubber dissolution was determined to improve the low- and intermediate-temperature rheological properties of a binder (Billiter *et al.*, 1997b).

After the initial increase in high-temperature viscosity with the addition of rubber, the high-temperature viscosity decreased significantly with increased rubber dissolution. Furthermore, by using high temperature and high shear, along with extended curing time, the rubber particles can be devulcanized and depolymerised into the bitumen to produce an asphalt-rubber binder that is both homogeneous and truly elastic (Billiter *et al.*, 1997b).

The evolution of the bitumen phase properties is mainly due to the interaction with crumb rubber. (Ould-Henia and Dumont, 2006):

- Viscoelastic properties of asphalt rubber are mainly related to rubber content and bitumen composition;
- The evolution of the rheological properties of the bitumen recovered from asphalt rubber is more important for base bitumen with low aromatic fraction content. This change is mainly due to light fraction migration and cannot be entirely attributed to bitumen aging;
- The residual rubber phase recovered from asphalt rubber exhibits viscoelastic properties, strongly affected by the base bitumen composition.

Rubber content is the key factor affecting the viscoelastic properties of asphalt rubber binders. Increasing rubber content in asphalt rubber induces, for all frequencies, a tightening of modulus range on the Black’s curve as well as a reduction of the phase angle for both base bitumen (Ould-Henia and Dumont, 2006).

In general, by increasing the rubber content, the observed changes are the following ones (Ould-Henia and Dumont, 2006):

- an increase in stiffness modulus at high temperatures;
- a decrease in stiffness modulus at low temperatures;
- a decrease in phase angle.

The rubber confers a part of its elasticity to the blend at low temperature and reduces the flow behaviour by the presence of dispersed polymer networks (Ould-Henia and Dumont, 2006). The mechanical contribution of rubber dominates for high temperatures, whereas the one of bitumen is determinant for low temperatures (Ould-Henia and Dumont, 2006).

The results of dynamic shear testing show small improvements in performance grade (PG) by the incorporation of tire rubber. However, the results appear to be insensitive to the particle size of the rubber modifier in the binder (Coomarasamy and Hesp, 1998).

Putman and Amirkhanian (2006) affirm that the addition of crumb rubber to bitumen binders increases the rheological properties of the binders. They found that the viscosity increased with decreasing particle size, while the G* increased with particle size.

The viscosity and G* of the drained binders are greater than those of the base binders. This indicates that the crumb rubber particles do, in fact, absorb some of the lighter fractions of the binders as a result of the CR-bitumen interaction (Putman and Amirkhanian, 2006).

The addition of ground tire rubber considerably enhances the low-temperature properties of bitumen. The effect is particularly good in bitumens that originally have a high degree of stiffness. At intermediate temperature, the complex viscosity is considerably increased by rubber addition which should increase rutting resistance. Temperature susceptibility is considerably improved by rubber addition. All of these effects are bitumen dependent (Billiter *et al.*, 1997a).

The Texas Transportation Institute (TTI) study showed the binder creep stiffness decreased with time and the logarithmic creep rate increased with time, both property improvements. For bitumen with poor low temperature properties, increased interaction time caused further improvement at a constant rate. For bitumens with good low temperature properties, after improvement during the first hour, the interaction time had a negligible effect on creep stiffness (Jensen and Abdelrahman, 2006).

The residual bitumens showed a considerable increase in high temperature viscosity, complex modulus and elastic response compared to both the virgin as well as the oxidised binders. In general, the increase in viscosity, stiffness and elastic response can be considered to be similar irrespective of crude source or penetration grade, although the absolute values for these parameters will be lower for the "softer" bitumens (Rahman, 2004).

4.3.2. Physical properties of asphalt rubber binders

The amount of crumb rubber added to the bitumen will influence blend properties with higher amounts providing greater changes in properties. Generally, as the rubber content increases: (i) the viscosity of the material at 175 °C increases; (ii) the resilience increases; (iii) the softening point increases; (iv) the penetration at 25 °C decreases (Fontes *et al.*, 2006).

Additional factors include: i) crumb rubber surface area; ii) grinding process; iii) crumb rubber chemical composition; iv) contaminants (water, fibre, metal) can also influence properties of asphalt rubber (Fontes *et al.*, 2006).

Parameters of the interaction process used in developing performance related specifications of asphalt rubber binders can be varied by selecting different combinations of material properties and interaction variables. For example (Jensen and Abdelrahman, 2006):

- Interaction temperature controls progression of interaction activities. For a specific asphalt rubber combination, lower interaction temperature results in particle swelling that will continue for a relatively longer period of time while higher interaction temperature results in particle swelling for only a short period of time followed by depolymerization;
- The effect of interaction time at different temperatures shows there is an initial period when most of the modified binder properties develop followed by a stabilizing period. The duration of the initial period varies depending on CR material properties such as rubber source and particle size;
- Shearing energy controls crumb rubber particle size; higher energy converts coarser particles into finer particles. Finer particles help stabilize the binder production process;
- Higher crumb rubber concentrations have significant effects on the matrix and the liquid phase of the binder. Higher crumb rubber concentrations congest the matrix with swollen particles at low interaction temperatures. At higher interaction temperatures, a higher concentration of smaller particles depolymerise more quickly, which produces greater changes in modified binder properties. Higher crumb rubber concentrations also absorb more binder volatiles, stiffening the liquid phase more than lower crumb rubber concentrations. Higher crumb rubber concentration did not

significantly modify the interaction conditions required for the development of G* and δ when compared to lower CR concentrations;

- The high temperature properties, G* and δ, were not developed by the same process. The increase in G* is mainly due to particle swelling. The decrease in δ continues even during the early stages of depolymerization, indicating that swelling is not the sole factor affecting the development of the phase angle (δ). Component exchange between bitumen and rubber in the early depolymerization stages stiffens the binder liquid because depolymerization (of rubber) adds more elasticity to the binder. Depolymerization of rubber appears to have the largest effect on modifying δ;
- Binder stability can be achieved through high speed mixing and/or through extending the interaction time, up to a maximum of about eight hours.

It can be observed that the increase of the specific surface (smaller particles) increases the rotational viscosity, softening point and resilience of asphalt-rubber samples tested (Neto *et al.*, 2006).

Elastic recovery describes the ability of a bitumen binder to elongate when tension is applied and to recover its original shape when the tension is released. This property is important in both fatigue and rutting resistance. Elastic recovery is a property that is indicative of the quality of polymer components in bitumen binders (Jensen and Abdelrahman, 2006).

Oliver (1981) concluded that elastic recovery of the asphalt-rubber binders tends to increase as the rubber particle size decreases. Chehovits *et al.* (1982) showed that coarser particles create a mix that is more sensitive to rubber concentration or bitumen grade. Frobel *et al.* (1978) concluded that finer rubber particles result in higher ductility than larger particles, and that toughness increases as particle size decreases. Lalwani *et al.* (1982) reported that toughness increased as particle size decreased and that particle size had no effect on elastic recovery (Jensen and Abdelrahman, 2006).

Oliver (1981) examined the general trend of the progression of elastic strain recovery as a function of both time and temperature. A combined effect of both time and temperature was noted, with minimum elastic recovery value developed at maximum time and maximum temperature, two hours and 240 °C, respectively (Jensen and Abdelrahman, 2006).

Unmodified bitumen shows practically no recovery. Binders modified with crumb rubber from car tyres recover less than those modified with crumb rubber from truck tyres (Figure 4.6). Truck tyre rubber hardened and absorbed more bitumen than car tyre. Equilibrium swelling mass uptake depended on bitumen origin and grade. Bitumens with high asphaltene content were less prone to swell rubber.

Interaction with rubber stiffened the residual bitumen. G* increased and δ decreased. The rubber modified binders recovered between 4 and 12% depending on rubber origin and mixing conditions (Khalid, 2005).

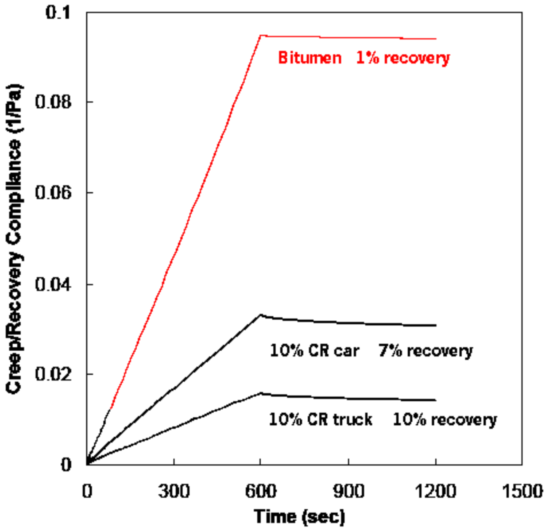


Figure 4.6 – Effect of the addition and crumb rubber (CR) origin (truck or car) in the binder recovery (Khalid, 2005)

Binder elasticity was drastically reduced (by as much as three times) when temperature was increased from 200 to 300 °C, while no significant differences occurred due to changing temperature from 150 to 200 °C. In all cases, rubber concentration was the main controlling factor, particularly in reducing temperature sensitivity. Jimenez (1978) reported that AR ductility was not affected by interaction temperature (Jensen and Abdelrahman, 2006).

Modified binders underwent a significant enhance on the elastic recovery, and, in contrast, the ductility decreased with respect to unmodified binders (Martinez *et al.*, 2006).

Rosner and Chehovits evaluate the effects of rubber type and concentration on the properties of asphalt-rubber binders and fond that rubber type affects the viscosity at 60 °C and the force ductility properties at 4 °C. They also found that viscosity increase with the increase in rubber concentration and, from the force ductility test at 4 °C, that the load failure increases, and the elongation at failure decreases as rubber concentration increases. The same authors concluded that low-viscosity base bitumen produce lower viscosities, lower failure stresses, and higher failure strain properties in asphalt-rubber binders (Epps, 1994).

The viscosity is a continuously increasing non linear function of rubber content, and the relative increase is a function of temperature (Bahia and Davies, 1995).

CR content and temperature are found to have a statistically significant effect on the increase in viscosity. The CR content effect, however, is found to be more significant than temperature and is found to be independent of the effect of temperature (Bahia and Davies, 1995).

Oliver (1979) concludes that when curing asphalt rubber at high temperature and mechanical energy (from agitation) the viscosity first increases and eventually begins to decrease (Billiter *et al.*, 1997a).

The wet process, where the bitumen and the rubber react at elevated temperatures (190 to 260 °C) is the increasingly preferred method. This process produces asphalt-rubber binders that are heterogeneous, consisting of rubber particles in the bitumen medium and that are highly viscous compared to bitumen binders (Leite and Soares, 1999).

Asphalt rubber production according to the wet process is assumed to be essentially a physical interaction between bitumen and rubber particles (PIARC, 1999; Rouse, 1997; Singleton et al, 2000). The main change in the composite system bitumen-rubber is the swelling of the rubber due to the migration of light fractions of bitumen through the cross-linked polymeric network. The swelling of rubber is demonstrated by an increase in viscosity which has to be controlled to satisfy the pumping and the mixing conditions (Ould-Henia and Dumont, 2006).

Finer sized crumb rubber materials will generally experience quicker swelling due to their increased surface area and will produce higher viscosities than crumb rubber with larger particle sizes (Fontes *et al.*, 2006). Ground tire rubber materials with greater specific surface area and more irregular-shaped particles also produced asphalt rubber binders having higher viscosities (Fontes *et al.*, 2006).

The change in rubber particle sizes and formation of gel structures, during asphalt rubber production, results in a reduction in the inter-particle distance and produces a modified gel which produces a viscosity increase of up to a factor of ten (Jensen and Abdelrahman, 2006).

4.3.3. Influence of rubber in the pavement performance

The use of reclaimed rubber obtained from tires has been taken into consideration in order to improve conventional bitumen properties such as higher resistance to rutting and to thermal cracking (Lima *et al.*, 2006). The addition of crumb rubber into a bitumen binder also improves its elastic and energy absorption properties, which are directly related to the binder's resistance to cracking and rutting failures (Gopal *et al.*, 2002).

There is moderate improvement in thermal cracking resistance of mixes containing rubber modified binders, with systems containing smaller particles performing better than the others (Coomarasamy and Hesp, 1998).

The crumb rubber size did not have significant effect on the low temperature properties. The effect of the size of the crumb rubber on the resistance to thermal cracking is dependent on the bitumen binder source (Gopal *et al.*, 2002). However, increasing the crumb rubber content decreased the creep stiffness which improves thermal cracking resistance (Gopal *et al.*, 2002).

Fracture toughness is a material parameter that measures the resistance of the material to crack. Fracture toughness is directly related to the energy released during crack propagation. As such, fracture toughness is a better parameter for measuring the ability of bitumen to relieve internal stresses before they build up and lead to catastrophic failure. The rubber modification improves the fracture toughness of the binder (Coomarasamy and Hesp, 1998).

The higher rubber contents better the cold stiffness properties and fatigue resistance and lower the aging index (Leite and Soares, 1999).

Asphalt rubber had an excellent fatigue and permanent deformation resistance behaviour, and presented the best rheological behaviour after aging by the SuperPave methods (Martinez *et al.*, 2006). The better fatigue properties of the asphalt rubber binder course layer can be useful to prolong the pavement life without significantly compromising the deformation resistance (Rahman, 2004).

To increase the capability of the bituminous pavement in sustaining temperature changes, several countries are employing rubber and synthetic polymers in the binder formulation (Lewandowsky, 1994). Some beneficial effects of polymer addition on bitumen binder include decreased thermal susceptibility and permanent deformation, increased fatigue and low temperature resistance. In addition to virgin rubbers, elastomers and thermoplastics, the employment of ground tire rubber GTR has an economical interest (Leite and Soares, 1999).

Discarded rubber tires have found end-use applications in bitumen binders in order to improve the low- and high-temperature performance of the road surface (Coomarasamy and Hesp, 1998).

At higher temperatures, i.e., hot days, the rutting effect is reduced compared to the original bitumen by increased viscosity contributions from the partially digested tire rubber solids. The elastic contribution of the added material would reduce thermal cracking at temperatures below freezing, and fatigue cracking is also benefitted by the higher elasticity at more common daily temperatures (Glover *et al.*, 2002).

The resistance to rutting of mixes based on crumb rubber modified binders is significantly better than that of the reference samples. By crumb rubber modification of a softer grade (150-200 pen) bitumen, it may be possible to obtain comparable rutting resistance to that of an 85-100 pen grade bitumen (Coomarasamy and Hesp, 1998).

Huff and Vallerga (1979) note that bitumens low in aromatic oil produced an asphalt rubber product with poor adhesive properties (Glover *et al.*, 2002).

There is much research indicating that crumb rubber can improve certain characteristics of bituminous pavements. The obvious benefit of adding rubber to bitumen is that the rubber imparts elasticity to the binders, which helps increase pavement fatigue life or fatigue resistance, as well as reduces reflective cracking. This elasticity also makes the pavement more flexible, thus improving the pavement's susceptibility to low-temperature cracking. It has been reported that rubber also imparts tensile strength, ductility, toughness, resiliency, tenacity and thus, durability to the binder. Asphalt-rubber binder has a higher softening point than bitumen, which improves resistance to rutting. The improved adhesion of asphalt-rubber binder promotes chip retention when it is used as a chip seal. Rubber-modified pavement improves skid resistance even under icy conditions. Furthermore, the practice of utilizing rubber in bitumen is environmentally friendly since it eliminates solid waste and reduces traffic noise. On the other hand, the addition of rubber increases the viscosity of the binder at high temperatures, which can make compaction more difficult. The high compaction viscosity can lead to high air void content and thus, high rates of oxidation which, overtime, leads to pavement brittleness (Billiter *et al.*, 1997a).

The performance of asphalt rubber mixtures can be enhanced with respect to conventional bituminous mixes, provided that mix formulation is carefully studied and adequate construction practices are followed (Antunes, 2006).

In conclusion, asphalt-rubber binder with improved low temperature cracking resistance, improved mid-temperature rutting resistance and temperature susceptibility, and a non-detrimental high-temperature compaction viscosity, all relative to the base bitumen, can be produced with success (Billiter *et al.*, 1997a).

4.4. Influence of Aging in the Binder Properties

The role played by weather and environmental factors on bituminous pavement distress is a subject of continuous interest (Campbell and Wright, 1962).

Earlier studies carried out on the effect of temperature and relative humidity on the oxidation of air-blown bitumens, as a function of exposure time, showed that the rate of oxidation is dependent on both of these environmental factors (Chipperfield and Dutie, 1970).

Bitumen ageing occurs during the mixing and construction process as well as during long-term service in the road. The circumstances at different ageing stages vary considerably. The factors affecting bitumen ageing include characteristics of the bitumen and its content in the mix, nature of aggregates and particle size distribution, void content of the mix, production related factors, temperature and time. All these factors operate at the same time, making the process of bitumen ageing very complex. The simulation of field ageing entails increasing the temperature, decreasing bitumen film thickness, increasing oxygen pressure, or using combinations of these factors. Kinetics of bitumen ageing may vary with test conditions (Lu and Isacsson, 2002).

By comparison with changes induced by field ageing, it has been established that binder ageing is characterised by (FEHRL, 2006):

- Changes in the generic composition;
    - appearance of oxidised functions (development of ester, acid and sulfoxide functions) and transformation of the cyclic compounds into resins and then into asphaltenes;
    - with preferential formation and accumulation of resins during field ageing;
    - with preferential formation of asphaltenes during the “in construction” ageing;
- Modifications of the properties;
    - increase of R&B softening point;
    - decrease of penetration;
- Variations in rheological properties;
    - viscosity;
    - complex modulus;
    - phase angle.

4.4.1. Bitumen aging chemistry

The chemical composition of bitumen determines its physical properties. However, the chemical composition of bitumens changes during both the short term (handling and pumping) and long term (field service) (Glover, 2007).

Bituminous binder aging is a main factor that reduces pavement service life (Lima *et al.*, 2006). Oxidation adds to age hardening and brittleness of bitumen by contributing to the structures zones within binder (Robertson, 1991).

In bitumen ageing, two types of mechanisms are involved. The main ageing mechanism is an irreversible one, characterised by chemical changes of the binder, which in turn has an impact on the rheological properties. The processes contributing to this type of ageing include oxidation, polymerization, condensation, loss of volatile and exudation (migration of oily components from the bitumen into the aggregate) (Lu and Isacsson, 2002). The second mechanism is a reversible process called physical hardening. Physical hardening may be attributed to molecular structuring, i.e. the reorganisation of bitumen molecules (or bitumen microstructures) to approach an optimum thermodynamic state under a specific set of conditions (Lu and Isacsson, 2002).

However, reaction with oxygen (oxidative hardening) has been shown to be the principal factor responsible for a more brittle structure and an increase in susceptibility to cracking. Oxidative hardening happens at a relatively slow rate and varies seasonally. It occurs faster at higher temperature as diffusion of oxygen increases. Therefore, aging is considered as a chemical as well as a physical problem (Glover, 2007).

The mechanism of bitumen oxidation is very complex. It could be that oxidation of methylene and degradation of unsaturated chains and/or naphthenic rings of benzene systems lead to ketones and carboxylic acids, respectively, and oxidation of thio-ethers to sulfoxides. In addition, aromatization and chain scission may occur during oxidative ageing, which do not result in oxygen incorporation in the bitumen. The functionalities formed should introduce an increase in the overall polarity of the bitumen, which in turn will influence bitumen rheology (Lu and Isacsson, 2002).

The aging (hardening) of bitumen binder is usually associated with the loss of volatile components and oxidation of the bitumen binder during bituminous mixture construction (short-term aging) and progressive oxidation of the in-place material in the field (long-term aging) (Airey, 2003).

Chemical changes during the mixing/laying operations (Figure 4.7) reveal an appreciable degree of oxidation and polymerization of the cyclic molecules to form resins, whilst to a lesser extent the resins have been similarly oxidized and polymerized to form asphaltenes. The saturates content of some bitumens remain substantially unchanged, whereas the saturates contents of other bitumens increased with time (Chipperfield *et al.*, 1970).

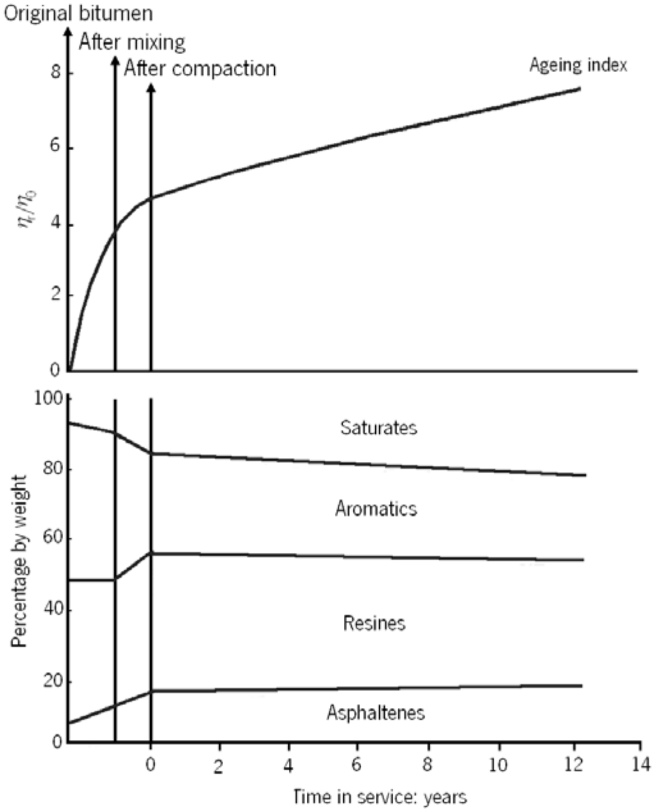


Figure 4.7 – Changes in bitumen composition during mixing, laying and in service (Chipperfield *et al.*, 1970)

The principal cause of ageing in service of bituminous binders is the oxidation by oxygen from the air of certain molecules. This oxidation results in the formation of highly polar and strongly interacting oxygen containing functional groups (Mouillet *et al.*, 2008).

During service, an bituminous pavement becomes aged, that is, the brittleness of the material gradually increases due to physico-chemical changes in the binder. Four principal mechanisms are related to bitumen ageing: (i) exudation; (ii) evaporation; (iii) oxidation and; (iv) physical ageing. The most important of these is the oxidation. In bitumen oxidative ageing, formation of functionalities containing oxygen as well as transformation between different binder components can be observed. Usually, the asphaltene content increases while the content of aromatics decreases. Saturates are inert to oxygen, and thus only slight changes in this fraction may occur due to volatilisation, as it can be observed in

Figure 4.8. The transformation between bitumen components during oxidative ageing may be written as: Aromatics ⇨ Resins ⇨ Asphaltenes (Isacsson and Zeng, 1997).

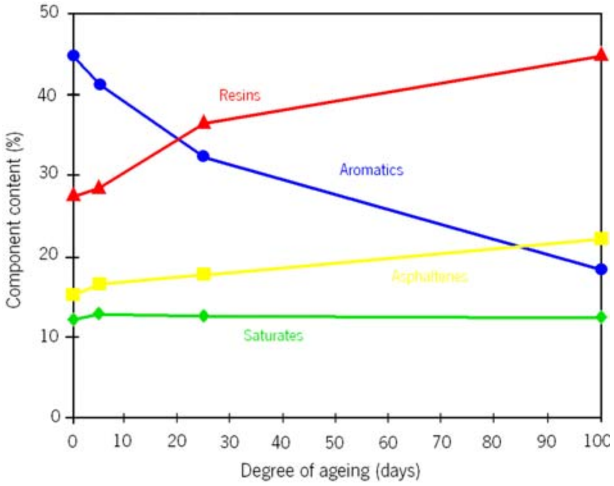


Figure 4.8 – Effect of ageing on chemical composition of a binder recovered from porous bituminous pavement (Isacsson and Zeng, 1997)

Several previous studies of thin film bitumen aging have been performed. As bitumen ages, it quickly passes through a rapid aging rate regime, during which the viscosity and carbonyl area have been shown to rapidly climb. This rapid aging is attributed to the presence of sulfoxide materials and highly reactive carbonyl-forming sites. After this initial-jump phenomenon, a constant rate state is reached (Glover *et al.*, 2002). The asphaltenes increase after the aging test is result of both oxidation and volatilization process (hardening) which is reflected in enhance on the binder stiffness (Martinez *et al.*, 2006).

Because the main cause for ageing of bituminous binders is oxidation, the chemical transformations of the binders during ageing can be determined by analytical techniques such as the infrared spectroscopy, which informs on the nature and concentration of functional and structural groups (Mouillet *et al.*, 2008).

The changes in bitumen generic SARA (saturates, aromatics, resins and asphaltenes) fractions and Fourier transform infra-red spectroscopy (FTIR) observation show a small difference between TFOT and RTFOT (Lu and Isacsson, 2002).

Gel-permeation chromatography (GPC) analysis can be used to demonstrate that association of smaller molecules with higher polarity may contribute to the high molecular weight fraction of the bitumen. This may also be indicative of the formation of highly polar functional groups during ageing (Lu and Isacsson, 2002).

The aging of conventional bitumens in service results in carbonyl growth. This reaction produces asphaltenes which then harden the material. The oxidation rate ultimately determines the hardening rate, but the hardening susceptibility, a characteristic of each bitumen, is important for establishing the extent to which oxidation causes hardening (Glover *et al.*, 2002).

Figure 4.9 shown clusters of ten or more individual micelles, illustrating the relative increase in size of the asphaltenes which occurs during aging due to oxygen uptake. Studies of the asphaltenes from the same AC-5 binders before and after aging indicate that no significant weight loss or decomposition occurs until the temperature exceeds 350 °C. Nevertheless, the particle size varies from 0.2-0.3 μm before aging to 0.8-1.2 μm after aging (Rozeveld *et al.*, 1997).

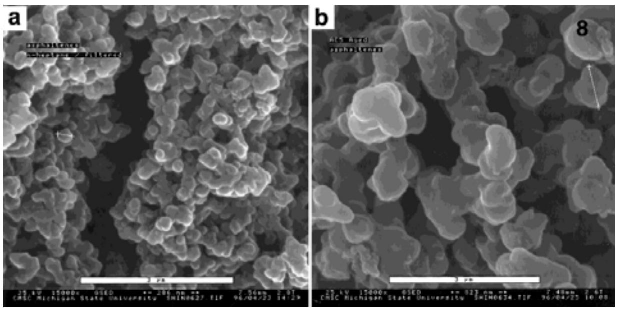


Figure 4.9 – ESEM images of asphaltene fraction for (a) an AC-5 binder and (b) an aged AC-5 binder (Rozeveld *et al.*, 1997)

Aged bitumens examined in the ESEM showed a significant change in network morphology. The network in aged bitumens was significantly coarser, with a corresponding increase in the fibril diameter, approximately 15 μm *vs.* 10 μm for the unaged samples. The fibrils in the network structure are considered to consist of the high molecular weight asphaltene/resin micelles. These microstructural observations correlate well to known changes in binder properties during aging (i.e., an increase in the molecular weight and viscosity) (Rozeveld *et al.*, 1997).

4.4.2. Rheology of aged bitumen

Bitumen is a viscoelastic material, which displays either elastic or viscous behaviour, depending on temperature and time of loading. At sufficiently low temperatures and/or short loading times, bitumen behaves essentially as an elastic solid. As temperature increases and/or loading time increases, the viscous property of bitumen becomes more obvious. At sufficiently high temperatures and/or long loading times, bitumen is essentially a Newtonian liquid, and can be described by a shear rate independent viscosity value. The temperature and time dependence of bitumen rheology may be changed by the process of ageing (Lu and Isacsson, 2002).

The aging dependency of rheological properties of bitumen is similar to the temperature dependency of bitumen, but is reversed in nature. An increase in aging level corresponds to a decrease in temperature (Huang and Zeng, 2007).

Gel-type bitumens tend to lose complex flow (a measure of non-Newtonian behaviour) upon heating. The phenomenon of isothermal, reversible age hardening, termed *steric* hardening, is a strong evidence for the formation of secondary structures in the bitumen unstable to heat and mechanical agitation (Petersen *et al.*, 1994).

For practical purposes it is important to correlate chemical changes due to oxidative hardening with changes occurring in physical properties. Upon aging, in-service bituminous binder becomes stiffer, suggesting systematic microstructural changes as *steric* hardening observed with rheological measurements (Petersen, 1984; Glover, 2007).

Ageing influences bitumen chemistry and rheology significantly. Chemical changes include the formation of carbonyl compounds and sulfoxides, transformation of generic fractions, and increases in amount of large molecules (or molecular association), molecular weight and polydispersity. As a result of the chemical changes, the mechanical properties of aged bitumens become more solid-like, as indicated by increased complex modulus and decreased phase angle. However, the chemical and rheological changes are generally not consistent. Consequently, ageing susceptibility of bitumens may be ranked differently when different evaluation methods are used. Using either chemical analyses or rheological measurements, a strong correlation is observed between TFOT and RTFOT, and the two methods show similar severity (Lu and Isacsson, 2002).

With ageing, the complex modulus (G*), storage modulus (G') and the loss modulus (G'') increase and the phase angle (δ) decreases. These indicate that aging makes the mechanical properties of the bitumen more solid-like (Lu and Isacsson, 2002).

With the increase in LMS due to the aging effects, the rutting parameter ($G^*/\sin\delta$) increases significantly. There is a significant correlation between molecular size distribution (MSD or LMS) and the rutting resistance property (Amirkhanian and Kim, 2004).

4.4.3. Asphalt rubber aging

The ageing of the asphalt rubber mixtures leads to an increase in stiffness through excessive loss of the lighter fraction of bitumen because of the combined effect of normal oxidation and rubber-bitumen interaction following short-term and long-term ageing. Consequently, the brittleness of the mixtures increased due to the loss of adhesive and cohesive strength of the material resulting in a reduction in fatigue life and resistance to permanent deformation of the long-term aged mixtures. However, the predicted strain and fatigue lives, calculated from fatigue and strain equations, were still better than similarly aged corresponding conventional mixtures. In addition, the compaction effort did not appear to have further significance on the long-term ageing properties for the asphalt rubber mixtures then it had on the control mixtures (Rahman, 2004).

The incorporation of rubber in bitumen binders provides enhanced aging characteristics. Low-cure blends have very low hardening rates and decreased hardening susceptibilities (hardening in response to a given amount of oxidation), mainly due to the predominance of suspended particles that elevate bulk viscosity, while not necessarily improving the bitumen phase (Glover *et al.*, 2002).

A higher rate of mixing and curing temperature worsened the aging index. Generally, higher the rubber content, lower the aging index. Bitumen with lower molecular weight improved the aging characteristics of the binder (Leite and Soares, 1999).

The impact of the crumb rubber modification improved the aging susceptibility, decreasing the binder aging ratio (Martinez *et al.*, 2006). The bitumen and asphalt rubber binders aging studies, using RTFOT and PAV, showed that the crumb rubber contributed to binder stability, acting as an antioxidant in the aging process (Lima *et al.*, 2006).

A series of rotational viscometer and gel-permeation chromatography (GPC) tests were conducted. From these results, the following conclusions were drawn (Lee *et al.*, 2006):

- The longer blending time and the higher blending temperature for the rubber modified binder seemed to lead to an increase in the viscosity at 135 °C, which is related to the increase in the rubber mass through binder absorption;
- The asphalt binder with the higher rubber content exhibited slightly higher LMS values, and the increase in rubber content is thought to result in the additional loss of the low molecular weight maltenes of the asphalt binder during the blending;

- In general, the higher rubber content resulted in the higher increase in the LMS value of asphalt binder under the aging conditions used in this study. With relatively higher rubber contents such as 15% and 20%, the asphalt binders showed a tendency that the LMS values decrease after a certain level;
- The results of LMS values of all mixtures subjected to the short-term and longterm aging indicated that the same aging level was produced comparing control sample with rubber-modified binders.

There are several available methods to investigate physical properties in the rubber modified bitumen under aging conditions. One of the most used equipments is the dynamic shear rheometer (Lima *et al.*, 2006).

4.4.4. Effects of aging in the pavement performance

Bitumen ageing is one of the principal factors causing the deterioration of bituminous pavements. Important ageing related modes of failure are traffic and thermally induced cracking, and ravelling (Lu and Isacsson, 2002). Furthermore, bitumen aggregate de-bonding (adhesion failure) and/or bitumen phase separation (cohesion failure) is a result of oxidative hardening (Glover, 2007).

The quantity of low molecular weight and of nonpolar molecules is reduced when bitumen ages (Branthaver *et al.* 1993). This reduction occurs due to the conversion of nonpolar molecules to polar carbonyl group. These new polar sites will form associations with other polar molecules, making the bitumen molecules to which it is attached act as strong polar, associating molecules. Certainly bitumens that have too many polar materials will be subjected to thermal cracking, brittleness and fatigue cracking in the pavements. On the other hand, bitumens that have too much nonpolar material will suffer from rutting and moisture damage as well (Huang and Zeng, 2007).

The bituminous binder loses lighter components upon its exposure to air (Lima *et al.*, 2006). The increased content of high molecular components (resins, asphaltenes) results in increased hardness of the binder, which in turn means higher fracture temperature (Isacsson and Zeng, 1997).

5. EXPERIMENTAL STUDY OF BITUMEN, RUBBER AND THEIR INTERACTION IN ASPHALT RUBBER BINDERS

5.1. Experimental Procedure: Materials and Methodology

5.1.1. Preparation of the Materials

In order to accomplish the objective of this work, and to prevent possible errors due to the variability of the characteristics of the materials, the bitumens to be used in this work were carefully selected. Therefore, the used bitumens were collected from the same batch of bitumen production at the refinery, because, as mentioned earlier, the characteristics of bitumens highly depend on their sources and processing.

Furthermore, it is known that asphalt rubber (AR) characteristics depend on the bitumen used. In order to better understand how different graded bitumens affect AR properties, a wide range of graded bitumens were chosen to conduct this research. Due to the difficulty that the refinery experienced in order to supply bitumens different from those of the commercial line, all the commercial base bitumens of the Spanish refinery (10/20, 40/50, 60/70 and 150/200) were used to obtain a great variety of bitumens in a wide pen range.

5.1.1.1. Bitumen samples

The referred commercial bitumens were combined in different proportions to obtain 16 samples of bitumen as indicated in Table 5.1.

Table 5.1 – Proportions of commercial bitumen combined to obtain the 16 different bitumen samples

Sample designation		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Commercial bitumen	10/20	100%	75%	50%	25%						25%	50%	75%				
	40/50		25%	50%	75%	100%	75%	50%	25%								
	60/70									100%	75%	50%	25%		25%	50%	75%
	150/200						25%	50%	75%					100%	75%	50%	25%

The characterisation of these 16 bitumen samples was based in two groups of properties:

- Physical properties (Pen at 25 °C – NP82/1964, dynamic viscosity – ASTM D4402, ring and ball softening point – E34/1955);
- Rheological properties, using the dynamic shear rheometer (DST) in 8 selected bitumens.

Besides these determinations on the new samples, the four commercial bitumens were also subjected to other procedures in order to assess their reaction to the process of asphalt rubber (AR) binder production, bituminous and AR mixtures production and compaction, namely:

- RTFOT (EN 12607-1);
- “Sphere AR production simulator” (procedure developed in this work).

After these procedures, the physical and rheological properties of the bitumen obtained were assessed, and the changes in the binder were measured.

5.1.1.2. Crumb rubber sample

The crumb rubber used in this work was obtained by the cryogenic process. According to the supplier, the crumb rubber was constituted by 30% of truck tyres and 70% of car tyres.

The supplied crumb rubber was sieved through a sequence of sieves in the laboratory, in order to use only the fraction passed through the sieve ASTM #20 (0.850 mm) and held on the sieve ASTM #40 (0.425 mm).

The sieved crumb rubber obtained in the laboratory was washed with toluene and dried in an oven at 135 °C. The clean and dry rubber particles where observed and measured, using an optical microscope (results are presented in Chapter 5.5.5). Crumb rubber was also analyzed to determine its soluble percentage (ASTM D 6814-02) and density (apparent and bulk density – AG:PT/T144).

5.1.2. Methodology

5.1.2.1. Asphalt rubber production

The method used to produce and collect the desired samples of AR, swelled rubber and residual bitumen was a modified “Basket drainage method” (Rahman, 2004).

The asphalt rubber production facility was constituted by an assemblage of equipments in a laboratory ventilator (Figures 5.1 and 5.2).

The wire basket used was manufactured with a wire mesh. This mesh was observed in an optical microscope (Figure 5.3). The average wire square mesh opening was 0.470 mm.

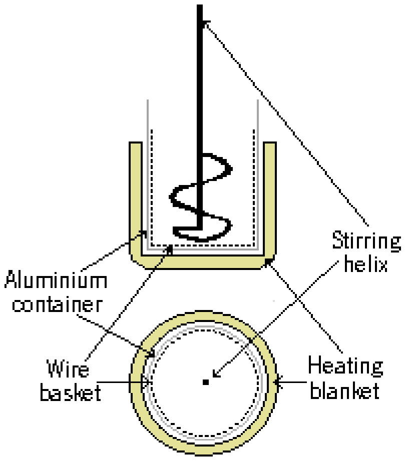


Figure 5.1 – Scheme of AR production facility

Figure 5.2 – Equipment used to produce the AR binders

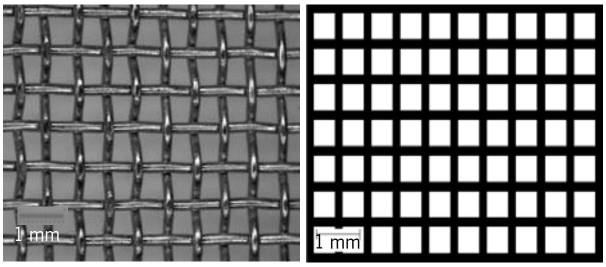


Figure 5.3 – Photograph and scheme of the wire mesh used to manufacture the basket

The procedures for the production and collection of samples followed the next steps:

- Heating approximately 1 kg and collection of a sample of base bitumen (B) at 180 °C;
- Measurement of the bitumen density;
- Introducing 21.0% w/w of crumb rubber (CR) and re-heating of the mix at 180 °C;
- Measurement of the “asphalt rubber” density;
- Maintain the temperature at 180 °C, while stirring the “asphalt rubber” at a velocity at 230 rot/min for 60 minutes (Figure 5.4);
- Measurement of the “asphalt rubber” density every 5 min, only for the commercial bitumens;
- Measurement of the density and collection of a sample of the asphalt rubber (AR) produced;
- Suspension of the basket in a oven at 180 °C for 15 min (Figure 5.5);
- Collection of a sample of the recovered rubber (RR) retained in the basket;
- Measurement of the density and collection of a sample of residual bitumen (Res) (Figure 5.6).

5.1.2.2. “Sphere AR production simulator”

One of the objectives of this research is to determine the extension of changes produced in the bitumen due to the interaction with crumb rubber.

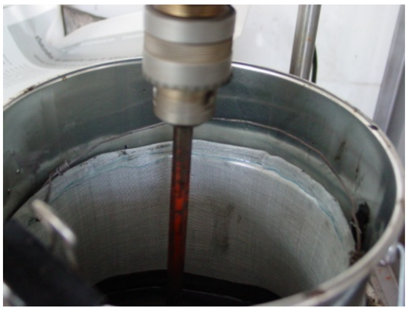


Figure 5.4 – Stage of production of the asphalt rubber binder

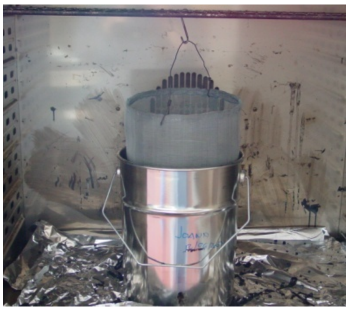


Figure 5.5 – Separation of the crumb rubber and residual bitumen from the AR binder

Figure 5.6 – Appearance of the residual bitumen and recovered rubber from the AR binder

As mentioned in Chapters 2.1 and 4.4, when heated bitumen oxidises, restructures and loses volatile molecules. Throughout the production of the AR binder, the mix is heated and stirred during 60 min. Moreover, when bitumen interacts with rubber, the rubber particles absorb the light parts of bitumen and swell.

Since the light molecules of bitumen possibly will evaporate during AR production, while other molecules will oxidise and associate, it is impossible to assess separately the changes produced by rubber and by the referred mechanisms. Thus, a new method was developed during this research in order to determine the changes induced only by heat and stirring of bitumen during AR production, being designated “Sphere AR production simulator”.

This method simulates the AR production, replacing the rubber particles by metallic spheres with approximately the same dimensions of crumb rubber particles, to reproduce the oxidation, evaporation and association (restructuration) processes, independently from the rubber swelling and interaction.

Before beginning the experimental procedure, the metallic spheres were observed and measured (Ø ≈ 0.825 mm) with an optical microscope (Figure 5.7) and their density was determined (7.75 kg/dm^3).

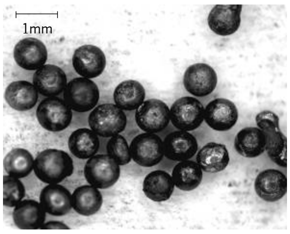


Figure 5.7 – Appearance of the metallic spheres used to simulate the crumb rubber particles

The assemblage used in the "Sphere AR production simulator" was similar to that where AR is produced, but in a reduced scale. The experimental procedure was the following:

- Heating approximately 150 g of a sample of base bitumen (B) at 180 °C;
- Introducing the equivalent volume to 21.0% w/w of crumb rubber of metallic spheres (≈ 240 g);
- Re-heating of the mix at 180 °C;
- Maintaining the temperature at 180 °C, while stirring at a velocity of 230 rot/min for 60 minutes;
- Suspension of the basket in a oven at 180 ° C for 15 min;
- Collection of a sample of the resulting "sphere" bitumen (Sb).

The physical properties of the resulting bitumen samples were immediately determined.

5.1.2.3. Aging of bitumen by the RTFOT method

A phenomenon of aging of the binder occurs during the process of production and compaction of bituminous mixes. The extension of this aging phenomenon is usually determined by applying a standard test method designated by RTFOT (EN 12607-1). In this work, the RTFOT method was applied to three bituminous binders in order to determine the difference of aging between these materials and to assess the effect of the presence of rubber particles in the AR binder during the aging process.

In order to evaluate, in a global perspective, the aging process in the presence of different grade bitumens, the four commercial bitumens and the resulting AR binders and residual bitumens were subjected to the RTFOT procedure. The physical properties of the resulting materials were immediately determined, and samples of these materials were also stored for further rheological analysis.

5.1.2.4. Recovery and analysis of AR rubber particles

Throughout the process of AR production, the rubber particles suffer great changes in their morphology. These changes are caused by the interaction with bitumen, which diffuses through the rubber reticulated structure causing them to swell, while transforming rubber from an elastic solid into a gel structure.

Furthermore, the AR production process involves aggressive stirring at high temperatures. These conditions favour the swelling process, but as rubber particles turn into gel structures they also become more fragile, and the stirring and eventual localized depolymerisation of the gel rubber particles can break them into little pieces. The wire basket mesh chosen guarantees that the rubber particles, in their initial shape, were not able to pass through the wire of the basket during the drainage of the residual bitumen, but it cannot assure that the final little pieces of depolymerised rubber will be retained.

The reported phenomena may vary when rubber particles interact with different grade base bitumens. In order to evaluate this phenomenon, the rubber particles recovered (RR) from ARs produced with the commercial bitumens and filtered from the respective residual bitumens (FR) were observed and measured with an optical microscope.

The preparation of the rubber particles from the recovered rubber for microscopic observations followed the next steps:

- Introducing 2.0 g of recovered rubber in a bottle with approximately 200 mL of toluene;
- Agitation of the bottle until the rubber particles were totally separated;
- Filtering the resulting solution with a filter paper, and washing it with toluene until the filtered solution appears absolutely clean;
- Drying the filter paper with the resulting recovered rubber in an oven at 135 °C;
- Observation and measurement of the clean particles in an optical microscope.

The preparation of the rubber particles, which have passed through the wire basket and were suspended in the residual bitumen for the microscopic observations, followed the next steps:

- Introducing 2.0 g of residual bitumen in a baker of 250 mL capacity;
- Dilution of the residual bitumen with small amounts of toluene while stirring the solution with a glass rod;
- The residual bitumen is diluted and the resulting solution is filtered through a filter paper. Then it is washed with toluene until the filtered solution appears absolutely clean;
- Drying the filter paper with the resulting filtered rubber in an oven at 135 °C;
- Observation and measurement of the clean particles in an optical microscope.

5.1.3. Rheological characterization

From the initial 16 samples of base bitumen, eight representative samples were selected for rheological evaluation, according to the variation of the physical properties of the base bitumens. The rheological properties of those 8 base bitumens, ARs and residual bitumens were assessed using a DSR.

The test selected temperatures to determine the rheological variation of the binder properties, in all its live stages, were 25, 35, 50, 80, 110, 140, 160 and 180 °C. For each temperature, frequency sweep tests between 0.1 and 10.0 Hz were performed in the linear viscoelasticity range, using a parallel plate geometry with 40 mm of diameter and a gap of 1.0 mm.

Primarily it was necessary to establish the input stress at each temperature. Therefore, previous stress sweep tests at 1.0 Hz were performed to determine the linear viscoelasticity region (Figure 5.8). It can be identified in the Figure as the range of stresses where no changes are observed in the values of the rheological measured characteristics at each temperature.

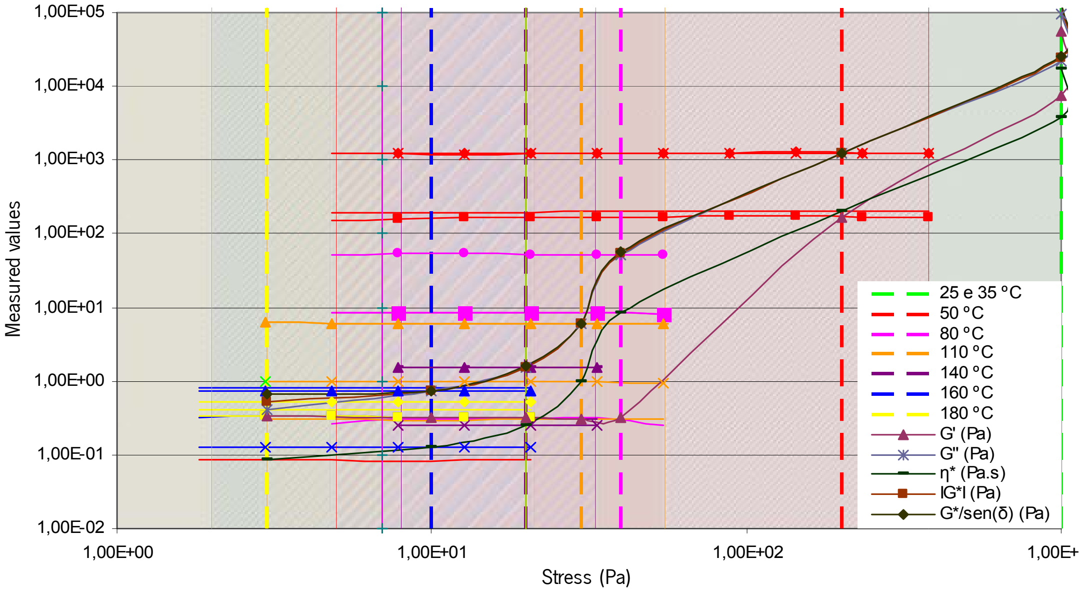


Figure 5.8 – Stress sweep tests at 1.0 Hz

Time sweep tests, at a constant temperature, stress and frequency were also performed to confirm that no structural modifications occurred during the time required for each test. The rheological characteristics assessed in the testes carried out with the DSR were the complex modulus – G*, storage or elastic modulus – G’, loss or viscous modulus – G’’, complex viscosity – η^*, phase angle – δ and rutting parameter – G*/sen(δ).

The linear viscoelasticity range can be identified in Figure 5.8 as being the range of stresses where no change in the values of the rheological measured characteristics at each temperature is observed.

The choice of stress values to be applied on the tests at each temperature was made to guarantee the linear viscoelasticity region for all the materials tested. This care had to be observed to provide the possibility of further comparative analysis between the rheological characteristics of each studied material.

5.1.4. Analytical determinations

During this work many analytical determinations (Penetration – Pen; Ring and ball – R&B; Dynamic viscosity – CV; Elastic recovery – ER; Density – Den; Microscopy – Micr; and DSR tests) were performed in different ways and for a variety of studied materials (Base bitumen – B; Asphalt rubber – AR; Residual bitumen – Res; "Sphere" bitumen – Sb; Recovered rubber – RR; and Filtered rubber – FR).

Besides the characterization tests performed on crumb rubber to determine its morphology, in Table 5.2 a systematized approach of the research analysis carried out in this work is presented.

Table 5.2 – Analytical determinations carried out in this work

Sample	Analytical determinations						
	Pen	R&B	DV	ER	Den	Micr.	DSR
A, E, I and M	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ AR ▪ RTFOT (AR)	▪ B, AR, Res, Sb	RR, FR	▪ B, AR, Res ▪ RTFOT (B, AR, Res)
B, J, O and P	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ AR ▪ RTFOT (AR)	▪ B, AR, Res		▪ B, AR, Res ▪ RTFOT (B, AR, Res)
C, D, F, G, H, K, L and N	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ B, AR, Res, Sb ▪ RTFOT (B, AR, Res)	▪ AR ▪ RTFOT (AR)	▪ B, AR, Res		

5.2. Study of the Bitumen

5.2.1. Characterization of the base bitumens

The experimental work began with a raw material characterization, namely, the four commercial bitumens. Simultaneously, these bitumens were combined in different proportions (Table 5.1) and the resulted base bitumens were also characterized.

5.2.1.1. Physical properties of the base bitumens

The first performed tests provided values of the physical properties of these materials, which are graphically presented in Figure 5.9:

- Penetration at 25 °C (1/10 mm) – Pen;
- Dynamic viscosity (cP) – DV;
- Ring and ball softening point (°C) – R&B;

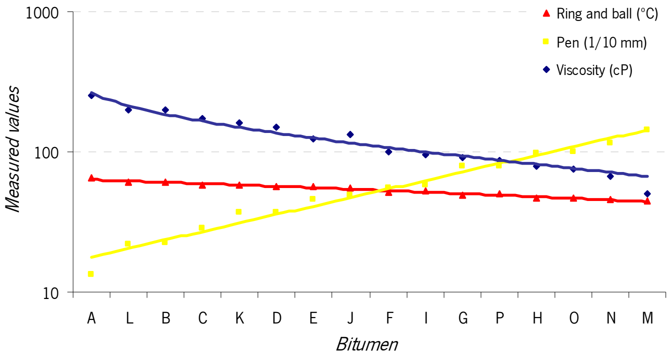


Figure 5.9 – Graphic representation of the physical properties of base bitumen

It was possible to set in order the different bitumens based on their physical properties. The results of the different tests were very consistent with the proportions of commercial bitumens used to produce the sixteen base bitumens. Actually, the changes in the constitution of the samples (from harder to softer bitumen) originated an ordered sequence for the evaluated properties, represented by a trend line.

To assess the variation of the physical properties it was necessary to represent them in a known scale. Figure 5.10, shows how Ring and Ball and Dynamic Viscosity vary with Penetration.

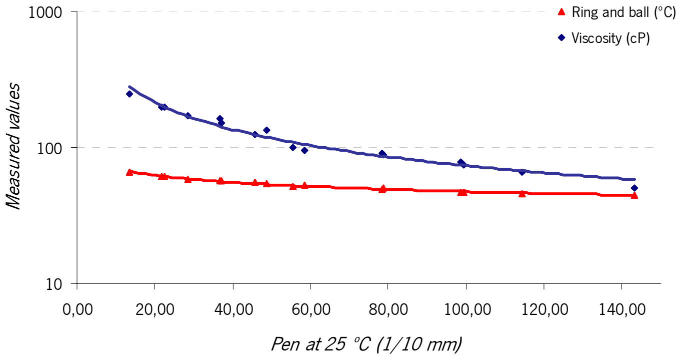


Figure 5.10 – Variation of R&B and DV with the Pen at 25 °C (1/10 mm)

Based on the graphic, it was possible to select a more reduced collection of representative bitumens for further specific analyses, since the bitumen distribution is not regular. The relationship between R&B and DV with Pen is approached by potential trend lines, what means that the variation of the R&B and DV properties with Pen is more sensitive for bitumen Pen under 6 mm.

5.2.1.2. Rheological properties of the base bitumens

Bitumen is a viscoelastic material, and this characteristic is plotted in Figure 5.11, representing τ *vs.* $\dot{\gamma}$ for bitumen M (150/200).

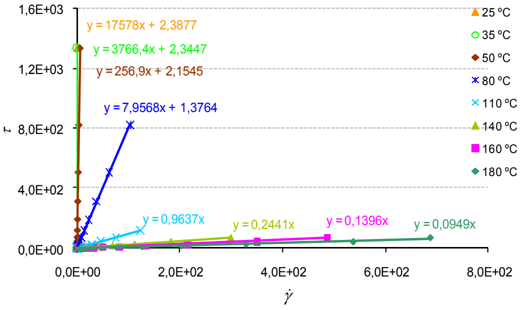


Figure 5.11 – Curves of τ (Pa) versus $\dot{\gamma}$ (s^{-1}) for base bitumen M at different temperatures

Figure 5.11 indicates that this bitumen (M – 150/200) is a non-Newtonian linear viscoelastic material, or a Bingham solid, for temperatures below 110 °C. Above the referred temperature it behaves as a Newtonian fluid. Another observation is the increase of the yield stress (σ_0) and the lines inclination as temperature drops, reflecting a rise in the stiffness.

The rheological tests were performed for each base bitumen under the next conditions (Table 5.3):

Table 5.3 – Test temperatures and respective stresses used in the DSR

T (°C)	25	35	50	80	110	140	160	180
Stress (Pa)	1000	1000	200	40	30	20	10	3

The stress applied at each temperature was determined in order to develop the test in the linear viscoelasticity range (Figure 5.8). For each pair temperature/stress frequency, sweep tests were performed between 0.10 and 10.0 Hz.

After choosing the rheometer geometry, parallel plates of 40 mm of diameter, the initial input values were the temperature – T (°C), the gap between the parallel plates, the frequencies (Hz) and the stress – σ (Pa) to be applied. For each pair temperature/frequency, the rheometer read the torque, phase angle – δ (°) and the angular velocity – θ (rad/s). With these values the rheometer software calculate the values of the strain – ε, G* (Pa), G' (Pa), G'' (Pa) and η^* (Pa.s).

One of the most significant values normally used to describe the bitumen rheology is the rutting parameter – G*/sen(δ), especially in the SuperPave method developed in the context of the SHRP programme. This parameter was manually calculated and studied in parallel with the other rheological parameters.

From the 16 initial base bitumens, eight were selected to perform rheological essays. In order to exemplify the rheological behaviour of bitumen, the results of only one of the tested bitumens (base bitumen I (60/70) are presented individually, once it is a commercial bitumen that presents average characteristics of the studied bitumens. The data obtained on the DSR for bitumen I, are presented in Figure 5.12 as isotherm plots of G*, G', G'', δ, η* and G*/sen (δ) versus frequency.

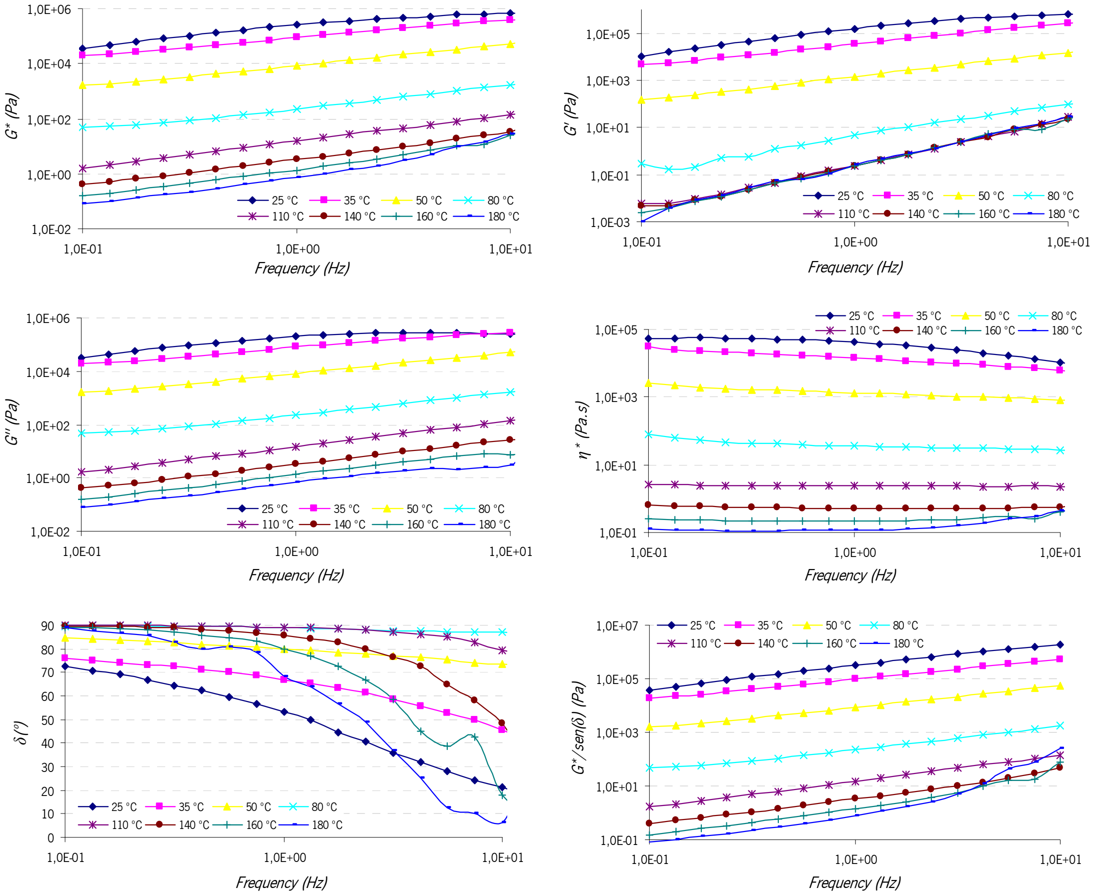


Figure 5.12 – Rheological characteristics *vs.* frequency for bitumen I

The isotherm plots show, as expected, an increase on the values of G*, G’, G’’ and G*/sen(δ) for all tested temperatures with the increase of the applied frequency, since the determination of all these parameters is a function of the frequency. This variation is less important when compared with the effect of the temperature on the stiffness of the material that drops significantly with the increase of temperature. However, the storage modulus (G’) stabilizes for temperatures above 80 °C.

The complex viscosity (η^*) is almost independent of the frequency. This characteristic depends on shear stress and shear rate and these variables are function of the torque, gap and angular velocity.

The increase of the applied frequency has a great impact on the measured phase angle (δ), its values presented a great variation for temperatures below 50 °C and above 110 °C, the most significant variation is shown for 180 °C; at this temperature the δ values covers nearly all possible ranges from 5° at 10.0 Hz to 90° at 0.1 Hz.

The plotted data are obtained directly from the DSR. To better understand the effect of temperature on the rheological behaviour of the bitumen at different frequencies the output data was rearranged and the resulting graphics are presented in Figure 5.13; those show the evolution of G´, G’’ and δ with the temperature, and how this rheological parameters affect G*, G*/sen(δ) and η^*.

The elastic modulus (G’) behaviour with the temperature has two parts. For temperatures below 90 °C, G’ decreases with the increase of temperature, but above 90 °C the elastic behaviour of bitumen reaches the minimum value of G’ at each frequency, and does not change with the temperature increase. However, the variation is not independent from the frequency; at 20 °C the range of G’ values is more restricted than the one presented at 180 °C. The values of G’ decrease with the applied frequency. The viscous modulus (G’’) shows a different behaviour. In spite of maintaining the expected decrease with frequency, G’’ decreases regularly as the temperature increases.

Contrarily to the other graphics, the plot of the phase angle versus temperature presents lines with different shapes at each frequency. For the lowest frequency value (0.1 Hz), the δ increases from 70° at 25 °C to 90° at 90 °C and stabilizes at that value. For higher frequencies, the line describing δ behaviour with temperature presents a bell shape. The lowest value of δ is ≈ 8° at 180 °C and the maximum value of δ (≈90°) is reached at ≈ 90 °C for all applied frequencies.

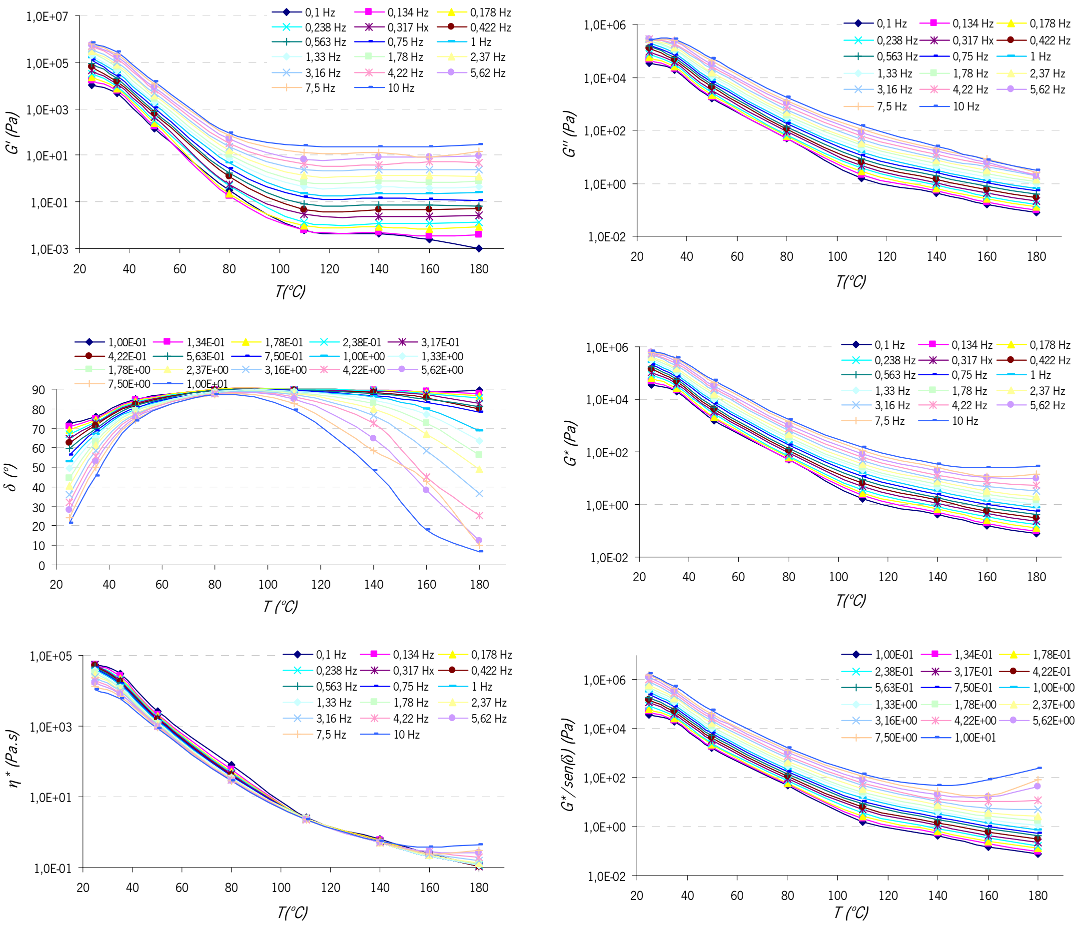


Figure 5.13 – Isochrones of the rheological properties of bitumen I

The best way to visualise any changes in the molecular structure of the material, such as relaxation processes is to represent tgδ versus temperature and/or frequency (Figure 5.14).

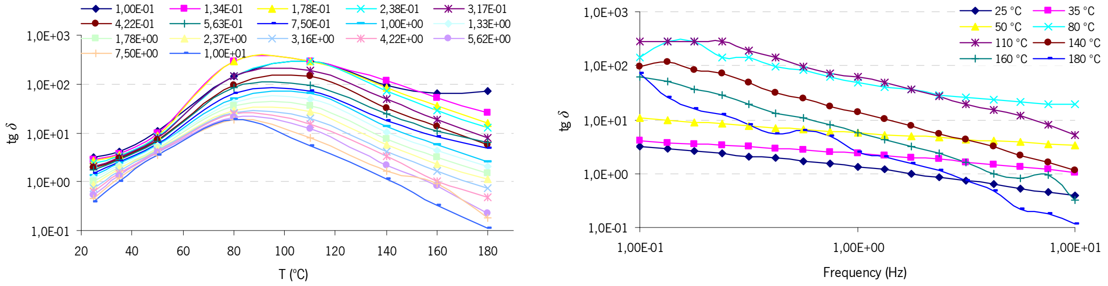


Figure 5.14 – Isochrones and isotherms of the tgδ of bitumen I

In the graphic of tgδ versus temperature it is possible to see that some changes happen within 80 °C and 110 °C where tgδ show its maximum value. The referred temperature range marks an alteration on the material. Bitumen behaves like two different materials, being a viscoelastic solid below 80 °C and a fluid above 110 °C, as showed in the plot of tgδ *vs.* frequency by the sudden change in the inclination of the isotherms above and below 100 °C.

In this work, the temperature at which the 1.0 Hz isochrones of tgδ reach its maximum value will be defined as T_c, which is a characteristic of each bitumen. Figure 5.15 shows the relationship between the rheological parameters measured at 1.0 Hz and the determination of T_c.

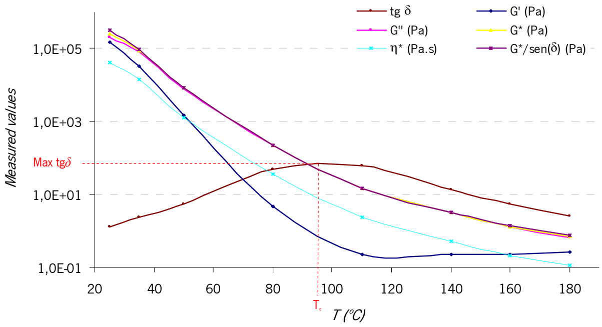


Figure 5.15 – Comparative isochrones (at 1.0 Hz) of bitumen I

In order to simplify the graphics presented above, a plot of the output rheological parameters versus the temperature at 1.0 Hz was constructed. By the analysis of this graphic it is easy to assess the relationship among all the measured values. The G'', G* and G*/sen(δ) show a very similar behaviour, indicating that the G' value is not significant if compared to G'', especially above 110 °C, what means that, at this range of temperatures, bitumen behaves mainly as a viscous material.

The tgδ values clearly reflect the relationship between the viscous and the elastic parts of the bitumen behaviour. For temperatures below 90 °C, the difference between G' and G'' increases, but for temperatures above 90 °C the stabilization of G' and continuous decrease of G'' reduces the difference between them. The line representing the evolution of the complex viscosity (η^*) is a parallel to that of the G* line, which is dislocated down. This is a consequence of the η^* determination (Equation 3.13).

A practical way to understand the rheological property-dependency on the phase angle variation is to construct the Black space (Figure 5.16). These curves are constructed using the values of the rheological variables at different temperatures and frequencies plotting them in function of their phase angle (δ). This procedure should result in an apparently continuous curve that describes the bitumen behaviour along the tested range of temperatures and frequencies.

With exception of the plot η^* *vs.* δ, all other graphics show a continuous curve using the points obtained for the different frequencies up to 110 °C. For higher temperatures, the obtained curves are independent, with a very similar design to that of the first curve constructed using several different temperatures. As temperature increases above 110 °C, the resulting points spread over a large range of phase angles.

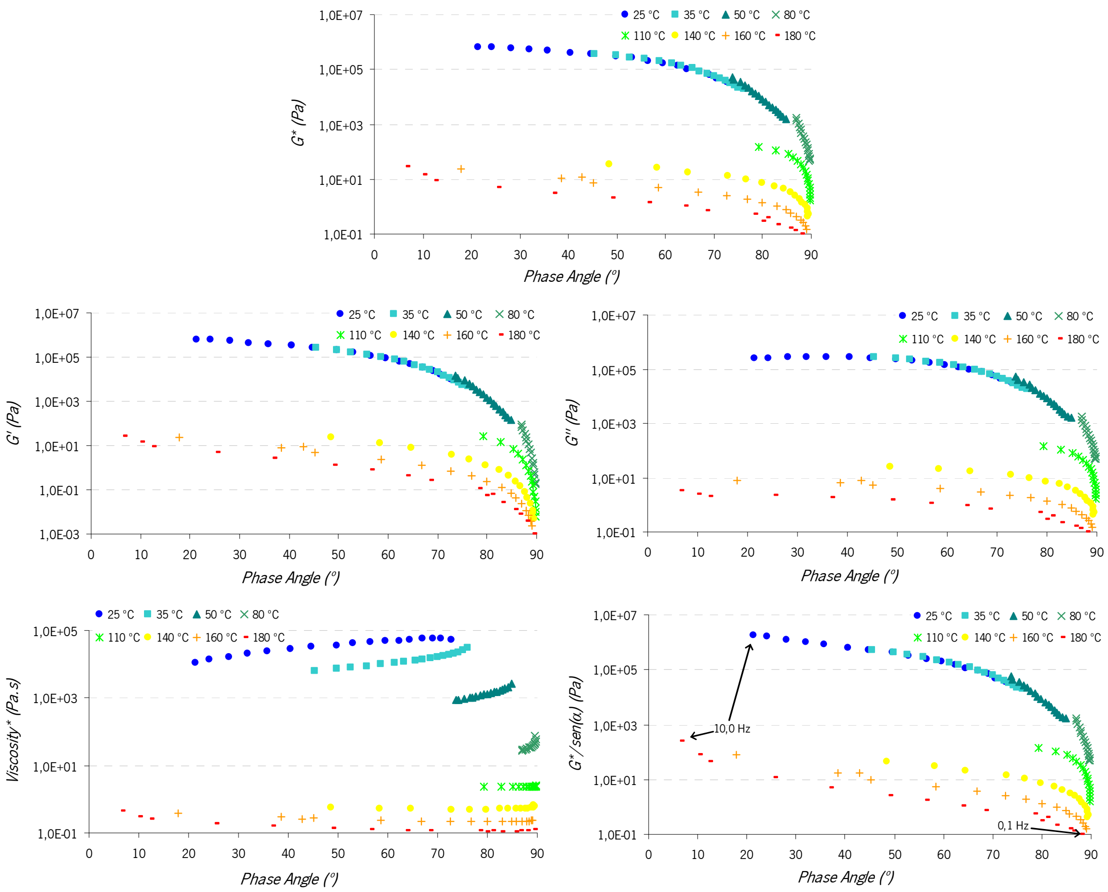


Figure 5.16 – Black space of the rheological properties of bitumen I

Other way to represent the data that describe bituminous materials behaviour is the Cole-Cole plane (Figure 5.17). The Cole-Cole plane is constructed plotting the values obtained for different frequencies at different temperatures of G'' in function of G'.

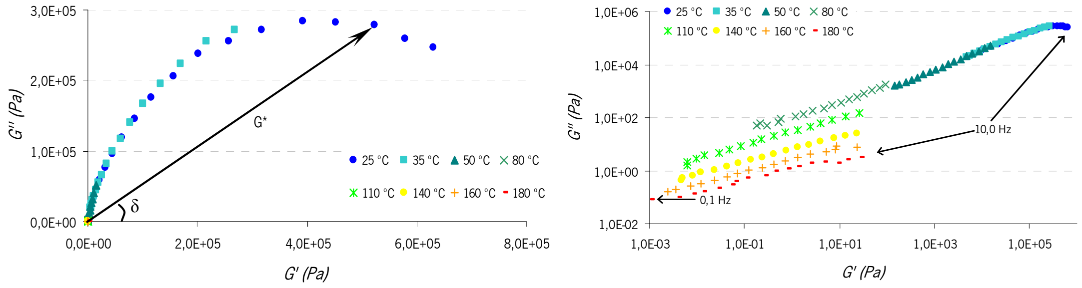


Figure 5.17 – Cole-Cole plane representation of bitumen I

The distance between the axis origin and each point corresponds to G*, and the angle formed by this line and the xx axis is the phase angle (δ).

At 25 °C, bitumen has an elastic component (G') much higher than its viscous part (G''), namely for the highest measured frequencies (10.0 Hz). This behaviour begins to change at 35 °C; at this temperature, for 10.0 Hz G'' is much inferior to G', whereas for 0.10 Hz G'' is superior to G'. The behaviour of the last one is accentuated at 50 °C. For higher temperatures (T > 50 °C) it is necessary to plot the values in the logarithmic axis, since the variation that occurs at a little scale, is not perceptible in the normal representation. This procedure is unusual and does not correspond to the original Cole-Cole plane.

One of the most effective ways of representing the data obtained in the DSR rheometer is the Master curves. These curves can be constructed because it is generally accepted that bitumen is a rheologicaly simple material, being applicable the time-temperature superposition principle (TTS), either by using the Arrhenius equation (5.1) or the Williams-Landel-Ferry's (WLF) (5.2).

$$\eta^* = k \cdot \exp^{[E_a/(R \cdot T)]} \quad \text{for} \quad \mathrm{T} < \mathrm{T_g} \tag{5.1}$$

$$\log a_T = \frac{-C_1 \cdot (T - T_g)}{C_2 + T - T_g} \quad \text{for} \quad \mathrm{T} > \mathrm{T_g} \tag{5.2}$$

The master curves are the result of the superposition of curves at different times (frequencies) and temperatures and cover a large range of time or frequency domains.

With the initial data it is not possible to find out the glass transition temperature (T_g) value. Consequently it is not possible to identify the function that better approaches the data used to construct the master curves.

The easy way to choose the best function is to construct a graphic of logarithms of any of the stiffness parameters versus the inverted temperature. If the result line is a linear relation among the plotted data, the Arrhenius equation should be used, otherwise, the best approach is obtained by using the WLF equation, as in the present case as depicted in Figure 5.18.

In the plot of η^* *vs.* 1/T it is possible to see that, for temperatures above 110 °C, the curve is not a linear relation among the plotted parameters. Therefore the equation which should be used to construct the master curve must be the WLF. The master curve for temperatures between 25 °C and 100 °C shows a point of interception of G' and G'' lines (tgδ = 1), what indicates that the material experienced some changes. It is also possible to observe that between 50 °C and 80 °C it would be useful to test at least one more temperature to obtain a perfect superposition time/temperature.

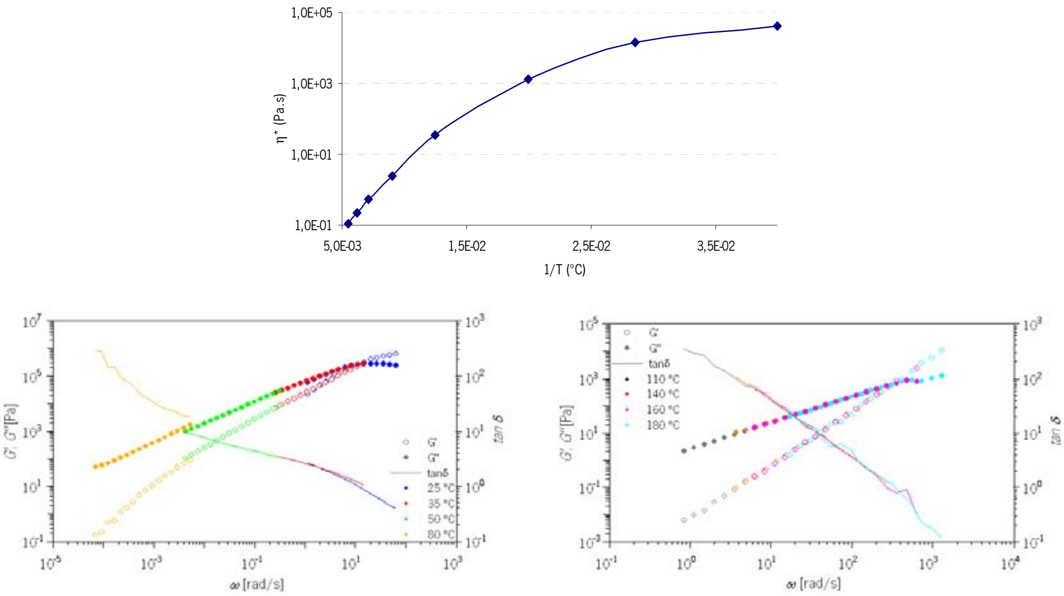


Figure 5.18 – Master curves of bitumen I

The application of the WLF equation has three values as output, C1, C2 and Tg. This last parameter is a characteristic of each material. However, its determination depends on the geometry used to assess the rheological parameters and the material behaviour. In this case the Tg parameter could only be achieved by using another geometry, due to the irregular evolution of the master curve which, with this geometry (parallel plates), suggests an erroneous Tg.

Above 100 °C the graphic of η^* *vs.* 1/T can be approached to a straight line, indicating that for these temperatures the equation that better defines the bitumen is the Arrhenius equation. The resulting master curve also shows a point of interception of G' and G'' lines that corresponds to a new change in the material. The Arrhenius equation also provides a characteristic value of each material, the activation energy (Ea). In this case, the Ea value cannot be considered, since there are changes in the bitumen structure, and also because the accuracy of the equipment at high temperatures is not adequate. To assess more significant values it would be necessary to use another test to relate geometries and temperatures.

With the present results it is not possible to construct an unique master curve covering the entire range of tested temperatures. In order to achieve that, it would be necessary to use a variety of geometries corresponding to the different ranges of temperatures and more temperatures between 80 °C and 110 °C should be tested, because, at this temperature range the most significant changes in the bitumen structure occur. Thereby, due to all the exposed constrictions, the master curves will not be used as a tool to compare the rheological characteristics of the different bituminous materials studied in this work.

5.2.1.3. Rheological characterization of the several base bitumens

In order to understand how the rheological characteristics of the bitumen evolve, during the production process of the different penetration grade bitumen, eight (8) bitumens were selected. The selection criterion was to obtain a regular distribution of the bitumen characteristics. The data obtained in the physical characterization of bitumen was used to accomplish this purpose.

The eight bitumens selected to carry out the rheological tests (A, B, E, I, J, M, N and P) were tested in the DSR, using the experimental protocol presented earlier. The results presented in Figure 5.19 correspond to the different rheological parameters (G', G'', G*, η^*, δ and G*/sen(δ)) measured at a frequency of 1.0 Hz and at temperatures between 25 and 180 °C.

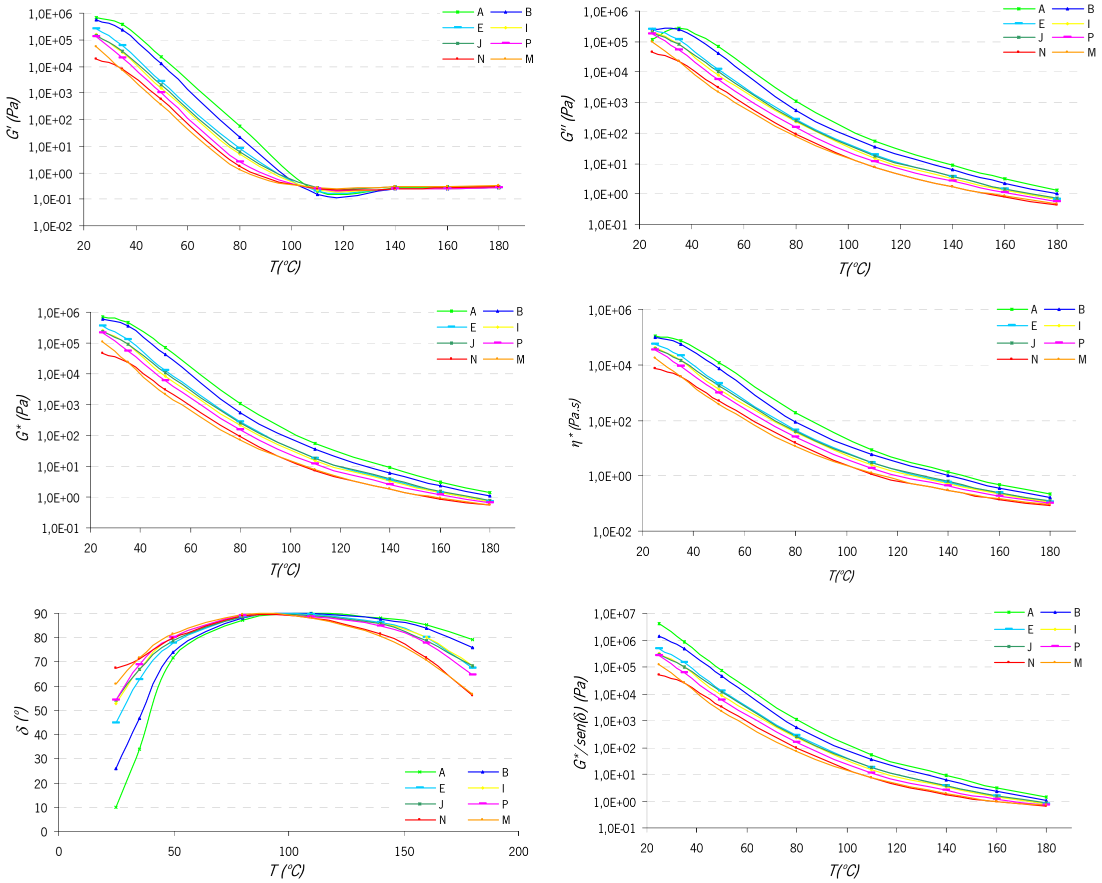


Figure 5.19 – Comparative isochrones (at 1.0 Hz) of the rheological properties of a set of bitumens

The isochronal plot of the rheological properties of the bitumens illustrates the variation of their stiffness and viscoelastic nature with the temperature and type of bitumen evaluated. The lines representing the rheological properties of the different bitumens are in conformity with the previous physical characterisation, i.e. the harder bitumen with lower penetrations and higher R&B and DV also present the highest values of G', G'', G*, η^* and G*/sen(δ) in the rheological tests for every tested temperature.

The change in the gradient of the isochrones at 1.0 Hz demonstrates a variation in the nature of the bitumen. It is mostly a viscoelastic semisolid material below 100 °C (when the rapid reduction of stiffness results mainly from the loss of the elastic component), becoming a viscous liquid at higher temperatures (when the stiffness decrease is a consequence of the reduction of viscosity), and near 180 °C the bitumen behaves almost independently of the bitumen type, trending for a constant and very low value of rheological parameters.

The plot of δ *vs.* T (°C) shows a maximum value of δ within 80 and 110 °C for all the studied bitumens, but is very difficult to determine the exact temperature at which, for each bitumen, the maximum δ is achieved. This behaviour indicates that in this range of temperatures a phenomenon of relaxation happens in all the bitumens and that it is reversible, once the same results were obtained, in sequential repeated test of the same sample of bitumen (without removing it from the rheometer).

The value of δ shows the relation between G'' and G', but this parameter has a very short range of variation (0 – 90°). One way to transform δ into a more sensitive parameter is to calculate its tangent. In Figure 5.20 the tgδ *vs.* T (°C), frequency (Hz) and T_c (°C), for every selected bitumen, are represented.

The value of tgδ is the ratio between G'' and G'. When tgδ is represented in function of temperature is possible to obtain a characteristic value of T (°C), at one frequency, for each studied bitumen – T_c (°C). The tested bitumens were obtained from the same distillation column. This fact, combined with the similar shape of the curves of tgδ *vs.* T (°C), confirm the reversibility of the eventual relaxation process.

Every tested bitumen showed a maximum tgδ at temperatures between 80 and 112 °C, that correspond to the point of relaxation on the bitumen molecular structure. The temperature (at each frequency) at which this phenomenon occurs is a characteristic of the bitumen and depends on its chemical constitution.

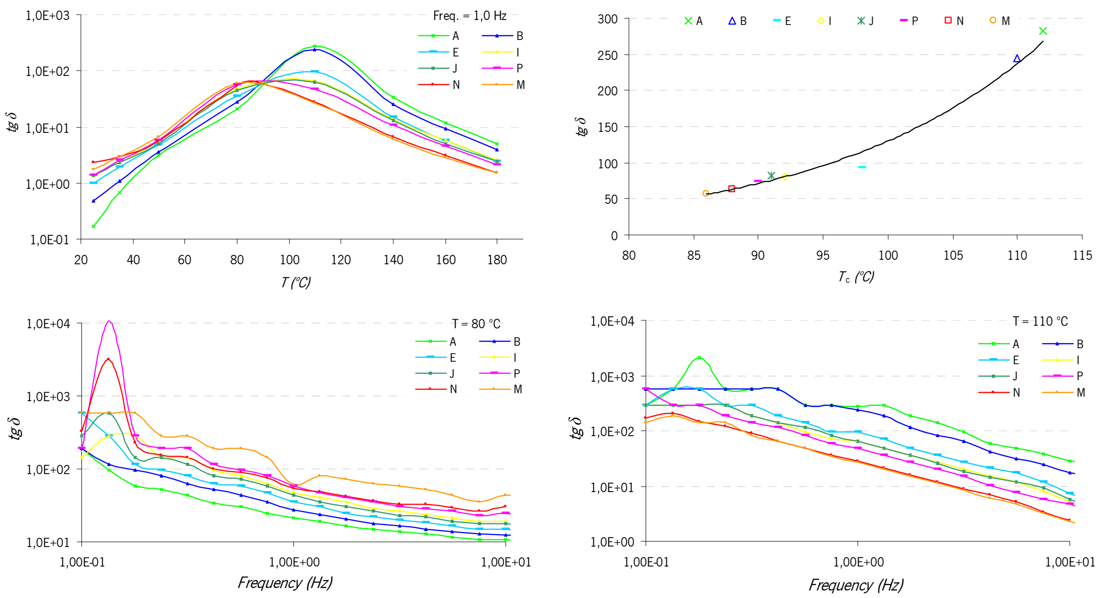


Figure 5.20 – Comparative isochrones and isotherms of tgδ of a set of bitumens

With the data collected in the graphic of tgδ *vs.* T (°C), another graphic of tgδ *vs.* T_c (°C) was constructed. The characteristic points of each bitumen, at this frequency (1.0 Hz), appear to describe a proportional exponential line. This behaviour is coherent with the results obtained in the physical characterization of the bitumens.

Furthermore, since tgδ is a ratio between the viscous and the elastic part of bitumen, it is possible to speculate about the way that each chemical fraction of the bitumen constitution contributes more for the present behaviour. It is noticeable that, for harder bitumens, the viscous part of bitumen is predominant in relation to its elastic part. This predominance is reduced as the bitumen gets softer. It is also recognized that a harder bitumen is rich in asphaltenes. Apparently the concentration of asphaltenes is a factor responsible for the changes in the viscous behaviour of bitumen.

By the analysis of the graphics of tgδ *vs.* T (°C), the most significant changes in the bitumen characteristics happen between 80 and 110 °C, where the maximum value of tgδ is achieved. Moreover, it is also possible to distinguish different declivity of the curves at 80 °C and at 110 °C, which indicates that the material behaves differently under those two conditions, making unfeasible the construction of a unique master curve. Within 80 and 110 °C the proportion of viscous and elastic part of the rheological performance of bitumen inverts. At the same frequency, at 80 °C the hardest bitumens are proportionally less viscous than the softest ones, but at 110 °C inverse results are observed.

In Figure 5.21 the Black space diagrams of the eight studied bitumens are presented.

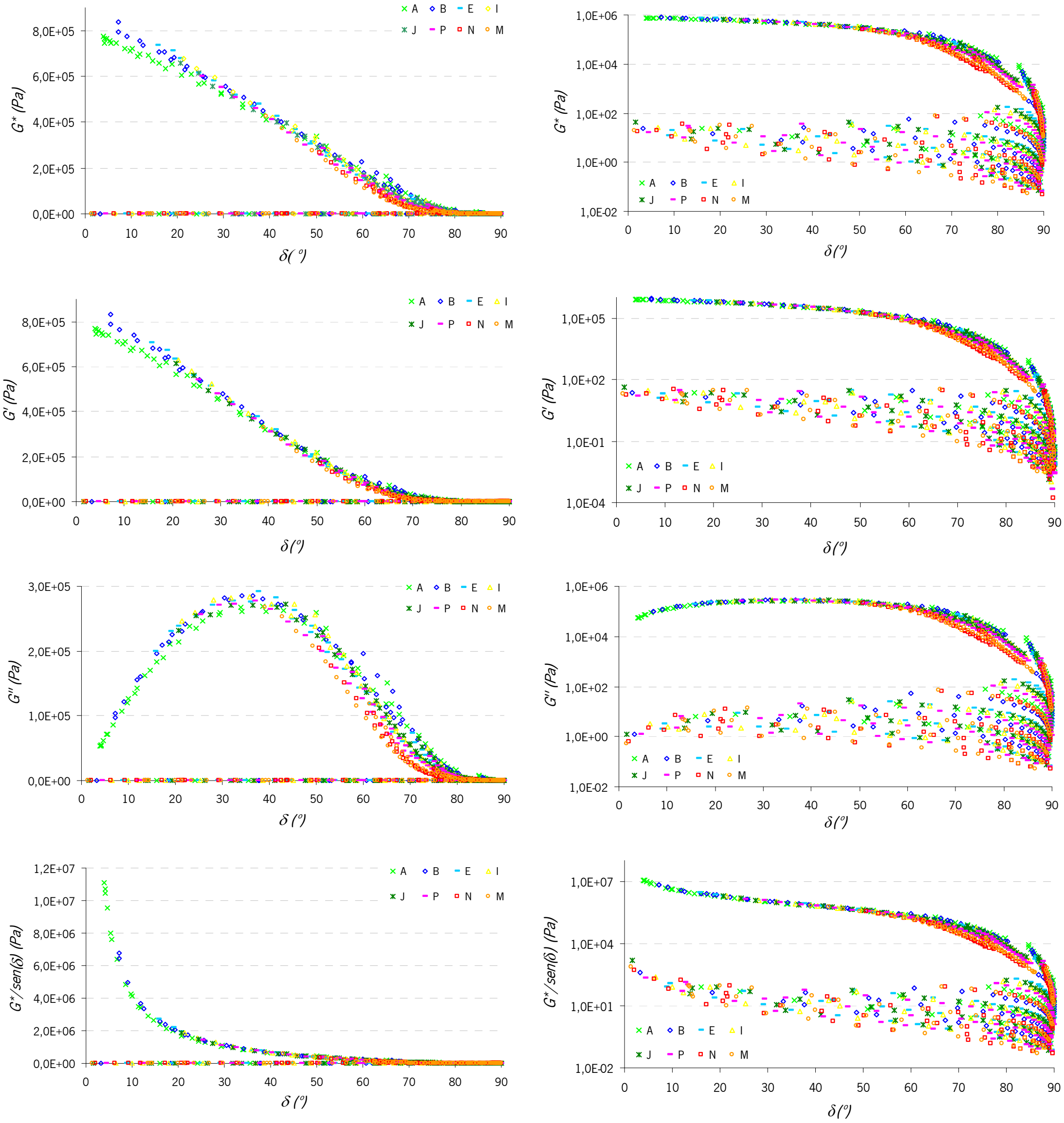


Figure 5.21 – Comparative Black space of a set of bitumens

The Black space provides very useful information about the viscoelastic behaviour of bitumen for temperatures below T_c, particularly, when only a bitumen is analysed. This information can also be assessed by constructing the Cole-Cole plane. This representation allows a better differentiation between different bitumens. Hence, this will be select tool to analyse the subsequent materials.

In Figure 5.22, a comparative representation of the data of the eight bitumens in the form of Cole-Cole plane is presented. The representation of the rheological behaviour of bitumen in Cole-Cole plane can provide some useful information at temperatures below 50 °C (in the left side of the Figure).

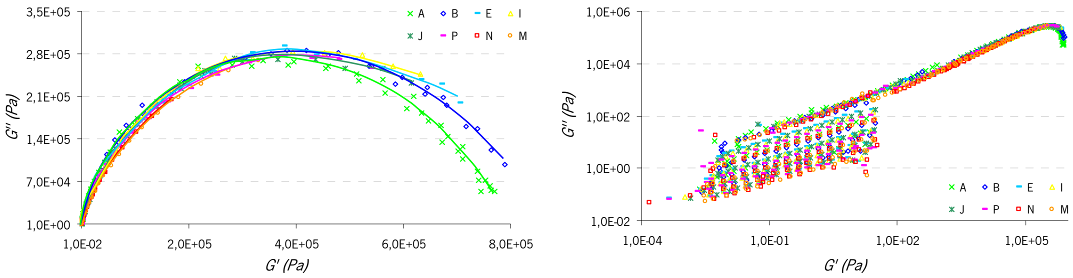


Figure 5.22 – Comparative Cole-Cole plane of a set of bitumens

As observed in the other representations, it is noticeable that when a bitumen is softer its G* (Pa) reduces and its δ(°) increases (at each frequency), with exception for bitumen A, which, being harder than B, shows the lowest G* at 25 and 35 °C. Additionally, with the exception of bitumens N and M, all bitumens present a curve with a maximum point for G' = G''; this point repeats at different frequencies for 25 and 35 °C, what indicates a reversible alteration on the rheological behaviour of bitumen. Stiffer bitumen has a high value of G', *i.e.* it is a more elastic material. This elastic characteristic of bitumen decreases when it becomes softer.

For temperatures above 50 °C (right side of the Figure) the Cole-Cole plane is not a very useful tool to distinguish different bitumens, once the values of the G' and G'' parameters are very small. The space must be represented in logarithmic scale, and still, very few differences can be noticed.

5.2.1.4. Comparison between the rheological and physical properties of the base bitumens

During the pavement life cycle, the asphalt binders used in bituminous materials should always present the adequate characteristics, initially during the mixing and application phases at elevated temperatures (Figure 5.23), then during the operating phase, in order to resist to the weather and traffic actions at low and medium temperatures (Figures 5.24 and 5.25) and, finally, in the removal and recycling of the distressed mixtures (this last phase was not studied in this work).

Next results of the two different approaches used to assess the binder behaviour (physical and rheological for a reference frequency of 1.0 Hz) will be compared for the eight bitumens (A, B, E, I, J, M, N and P) evaluated in this study. At medium operating temperatures causing fatigue cracking distresses, the physical parameter measured in this work was penetration at 25 °C. Thus, Figure 5.23 relates the penetration value of the several binders to the rheological properties measured at 25 °C.

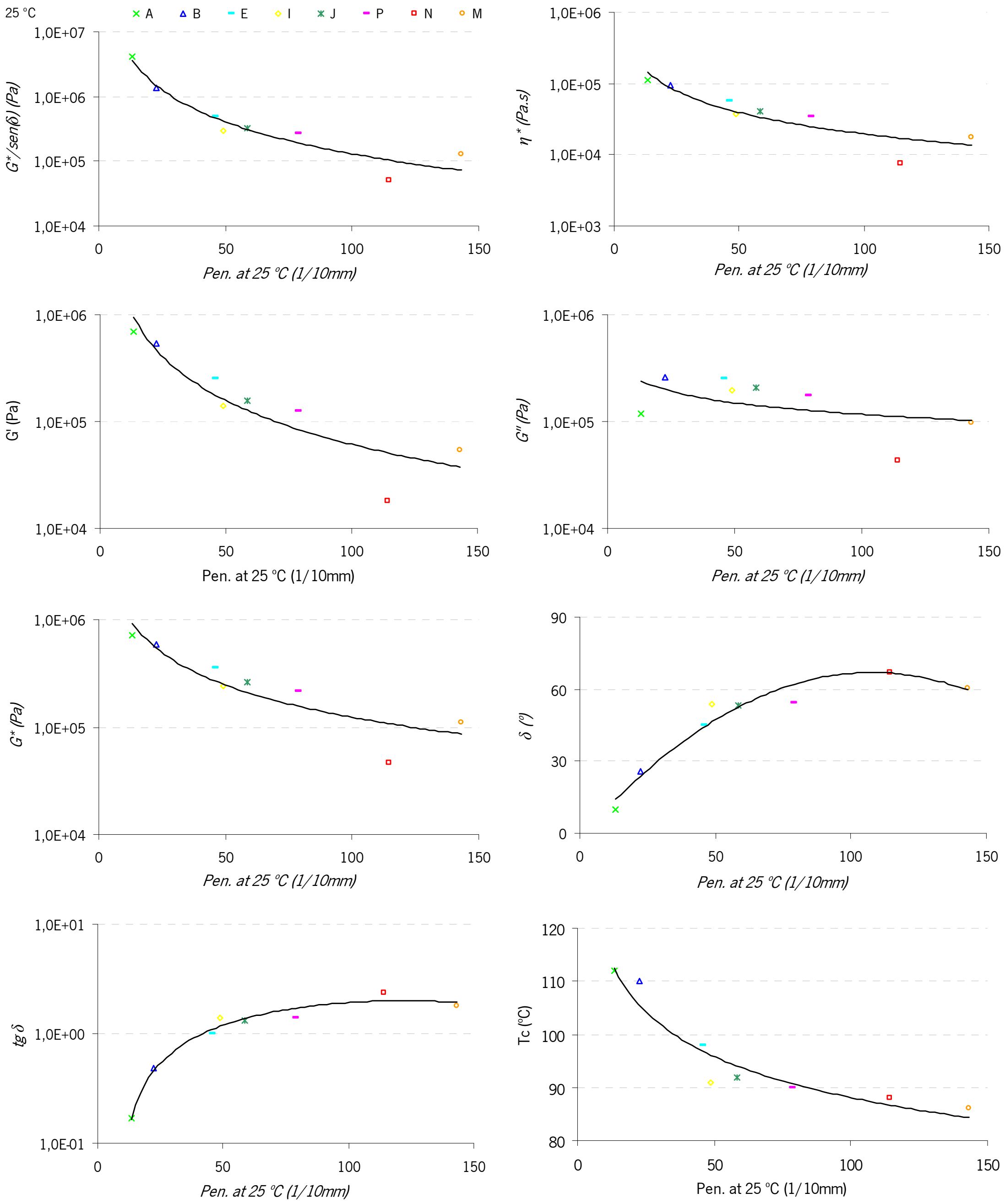


Figure 5.23 – Rheological *vs.* physical properties at 25 °C and 1.0 Hz for the base bitumens

The potential trending lines shown presented the best fit to the relation between the physical and rheological properties measured at 25 °C, with exception of δ and tgδ, to which the best fit is a 2nd grade polynomial line. Apparently the relation between both properties is not so good at this temperature, since the dispersion of the several points is significant (probably due to the type of rheometer used in this work).

The range of values of the penetration results is visibly inferior to the rheological classification, and thus the rheology axis is presented in a logarithmic scale.

At high operating temperatures causing rutting distresses, the physical parameter measured in this work was the R&B softening temperature. Figure 5.24 compares the R&B temperature with two rheological properties measured at 50 °C.

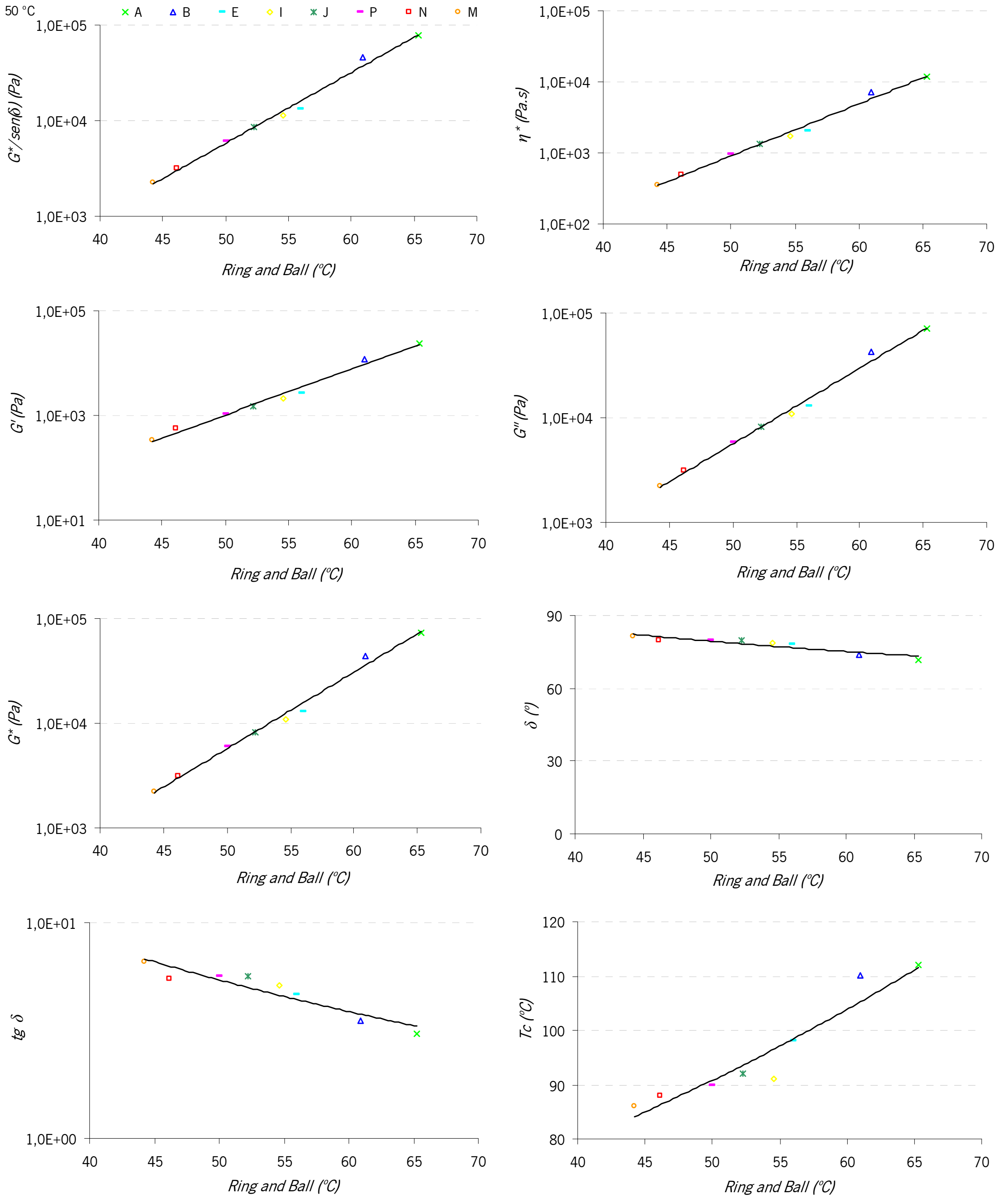


Figure 5.24 – Rheological *vs.* physical properties at 50 °C and 1.0 Hz for the base bitumens

At mixing and application temperatures, the physical parameter measured in this work was the dynamic viscosity at 175 °C. Figure 5.25 compares the DV at 175 °C with the rheological properties measured at 180 °C.

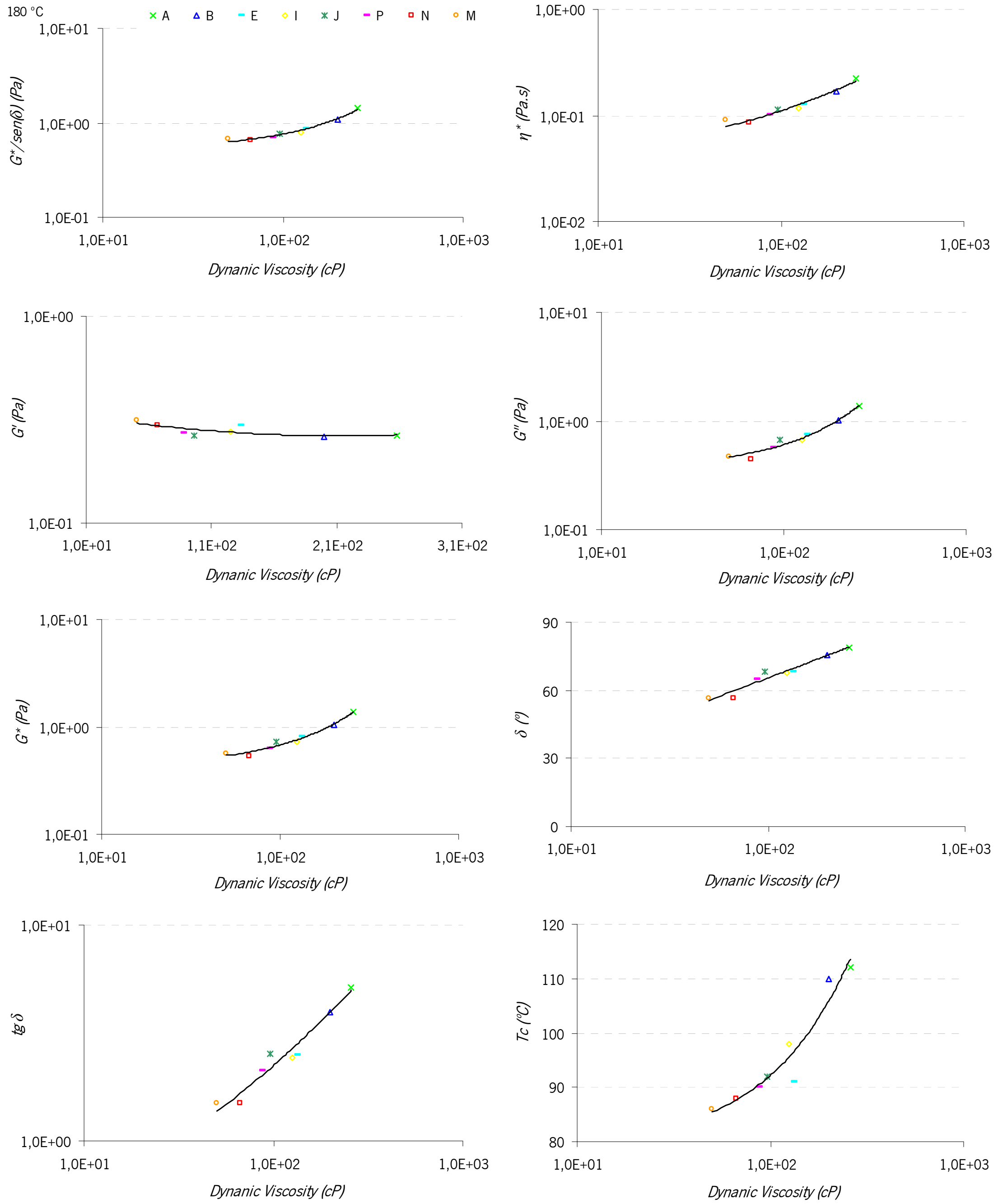


Figure 5.25 – Rheological *vs.* physical properties at production/application temperatures and at 1.0 Hz for the base bitumens

The set of lines show an exponential relation between the R&B physical properties of all the binders and the corresponding rheological parameters measured at 50 °C. The range of values of the R&B results is visibly inferior to the rheological classification, and thus the rheology axis is presented in a logarithmic scale. At 50 °C the R&B temperature has a very good correspondence to the rheological properties.

The values of G* are approximately the same of G*/sen(*δ*) at this temperature (175 °C), because the phase angle (*δ*) is nearly 90°. In fact, at this temperature the binders behave as a viscous liquid with very low values of G* and an insignificant elastic component (G') when compared with the viscous part of the stiffness (G'').

Contrarily to the other represented physical characteristics (Pen at 25 °C and R&B) the DV at 175 °C appears to be more accurate when describing the behaviour of bitumen than the rheological parameters, since the range of the DV at 175 °C results is visibly superior to the rheological classification, and thus the physical axis is presented in a logarithmic scale. The relations between the physical and rheological properties represented in the graphics are nearly linear. The comparison between the dynamic viscosity (physical) and the complex viscosity (rheology) presented the best relation, being the slope nearly equal to 1 (because 1 Pa.s = 1000 cP).

5.2.2. Characterization of the base bitumen after RTFOT

The four commercial bitumens were subjected to the Rolling Thin Film Oven Test – RTFOT procedure and the resultant RTFOT aged bitumens were characterized in relation to their physical and rheological properties.

5.2.2.1. Physical properties of RTFOT aged bitumen

The first performed tests provide the physical properties of these materials, namely the penetration at 25 °C, the dynamic viscosity and the ring and ball softening point. The measured values of the physical properties are graphically presented in Figure 5.26.

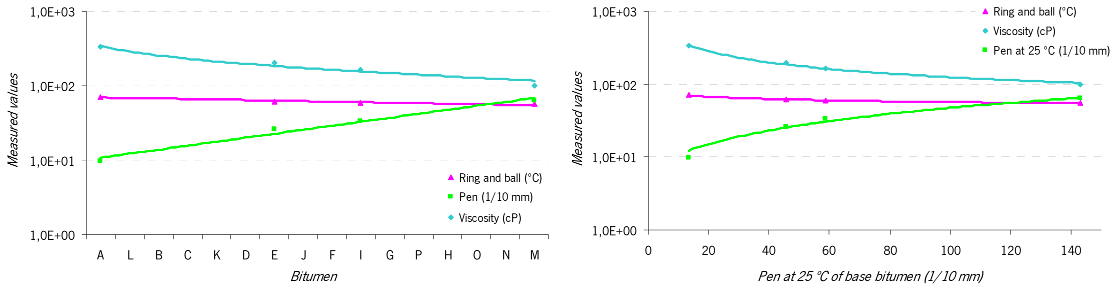


Figure 5.26 – Graphic representation of the physical properties of RTFOT aged bitumen

The shape of the curves is similar to the curves representing the base bitumen (Figures 5.9 and 5.10), for all the assessed parameters. This means that, during the production and compaction of the bituminous mixes, the bitumen alterations do not change its basic structure. In spite of that, it is useful to quantify those changes (Figure 5.27).

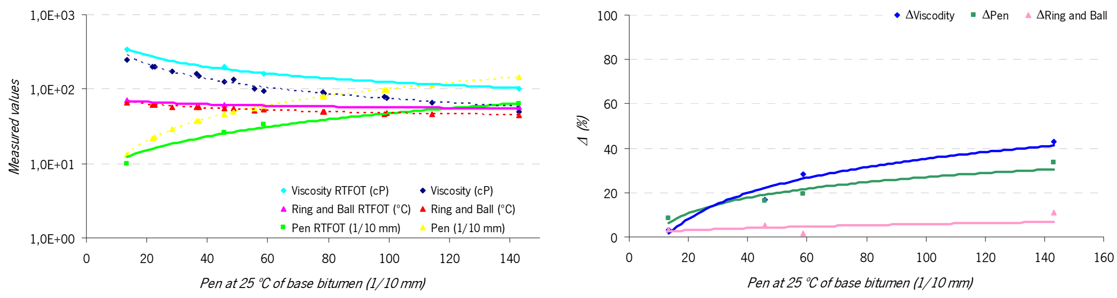


Figure 5.27 – Comparative representation of the physical properties of the base and aged bitumen

As documented, the most affected property during the RTFOT aging of the bitumen is viscosity. This physical parameter shows a great variation, especially in respect to the softest bitumen (M), this behaviour is also observed in the other physical parameters.

These observations suggest that the aging process highly alters the softest bitumen. These results presuppose that, during the aging of bitumen, the small molecules that confer softness to the bitumen evaporate or associate into bigger molecules and, as a result, bitumen becomes stiff.

5.2.2.2. Rheological properties of the RTFOT aged bitumen

After RTFOT aging process, the rheological properties of the four commercial bitumens were assessed and compared with the base bitumen. In Figure 5.28 the comparative isotherms of the rheological parameters, at different temperatures, for bitumen I (base and RTFOT) are presented.

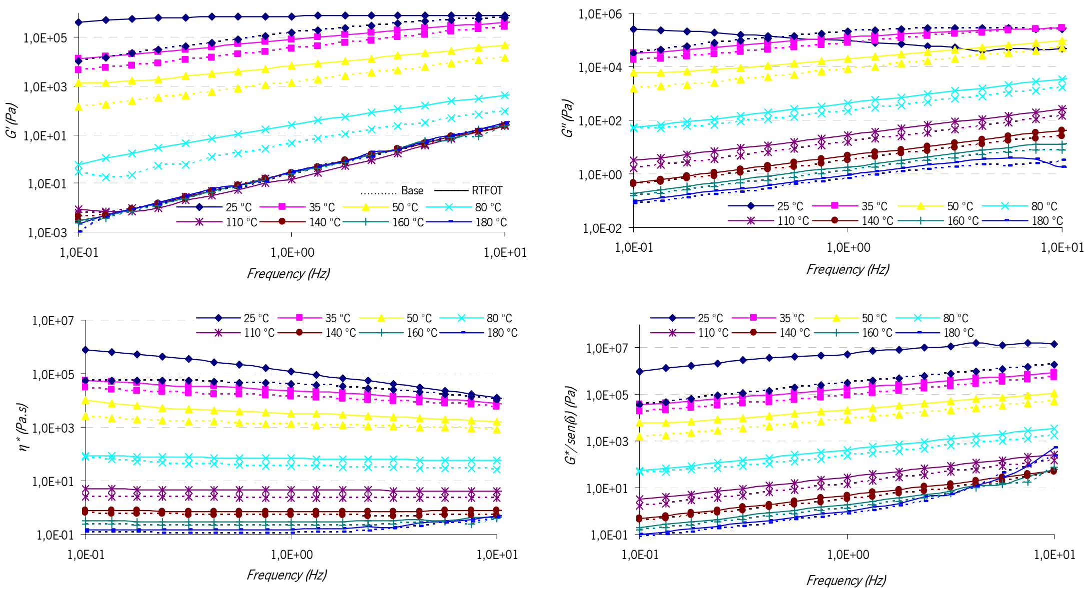


Figure 5.28 – Comparative isotherms of the rheological properties of base and aged bitumen I

The isotherms of base and aged bitumen have roughly the same form, indicating that the changes induced in the bitumen by the RTFOT do not affect the behaviour of bitumen. However, it has been noticed that the complex viscosity (η^*) of bitumen increases, especially at low temperatures. This behaviour corresponds to the increase in the bitumen modulus (G', G'' and G*/sen(δ)).

Moreover, the isochrones (Figure 5.29) also present a similar behaviour to the base bitumens.

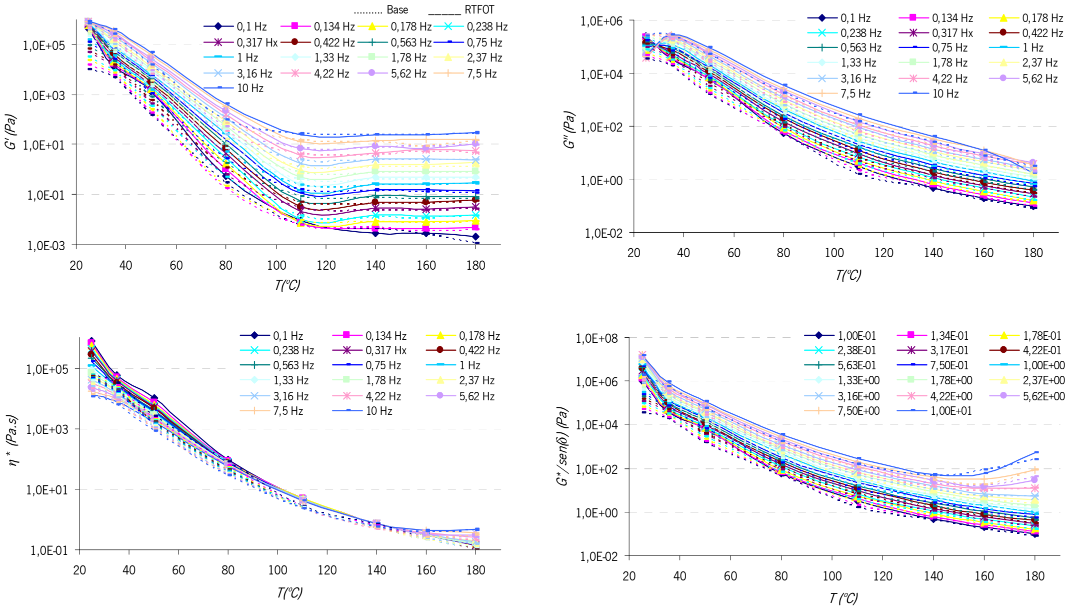


Figure 5.29 – Comparative isochrones of the rheological properties of base and aged bitumen I

The most significant differences between base and aged bitumen occurred at the lowest temperatures at which all the rheological parameters indicate an increase in the bitumen stiffness. It appears that RTFOT confers less dependence on the temperature and makes bitumen stiffer at service temperatures, maintaining the softness at production temperatures.

Depending on the physical characteristics of bitumen and on the service temperatures, the process of production and compaction of bituminous mixtures can enhance bitumen properties.

The earlier observations, indicating that RTFOT have no influence on the structure of the bitumen, only making it stiffer at low temperatures, is questioned by the graphics of tgδ *vs.* T (°C), frequency (Hz) shown in Figure 5.30.

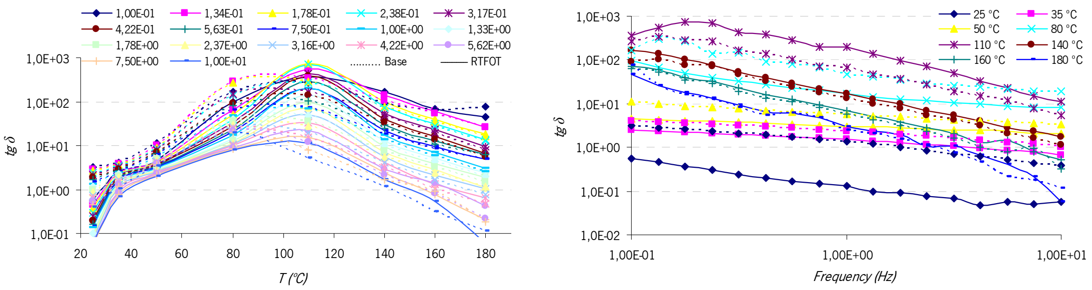


Figure 5.30 – Comparative isochrones and isotherms of the tgδ of base and aged bitumen I

As expected in the plot of tgδ *vs.* T (°C) (on the left side of the Figure) it is detected that the tgδ value reaches its maximum at a higher temperature in bitumen after RTFOT. However, by looking at the right side of Figure 5.28, it is observable that the proportions between the viscous (G'') and the elastic (G') part of bitumen, at the different temperatures, changes due to RTFOT (tgδ = G''/G').

Comparing the tgδ isotherms of bitumen before and after RTFOT (on the right side of the Figure), it is noticeable that, between 25 and 80 °C, the aged bitumen presents a slight reduction of the value of tgδ due to a more significant increase of the elastic part than that of the viscous one. The inverse behaviour is observed at 110 °C and, for superior temperatures, the values of tgδ show no alteration.

This observation indicates that the relaxation experienced by the bitumen, according to The Micellar Model of Bitumen (Jones and Kennedy, 1992), shall be inherent to the asphaltenes and resins, since, those molecules are the principal responsible for the stiffness of the bitumen as those are concentrated during the RTFOT.

Figure 5.31 illustrates the changes induced by the RTFOT in the rheological characteristics of bitumen compared with the base bitumen. It is noticeable that below 100 °C, with the exception of tgδ, all other parameters present higher values for the bitumen after the RTFOT corresponding to the increase of stiffness. For this range of temperatures, the elastic modulus (G') of the aged bitumen suffer a more extensive increase, what indicates that asphaltenes are the molecules responsible for the elastic characteristic of bitumen, especially at lower temperatures, since above 100 °C the relaxation of the asphaltenes leads the values of the aged bitumen approximately to the same values of the base bitumen.

The previous observation is also obvious when representing the binders in the Cole-Cole plane (Figure 5.32).

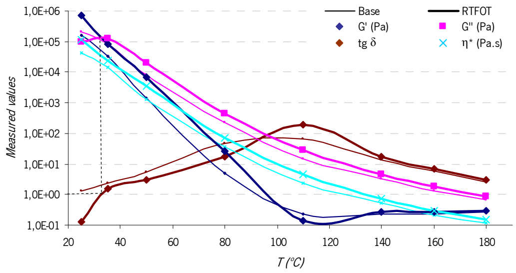


Figure 5.31 – Comparative isochrones, at 1.0 Hz, of base and aged bitumen I

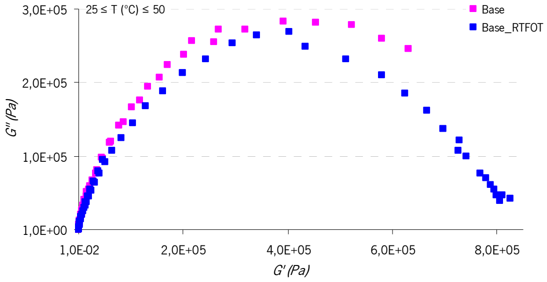


Figure 5.32 – Cole-Cole plane of bitumen I before and after RTFOT

As mentioned before, the Cole-Cole plane is a useful tool for identifying changes in the bitumen at low temperatures. When comparing aged and base bitumen it can be noticed that the most obvious changes in the rheological characteristics of the aged bitumen occur at 25 and 35 °C where the big rise in the value of G’ is combined with the decrease of G’’, demonstrating that at this range of temperatures, bitumen behaves more as an elastic than as a viscous material.

Figure 5.33 illustrates how the molecular structure of bitumen changes during the aging process induced by the RTFOT.

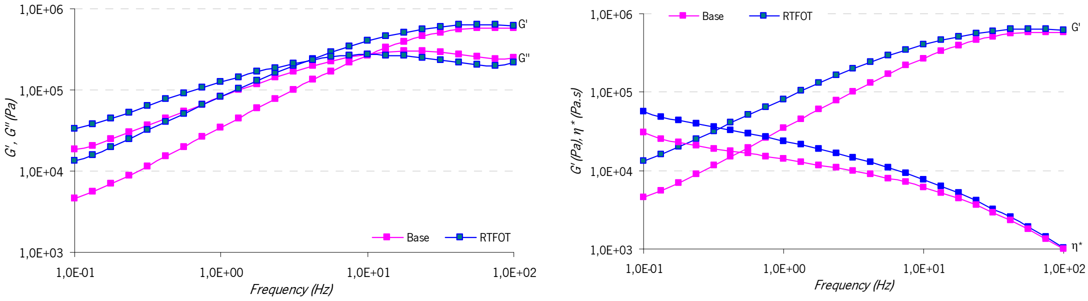


Figure 5.33 – Effect of the RTFOT on molecular weight (Mw) and structure of the bitumen I at 35 °C

On the left side of Figure 5.33 is noticed that the G’ and G’’ isochronal lines dislocate horizontally at lower frequencies as the molecular weight (Mw) increases, since the greatest complexity in the molecular arrangements induces a more pronounced viscous character of the bitumen.

Besides the Mw, it is also important to consider its distribution, the modulus, at the point of interception between the curve of G' and G'' reduces with the increase in the amplitude of the MWD. Additionally, the aged bitumen with a major amplitude in the molecular weight distribution (MWD) is more sensitive to the frequency and the initial values of G' and η^* (right side of the Figure).

The plot of G', η^* *vs.* frequency is also elucidative in relation to the ramification of the asphaltene networks formed in the bitumen, since the viscosity varies with the number, the length, the flexibility and the distribution of the side chains along the principal chains.

The higher viscosity and a major dependency on the frequency of aged bitumen indicate that the chains formed after RTFOT have reactively pitiable ramification, but longer branches that cause interlacing.

5.2.2.3. Rheological characterization of the several RTFOT aged bitumens

To assess the effect of the RTFOT in the four commercial bitumens (A, E, I and M), rheological tests were performed in the bitumens after RTFOT and the results were compared with the base bitumen.

In Figure 5.34 the isochrones obtained for the different rheological parameters and slopes between each base and aged bitumen are plotted.

It was noticed that the softest bitumen (M) presented, in all the rheological parameters measured, the most significant variations between the base and the aged bitumen. In contraposition, the hardest bitumen A showed an inverse tendency, especially at lower temperatures. The rheological parameter that had the greatest variation was the storage modulus (G'), namely below 100 °C, that, at these temperatures, achieved variations superior to 80% in all the different bitumens. This variation is reflected in the values of tgδ that also presents significant variations (above to 60%). The shape of the curves that represent all the parameters is slightly the same for the different bitumens, although it dislocates up and to the right.

Furthermore, it is also noticed that the values of temperature at which the maximum values of tgδ occur, dislocated to the right (higher temperatures) in all the bitumens and achieved higher values, reflecting the presence of bigger molecules in a superior concentration to those of the base bitumen.

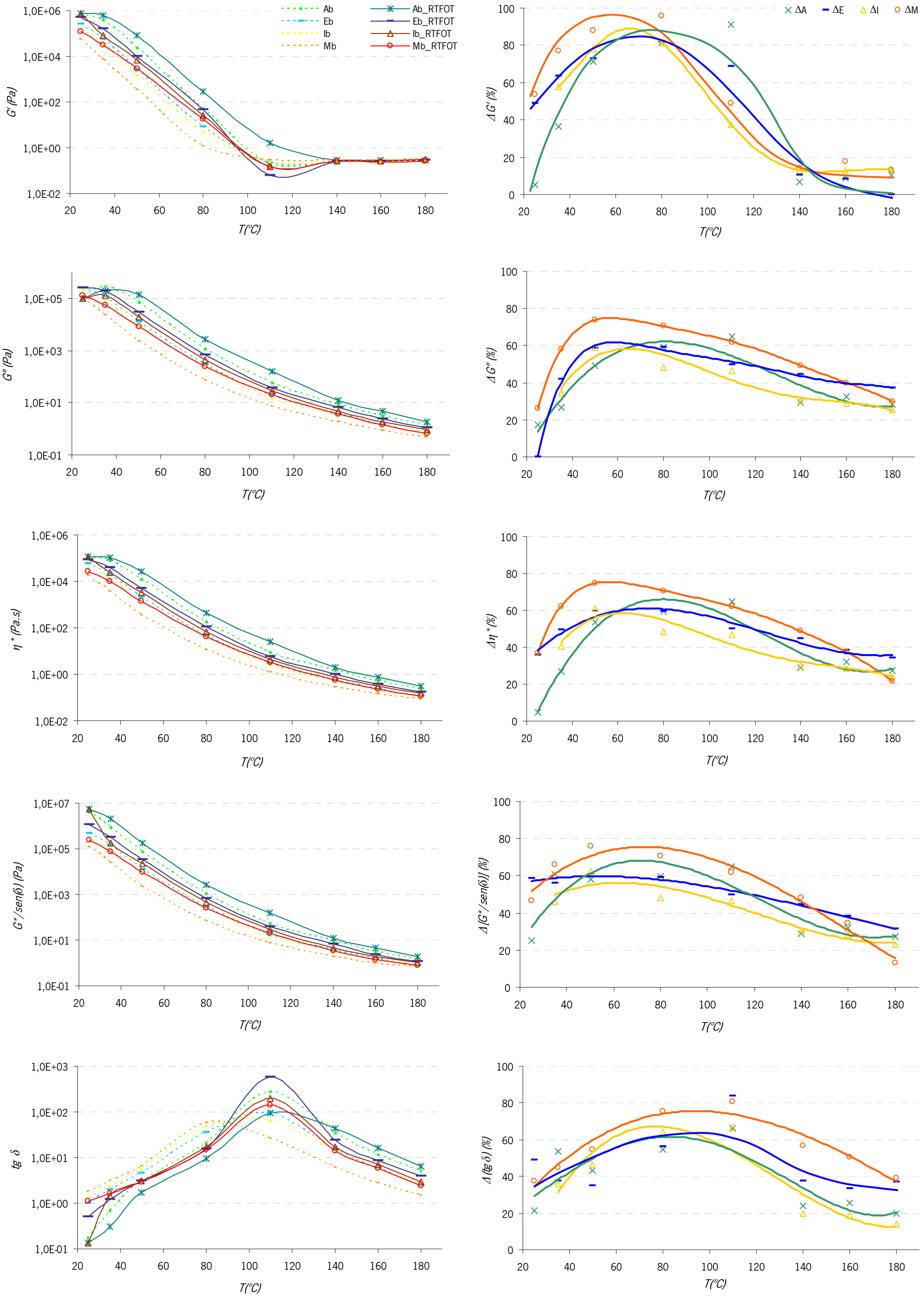


Figure 5.34 – Comparative graphics of the rheological properties of the base and aged bitumens

At the lowest temperatures tested (25 and 35 °C) the changes can be clearly assessed by the construction of the Cole-Cole plane (Figure 5.35).

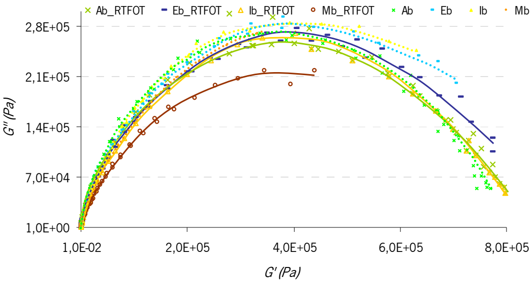


Figure 5.35 – Comparative Cole-Cole plane for the commercial base and aged bitumens

All aged bitumen showed an increase of G’ and a decrease of G’’ at each frequency. The lower variation occurs for bitumen A and highest for bitumen M, as expected. The similarity between the form and the evolution of the different curves indicate that the RTFOT is a process that approaches the distillation process by which the different grade bitumens are produced.

5.2.2.4. Comparison between the rheological and physical properties of the base and aged bitumens

After being submitted to the RTFOT aging process, bitumen presents the same characteristics of the bitumen that constitute the pavement and that control a great part of its behaviour.

The plots showed in Figure 5.36 clarify the effect of the aging process that occurs in the bitumen during the production of mixtures and during the construction of the pavement in the physical properties of bitumen that affect the performance of the pavement at low service temperatures (25 °C) that control the pavement fatigue distresses.

The physical parameter measured at this temperature is penetration at 25 °C. The measured values of this property presented a significant reduction for all the different bitumens, especially for bitumen M. The curves representing the aged bitumen have the same shape of the curve of the base bitumen (potential trending lines), what indicates that, during the RTFOT process, there were no significant structural alterations in the material.

In spite of the increased scattering of the values relating the rheological properties after RTFOT with the penetration at 25 °C, it is noticed that the aged bitumen curves are not a continuation or superposition of the base bitumen curves. The range of values of the penetration results is visibly inferior to that of the rheological classification, especially for the RTFOT aged bitumen, and thus the rheology axis is presented in a logarithmic scale. Actually, the penetration of the RTFOT aged bitumen shows little variation, always inferior to 65 dmm.

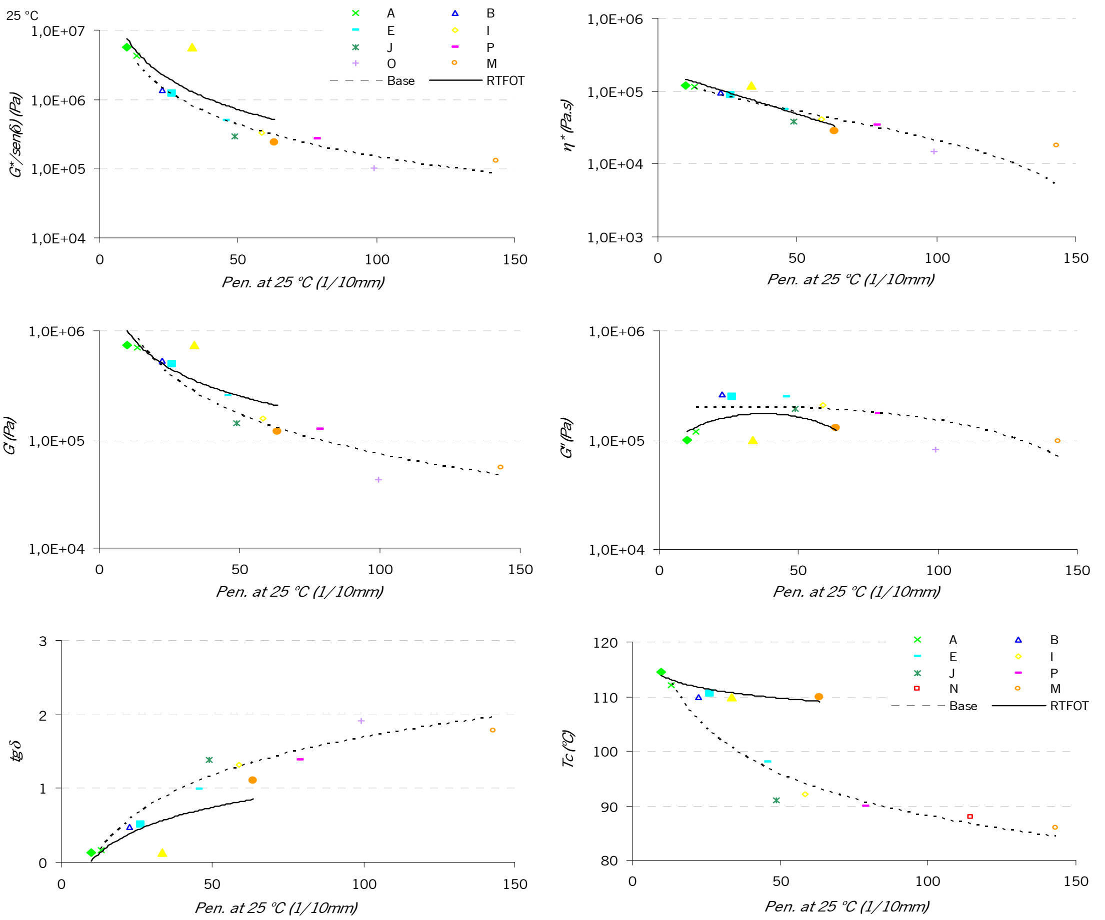


Figure 5.36 – Rheological *vs.* physical properties, at 25 °C and 1.0 Hz, for commercial bitumens, before and after RTFOT

The effect of RTFOT aging of bitumen for operating temperatures can be assessed by comparing the plots of R&B *vs.* rheological parameters at 50 °C of the aged and of the base bitumen (Figure 5.37).

At the reference temperature (50 °C) the differences between the base and aged bitumen are clear, since the lines relating the physical and rheological properties of those bitumens are visibly disconnected (with exception of G'). This occurs because the softening temperature of several binders is superior to 50 °C, mainly that of the aged bitumens, that only melt above 56 °C.

The most significant difference in the behaviour of the aged and of the base bitumen is observable in the plots of tgδ and T_c *vs.* R&B. In combination with the rise in the values of R&B for all bitumens, the values of tgδ suffer a considerable reduction, since the RTFOT turns aged bitumen, besides the elevation in the stiffness, in a more viscous material, namely for the softest bitumen.

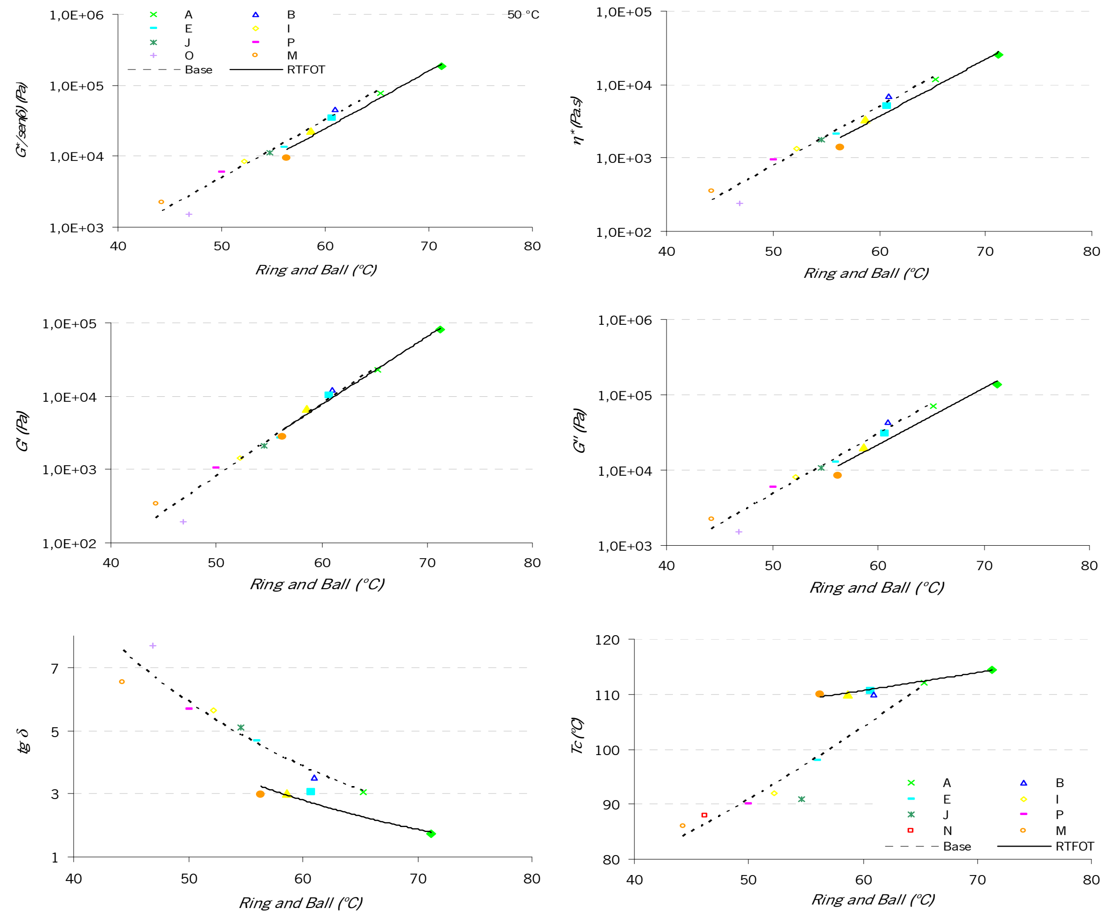


Figure 5.37 – Rheological *vs.* physical properties, at 50 °C and 1.0 Hz, for commercial bitumens, before and after RTFOT

Even more noteworthy is the change in the slope of the lines of the base and the aged bitumen in the plot of T_c *vs.* R&B, because the variation in the softest bitumens is much larger than the one that occurs in the hardest bitumen. The approximate angle formed between the lines and the xx axis varies from 76° for the base bitumen to 19° for the aged bitumen, what indicates that the bitumen is highly changed by the aging occurred in the bituminous mixes production and during the pavement construction, especially the softest ones.

At temperatures of production and compaction of the bituminous mixes (175-180 °C) the comparison between the dynamic viscosity and the rheological parameters for the base and RTFOT aged bitumen is presented in Figure 5.38.

The lines depicted in this Figure correspond to the evolution of the base and RTFOT aged bitumen. With the exception of G' and T_c, all rheological properties show a continuity of the base bitumen data with the aged bitumen.

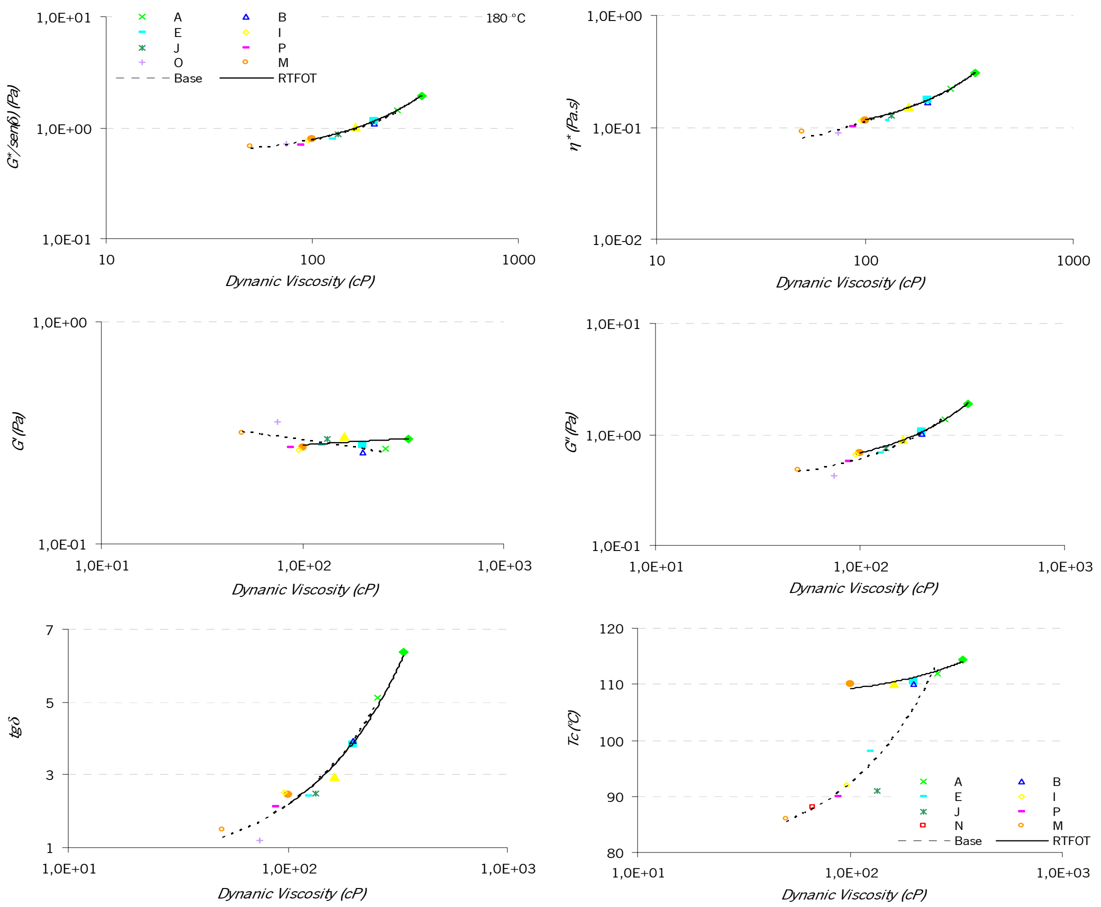


Figure 5.38 – Rheological *vs.* physical properties at production and application temperatures and 1.0 Hz for commercial base and aged bitumens

Both lines almost form a single and continuous line where the values of RTFOT present a proportional increase in the dynamic viscosity and in the rheological parameters values. In the plot of T_c *vs.* dynamic viscosity two different lines showing the different changes that occur in the different grade bitumens are presented.

Contrarily to the other physical properties of bitumen, the dynamic viscosity is more accurate than the rheological parameters of bitumen at this temperature, since the resulting lines spread more along the xx axis, which is represented in a logarithmic scale covering a large range of values.

5.2.3. Characterization of the bitumen obtained in the "*sphere AR production simulator*"

The "sphere AR production simulator" is a test designed for this work with the purpose of assess the alterations that occur in the base bitumen during the production of AR that are independent from the interaction between bitumen and crumb rubber, so that, in posterior tests, it would be possible to individualise the changes in the bitumen due to the presence of rubber particles. This test is, as RTFOT, a simulation of the production conditions test that results on an aging of the bitumen.

To assess the changes that the “sphere AR production simulator” induced in bitumen, some characterization of the physical properties of a set of bitumens was performed. Figure 5.39 presents the results obtained in comparison with the results previously obtained for the base and RTFOT bitumen.

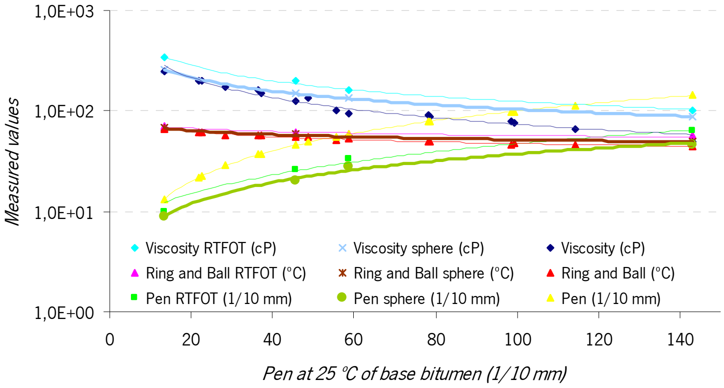


Figure 5.39 – Representation of the physical properties of the sphere bitumens compared to the base and aged bitumens

As expected, the shape of the lines representing each physical property for the sphere aged bitumen is similar to the lines that correspond to the base and RTFOT bitumen, confirming that this is really an aging process. However, the reduction in the penetration due to this process is more pronounced than the observed in the RTFOT bitumen, while in respect to the dynamic viscosity and the R&B parameters the values of the sphere bitumen remain between those of the base and the RTFOT aged bitumen.

In this “sphere AR production simulator” there is not a thin layer of bitumen expose simultaneously to heat and air, as in RTFOT. By the contrary the surface exposed to the air is reduced, this conditions difficult the evaporation of the light fractions of bitumen. Furthermore, the processes have different times in which bitumen is exposed to the aging conditions and in the RTFOT the air is circulating at a pressure superior to the atmospheric.

It is important to attend that, in relation to the effect of aging in the bitumen, of the processes of production of AR, production of the bituminous mixes and the pavement construction the aging process effects in bitumen are the addition of all the effects produced in the tree stages of the construction of a pavement with AR binder, simulated by the RTFOT and by the “sphere AR production simulator” disregarding the effects of the crumb rubber present in the AR binder.

5.3. Study of the Asphalt Rubber (AR)

5.3.1. Characterization of the asphalt rubber

The eight selected bitumens were used to produce asphalt rubber and the eight resultant ARs were characterized in order to assess their physical and rheological properties. Furthermore, the variation of the density during the time of interaction was monitored for the four commercial bitumens and for ARs produced with them.

5.3.1.1. Physical properties of the asphalt rubber

The first performed tests provide the physical properties of these materials:

- Penetration at 25 °C (1/10 mm) – Pen;
- Dynamic viscosity (cP) – DV;
- Ring and ball softening point (°C) – R&B;
- Elastic recovery (%) – ER;
- Density (g/cm^3) – Den.

The physical characteristics of the different samples of binder (base bitumen – B; asphalt rubber– AR) collected throughout the AR production were assessed in this part of the work, in order to evaluate the changes in the binder properties caused by the addition of rubber to the bitumen. Thus, the physical characteristics (Pen, R&B and DV) of the sixteen different base bitumens (A to P) used in this study are presented in Figure 5.40, as well as the properties of the corresponding AR binders. The elastic recovery property for AR binders is also presented as well as the measured values and corresponding differentials of the physical properties.

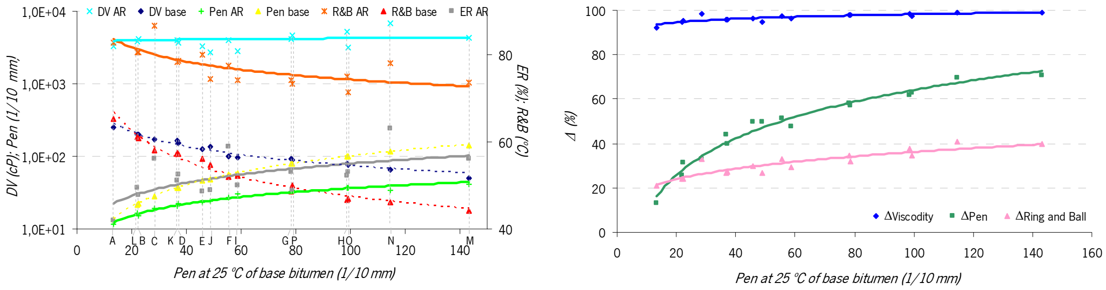


Figure 5.40 – Graphic representation of the physical properties of AR compared to the base bitumen and the calculated differential

The results of the different tests were very consistent with the proportions of the commercial bitumen used to produce the sixteen ARs. In fact, the changes in the constitution of the samples (from harder to softer bitumens) originated an ordered sequence for the evaluated physical properties, represented by a potential trend line.

For every physical property evaluated, the AR binder results presented the greatest dispersion, mainly due to the heterogeneity of this material. As expected, the AR binders presented much lower penetration values and higher R&B temperatures and dynamic viscosities than the corresponding base bitumens.

The dynamic viscosity test is the most effective to find variations in the behaviour of the different materials, as it allows distinguishing the several base bitumens (A to P) very well and the corresponding types of AR. The greatest variation of all the physical characteristics among the sixteen bitumens was observed for the base bitumens, whereas for the AR binders produced with the different bitumens were very similar, mainly the dynamic viscosity and the elastic recovery which hardly varied.

The comparison between the several types of bitumen used to produce AR showed that the highest variations in the physical characteristics of the binder (ARs compared with the Base bitumens) are obtained by softer bitumens. This result is consistent with the microscopic evaluation of the most significant changes in the morphology of rubber particles when softer bitumens are used to produce AR binders (Chapter 5.5). Thus, even using the 150/200 bitumen (M), which is not generally applied to produce asphalt rubber or hot asphalt mixtures, the experimental results showed that it presents the greatest interaction with the crumb rubber, thus being a very good alternative to produce AR binders with final penetration similar to that of AR made with 60/70 bitumen (I).

During the production of the AR binders the density (Den) (of base bitumen, rubber and AR) changes significantly. The study of the variations of the material density, throughout the AR production process, is very important to adequately design the production equipment and to understand the interactions between the bitumen and the rubber particles.

In Figure 5.41 the variation of the density of the bitumen, rubber and ARs of the four commercial base bitumens are graphically represented.

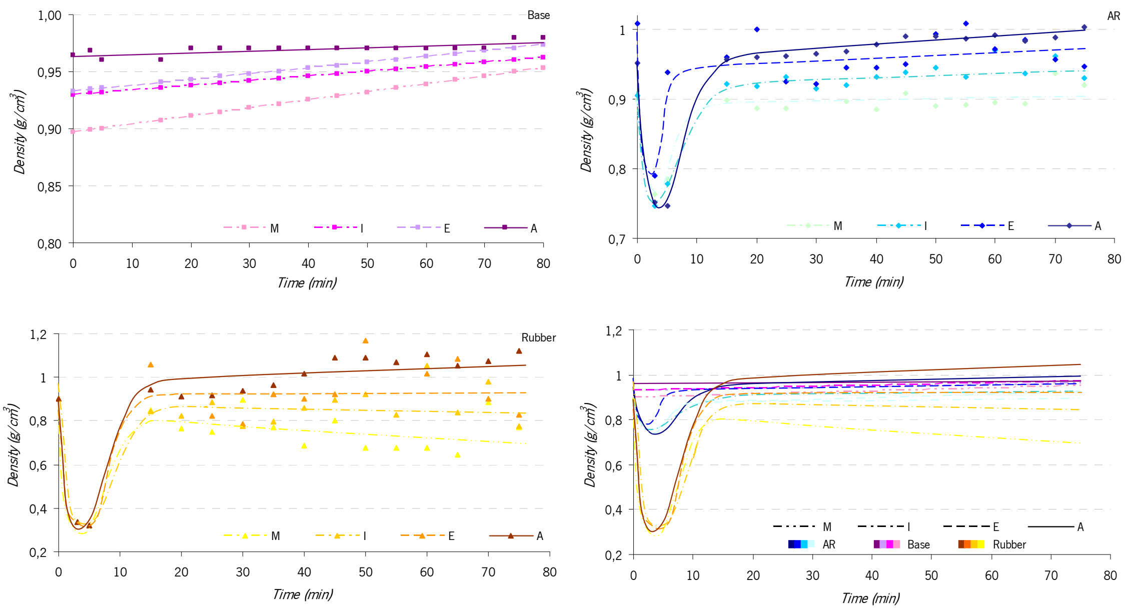


Figure 5.41 – Screening of the evolution of the density of the ARs constituents

The ARs are initially composed by base bitumen and crumb rubber. During the time of interaction a collection of phenomena occurs, some of which are independent of the interaction between the materials:

- Bitumen becomes denser and harder after being subjected to heat and stirring for more than 60 minutes (Base);
- Crumb rubber contains large quantity or air and moisture, in and within their particles. When exposed to eat, the air and water expand their volume, before being replaced by the warm and liquid bitumen (Rubber).

Furthermore, during the rubber-bitumen interaction other phenomena also occur, such as:

- Some compounds of the rubber, as extender oils, carbon black and other additives solubilise in the bitumen;
- The rubber particles swell, due to the diffusion of small molecules of the bitumen in the reticulated molecular structure of rubber;
- The molecules of bitumen diffused in the rubber structure, also induce a relaxation of the links between the rubber atoms causing a decrease in the bulk density of rubber;
- The rubber particles saturated with bitumen molecules transform into a fragile gel which split by the action of the stirring, heat and punctual depolymerisation;
- Parts of the rubber molecules, that were not totally reticulated, can be depolymerised and solubilised in the bulk of the bitumen.

The compounds of rubber that were solubilised in bitumen, combined with the absorption of the smallest molecules of the bitumen, that contribute to its fluidity and softness, turns bitumen denser. This phenomenon together with an increase in density due to the heat which causes the evaporation of its lighter molecules adds more density to bitumen.

The AR is the final product of a chain of physic-chemical interactions, not only between bitumen and rubber, but also with the air and the water. The big reduction of density, in the beginning of the production of the AR, is clearly due to the changes that occur among the rubber particles produced by a warm liquid (this is independent of the liquid characteristics). The reported reduction of density corresponds to a significant increase in the volume of the AR, which leads to other questions, such as:

- How should an AR production plant be dimensioned?
- How long does it take to the air and the moisture contained in the rubber to be expelled?

After these initial events, even more interesting things occur. Bitumen and crumb rubber particles begin to interact and the different bitumen display different evolutions on the rubber density. For instance, during the interaction time (after the first 15 minutes of contact), the rubber that interacts with the hardest bitumen (A) presents a positive linear trend line, showing, in the end of the interaction time, that the density value is superior to its apparent density (0.86 g/cm^3), but inferior to its bulk density (1.21 g/cm^3).

On the contrary, when rubber interacts with the softer bitumen (M) a negative linear trend line appears being the final value inferior to its apparent density. A similar, but less evident behaviour, is registered when bitumen I is used as a base. During the rubber-base bitumen E interaction, practically no changes occur in relation to the density of the rubber particles.

After an analysis, the AR produced with base bitumen A was denser than the residual bitumen – Res (base bitumen after time-rubber interaction), but the density of the swelled rubber particles is inferior to the bulk density of the initial crumb rubber particles. This is explained by the bulk density of the crumb rubber and insufficient quantity of small molecules in the base bitumen, to further swell the rubber particles. The bulk density of the crumb rubber (1.21 g/cm^3) is largely superior to any other material used in the AR production. The density of the recovered rubber particles from the AR is 1.12 g/cm^3, i.e., their density was reduced but continue to be superior to the density of the residual bitumen. The densification of the bitumen due to the loss of the small maltenes is not balanced by the reduction of rubber density.

All other produced ARs have densities inferior to those of their residual bitumen. In the case of the softest bitumens I and M, the final density is even inferior to their base bitumen, because the undersized bitumen molecules profoundly diffuse into the rubber bulk, causing it to swell and changing its crosslink density by punctual depolymerisation and relaxation of the links between atoms, reducing the bulk density of the rubber particles. In fact, when rubber interacts with softer bitumens, its final density is inferior to the initial apparent density.

However, in spite of the significant reduction in the apparent density of rubber particles that interacts with the softest bitumens, I and M, and despite keeping the apparent density of the rubber that interact with bitumen E, all ARs showed an increase in density, except for the AR produced with base bitumen M, which kept its density. The balance between the significant reduction of the rubber density and the increase of the residual bitumen density results in an increase of the AR density, since the percentage of natural and polymeric rubber (not taking in account the bitumen molecules diffused in the swelled rubber) is largely inferior to that of the bitumen.

The graphics depicts the scattering of values, namely in the AR and rubber plots. Nevertheless, it was possible to determine a clear trend line in both cases. The dispersion of values is due to the great heterogeneity of the material (AR), which never presented a flat surface, thus making the measurements difficult.

5.3.1.2. Rheological properties of the AR produced with base bitumen I

Figures 5.42 and 5.43 exemplify the typical variation of the rheological behaviour of the different types of binder evaluated (base bitumen and AR binder) in relation to one of the tested bitumens (60/70 or I). Figure 5.42 illustrates the isothermal plots (for temperatures between 25 and 180 °C) of the base bitumen I and AR I from 0.1 to 10.0 Hz. Figure 5.43 illustrates the isochronal plots (for frequencies between 0.1 and 10.0 Hz) of the binders from 25 to 180 °C.

The comparison between the base bitumen and the AR binder showed that, if the temperature increases, the rheology of the Base bitumen evolves differently from the AR binder (which is clearly stiffer). By observing the isothermal plots of the AR binder, it is noticeable that its rheological behaviour is analogous to that of the Base bitumen for temperatures inferior to 100 °C at all frequencies. However, for temperatures above 100 °C the rheological parameters of the AR, trend for values clearly superior to the ones of the Base bitumen (except for frequencies near 10.0 Hz).

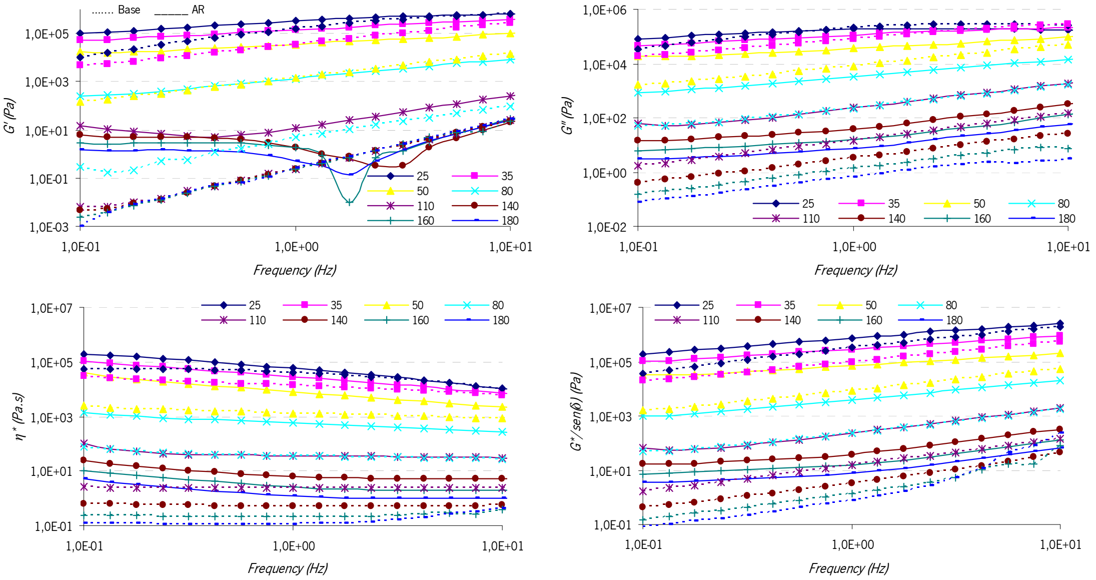


Figure 5.42 – Comparative isotherms of the rheological properties between the base bitumen I and the correspondent AR

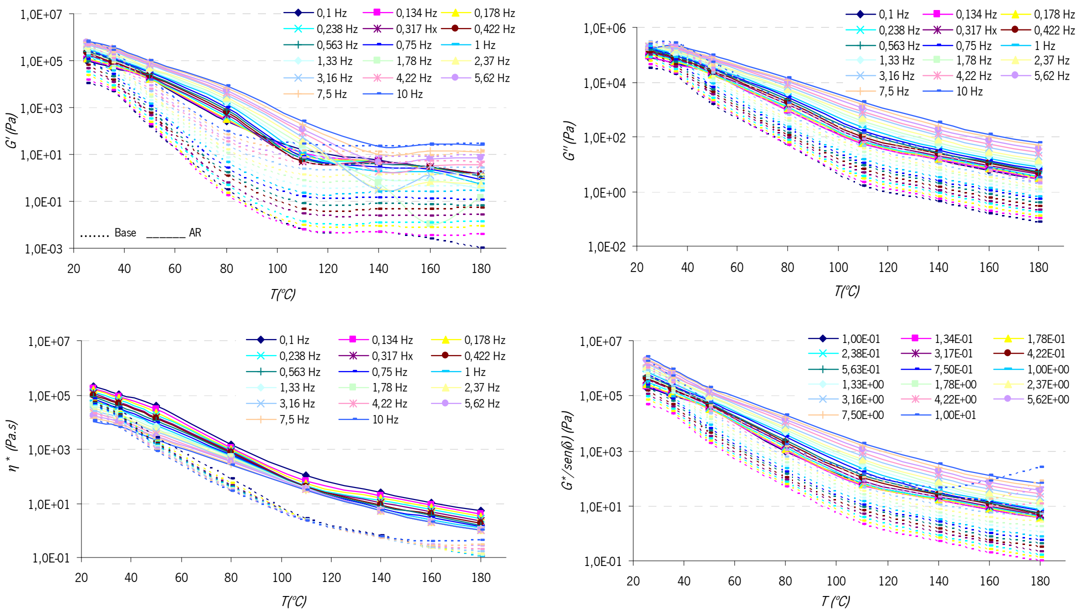


Figure 5.43 – Comparative isochrones of the rheological properties between the of base bitumen I and the correspondent AR

By analysing the effect of the frequency in the rheology of the binders for the different isothermal curves, it is possible to observe that all curves have the same shape (being almost parallel), for the two materials, for temperatures below 100 °C. It can be observed that those curves present higher values for the rheological parameters when the temperature decreases and the frequency increases. The influence of the frequency is still the same for the AR binder at higher temperatures and frequencies, but for the Base bitumen the influence of the frequency in the rheology increases substantially for temperatures above 150 °C and frequencies superior to 3.0 Hz.

The isochronal plots of the different rheological parameters of the AR show a similar development to that shown by their analogous parameters of the Base bitumen. At temperatures of 25 °C, few differences exist on the rheological values of the two binders, but, as temperature rises, the gradient of the curves that define the progress of AR rheological characteristics is inferior to those of the base bitumen. All the rheological parameters show that, for temperatures superior to 25 °C, the AR is stiffer than the corresponding Base bitumen.

The rheological parameter that present a different behaviour is the complex viscosity (η^*), since at temperatures superior to 80 °C the lines describing AR progress are more disperse than the Base bitumen, namely for frequencies above 0.238 Hz. The frequency has more effect in the AR than in the Base bitumen. In fact, for the AR binder the more the frequency increases the more the η^* drops, while the correspondent base bitumen maintains its value at all tested temperatures.

The behaviour described above is due to the rubber particles in the bitumen, which move during each vibratory test, aligning themselves when frequency increases. This causes less particle attrition and a decrease in the complex viscosity. However, as temperature increases, the rheological behaviour of bitumen changes abruptly from a viscoelastic material with a modulus similar or superior to the rubber particles, with the capacity of holding them in its bulk, to a viscous liquid, the modulus of which is clearly inferior to the rubber particles allowing them to move more freely.

In Figures 5.42 and 5.43 it can be observed that the elastic or storage modulus (G') shows a divergent behaviour for temperatures superior to 140 °C and at frequencies between 0.238 and 5.62 Hz, since at these temperatures the G' of bitumen is very small and bitumen behaves as a viscous liquid. However, in AR there are rubber particles in the bulk of bitumen that act independently when bitumen melt and may interfere with the rheometer parallel plate movement inducing abrupt changes in the G' values.

The previous observations are evidenced in Figure 5.44, in the tgδ *vs.* temperature and frequency plots

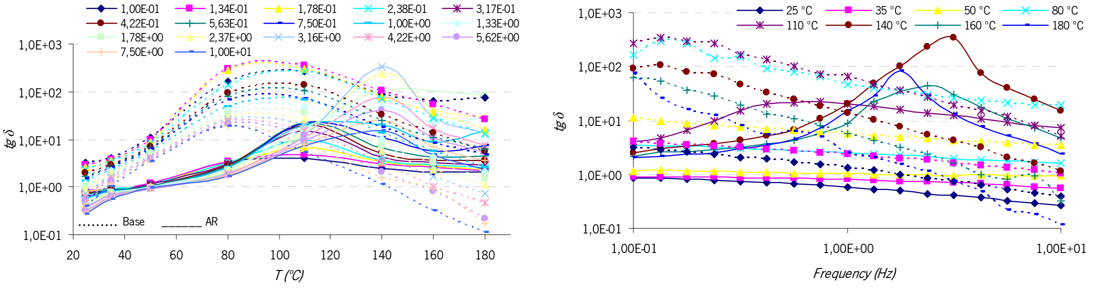


Figure 5.44 – Comparative Isochrones and isotherms of the tgδ of the base bitumen I and respective AR

Considering what said above and ignoring the frequencies between 0.562 and 5.62 Hz for temperatures above 110 °C, the graphics show that the tgδ for the AR does not achieve the values of the Base bitumen, since the presence of the rubber particles increase the value of G' significantly, when compared with the increase in G''.

Regarding the temperature at which the tgδ riches its maximum value (T_c), a displacement to the right can be observed at higher temperatures and frequencies. Furthermore, the behaviour of tgδ for AR is similar to that presented by the Base bitumen. The lines appear concentrated at the bottom of the graphic (for lowest values of tgδ) and to the right (for highest values of temperature), what indicates that the rubber particles provide more elasticity to the binder, without altering its basic rheological behaviour. During the tests, it was observed that the liquid bitumen drained from the rheometer parallel plate geometry, leaving the rubber particles partially uncovered by the bitumen at 180 °C. This fact promoted the partial burning of the rubber particles causing the loss of its elastic properties. Thus, an increase of rigidity and of fragility that provoked the splitting of the rubber particles was observed, especially when exposed to high frequencies, what explains the sudden rise in the values of tgδ.

The study of the rheological behaviour of AR I compared with the Base bitumen I at 1.0 Hz is summarized and reported in Figure 5.45.

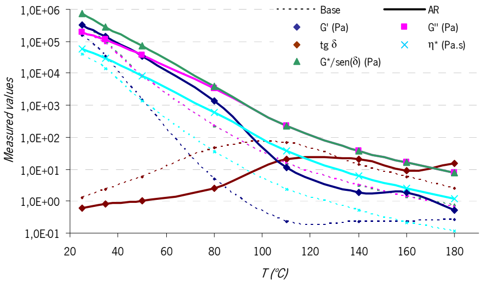


Figure 5.45 – Comparative isochrones of the rheological properties, at 1.0 Hz, of bitumen I and respective AR

The analysis of the graphic allows understanding some rheological behaviours of AR in contraposition to those of the Base bitumen. It can be easily observed a detachment of the lines that define G'' and G*/sen(δ) for temperatures below 80 °C that does not occur in the Base bitumen. This is explained by the more significant increase of the values of G' in relation to G'', the form of calculation of G* and the reduction of the values of the phase angle (δ).

The inclusion of the crumb rubber in the bitumen not only causes a rise in the stiffness of the new binder (AR), but also causes a differentiated increase in the storage (G') and loss (G'') modulus of the binder, where G’ suffers the greatest rise due to the presence of the rubber that, being an elastic solid, confers more elasticity to the AR. Actually, G’ presents higher values than G’’ in the AR, at temperatures below 35 °C. This fact is coherent with a better resistance to rutting and fatigue distresses and to reflective cracking of pavements at service temperatures.

Between 80 and 160 °C, the behaviour of the AR for all reported rheological parameters at the selected frequency (1.0 Hz), is similar to that of the Base bitumen. There is a more evident difference in what respects to the values of G’, G’’ and G*/sen(δ), as they are higher, but proportionally equal to the one of the Base bitumen, as corroborated by the almost superposition between the lines of tgδ for the AR and Base bitumen. This means that, in spite of being stiffer than the Base bitumen, the rheological behaviour at production and application temperature of AR is similar. At 180 °C the behaviour of the AR should be ignored for the previously exposed reasons concerning to the test conditions.

The Cole-Cole plane presented in Figure 5.46 confirms the previous indications about the performance of the AR at service temperatures.

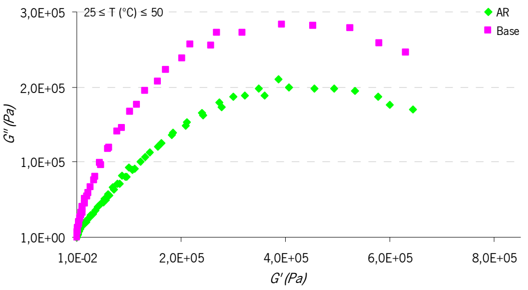


Figure 5.46 – Comparative Cole-Cole plane of bitumen I and respective AR

By observing the curves defined by the interception of G’ with G’’ at each frequency for the base bitumen I and the AR produced with it, it is possible to confirm that the presence of the crumb rubber in the binder does not change its rheological characteristics at the reference temperatures, since the two curves present the same exact shape. The only difference is that the line for the AR is lower than that for the base bitumen, meaning it is a stiff material.

5.3.1.3. Rheological properties of the several asphalt rubbers

Figure 5.47 shows the isochronal plots of the rheological parameters of the Base bitumen and of the resultant AR binder at a frequency of 1.0 Hz and temperatures between 25 and 180 °C for the eight bitumens selected to carry out the rheological tests (A, B, E, I, J, M, O and P).

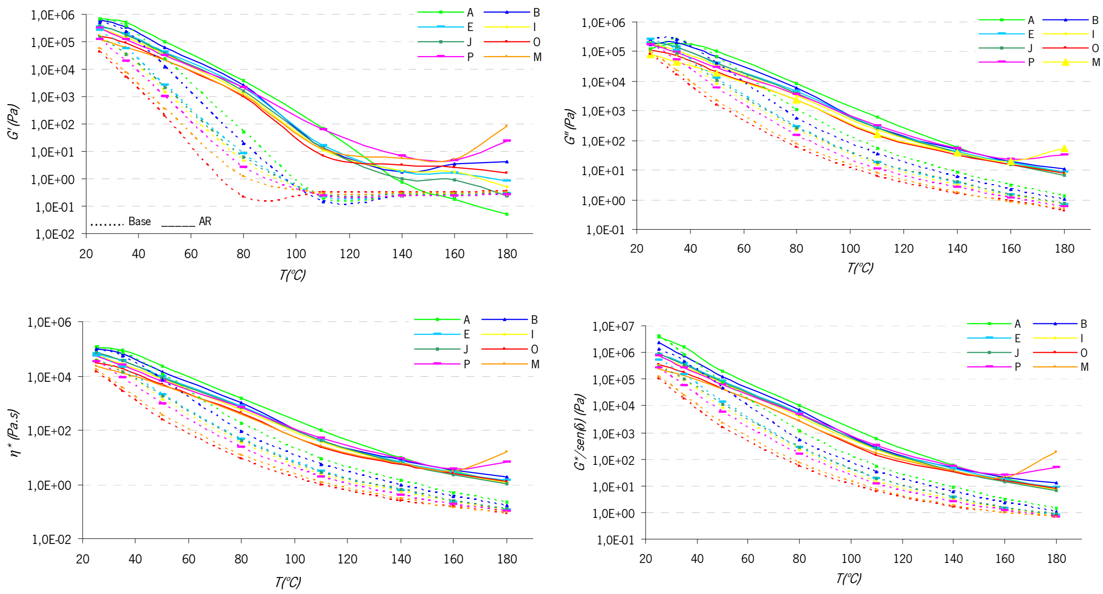


Figure 5.47 – Isochronal plots of the rheological characteristics of the studied binders at 1.0 Hz

The analysis of the rheology of the AR binder showed that it is the stiffest material, being the less susceptible to changing the base bitumen type (plots are very similar) and to temperature variations. In fact, the high increase in the elasticity of the AR binder at all the studied temperatures, caused by the presence of rubber particles, totally changes the rheology of the binder, as it reduces the influence of the temperature in the binder behaviour, mainly for temperatures above 100 °C (the AR does not totally become a viscous liquid).

Asphalt binders must have a set of characteristics, in order to allow its adequate use in road pavement construction at different temperatures. Binders should not be very rigid at low and medium operating temperatures to avoid cracking distresses, but they should be sufficiently stiff at high operating temperatures to improve their resistance to permanent deformation.

The AR binders fulfilled these demands for every base bitumen used, even for the softer bitumen 150/200 (M), since the values of the rheological parameters at 25-35 °C are similar to the Base bitumen, being much higher at 60-80 °C However, the several AR binders presented elevated viscosities at high temperatures, difficulting the mixing and application of AR mixtures.

Figure 5.48 depicts the changes on the viscoelastic nature of bitumen induced by the presence of the crumb rubber after the interaction time throughout the tested range of temperatures at 1.0 Hz and frequencies at 110 and 140 °C..

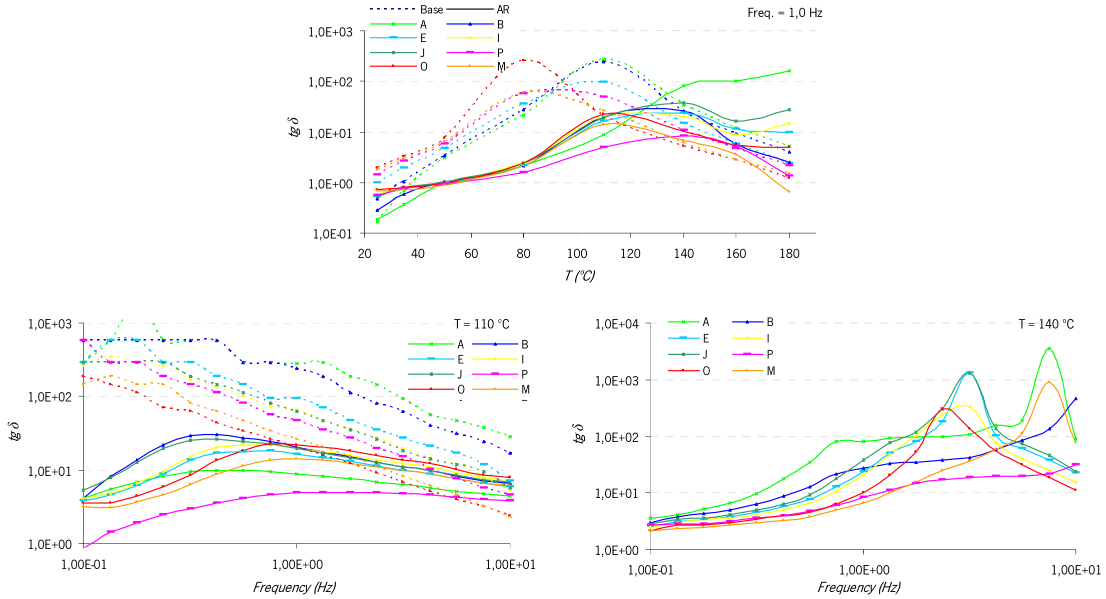


Figure 5.48 – Comparative Isochrones and isotherms at 1.0 Hz of tgδ of the base bitumens and resultant ARs

The graphics show that, for all the ARs, the temperature at which tgδ reaches its maximum dislocation to the right in comparison to the base bitumen, varying from 80-110 °C to 120-150 °C. Additionally, all ARs present inferior values of tgδ than those presented by their correspondent Base bitumens at temperatures below 110 °C, whereas above 110 °C the AR values of tgδ are similar to those presented by the Base bitumen. This behaviour is akin to that presented by AR I. A very interesting result is the quasi-independence values of tgδ from the AR tipe between 35 and 80 °C in spite of their different modulus and viscosity.

There exist an evident disparity between the isotherms of the tested set of ARs at 110 °C and 140 °C, but very different from the behaviour or the base bitumen. At 110 °C for frequencies bellow 1.0 Hz, the values of tgδ augment with the frequency due to the diminution of G' influenced by the melt of the residual bitumen and the alignment of the rubber particles. For frequencies above 1.0 Hz, is observed a light diminution in the values of tgδ, as those develop in an almost independent way of the frequency.

At 140 °C the tgδ values maintain nearly constant until 0.5 Hz, presenting an increase followed by a new stabilization, after which a sudden peak in the values of tgδ occurs.

The development of the viscoelastic characteristics, for temperatures between 25 and 50 °C, of the different ARs and respective Base bitumen, are presented in Figure 5.49.

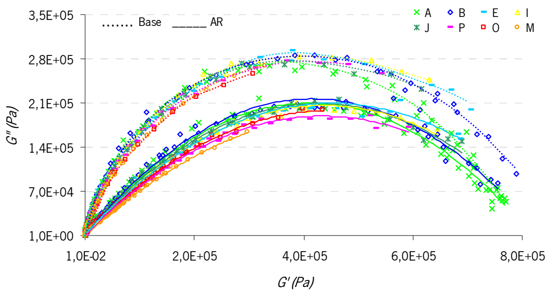


Figure 5.49 – Comparative Cole-Cole plane of the base bitumens and respective ARs

The viscoelastic behaviour of the tested set of ARs, in relation to their origin Base bitumen, is the same previously observed in AR I. By the observation of the set of base bitumen in comparison with the collection of ARs, it can be noticed that the Cole-Cole curves of the latter are more spread, denoting a major influence of the modification of the binder with the crumb rubber in the softer bitumen. This fact is explained by the major extension of the interaction between the softer base bitumen and the crumb rubber during the interaction time. The AR binders that present the best rheological characteristics at service temperatures are those produced with the softer Base bitumen. This indicates that a profound interaction between bitumen and rubber is undoubtedly advantageous.

5.3.1.4. Comparison between the rheological and physical properties of base bitumens and asphalt rubbers

In this section the two binders studied in this work will be compared, with the purpose of understanding the differences between them and of defining the parameters (rheological or physical) that better characterize them and that properly describe their performance along the different life stages of the pavement. In this work the physical parameters used to characterize the performance of the binders at service temperatures that control the fatigue cracking distresses in the pavement are: (i) penetration at 25 °C; (ii) elastic recovery (ER) of the AR binders.

The values of penetration of the different binders are plotted against the respective measured rheological parameters in Figure 5.50.

The range of values in relation to the penetration results is visibly inferior to the rheological classification for AR binders, and thus, the rheology axis is presented in a logarithmic scale. Actually, the penetration values of the AR binders show a slight variation, being always inferior to 50 dmm.

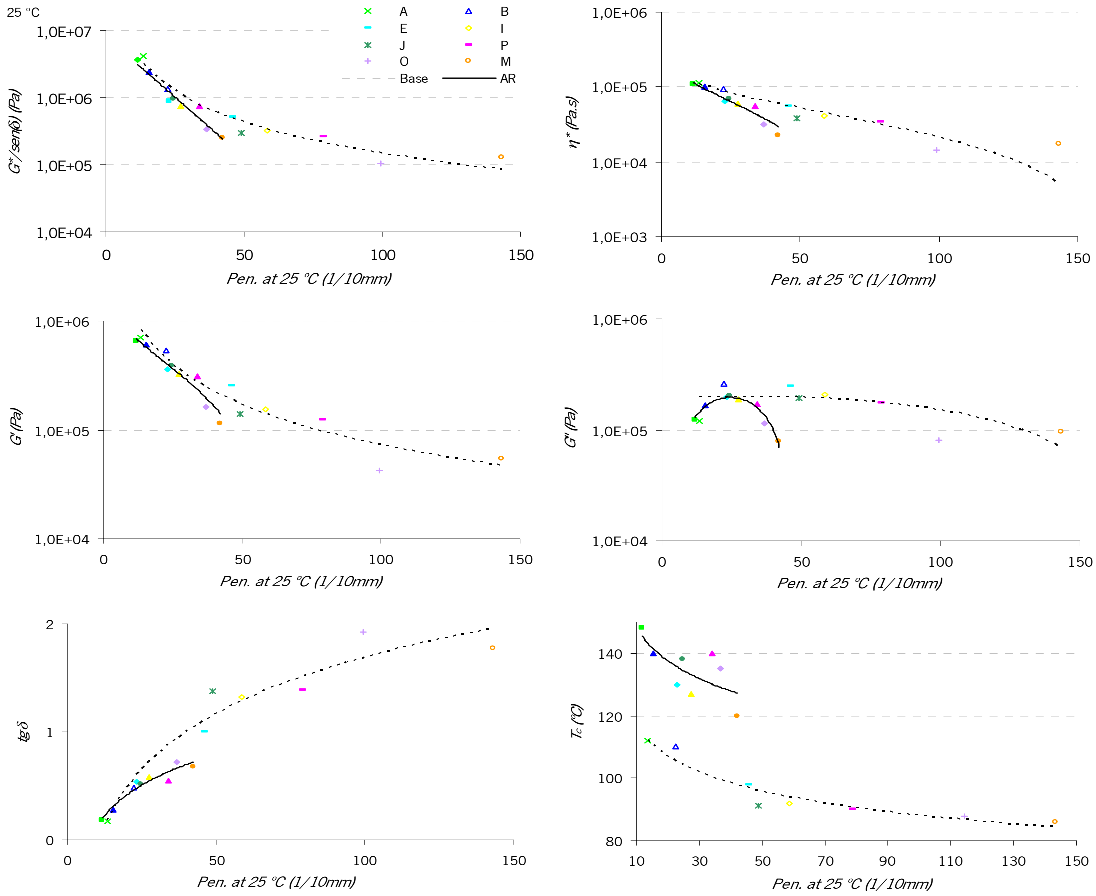


Figure 5.50 – Rheological *vs.* physical properties, at 25 °C and 1.0 Hz, for base bitumens and resultant ARs

It is worth to mention that by analysing the rheology of the different binders (base bitumen and AR), for the same penetration value, the AR binder is the softest material (this result is consistent with the best fatigue cracking resistance of this material).

The lines representing the evolution of T_c *vs.* Pen for the Base bitumen and the AR binders are parallel. The AR binder lines are shorter and displaced up for higher temperatures, what indicates an increase in the binder stiffness. This rheological characteristic of the binder is clearly the most sensitive in relation to bitumen modified with crumb rubber.

The most considerable changes in the characteristics of the binder, before and after the introduction and interaction the crumb rubber, were observed in bitumen M (150/200). In terms of penetration, the Pen of the AR produced with Base bitumen M (Pen = 42.1 dmm) is similar to bitumen E (40/50). However, in terms of rheological characterization the changes are not so drastic, since the measurements indicate similar values between AR M and Base bitumen P (Pen = 78.8 dmm).

Contrarily, when assessing the physical and the rheological characteristics of Base bitumen A and the correspondent AR, almost no alterations were detected, as if the presence of rubber in the binder had not affected the AR behaviour at that temperature (25 °C). Thus, rubber confers the AR binder a property that does not exist in the base bitumen: the Elastic Recovery (ER).

Figure 5.51 depicts the evolution of the rheological properties of the different AR binders with the Elastic Recovery property.

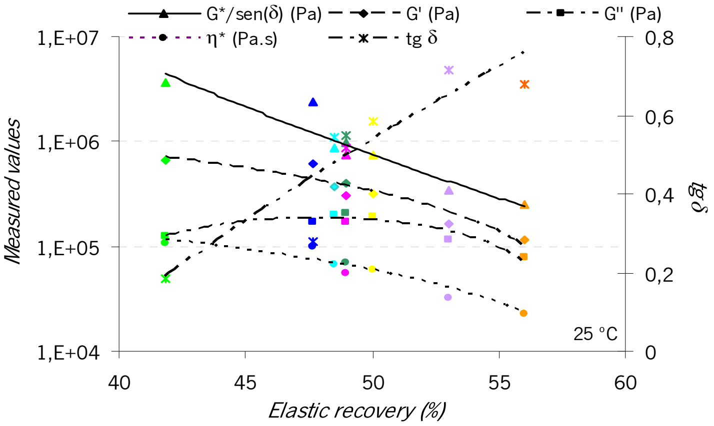


Figure 5.51 – Relation between the elastic recovery at 25 °C and the rheological parameters of the different AR binders

Determining the elastic recovery in the AR binder is undoubtedly important, especially if previous rheological and physical results obtained for AR A are considered, since this is a property that only demonstrates the changes that occur in this binder (ER = 41.82%) in comparison with the base bitumen A (ER ≈ 0%).

It is noticed that the ARs elastic recovery increases when the base bitumen used for their production gets softer. This occurs because the residual bitumen surrounding the rubber particles in the AR binder is less rigid and that allows returning to their initial form.

With the exception of the tgδ lines, it is observed a decrease in the rheological properties when the ER increases, what indicates that this is an important property to characterize the binder (relative to resistance to rutting distresses in the pavement), which is not reported by the rheological measurements.

The rheological properties *vs.* R&B at high operating temperatures (50 °C) for the base bitumen and the correspondent ARs are presented in Figure 5.52.

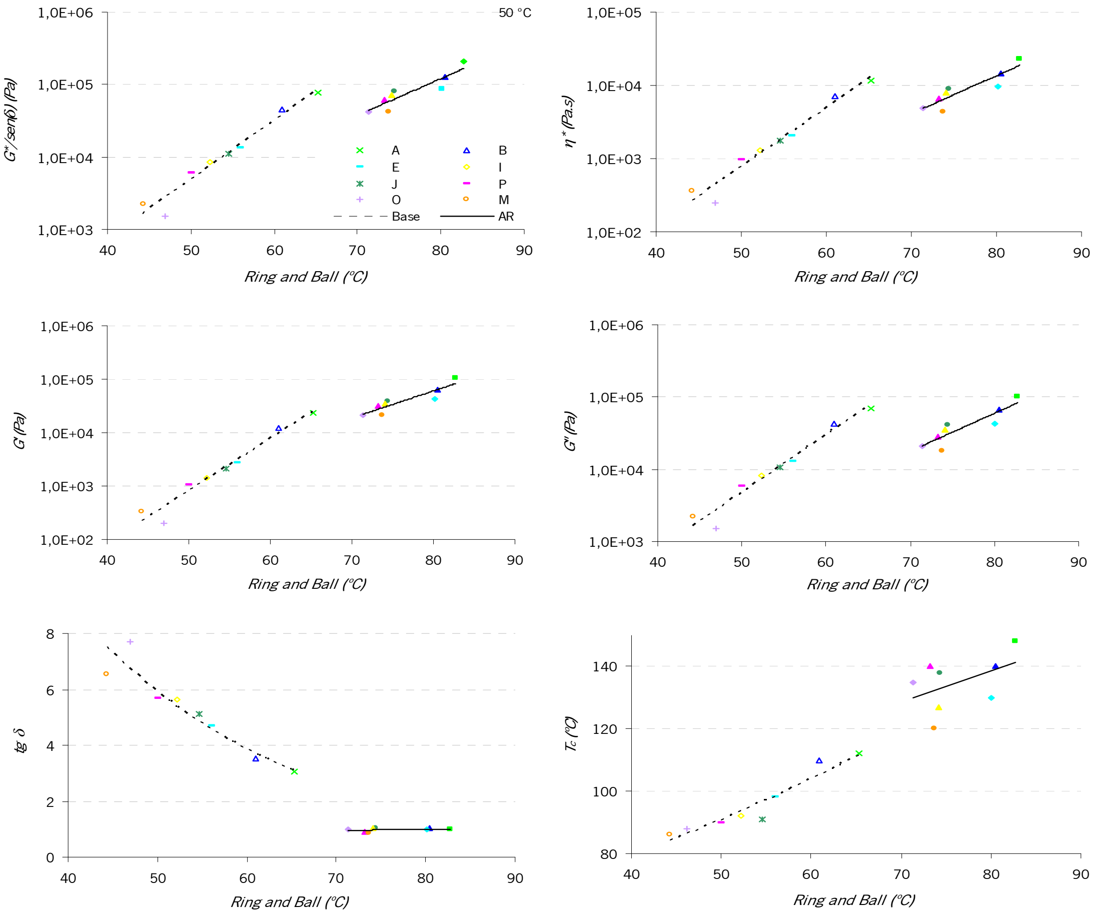


Figure 5.52 – Rheological *vs.* physical properties, at 50 °C and 1.0 Hz, for base bitumens and resultant ARs

There are evident differences between the various binders (Base and AR), since the lines related to the physical and rheological properties of those binders are visibly disconnected. This occurs because the softening temperature of several binders is superior to 50 °C, mainly the AR binders that only melt above 70 °C. The graphic also confirms the previous observations: the softer AR binder is stiffer than all the Base bitumen.

At this temperature the rheological parameters are more accurate to describe the behaviour of the two binders, with the exception of the tgδ. This parameter is less accurate than the R&B parameter for the base bitumen, for AR binders is clearly inefficient presenting slightly the same value for all tested AR binders.

As mentioned earlier, during the rheological tests at high temperatures, the liquid bitumen drained from the rheometer parallel plate geometry, the rubber particles partially uncovered by the bitumen partially dried and burnt. Thereby the comparison between the Dynamic Viscosity at 175 °C with the rheological properties did not present any relation.

5.3.2. Characterization of the AR after RTFOT

The ARs produced with the four commercial base bitumens, were subject to the RTFOT procedure and the resultant RTFOT aged ARs were characterized for their physical and rheological properties.

5.3.2.1. Physical properties of the aged asphalt rubber

The first performed tests provided the physical properties of these materials:

- Penetration at 25 °C (1/10 mm) – Pen;
- Dynamic viscosity – DV;
- Ring and ball softening point – R&B;
- Elastic Recovery (%) – ER.

The measured values of the physical properties are graphically presented in Figure 5.53.

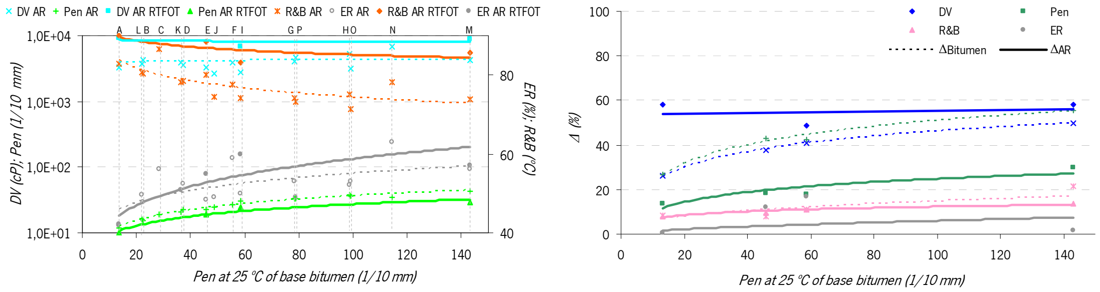


Figure 5.53 – Comparative graphic representation of the physical properties of bitumen and AR (before and after RTFOT)

As documented, the more affected property during the RTFOT aging of the AR is, once more, the viscosity (DV). This physical parameter shows a great variation, especially in relation to the AR produced with the hardest bitumen (A), contrarily to all the other parameters to which the greatest variation is attained for the softer bitumen M and the related AR.

The method used to determine the AR viscosity (ASTM D 4402) is not sufficiently accurate. During each test the DV values decrease significantly and the repeated tests offer different results which lead to a noteworthy dispersion of points. This behaviour is due to the heterogeneity of the AR binder and the different density of its components.

The property that was less affected by the RTFOT aging of the AR binder was the Elastic Recovery (ER). Besides, it is the only property that indicates an improvement in the physical characteristics of the material (AR) after the aging process. However, it is useful to observe that the AR produced with the hardest and the softest bitumens, hardly shows any variations in their ER after RTFOT.

With the exception of the DV, all other properties presented less variation in the AR aging that in the bitumen aging. These observations suggest that AR binder is less sensitive to aging, during the mixes production and compaction, than Bitumen. However, during the AR production the base bitumen is "aged" and the RTFOT favours the continuation of the rubber swelling and the re-vulcanization. Since the bitumen surrounding the rubber particles (Res) has very different characteristics than the Base bitumen, it is not possible, with the present data, to conclude whether the rubber protects the AR binder from aging. It is important to indicate that the Pen and the R&B tests are performed at temperatures below 100 °C, i.e. under the temperatures at which the relaxation of the bitumen occurs. Thus, the measured properties are mainly affected by the bitumen behaviour. On the contrary, the DV values are obtained for high temperatures, at which the bitumen behaves as liquid oil. Under these conditions the performance of AR is largely controlled by the rubber and it is possible to assess the changes that occur in this material during the RTFOT aging process. According to the results many alterations occurred in AR throughout the RTFOT.

5.3.2.2. Rheological properties of the RTFOT aged asphalt rubber

After RTFOT aging process, the rheological properties of the four ARs were assessed and compared with the initial AR. In Figure 5.54 the comparative isotherms of the rheological parameters, at different temperatures, for AR I (initial and RTFOT) are presented.

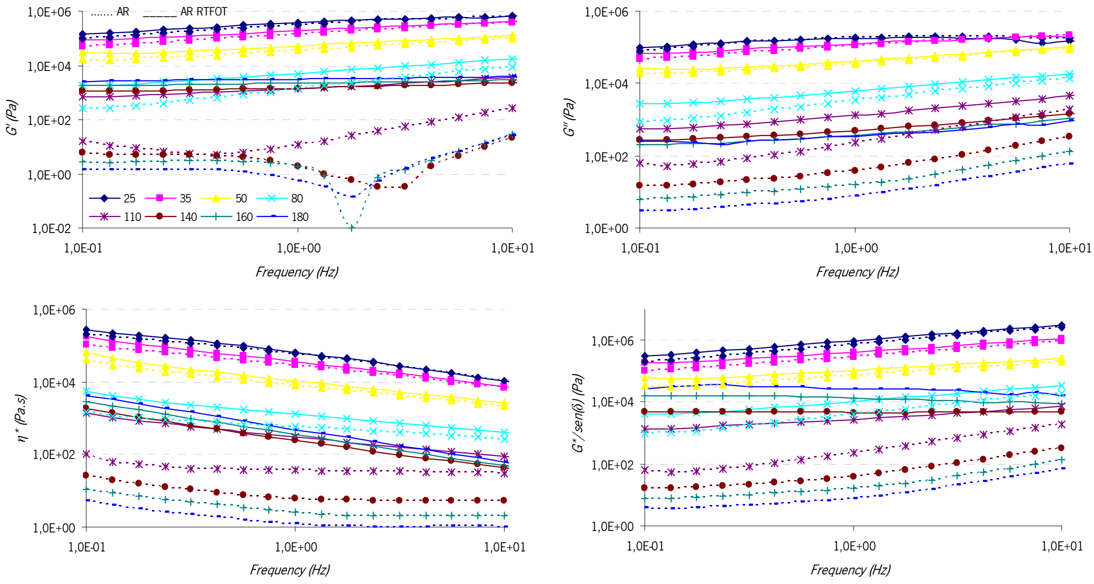


Figure 5.54 – Comparative isotherms of the rheological properties of the AR I before and after RTFOT

By the analysis of the graphics is possible to differentiate two stages, under and above 100 °C. Below 100 °C, the behaviour of the AR binder is largely influenced by the bitumen and the most significant changes in the properties of this material take place around 100 °C. Thus, the rheological parameters present a very slight increase, despite the significant increase in the residual bitumen stiffness due to the aging process and to the interaction with the rubber. Above 100 °C, the rheological behaviour of the AR is conducted by the rubber particles. However, the phenomenon that occur in the AR during the rheological tests do not replicate after the RTFOT, allowing the measurement of the rheological properties at these temperatures. During the RTFOT the residual bitumen gets stiff, allowing the performance of all the tests, without the bitumen draining off the parallel plates.

The isotherms of the G', G'' and η^*, for temperatures beyond 100 °C, present the same slope of the lines under that temperature and a modest amplitude of variation. The lines of the G*/sen(δ) present a different sensibility to the frequency under and above 100 °C, having a positive slope for the lowest temperatures and being almost independent from the frequency at higher temperatures. Other remark that should be made, based on the observation of the graphic of η^* *vs.* frequency, is the great dependency of the viscosity (η^*) on the frequency. The isotherms in this graphic present a negative slope, indicating a reduction of the viscosity with the increase of frequency. The lines of the aged AR are parallel to the unaged until 100 °C, but that dependency gets stronger as the temperature increases.

In Figure 5.55 the isochrones of the rheological parameters for the aged and initial AR produced with bitumen I are displayed.

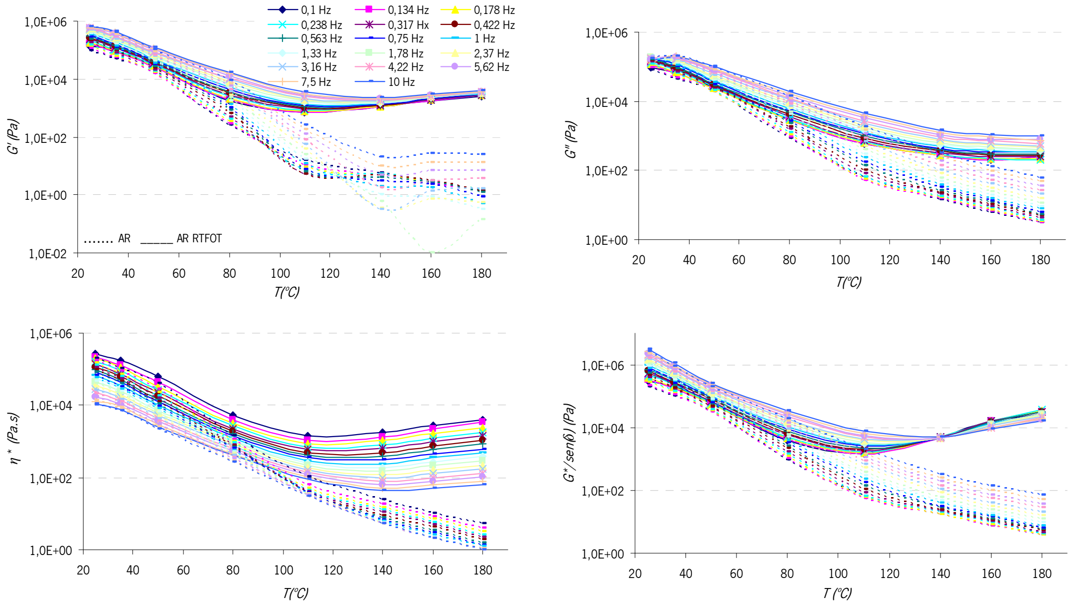


Figure 5.55 – Comparative isochrones of the rheological properties of the AR I before and after RTFOT

Again, by the observation of the graphics it is possible to divide the behaviour of the aged AR into two phases, above and below 100 °C.

In the range of temperatures between 25 and 80 °C there is almost no alteration in the behaviour of the AR before and after RTFOT. Additionally, the shape of the curves at these temperatures is similar to the curves describing the rheological behaviour of the base bitumen, but they indicate a stiffer material. These observations point to control the AR from the behaviour of the bitumen, since at this range of temperatures (25-80 °C), the enclosed rubber particles in the rigid structure of the bitumen have restricted movements. At this stage bitumen is harder than ever before. Hence, the behaviour of the swelled rubber particles is influenced by the bitumen molecules within its reticulated structure.

Between 80 and 110 °C, an alteration in the aged AR behaviour is noticeable, what coincides with the beginning of the relaxation of the bitumen structure. After this point, it is possible to observe a behaviour clearly affected by the rubber.

During the aging of AR using the RTFOT several processes take place, such as:

- The residual bitumen that surrounds the rubber particles is subjected to a more intense aging than the base bitumen aging, since it is exposed to the same conditions in a thinner layer;
- The rubber particles, which have not achieved saturation during the AR production, continue to swell;
- The volume fraction of rubber particles in the AR increase to a clearly superior level than that of the residual bitumen;
- At these temperatures and in presence of sulphur, the vulcanization and polymerization processes may take place within the rubber particles;
- Simultaneously, the rubber particles, swelled to saturation by the action of temperature and pressure of the bitumen molecules held in the rubber reticules, start to depolymerise and break;
- In the end of the RTFOT, it is almost impossible to drain the bitumen from the AR material, since bitumen is entrapped in the swelled rubber and the re-vulcanized particles.

The majority of these processes occur due to the characteristics of the rubber and reflects the chemical reactions that take place during the rubber polymerization and vulcanization. During the AR production and later, during the AR mixes production and compaction, the rubber particles are exposed to approximately the same conditions of those of the production of tyre rubber (see Chapter 2.2), in the presence of vulcanization and polymerization inducers, that are not totally consumed in the primary reaction, the broken and unvulcanized rubber chains can be polymerized and vulcanized.

For temperatures superior to 100 °C, the isochronal lines reproduce the previous arguments. The presence of bitumen in the aged AR is imperceptible, because at these temperatures it is softer than the swelled rubber. Furthermore, the interaction between the rubber and the bitumen and the reactions among the swelled rubber particles, initiated during the AR production and continued in the RTFOT, result in a mass controlled by the rubber rheological behaviour, with values of G’ visibly superior to the values of G’’.

The analysis of the graphics of G’, η^* and G*/sen(δ) between 140 and 180 °C showed an increase of the rheological parameters with temperature, mainly due to (i) the increase in the viscous part of the residual bitumen that released the rubber particles and (ii) the dilatation of the links in the rubber structure and more amplitude of vibration of the atoms induced by temperature.

The evolution of the values of tgδ for the aged AR compared with the initial AR (Figure 5.56) confirms the previous observations.

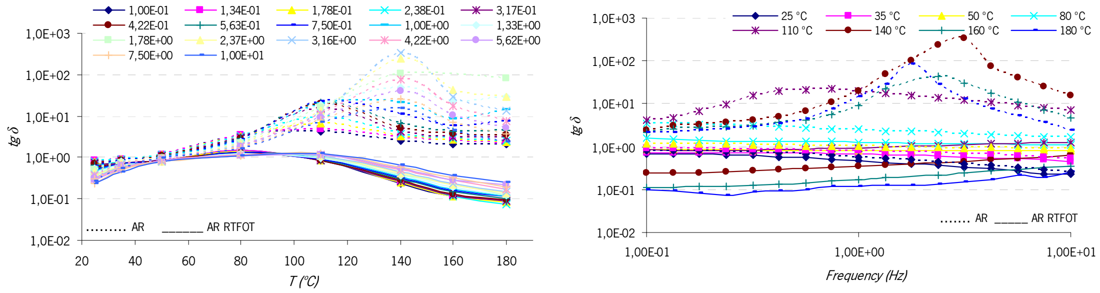


Figure 5.56 – Comparative Isochrones and isotherms of the tgδ of the AR I before and after RTFOT

In the previous studied materials (base and aged bitumen, AR) the isochrones of tgδ present a peak, and the isotherms present a sudden change in slope, for temperatures at which the bitumen alters its characteristics, mainly from a elastic material to a viscous material (T_c). However, there is a smoothening of the peaks in the isochrones and a reduced variation of the slope of the isotherms after AR is subjected to RTFOT. The behaviour of tgδ for the aged AR below 80 °C is similar to the initial AR and coherent with the behaviour of the base and aged bitumen. Nevertheless for temperatures above that value and after a phase of stabilization, the values of tgδ decrease because of the increase of the G’ of the material, corroborating the control of the aged AR by the rubber.

Figure 5.57 illustrates the changes induced by the RTFOT in the rheological characteristics of AR compared with the initial AR at 1.0 Hz.

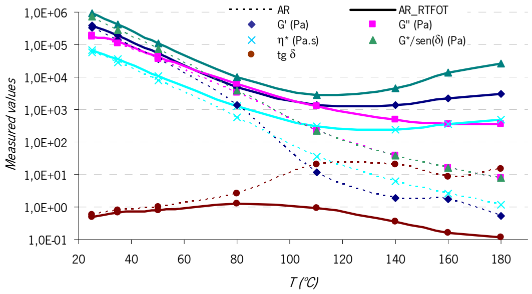


Figure 5.57 – Rheological characteristics, at 1.0 Hz, of AR I before and after RTFOT

Analysing the graphic, it is possible to verify that, contrarily to what was observed in the materials previously considered, the lines describing the evolution of G'' and G*/sen(δ) are not coincident at any temperature interval showing distinct forms that diverge for temperatures superior to 110 °C. The referred behaviour is due to the fact that the G' parameter of this material always present values superior to the G'' parameter, *i.e.*, the elastic component of the material is slightly superior to its viscous part, showing both parameters (in average) higher values than all other materials studied until this moment, specially for temperatures superior to 80 °C. The aged AR is clearly the stiffest and most elastic material.

For temperatures inferior to 80 °C the aged AR presents values of the rheological parameters vaguely higher to the initial AR, and the evolution in this range of temperatures is similar, indicating the preponderance of the bitumen behaviour in relation to that of the rubber. Above 80 °C, the evolution of the rheological parameters diverges from the earliest observations, being dominated by the rubber rheological performance. Beyond 110 °C the value of G' increases significantly with temperature, while the value of G'' suffers a moderate decrease, reflecting the amplified liquefaction of the bitumen, originating very little values of tgδ. Thus, the complex viscosity values increase with temperature, since the rubber applies an attrition force to the plates which restricts its movement.

The relation between the storage and the loss modulus of the aged AR related to the correspondent initial AR, at service temperatures, is graphically represented in Figure 5.58 by the Cole-Cole plane.

By the observation of the two curves depicted by the points that relate G' with G'' at the different frequencies and temperatures, it is perceptible that the two materials (initial and aged AR) performed in an analogous form. The line representing the aged AR indicates that this is a harder material (higher values of G* at each frequency).

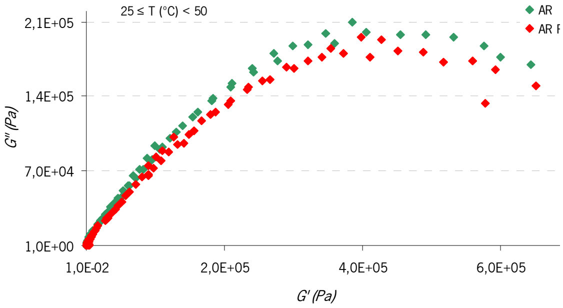


Figure 5.58 – Comparative Cole-Cole plane of AR I before and after RTFOT

Furthermore, the ratio between the viscous and the elastic components of the aged AR is inferior to the initial AR, what indicates a special increase in the elasticity of the material during the RTFOT with impact in this range of temperatures, and consequently, in the performance of the constructed pavement.

5.3.2.3. Rheological characterization of the several RTFOT aged asphalt rubbers

To assess the effect of the RTFOT in the AR produced with the four commercial bitumens (A – 10/20; E – 40/50; I – 60/70; M – 150/200), rheological tests were performed in the bitumens after RTFOT and then, the results were compared with the initial AR.

In Figure 5.59 the isochrones obtained for the different rheological parameters and variation between each initial and aged AR are plotted.

By the analysis of the graphics it is possible to distinguish two phases in the evolution of the rheological characteristics of the different materials in the tested range of temperatures. Therefore, as already verified for the initial and aged AR I, at temperatures inferior to 80 °C the behaviour of all the aged ARs is similar to the initial AR, although it presents slightly higher values in the rheological parameters (except tgδ). However, some differences in the rheological behaviour of the aged AR are noticeable, in accordance to the base bitumen used in its production, namely:

- The AR produced with the softest bitumen (M) showed the highest variation between the initial and the aged binder;
- The smallest variation is verified when comparing the aged and initial AR produced with the harder bitumen (A), in exception of the G'.

Under 80 °C, the property that suffers the most significant variation, when comparing all the initial ARs with the resultant aged ARs, is the elastic modulus (G').

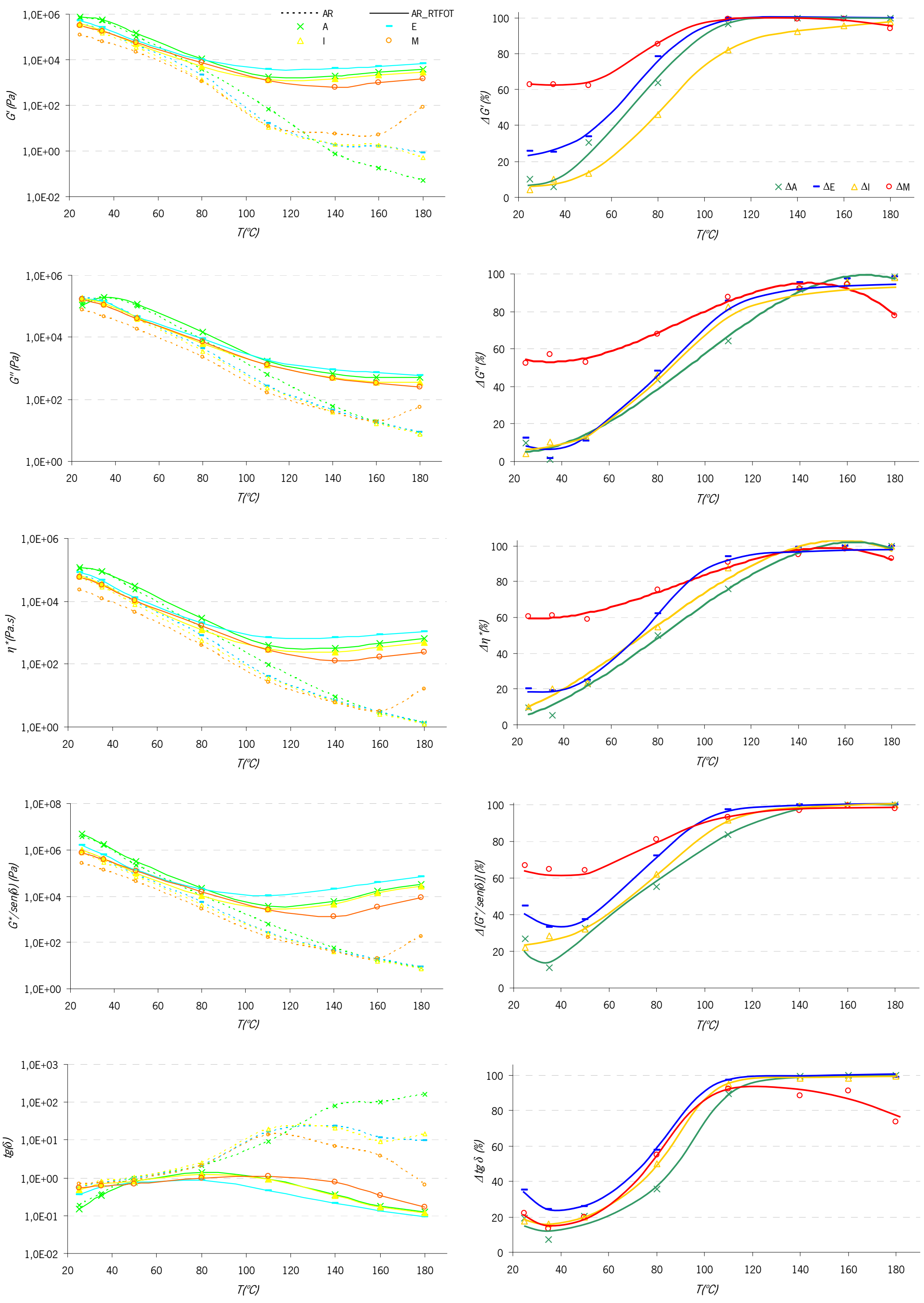


Figure 5.59 – Comparative graphics of the rheological properties of the initial and aged AR

The isochrones of the rheological properties of the four aged ARs present the same shape and little scattering. The most elevated values are those of the rheological parameters (except tgδ) observed for the aged AR produced with bitumen E. The smallest values are those of the aged AR produced with bitumen M.

The greatest increase in the variation of the rheological parameters for the initial and RTFOT aged ARs occur within the range of temperatures between 50 and 110 °C. Above 110 °C, it is observable an enormous variation in the values of the rheological properties in all the materials of approximately 100%. However, these results do not correspond to a real variation in the rheological parameters, since the values measured for the initial AR are affected by a lack of accuracy.

The most important information needs to assess the binder performance in the pavement. This can be obtained by the analysis of the Cole-Cole plane of the aged binders. Figure 5.60 depicts the Cole-Cole plane of the initial and aged ARs produced with the four commercial bitumens.

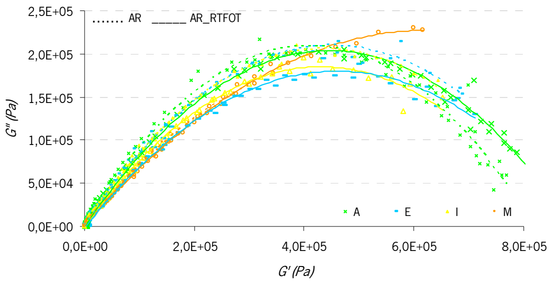


Figure 5.60 – Comparative Cole-Cole plane of the commercial base and aged AR

In previous paragraphs it was referred that between 25 and 50 °C the changes in the behaviour of the ARs, initial and aged, were small. However, aging has a dissimilar impact in the diverse initial ARs. The effect of the RTFOT in the initial ARs, between 25 and 50 °C, produced changes in the relation between the elastic and the viscous components of the tested materials.

The Cole-Cole curves of the aged ARs produced with bitumen E and I show a similar form in the Cole-Cole plane of the initial ARs. Only a curve translation upwards and to the right, is noticeable, what represents that the material became stiffer. These results indicate that, during the RTFOT, the interactions between the rubber and the bitumen initiated in the production of the ARs continue, since the residual bitumen still contains small molecules that can diffuse in the rubber and the rubber particles did not achieve saturation.

On the other hand, the ARs produced with the Base bitumen A and M present significant changes in their behaviour before and after aging. Thus, the Cole-Cole curves of AR A after and before the RTFOT intercept and no hardening is detected in the aged material. In fact, the Cole-Cole plane of the aged AR A even shows a slight softening of the material. This performance is due to the fact that during the production of AR A the quasi-totality of the small molecules contained in the Base bitumen A was consumed by the rubber particles. Therefore, throughout the RTFOT there is hardly interaction between bitumen and rubber, but the molecules of bitumen diffused into rubber reticules continue to progress in the bulk of the rubber particles, causing the relaxation of the rubber molecular links.

As it would be expected, taking into account the previous observations, the AR produced with the Base bitumen M suffered noteworthy changes in the aging process. Since the residual bitumen (Res) in the AR M still bears a considerable amount of small and volatile molecules, they can continue to diffuse into the rubber particles until it is saturated (gel rubber).

The particles of gel rubber fracture, releasing little pieces which increase the volume fraction of the gel rubber in the AR. The aged AR M is softer than the initial AR because the Base bitumen M has a small quantity of big molecules that confer stiffness to the bituminous binders and the more swelled the rubber particles are the softer they can get.

5.3.2.4. Comparison between the rheological and physical properties of the asphalt rubbers before and after RTFOT aging

The rheological and physical characterization of a bituminous binder after RTFOT is of primordial importance, since this is the material which actually constitutes the pavement, conferring it an adequate performance and which will suffer the distresses caused by the traffic, weather, pollution, and others.

To understand how the rheological characteristics of the aged ARs relate with the Pen, and to assess the evolution of these properties, from the initial ARs, several graphics are displayed in Figure 5.61.

By the analysis of the graphics, a great consistency can be noticeable between the rheological and the physical properties, pointing to an improvement of the AR after RTFOT, especially when the Base bitumen used for the AR production is softer. In fact, the AR A is less affected by the RTFOT. It hardly shows any variation in the rheological and the Pen at 25 °C. By opposition to AR A, AR M shows significant changes in its rheological and physical properties after the aging test (RTFOT). The reduction in the Pen of the AR M after RTFOT is conjugated with the increase of the rheological parameters (except tgδ). These results indicate a very resistant material, with an elevated complex modulus and viscosity and also very resistant to fatigue cracking since it preserves an adequate softness. The ARs produced with base bitumen E and I show an intermediate behaviour after RTFOT that can be related with the base bitumen used.

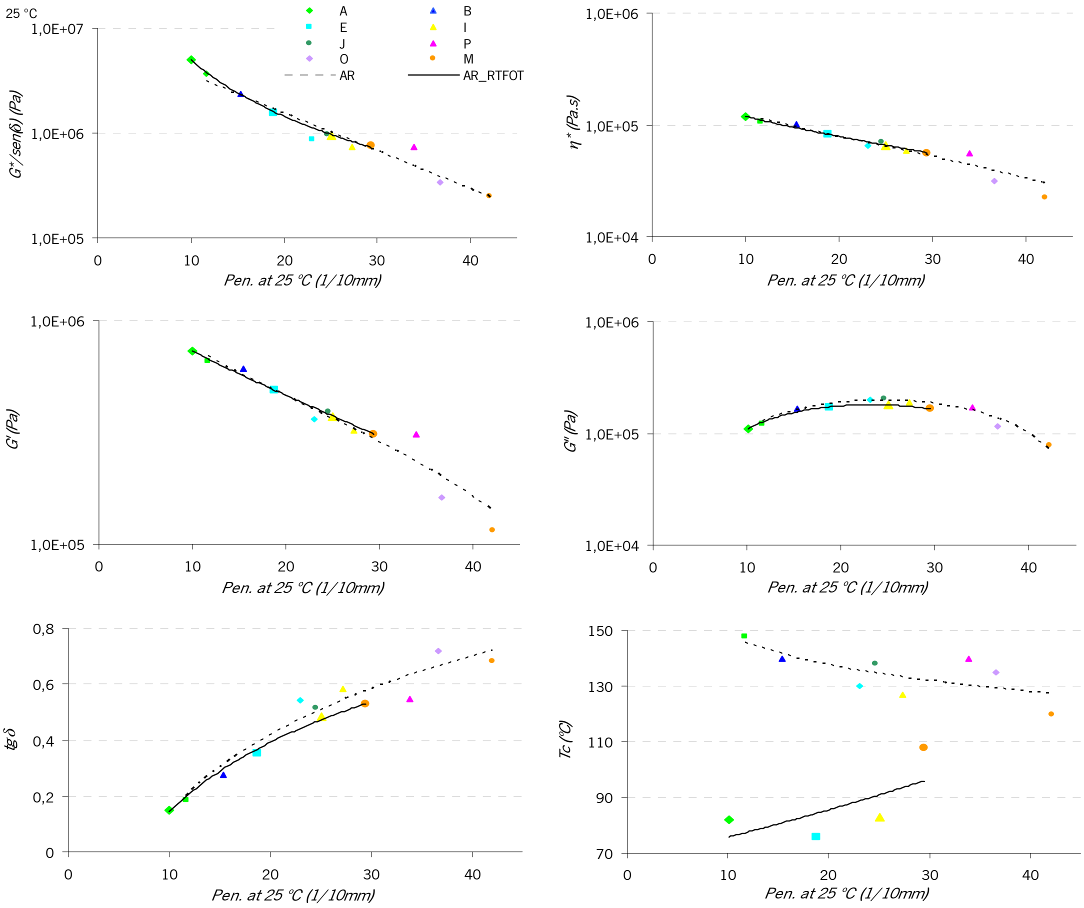


Figure 5.61 – Rheological *vs.* physical properties at operating temperatures causing fatigue cracking of AR and RTFOT aged AR

Finally, it is noticeable the good adjustment of the points relating the rheological and the Pen at 25 °C of the aged ARs to logarithmic trending lines with the exception of the values of G'', which are adjusted by 2^{nd} degree polynomial lines.

Besides the Pen at 25 °C, at this temperature another physical property was assessed and compared with the rheological characteristics of the ARs before and after RTFOT (Figure 5.62).

The elastic recovery is a property characteristic of elastomers used to classify them and especially to survey the polymerization reactions in the rubber production and the crosslink density during the vulcanization process. The introduction of rubber in the bituminous binders confers to the pavement the capacity of recovering the form after being subjected to a deformation for numerous times without showing signs of fatigue. The interaction between rubber particles and bitumen enhances the rubber abilities. The rubber particles can be compared to springs; when a spring is compressed it recovers its initial form, so the longer spring the larger the length recovered.

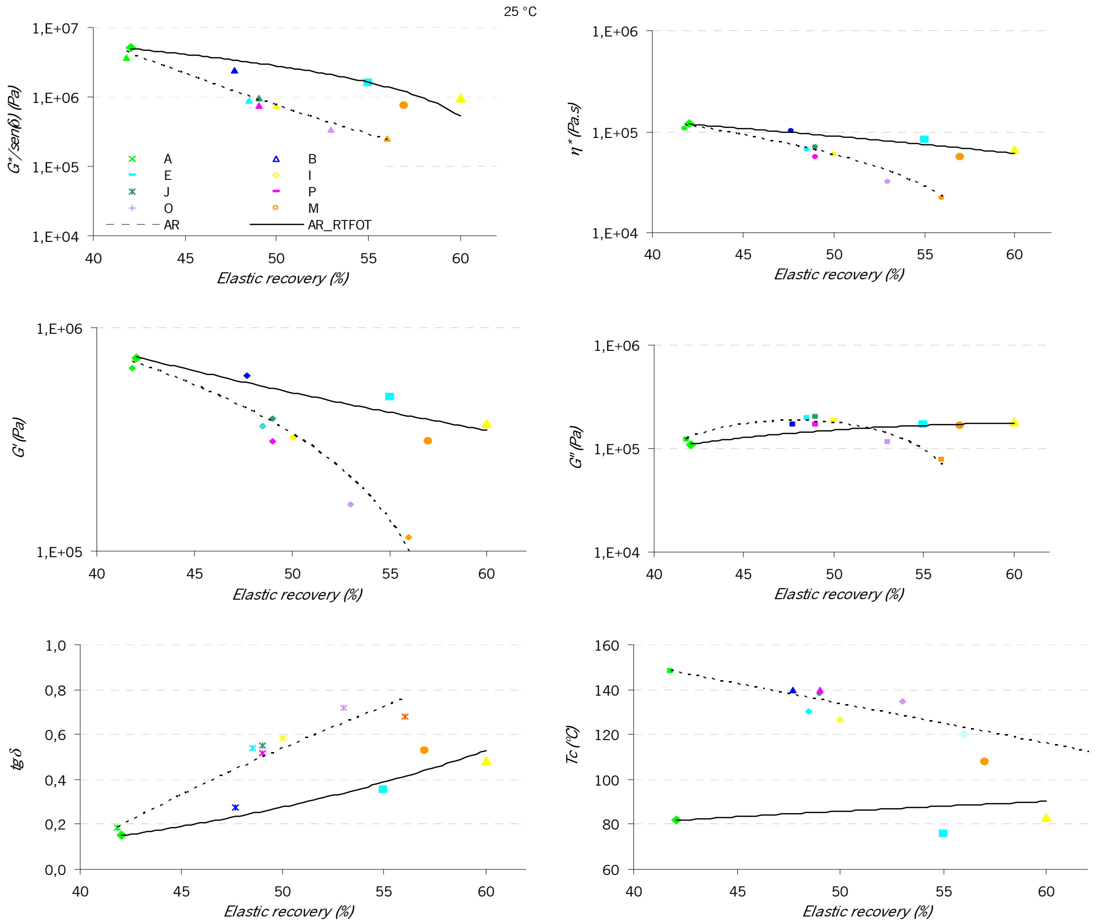


Figure 5.62 – Rheological properties vs. Elastic Recovery of AR and RTFOT aged AR

When AR binders are aged, the RTFOT acts like a continuation of the time used to produce AR. During the aging test the rubber particles continue to swell until their saturation, after what the rubber particles begin to split. As noticed from the graphics, the rubber swelling phenomenon increases the dimension of the AR elastic recovery, since the larger the rubber particles get, the more extended their recovery is. Furthermore, the rubber particles swelling is proportional to the quantity of small molecules in them. The swelling process ends up when the rubber particles are saturated and when there are no more molecules to be absorbed.

The changes in the ER of the ARs after the RTFOT mainly reflect the swelling extent of the rubber particles that induces an expansion of their volume. However, the characteristics of the residual bitumen (Res) around the rubber particles in the AR before and after aging should also be considered. The exposed observations can be clarified by assessing each aged AR separately:

- The changes in the ER and in the rheological parameters of the AR produced with Base bitumen A after RTFOT are quasi null, since the base bitumen is mainly constituted by big molecules which cannot diffuse into the rubber particles. Consequently the rubber particle swelling is very reduced during the AR production and aging due to a poor absorption of little molecules of bitumen and restricted by the increase of Res bitumen stiffness;

- The velocity and extent of the swelling of rubber particles in the AR depend on the concentration of molecules capable of diffusing into the rubber bulk. This is the principal reason why the aged AR produced with bitumen E presents an inferior increase in its ER in relation to the initial AR, when compared with the aged AR produced with Bitumen I;
- Base bitumen M used to produce AR M is very rich in small molecules which are easily and quickly absorbed by the rubber particles. However, the 60 minutes of interaction with bitumen during the production of AR are not enough to the complete the saturation of all the rubber particles. Therefore the diffusion of molecules of bitumen into rubber continues until its saturation. Simultaneously the saturated particles of rubber split up releasing little pieces. In the end of the aging test, the average volume of the rubber particles in aged AR M is lower than the rubber particles of the aged AR I leading to an inferior value of ER for the AR M after RTFOT.

Finally, it is important to refer that the rheological parameters do not reflect properly the presence and changes that rubber provokes in the AR binder performance, since that at this temperature the rheology is controlled by the bitumen.

Another important physical property to assess the binder performance in the pavement is the Ring and Ball softening temperature. Figure 5.63 graphically represents the relation between the R&B and the rheological properties at 50 °C of the ARs before and after RTFOT.

The bitumen rigidity is largely affected by temperature. At 50 °C bitumen is softer than at 25 °C allowing the perception of the presence of the rubber in the AR binder by the changes in the physical and rheological properties of the binder.

By observing the graphics it is possible to find out a correlation between the rheological parameters and the R&B property. In spite of the same scattering of values, both approaches reflect the differentiated effect of RTFOT in the ARs. If the rubber acts as an inert during the RTFOT and if all the interactions and changes in the rubber particle shape took place during the AR production, the effects of aging would only depend on the residual bitumen characteristics. Thus at the end of the aging process the aged ARs would be organized in the same order than the initial ARs. However, the aged AR M switches place with the aged AR I due to the alterations in the rubber shape that occur during the RTFOT. Moreover, an increase of the measured properties of the ARs after RTFOT is also observed. Those concentrate in a reduced range of values indicating that after RTFOT the material gets stiffer.

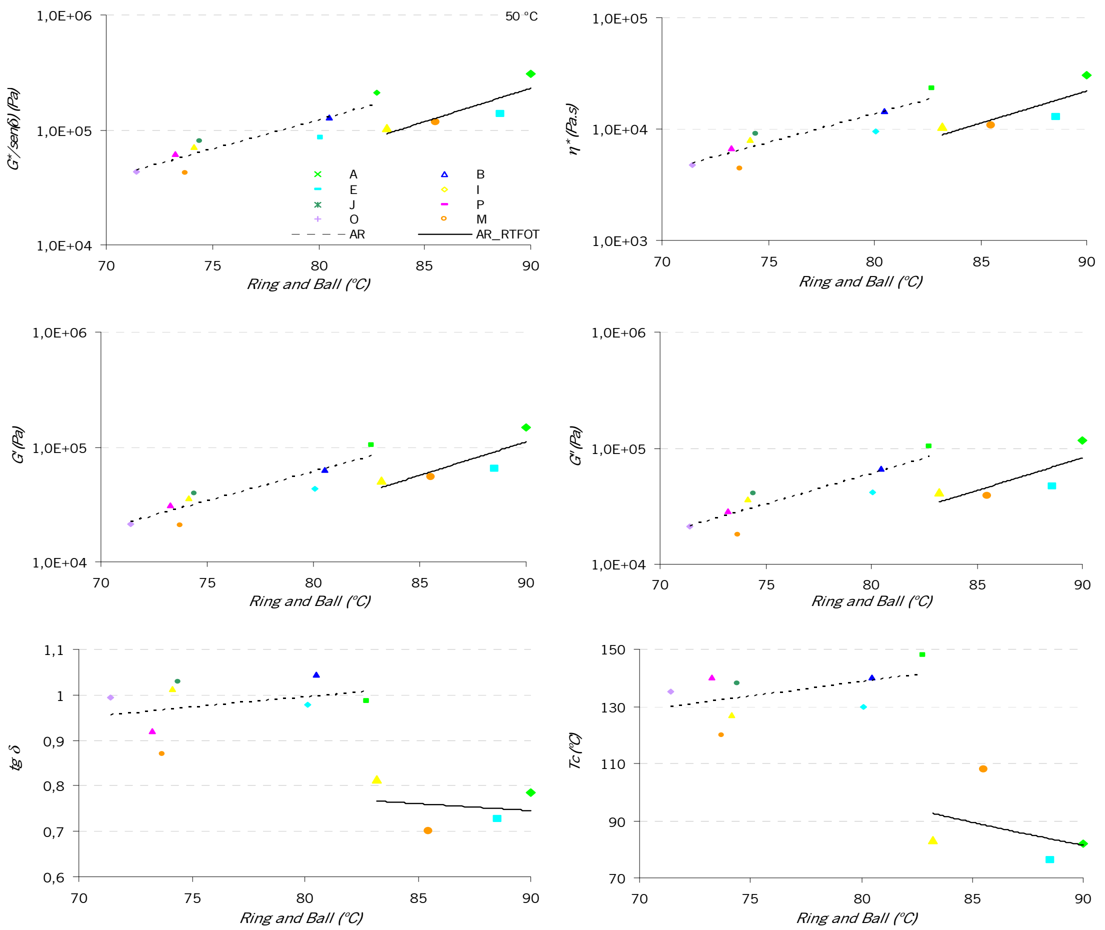


Figure 5.63 – Rheological *vs.* physical properties at high operating temperatures causing rutting of the initial and RTFOT aged AR

The relation between the dynamic viscosity and the rheological parameters of the aged AR will not be presented since, despite the restrictions verified in the rheological characterization of the unaged AR at this temperature (175 °C); as it did not occur in the rheological tests of the aged AR, the scattering of the four measured values only allows an adjustment of trend lines with an R^2 always inferior to 0.7. Additionally, no comparison between the ARs before and after aging would be possible.

5.4. Study of the Residual Bitumen (Res)

5.4.1. Characterization of the residual bitumen

One of the objectives of this work is to clarify the physical and chemical mechanisms involved in the AR binder production and to relate them to the AR binder performance. In order to achieve that goal the different factors that affect the final product should be analysed separately. In Chapter 5.2.2 the impact of the conditions of the production of the AR in the bitumen was assessed independently of the interaction between rubber and bitumen. In this section the changes induced in the bitumen used during AR production (residual bitumen – Res) will be analysed.

Being the AR a heterogeneous material, it is possible to separate the AR into two distinguished components: the swelled rubber and the residual bitumen. In fact, the swelled rubber by itself does not promote the adhesion between the aggregates. Thus, it is reasonable to include the swelled rubber in a special category of aggregate, being the binder constituted by the residual bitumen.

Therefore, it is essential to understand the behaviour of this new binder (residual bitumen) to develop an AR pavement with an optimized performance.

5.4.1.1. Physical properties of the residual bitumen

The first performed tests provide the physical properties of these materials:

- Penetration at 25 °C (1/10 mm) – Pen;
- Dynamic viscosity – DV;
- Ring and ball softening point – R&B.

The measured values of the physical properties are graphically presented in Figure 5.64. The chart on the left represents the evolution of the physical properties of the residual bitumen, the sphere bitumen and the base bitumen. The graphic on the right exhibits the percent variation induced in the different physical properties by the bitumen interaction with the rubber and the spheres in relation to the base bitumen.

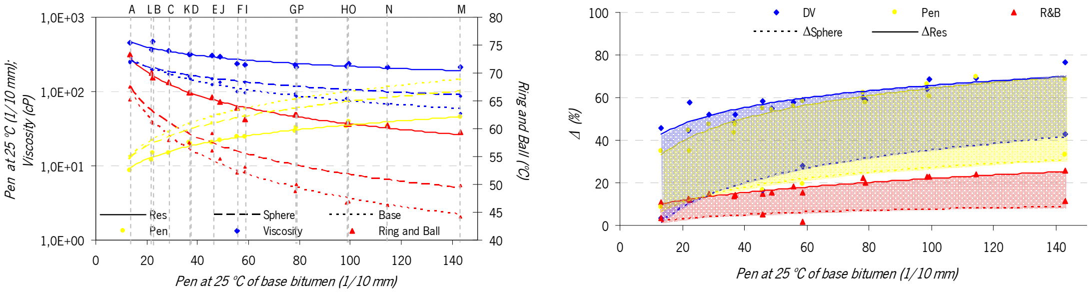


Figure 5.64 – Graphic representation of the physical properties of the residual bitumens

By the observation of the graphics it is apparent that the most sensitive property to variation in the bitumen constitution is the Dynamic Viscosity, followed by the Penetration. The least sensitive is the Ring and Ball softening point.

The results obtained for the bitumens after tests with the spheres constitute an indication of the changes that happened during the production of the AR that do not depend on the interaction of the bitumen with the rubber, mainly caused by oxidation, restructuration and volatilization of parts of bitumen. The variation on the physical properties of the bitumen, after the test with the spheres, point out a considerable "aging", superior to 10% in Pen and 40% in DV.

The variation of the results obtained for the residual bitumen is highly superior to that observed for the sphere bitumen, what indicates a clear absorption of parts of the bitumen by the rubber particles. Additionally, considering the constitution and dimension of crumb rubber and the interaction time-temperature between bitumen and rubber during the AR production, it is noticeable that in the materials produced with base bitumen with Pen superior to 30 dmm, the variation in the physical properties, is a product of the interaction between bitumen and rubber, remains constant in all the materials, as indicated by the shaded band of each property on the right side of the Figure.

For the materials produced with base bitumen with Pen superior to 30 dmm, the variation in the physical properties for the residual bitumen nearly doubles the variation achieved by the sphere bitumen. Thus, when a bitumen has a sufficient concentration of molecules it can be absorbed by the rubber and volatilized due to the temperature and stirring. These two phenomena are alike. However, harder bitumens (Pen inferior to 30 dmm) originate materials with an absorption/volatilization ratio clearly superior to 1. For these materials the difference due to the evaporation of the volatile molecules of bitumen is considerably inferior to the variation measured after the interaction rubber/bitumen. These results indicate that: (i) when bitumen is stiff, the phenomenon of diffusion of the smaller molecules into the rubber reticulated bulk is more efficient than the process of volatilization; (ii) the absorbed molecules are not volatile.

Finally, the quantification of the part of bitumen that volatilizes during the process of production of AR, using the "sphere AR production simulator" procedure, is affected by a large number of uncertainties, since through the AR production several alterations occur simultaneously in rubber and bitumen and are inter-dependent, such as diffusion and volatilization of parts of bitumen. However, the results have a sufficient dimension that allows the understanding and extension of these two phenomena.

5.4.1.2. Rheological properties of residual bitumen I

The eight residual bitumens were tested in a DSR to assess their rheological properties. In Figure 5.65 the isotherms obtained from the residual compared to the base bitumen I are depicted.

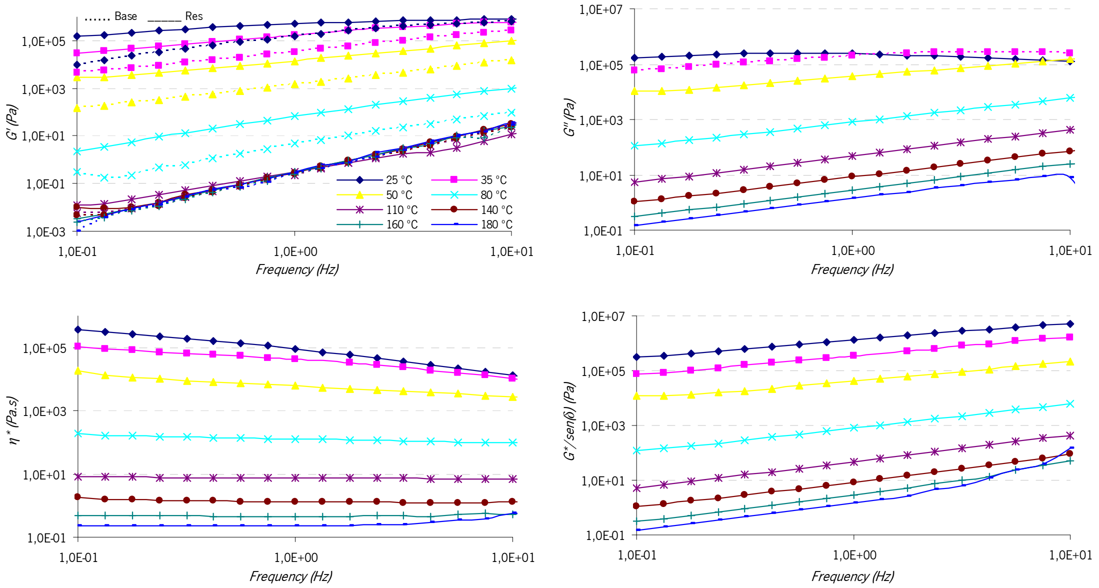


Figure 5.65 – Isotherms of the rheological properties for the residual and base bitumen I

The analysis of the isotherms shows a rheological behaviour of the residual bitumen which is very similar to the base bitumen. They present a dislocation to higher values, what indicates a hardening of the bitumen.

This is a behaviour already observed in the RTFOT aged bitumen, but the results were less perceptible. The isochronous correspondent to the residual and base bitumen throughout the range of temperatures between 25 and 180 °C are represented in Figure 5.66.

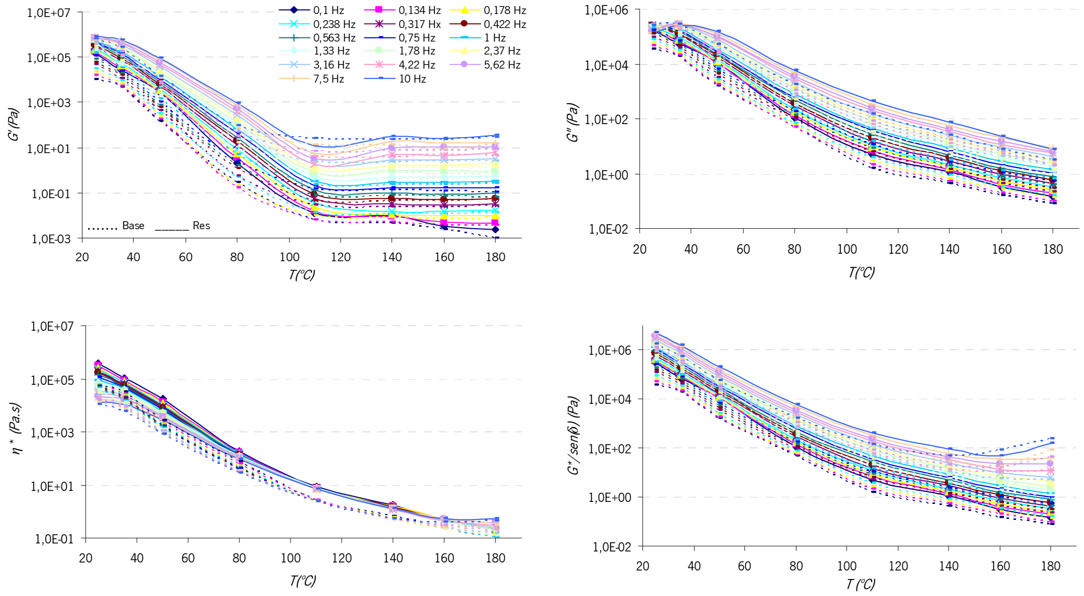


Figure 5.66 – Comparative isochrones of the rheological properties between the of base and residual bitumen I

The isochrones also dislocate to higher values of the rheological parameters. However, this behaviour is more pronounced for temperatures between 25 and 80 °C, that is, in-service temperatures. For temperatures above 140 °C (production and compaction temperatures) there are slight differences in the rheological parameters, what indicates that the enormous alterations in the rheological behaviour of the AR (Chapter 5.3.1) are largely due to the presence of the swelled crumb rubber.

The isochrones and isotherms of tgδ for the base and residual bitumen I are presented in the following charts (Figure 5.67).

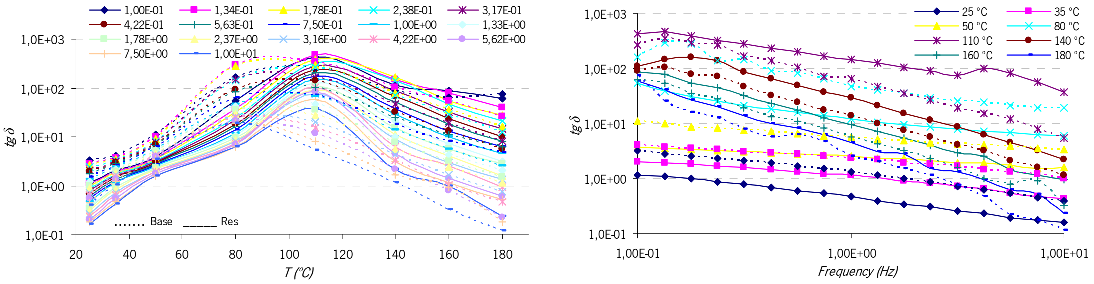


Figure 5.67 – Comparative Isochrones and isotherms of the tgδ of the base and residual bitumen I

The form of the isochronal lines of tgδ (left side of the Figure) for the residual bitumen is similar to the base bitumen isochrones and nearly equal to those of the RTFOT aged base bitumen (Chapter 5.2.2, Figure 5.30). The "hill" formed by the residual bitumen is higher than the pike formed by the base bitumen set of isochrones and, at superior temperatures, for example at 1.0 Hz, the tgδ of the residual bitumen (146.2) is superior to the tgδ of the base bitumen (81.0). T_c of the residual bitumen (110.5 °C), is superior to T_c of the base bitumen (92 °C). Furthermore, when compared with the aged base bitumen it is noticeable that T_c of the residual bitumen (110.5 °C) is slightly superior to T_c of the aged base bitumen (110.0 °C) while the tgδ of the residual bitumen (146.2, 1.0 Hz), being inferior to the tgδ of the aged base bitumen (199.0, 1.0 Hz) at frequencies below 1.33 Hz, is superior at frequencies above 1.33 Hz (for Freq. = 1.78 Hz, tgδ(Res) = 155 > tgδ(aged bitumen) = 96.1).

The described behaviour is confirmed by the isotherms of the residual bitumen (right side of the Figure) that have identical shapes to the lines of the base bitumen. Although the sets of isotherms are parallel, the isotherms of the residual bitumen are below the base bitumen lines at temperatures inferior 110 °C and at temperatures superior 110 °C they are above.

The comparison between the evolution of the rheological properties of the residual and base bitumen is presented in Figure 5.68.

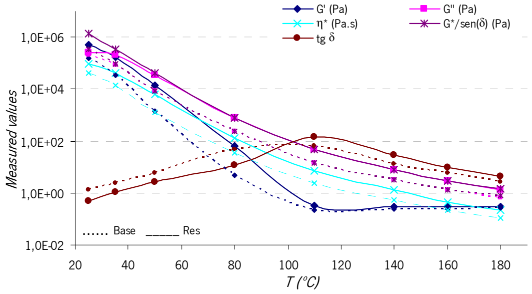


Figure 5.68 – Comparative isochrones of the rheological properties, at 1.0 Hz, of base and residual bitumen I

By analysing of the graphic, it is possible to distinguish two phases in the evolution of the rheological characteristics of the residual and of the base bitumen through temperature. On the one hand, at temperatures inferior to 100 °C, the differences in the rheological properties between the residual and the base bitumen are evident, presenting the maximum disparity between 50 and 80 °C. In this range of temperatures, the residual bitumen is clearly stiffer than the base bitumen. On the other hand, at temperatures superior to 110 °C the differences between the rheological properties of the residual bitumen and the base bitumen diminish as temperature increases trending to the same value.

This behaviour confirms the conclusions drawn in Chapter 5.2.2 (Figure 5.30) in relation to the alterations in the molecular structure of bitumen. That is, when T_c is achieved for a specific bitumen, the molecular structure of the bitumen relaxes. The weak interactions that maintain the “networks” formed by the polar molecules of bitumen (asphaltenes and resins) are broken, bitumen lives its colloidal behaviour and assumes a Newtonian fluid behaviour as the asphaltenes are peptized by the resins being totally disperse in the maltenes phase (non-polar). The new molecular organization of the bitumen has predominance in the rheological behaviour of bitumen masking the changes in the concentration of the smallest molecules that were responsible before for the viscous behaviour of the bitumen.

Figure 5.69 evidences the changes that occur in the viscoelastic character of the bitumen after the AR production at service temperatures (25 ≤ T (°C) < 50).

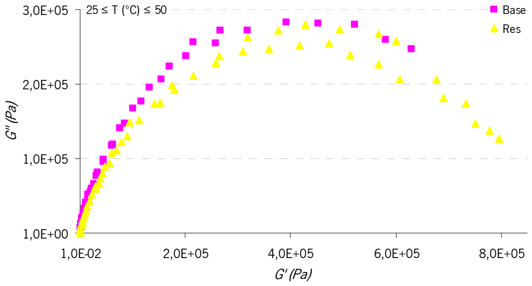


Figure 5.69 – Comparative Cole-Cole plane of base and residual bitumen I

By the observation of the Cole-Cole plane is perceptible that, as it was expected, the residual bitumen is stiffer (higher G*) than the base bitumen. The curve representing the evolution of the viscoelastic characteristics of the residual bitumen at service temperatures is similar to the base bitumen, indicating that during the AR production there were no changes in the structure of bitumen that may affect the characteristic viscoelastic behaviour of this material.

The observable changes in the viscoelastic characteristics of residual bitumen at these temperatures resume to an increase in its elastic character (G') with a reduction of its viscous part (G''). This behaviour can be explained by the fact that in the AR production process an important part of the non-polar less weighted molecules of bitumen (maltenes) are volatilized and absorbed by the rubber, leading to an increase in the concentration of the polar high Mw molecules of bitumen (asphaltenes and resins), conferring to the residual bitumen a pronounced elastic character (superior G') at these temperatures. The loss of the maltenes of bitumen is responsible for the reduction of the viscous character of the residual bitumen (G'') at these temperatures.

In Figure 5.70 two graphics that allow the identification of the alterations that occur at a molecular level in the residual bitumen are displayed in contrast with aged and base bitumen, by the analysis of the evolution of three rheological properties (G', G'' and η^*) at 35 °C.

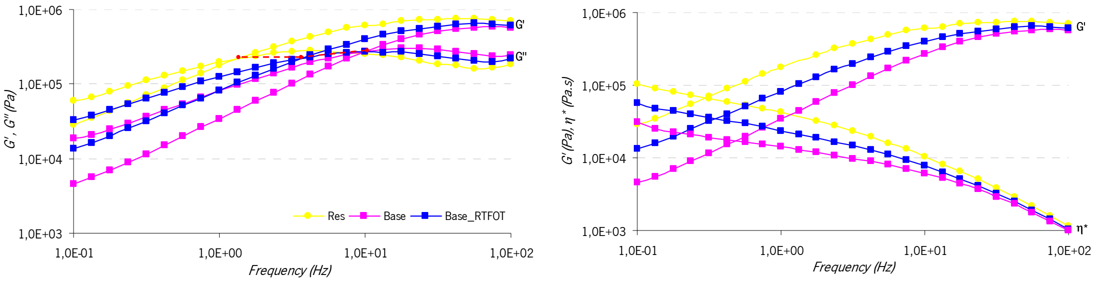


Figure 5.70 – Effect of the AR production on the molecular weight (Mw) and structure of the bitumen at 35 °C when compared with RTFOT

By the observation of the graphic on the left it can be noticed that the interception point of the isotherms of G' and G'' for the residual bitumen dislocate to the left (inferior frequencies) and down, having a modulus value inferior regarding the base bitumen, what means that during the AR production a widening of the MWD of the bitumen with an increase in the average Mw occurs. However, by comparing the interception point of the G' and G'' isotherms of the residual bitumen to the RTFOT aged bitumen is obvious that, in spite of the superior value of the Mw for the residual bitumen, the MWD is maintained.

By looking at the chart on the right side of Figure 5.70, an increase of the values of the G’ and η^* is obvious at low frequencies for the aged RTFOT bitumen and even more for the residual bitumen, if compared with the base bitumen, corresponding to an increase in the Mw average (> η^*) and to a widening of the MWD (> G’).

These results indicate that both, during the RTFOT aging of bitumen and during the AR production there is an increase in the molecular weight average, due to the volatilization of small molecules and to the aggregation of aromatic molecules, from the maltenes of the bitumen to the molecules of asphaltenes, enlarging them. Thus, as the average of Mw rises with the sprouting of more weighted molecules, the MWD also increases, since the other molecules continue to exist in the bitumen, even in less quantity.

5.4.1.3. Rheological characterization of the several residual bitumens

The graphics presented in Figure 5.71 allow assessing the extension of the changes induced by the AR production process in the rheological properties of bitumen (res) at 1.0 Hz.

As already observed for residual bitumen I, the remained seven residual bitumens present a similar behaviour to the RTFOT aged bitumen, although it is more perceptible. By the observation of the charts on the left side column of the Figure it is noticeable that the isochrones relative to the residual bitumen are less dispersed than those of the base bitumen, particularly at higher temperatures.

The rheological property that better reflects the described behaviour is the storage modulus (G’). The G’ isochrones that define the evolution of the elastic characteristic of the different materials became completely independent from the different constitution of the residual and base bitumen and also from the temperature, since the isochrones nearly overlap defining a parallel line to the xx axis above 140 °C. The weak interactions than maintained the “networks” of asphaltenes/resins, at 140 °C no longer exist and the bitumen assumes the behaviour of Newtonian fluids, in which the asphaltenes are totally peptized by the resins and dispersed in the maltenes.

As expected, the graphics on the right column of the Figure confirm the behaviour detected by the analysis of the physical properties of the residual and base bitumen. Therefore, the constitution of the base bitumen has a great influence in the rheological and physical characteristics of the residual bitumen. It is observable that the softer bitumen presents the greatest variations in the rheological properties after the AR production, principally between 25 and 35 °C.

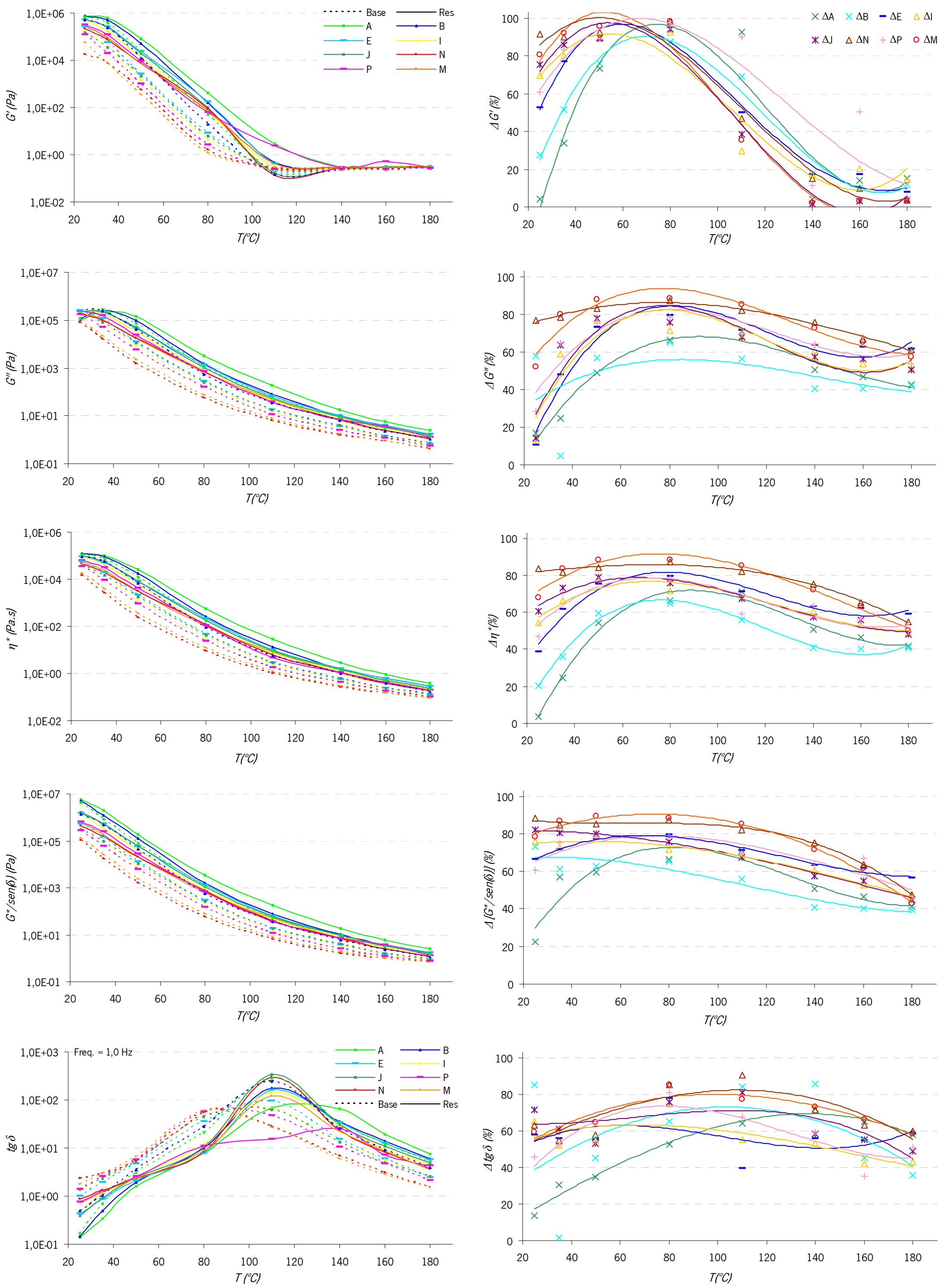


Figure 5.71 – Comparative graphics of the rheological properties of base and residual bitumens

However, it is between 35 and 110 °C that the maximum variations in the rheological properties of the base and residual bitumen can be observed.

Finally, the softer base bitumen is the most affected in the AR production process, as it detaches considerably from its initial characteristics. Thus, it becomes significantly stiffer and eventually more adequate to be applied. It confers the pavement more resistance to climatic aggressions and traffic.

Figure 5.72 presents the evolution of the viscoelastic characteristic at in-service temperatures of the eight residual bitumens, in comparison with their corresponding base bitumens in a Cole-Cole plane.

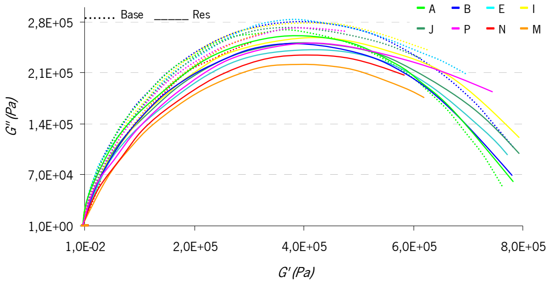


Figure 5.72 – Comparative Cole-Cole plane of the commercial base and residual bitumens

By analyzing the two sets of curves for the residual and base bitumen, it is detectable a generalized hardening of the residual bitumen, due to the increase of G' and the decrease of G''. The curves representing the residual bitumen slightly present the same form of the base bitumen and they are organized in the same order. Thus, the softest bitumen corresponds to the down shorter curve of each set and the hardest bitumen to long and up curve. The remaining six bitumens are organized in the middle of those two, following the same logics. The relative position of the two sets of bitumens, base and residual, follows the previous logics. The curve represents the residual bitumen positioned under the curves of the base bitumen, as it already occurs with the aged RTFOT bitumen, in a less evident way. Once again, there is no symptom of any specific structural change in the residual bitumen caused by the interaction with the rubber.

In terms of rheological properties, the effect of the rubber in the bitumen resemble to an more intense RTFOT, which signify that the quantity of rubber elements that react and diffused/suspend in the bitumen bulk constitute vestiges which cannot be perceived using this DSR rheological tests.

5.4.1.4. Comparison between the rheological and physical properties of the base and residual bitumens

In this section the relation between the physical and rheological properties of the residual bitumen is analysed, in comparison to the base bitumen.

In Figure 5.73 the comparative relation between the Pen and the assessed rheological properties at 25 °C are plotted.

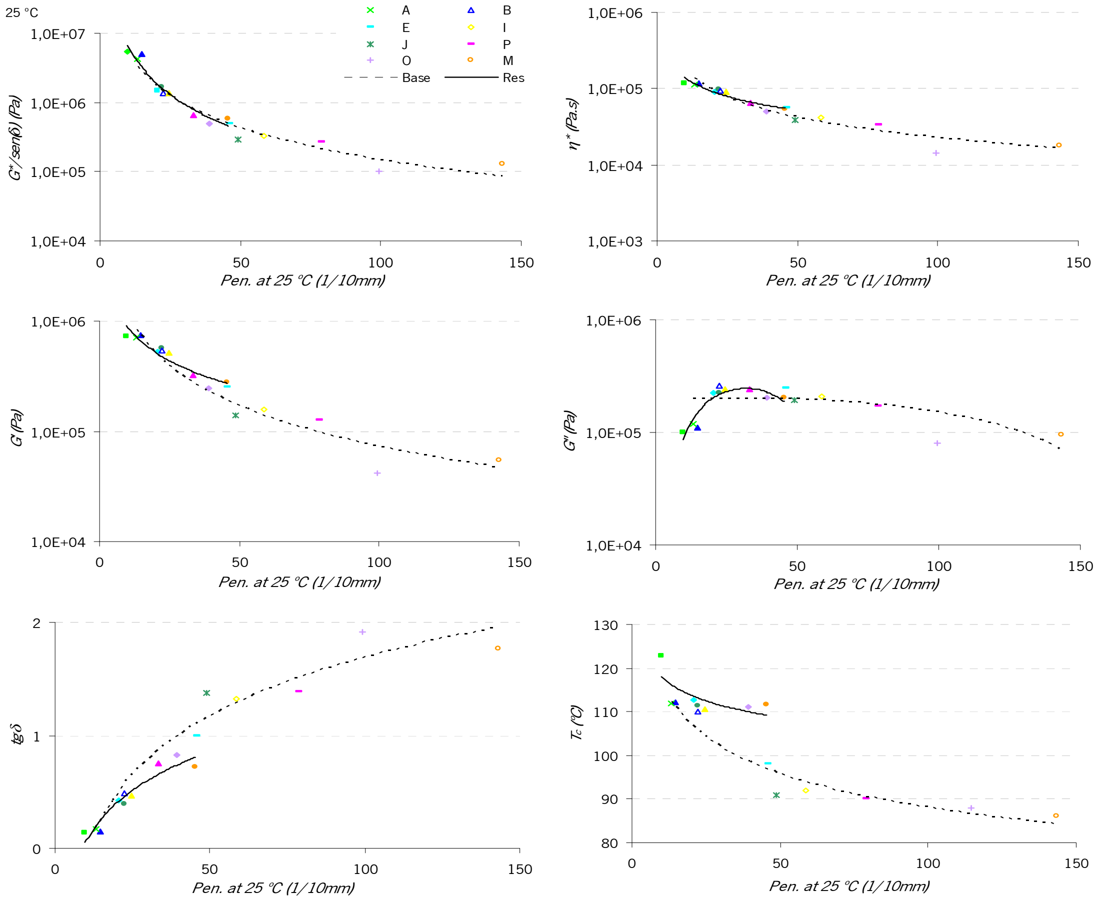


Figure 5.73 – Rheological *vs.* physical properties at operating temperatures cause fatigue cracking for base and residual bitumens

Through the observation of the graphics the increase in the stiffness of the residual bitumen (9 < Pen (dmm) < 50) is evident if compared to that of the base bitumen (10 < Pen (dmm) < 150), followed by the rheological properties that also show superior values in the residual bitumen (exception for the G'' and tgδ of residual bitumen A).

In terms of Pen, the softest residual bitumen (45.4 dmm) is the resultant of the use of base bitumen M (150/200), which corresponds to a 40/50 graded bitumen. This is one of the most common grade bitumen used to produce conventional bituminous mixtures.

Furthermore, it is possible to establish a relation between the Pen and the rheological properties at 25 °C, through the resultant potential trending lines, with the exception of G'' (2nd degree polynomial trending lines) and tgδ (exponential trending lines).

Additionally, the rheological properties are more accurate than the Pen to characterize the bitumen at 25 °C, since the axes where they are represented are in a logarithmic scale. It is worth to mention that the sets of lines for the residual and the base bitumen present very similar forms, namely in the case of G*/sen(δ) where the line that corresponds to the residual bitumen seems to be a prolongation of the line of the base bitumen.

Finally, the greatest variations in the Pen and in the rheological properties are observed for the softer bitumen, being detect meagre variations in the properties of the bitumen after AR production when stiffer base bitumen is used.

Figure 5.74 presents the graphics that represent the relation between the ring and ball softening point and the rheological properties of the residual bitumen compared to the base bitumen at 50 °C.

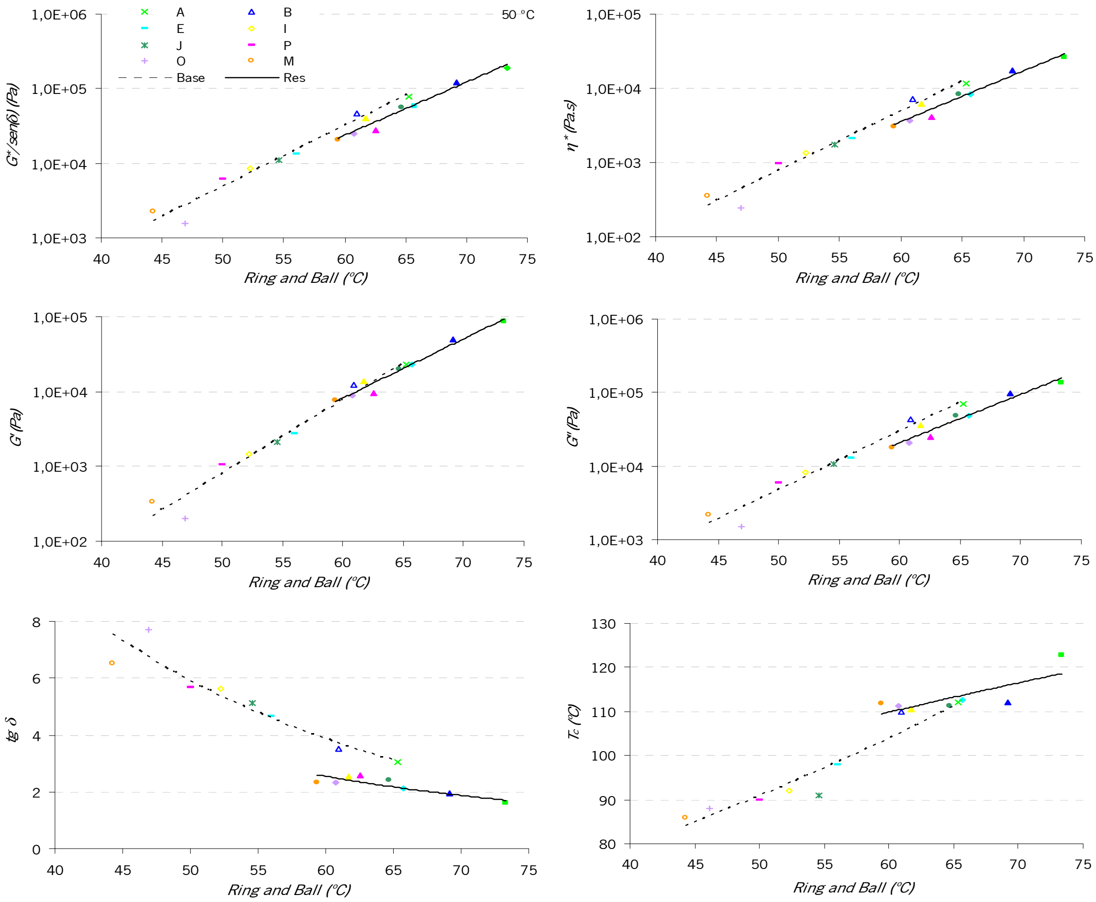


Figure 5.74 – Rheological *vs.* physical properties at high operating temperatures that cause rutting for base and residual bitumens

The most obvious observation that can be made by observing the graphics is the exponential relation between the rheological properties and the R&B physical property.

Furthermore, the slope of the curves related to the residual bitumen is identical to that of the base bitumen, with the exception of tgδ that presents a different alignment of its residual and base bitumen lines. Additionally, the range of values of R&B and of the rheological properties in which the residual and base bitumen develop confirm the significant increase in the stiffness of the binder after the AR production. Once again, the most accurate properties to define the residual and base bitumen characteristics are the rheological ones. However, contrarily to what can be observed in the graphics representing Pen at 25 °C *vs.* rheological properties, all the residual bitumen presented considerable variations of their R&B and rheological properties in relation to the base bitumen, being the softer bitumen the most affected.

Finally, when comparing the characteristics of the residual bitumen M to the eight base bitumen, it is noticeable that it presents values of R&B and rheological properties between base bitumen B and E (40/50), with the exception of tgδ, corresponding to a superior increase in the stiffness of this material at this temperature than that observed at 25 °C.

Figure 5.75 presents a set of charts where measured rheological properties are plotted against the dynamic viscosity at 180 °C for the residual and base bitumen.

The relation between the dynamic viscosity and the rheological properties is defined by exponential trending lines, as in the charts of rheological properties *vs.* R&B showed in Figure 5.74.

However, at test temperature (180 °C), the most accurate property is the dynamic viscosity and not the rheological properties, as at temperatures of 25 and 50 °C. Since at 180 °C any bitumen behaves as a Newtonian fluid, the rheological changes that could characterize the different materials are imperceptible when compared to the DV. Nevertheless, at this temperature (180 °C) all residual bitumens are stiffer than the base bitumen. This difference is visible by the increase in the values of the DV and of the rheological properties.

Finally, bitumen M experiences more changes in the AR production process. At this temperature the residual bitumen M presents values of DV and rheological properties between the values of the base bitumens A (10/20) and B.

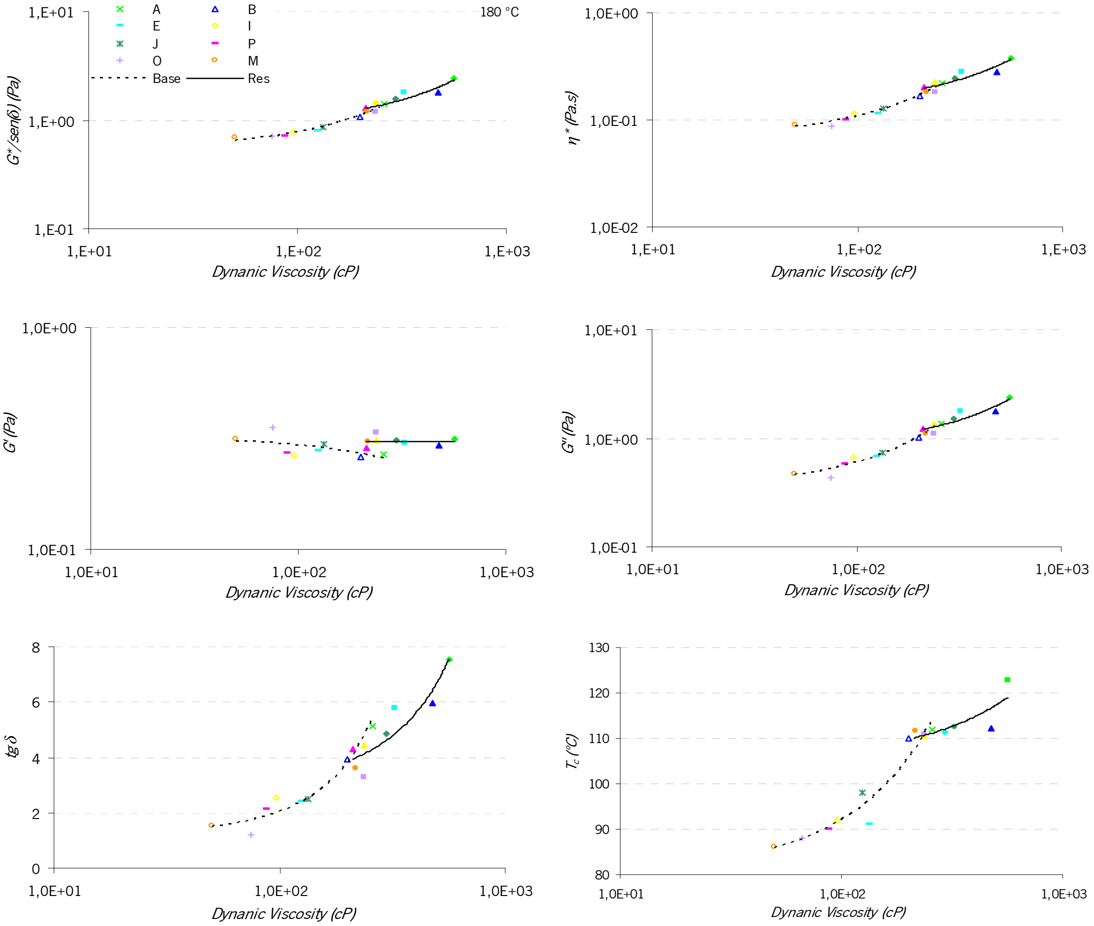


Figure 5.75 – Rheological vs. physical properties at production and application temperatures for base and residual bitumens

5.4.2. Characterization of the RTFOT aged residual bitumens

To understand the aging process in the AR mixtures during their production and compaction, in comparison to the conventional mixtures, the changes in the binder should consider the changes in the residual bitumen, since in the AR mixtures this is the effective binder. However, during the production and compaction of the AR mixtures, bitumen and rubber continue to interact. The final properties of the residual bitumen in the constructed pavement will be different from the residual bitumen after RTFOT.

5.4.2.1. Physical properties of the RTFOT aged residual bitumens

The first performed tests provide the physical properties of these materials:

- Penetration at 25 °C (1/10 mm) – Pen;
- Dynamic viscosity – DV;
- Ring and ball softening point – R&B.

The measured values of the physical properties of the residual bitumens, before and after aging, compared to respective base bitumens, are graphically presented in Figure 5.76.

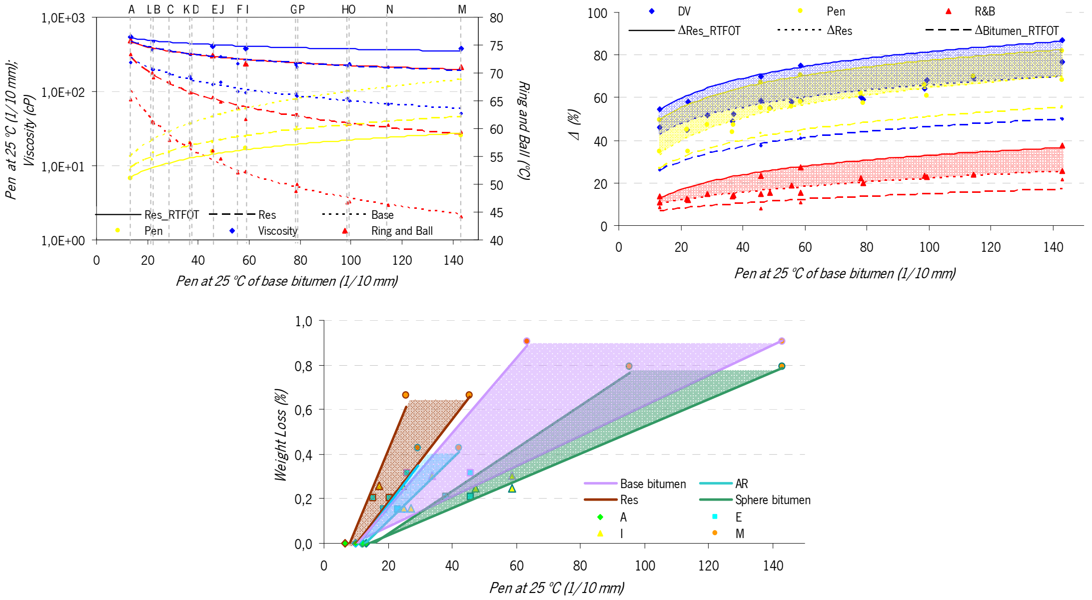


Figure 5.76 – Comparative representation of the physical properties of the commercial base, sphere and residual bitumens and ARs, after and before aging

In the charts, it is noticeable that the aging process of the different residual bitumens provokes significant changes in their physical properties. The hardest binders are the least affected by RTFOT. The aging process induces more changes in softest materials than in the hardest ones. Thus, during the AR production the resulting bitumens become harder and the performed RTFOT over these residual bitumens produces inferior variations than when applied in the base bitumens.

One of the results obtained by the RTFOT application in the bituminous materials is their weight loss (%). In the graphic it is noticeable that the variation of this parameter with the Base bitumens Pen is a linear trending line, with a positive slope. By the observation of the changes in the values of the Pen in the tested materials and the correspondent weight loss, it is apparent a direct correlation between these two parameters. Therefore, the greatest alterations in the Pen and weight loss are observed for the base bitumens, followed by the sphere bitumen and then by the residual bitumen, being the inferior changes observed in the ARs RTFOT.

However, it would be expected that the variations in the weight losses were proportional to the values of the Pen, i.e., the hardest binders should present the inferior weight loss, but, despite the smallest Pen values of the residual bitumen, before and after aging, it loses more weight than the AR binders due to the RTFOT. Surprisingly, binders with the same Pen before RTFOT present very different weight loss during the aging process. For instance, a base bitumen with Pen 40 dmm would lose 0.21% of its weight during RTFOT wile an AR binder would lose 0.38% of its weight and a residual bitumen would lose 0.56%. These results indicate that a residual bitumen with an equal Pen to that of a base bitumen has more volatile molecules, suggesting that only some classes of volatile molecules diffuse into rubber particles during the AR production. Finally, it is worth to refer that no process to which base bitumen A was exposed caused weight loss, but noticeable changes in the physical properties were observed, indicating that the aging process of bituminous materials is complex and that it involves restructuration and oxidation of their molecules.

5.4.2.2. Rheological properties of the residual bitumen I after RTFOT aging

The rheological properties of the four aged residual bitumens were determined and the following Figures are an exemplification of the rheological changes induced in the bitumen by the RTFOT using the data obtained for residual bitumen I before and after aging.

The alterations in the rheological behaviour of the residual bitumen with the frequency and temperature are displayed in Figures 5.77 and 5.78, respectively.

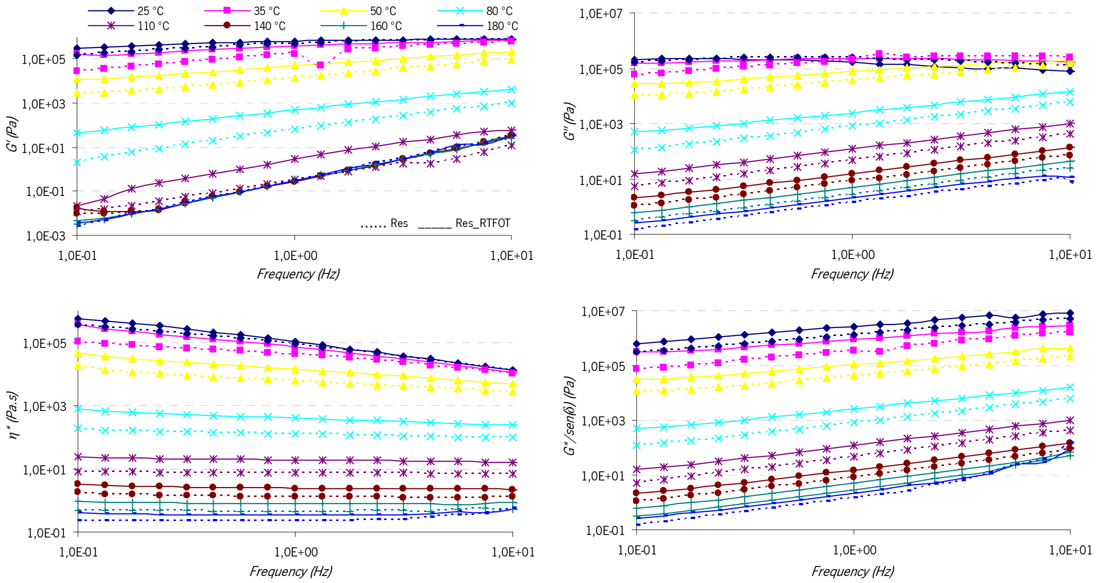


Figure 5.77 – Isotherms of the rheological properties of residual bitumen I before and after aging

The graphics suggest that the changes induced by the aging of the residual bitumen had as consequence its hardening with no quantifiable changes in its structure, according to the parallelism between the lines of the residual bitumen before and after RTFOT. The most significant changes in the rheological properties due to the aging of the residual bitumen are apparent between 50 and 140 °C.

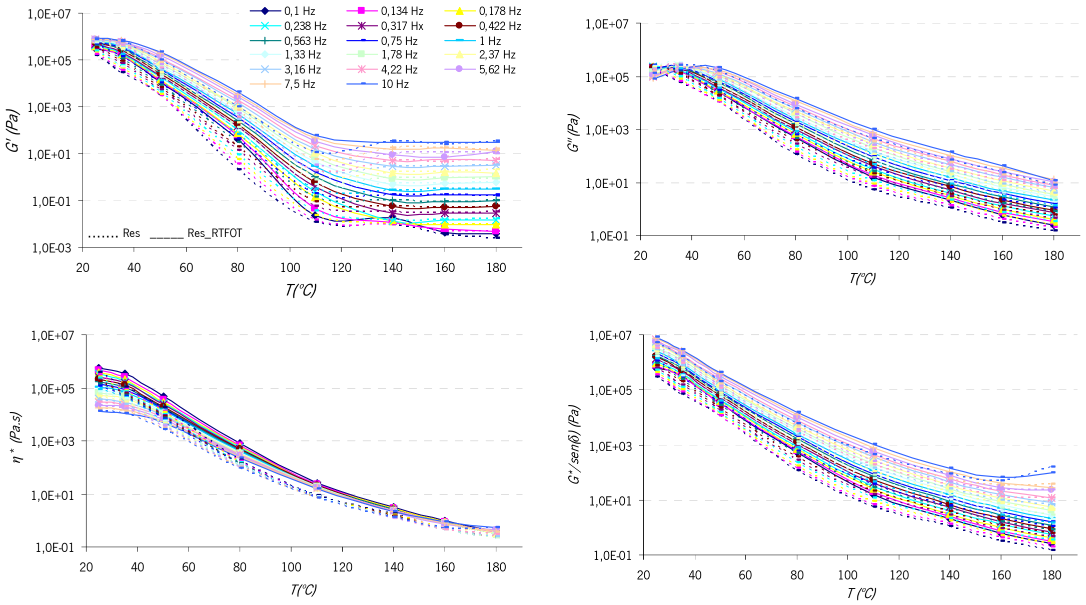


Figure 5.78 – Isochrones of the rheological properties of residual bitumen I before and after aging

The isochrones confirm the earliest observations. Hence, the RTFOT provokes very few changes in the rheological behaviour of the residual bitumen.

The isochrones and isotherms of tgδ for the residual bitumen I, before and after aging, are presented in the following charts (Figure 5.79).

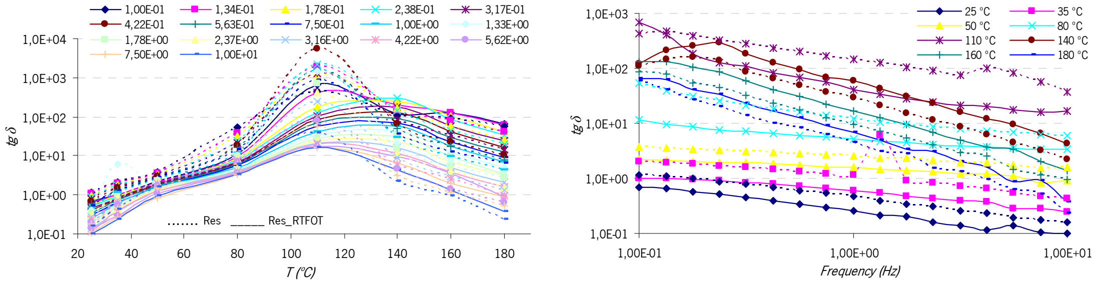


Figure 5.79 – Isochrones and isotherms of tgδ of the residual bitumen (extracted from the AR produced with base bitumen I) before and after aging

The observed behaviour of the aged residual bitumen is similar to the one of the aged base bitumen. The "hill" formed by the isochronal lines dislocates to the right at higher critical temperatures. This phenomenon is reflected in the Res bitumen isotherm lines by the temperature at which the change of slope of the lines occurs, between 50 and 80 °C, before aging and between 80 and 110 °C after aging.

This behaviour is due to the alterations in the molecular structure of bitumen when temperature increases. That is, when a critical temperature for a specific bitumen is achieved, the relaxation of the molecular structure of the bitumen occurs. The weak interactions that maintain the “networks” formed by the polar molecules of bitumen (asphaltenes and resins) are broken, bitumen lives its colloidal behaviour and assume a Newtonian fluid behaviour, as the asphaltenes are peptized by the resins, being totally disperse in the maltenes phase (non-polar). The new molecular organization of the bitumen has predominance in its rheological behaviour, masking the changes in the concentration of the smaller molecules that earlier were responsible for the viscous behaviour of the bitumen.

Figure 5.80 illustrates the changes induced by the AR RTFOT in the rheological characteristics of the residual bitumen I at 1.0 Hz.

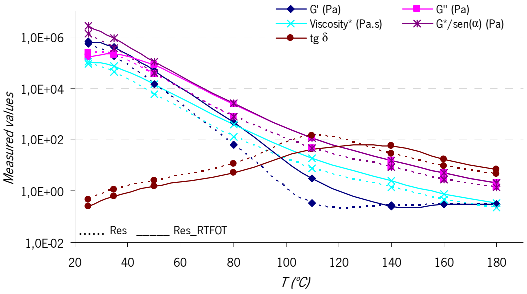


Figure 5.80 – Comparative graphic of the rheological properties of the residual bitumen I before and after RTFOT at 1.0 Hz

By observing the graphic, several alterations are noticed in the residual bitumen provoked by the aging process. The 1.0 Hz isochrones defining the rheological behaviour of the aged residual bitumen appear to dislocate to the right, to the correspondent non aged material. The changes in the rheological properties are due to the loss of some volatile maltenes, responsible for the viscous character of the bitumen (G’’) at low temperatures. The increased concentration of the polar non volatile molecules induces an increase in the elastic part of bitumen (G’) at temperatures below T_c. The enlargement of the resine/asphaltene “networks” delays the relaxation process, what confers bitumen its Newtonian fluid behaviour at high temperatures.

Figure 5.81 evidences the changes that occur in the viscoelastic character of the residual bitumen before and after aging at service temperatures (25 ≤ T (°C) < 50).

The changes in the viscoelastic character of the residual bitumen induced by the RTFOT indicate a stiffer aged material due to a reduction in its viscous part and a slight increase in its elastic part, caused by oxidation, restructuration and volatilization of some bitumen molecules and by the increase in the Mw (or particle size).

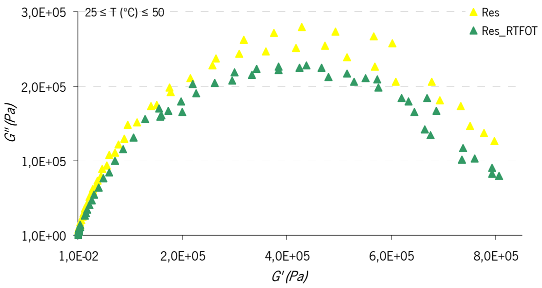


Figure 5.81 – Cole-Cole plane of the residual bitumen (from the AR produced with base bitumen I) before and after aging

Figure 5.82 displays two graphics that allow the identification of the alterations that occur at a molecular level in the base and residual bitumen I in contrast with the aged materials, through the analysis of the evolution of three rheological properties (G', G'' and η*) at 35 °C.

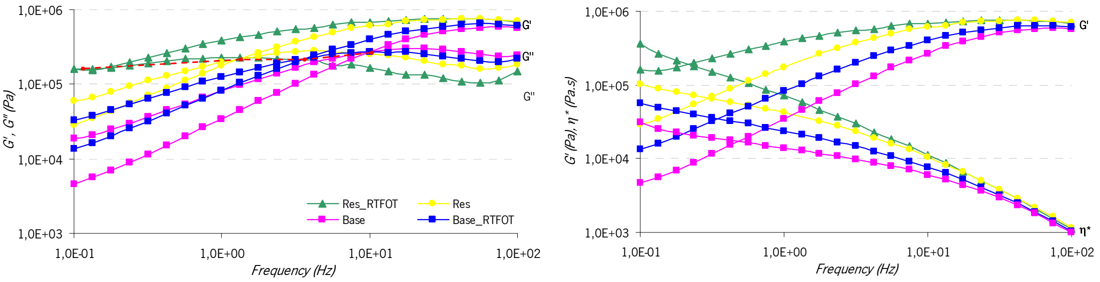


Figure 5.82 – Effect of the RTFOT on the molecular weight (Mw) and structure of the base and residual bitumen I at 35 °C

By the observation of the graphic on the left side of the Figure it is noticeable that the interception point of the isotherms of G' and G'' for the residual bitumen dislocate to the left (inferior frequencies) and down. They have a module value inferior in relation to the base bitumen, what means that during the AR production a widening of the MWD of the bitumen occurs with an increase in the average Mw.

Furthermore, when comparing the interception point of the G' and G'' isotherms of the residual bitumen to the RTFOT aged bitumen is evident that, despite the superior average value of Mw for the residual bitumen, the MWD broad maintains. However, the greatest changes in the molecular structure of bitumen occur when the residual bitumen is aged: it presents a significant increase in the average Mw and simultaneously a widening of the MWD superior to the that observed when aging the base bitumen.

On the right side of Figure 5.82 an increase of the values of the G' and η* at low frequencies for the aged base bitumen and the residual bitumen is obvious. It is even more evident for the aged residual bitumen if compared with the base bitumen, what corresponds to an increase in the Mw average (superior η*) and to a widening of the MWD (higher G').

These results indicate that either during the RTFOT aging of bitumen or during the AR production there is an increase in the average of the molecular weight due to the volatilization of small molecules and to the aggregation of aromatic molecules from the maltenes of the bitumen to the molecules of asphaltenes, enlarging them.

Thus, as the average of Mw rises with the sprouting of more weighted molecules the MWD also increases, since the other molecules continue to exist in the bitumen, even if in less quantity. The considerable increase of the values of Mw and in the widening of the MDW, during the aging of the residual bitumen, indicates that the aromatic molecules in the bitumen must be more concentrated in the residual bitumen than in other materials, what facilitates their aggregation to the cores of resins/asphaltenes making them grow substantially. This happens because the rubber absorbs preferentially the saturate fraction of the maltenes.

5.4.2.3. Rheological characterization of the several residual bitumens before and after RTFOT aging

The rheological properties measured before and after RTFOT for the residual bitumens resulting from the AR production process using the commercial bitumens A, E, I, M are compared in Figure 5.83.

According to the graphics, the residual bitumens before and after RTFOT presents approximately the same behaviour of the base and aged bitumens, but at higher values of the rheological parameters, except for tgδ.

Additionally, when comparing the rheological values of the aged residual bitumens to the aged AR binders at temperatures inferior to 80 °C it is noticeable that the residual bitumens are stiffer than the corresponding AR binders and continue stiff after aging.

Finally, at the referred temperatures ($T < 80$ °C) the variations of the rheological parameters of the residual bitumens before and after RTFOT are larger than the observed for the ARs.

These observations confirm the previous observations that indicate that the presence of the rubber particles in the binder protect it from aging.

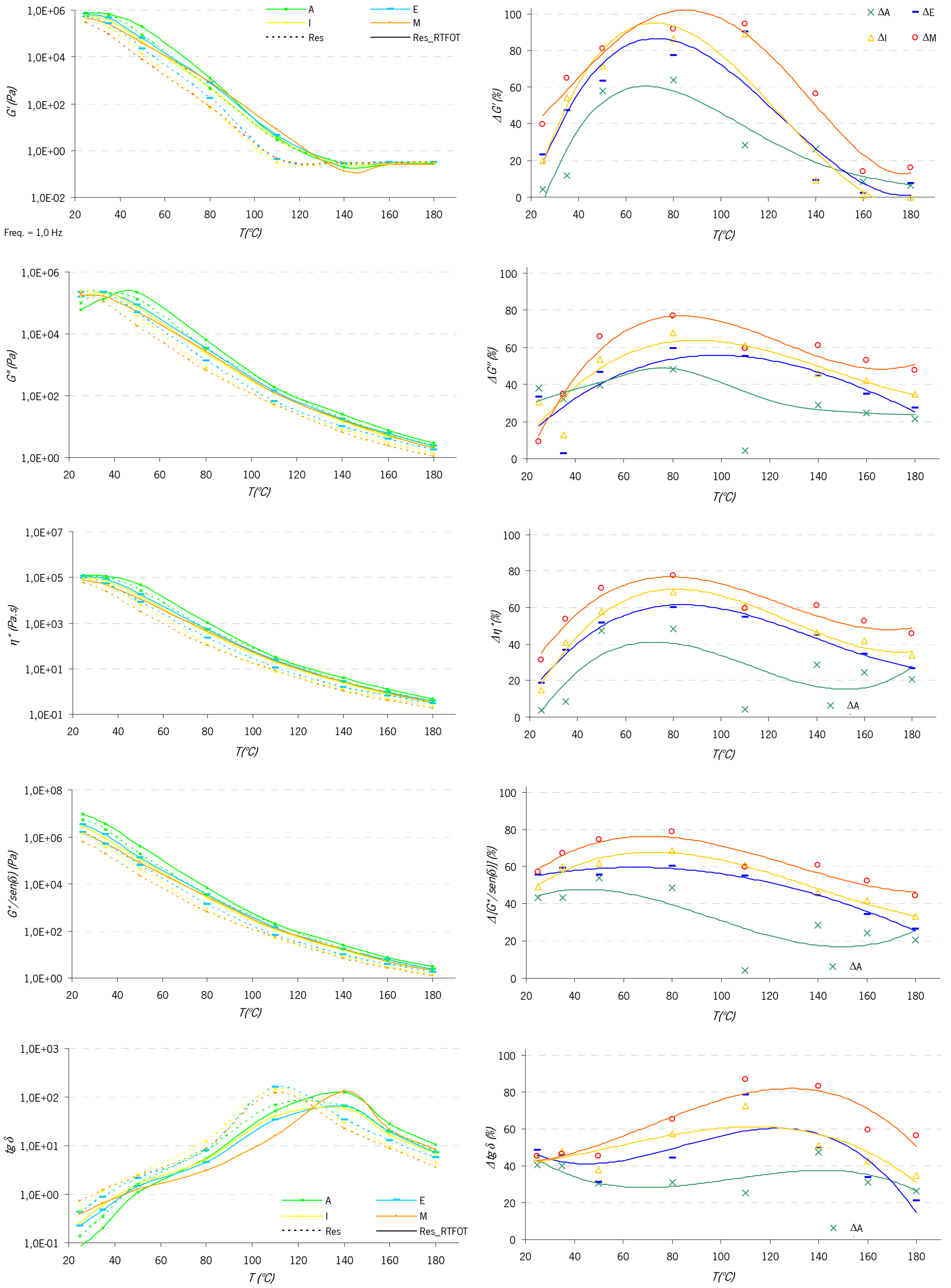


Figure 5.83 – Comparative graphics of the rheological properties of the residual bitumens before and after aging

Some of the most important information needed to assess the performance that the binder will have in the pavement can be obtained through the analysis of the Cole-Cole plane of the aged binders, where at the lowest temperatures tested (25 and 35 °C) the changes can be clearly assessed (Figure 5.84).

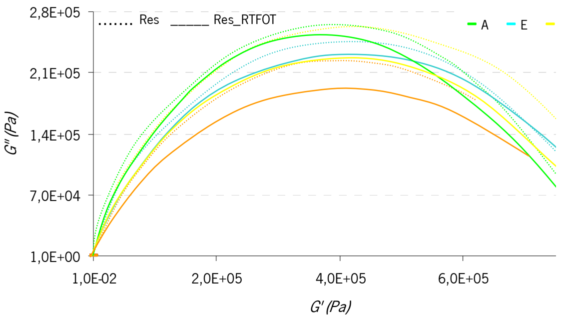


Figure 5.84 – Comparative Cole-Cole plane of the residual bitumen after and before aging

Observing the graphic it is noticeable a spread in the lines of the residual bitumens before aging, due to the differentiated effect of the rubber in each bitumen. Although the behaviour within each set of residual bitumens (before and after aging) is consistent with the previous observations, the lines of the residual bitumens are above the aged ones.

In spite of the fact that the average values of the G'' of these materials are between the base bitumens and the ARs, they achieve superior average values of G', what indicates that the residual bitumens are the stiffest materials before and after RTFOT, reflecting the greatest alterations in its chemical structure and composition.

5.4.2.4. Comparison between the rheological and physical properties of the residual bitumens before and after RTFOT aging

In Figure 5.85 to 5.87 the lines relating the three measured physical properties to the rheological parameters of the aged residual bitumen compared with the base bitumen are depicted.

The relation between the rheological properties and the Pen of the aged residual bitumen is coherent with the results obtained for the residual bitumen. Despite the line that represents the aged residual bitumen being shorter than the line of the residual bitumen before RTFOT, there is a slight extension of the line referring to the residual bitumen when combined to the plotted data of the aged residual bitumen to lower values of the measured properties, except for Tc.

The values of Tc increased disproportionally, being almost independent of the values of the Pen. This behaviour shows the structural and molecular differences that the aging process induces in the bitumen, and that bitumens with slightly the same Pen and rheological properties can have distinct chemical structures.

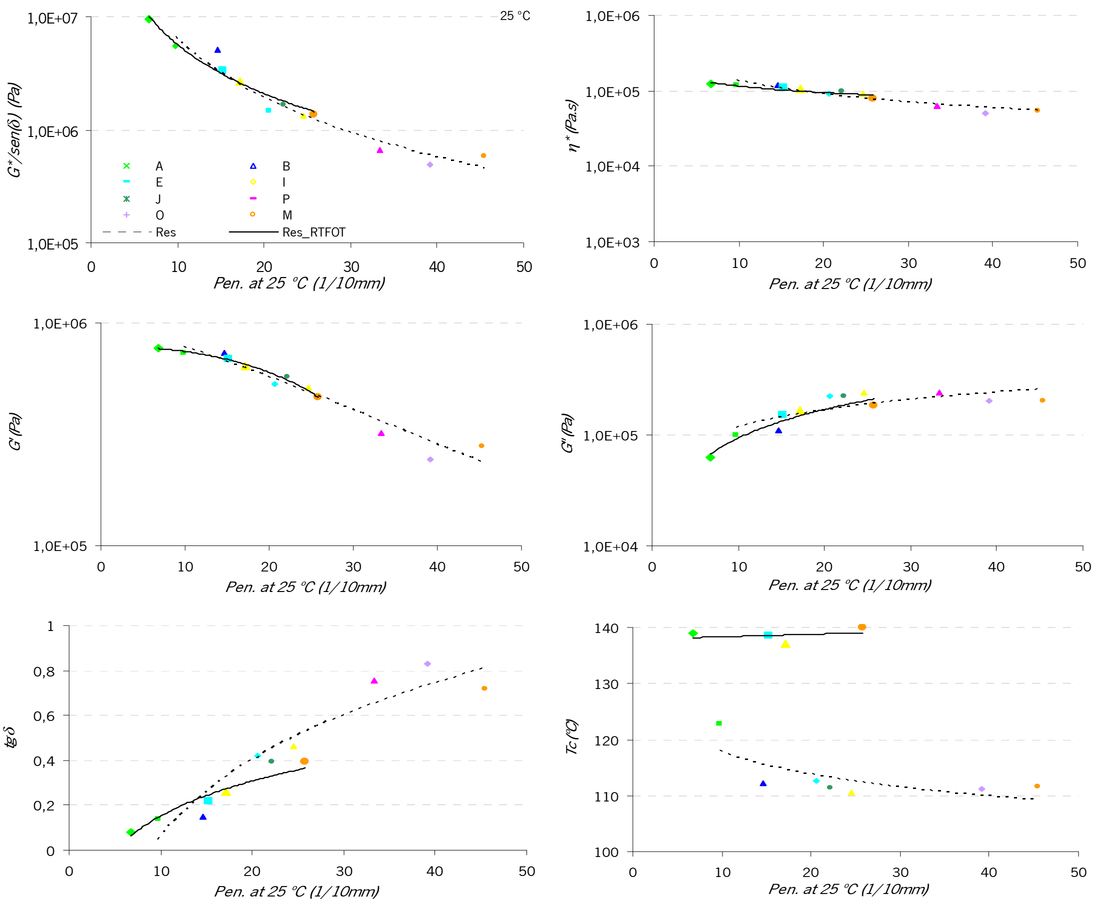


Figure 5.85 – Rheological *vs.* physical properties, at operating temperatures, causing fatigue cracking of base and residual bitumens

At this temperature an increase of the storage modulus (G') and a decrease in the loss modulus (G'') can be observed, what indicates that the RTFOT reinforces the elastic character of the residual bitumen mainly due to the enlargement of the resine/asphaltene "networks". These graphics are very similar to the graphics relating the base and aged bitumens. However, according to the range of values in which the properties develop the residual bitumen before and after aging is a much stiffer material.

At 50 °C, the physical property selected to be correlated with the rheological parameters is the Ring and Ball softening point (Figure 5.86).

By the observation of the graphics an increase in the values of the rheological parameters due to the aging of the residual bitumen is noticeable. As expected the more affected bitumens were the softest ones. The lines representing R&B *vs.* rheological properties for the aged residual bitumen present a higher slope than before RTFOT, since the rheological parameters are more sensitive to the changes in the bitumen than the R&B.

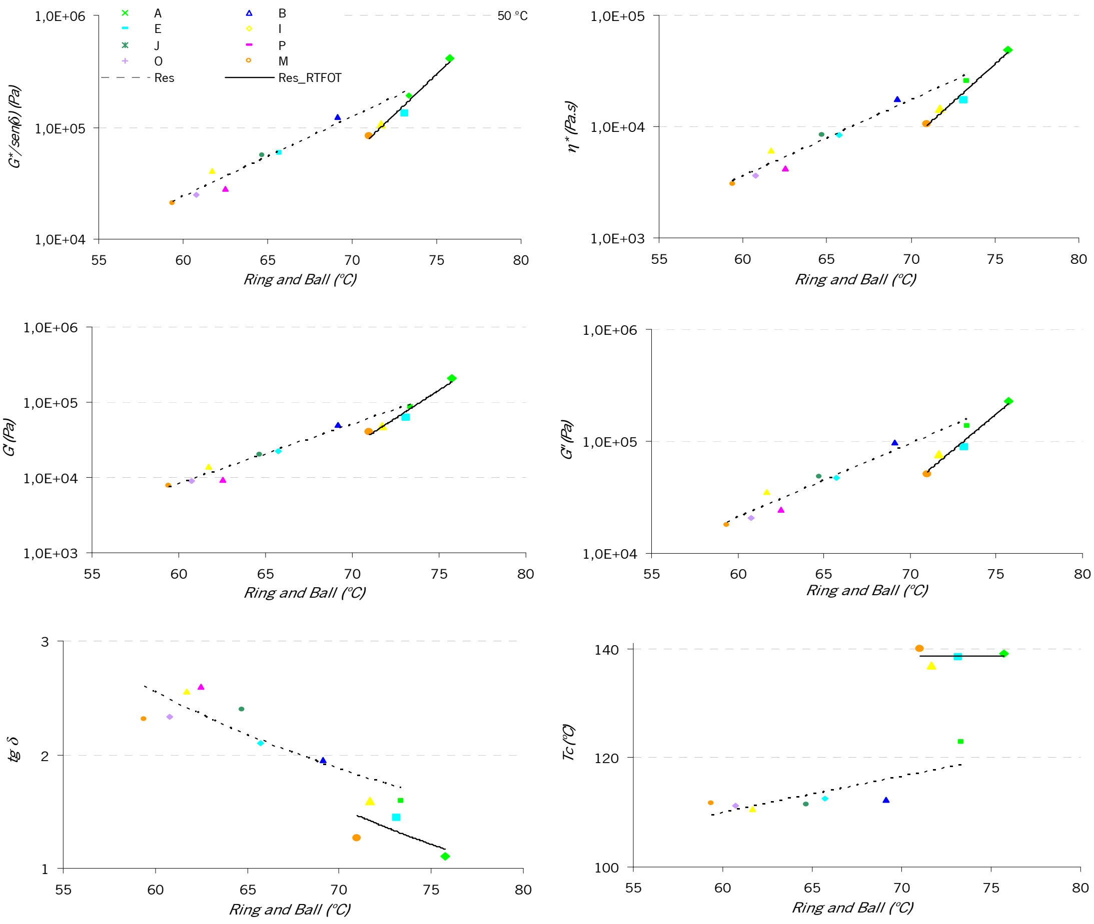


Figure 5.86 – Rheological *vs.* physical properties at high operating temperatures that cause rutting for base and residual bitumens

Additionally, a superior increase in the elastic character of the residual bitumen after RTFOT is detected than in the viscous part of the material. This fact is reflected in the tgδ, where the lines referent to the residual bitumen before and after aging are completely disconnected, being the line of the aged material drawn at a inferior range of values of tgδ.

The values of T_c are very similar for the four aged residual bitumens, being clearly superior to the values of residual bitumen before RTFOT, confirming the increased stiffness of the aged material. The fact that the values of T_c almost double the R&B temperatures indicates that the bitumen continues to behave as a viscoelastic material when R&B softening point is achieved.

The performance of a flexible pavement, during its life cycle, is clearly affected by the phases of the bituminous mixture production and compaction. These activities demand that the binders remain at high temperatures. Therefore, in Figure 5.87 the alterations in the residual bitumen during those activities on the rheological properties *vs.* the Dynamic Viscosity at 180 °C are represented.

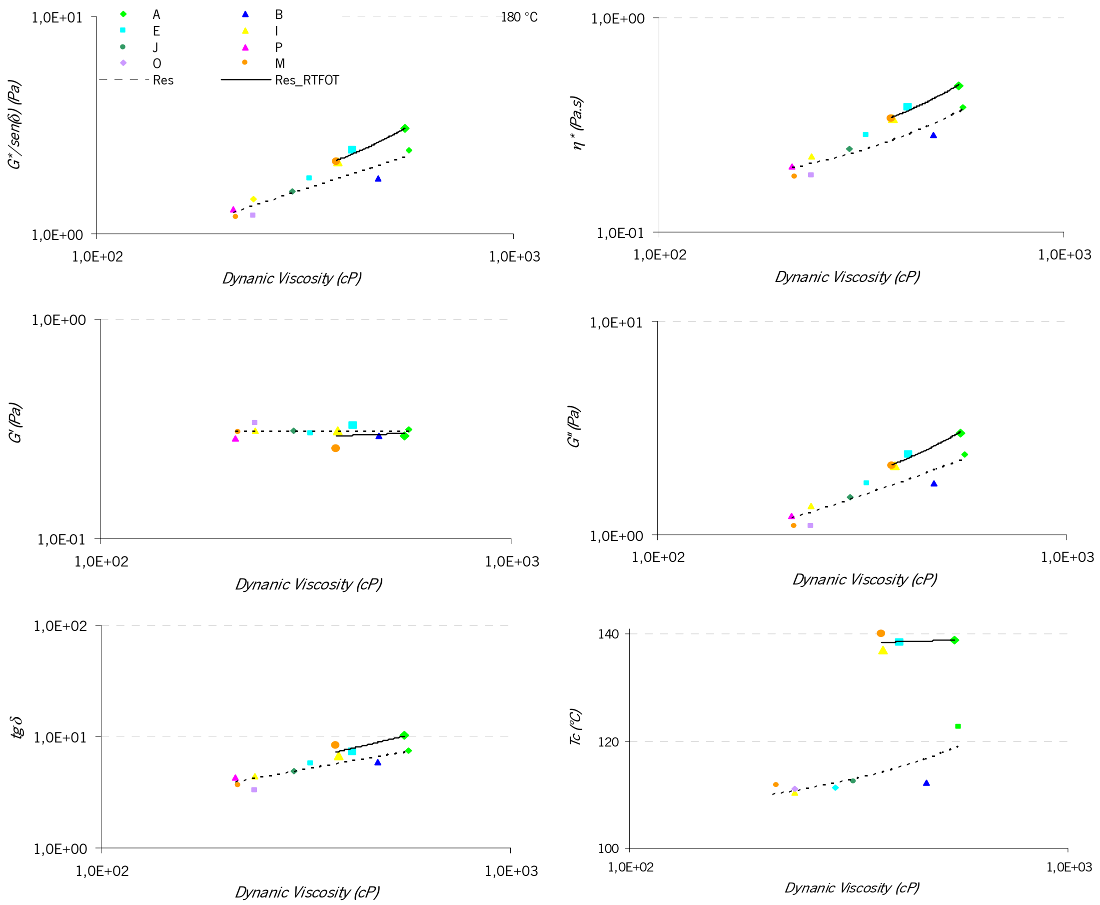


Figure 5.87 – Rheological *vs.* physical properties at production and application temperatures for base and residual bitumens

By the analysis of the charts, the maintenance of the values of G' and the increase of the values of G'' for all the aged residual bitumens is obvious. This fact is reflected in the increased values of G*/sen(δ), tgδ and η*. The changes in the DV and in the rheological properties verify the hardening of the residual bitumen due to the RTFOT and indicate that, at this temperature (180 °C), the viscous character of bitumen is intensified. In spite of the major accuracy of the DV at 180 °C, this physical property does not detect any alteration in the hardest residual bitumen (A) after RTFOT.

Finally, the lines of the aged residual bitumens are shorter than the ones of the residual bitumen before RTFOT, since the softest residual bitumens are more sensitive to the aging processes.

5.5. Study of the Morphology of the Crumb Rubber Particles

The importance of the study of the morphology of the rubber particles, before and after the interaction with bitumens of different chemical constitution, is due to two facts: (i) the morphology of the crumb rubber (CR) determines the form and extension of interaction with bitumen and has a significant influence in the viscosity of the AR, and (ii) bitumens with different constitution interact with rubber particles in different extension and rate, promoting changes in the rubber particles morphology.

5.5.1. Density of the crumb rubber particles

The crumb rubber from used tyres applied in this work is constituted by small particles (425.0 < $Ø_{eq}$ (μm) < 850.0), that entrapped air and moisture between them. Furthermore, rubber is a porous material containing air and moisture in the pores. There are several ways to determine the apparent density of a material:

- Through the comparison between the volume (water displacement) and the mass of a sample – volume analysis;
- Through the difference between the mass of the sample measured in and out of a liquid – mass analysis.

5.5.1.1. Apparent density

The assessment of the apparent density of the crumb rubber by volume analysis using water is not possible since that the average of the crumb rubber density is inferior to the density of the water, as documented in Figure 5.88 by the way the crumb rubber particles distribute in contact with water.

Therefore, the apparent density of the rubber was determined by mass analysis, using a liquid with a density inferior to the pre-supposed apparent density of the rubber. The liquid used was the isopropyl alcohol with a density of 0.783 g/cm^3, since it does not react with rubber and even if some interaction could occur, it would not be possible at the temperature and time of the test.

The procedure used to assess the apparent density of the used crumb rubber is described next. Thus it is possible to calculate its value through the Equation 5.3:

- Weigh approximately 2.0 g of crumb rubber in an analytical proportion;
- Weigh a piece of sieve with pores of inferior length to the size of the smaller rubber particles;
- Weigh the sieve in the Isopropyl alcohol in the same proportion used before;
- Seal the rubber particles with the sieve and weigh.

$$\rho_{\mathrm{a}} = 0.0012 + \left(m_{ds} \times \rho_{ip}\right) / \left[0.99983 \times \left(m_{ssl} - m_{sl}\right)\right] \tag{5.3}$$

Where:

ρ_a – Apparent density of the crumb rubber (g/cm^3);

m_{ds} – Mass of the dry sample of crumb rubber (g);

ρ_{ip} – Density of the isopropyl alcohol (g/cm^3);

m_{ssl} – Mass of the sealed sample of crumb rubber in isopropyl alcohol (g);

m_{sl} – Mass of the sieve in isopropyl alcohol (g).

The average of the values obtained in the repeated tests indicates that the apparent density of the used crumb rubber is 0.9 g/cm^3.

5.5.1.2. Bulk density

To assess the bulk density of the used crumb rubber it was necessary to expel all the air in and within the rubber particles. This was achieved by boiling a sample of rubber previously weighed and by stirring to release all the air. The volume occupied by the boiled crumb rubber (Figure 5.89) was measured.

Figure 5.88 – Appearance of the crumb rubber in water at 25 °C

Figure 5.89 – Appearance of the crumb rubber in water at 25 °C after application of standard test AG:PT/T144

The analytical procedure followed is the described in the standard test AG:PT/T144. The average of the bulk density determined in the repeated tests indicates a value of 1.21 g/cm^3.

5.5.1.3. Percentage of devulcanization based on the crosslink density

The crumb rubber solubility was assessed according to ASTM D 6814-02 standard, in order to indirectly evaluate the potential depolymerisation of the studied rubber after interacting with bitumen. Two solvents were used in this test, toluene and cycle-hexane, being the crumb rubber mass loss equal to 10.9% and 10.7% respectively, indicating a low depolymerisation potential. It is worth to refer that behind the depolymerisation potential, the mass loss of the rubber is also due to some soluble additives and fillers present in the rubber constitution.

5.5.2. Form and dimension of the crumb rubber particles

The crumb rubber used in this work was obtained by the cryogenic gridding of used tyres. The resulted rubber particles used are very small (Figure 5.90), therefore, it was not possible to evaluate their form with the naked eye.

Figure 5.90 – Macroscopic and microscopic appearance of the crumb rubber particles

In order to assess the form and average of the rubber particles dimension, an optical microscope was used. Observing the photos, it is noticed that the rubber particles present slightly the same size, with an equivalent average diameter of 620.1 *µm*. The form of the particles is irregular and angular, but their faces are almost plan (some appendixes increase their surface area).

5.5.3. Morphology of the recovered rubber particles

The crumb rubber particles collected during the AR production, before (CR) and after (RR and FR) interacting with different types of bitumen, were cleaned with toluene and analysed through microscope methods. The results of the microscopic analysis of the rubber that have interacted with the four commercial bitumens used in this work (A, E, I and M) are presented in following Figures.

- **Rubber particles recovered from asphalt rubber A**

The rubber particles recovered from the AR produced with base bitumen A (10/20) and washed with toluene were observed and photographed (Figure 5.91).

Figure 5.91 – Macroscopic and microscopic appearance of the rubber particles recovered from the AR produced with the base bitumen A

By the observation of the photograph presented on the right side of the Figure, it is noticeable that the recovered rubber particles present very different shape and size from the original crumb rubber.

Despite the average of the equivalent diameter ($Ø_{eq}$ = 620,648 *µm*) of the recovered rubber particles similar to those of the crumb rubber, this does not mean that during the AR production the rubber particles were not affected.

Actually, during the AR production using the base bitumen A, the rubber particles swelled and broke. In the end of the AR production process, the rubber particles present very irregular forms and very little pieces of rubber among larger ones are observed.

The swelling dimension was assessed using the “Basket drainage method” combined with the “Sphere AR production simulator” method. Thus, the two methods combined indicated the variation of the rubber weight during the AR production. To produce the AR A 428.6 g of crumb rubber were added to the bitumen. In the end of the process, the weight of the recovered rubber in the basket, subtracted from the weight of the bitumen that remained around the rubber particles after bitumen drainage was 574.4 g, indicating an increase in the weight of the rubber particles of 25.23%.

The crumb rubber concentration in the beginning of the AR production was 21.0% w/w, in the final AR A the concentration of swollen rubber particles in the bitumen was 70.1% w/w, corresponding to an increase of 50%. This is coherent with earlier observations, indicating that the rubber swelling was due to the diffusion of bitumen molecules in its reticulated structure.

- **Rubber particles recovered from asphalt rubber E**

In Figure 5.92 two photographs of the rubber particles that were removed from the AR produced with base bitumen E (40/50) are presented.

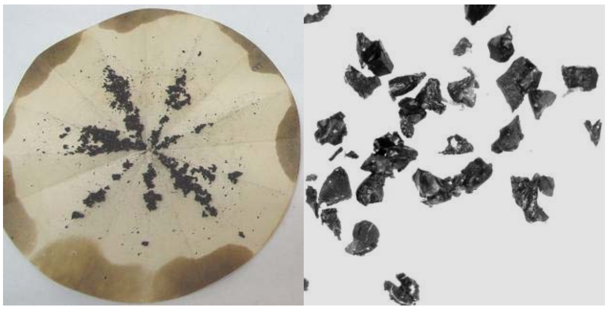


Figure 5.92 – Macroscopic and microscopic appearance of the rubber particles recovered from the AR produced with the base bitumen E

By the observation of the photograph in the right side of the Figure it is noticeable that some rubber particles are larger than the initial rubber and others are tiny, smaller than the smallest particles that appear in the recovered rubber form AR A. The medium equivalent diameter of the rubber particles recovered from AR E was 626.71 *μm*. The faces of the particles of the rubber are much more irregular and present holes, what is an evident sign of degradation.

To produce the AR E 210.74 g of crumb rubber were added to the base bitumen E, corresponding to a concentration of rubber of 21% w/w. In the end, 349.03 g of swollen rubber were recovered from the AR E, which is a quantity equivalent to a concentration of rubber in the AR of 81.13% and indicates an increase in the rubber weight of 39.6%.

- **Rubber particles recovered from asphalt rubber I**

Bitumen I (60/70) is the softest bitumen usually used to produce AR. The appearance of the rubber particles recovered from AR I is reported in Figure 5.93.

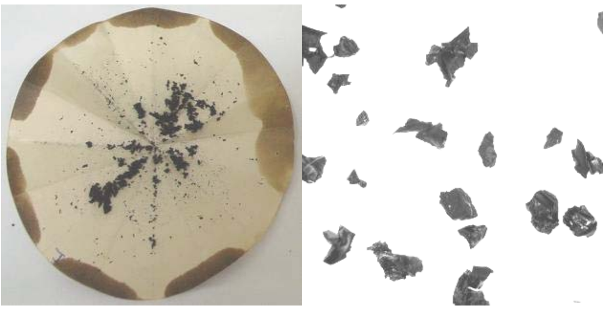


Figure 5.93 – Macroscopic and microscopic appearance of the rubber particles recovered from the AR produced with the base bitumen I

The photograph taken through the optical microscope (right side of the Figure) shows a collection of rubber particles recovered from the AR I. There are rubber particles of all sizes, forming a continuous particle size distribution. In average, the equivalent diameter of these particles is 634.19 *μm*. The signs of degradation, holes and irregularity on the particles are more patent than in bitumen E (Figure 5.92).

The percentage of crumb rubber used to produce AR I was the same of that of the other ARs, 21.0% w/w, which in this case corresponds to 210.84 g. The weight of the swollen rubber recovered from the AR I was 379.57 g, indicating an increase in mass of 44.45%. The concentration of the rubber particles in the bitumen pass from 21.0% in the beginning to 77.87% in the final AR I.

- **Rubber particles recovered from asphalt rubber M**

Bitumens in the range of Pen of bitumen M (150/200) are not usually used to produce bituminous mixtures in highways construction, whether rubberized or not. However, in this work, an AR binder was produced with base bitumen M. The photographs of the recovered rubber from the AR M are presented in Figure 5.94.

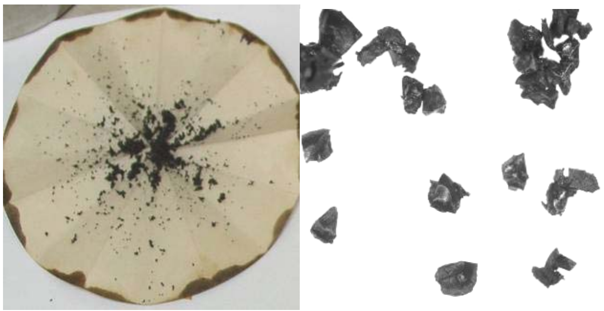


Figure 5.94 – Macroscopic and microscopic appearance of the rubber particles recovered from the AR produced with the base bitumen M

By the analysis of the images, some surprising observations can be made. Thus, contrarily to the recovered rubber from ARs A, E and I, the rubber particles recovered from AR M have slightly the same size, i.e., the particle size distribution is narrow and sharp. Additionally, the rubber particles are not individualized, as the recovered rubber from the other ARs, giving the impression of being stuck to each other forming little clusters.

Once more, the percentage in mass of crumb rubber added to the base bitumen to produce AR M was 21.0% (210.11 g). During the interaction time the rubber particles experienced an increase in their weight of 51.6% (434.39 g). Consequently in the final AR M the concentration of swollen rubber was 81.84% and the particles presented an equivalent diameter of 608.42 *μm*.

5.5.4. Morphology of the filtered rubber particles

During the process of AR production the rubber particles split into little pieces and some of them passed through the basket. Therefore, to quantify and make a visual inspection of these little pieces of rubber the residual bitumen was diluted and the rubber particles were filtered. To assess the concentration of rubber in the residual bitumen, the mass of the insoluble material in the base bitumen and in the residual bitumen was determined, using the European standard EN 12592. The comparison between the two values indicate the mass concentration of FR in the residual bitumen.

The filters containing the filtered rubber (FR) particles were observed with the naked eye and some of the particles were removed from the filter and observed through an optical microscope. The next figures contain the photos of the filtered rubber (FR) particles.

- **Rubber particles filtered from asphalt rubber A**

In the microscopic photograph of Figure 5.91 the presence of little pieces of rubber, which could pass through the basket sieve can be seen. In fact, a little amount of rubber particles were filtered form the residual bitumen. In Figure 5.95, the photographs of the filter containing the FR and the microscopic image of the FR particles are presented.

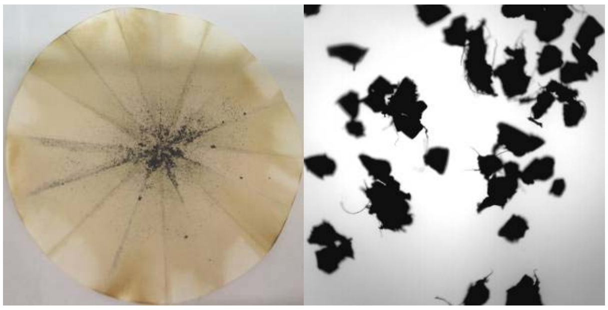


Figure 5.95 – Macroscopic and microscopic appearance of the rubber particles filtered from the residual bitumen of the AR produced with the base bitumen A

By observing the photograph on the left it is evident that the dimension of the rubber particles retained in the filter is very inferior to that previously observed. However, it is possible individualize the same rubber particles with the naked eye.

By the examination of the photograph in the right side of the Figure, it is noticeable a surprising uniformity in the size of the FR particles. Their equivalent diameter is 378.67 *µm*, showing that the size of these particles is in fact inferior to the CR and to the Recovered rubber. The mass concentration of the FR in the residual bitumen was 1.01% w/w. This quantity of rubber particles in the residual bitumen is so reduced that was undetectable in the physical and rheological characterization of this material.

- **Rubber particles filtered from asphalt rubber E**

Figure 5.96 presents macroscopic and microscopic photographs of the filtered rubber from the residual bitumen obtained from the AR E, in the sequence of the application of the "basket drainage method".

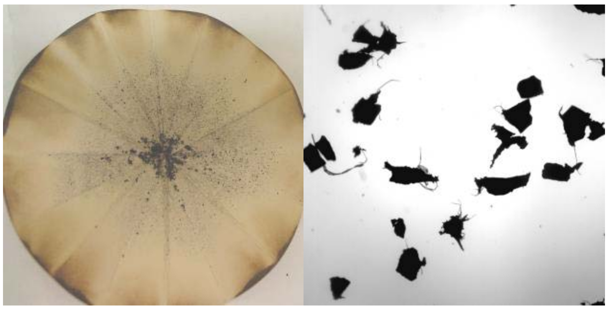


Figure 5.96 – Macroscopic and microscopic appearance of the rubber particles filtered from the residual bitumen of the AR produced with the base bitumen E

By observing the rubber particles in the filter (right side of the Figure), it is noticeable that they are smaller than the FR from AR A. This remark is confirmed by the microscopic analysis of the FR E.

The FR particles present very irregular surfaces and dimensions (left side of the Figure). Tiny particles can be observed among others significantly bigger. In average the equivalent diameter of the FR particles from the residual bitumen E is 311.05 *μm*. The mass concentration of the rubber particles in the residual bitumen E is 0.75%.

- **Rubber particles filtered from asphalt rubber I**

The rubber particles filtered from the residual bitumen I were photographed in the respective filter and observed and photographed at an optical microscope (Figure 5.97).

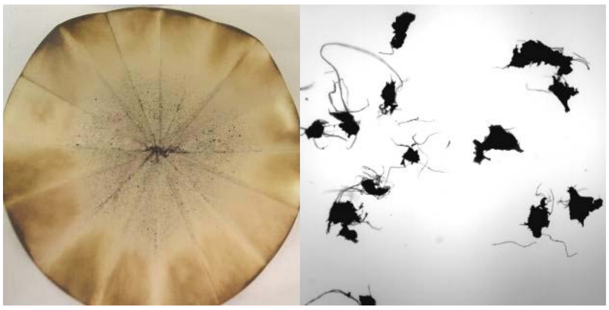


Figure 5.97 – Macroscopic and microscopic appearance of the rubber particles filtered from the residual bitumen of the AR produced with the base bitumen I

By the analysis of the photograph of the filter with the FR from the residual bitumen I (right side of the Figure), a reduction of the quantity of the rubber particles is evident, when compared to the previous FRs from residual bitumens A and E. The FR was quantified and its mass concentration in the residual bitumen was 0.336%.

Assessing the form and dimension of the FR particles, it is immediately noticeable that the FR in the filter looks like dust. They seem to be much littler than the FR observed earlier. This observation is completed by the microscopic examination (left side of the Figure) by which an average equivalent diameter of 278.76 *μm* was determined.

- **Rubber particles filtered from asphalt rubber M**

In Figure 5.98 the macroscopic and microscopic photographs of the filtered rubber particles from the residual bitumen M can be shown.

Figure 5.98 – Macroscopic and microscopic appearance of the rubber particles filtered from the residual bitumen of the AR produced with the base bitumen M

By the examination of the photograph on the right, it is noticeable a even dustier appearance of the FR and the quantity of rubber retained on the filter is inferior to the previous observed FRs (A, E, I). In fact, the residual bitumen M contains only 0.14% w/w of rubber particles.

Unsurprisingly, the equivalent diameter of the FR, form residual bitumen M, is the smallest, only 282.98 *μm*. Furthermore, the FR particles appear to be stuck to each other (left side of the Figure) as earlier observed in the recovered rubber from AR M.

5.5.5. Changes in the morphology of the rubber particles after the interaction with the different base bitumens

Figures 5.99, 5.100, and 5.101 are the quantitative representation of the results obtained in the performed tests to assess the changes in the morphology of the rubber particles during the production of AR with various bitumen pen, already documented in the Figures presented above. Those Figures and Figure 5.102 are a summary of the observations made in this part of the work, which will allow a holistic understanding of the AR production process form the point of view of the rubber particles.

Therefore, in Figure 5.99 the lines representing the evolution of the equivalent diameter of the crumb rubber added initially added to the four commercial base bitumens in the form of recovered rubber and filtered rubber were depleted.

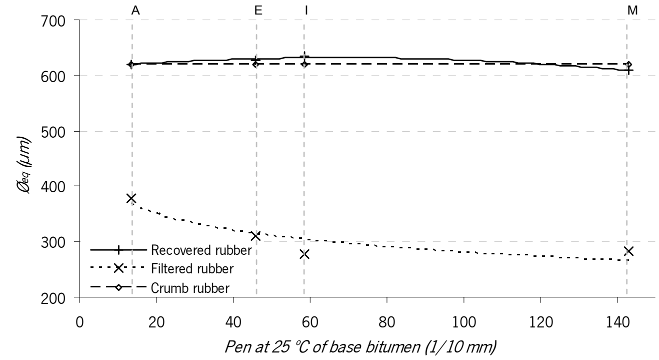


Figure 5.99 – Dimension of recovered rubber (RR) and filtered rubber (FR) particles after interact with the four commercial bitumens, compared to the added crumb rubber (CR)

In the production process of the different ARs the same crumb rubber was always used, with an $Ø_{eq}$ of 620.10 μm. The added crumb rubber is represented in the graphic by a straight line (dashes) independent from the base bitumens Pen.

At the end of the ARs production the swollen rubber particles were recovered and their equivalent diameter was assessed. The evolution of the $Ø_{eq}$ of the rubber particles with the base bitumen Pen is described by a quadratic function. Therefore, it is noticeable a slight increase of the volume of the rubber particles for base bitumens with a Pen inferior to 70 dmm, but for softer bitumens the average of the rubber particles dimension decreases.

Meanwhile, the size of the rubber particles filtered from the residual bitumen is considerably inferior to the crumb rubber particles and varies significantly. The relation between the variation of the FR particles with the Pen of the base bitumen is approach by a logarithmic trending line, being the particles filtered from the residual bitumen A the largest and the filtered from residual bitumen M, the smallest.

The mass of the crumb rubber initially added to the base bitumen, to produce the AR, was registered. In the end of the AR production, and by combining the application of the “basket drainage method” with the “sphere AR production simulator” method it was possible to assess the mass of the swollen rubber in the AR. The comparison between the mass of the crumb rubber, before and after the interaction with the four commercial base bitumens, allowed determining the percent variation of the rubber mass (Figure 5.100), which is a direct indication of rubber swelling.

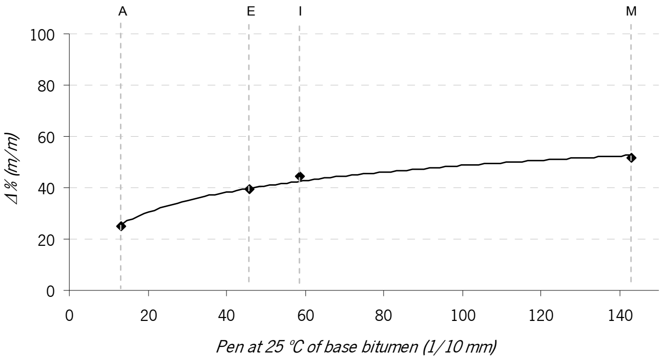


Figure 5.100 – Mass percentage of the swollen rubber particles, after interacting with the four commercial bitumens (recovered rubber)

The differential mass percentage between the added and the recovered rubber from each AR, *i.e.*, the rubber swelling percentage, plotted in function of the base bitumen Pen, originates a logarithmic trending line.

The swelling of the rubber increases with the base bitumen Pen, trending to a maximum value that corresponds to the saturation of the rubber particles. When this point is achieved, the rubber particles are in the form of a gel and the diffusion process of bitumen molecules into rubber reticules cannot continue. When comparing these observations to the previous results it is obvious that during the AR production process the rubber particles swell and transform into a fragile gel. The stirring and high temperature provoke the rupture of the particles, exposing the centre of each particle to the bitumen, helping to prolongate the swelling process. Simultaneously, parts of the gel rubber particles are partly or completely depolymerised, depending on the concentration of little molecules in the bitumen. In fact, when the swelling process of the rubber particles is complete, the phenomena that occur in the AR are the splitting and the degradation of the rubber gel particles.

Attending to the facts previously exposed, it is evident that, as the AR production process takes place, the relative importance of the rubber particles in the binder increases. Therefore, the evolution of the rubber mass concentration (%) in the AR and in the residual bitumen with the Pen of the used base bitumen was quantified and compared to the concentration of the crumb rubber in the beginning of the ARs production process (21% w/w).

In Figure 5.101, the lines that represent the rubber concentration in the beginning and end of the AR production and in the residual bitumen in function of the base bitumen Pen are depleted.

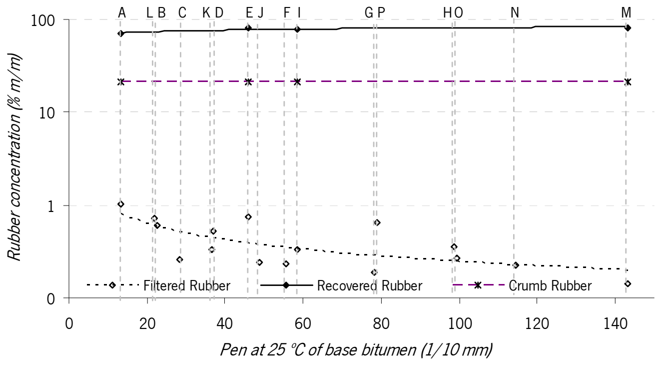


Figure 5.101 – Mass percentage of rubber particles in the base bitumen (added for AR production), in the AR and in the residual bitumen

The concentration of rubber particles in the AR binder is of major importance due to several reasons:

- In the bituminous mixtures produced with AR binder, the element that promotes the liaison among the aggregates is the residual bitumen, since the swollen rubber particles by themselves do not adhere to the aggregate. It was observed that the clean swollen rubber particles are not sticky and dry (burn) when heated when bitumen is absent;
- Behind the binding function, the bitumen binders are responsible for the lubrication of the aggregates particles allowing the adequate compaction of the bituminous mixtures;
- The performance of flexible pavements is largely dependent on the mineral skeleton, which depends on the organization and attrition forces between the aggregates that are controlled by the binder;
- In the pavement it is possible to approach the rubber particles to a special aggregate. However, by taking the place of some of the mineral aggregates, the rubber particles make difficult the contact (attrition) between mineral aggregates;
- One of the most important rheological characteristics of a suspension is its volume fraction of solids. This factor largely controls the viscosity of the suspension;
- In the case of the AR binders, it was observed that the density of the swollen rubber particles is slightly the same of the bitumen, indicating that the volume fraction of rubber in the ARs, produced in his work, is always superior to 70%, achieving the 82% for AR produced with base bitumen M.

In the graphic three lines are depleted relating the logarithm of the rubber mass concentration in the initial base bitumen, in the final AR and in residual bitumen in function of the base bitumen Pen. Thus, the behaviour of the mass concentration of rubber in the AR as the bitumen gets softer is approached by a potential trending line.

When comparing the referred line to the graphic presented in Figure 5.102, it is noticeable that the increase of the differential between the initial and the final concentration of crumb rubber corresponds approximately to the double of the percentage of the swollen rubber particles, confirming that the swelling phenomenon is due to the absorption of parts of the bitumen.

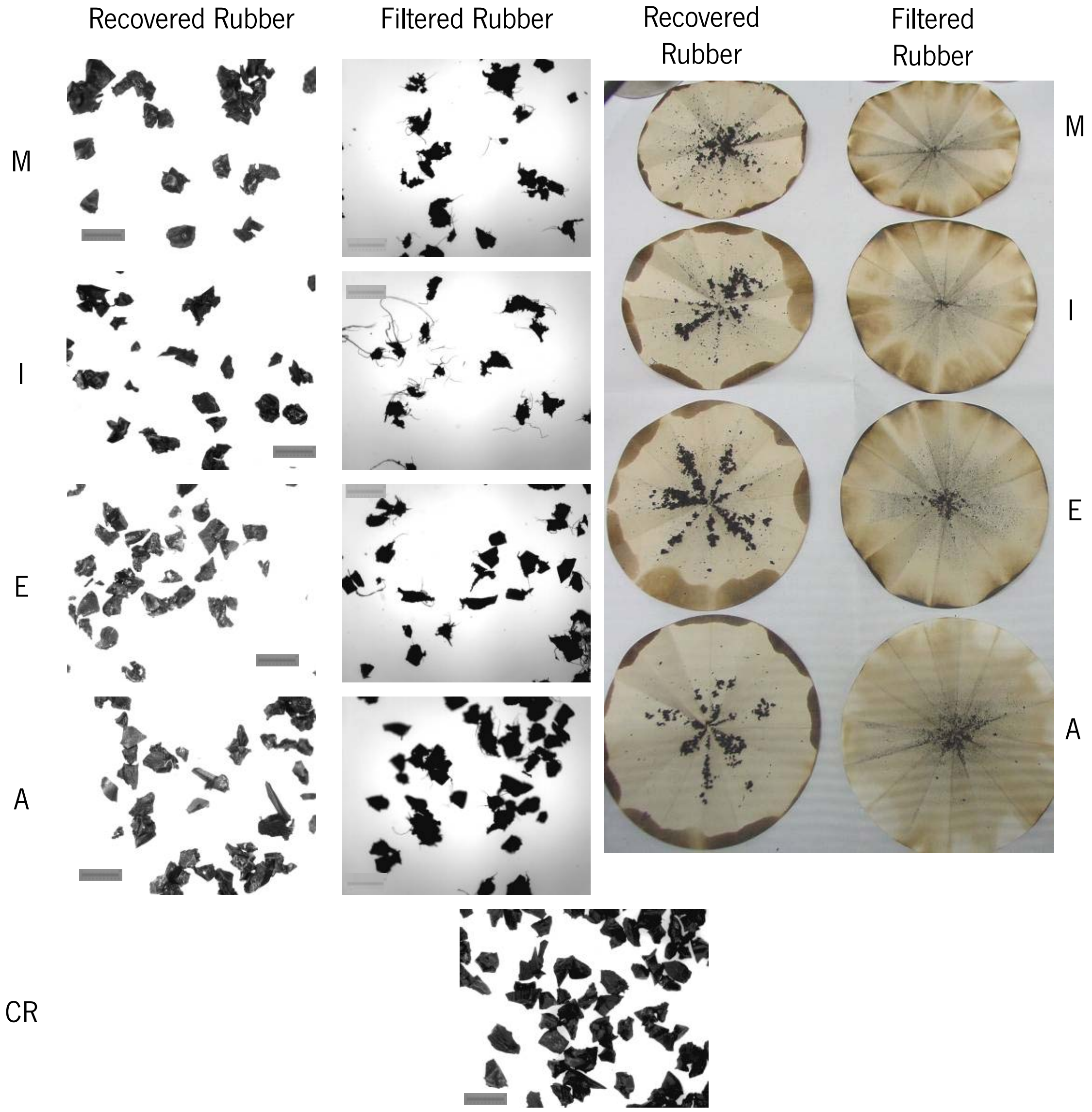


Figure 5.102 – Microscopic and macroscopic photographs of crumb rubber before and after interacting with the four base bitumens

Additionally, it is useful to remark that the greatest change in the mass concentration of the rubber particles is nearly independent of the base bitumen Pen. It is noticeable that even when bitumen A (10/20) is used to produce AR, the increase in the rubber mass concentration is from about 49%, being from about 61% when bitumen M (150/200) is used. The difference between the utilization of bitumens A and M to produce AR, in relation to rubber concentration is of 12% only. Since the rubber particles achieve the saturation when bitumens harder than M are used, its expectable that by using an initial mass concentration of rubber of 21% the final concentration of rubber, independently from the base bitumen Pen, will never surpass 82% (21% + 61%).

Therefore, the rubber swelling is mostly due to the diffusion of specific light fractions of bitumen that are not volatile. In fact, rubber particles present a significant increase in mass and volume after interacting with all bitumens, even with base bitumen A, which did not lose weight in the RTFOT aging method.

When assessing the potential trending line describing the evolution of the rubber particles mass concentration on the residual bitumen a decrease was noticed as the base bitumen used became softer. This fact indicates a degradation of the rubber particles suspended in the residual bitumen. Moreover, when softer bitumens are used, the rubber swells until saturation. If the volume fraction of crumb rubber is considerable, re-vulcanization and re-polymerization of the rubber particles can occur, and the clusters formed by the assembly of rubber particles do not pass easily through the wire basket.

In Figure 5.102 it is possible to visualise the changes in the morphology of rubber particles induced by the interaction with the different bitumens. The differences between the initial crumb rubber particles and the recovered rubber are evident for all the AR binders produced with the four commercial bitumens. The recovered rubber particles vary in shape and size, whereas the initial crumb rubber particles are clearly more homogeneous. These changes in the crumb rubber morphology cannot simply result from its solubility in the solvent constituents of the bitumen, since the observed changes are visibly superior to 11% (depolymerisation and devulcanization changes may occur).

When comparing the recovered rubber particles from ARs produced with different bitumens, it was possible to observe that the interaction with softer bitumens (M) resulted in a greater variability in the shape and size of the rubber particles than in harder bitumens (A), suggesting that the bitumen constitution has a significant influence in its interaction with the crumb rubber.

A clear evidence of the changes in the rubber particles properties during the AR production can be observed in the microscopic photos of the rubber particles filtered (FR) from the residual bitumen. In fact the size of the crumb rubber particles has inevitably changed during the AR production, since the residual bitumens present some residual rubber particles in its constitution, although the initial rubber particles cannot pass through the wire basket. In conclusion crumb rubber particles interact with the bitumen in the AR production, and the changes in the shape and size of the rubber particles are more evident in softer bitumens.

During the AR binder production, the interaction of the crumb rubber particles with softer bitumens is clearly superior than with harder bitumens, and thus the morphology of the rubber particles is clearly more influenced by softer bitumens (apparently the rubber particles in contact with softer bitumens swell much more, splitting and releasing a great amount of very small elements (recovered in the residual bitumen).

Finally, the appearance and quantity of the FR in the filters is an obvious sign of the diminution of the concentration and size of the rubber particles in the residual bitumen, indicating a solubilisation of the discrete particles of rubber in the presence of hot soft bitumen.

5.6. Conclusions

The development of this research included the achievement of specific objectives, which led to the conclusions presented below.

The analysis of the results of this work made possible to assess the changes in the physical and rheological properties of AR binders produced with different base bitumens. The results of the different tests were very influenced by the base bitumen used to produce the ARs. In fact, the change from harder to softer bitumens originated an ordered sequence for the physical properties evaluated, described by a potential trending line for the best fit between the R&B and the dynamic viscosity properties and the Pen at 25 °C (of the base bitumen) for all the materials studied in this work (base and residual bitumens, AR binders, before and after aging). The dynamic viscosity test was the most effective to detect variations in the behaviour of the different materials, since it adequately discriminates the several base bitumens (A to P) and the corresponding AR binders. The dynamic viscosity results showed a great variation, especially in the softest bitumen (M).

The comparison between the several types of bitumen used to produce AR binders showed that the highest variations in the physical characteristics of the binder (AR compared with the base bitumen) are obtained with softer bitumens. The softest bitumen (150/200), which is not generally used to produce AR or asphalt mixtures, presented the highest interaction with the crumb rubber, being a very appropriate alternative to produce AR binders with a penetration inferior to that of a 60/70 base bitumen.

The AR binders that present the best rheological characteristics are those produced with softer base bitumens. The rheological behaviour of the AR binder and that of the corresponding base bitumen are similar for temperatures inferior to 80 °C, at all frequencies. However, for temperatures above 112 °C the rheological behaviour of the AR binders is clearly different from that of the base bitumen.

The interaction between the rubber and the bitumen and the reactions among the swollen rubber particles, initiated during the AR binder production and continued in the RTFOT aging test, result in an AR material controlled by the rubber rheological behaviour for temperatures superior to 112 °C (being G' visibly superior to G'') and by the bitumen rheological behaviour for temperatures below 80 °C. The high viscosity/stiffness of the AR binders, even at temperatures superior to 112 °C, makes difficult their mixing and application. The AR binder rheology is more affected by the frequency (η^* reduces when frequency increases) than the base bitumen rheology (frequency does not change η^*).

At temperatures inferior to 80 °C the residual bitumen is stiffer than the corresponding base bitumen and AR binder and it remains stiff after aging. However, above 112 °C the residual bitumen is softer than the AR binder, having nearly the same stiffness as the base bitumen.

The rubber swelling phenomenon increases the elastic recovery (ER) of AR binders. At the end of the RTFOT aging test, the average volume of the rubber particles in aged AR binder M is lower than in the aged AR binder I. Thus it reduces the value of elastic recovery for the AR binder M after RTFOT.

During the production of AR binders the density (Den) of the base bitumen, rubber and AR binder changes significantly. The densities of the AR binders are inferior to those of their residual bitumen, being also inferior to their base bitumen for softer bitumens (I and M) Only. The solubilisation of rubber compounds in the bitumen, combined with the diffusion of the smallest molecules of the bitumen into the rubber, makes the bitumen denser. At the same time, the increase in the bitumen density is caused by the heat, because of the evaporation of its lighter molecules.

During the AR production and aging, as a consequence of the bitumen-rubber interaction several rheological and chemical changes can be identified in the bitumen. The greatest differences between the base and aged bitumen are visible at lower temperatures, at which all the rheological parameters indicate an increase in the bitumen stiffness. These results mean that during the aging of bitumen, and beyond the oxidation phenomenon, the small molecules that confer softness to the bitumen have evaporated or combined into bigger molecules, and thus the bitumen becomes stiffer.

During the RTFOT aging of the base bitumen and especially of the residual bitumen, as well as during the AR binder production, the values of Mw increase and the MWD widens. However, despite the superior average value of Mw of the residual bitumen, its MWD is similar to the aged base bitumen. Residual bitumen with the same Pen of base bitumen has more volatile molecules, suggesting that only some classes of molecules diffuse into rubber particles during the AR production. The greatest changes in the molecular structure of bitumen occur when the residual bitumen is aged (with a major increase in the average Mw and widening of the MWD in comparison with the aged base bitumen).

The processes to which the base bitumen A was exposed did not result in weight loss, but noticeable changes in the physical/rheological properties were observed, indicating that the aging of bitumens is a complex process involving restructuration and oxidation of molecules.

Several morphological alterations in the crumb rubber were detected during the AR production and were related to the base bitumen used. The rubber particles swell due to the diffusion of small molecules of bitumen in the reticulated molecular structure of rubber. The molecules of bitumen diffused in the rubber structure also induce a relaxation of the links between the rubber atoms causing a decrease in the bulk density of rubber. The swelling of rubber increases with the base bitumen Pen, until a maximum value that corresponds to the saturation of the rubber particles. The rate and extent of swelling of the rubber particles in the AR depend on the concentration of bitumen molecules capable of diffusing into the rubber bulk. The rubber particles saturated with bitumen molecules become a fragile gel that can easily split by the action of the stirring, heat and eventual depolymerisation. Therefore, a slight increase in the volume of the rubber particles for base bitumens with Pen inferior to 70 dmm was observed, although for softer bitumens the average dimension of the rubber particles decreased.

In the bituminous mixes produced with AR binder, the aggregates are bonded by the residual bitumen, since the swollen rubber particles, by themselves, do not adhere to the aggregates. Actually, after being cleaned, the swollen rubber particles are not sticky and burn when heated without bitumen.

One of the most important factors affecting the rheological properties of a chemical suspension (e.g. AR binder) is its volume fraction of solids, which largely controls the viscosity of the suspension. By using an initial mass concentration of crumb rubber of 21.0%, the volume fraction of rubber in the ARs produced in this work was always superior to 70%, with a maximum value of 82% for the AR produced with base bitumen M.

During AR binder production, the interaction of crumb rubber particles with softer bitumens is clearly superior, and the morphology of the rubber particles is clearly more influenced by those bitumens than by harder ones. Apparently the rubber particles in contact with softer bitumens swell much more, splitting into and releasing a great amount of very small elements. Thus, the particles filtered from residual bitumen A are the largest and the ones filtered from residual bitumen M are the smallest, due to a higher degradation of the rubber particles suspended in the softer bitumen. Furthermore, when softer bitumens are used in the AR, rubber particles can swell to their saturation and re-vulcanization and re-polymerization among the rubber particles can occur if the volume fraction of rubber particles is considerable. However, it must be referred that the amount of rubber particles in the residual bitumen is so reduced that they nearly do not change the physical and rheological properties of this material.

The rheological and physical characterization of the several binders after RTFOT aging is of primordial importance, since these materials are the ones that best simulate the binder performance in the pavement under traffic, weather and pollution actions. The aging of AR binders is caused by the production of the AR binder and then by the production and compaction of asphalt mixes. In order to assess the aging of the bitumen in the AR binders without the effects of the crumb rubber, a new procedure was developed using the RTFOT after the “sphere AR production simulator”.

The reduction of Pen in the “sphere AR production simulator” method was more pronounced than in the RTFOT aging of the base bitumen, but the DV and R&B changes in the “sphere” simulator are minor than in the RTFOT aging. Thus, the changes in the bitumen caused by both methods are different.

The RTFOT aging of the base bitumen causes more changes in softer bitumens than in the hardest ones, especially at lower temperatures (Pen values). Additionally, the binders become less dependent on temperature, since bitumen is stiffer at in-service temperatures and maintains the softness at production temperatures.

The most affected property by the RTFOT aging of AR binders was the dynamic viscosity. In opposition, the least affected physical property of the AR binder by aging was the elastic recovery, which improves after the RTFOT aging process. There is a clear improvement of the physical and rheological properties of the AR binder after RTFOT aging, especially for ARs produced with softer base bitumens. In fact, the aged AR produced with bitumen M has an elevated stiffness and viscosity at higher temperatures (adequate rutting resistance) and an adequate softness at lower temperatures (adequate fatigue cracking resistance).

The changes in the rheological properties of the base, “sphere” and residual bitumens after RTFOT aging were greater than the ones observed for the AR binders, indicating that the AR binder is less sensitive to aging during the mixing and compaction phases (mainly because the rubber particles have already interacted with the softer molecules of bitumen, hampering the aging of the AR). For temperatures superior to 80 °C the aged AR binders are clearly a stiffer and more elastic material.

The changes in the values of Pen and in the corresponding weight loss after aging of the studied materials have shown a direct and very good correlation. Therefore, the greatest changes in both values were observed in the base bitumens, followed by the sphere and by the residual bitumens, being the minor changes observed in the AR binders. It was also observed that binders with the same Pen values before RTFOT aging present very different weight loss during aging.

The establishment of a relationship between the physical and rheological properties of different bitumens and resulting AR binders provides additional information about the behaviour of binders and allows selecting the best technique to assess the properties of the binders at each studied temperature.

The physical and rheological characterization of bitumen confirms the singularity of this material. Bitumen behaves mostly as a viscoelastic semisolid material below 80 °C, becoming a viscous liquid at higher temperatures (superior to 112 °C). At approximately 180 °C the bitumen behaviour is almost independent of the bitumen type, trending to a constant and very low stiffness value.

The relationship between the physical and rheological properties of the studied binders depends on the test temperature. This relationship has proven to be excellent for all the studied materials (AR binder, base and residual bitumen) at higher temperatures (DV and R&B), but it is not so good at medium operating temperatures (Pen).

The Pen values of the base and residual bitumens, before and after aging, are related to their rheological properties by potential trending lines. However, the same relations for the AR binders, before and after aging, are adjusted by a logarithmic trend line. The relationship between the elastic recovery (ER) and the rheological properties at 25 °C can be approached by a logarithmic trending line. Additionally, the ER of the AR binders increase when the base bitumen used for their production is softer.

The relation between the R&B and the rheological properties of all tested materials was defined by exponential trending lines with the same slope. The R&B temperature has a very good correlation with the rheological properties of the same binders at 80 °C, either before or after RTFOT aging, resulting in a continuous single line that adjusts all the studied materials.

The physical property that showed the highest sensitivity to the changes in the characteristics of the binders was viscosity. The relations between the DV and rheological properties are exponential lines, which are nearly linear. The comparison between the DV (physical property) and the complex viscosity (rheology) presented the best relationship, being the slope nearly equal to 1 (since 1 Pa.s = 1000 cP).

For all the tested binders, the range of values of Pen and R&B results are visibly inferior to the ones of the rheological classification. The physical characterization of binders is more effective for bitumens than for AR binders, because the physical properties of the AR binders are poorly influenced by the type of base bitumen used (especially at higher temperatures).

The greatest variations in the physical and rheological properties were observed in the softest bitumen. In fact, the variation of the Pen value of the softer base bitumen M (150/200) after AR production is enormous (becoming a 40/50 bitumen), but the rheological changes are not so drastic. However, only small variations in the properties of the stiffer base bitumen (A) were detected, mainly after AR production.

For temperatures superior to 50 °C, the physical properties of the tested AR binders show high variations in comparison with the ones of their base bitumens. In fact, the AR binder is much stiffer than the base bitumen, and this can be especially observed at higher temperatures in the DV test, with a really high increase in the AR binder stiffness.

The final characteristics (Pen, R&B and rheological properties) of the residual bitumen obtained from the AR binder produced with the softer base bitumen (M) at in-service temperatures (between 25 and 80 °C) correspond to a base bitumen 40/50. When tested at production temperatures (180 °C), the same residual bitumen presents DV values and rheological properties similar to the ones of the base bitumen 10/20 (confirming that changes are more visible at higher temperatures).

6. CONCLUSIONS AND FUTURE RESEARCH

6.1. Introduction

The principal aim of this research was to characterise the influence of the bitumen constitution in the AR binder performance. This chapter presents the conclusions of this research work and recommendations for future investigation.

6.2. Conclusions

The main conclusions that can be drawn from the research carried out in this work are:

- The “sphere AR production simulator” combined with the “basket drainage method” were found to be simple and effective methods to evaluate the rubber-bitumen interaction. The “sphere AR production simulator” may also be used to deepen knowledge and understanding of the aging of bitumen during AR production and to assess the variations of density of the studied materials.
- The bitumen aging and the AR production originate physical and rheological changes, such as an increase in the density, stiffness, elasticity and viscosity and a reduction in the penetration. During AR production these changes are mostly due to the diffusion of light fractions of bitumen in the rubber particles, while the bitumen aging is caused only by oxidation, growth and restructuration of its molecules.
- The crumb rubber particles absorb bitumen and swell during AR production at mixing temperatures. The rate and amount of absorption is mainly dependent on the concentration of light molecules of bitumen that can diffuse into rubber and on the saturation characteristics of rubber (which depend on its chemical constitution and crosslink density). During the AR production the rubber particles swelled 250 to 300% their weight, respectively for the hardest (10/20) and softest (150/200) bitumens. However, the maximum increase in the equivalent diameter of the rubber particles was only 2.5% for bitumen 60/70. As a result, the maximum elastic recovery was obtained for the softest bitumen.
- Binders should not be very stiff at low and medium operating temperatures to avoid cracking distresses, but they should have enough stiffness at high operating temperatures to improve rutting resistance properties. The AR binders always fulfil these demands, especially the AR produced with softer bitumen M (its rheological properties at 25-35 °C are similar to the base bitumen 60/70, being much higher at 60-80 °C). The rheology of the AR binders indicates that they are softer than the base bitumens for the same Pen value, corroborating their best cracking fatigue resistance.

- The aged AR binders show a very high stiffness due to excessive loss of the lighter fractions of bitumen after the combined effect of short-term aging oxidation and rubber-bitumen interaction.
- The analysis of the aging effect on the different bitumens and AR binders (with similar characteristics at in-service temperatures) showed that the greatest changes in weight loss, rheological and physical properties occur to the base bitumen, followed by the “sphere” and residual bitumens, being the AR binder the one with minor alterations. Thus, the rubber particles protect the AR binder from aging.
- The rubber swelling is mostly due to the diffusion of specific light fractions of bitumen that are not volatile. In fact, rubber particles present a significant increase in mass and volume after interacting with bitumens that did not lose weight in the RTFOT aging method.
- Residual and base bitumens show similar physical and rheological properties. However, the RTFOT aging of base and residual bitumens with the same characteristics results in materials with different properties. Hence, bitumens with the same properties can have different chemical constitutions.
- It is possible to relate the physical and rheological properties of all tested materials through known mathematical equations with very good correlations (small dispersion), especially for the “sphere”, base and residual bitumens (before and after aging). The rheological properties are more sensitive to characterize the binders at in-service temperatures (inferior to 80 °C), but the dynamic viscosity characterization presented the best accuracy at production temperatures (near 180 °C).

6.3. Recommendations for Future Research

In spite of the different conclusions reached from this research project, further information remains unknown about the studied material. Thus, a list of recommendations is summarised in the following paragraphs:

- The great importance of the chemical constitution of the bitumen used in the production of AR binders was reported during this research. Actually, several changes in the chemical constitution of the materials during the production of AR binders and mixtures were evaluated based on indirect analysis of the tests. The confirmation of the indirect data by direct chemical analysis would be a useful tool to construct a model which relates the chemical constitution of bitumen with the physical and rheological properties and with the final characteristics of the resulting AR binders;
- The results of the research indicate that only a part of the small and volatile molecules of bitumen diffuse into the rubber. Hence, these molecules should be identified in order to develop additives that promote a better compatibility between rubber and bitumen, and later, between AR and aggregates;

- Further rheological characterization of the studied materials should be carried out using different temperature degrees, different test geometries and configurations and other rheometers, in order to obtain the master curves, the transition temperatures (Tg) and the fatigue resistance of the binders;
- The changes that occur in the bitumen during the AR production that are independent of the rubber interaction should be better understood, by assessing the rheological and chemical characteristics of the bitumen obtained after the use of the “sphere AR production simulator”;
- Since that crumb rubber morphology clearly affects the AR properties, this is a factor that must be carefully evaluated and related to the bitumen used in the AR binder;
- During the RTFOT aging procedure the rubber particles continue to interact with bitumen. This phenomenon induces additional changes in the morphology of the rubber particles and in the bitumen that should be investigated in the aged AR binders and in the residual bitumens;
- The AR production is largely controlled by physical factors such as temperature, digestion time and stirring velocity. The influence of these factors in the final characteristics of the binders and in the dimension of the swelled rubber particles should also be evaluated;
- If possible, crumb rubber particles and bitumens from other sources and produced through different methods should be analysed;
- The major problem that turns unfeasible the production and storage of AR binders with high percentage of rubber in proper and controlled industrial facilities is the segregation and sedimentation of rubber particles. During this work it was demonstrated that it is possible to control the density of the swelled rubber in order to avoid the referred phenomena, but this line of research should be continued;
- The conclusions of this work show that the use of softer bitumens originates AR binders with an improved behaviour in flexible road pavements. However, these conclusions were only obtained through binder characterization. Therefore, these results should be validated by carrying out tests in AR bituminous mixtures and by evaluating pavement trials constructed with this AR binder.

BIBLIOGRAPHY

AASHTO PP1-98, 1998. *Standard Practice for Accelerated Ageing of Asphalt Binder Using a Pressurized Ageing Vessel (PAV)*. American Association of State Highway & Transportation Officials.

AASHTO T314, 2007. *Determining the Fracture Properties of Asphalt Binder in Direct Tension*. American Association of State Highway & Transportation Officials.

AASHTO TP3-98, 1998. *Direct Tension (DT)*. Provisional standard. American Association of State Highway & Transportation Officials.

AASHTO TP5-97, 1997. *Determining the Permanent Deformation and Fatigue Cracking Characteristics of Hot Mix Asphalt (HMA) Using the Simple Shear Test (SST) Device*. American Association of State Highway & Transportation Officials.

Abdelrahman, M.A., Carpenter, S.H., 1999. "Mechanism of Interaction of Asphalt Cement with Crumb Rubber Modifier". *Transportation Research Record* 1661, TRB, National Research Council, Washington, D.C., pp. 106-113.

About.com, 1989. *Weatherometer*. The New York Times Company, CRC Press LLC. Web. 02 Apr. 2009. <http://composite.about.com/library/glossary/w/bldef-w6053.htm>.

Adhikari, B., De, D., Maiti, S., 2000. "Reclamation and Recycling of Waste Rubber". *Progress in Polymer Science*, Vol. 25 (7), pp. 909-948.

Airey, G.D., Rahman, M.M., Collop, A.C., 2003. "Absorption of Bitumen into Crumb Rubber Using the Basket Drainage Method". *International Journal of Pavement Engineering*, Vol. 4 (2), pp. 105-119.

Alcantara, M.R., 2003. *About Rheology*. Greso - Grupo de Reologia em Sistemas Organizados. Web. 14 May 2009. <http://www.iq.usp.br/wwwdocentes/mralcant/About_Rheo.html>.

Altgelt, K.H., Boduszynski, M.M., 1994. *Composition and Analysis of Heavy Petroleum Fractions*. Marcel Dekker: New York.

Altgelt, K.H., Harle, O.L., 1975. "The Effect of Asphaltenes on Asphalt Viscosity". *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 14 (4).

Amirkhanian, S.N., Kim, K.W., 2004. *Rutting Index Prediction of Rubber-Modified Binder Using HP-GPC*. Resource Library, Asphalt Rubber Technology Service.

Andersen, S.I., Speight, J.G., 2001. "Petroleum Resins: Separation, Character and Role in Petroleum". *Petroleum Science and Technology*, 19 (1&2), pp. 1-34.

Antunes, M., Batista, F., Fonseca, P., 2006. "Asphalt Rubber mixtures in Portugal: practical applications and performance". *Asphalt Rubber 2006 Conference*, Palm Springs, California, USA, pp. 283-298.

Artamendi, I., Eastmond, G.C., Khalid, H., 2002. "Influence of crumb rubber modifier (CRM) from tyre waste on the rheological properties of bituminous binders". *Proc. 3rd Int. Conf. Bituminous Mixtures and Pavements*, Thessaloniki, pp. 65-74.

Artamendi, I., Khalid, H.A., 2006. “Diffusion Kinetics of Bitumen into Waste Tyre Rubber”. *Journal of the Association of Asphalt Paving Technologists*. Proceedings of the Technical Sessions, Vol. 75, Savannah, Georgia, pp. 133-164.

Ashcroft, C., 2002. *What is Asphalt Rubber? What is RAC?* San José Asphalt Rubber Design and Construction Workshop. Rubber Pavements Association. Web. 4 Apr 2009. <http://www.asphaltrubber.org/ari/General_Information/Cliff_Ashcroft_What_is_AR_What_is_RAC.ppt#307,21,RESILIENCE>.

ASTM D 2007-03, 2003. *Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatographic Method*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 2170-95, 1995. *Standard test method for kinematic viscosity of asphalts (bitumens)*. American Society for Testing & Materials. ASTM, Pennsylvania.

ASTM D 2171-94, 1994. *Standard test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer*. American Society for Testing & Materials. ASTM, Pennsylvania.

ASTM D 2872, 1985. *Effect of Heat on Air on a Moving Film of Asphalt (Rolling Thin Film Oven Test)*. American Society for Testing & Materials, ASTM, Pennsylvania.

ASTM D 3279-97, 2001. *Standard Test Method for n-Heptane Insolubles*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 36-95 e1, 2000. *Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 4124-01, 2001. *Standard Test Method for Separation of Asphalt into Four Fractions*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 5-05a, 2005. *Standard Test Method for Penetration of Bituminous Materials*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 5603-96, 1996. *Classification of the Type of Ground Rubber in Terms of Maximum Particle Size, Size Designation, and Grades*. Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia.

ASTM D 5644-96, 1996. *Method for Determining Mesh Size for the Particular Rubber to Ensure Uniformity*. Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia.

ASTM D 6648-01, 2001. *Standard test Method for Determining the Flexural Creep Stiffness of Asphalt Binder using the Bending Beam Rheometer (BBR)*. American Society for Testing & Materials, ASTM, Pennsylvania.

ASTM D 6814–02, 2002. *Standard test Method for Determination of Crumb Rubber Based on Crosslink Density*. ASTM Annual Book of Standards, American Society for Testing and Materials, West Conshohocken, PA.

ASTM D 1754-97, 2002. *Standard Test Method for Effect of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)*. American Society for Testing & Materials. ASTM, Pennsylvania.

ASTM E 1290-02, 2002. *Standard Test Method for Crack-Tip Opening Displacement (CTOD) Fracture Toughness Measurement*. American Society for Testing & Materials, ASTM, Pennsylvania.

ASTM E 1820-01, 2001. *Standard Test Method for Measurement of Fracture Toughness*. American Society for Testing & Materials, ASTM, Pennsylvania.

Bahia, H.U., Davies, R., 1995. "Role of Crumb Rubber Content and Type in Changing Critical Properties of Asphalt Binders". *Journal of the Association of Asphalt Paving Technologists*, Vol. 64, pp. 130-162.

Bandurski, E., 1982. "Structural Similarities between Oil-Generating Kerogens and Petroleum Asphaltenes". *Energy Sources*, Vol. 6, pp. 47-64.

Behar, F., Pelet, R., Roucache, J., 1984. "Geochemistry of Asphaltenes". *Organic Geochemistry*, Vol. 6, pp. 587-595.

Bell, D., Claxton, M.J., 2000. "A novel Rheometer for Bitumens". *2nd Euroasphalt and Eurobitume Congress*, Vol. 1, Barcelona, pp. 35-43.

Benedetto, H., La Roche, C., 1998. "State of the Art on Stiffness Modulus and Fadigue of Bituminous Mixtures". *Rilem Report 17 – Bituminous Binders and Mixtures*. E&FN Spon, London and New York, pp. 137-180.

Berkers, R.F.A., 2005. *Influence of Chemical Composition on the Performance of Bitumen*. Master's Degree in Technology, Department of Civil Engineering, Tswane University of Technology, Republic of South Africa.

Billiter, T.C., Chun, J.S., Davison, R.R., Glover, C.J., Bullin, J.A., 1996. "Investigation of the Curing Variables of Asphalt-Rubber Binder". *American Chemical Society, Division of Fuel Chemistry*, 41 (4), pp. 1221-1224.

Billiter, T.C., Davison, R.R., Glover, C.J., Bullin, J.A., 1997a. "Physical Properties of Asphalt-Rubber Binder". *Petroleum Science and Technology* 15 (3&4), pp. 205-236.

Billiter, T.C., Davison, R.R., Glover, C.J., Bullin. J.A., 1997b. "Production of Asphalt-Rubber Binders by High-Cure Conditions". *Transportation Research Record 1586*, TRB, National Research Council, Washington, D.C., pp. 50-56.

Bouldin, M.G., Collins, J.H., Berker, A., 1990. "Rheology and Microstructures of Polymer/Asphalt Blends". *Rubber Chem. Technics.*, 64, pp. 577–600.

Branco, F., Pereira, P., Picado Santos, L., 2005. *Pavimentos Rodoviários*. Edições Almedina, Coimbra.

Bridgestone, 2008. *Tires*. Web. 23 Apr 2008. <http://www.bridgestone.eu>.

Bukka, K., Miller, J.D., Oblad, A.G., 1991. "Fractionation and Characterization of Utah Tar-Sand Bitumens: Influence of Chemical Composition on Bitumen Viscosity". *Energy & Fuels*, 5, pp. 333-340 .

Carbognani, L., Gonzalez, M.F., Pereira-Almao, P., 2007. "Characterization of Athabasca Vacuum Residue and Its Visbroken Products. Stability and Fast Hydrocarbon Group-Type Distributions". *Energy & Fuels*, 21, pp. 1631-1639.

Castro, A.G., Covas, J.A., Diogo A.C., 2001. *Reologia e suas Aplicações Industriais*. Ciência e Técnica, Instituto Piaget, Lisboa.

Chehovits, J., Dunning, R., Morris, G., 1982. "Characteristic of Asphalt-Rubber by the Sliding Plate Microviscometer". *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 51, p. 241.

Chesner, W., Collins, R., MacKay, M., Emery, J., 1998. *The User Guidelines for Waste and Byproduct Material in Pavement Construction - Scrap Tires, Turner-Fairbanks*. Highway Research Center, Federal Highway Administration, U.S. Department of Transportation, FHWA-RD-97-148. Web. 23 Apr 2008. <http://www.tfhrc.gov///hnr20/recycle/waste/st1.htm>.

Collins, J.H., Bouldin. M.G., Gelles, R., Berker, A., 1991. "Improved Performance of Paving Asphalts by Polymer Modification". *Journal of the Association of Asphalt Paving Technologists*, Vol. 60, pp. 43-79.

Continental, 2005. *Tyre Basics Passenger Car Tyres*. Web. 24 Apr 2008. <http://www.conti-online.com/generator/www/de/en/continental/automobile/themes/tyretips/download/tyre_basics_pasenger_car_tyres_2005_en.pdf>.

Continental, 2006. *Truck tyres - technical basics*. Web. 24 Apr 2008. <http://www.conti-online.com/generator/www/de/en/continental/transport/general/tech_info/download/tirebasics_pdf_en.pdf>.

Coomarasamy, A., Hesp, S.A., 1998. "Performance of Scrap Tire Rubber Modified Asphalt Paving Mixes". *Rubber World*, 218, p. 26.

Corbett, L.W., 1970. "Relationship between Composition and Physical Properties of Asphalt". *Proceedings of Am. Association of Asphalt Paving Technologists*, Association Asphalt Paving Technologists, Vol. 39, Seattle, pp. 481-491.

Donnet, J.B., Ducret, J., Kennel, M., Papirer, E., 1977. "Electron Microscopic Observations of the Morphology of Bitumens". *Fuel*, Vol. 56 (1), pp. 97-100.

Douglas, J.F., McKenna, G.B., 1993. "The Effect of Swelling on the Elasticity of Rubber: Localization Model Description". *Macromolecules*, 26 (13), pp. 3282-3288.

Dwiggins, C.W.Jr., 1978. "Study of the Colloidal Nature of Petroleum with an Automated Bonse-Hart X-Ray Small-Angle Scattering Unit". *Applied Crystallography*, Vol. 11, pp. 615-619.

Edwards, Y., 2005. *Influence of Waxes on Bitumen and Asphalt Concrete Mixture Performance*. Doctoral Thesis, Stockholm: KTH – Architecture and the build environment, 10044 Stockholm.

Edwards, Y., Isacsson, U., 2005. "State of the Art - Wax in bitumen Part 1 - Classifications and General Aspects". *Road Materials and Pavement Design* 6 (3), p. 281.

EN 12591, 1999. *Specifications for Paving Grade Bitumens*. Comité Européen de Normalisation.

EN 12593, 1999. *Bitumen and bituminous binders – Determination of Fraass Breaking Point*. Comité Européen de Normalisation.

EN 12595, 1999. *Bitumen and Bituminous Binders – Determination of Kinematic Viscosity*. Comité Européen de Normalisation.

EN 12596, 1999. *Bitumen and Bituminous Binders – Determination of Dynamic Viscosity by Vacuum Capillary*. Comité Européen de Normalisation.

EN 12606-1, 1999. *Bitumen and Bituminous Binders Determination of the Paraffin Wax Contents Part 1: Method by Distillation*. Comité Européen de Normalisation.

EN 12607-1, 1999. *Bitumen and Bituminous Binders – Determination of the Resistance to Hardening under the Influence of Heat and Air – Part 1: RTFOT Method*. Comité Européen de Normalisation.

EN 12607-2, 1999. *Bitumen and Bituminous Binders – Determination of the Resistance to Hardening under the Influence of Heat and Air – Part 2: TFOT Method*. Comité Européen de Normalisation.

EN 12607-3, 1999. B*itumen and Bituminous Binders – Determination of the Resistance to Hardening under the Influence of Heat and Air – Part 3: RFT Method*. Comité Européen de Normalisation.

EN 13587, 2003. *Bitumen and Bituminous Binders – Determination of the Tensile Properties of Modified Bitumen by the Tensile Test Method*. Comité Européen de Normalisation.

EN 13588, 2004. *Bitumen and Bituminous Binders – Determination of Cohesion of Bituminous Binders with Pendulum Test*. Comité Européen de Normalisation.

EN 13589, 2003. *Bitumen and Bituminous Binders – Determination of the Tensile Properties of Modified Bitumen by the Force Ductility Method*. Comité Européen de Normalisation.

EN 13702-1, 2003. B*itumen and Bituminous Binders – Determination of Dynamic Viscosity of Modified Bitumen – Part 1: Cone and Plate Method*. Comité Européen de Normalisation.

EN 13702-2, 2003. *Bitumen and Bituminous Binders – Determination of Dynamic Viscosity of Modified Bitumen – Part 2: Coaxial Cylinders Method*. Comité Européen de Normalisation.

EN 13703, 2003. *Bitumen and Bituminous Binders – Determination of Deformation Energy*. Comité Européen de Normalisation.

EN 14023, 2004. *Bitumen and Bituminous Binders – Specifications for Polymer Modified Bitumens*. Comité Européen de Normalisation.

EN 1426, 1999. *Bitumen and Bituminous Binders – Determination of Needle Penetration*. Comité Européen de Normalisation.

EN 1427, 1999. *Bitumen and Bituminous Binders – Determination of Softening Point – Ring and Ball Method*. Comité Européen de Normalisation.

EN 14769, 2005. *Bitumen and Bituminous Binders – Accelerated Long-Term Ageing – Pressure Ageing Vessel (PAV)*. Comité Européen de Normalisation.

EN 14770, 2005. *Bitumen and Bituminous Binders – Determination of Complex Shear Modulus and Phase Angle – Dynamic Shear Rheometer (DSR)*. Comité Européen de Normalisation.

EPA, 2005. *Profile of the Rubber and Plastic Industry*. 2nd Edition. EPA/310-R-05-003 SIC Code: 30. (158 pp). U.S. EPA Compliance Assistance and Sector Programs Division. Web. 24 Apr 2008.

<http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/rubplan.pdf>.

Epps, J.A., 1994. *Uses of Recycled Rubber Tires in Highways - Synthesis of Highway Practice. NCHRP Synthesis of Highway Practice 198*, Transportation Research Board, National Research Council, National Academy Press, Washington DC.

ESIS P1-92, 1992. *ESIS Recommendation for Determining the Fracture Resistance of Ductile Materials*. European Structural Integrity Society. Web. 22 Apr 2008. <http://www.esisweb.org>.

ESIS P2-92, 1992. *ESIS Procedure for Determining the Fracture Behaviour of Materials*. European Structural Integrity Society. Web. 22 Apr 2008. <http://www.esisweb.org>.

FEHRL, 2006. *BitVal - Analysis of Available Data for Validation of Bitumen Tests. Report on Phase 1 of the BiTVal Project*, Forum of European National Highway Research Laboratories, ed. Cliff Nicholls, TRL, UK.

Ferguson, J., Kemblowski, Z., 1991. *Applied Fluid Rheology*. Elsevier applied science, Elsevier science publishers Ltd, Essex, New York.

FHWA, 1993. *Defining the Terminology*. Session 2.0, Crumb Rubber Modifier Workshop Notes, Office of Engineering, Federal Highway Administration, Office of Technology Applications.

Flory, P.J., Rehner, J. Jnr., 1943. "Statistical Mechanics of Cross-Linked Polymer Networks, Part I. Rubber Elasticity". *The Journal of Chemical Physics*, Vol. 11 (11), p. 521.

Fontes, L.P.T.L., Pereira, P.A.A., Pais, J.C., Trichês, G., 2006. "Behaviour of Asphalt Rubber Mixtures with Different Crumb Rubber and Asphalt Binder Sources". *Asphalt Rubber 2006 Conference*, Palm Springs, USA.

Frenkel, J., 1940. "A Theory of Elasticity, Viscosity and Swelling in Polymeric Rubberlike Substances". *Rubber Chem. Technol.* 13, p. 264.

Fritsche, H., 1995. *Bitumen*. 57: 29.

Frobel, R., Jimenez, R., Cluff, C., 1978. *Laboratory and Field Development of Asphalt-Rubber for use as a Waterproof Membrane*. Report No. ADOT-RS-15(164), Arizona Department of Transportation.

Gawel, I., Czechowski, F., 1997. "Study of Saturated Components in Asphalt". *Petroleum Science and Technology*, 15 (7), pp. 729-742.

Gawel, I., Stepkowski, R., Czechowski, F., 2006. "Molecular Interactions between Rubber and Asphalt". *Ind. Eng. Chem. Res.*, 45 (9), pp. 3044-3049.

Gershkoff, D.R., 1991. *A Study of the Rheological Behaviour of Some Surface Dressing Binders*. MSc Thesis, School of Civil Engineering, the University of Nottingham.

Glover, C.J., Davison, R.R., Bullin, J.A., Estakhri, C.K., Williamson, S.A., Billiter, T.C., Chipps, J.F., Chun, J.S., Juristyarini, P., Leicht, S.E., Wattanachai, P., 2002. *A Comprehensive Laboratory and Field Study of High-Cure Crumb-Rubber Modified Asphalt Materials*. Texas Transportation Institute, The Texas A&M University System.

Glover, I.C., 2007. *Wet and Dry Aging of Polymer-Asphalt Blends: Chemistry and Performance*. A dissertation submitted to the graduate faculty of the Louisiana State University and Agricultural and

Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy - Department of Chemistry.

Goodrich, J.L., 1988. “Asphalt and polymer modified asphalt properties related to the performance of asphaltic concrete mixes”. *Proceedings of the Association of Asphalt Paving Technologists* 57, pp. 116-175.

Gopal, V.T., Sebaaly, P.E., Epps, J., 2002. “Effect of Crumb Rubber Particle Size and Content on the Low Temperature Rheological Properties of Binders”. *Transportation Research Board, Annual Meeting*, Washington D.C.

Green, E.L., Tolonen, W.J., 1977. *The Chemical and Physical Properties of Asphalt-Rubber Mixtures*. FHWA-AZ-HPR14-162, Arizona Department of Transport, Report ADOT-RS-14 (162).

Hagen, A.P., Jones, R., Hofener, R.M., Randolph, B:B:, Johnson, M.P., 1984. “Characterization of Asphalt by Solvent Profile”. *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 53, pp. 119-137.

Hamed, G.R., 1992. “Materials and Compounds”. *Engineering with Rubber: How to Design Rubber Components*, from Alan N. Gent, Hanser Publishers, Germany.

Heitzman, M., 1992. “Design and Construction of Asphalt Paving Materials with Crumb Rubber Modifier”. *Transportation Research Record* 1339, TRB, National Research Council, Washington, DC., pp. 1-8.

Heitzman, M., 1992. *State of the Practice for the Design and Construction of Asphalt Paving Materials with Crumb Rubber Additive*. Report No. FHWA-SA-92-022, Office of Engineering, Pavement Division, Federal Highways Administration.

Herzog, P., Tchoubar, D., Espinat, D., 1988. “Macrostructure of Asphaltene Dispersions by Small-Angle X-Ray Scattering”. *Fuel*, Vol. 67, pp. 245-250.

Jennings, P.W., 1980. *High Pressure Liquid Chromatography as a Method of Measuring Asphalt Composition*. Report No. FHWA-MT-7930, Dept. of Chemistry, Montana St. Univ., Bozeman, Mt.

Jensen, W., Abdelrahman, M., 2006. *Crumb Rubber in Performance-Graded Asphalt Binder*. Nebraska Department of Roads, Final Report, SPR-01 (05) P585, University of Nebraska-Lincoln.

Jimenez, R., 1978. *Testing Methods for Asphalt-Rubber*. Report ADOT-RS-15(164), Arizona Department of Transportation.

Jones, D.R.IV, Kennedy, T.W., 1992. *The Asphalt Model: Results of the SHRP Asphalt Research Program. SHRP A-001*. Center for Transportation Research University of Texas, Austin, Texas, USA.

Kariyo, S., Stapf, S., 2004. “NMR Relaxation Dispersion of Vulcanized Natural Rubber”. *Solid State Nuclear Magnetic Resonance*, Vol. 25 (1-3), pp. 64-71.

Khalid, H.A., 2005. *Recent Research on Use of Rubber in Asphalt*. WRAP Rubber in Roads Seminar, University of Liverpool.

Kumnuantip, C., Sombatsompop, N., 2003. “Dynamic Mechanical Properties and Swelling Behaviour of NR/Reclaimed Rubber Blends”. *Materials Letters*, Vol. 57 (21), pp. 3167-3174.

Labout, J.W.A., 1950. “Constitution of Asphaltic Bitumen”. *The Properties of Asphaltic Bitumen*. Pfeiffer, J.Ph. (Ed.). Elsevier, Amsterdam.

Labout, J.W.A., 1958. “The Micro-Elastometer. A Micro-Device for Measuring the Modulus of “Stiffness” of Small Samples of Thermoplastic Materials”. *Rheologica Acta*, Vol. 1 (2-3), pp. 186-189.

Lalwani, S., Abushahada, A., Halasa, A., 1982. “Reclaimed Rubber-Asphalt Blends Measurements of Rheological Properties to Assess Toughness, Resiliency, Consistency and Temperature Sensitivity”. *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 51.

Leite, L.F.M., Soares, B.G., 1999. “Interaction of Asphalt With Ground Tire Rubber”. *Petroleum Science and Technology*, 17 (9), pp. 1071-1088.

Leontaritis, K.J., Mansoori, G.A., 1989. “Fast Crude-Oil Heavy-Component Characterization Using Combination of ASTM, HPLC and GPC Methods”. *Journal of Petroleum Science Engineering*, 1.

Lewandowsky, L.H., 1994. “Polymer Modification of Paving Asphalt Binders”. *Rubber Chemistry and Technology*, 67 (3), pp. 447-480.

Lima, C., Tomé, L., Filho, C., Soares, S., Soares, J., 2006. “Aging Studies of Asphalt-Rubber Binder”. *Asphalt Rubber 2006 Conference*, Palm Springs, USA, pp. 797-812.

Loeber, L., Muller, G., Morel, J., Sutton, O, 1998. “Bitumen in Colloid Science: A Chemical, Structural and Rheological Approach”. *Fuel*, Vol. 77 (13), pp. 1443-1450.

Lu, X., Redelius, P., 2006. “Compositional and Structural Characterization of Waxes Isolated from Bitumens”. *Energy & Fuels*, 20 (2), pp. 653-660.

Lubbers, H.E., 1985. *Bitumen in de Wegen Waterbauw*. Netherlands Adviesbureau voor Bitumen to Epassingen, Gouda.

Mack, C., 1932. “Colloid Chemistry of Asphalts”. *The Journal of Physical Chemistry*, Vol. 36, pp. 2901-2914.

Martinez, G., Caicedo, B., Celis, L., González, D., 2006. “Rheological Behaviour of Asphalt with Crumbed Rubber and other Modifiers”. *Asphalt Rubber 2006 Conference*, Palm Springs, USA, pp. 863-884.

Masson, J.-F., Leblond, V., Margeson, J., 2006. “Bitumen Morphologies by Phase-Detection Atomic Force Microscopy”. *Journal of Microscopy*, Vol. 221 (1), pp. 17-29

Masson, J.-F., Pelletier L., Collins, P., 2001. “Rapid FTIR Method for Quantification of Styrene-Butadiene Type Copolymers in Bitumen”. *Journal of Applied Polymer Science*, Vol. 79 (5), pp. 1034-1041.

Masson, J.-F., Price, T., Collins, P., 2001. “Dynamics of Bitumen Fractions by Thin-Layer Chromatography/Flame Ionization Detection”. *Energy & Fuels*, 15 (4), pp. 955-960.

McDonald, C., 1966. “A New Patching Material for Pavement Failures”. *Highway Research Record* 146, HRB, p. 1.

McKenna, G.B., Flynn, K.M., Chen, Y., 1988. “Experiments on the Elasticity of Dry and Swollen Networks: Implications for the Frenkel-Flory-Rehner Hypothesis”. *Polymer Communications*, Vol. 29 (9), pp. 272-275.

McKenna, G.B., Flynn, K.M., Chen, Y., 1989. “Experiments on the Elasticity of Dry and Swollen Networks: Implications for the Frenkel-Flory-Rehner Hypothesis”. *Macromolecules*, 22, pp. 4507-4512.

McKenna, G.B., Flynn, K.M., Chen, Y., 1990. “Swelling in Cross-Linked Natural-Rubber - Experimental Evidence of the Cross-Link Density Dependence of X”. *Polymer*, 31, pp. 1937-1945.

McLean, J.D., Kilpatrick, P.K., 1997. “Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua”. *Energy Fuels*, 11, pp. 570-585.

Merdrignac, I., Espinat D., 2007. “Physicochemical Characterization of Petroleum Fractions: the State of the Art”. *Oil & Gas Science and Technology – Rev. IFP*, Vol. 62 (1), pp. 7-32.

Michon, L., Hanquet, B., Diawara, B., Martin, D., Planche, J.-P., 1997. “Asphalt Study by Neuronal Networks. Correlation between Chemical and Rheological Properties”. *Energy & Fuels*, 11 (6), pp. 1188-1193.

Miskolczi, N., Nagy, R., Bartha, L., Halmos, P., Fazekas, B., 2008. “Application of Energy Dispersive X-Ray Fluorescence Spectrometry as Multielemental Analysis to Determine the Elemental Composition of Crumb Rubber Samples”. *Microchemical Journal*, Vol. 88 (1), pp. 14-20.

Murgich, J., Abanero, J.A., Strausz, O.P., 1999. “Molecular Recognition in Aggregates Formed by Asphaltene and Resin Molecules from the Athabasca Oil Sand”. *Energy Fuels*, 13, pp. 278-286.

Nellensteyn, F.J., 1924. “The Constitution of Asphalt”. *Journal of the Institute of Petroleum Technology*, 10, pp. 311-325.

Neto, S.A.D., Farias, M.M., Pais, J.C., Pereira, P.A.A., Sousa, J.B., 2006. “Influence of Characteristics of Crumb Rubber and Digestion Time on the Properties of Asphalt Rubber Binders”. *Road Materials and Pavement Design*, Vol. 7 (2).

Netzel, D.A., 2006. “Apparent Activation Energies for Molecular Motions in Solid Asphalt”. *Energy & Fuels*, 20 (5), pp. 2181-2188.

Oliver, J., 1981. “Modification of Paving Asphalts by Digestion with Scrape Rubber”. *Transportation Research Record* 821, TRB, National Research Council, Washington, D.C.

Ortega-Rodriguez, A., Cruz, S.A., Gil-Villegas, A., Guevara-Rodriguez, F., Lira-Galeana, C., 2003. “Molecular View of the Asphaltene Aggregation Behavior in Asphaltene-Resin Mixtures”. *Energy & Fuels*, 17 (4), pp. 1100-1108.

Ortega-Rodriguez, A., Duda, Y., Guevara-Rodriguez, F., Lira-Galeana, C., 2004. “Stability and Aggregation of Asphaltenes in Asphaltene-Resin-Solvent Mixtures”. *Energy & Fuels*, 18 (3), pp. 674-681.

Ould-Henia, M., Dumont, A.-G., 2006. “Assessment of the Rheological Properties of Asphalt Rubber Binder and its Residual Phases”. *Asphalt Rubber 2006 Conference*, Palm Springs, USA, pp. 931-948.

Overfield, R.E., Sheu, E.Y., Sinha, S.K., Liang, K.S., 1989. “SANS Study of Asphaltene Aggregation”. *Fuel Sci. Tech. Intl.*, Vol. 7, pp. 611-624.

Oyekunle, L.O., 2006. "Certain Relationships between Chemical Composition and Properties of Petroleum Asphalts from Different Origin". *Oil & Gas Science and Technology – Rev. IFP*, Vol. 61 (3), pp. 433-441.

Oyekunle, L.O., 2007. "Influence of Chemical Composition on the Physical Characteristics of Paving Asphalts". *Petroleum Science and Technology*, Vol. 25 (11), pp. 1401-1414.

Park, S.J., Mansoori, G.A., 1988. "Aggregation and Deposition of Heavy Organics in Petroleum Crudes". *Energy Sources*, 10, pp. 109-125.

Pauli, A.T., Branthaver, J.F., Robertson, R.E., Grimes, W., Eggleston, C.M., 2001. *Atomic Force Microscopy Investigation of SHRP Asphalts: Heavy Oil and Resid Compatibility and Stability*. American Chemical Society. Division of Petroleum Chemistry, San Diego, California, pp. 110-114.

Petersen, J.C., 1984. "Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art", *Transportation Research Board* 999, pp. 13-30.

Petersen, J.C., Robertson, R.E., Branthaver, J.F., Harnsberger, P.M., Duvall, J.J., Kim, S.S., Anderson, D.A., Christiansen, D.W., Bahia, H.U., Dongre, R., Antle, C.E., Sharma, M.G., Button, J.W., Glover, C., 1994. *Binder Characterization and Evaluation, Volume 4: Test Methods. Report No. SHRP-A-370*. Strategic Highway Research Program, National Research Council, Washington, D.C.

Pfeiffer, J., Saal, R.N.J., 1940. "Asphaltic Bitumen as Colloid System". *The Journal of Physical Chemistry*, Vol. 44 (2), pp. 139–149.

Pfeiffer, J.P., Van Doormaal, P.M., 1936. "The Rheological Properties of Asphaltic Bitumen". *Journal of the Institute of Petroleum Technologists*, 22, p. 414.

PIARC, 1999. "Modified Binders, Binders with Additives and Special Bitumen". *Roads, PIARC Journal*, 303, pp. 88-91;106-107.

Polymer Science Learning Center, 2005. *The Macrogalleria – A Cyberwonderland of Polymer Fun!* Department of Polymer Science, The University of Southern Mississippi. Web. 22 Apr 2008. <http://www.pslc.ws/mactest/index.htm>.

Porter, J., 1991. *Highway Research, Sharing the Benefits. Proceedings of the Conference The United States Strategic Highway Research Program*. Institution of Civil Engineers, Thomas Telford ed., London.

prEN 15323, 2005. *Bitumen and Bituminous Binders: Accelerated long-term Ageing Conditioning by the Rotating Cylinder Method (RCAT)*. Comité Européen de Normalisation. Draft for CEN Enquiry.

Putman, B.J., Amirkhanian, S.N., 2006. "Crumb Rubber Modification of Binders: Interaction and Particle Effects". *Asphalt Rubber 2006 Conference*, Palm Springs, USA, pp. 655-677.

Rahman, M.M., 2004. *Characterisation of Dry Process Crumb Rubber Modified Asphalt Mixtures*. Thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy, University of Nottingham, School of Civil Engineering.

Raki, L., Masson, J.-F., Collins, P., 2000. "Rapid Bulk Fractionation of Maltenes into Saturates, Aromatics, and Resins by Flash Chromatography". *Energy & Fuels*, 14 (1), pp. 160-163.

Ravey, J.C., Ducouret, G., Espinat, D., 1988. “Asphaltene Macrostructure by Small Angle Neutron Scattering”. *Fuel*, Vol. 67, pp. 1560-1567.

Read, J., Whiteoak, C.D., 2003. *The Shell Bitumen Handbook*. Fifth edition, Shell Bitumen UK, Thomas Telford Publishing, London.

Recipneu, 2006. *Company, Products and Technology*. Recipneu, Empresa Nacional de Reciclagem de Pneus, Lda. Web. 23 Apr 2008. <http://www.recipneu.com/uk/empresa_tecnologia.html>.

Redelius, P., 2004. “Bitumen Solubility Model Using Hansen Solubility Parameter”. *Energy & Fuels*, 18 (4), pp. 1087-1092.

Reschner, K., 2006. *Scrap Tire Recycling - A Summary of Prevalent Disposal and Recycling Methods. Berlin*. Web. 23 Apr 2008. <http://www.entire-engineering.de/Scrap_Tire_Recycling.pdf>.

Robertson, R.E., 1991. *Chemical Properties of Asphalts and Their Relationship to Pavement Performance*. Western Research Institute, Strategic Highway Research Program, National Research Council, Washington, D.C.

Rodríguez-Valverde, M.A., Ramón-Torregrosa, P., Páez-Dueñas, A., Cabrerizo-Vílchez, M.A., Hidalgo-Álvarez, R., 2008. “Imaging Techniques Applied to Characterize Bitumen and Bituminous Emulsions”. *Advances in Colloid and Interface Science*, Vol. 136 (1-2) (15), pp. 93-108.

Rosner, J.C., Chehovits, J.G., 1982. *Chemical and Physical Properties of Asphalt-Rubber Mixtures – Part III, vol. 4 – Physical Properties of Field-Mixed Asphalt-Rubber Mixtures and Comparisons of Lab and Field-Mixed Asphalt-Rubbers*. Report no. FHWA/AZ-82/159/4, Arizona Department of Transportation.

Rouse, M.W., 1997. “Production, Identification, and Application of Crumb Rubber Modifiers for Asphalt Pavements”. *Asphalt Science and Technology*, Ed. Arthur M. Usmani, pp. 385-442.

Rozeveld, S., Shin, E., Bhurke, A., France, L., Drzal, L., 1997. “Network Morphology of Straight and Polymer Modified Asphalt Cements”. *Microscopy Research and Technique*, 38, pp. 529-543.

Senglet, N., Williams, C., Faure, D., Courieres, T., Guilard, R., 1990. “Microheterogeneity Study of Heavy Crude Petroleum by U.V.-Visible Spectroscopy and Small Angle X-Ray Scattering”. *Fuel*, Vol. 69, pp. 72-77.

Shulman, V.L., 2000. *Tyre Recycling After 2000: Status and Options*. European Tyre Recycling Association, Paris, France.

Simpson, W.C., Griffin, R.L., Miles, T.K., 1961. “Relationship of Asphalt Properties to Chemical Constitution”. *Journal of Chemical and Engineering Data*, Shell Development Co., Emeryville, California, pp. 426-429.

Singleton, T.M., Airey, G.D., Widyatmoko, I., Collop A.C., 2000. “Residual Bitumen Characteristics Following Dry Process Rubber-Bitumen Interaction”. *Asphalt Rubber 2000 Conference*, Vilamoura, Portugal, pp. 463-482.

Speight, J.G., 1999. *The chemistry and Technology of Petroleum*. 3rd. Marcel Dekker, New York.

Stangl, K., Jäger, A., Lackner, R., 2006. “Microstructurebased Identification of Bitumen Performance”. *Int J Road Mater Pavement Design*, 7, p. 111.

Stangl, K., Jäger, A., Lackner, R., 2007. “The Effect of Styrene-Butadiene-Styrene Modification on the Characteristics and Performance of Bitumen”. *Monatshefte für Chemie Chemical Monthly*, 138, pp. 301-307, Netherlands.

Stern, H.J, 1967. *Rubber: Natural and Synthetic*. Maclaren and Sons Ltd, London.

Storm, D.A., Sheu, E.Y., 1993. “Rheological Studies of Ratawi Vacuum Residue at 366 K”. *Fuel*, Vol. 72, pp. 233-237.

Tia, M., Ruth, B.E., 1987. “Basic rheology and rheological concepts established by H. E. Schweyer”. *Asphalt rheology: Relationship to mixture. ASTM STP 941*, O. E. Briscoe, Ed., American Society for Testing and Materials, Philadelphia, pp. 118-145.

Traxler, R.N., 1961. *Asphalt: Its Composition, Properties and Uses*. Reinhold, New York.

Usmani, A.M., 1997. *Asphalt Science and Technology*. CRC Press, Marcel Dekker Inc., New York – Basel – Hong Kong.

van der Poel, C., 1954. “A General System Describing the Visco-Elastic Properties of Bitumens and Its Relation to Routine Test Data”. *Journal of Applied Chemistry*, 4, pp. 221-236.

Whiteoak, D., 1990. *The Shell Bitumen handbook*. Fourth edition, Shell Bitumen UK, Chertsey.

Yapp, M.T., Durrani, A.Z., Finn, F.N., 1991. *HP-GPC and Asphalt Characterization Literature Review*. SHRP-A/ULR-91-503, SHRP, NRC, Washington, DC.

Yen, T.F., Erdman, J.G., Pollack, S.S., 1961. “Investigation of the Structure of Petroleum Asphaltenes by X-Ray Diffraction”. *Analytical Chemistry*, 33, pp. 1587-1594.

Youtcheff, J.S., 2006. *Asphalt technology handbook*. Marcel Dekker Inc.

Youtcheff, J.S., Jones, D.R.IV, 1994. *Guideline for Asphalt Refiners and Suppliers*. Strategic Highway Research Program, National Research Council, Washington, DC.

Zanzotto, L., Kennepohl, G.J., 1996. “Development of Rubber and Asphalt Binders by Depolymerization and Devulcanization of Scrap Tires in Asphalt”. *Transportation Research Record* 1530, TRB, National Research Council, Washington, DC., pp. 51-58.

Zhao, S., Kotlyar, L.S., Woods, J.R., Sparks, B.D., Gao, J., Chung, K.H., 2003. “The Chemical Composition of Solubility Classes from Athabasca Bitumen Pitch Fractions”. *Petroleum Science and Technology*, 21 (1), pp. 183-199.