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Modification of binder with tyre rubber and polymeric networks for usage in road asphalt mixes

Memoria para optar al grado de doctora
presentada por:

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Fecha de lectura: 17 de abril de 2020

Bajo la dirección de los doctores:

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Huelva, 2020

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MODIFICATION OF BINDER WITH TYRE RUBBER AND POLYMERIC NETWORKS FOR USAGE IN ROAD ASPHALT MIXES

Ph. D. Thesis

Doctoral Program in Industrial and Environmental Science and Technology

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2019

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Contents

Abstract

Hybrid modification is a relatively new concept of incorporating two or more polymeric modifiers of different nature to a bitumen, in order to take advantage of their complementary features. However, the problem of its inherent storage instability is a major concern that limits the industrial application. Hybrid Systems (HSs) were formulated by the addition of different copolymer (reactive and non-reactive) to a model rubberised binder (Crumb Tyre Rubber Modified Bitumen). The resulting HSs were evaluated by means of thermos rheological analysis, technological characterisation, fluorescence microscopy and modulated differential scanning calorimetry. The results obtained pointed out that both, in-service properties and storage stability were notably enhanced by the development of a complex multiphasic structure of: polymer-rich and asphaltene-rich phases, non-degraded rubber particles and digested rubber chains. This enhancement is attributed to the development of a multiphasic system composed of non-dissolved CTR particles, a polymer-rich phase and an asphaltene rich-phase. In the case of non-reactive HSs, droplets of swollen ethylene copolymer form a well-defined dispersed phase. By contrast, reactive HSs display a different morphology, almost invisible by optical techniques, as consequence to the development of a chemical network that yields by far the highest degree of modification.

Chapter I: LITERATURE REVIEW

1.1. INTRODUCTION

According to the current European specifications (EN 12597), bitumen is defined as a “virtually involatile, adhesive and waterproofing material derived from crude petroleum, or present in natural asphalt, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperatures”. In addition, a toluene solubility of greater than 99% is required for bitumen used in paving applications (EN 12591). This European definition of bitumen is equivalent to American definitions of asphalt or asphalt cement (Krishnan, Rajagopal 2003).
Nowadays bitumen is the most used binder for street paving, thanks to its properties that depend on the chemical composition. It is sticky, black and highly viscous liquid or semi-solid form of petroleum which can be found in “natural” form in the pitch lakes or it can be a refined product.

From a performance point of view, bitumen is one of the most important constituents of an asphalt mixture (mixture of aggregates, binder and fillers). A typical road pavement is composed by a mixture of mineral aggregates with only 5% of bitumen, which just acts as a binder. However, despite this small amount, bitumen controls the properties of the resulting pavement.

The use of bitumen in pavement construction started in the early nineteenth century (Abraham, 1960; Cebon, 1993). Bitumen is one of the oldest engineering materials. There are records of the use of bitumen in the ancient times as mortar between bricks and stones, as waterproofing agent, and as a material to embalm mummies (Egypt, B.C. 2600) etc. According to Roberts et al. (1996), a Sumerian who thrived on shipbuilding industry used the material in B.C. 6000. The Sumerians also used the black material for inlaying shells, precious stones, and pearls (WSDOT, 2006). Around 1500 A.D., there were records of the use of a material similar to the modern bituminous macadam to pave the Incas’ highway system in Peru. In modern times, the first roadway in the U.S. to be paved using asphalt was Pennsylvania Avenue in Washington D.C., in 1876 (Roberts et al., 1996).

Krishnan and Rajagopal (2003) referred to the Shell Bitumen Handbook to summarize more than 250 known current uses of bitumen in agriculture, construction, hydraulics, erosion control, automobile industry, electrical industry, railways, paving industry, etc. According to the authors, however, the most widespread use of bitumen is in the construction of roadways and runways.

1.2. BASIC CONCEPTS OF BITUMEN

Bitumen is a complex material with a complex response to stress. The response of bitumen to stress is dependent on both temperature and loading time and the degree to which their behaviour viscous and elastic is a function of both temperature and loading time. At high temperatures or long loading times, bitumens behave as viscous liquids whereas at very low temperatures or short times of loading they behave as elastic (brittle) solids. The most typical conditions in service result in viscoelastic behaviour (Whiteoak et al., 2003).

Changing bitumen' viscoelastic characteristic in production and in-service temperatures is the main part of most of the recent technologies.

For this reason, it is vitally important to have solid knowledge about bitumen properties and their influence on the viscoelastic behaviour in order to determine the right production and paving temperature and predict asphalts behaviour for long term in-service life.

1.2.1. Bitumen Composition and Structure

Both the chemical (constituent) and the physical (structural) part of the bitumen comprise mainly hydrocarbons with minor amounts of heteroatoms such as oxygen, nitrogen and sulphur. As bitumen is extracted from crude oil, which has variable composition according to its origin, the precise breakdown of hydrocarbon groups in bitumen is difficult to determine. However, elementary analysis of bitumen manufactured from a variety of crude sources show that most bitumens contain:

- Carbon: 82-88%
- Hydrogen: 8-11%
- Sulphur: 0-6%
- Oxygen: 0-1.5%
- Nitrogen: 0-1%

The precise composition of bitumen varies according to the crude source. Although the chemical composition is very complex, it is possible to separate bitumen into four main chemical compositions (Whiteoak, 1990; Airey, 1997) known as SARA fractions;

- Asphaltenes
- Resins
- Aromatics
- Saturates

These four groups are not well defined and there is inevitably some overlap between them. A schematic representation of the bitumen structure is presented in Figure 1.1.

Asphaltenes are black or brown amorphous solids. They are highly polar, complex materials of high molecular weight (between 1,000 and 100,000 g/mol). Within an oily medium they tend to associate together to form micelles with a molecular weight between 20,000 and 1,000,000 g/mol (The Shell Bitumen Industrial Handbook, 1995). Asphaltenes typically constitute 5% to 25% of the bitumen. The molecular weight relates to the size of each molecule, so the higher the molecular weight the larger the molecules.

The asphaltenes content has a considerable effect on the rheological characteristics of bitumen. The higher the asphaltenes content, the higher the softening point and viscosity and the lower the penetration index. The association of asphaltenes is not fixed; on heating the gel structure (Figure 1.1) of the micelles is broken down and reformed on cooling. During long-term heating the asphaltenes micelles may break down, therefore, it is not unusual for the molecular weight of bitumen to decrease after heating. In short, asphaltenes define the stiffness and rigidity of the bitumen.

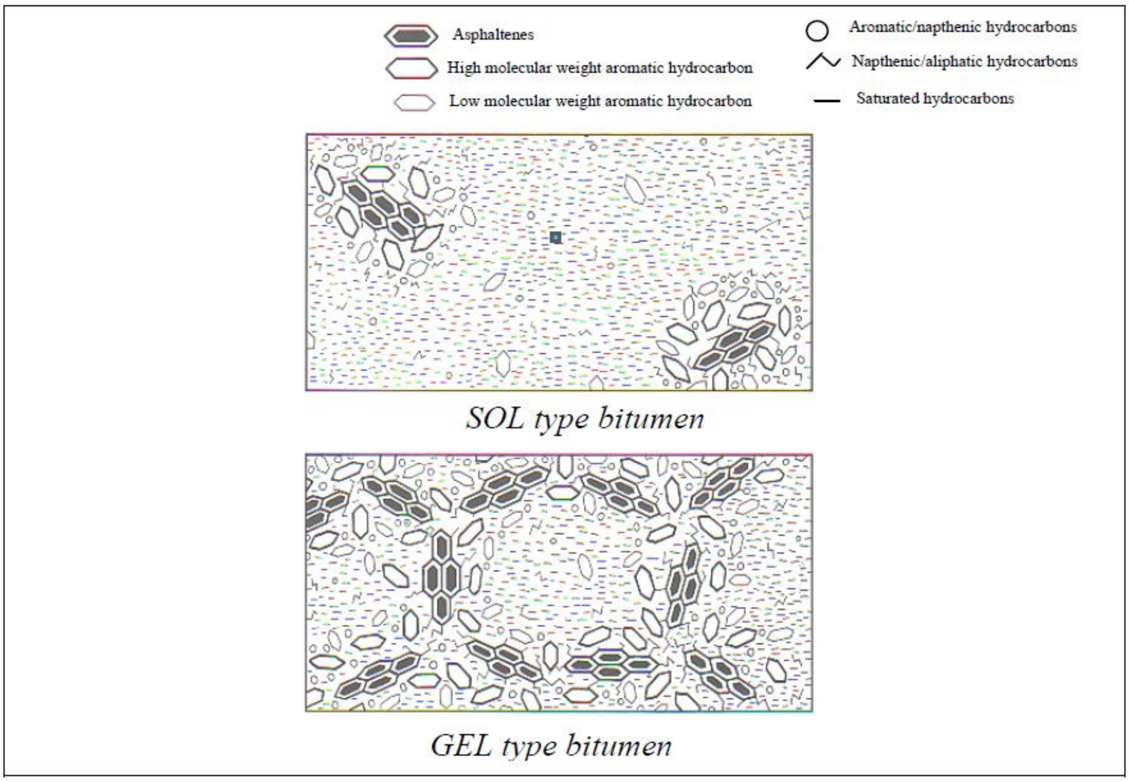


Figure 1.1: Schematic representation of typical bitumen structure (Whiteoak, 1990)

Resins are black or brown solid or semi-solid highly polar molecules. The high polarity makes the resins very adhesive. The molecular weight ranges from 500 to 50,000 g/mol. The resins act as a peptising agent for the asphaltenes, therefore an increase in resins results in a solution (sol) structure whereas a reduction forms a gelatinous (gel) structure in the bitumen (Figure 1.1) (The Shell Bitumen Industrial Handbook, 1995). Resins work as stabilisers, which hold everything together in the bitumen (Kerbs and Walker, 1971).

Aromatics have the lowest molecular weight and form the major proportion of the bitumen (40-65%). They present a very low polarity and form a dark brown viscous liquid that acts as a dispersion medium for the asphaltenes in the bitumen and have a molecular weight in the range of 300 to 20,000 g/mol (The Shell Bitumen Industrial Handbook, Shell Bitumen, Surrey, 1995). They give the adhesive properties of the bitumen.

Saturates are similar to oil and give the fluid properties of the bitumen. They have the lowest molecular weight (similar to aromatics) and are straw or white in color and form between 5-20% of the bitumen (The Shell Bitumen Industrial Handbook, 1995).

Bitumen, from a structural point of view, is a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in lower molecular weight oily medium (maltens) (Read, et al., 2003). The colloidal nature is responsible for the time dependence of the deformations of this material.

1.3. BITUMEN MODIFICATION

The properties and performance of bitumen can be improved by increasing the structure/composition (upgrading) and/or by adding additives to the bitumen (modification).

Thermoplastic polymers, thermo-set polymers, reinforce agents; adhesion, promoter, catalyst, chemical reaction, crumb rubber and aging inhibitors are used in modified of bitumen, in order to strength the road pavement and avoid the maintenance every year. However, not all types of modifiers are being currently used. The frequency of use varies significantly depending on the marketing of the modifiers, experience of contractors and agencies and cost (Bahia, 2007).

Some big oil companies have developed technologies (refinery processes) to produce upgraded bitumen. These so-called semi-hard multi-grade bitumen are stiffer at high temperature and less brittle at low temperature than conventional bitumen with the same penetration value at 25° C (i.e. they are less temperature susceptible). They are mainly applied to improve the permanent deformation. Only a few oil companies have the facilities and knowledge to produce these bitumens. Therefore, this technology cannot be applied to upgrade local bitumen.

1.3.1. Polymeric modification

Most of the modified bitumen for pavement applications are formulated with polymers. Therefore, Polymer Modified Bitumen (PMBs) are studied in this thesis. There are basically two types of polymers used for bitumen modification: thermoplastic elastomers and plastomers.

Thermoplastic elastomers increase stiffness and viscosity of the bitumen. The effect of these types of additives diminishes above their melting temperature (50 to 80 °C). Thermoplastic elastomer modified bitumen are mainly applied to improve the resistance to permanent deformation. Since they are often prone to phase separation, continuous mixing during storage is required. Examples of thermoplastic plastomers are Ethylene-Vinyl Acetate (EVA) and Polyethylene (PE). Copolymers such as styrene-butadienestyrene (SBS) triblock elastomers are most commonly used in commercially available polymer modified bitumens. Various studies have confirmed that bitumens modified with SBS present superior performance compared to pure bitumens. For example Qi et al. (1995) and Martinez-Boza et al. (2001) showed that SBS improves the thermal susceptibility of bitumen, while experiments by Elseifi et al. (2003) demonstrated that SBS increases the rutting and fatigue resistance of bitumen.

The effect of polymer modification not only depends on the type of polymer but also on the amount of polymer. In bitumen for road pavements polymers swell to maximum nine times their original volume.

In general, up to about 4% of polymer (by mass) the bitumen usually remains the continuous phase. The properties of these PMBs are dominated by the properties of the base bitumen. However, the polymer can already have a significant effect.

1.3.2. Rubberised binder

The use of crumb rubber in asphalt pavements is a technology developed by Charles McDonald, a City of Phoenix engineer. Asphalt rubber comes from the mixing of crumb rubber from waste tires and bitumen. This technology was first introduced in the late 1960’s as a surface treatment such as crack sealing and chip seals. By that time, the stockpiles of scrap tires where in the hundreds of millions of tires, so McDonald found that he could use a waste product at a low cost to improve the properties of asphalt binder. In his research, he found that a minimum of 15% of crumb rubber was needed to achieve the desired properties. McDonald’s work led to patented process, referred to as the wet mix process wherein the asphalt binder is mixed with the crumb rubber at 177 °C for about 45 minutes to let the binder digest the crumb rubber.

Crumb rubber modified asphalt was first introduced in asphalt pavements in the 1980’s and is especially used in gap and open graded mixes. The use of crumb rubber in asphalt pavement improved the mechanical properties of pavements, resistance to cracking and rutting as well as the reduction of environmental issues such as noise, energy consumption and CO_2 emissions (Way 2012).

Physical properties of rubber such as type, quantity, shape, gradation are said to affect the performance of rubber modified asphalt mixtures (Norhidayah et al., 2014).

To modify the asphalt pavement, two processes have been developed: the dry process and wet process. The dry process involves the blending of crumb rubber with hot aggregates prior to mixing with bitumen and substitutes a proportion of the mix aggregate with coarse rubber, thereby causing the rubber to function essentially as an elastic aggregate within the mixture while wet process is a whereby fine rubber is blended with hot bitumen to produce a 'rubberised bitumen' binder (Norhidayah et al., 2014). Although decades of research have been dedicated to the study of Crumb Tired Rubber (CTR) mixtures, results produced have been largely inconsistent. The difference in wet mixing process and dry mixing process are illustrated in below Figure 1.2 and Figure 1.3. Figure 1.2 show the wet process method where rubber particles are mixed with asphalt at elevated temperature prior to mixing with the hot aggregates. Figure 1.3 show the dry process, where rubber particles replace a small portion of the mineral aggregate in asphalt mix before the addition of the bitumen.

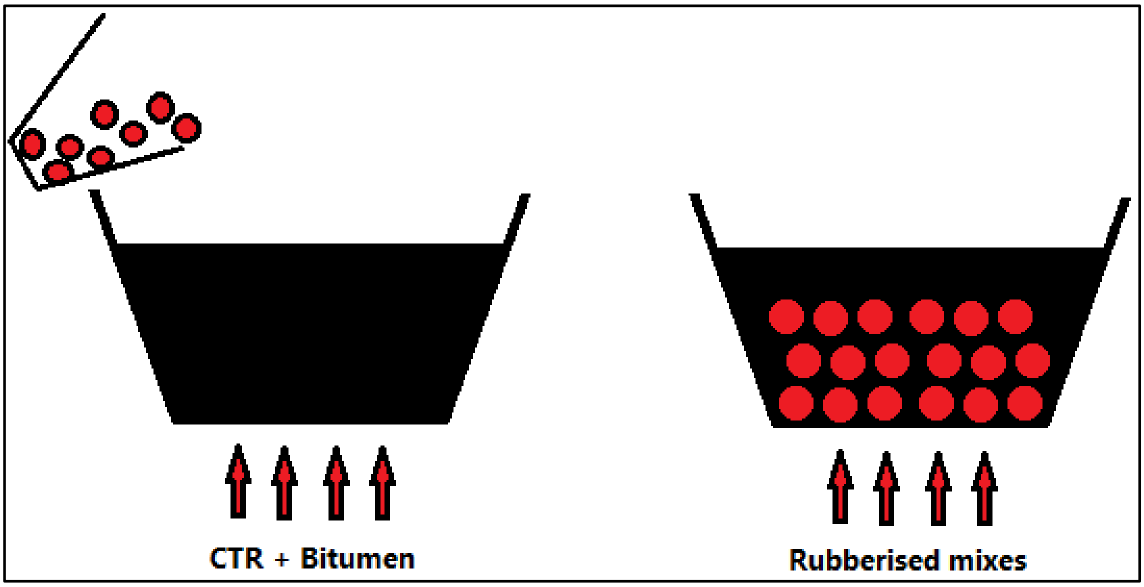


Figure 1.2 Wet Process method

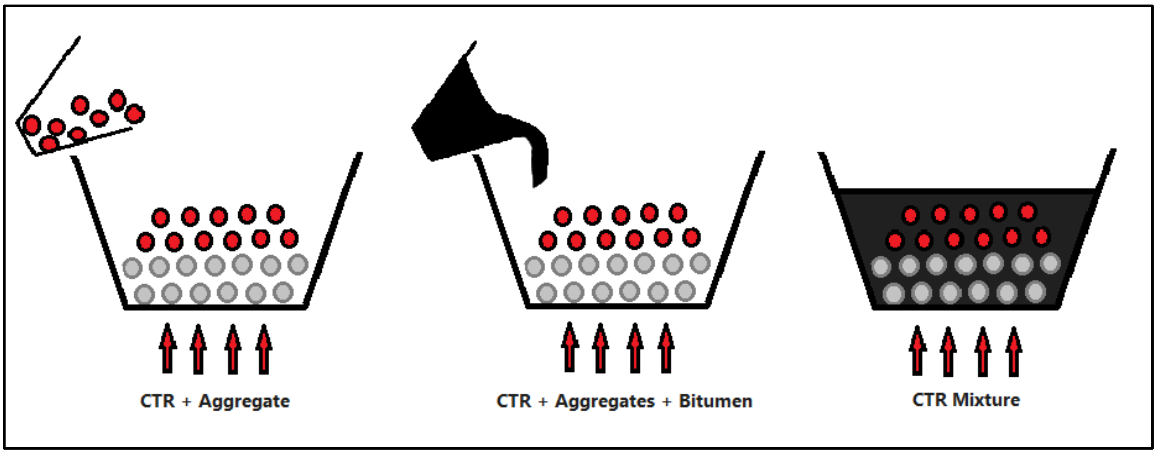


Figure 1.3 Dry Process method

The main differences between these processes are listed below:

- particle size is much finer in the wet process rubber.
- the amount of rubber in the dry process is from 2 to 4 times lower than in the wet process.
- in the dry process, it acts more like the filler, and finally the ease of incorporation into mix; the dry process no special equipment is required while in the wet process special mixing chambers, reaction and blending tanks, and oversized pumps and required.

1.4. BITUMEN RHEOLOGY

Rheology is the science of deformation and flow of matter (Barnes, et al., 1989), a discipline that studies the stress-strain interaction in the materials and it allows to forecast its behaviour under well-defined conditions. Together with chemical inquiries and large-scale tests, the study of bitumen rheology is central in the project of long-life pavements.

If a load is applied to a purely elastic material, the deformation produced will return to zero immediately after the removal of the stress. For a purely viscous material deformation increases as long as a stress is applied but this deformation remains at its maximum after removing the stress. However, for a viscoelastic material such as bitumen, part of the deformation is recovered while part remains after removing the stress. The viscoelastic properties of bitumen are therefore a combination of those found for purely elastic and purely viscous materials. Prior to any attempt to characterise the behaviour of the bitumen, a thorough understanding of the structure and properties of its components is necessary.

The classical theory of elasticity (from 1678) deals with mechanical properties of elastic solids, for which, in accordance with Hooke´s law, stress (τ) is always directly proportional to strain (γ) in small deformations but independent of the rate of strain . The proportionality constant (G) is called the elastic modulus:

$$\tau = G \cdot \gamma \tag{2.3}$$

The classical theory of hydrodynamics (from 1687) deals with properties of viscous liquids, for which, in accordance with Newton´s law, the stress is always directly proportional to the rate of strain but independent of the strain itself. The proportionality constant (η) is called viscosity:

$$\tau = \eta \cdot \dot{\gamma} \tag{2.4}$$

These two categories are idealizations. However, the vast majority of materials show a rheological behaviour that classifies them to a region somewhere between the liquids and the solids.

The rheological properties of materials are established analysing the relation between stress or strain applied to a material and the flow or/and the resultant deformation (Whorlow, 1992). However, before making a classification of fluid behaviour, it would be appropriate to understand some important concepts.

Rheological properties define the relationship between stress and strain/strain rate in different types of shear and extensional flows. As shown in Figure 1.4, in shear flows liquid elements flow over or past each other; in extensional flow, instead, adjacent elements flow towards or away from each other (Barnes et al., 2000).

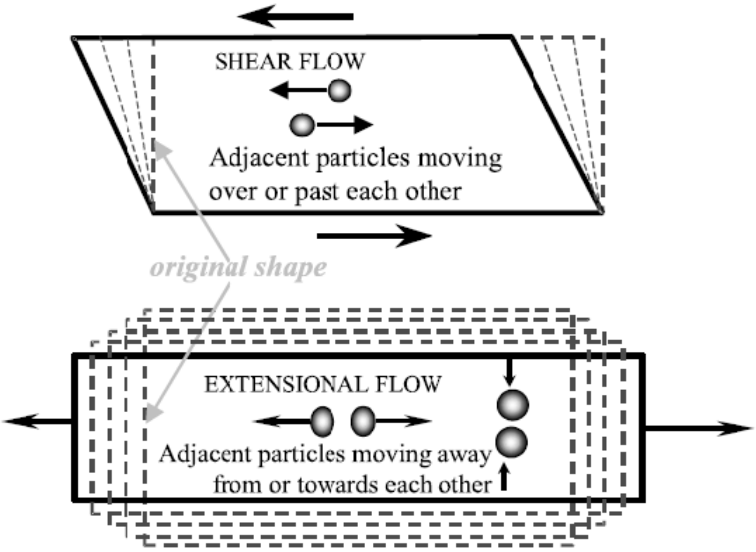


Figure 1.4. Particle motion in shear and extensional flows.

The stress is defined as the force F acting on a unit area A. Since both force and area have directional as well as magnitude characteristics, stress is a second order tensor and typically has nine components. Strain is a measure of deformation or relative displacement and is determined by the displacement gradient. Since displacement and its relative change both have directional properties, strain is also a second order tensor with nine components.

When a force F is applied to a piece of material (Figure 1.5), the total stress acting on any infinitesimal element is composed of two fundamental classes of stress components (Darby, 1976):

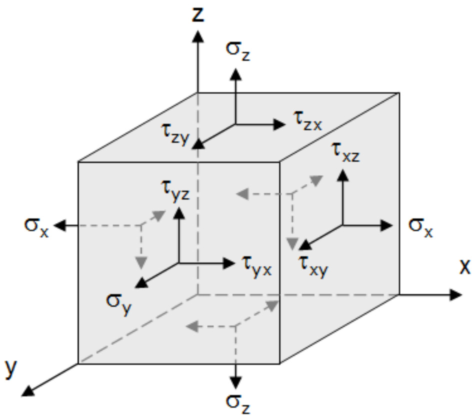


Figure 1.5. Stress components on a cubical material element.

Normal stress component, applied perpendicularly to the plane (σx, σy, σz). Shear stress components, applied tangentially to the plane (τxy, τxz, τyx, τyz, τzx, τzy).

There are a total of nine stress components acting on an infinitesimal element (i.e., two shear components and one normal stress component acting on each of the three planes). Individual stress components are referred to as τij, where i refers to the plane the stress acts on, and j indicates the direction of stress component (Bird et al., 1987). The stress tensor can be written as a matrix of nine components as follows:

$$\tau = \begin{Bmatrix} \sigma_x & \tau_{xy} & \tau_{xz} \\ \tau_{yz} & \sigma_y & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_z \end{Bmatrix} \tag{2.5}$$

One of the most useful types of deformation for rheological measurements is simple shear. In this type, a material element is placed between two parallel plates (Figure 1.6) where the bottom plate is stationary and the upper plate is displaced in x-direction by applying a force F tangentially to the surface A. The velocity profile in simple shear is given by the following velocity components:

$$v_x = \dot{\gamma} \cdot y \qquad v_y = 0 \qquad v_z = 0 \tag{2.6}$$

The corresponding shear stress is given as:

$$\tau = \frac{F}{A} \tag{2.7}$$

In this simple case, the shear rate may be expressed as the velocity gradient in the direction perpendicular to that of the shear force, i.e.,

$$\dot{\gamma} = \frac{dV_x}{dy} = \frac{\tau}{\eta} \tag{2.8}$$

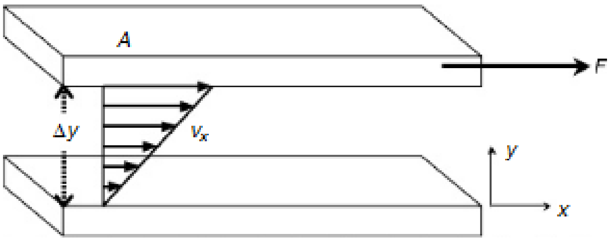


Figure 1.6. Simple shear between two parallel plates.

1.4.1. Classification of fluid behaviour

1.4.1.1. Newtonian fluid behaviour

A Newtonian fluid is characterized by a linear relationship between the applied shear stress and the rate of shear:

$$\tau_{yx} = \frac{F}{A} = \eta \cdot \dot{\gamma}_{yx} \tag{2.9}$$

According to the above-described Newton´s law, the proportionality constant (η) is called shear viscosity. This parameter is a property of the material and depends on its physical constitution, pressure and temperature. A Newtonian fluid is, of course, an idealization, but in many cases it is a very good representation of a large number of liquids under normal “everyday” conditions.

1.4.1.2. Non-Newtonian fluid

A non-Newtonian fluid is one whose flow curve (shear stress versus shear rate) is nonlinear or does not pass through the origin. So, its apparent viscosity, shear stress divided by shear rate, is not constant at a given temperature and pressure, but it depends on flow conditions (such as flow geometry, shear rate, etc.) and sometimes even on the kinematic history of the fluid element under consideration. Such materials may be conveniently grouped into three general classes, although most of real materials often exhibit a combination of two types of non-Newtonian features:

(1) Fluids for which the rate of shear at any point is determined only by the value of the shear stress at that point at that instant; these fluids are variously known as “time independent”, “purely viscous”, “inelastic” or “generalized Newtonian fluids” (GNF).

(2) More complex fluids for which the relation between shear stress and shear rate depends, in addition, upon the duration of shearing and their kinematic history. They are called “time-dependent fluids”.

(3) Substances exhibiting characteristics of both ideal fluids and elastic solids and showing partial elastic recovery, after deformation; these are categorized as “visco-elastic fluids”.

Each type of non-Newtonian fluid behaviour will now be dealt with in some detail.

1.4.2. Time-independent fluid behaviour

In simple shear, the flow behaviour of this class of materials may be described by a constitutive relation of the form:

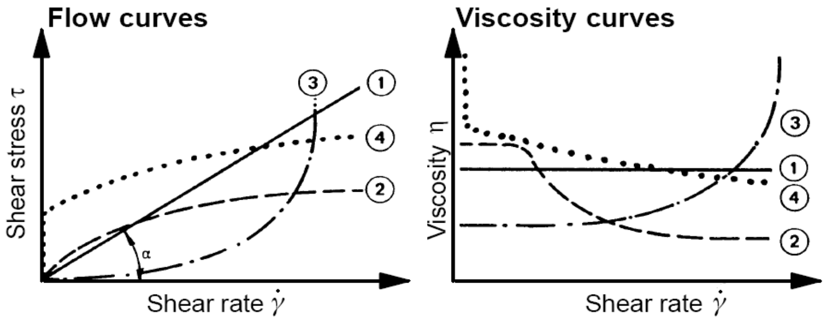
$$\dot{\gamma}_{yx} = f(\tau_{yx}) \tag{2.10}$$

This equation implies that the value of $\dot{\gamma}_{yx}$ at any point within the sheared fluid is determined only by the current value of shear stress at that point or vice versa. Depending upon the form of the function in equation (2.10), these fluids may be further subdivided into three types (Figure 1.7):

(a) Shear-thinning or pseudoplastic.

(b) Viscoplastic.

(c) Shear-thickening or dilatant.



(a) (b)

Figure 1.7. Flow curves (a) and viscosity curves (b) for fluids: [1] Newtonian, [2] shear-thinning, [3] shear-thickening and [4] viscoplastic.

1.4.2.1. Shear-thinning or pseudoplastic

It is the most common type of time-independent non-Newtonian fluid behaviour, characterized by an apparent viscosity which decreases with increasing shear rate. Many substances such as emulsions, suspensions, or dispersions of high technical and commercial importance belong to this group (Gebhard Schramm, 1998).

For most fluids, the shear-thinning effect is reversible, often with some time lag. It should be mentioned that the shear-thinning or pseudoplastic behaviour is not uniform over the range of very low to very high shear rates.

1.4.2.2. Viscoplastic fluid behaviour

This type of fluid behaviour is characterized by the existence of a yield stress (τ_y) which must be exceeded before the fluid will deform or flow. Conversely, such a material will deform elastically (or flow *en masse* like a rigid body) when the externally applied stress is smaller than the yield stress. Once the magnitude of the external stress has exceeded the value of the yield stress, the flow curve may be linear or non-linear but will not pass through origin. A fluid with a linear flow curve for $|\tau_{yx}| > |\tau_y|$ is called a Bingham plastic fluid.

It is interesting to note that a viscoplastic material also displays an apparent viscosity which decreases with increasing shear rate. At very low shear rates, the apparent viscosity is effectively infinite at the instant immediately before the substance yields and begins to flow. It is thus possible to regard these materials as possessing a particular class of shear-thinning behaviour.

Strictly speaking, it is virtually impossible to ascertain whether any real material has a true yield stress or not, but nevertheless the concept of a yield stress has proved to be convenient in practice because some materials closely approximate to this type of flow behaviour (Barnes and Walters, 1985; Schurz, 1990; Evans, 1992).

1.4.2.3. Shear-thickening or dilatant fluid behaviour

Shear-thickening fluids are similar to shear-thinning systems in that they show no yield stress, but their apparent viscosity increases with increasing shear rate. This type of fluid behaviour was originally observed in concentrated suspensions.

Of the time-independent fluids, this sub-class has received very little attention. Consequently very few reliable data are available. Until recently, shear-thickening fluid behaviour was considered to be much less widespread in the chemical and processing industries. However, with the growing interest in the handling and processing of systems with high solids loadings, it is no longer so, as is evidenced by the number of recent review articles on this subject (Barnes, 1989; Boersma et al., 1990; Goddard and Bashir, 1990).

1.4.3. Time-dependent fluid behaviour

Apparent viscosities may depend not only on the rate of shear but also on the time for which the fluid has been subjected to shearing.

Time-dependent fluid behaviour may be further sub-divided into two categories: thixotropy and rheopexy or negative thixotropy.

1.4.3.1. Thixotropy

A material is said to exhibit thixotropy if, when it is sheared at a constant rate, its apparent viscosity (or the corresponding shear stress) decreases with the time of shearing. If the flow curve is measured in a single experiment in which the shear rate is steadily increased at a constant rate from zero to some maximum value and then decreased at the same rate to zero again, a hysteresis loop of the form shown in Figure 1.8 is obtained; the height, shape and enclosed area of the hysteresis loop depend on the duration of shearing, the rate of increase/decrease of shear rate and the past kinematic history of the sample. Broadly speaking, the larger the enclosed area, stronger is the time-dependent behaviour of the materials.

1.4.3.2. Rheopexy or negative thixotropy

The relatively few fluids for which the apparent viscosity (or the corresponding shear stress) increases with time of shearing are said to display rheopexy or negative thixotropy. Again, hysteresis effects are observed in the flow curve, but in this case it is inverted, as compared with a thixotropic material.

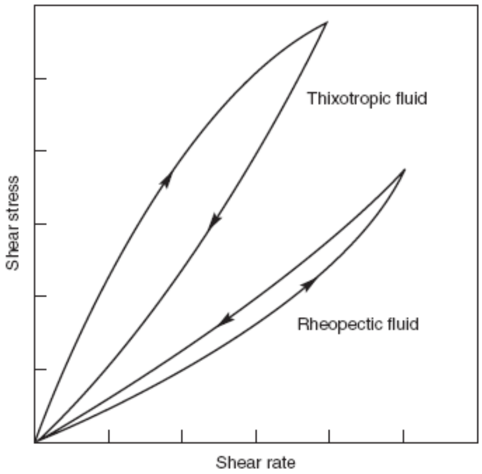


Figure 1.8. Schematic shear stress-shear rate behaviour for time-dependent fluid behaviour.

1.4.4. Viscoelastic fluid behaviour

The behaviour of linear viscoelastic materials combines both linear elastic and linear viscous behaviour. If a constant strain is applied to this material, the stress, which is required to maintain this deformation, decreases gradually or relaxes. Also, when a constant stress is applied, deformation increases slowly with time or creeps. Under oscillatory testing, the stress in a viscoelastic material is not exactly in phase with strain (pure elastic solid), and also not 90° out of phase with strain (pure viscous fluid) but is between these two extremes (Figure 1.9). The difference between linear viscoelastic and non-linear viscoelastic materials is that in linear viscoelastic materials the ratio of stress and strain is a function of time (or frequency) and temperature but not of stress magnitude (Darby, 1976).

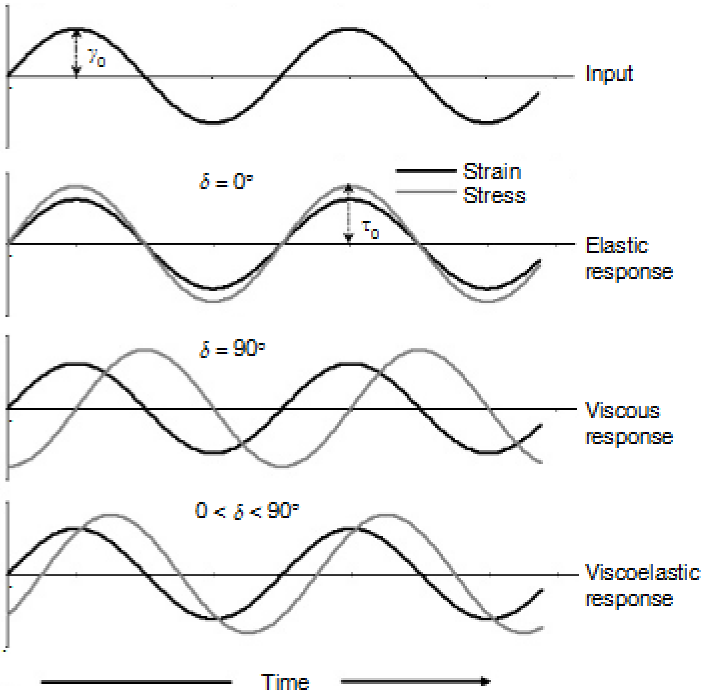


Figure 1.9. Input and response functions differing in phase by the angle δ.

Viscoelastic properties can be measured by experiments which examine the relationship between stress and strain, and strain rate in time dependent experiments. These experiments consist of stress relaxation, creep, and small amplitude oscillatory measurements. Stress relaxation (or creep) consists in instantaneously applying a constant strain (or stress) to the test sample and measuring change in stress (or strain) as a function of time (transient response). Dynamic testing consists in applying an oscillatory stress (or strain) to the test sample and determining its strain (or stress) response as a function of frequency. All linear viscoelastic rheological measurements are related, and it is possible to calculate one from the other (Ferry, 1980; Macosko, 1994).

1.4.4.1. Stress Relaxation

In a stress relaxation test, a constant strain (γ_0) is applied to the material over a very short period of the time, and the change in the stress $\tau(t)$ is measured (Darby, 1976; Macosko, 1994). Ideal viscous, ideal elastic, and typical viscoelastic materials show different responses to the applied step strain as shown in Figure 1.10. Shear strain and stress reach a maximum value after the loading time, but while the strain remains constant, shear stress begins to decrease.

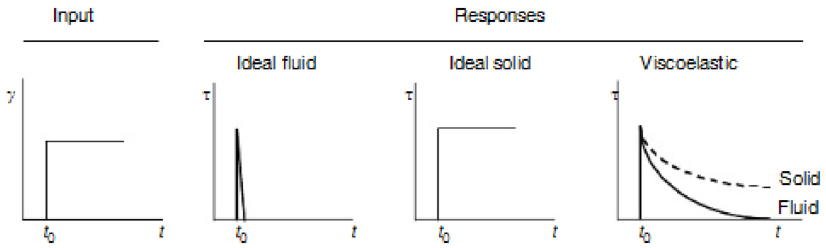


Figure 1.10. Response from stress relaxation test.

A relaxation modulus, which relates the measured shear stress and the applied shear strain, can be calculated from the following equation:

$$\tau(t) = \gamma_0 \cdot G(t) \tag{2.11}$$

The relaxation modulus is a time-dependent parameter in the linear region but it is a function of both time and strain in the non-linear range of response. The relaxation modulus has unit of stress (Pascal in S.I.).

1.4.4.2. Creep Response

In a creep test, a constant stress (τ_0) is applied at time t_0 and removed at time t_1, and the corresponding strain *γ(t)* is measured as a function of time. As in the case with stress relaxation, various materials respond in different ways as shown by typical creep data given in Figure 1.11. In a stress relaxation test, stress decreases for constant strain, whereas in creep, strain increases at constant stress.

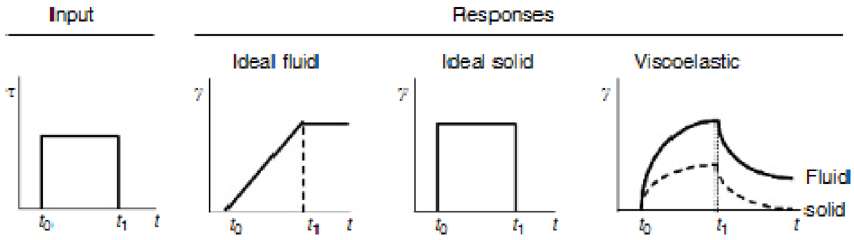


Figure 1.11. Response from creep test.

Data are usually expressed in terms of the compliance as follows:

$$J(t) = \frac{\gamma(t)}{\tau_0} \tag{2.13}$$

The compliance has the units of reciprocal modulus but in general it does not equal 1/G. However, because in the linear viscoelastic regime strain is linear with stress, strain versus time data at different τ_0 collapse into one J(t) plot. This is analogous to the reduction of stress relaxation curves to one G(t).

A *steady state creep compliance*, J_e^0, is defined by extrapolation of the limiting slope to t=0. The slope is the inverse of the viscosity at low shear rate, η_0. Thus, in the steady creeping regime, we have:

$$J(t) = \frac{\gamma_0}{\tau_0} + \frac{t\,\dot{\gamma}_\infty}{\tau_0} \tag{2.14}$$

or

$$J(t) = J^0{}_e + \frac{t}{\eta_0} \tag{2.15}$$

1.4.4.3. Dynamic Response

Dynamic mechanical analysis is the most widely used method for characterizing viscoelastic behaviour. Dynamic (oscillatory) tests may be performed in stress controlled or strain controlled modes. In stress controlled testing, a sinusoidal stress is applied to the sample and the resultant strain is monitored with time, whereas in strain controlled testing a sinusoidal strain is applied to the sample and the resultant stress is monitored with time. When considering tests in the controlled strain mode, the applied strain is expressed according to the following equation:

$$\gamma(t) = \gamma_{\max} \cdot \sin(\omega \cdot t) \tag{2.16}$$

where: ω=2·π· *f*

f = frequency of the sinusoidal strain (Hz), and

γ_{max} = the amplitude of strain.

Differentiating equation 2.16 results in the strain rate:

$$\dot{\gamma}(t) = \omega \cdot \gamma_{\max} \cdot \cos(\omega \cdot t) \qquad (2.17)$$

On the other hand, the corresponding stress can be represented as

$$\tau(t) = \tau_0 \cdot \sin(\omega \cdot t + \delta) \qquad (2.18)$$

where τ_0 is the amplitude of stress and δ is shift angle (Figure 1.13).

By employing complex notation, the complex modulus, *G*(ω)*, is defined as

$$G^*(\omega) = \frac{\tau(t)}{\gamma(t)} = G'(\omega) + iG''(\omega) \qquad (2.19)$$

$$|G^*(\omega)| = \frac{\tau^*}{\gamma^*} = \sqrt{(G'(\omega))^2 + (G''(\omega))^2} \qquad (2.20)$$

where: τ(t)=dynamic oscillatory shear stress

γ (t)=dynamic oscillatory shear strain

As previously mentioned, the behaviour of viscoelastic materials, such as bitumen, falls between ideal elastic solid behaviour and ideal viscous fluid response. A solid-like viscoelastic material exhibits a phase angle smaller than 45°, while a liquid-like viscoelastic material exhibits a phase angle greater than 45°. Thus, from dynamic tests, the following two rheological properties can be defined:

$$G'(\omega) = \frac{\tau_0}{\gamma_0} \cdot \cos\delta \qquad (2.21)$$

$$G''(\omega) = \frac{\tau_0}{\gamma_0} \cdot \sin\delta \qquad (2.22)$$

$G'(\omega)$ and $G''(\omega)$ are two frequency dependent functions, termed the shear storage and loss moduli, respectively. The storage modulus, *G΄,* is related to the elastic character of the fluid (energy storage during deformation), whilst the loss modulus, *G΄΄,* is related to the viscous character of the material (energy dissipation during the experiment). Therefore, for a perfectly elastic solid, all the energy is stored, that is, *G´´* is zero and the stress and the strain will be in phase. However, for a perfect viscous material all the energy will be dissipated, that is, *G´* is zero and the strain will be out of phase by 90º.

Another commonly used dynamic viscoelastic property, the loss tangent, tan δ(ω), denotes ratio of viscous and elastic components in a viscoelastic behaviour:

$$\tan\delta(\omega) = \frac{G''(\omega)}{G'(\omega)} \tag{2.23}$$

If the equations (2.21) and (2.22) are expressed for complex compliance, the following equations are derived (Ferry, 1980):

$$J^*(\omega) = \frac{\gamma(t)}{\tau(t)} = J'(\omega) + iJ''(\omega) \tag{2.24}$$

$$|J^*(\omega)| = \frac{\gamma^*}{\tau^*} = \sqrt{(J'(\omega))^2 + (J''(\omega))^2} \tag{2.25}$$

where: *J** = the complex compliance,

J′ the storage compliance, and

J′′ the loss compliance.

The relationship between these parameters is shown in Figure 1.12.

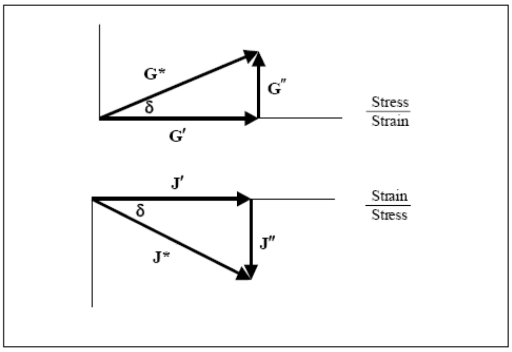


Figure 1.12. Components of complex modulus and compliance in sinusoidal shear deformation.

1.4.4.4. Conversion among Viscoelastic Functions

The ability to convert a viscoelastic function from one form to another is extremely useful. The following approximate equation is one of the simplest equations, which can be used to convert shear modulus to an uniaxial modulus for bitumen. This equation is based on the assumption that the Poisson’s ratio is 0.5 (Anderson and Christenson, 1991).

$$E^*(\omega) = 3G^*(\omega) \tag{2.26}$$

Where: $E^*(\omega)$ = the uniaxial complex modulus, and

$G^*(\omega)$ = the shear complex modulus.

The same equation can be used for calculating the uniaxial creep compliance, *D(t)*, from the shear creep compliance, *J(t)* (Anderson and Christenson, 1991).

$$D(t) = \frac{J(t)}{3} \tag{2.27}$$

Other important conversions are the equations used for converting creep stiffness parameters to dynamic complex modulus parameters. Van der Poel (1954) defined the following equation for direct conversion between creep compliance and dynamic complex modulus:

$$\begin{aligned} &G^*(\omega) \approx 1/J(t) \\ &t \rightarrow 1/\omega \end{aligned} \tag{2.28}$$

This means that the dynamic complex modulus at a frequency of $\frac{1}{t}$ equals the inverse of the creep compliance at time *t*.

The following equations can be used for direct conversion between the storage/loss compliance and the storage/loss modulus (Ferry, 1980):

$$J' = \frac{G'}{(G'^2 + G''^2)} = \frac{1/G'}{1 + \tan^2 \delta} \tag{2.29}$$

$$J'' = \frac{G''}{(G'^2 + G''^2)} = \frac{1/G''}{1 + (\tan^2 \delta)^{-1}} \tag{2.30}$$

$$G' = \frac{J'}{(J'^2 + J''^2)} = \frac{1/J'}{1 + \tan^2 \delta} \tag{2.31}$$

$$G'' = \frac{J''}{(J'^2 + J''^2)} = \frac{1/J''}{1 + (\tan^2 \delta)^{-1}} \tag{2.32}$$

where tan δ= G′′/G′=J′′/J′=E′′/E′. These methods of converting are approximate; however, in most cases, they are accurate enough for engineering calculations.

1.4.5. Parallel Plate Rheology

The most used configuration to analyse bitumen rheology behaviour is using dynamic oscillatory measurements on parallel plate geometry.

It applies a sinusoidal shear strain to a sample of bitumen sandwiched between two parallel disks and is shown schematically in Figure 1.13 and as a picture of a modern Dinamic Shear Rheometer (DSR) machine in Figure 1.14. If the bitumen test specimen is seen as a series of circular layers, rotating one with respect to another, the shear strain is defined as the distance the point rotates divided by the specimen thickness. Therefore, the shear strain is zero at the centre and it increases to the maximum at the outer edge of the specimen, where, also, most of the shear resistance is developed.

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 (τ) and angular rotation (θ), the remaining mechanical properties are calculated by using these two parameters.

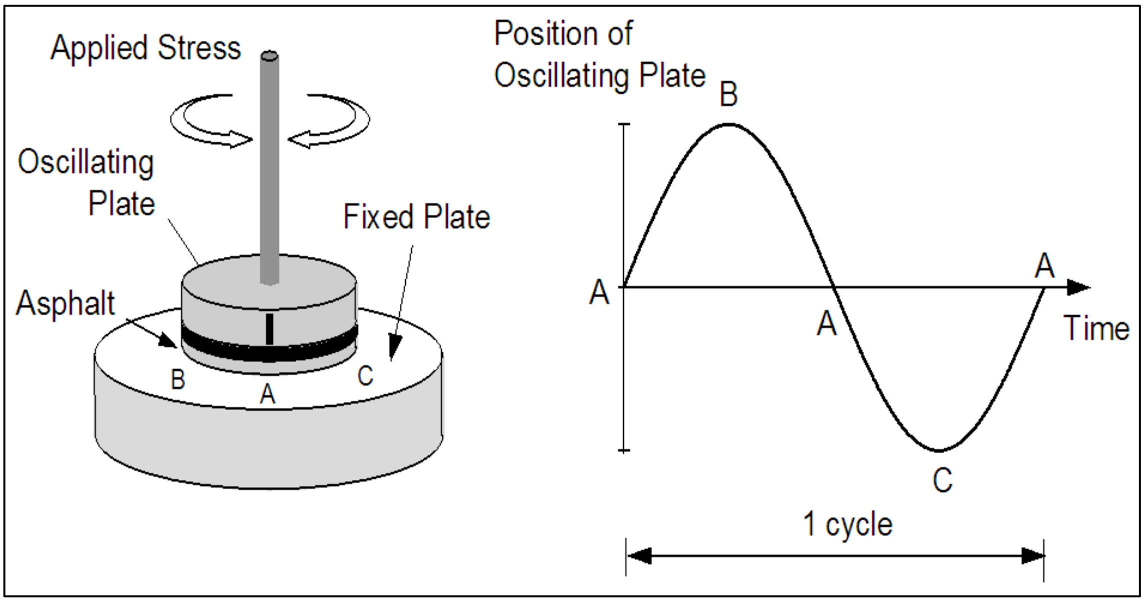


Figure 1.13: Schematic of DSR testing arrangement

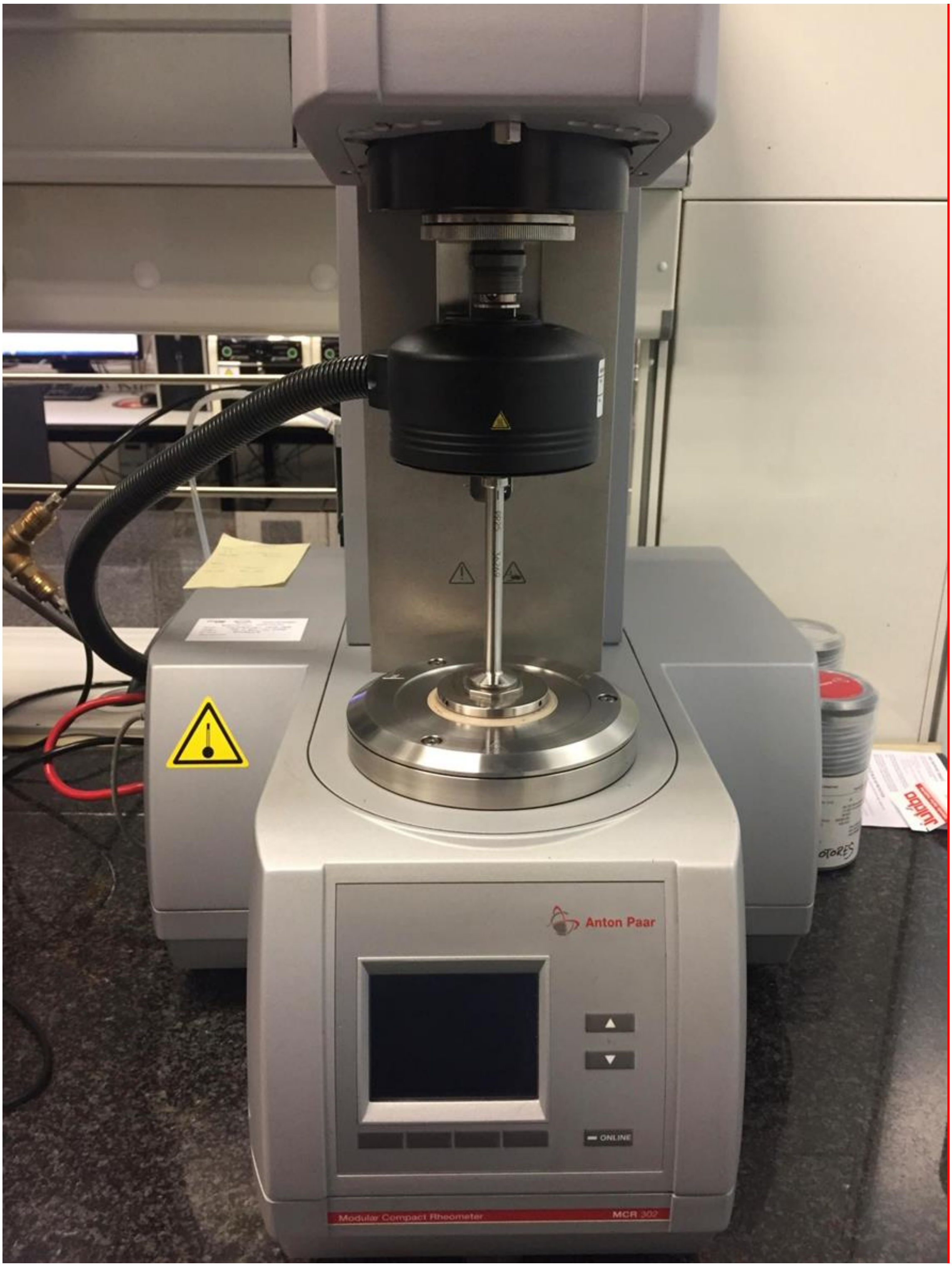


Figure 1.14: Anton Paar dynamic shear rheometer

Two basic equations are used to calculate stress and strain parameters (Airey et al., 1998, Gandiner and Newcomb, 1995):

$$\boldsymbol{\tau} = \frac{\boldsymbol{2T}}{\boldsymbol{\pi r^3}} \qquad (2.33)$$

Where,

τ = maximum shear stress (N/ mm^2)

T = torque (N·m)

r = radius of the parallel disks (mm) (Figure 1.5)

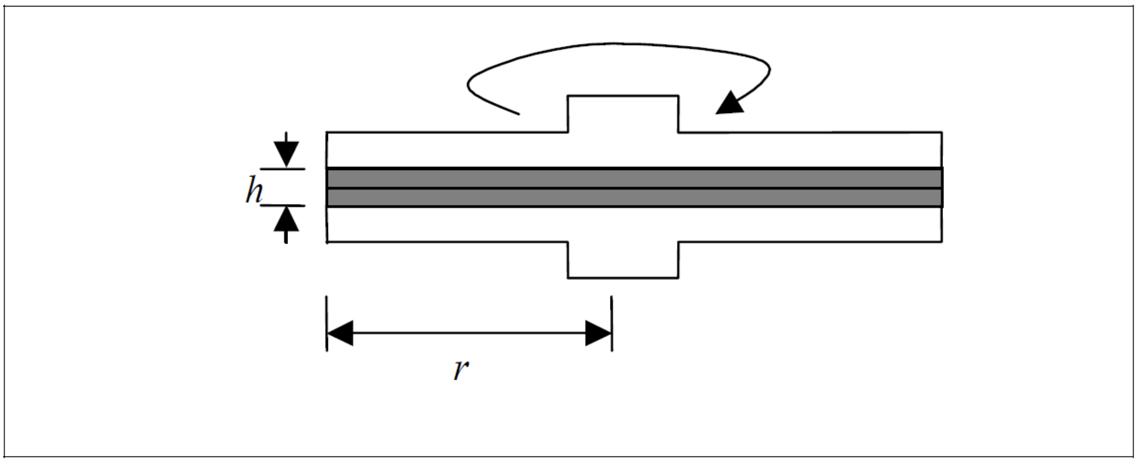


Figure 1.15: Testing geometry of DSR

$$\gamma = \frac{\theta r}{h} \qquad (2.34)$$

Where,

γ = shear strain

θ = deflection angle (radians)

h = gap between parallel disks (mm) (Figure 1.15)

The shear stress and strain in equations 2.33 (τ) and 2.34 (γ) 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.

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 1.14 (Peterson et al, 1994).

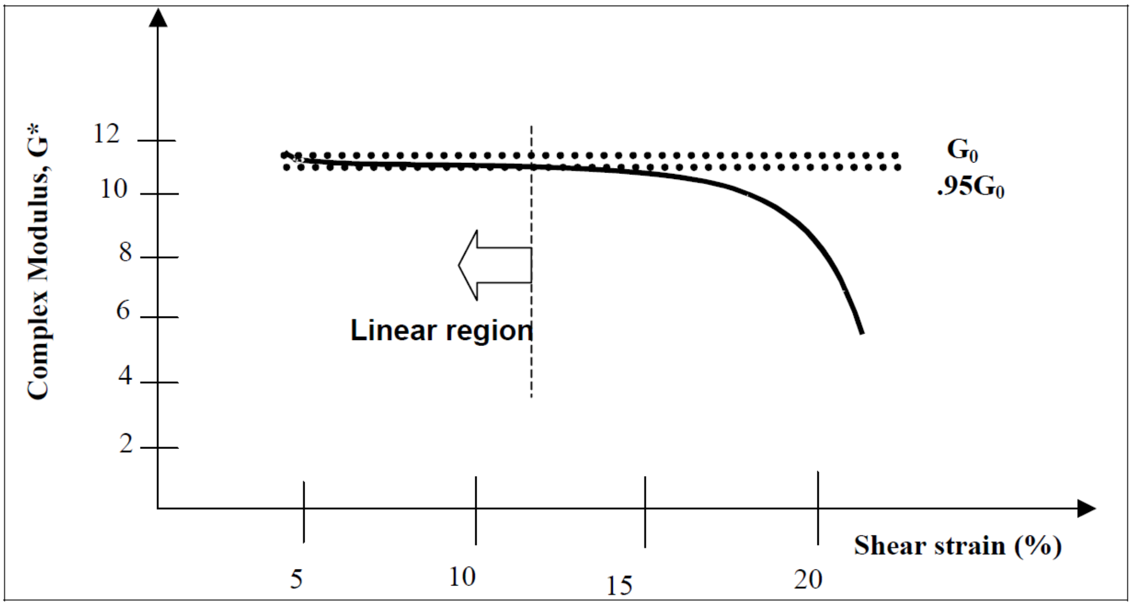


Figure 1.14: Strain sweep to determine linear region

1.4.5.1. Plate Diameter

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. But the most widely used method is suggested by SHRP Project A-002A (Anderson et al., 1994), as presented in Table 1.1.

Table 1.1 SHRP suggested disk diameters for DSR rheology testing (Anderson et al., 1994)

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 (Collins et al., 1991) 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 (Carswell et al., 1997).

1.4.5.2. Gap Width

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 30MPa, parallel plate geometry should not be used as the compliance of the rheometer can be sufficient to cause errors in the measurements (Peterson et al, 1994). According to SHRP, the following guidelines should be used,

- Bending Beam Rheometer (BBR) or torsional bar geometry when G*> 30 MPa

- 8 mm parallel plates with a 2 mm gap when 0.1MPa <G* < 30 MPa
- 25 mm parallel plates with a 1 mm gap when 1kPa <G* < 100 kPa
- 50 mm parallel plates 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.

1.4.6. 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.

1.4.6.1. Time Temperature Superposition Principle (TTSP)

Temperature has a dramatic influence on rates of viscoelastic response, and in practical work it is often necessary to adjust a viscoelastic analysis for varying temperature.

For this purpose, it is often necessary to utilize the time-temperature superposition (TTS) principle (Ferry JD. 1980)

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 (described below), 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 (Anderson et al, 1991).

TTSP procedure is frequently applied:

- To determine the temperature dependence of the rheological behaviour of a viscoelastic material
- To expand the time or frequency regime at a given temperature at which the material behaviour is studied.

This is due to the fact that the various relaxation times belonging to a given relaxation process have the same temperature dependence: the effect of lowering the temperature is simply to shift the viscoelastic response (plotted against log time) to the right without change in shape (Roylance, 2001; Van Gurp, et al., 1998)

1.4.6.2. Master Curves

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 (Anderson et al, 1991, Airey, 1997). A numerical factor, called the shift factor (Williams et al, 1955, Dickinson and Witt, 1974), is used to shift the data at a specific temperature to the reference temperature. 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.

1.4.7. Multi Stress Creep Recovery Test (MSCRT)

The repeated creep test is proposed as a method of separating the dissipated energy and estimating the resistance to accumulation of permanent strain for asphalt binders. The RCR test was developed during the NCHRP 9-10 project. Bahia et al. (2001) recommended the repeated creep recovery test (RCR) using the dynamic shear rheometer (DSR) to evaluate the resistance of asphalt binders to permanent deformation. The NCHRP 9-10 project recommend a shear stress in the range of 30 Pa to 300 Pa for 100 cycles at a rate of 1s loading time followed by a 9 s unloading time (Bahia et al., 2001).

The MSCR test was developed to reduce the number of samples at each stress level and it is the following development of RCR test. The test uses 1 (s) creep loading followed by 9 (s) recovery for the following stress levels: 25, 50, 100, 200, 400, 800, 1600, 3200, 6400, 12800 and 25600 Pa at 10 cycles for each stress level. The test starts at the lowest stress level and increase to the next stress

level at the end of every 10 cycles, with no rest periods between creep and recovery cycles or changes in stress level. (D'Angelo et al., 2007).
D'Angelo selected two stress levels, 0.1 kPa and 3.2 kPa, upon correlation between binder and mixture rutting results for performing the MSCR test. Ten cycles are run for each stress level for a total of 20 cycles. The average non-recoverable strain for the 10 creep and recovery cycles is then divided by the applied stress for those cycles yielding the non-recoverable creep compliance (J_{nr}). J_{nr} for 0.1 kPa is calculated by divided the strain after 10 cycles to 0.1 kPa. The Jnr parameter was suggested as a measure of the binder contribution to mixture permanent deformation (D'Angelo et al., 2007).

1.5. RUBBER AND TYRES

There are two types of rubber used in tyres; natural and synthetic. Natural rubber latex is obtained from the rubber tree called Hevea braziliensis. The primary composition of 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 (Blow, 1971).

Natural rubber is insoluble with water, alkali and weak acids, but it is soluble in benzene, gasoline, chlorinated hydrocarbons and carbon bisulphate (Blow, 1971). While it is easily oxidised by chemical oxidising agents, atmospheric oxygen produces a very slow reaction.

Synthetic rubbers are made from petroleum products and other minerals and produced in two main stages: first the production of monomers (long molecules consisting of many small units), then polymerisation to form a rubber. There are various types of synthetic rubber available for different applications. Some of them are: Styrene-Butadiene Rubber (SBR, used in bitumen, tyres etc); Silicon rubbers (used in gaskets, seals etc); Fluorocarbon rubber (resistant to heat and chemical attack); and Epichlorohydrin rubber (jackets, hose, cable, packing etc) (Blow, 1971).

The functionality of the rubber depends on how the molecules are arranged. There are three types of molecular arrangements; linear, side branched and cross-linked.

1.5.1. Molecular Structure of Rubber

The mechanical properties of this type of polymer are dependent on the length and shape (side branch) of the molecule. Both the linear and side branched polymers can be reversibly heated to melt and then cooled to crystallise time and time again. On melting they flow as a liquid and are therefore called thermoplastic. The number of the side branches can be varied by changing the polymerisation conditions. Even small variations in the number of side branches can cause appreciable changes in elastic modulus, creep resistance and toughness. Microwaveable food containers, Dacron carpets and Kevlar ropes are examples of products made with linear polymers. Soft, flexible shampoo bottles and milk jugs are examples of products generally made using branched polymers.

In cross-linked polymers, the chains are joined chemically at the tie points with cross-linking agents and formed into one simple giant molecular network. Many cross-linked networks are produced by chemical reactions triggered by heating.

After heating, the network gets permanent shape and this state is called "Thermoset". Cross-linked polymers do not flow when heated. Tyres and bowling balls are two examples of products composed of cross-linked polymers. The mechanical behaviour of an elastomer depends strongly on cross-link density, which is shown schematically in Figure 1.15 (Hamed, 1992). It shows that the modulus and hardness increase monotonically with cross-link density and the network becomes more elastic. Fracture properties such as tear and tensile strength pass through a maximum as cross-linking is increased.

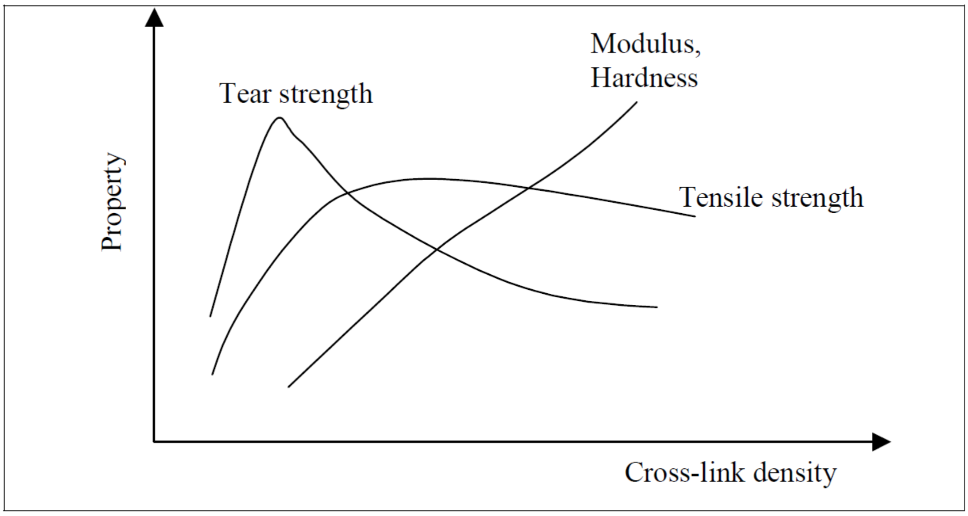


Figure 1.15: Effect of cross-link density on some mechanical properties of rubber (Hamed, 1992)

1.5.2 Processing of Rubber

There are many types of rubber products such as tyres, mats, moulded products, extruded products, etc. These rubber products have their unique specification of manufacturing. However, most of the rubber products are processed with four major steps and are listed below.

- Mixing
- Shaping
- Vulcanizing
- Compounding

1.5.2.1 Mixing

The additives must be thoroughly mixed with the base rubber to achieve uniform dispersion of ingredients. If vulcanizing agents were present from the start of mixing, premature vulcanization would result spoiling the product. To avoid premature vulcanization, a two-stage mixing process is usually deployed by the processing units:

1. carbon black and other non-vulcanizing additives are combined with the raw rubber. The term master batch is used for this first-stage mixture

2. after stage 1 mixing has been completed, and time for cooling has been allowed, stage 2 mixing is carried out in which vulcanizing agents are added

1.5.2.2 Shaping

This process helps in providing the shape to the product in the required form. Shaping and related processes for rubber products can be divided into four basic categories:

1. Extrusion

2. Calendering

3. Coating

4. Moulding and casting

Some products require several basic processes plus assembly work such as tires which uses all the basic shaping process to manufacture the final product.

Calendering

Rubber roll is passed through a series of gaps of decreasing size made by a stand of rotating rolls. Rubber sheet thickness determined by final roll gap. Some of the end products include conveyor belts, bonding gum, etc.

Coating

This process is used when a fabric is coated with rubber. The equipment is similar to calendaring equipment. Some of the products made by this process are automobile tires, conveyor belts, inflatable rafts, and water proof cloth tents and rain coats.

Roller Die Process

This process involves a combination of extrusion and calendaring which results in better quality product than either extrusion or calendaring alone.

Moulding

Moulded rubber products include rubber mats, gaskets and seals, bush, footwear soles, straps and bottle stops. Also, many foamed rubber parts are produced by moulding. In addition, moulding is an important process in tyre Production as well.

There are different types of moulding processes followed. The major types are as follows:

- Compression moulding
- Transfer moulding
- Injection moulding

Compression moulding is the most followed technique for most of the moulded rubber product and it is used in tire manufacturing process as well. Curing (vulcanizing) is accomplished in the mould in all three processes. But for other shaping processes such as extrusion and calendaring, separate curing/vulcanization process needs to be performed.

1.5.2.3 Vulcanisation

Vulcanisation is generally a heating process that accomplishes cross-linking of elastomer molecules, so that the rubber becomes stiffer and stronger but retains extensibility. During the vulcanization process, the number of cross-links increases, the polymer becomes stiffer and behaves more and more like a thermosetting plastic (hard rubber).

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 1.2 shows the effect of temperature on rubber.

Table 1.2: Effect of Different Temperatures on Rubber

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
~182 °C	Break down as in the masticator
200 °C	Decomposes

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 (Shulman, 2000). 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 (Blow, 1971). 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 (Fig. 2.16).

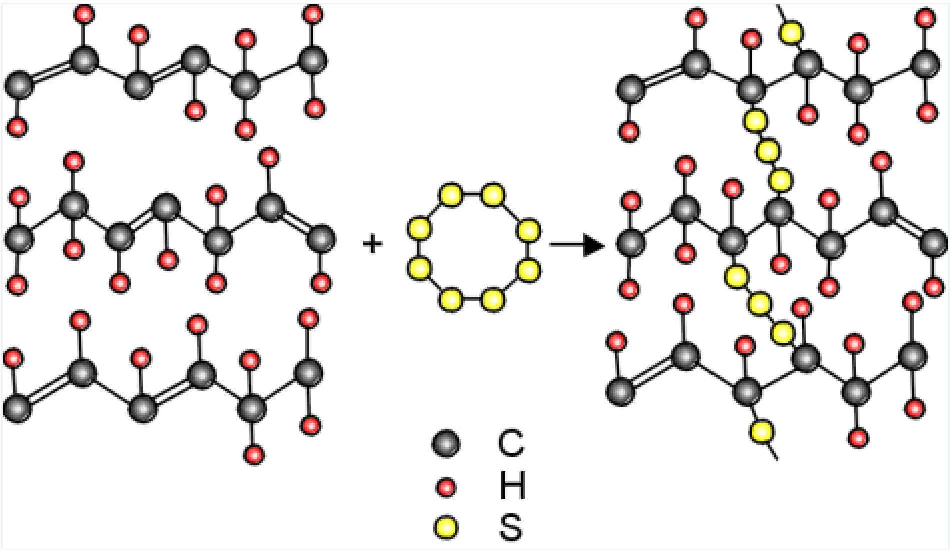


Figure 1.16: Vulcanisation process.

1.5.2.4 Compounding

Compounding is the process by which a number of ingredients are added to modify and improve the physical properties of rubber. The first reason for compounding is to incorporate the ingredients and ancillary substances necessary for vulcanisation. The second is to adjust the hardness and modulus of the vulcanised product to meet the end requirement. Different techniques are available to do compounding using the same fundamental constituents (Stern, 1954), such as base polymer, cross-linking agent, accelerator for the cross-linking reaction, reinforcing filler (carbon black, mineral), processing aids (softeners, plasticisers, lubricants), diluents (organic materials, extending oils), colouring materials (organic or inorganic), specific additives (blowing agent, fibrous materials). When designing a mixture formulation for a specific end use, it is necessary to take account not only of those vulcanisation properties essential to satisfy service requirements but also the costs of the raw materials involved and the production processes by which these will be transformed into final products.

The rubber compound used in rubber tyres is a complex mixture. In the compounding process, a number of ingredients are added to modify and improve the physical properties of the rubber and to make it more readily useable (modify the hardness, strength, toughness and to increase resistance to abrasion in oil, oxygen, chemical solvents and heat) for various applications. It is important to note that some of the ingredients still remain when the tyres are recycled at the end of their life. As an example, the stabilisers which provide resistance to cracking and degrading of the tyre, also prolong the life of roads, sports and safety surfaces etc; the pigments which produce uniform colour in the tyre also contribute to the consistent and long-term colour of roads which utilise post-consumer tyre materials.

1.5.3 Tyres

The first rubber tires appeared in the mid-1800s. They were solid or cushion tires in which the rubber itself carried the load, absorbed shocks, and resisted cutting and abrasions. The pneumatic or air-filled tire, which carried the load and absorbed shocks by the compressed air in the tire casing, was patented as early as 1845. Solid rubber tires were preferred over pneumatic tires because of their durability, so pneumatic tires fell into disuse. The popularity of bicycles in

the late 1800s revived the idea of the pneumatic tire, and in 1888 a Belfast veterinary surgeon named John Boyd Dunlop obtained a patent for a pneumatic bicycle tire. Goodyear finally produced a radial tire in 1977 by investing billions of dollars in radial technology. Other American tire companies either merged or were bought out. All American new cars came with radial tires by 1983.

In 1898 Goodyear Tire and Rubber Company - named after George Goodyear, the discoverer of vulcanized rubber - was formed in America by Frank Seiberling. Then Firestone Tire & Rubber Company was started by Harvey Firestone in 1900. Other tire makers followed.

In 1992 by Michelin introduces the first durable silica-filled tire, also known as "green tires". Then at 1998 Michelin develops tire that’s vertically anchored and unseatable, allowing it to run flat after a loss of pressure.

In 2000 by Firestone recalls tires after Congressional hearings into rollover accidents of Ford Explorers in Firestone and Ford tire controversy.

1.2.3.1 Production

A tyre is made up of three main materials; elastomeric (rubber) compound, fabric and 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 (Figure 1.17). 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.

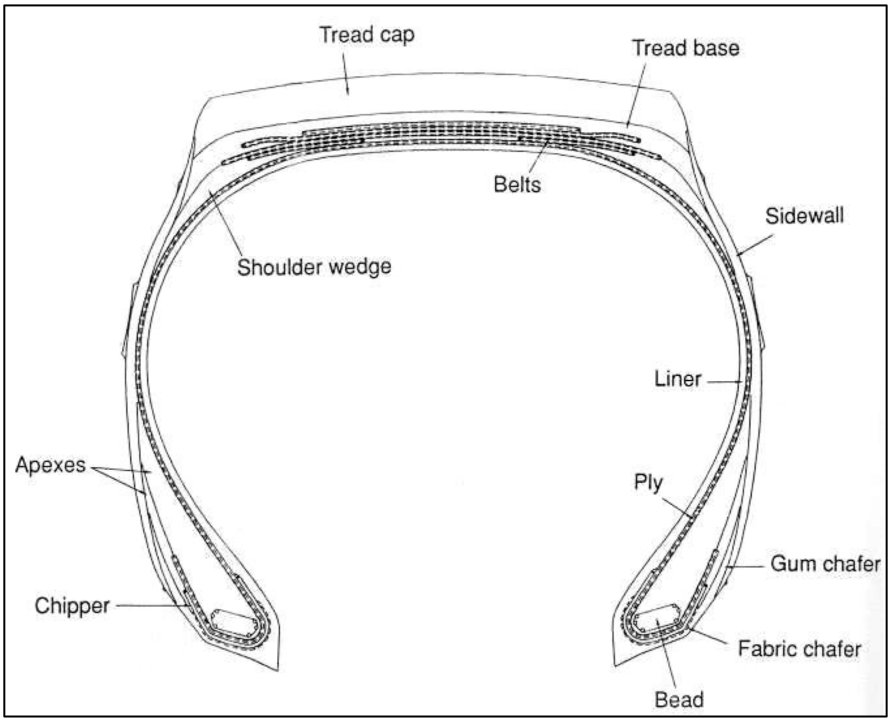


Figure 1.17: Schematic diagram of a typical truck tyre cross-section (Merk et al, 1994)

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 excessively deforming. Tyre construction is a complex process of compounding to combine the elastomer (rubber), process the steel and fabric with the rubber, extrude the treads, sidewalls and then cure the tyre under heat and pressure. 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, ultraviolet 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%.

1.5.3.2 Composition

The composition of tyres consists of four main ingredients: rubber, carbon black, metal and textiles. The remaining materials are additives, which facilitate compounding, and vulcanisation. Table 1.3 is a summarised version of general tyre composition in cars and truck tyres in the EU (Shulman, 2000).

Table 1.3: Comparison of passenger car and truck tyres in the EU

Material	**Car**	**Truck**
Rubber/Elastomers	48%	45%
Carbon Black	22%	22%
Metal	15%	25%
Textile	5%	--
Zinc oxide	1%	2%
Sulphur	1%	%1
Additives	8%	5%

In general, tyres are composed of natural and synthetic rubber. The proportion 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. 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; in sidewalls to add flexibility and to reduce heat build-up (HBU) (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.

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.

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.

1.5.3.3 Tyre Recycling

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 retreated. 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 1.18.

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.

Whole tyre: Typical weights of scrapped automobile (car and truck/bus) tyres are presented in the Table 1.4 including amount of recoverable rubber and percentage of natural and synthetic rubber. 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 28,000kJ/kg to 35,000 kJ/kg, which is the same as coal, and therefore, have been widely used as a cement-making fuel worldwide for the last ten years (Shulman, 2000).

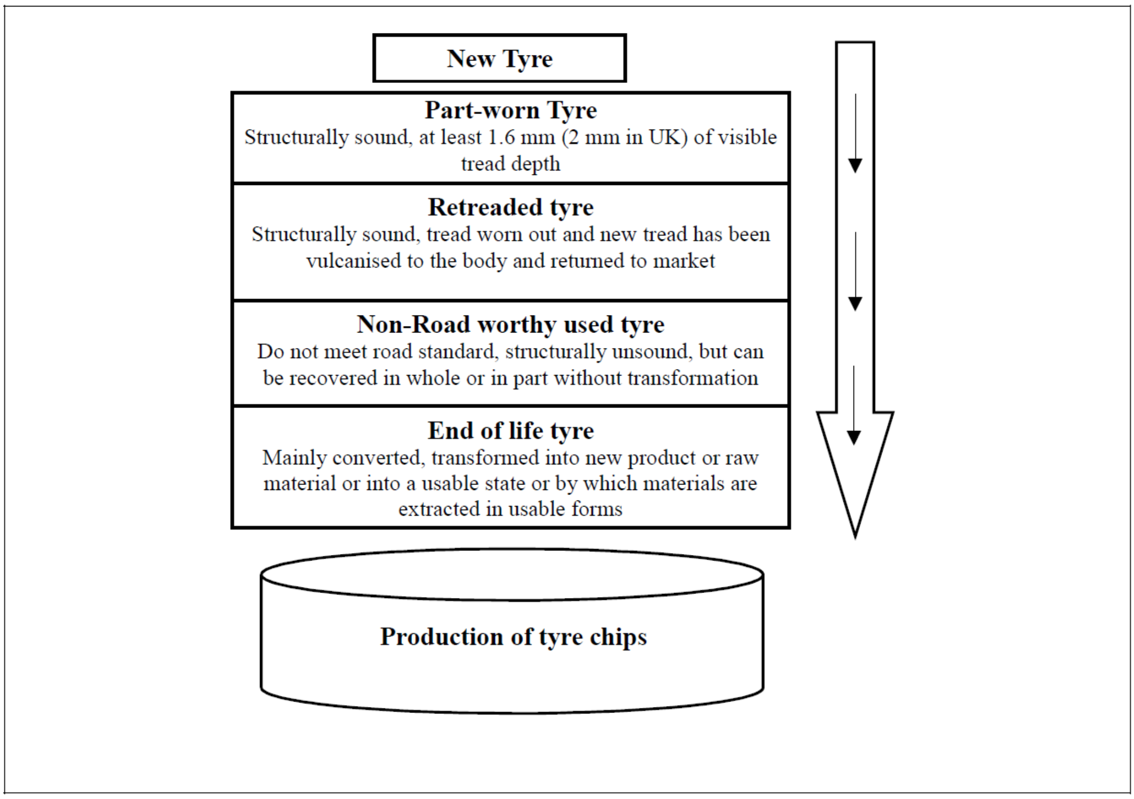


Figure 1.18: Flow chart of service life of a tyre

Slit tyres: Slit tyres are produced in tyre cutting machines. These cutting machines can slit the tyre into two halves or can separate the sidewalls from the tread of the tyre.

Table 1.4: Comparisons of car and truck tyres

Type of tyre	**Weight (kg)**	**Recoverable rubber (kg)**	**% Rubber**
Passenger car	9.1	5.4-5.9	35% natural, 65% synthetic
Truck	18.2	10-12.5	65% natural, 35% synthetic

Shredded or Chipped Tyres: In most cases the production of tyre shreds or tyre chips involves primary and secondary shredding. When the tyres are disposed, they can be used whole and/or as chips for different applications.

1.5.4. Crumb rubber

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 (Heitzman, 1992, Schnormeier, 1992).

1.5.5 Production and Specifications of Crumb Rubber

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.

1.5.5.1 Ambient Process

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.

1.5.5.2 Cryogenic Process

In this process liquid nitrogen or a similar material/method is used to freeze tyre chips prior to size reduction. Most rubber becomes embrittled or “glass-like” at temperatures below –80°C. 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.

1.5.5.3 Specifications

Crumb rubber is classified as number one, two and so on, depending on quality and size. Table 1.5 presents a summary of crumb rubber grades. However, crumb rubbers produced in industry should maintain certain quality requirements with respect to their grades and specifications. There is no national standard available in Spain, but a European standard is now underway. Most industries in the UK use their own specifications, although ASTM standards are widely used in many parts of the world. ASTM D5603-96 and ASTM D5644-96 are the two most widely used grading standards.

Table 1.6: Summary of crumb rubber grades

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.

1.6. POLYMERS FOR BITUMEN MODIFICATION

Polymers for bitumen modification can be classified on the basis of the mechanism by which the modifier alters the binder properties, the composition and physical nature of the modifier and the target bitumen property that must be modified (Bahia et al., 1995). A large number of bitumen modifiers are used in paving applications. These materials have been classified into different groups by different researchers or institutes. For example, SHRP has classified modifiers in eight categories (Mortazaviet al., 1990): thermoplastics, anti-stripping agents, mineral fillers, antioxidants, fibres, extenders, recycling agents and oxidants. Different kinds of modifiers are shown in Table 1.7 (Bahia et al., 1995). This study will focus only on polymers.

Table 1.7: Different types of bitumen modifiers used for pavement applications

Type of modifier	**Class**
Fillers	Carbon black Mineral: Hydrated lime Fly ash Portland cement Baghouse fines
Extenders	Sulphur Wood lignin
Polymers-Elastomers	Styrene butadiene diblock (SB) Styrene butadiene triblock/radial block (SBS) Styrene isoprene (SIS) Styrene ethylbutylene (SEBS) Styrene butadiene rubber latex (SBR) Polychloroprene latex
Polymers-Plastomers	Ethylene vinyl acetate (EVA) Ethylene propylene diene monomers (EDPM) Polyisobutylene Polyethylene Polypropylene
Crumb rubber	Different sizes, treatments and processes

Oxidants	Manganese compounds
Hydrocarbons	Aromatics
	Napthenics
	Paraffinics/wax
	Vacuum gas oil
	Asphaltenes: ROSE process resins
	SDA asphaltenes
	Tall oil
	Natural bitumens: Trinidad
	Gilsonite
Antistrips	Amines: Amidoamines
	Polyamines
	Hydrated lime
	Organo-metallics
Fibres	Polypropylene
	Polyester
	Reinforcement
	Natural: Cellulose
	Mineral
Antioxidants	Carbamates: Lead
	Zinc
	Carbon black
	Hydrated lime
	Phenols
	Amines

The use of polymers in binders can be traced back to the early 1950s in Europe (Roberts, 1991).

Gregg and Alcocke (Gregg 1954) published the earliest research available on polymermodified asphalt in 1954. They studied bitumen modified with the polymer styrene butadiene and found the addition of polymers to bitumens improved or reduced temperature susceptibility. Thompson (Thompson, 1964) in 1964 concluded that modification of bitumen with neoprene improved the toughness and ageing characteristics of bitumens.

Polymers are large chain-like molecules formed by the conjunction of small chemical units, called monomers. There are two stages in classifying various groups of polymeric materials (Lancaster, 1996).

- Classification based on the overall composition of the polymers, i.e. if the polymer contains only one type of unit or monomer then it is known as a homopolymer, whereas if more than one unit is present then it is known as a copolymer.
- Classification based on structural considerations, i.e. from knowledge of how the individual components of the polymers fit together. Polymers have three main structures: linear, branched and block polymers. The structure of the homopolymers is solely linear and branched, whereas the copolymers can be found in various forms, e.g. linear-random and linear-block (Walker, 1993).

Polymers can also be classified in two general categories:

- Elastomers, and
- Plastomers.

The mechanism of resistance to deformation is different between elastomeric and plastomeric polymers. The load-deformation behaviour of elastomers is similar to rubbers, i.e. increasing tensile strength with increased elongation and ability to recover to the initial state after removal of load. Under a given load, elastomers deform faster than plastomers and recover early strength but are less flexible and more prone to fracture under large strains compared to plastomers.

1.6.1 Thermoplastic elastomers

Elastomeric polymers or thermoplastic rubbers (TR) are the most important group of thermoplastic elastomers used for paving applications (Whiteoak, 1990). Examples of these polymers are styrene butadiene diblock (SB), styrene butadiene triblock/radial block (SBS), styrene isoprene (SIS), styrene ethylbutylene (SEBS), styrene butadiene rubber latex (SBR) and polypropylene (Bahia, 1995). Several benefits have been found when elastomeric polymers are added to bitumens. First, these materials have increased softening point, ductility, adhesion to aggregate and resistance to the effects of motor fuels. In addition, they improve the resistance to ageing and the elastic recovery of bitumen (Zielinski, 1997). Finally, because of their high elastic response, they resist permanent deformation by stretching and recovering their initial shape (Airey, 1998). Elastomeric polymers have a linear or branched structure (Whiteoak et al., 1990). Of the thermoplastic elastomers, the best-known group is the block copolymer, styrene butadiene styrene (SBS). They are characterised by their styrene content, their molecular weight and their configuration (linear or star shaped) (Usmani, 1997). SBS elastomers consist of polystyrene endblocks and polybutadiene midblocks with a star (tetrabranched) or linear structure (Usmani et al.,1997; Whiteoak et al., 1990). Star shaped SBS elastomers have high viscosity, a high softening point and better low temperature flexibility of the compound, whereas linear SBS elastomers have low viscosity, a low softening point and increased toughness (Usmani, A. M.,1997).

1.6.1.2 Plastomers

Major plastomeric polymers used for paving applications are ethylene vinyl acetate (EVA), ethylene propylene diene monomer (EPDM), polyisobutylene, polyethylene, polyvinylchloride (PVC) and polypropylene (Bahia et al., 1995). These polymers are characterised by softening on heating and hardening on cooling. One of the advantages of thermoplastic polymers is that the viscosity and the stiffness of the bitumen modified by these polymers increases at ambient temperature. However, most of the thermoplastic polymers can separate when heated and do not significantly improve the elastic properties of bitumen (Hoban, 1990; Whiteoak ,1990). One of the most popular thermoplastic polymers, which has been widely used as a polymer modifier in asphalt in European countries, is EVA. These copolymers have a random structure derived from the copolymerisation of ethylene and vinyl acetate (Whiteoak,1990). The molecular weight, in terms of melt flow index (MFI), and vinyl acetate content governs the properties of EVA copolymers, i.e. if MFI is 150 g/10 min and the vinyl acetate content is 19%, the grade of EVA will be 150/19. The higher the MFI value, the lower the molecular weight and viscosity (Whiteoak, 1990). The structure of EVA consists of two parts (Whiteoak, 1990).

- The polyethylene segments, which are packed closely together and form the crystalline region, and
- The massive vinyl acetate groups, which produce the non-crystalline or amorphous rubbery region.

The crystalline regions, which are stiff, provide the strength of EVA while the amorphous regions have rubbery properties. Therefore, the higher vinyl acetate content causes a higher proportion of rubbery regions and a lower proportion of the crystalline regions (Whiteoak,1990).

EVA has been shown to improve the workability of asphalt as it is slightly softer than bitumen and is also more susceptible to shear. However, asphalt workability drops rapidly when using EVA in asphalt at cold ambient conditions. This is because of the hardening of the EVA modified bitumen as a result of EVA polymer crystallisation (Whiteoak, 1990).

1.6.1.3 Reactive polymers

The modification of bitumen by chemical reaction using “reactive agents” (non-polymeric products) is not a new subject. Air-blowing of soft bitumen is an industrial application of the chemical reactivity of bitumen, in use more than a century. However, the process was quite complicated and could only be done in specific production units available to refiners (Lesueur, 2009).

Still, it was early observed that bitumen could be reacted with other compounds such as sulphur, chlorine or various acids (sulphuric, nitric, acid sludge, fatty acids, etc.) in normal storage tank. For example, the reaction of Venezuelan bitumen with chlorine at 200 ºC gave a final bituminous binder with properties comparable to those obtained by air-blowing process.

However, these processes did not get industrial success because of the corrosion problem involved with manipulating such products and their reaction by-products, together with the low economical interest given that the same effect on properties could be obtained by the cheaper air-blowing process (Siegmann, 1950). In parallel, air-blowing was progressively abandoned for paving bitumen because of the increased fragility of the binders and higher ageing susceptibility.

Recently, bitumen acid modification was rediscovered because it turned out to start to make economical sense and seemed to lack the fragility problem of air-blown bitumens (Edwards et al., 2006; Herrington et al., 1999). In particular, polyphosphoric acid (PPA) modification is currently gaining industrial importance since it permits to significantly harden bitumen in an easily controllable way. As a result, the reaction of 1 wt.% of PPA to bitumen typically allows for a change of one class of paving grade (Orange et al., 2004).

Some works proposed that PPA acts through the neutralisation of polar interactions between the stacked asphaltenes molecules, either by protonation of basic sites or by esterification. The overall effect is to increase the solvation of the asphaltenes, increasing in turn the solid fraction and hence, the viscosity (Orange et al., 2004). However, other researchers (Baumgardner et al., 2005) proposed various bitumen-dependent mechanism of PPA modification which also affect the lower weight components of the bitumen: co-polymerisation of the saturates, alkyl aromatisation of the saturates, cross-linking of neighboring bitumen segments, the formation of ionic clusters and the cyclisation of alkylaromatics.

Therefore, although the oxidative effect of acids was long recognized as well as its similarities with air-blowing (Siegmann, 1950), the reactivity of bitumen towards acids is still not completely understood. It is known that not all bitumens show the same reactivity, depending primarily on their crude source (Orange et al., 2004; Bonemazzi and Giavarini, 1999; Baumgardner et al., 2005).

Recently, reactive polymers are being considered as new bitumen modifiers, aimed to improve bitumen-polymer compatibility, and reducing the quantity of additives required. Reactive polymers are capable of forming chemical bonds with some bitumen molecules, improving the mechanical behaviour, storage stability and temperature susceptibility of the resulting binder (Bitumen modification with reactive and non-reactive (virgin and recycled) polymers: A comparative analysis). Different kind of reactive polymers have been involved in bitumen modification, such as isocyanate (H. Tarannum et al., 2003; A. Perez-Lepe et al., 2006; F.J. Navarro et al., 2007; G. Polacco et al., 2004 ; G. Polacco et al., 2004; Sekar et al., 2002; B. Singh et al., 2004).

1.6.2 Polymer Modified Bitumen

One of the prime roles of a bitumen modifier is to increase the resistance of the asphalt to permanent deformation at high road temperatures without adversely affecting the properties of the bitumen or asphalt at other temperatures. As a matter of fact, adding polymer to bitumen allows to greatly increase the high temperature end of paving grade, leaving the low temperature slightly better. The use of a polymer has no value if it does not substantially improve the life cycle cost of the material in which it is used or solve a specific problem (Lesuer, 2009). The selection of polymer modification should almost always be based on improved performance related to cost (FHWA, 2011).

Bitumen modification involving natural and synthetic polymers were patented as early as 1843, even if experiences with modified bitumen seriously started in 1970s with the introduction of styrene butadiene styrene (SBS) as a bitumen modifier (Airey, 2002).

1.6.2.1 Interaction and compatibility polymer-bitumen blends

Mayor restrictions related to polymer modification of bitumen involve the incompatibility issue of bituminous base and polymeric matrix. In general, polymer incorporation in a bitumen matrix results in a multiphase material with a great tendency to phase separate (Hesp et al., 1992).

Due to the tendency of phase separating of modified binders, the storage stability is an extremely important characteristic to be assessed. Since these binders consist of two distinct phases, they are subject to the same physical principles as those governing the separation or sedimentation of bitumen emulsions (Stokes‟ law). In other words, the velocity of displacement of dispersed particles (polymer phase in the case of a bitumen matrix and bitumen phase in the case of a polymer matrix) increases as:

- The particle size increases,
- The difference in density between the two phases increases, and
- The viscosity of the continuous phase decreases.

Making polymer-modified bitumens with good storage stability therefore implies micronising the dispersed phase (effect of the process and manufacturing process) or both phases of equal density at the storage temperature (effect of the chemical composition of the bitumen).

In order to improve compatibility, therefore prevent phase separation, it is fundamental to choose the right materials to blend and optimise all the variables that play an important role in the production of a PMB.

1.7. ASPHALT MIXTURES

The aim of a road pavement is to support the loads induced by traffic and to distribute these loads in such a way that the transmitted stresses do not exceed the capacity of the subgrade. Typically, flexible pavements consist of two main layer types (Figure 1.19): the bituminous layer including surfacing, binder course and base, and foundation layer including sub-base layer and subgrade. However, each layer of the pavement contributes to the overall performance of the road structure. Surfacing is principally to provide adequate skid resistance and has little structural significance. The binder course is to provide a smooth surface on which to construct the relatively thin surfacing and also to help to distribute the traffic load to the base, which is the main structural load bearing layer.

Brown (1997) suggested that in designing materials for bituminous layers, the designer should take account of the essential requirements of the following mechanical properties:

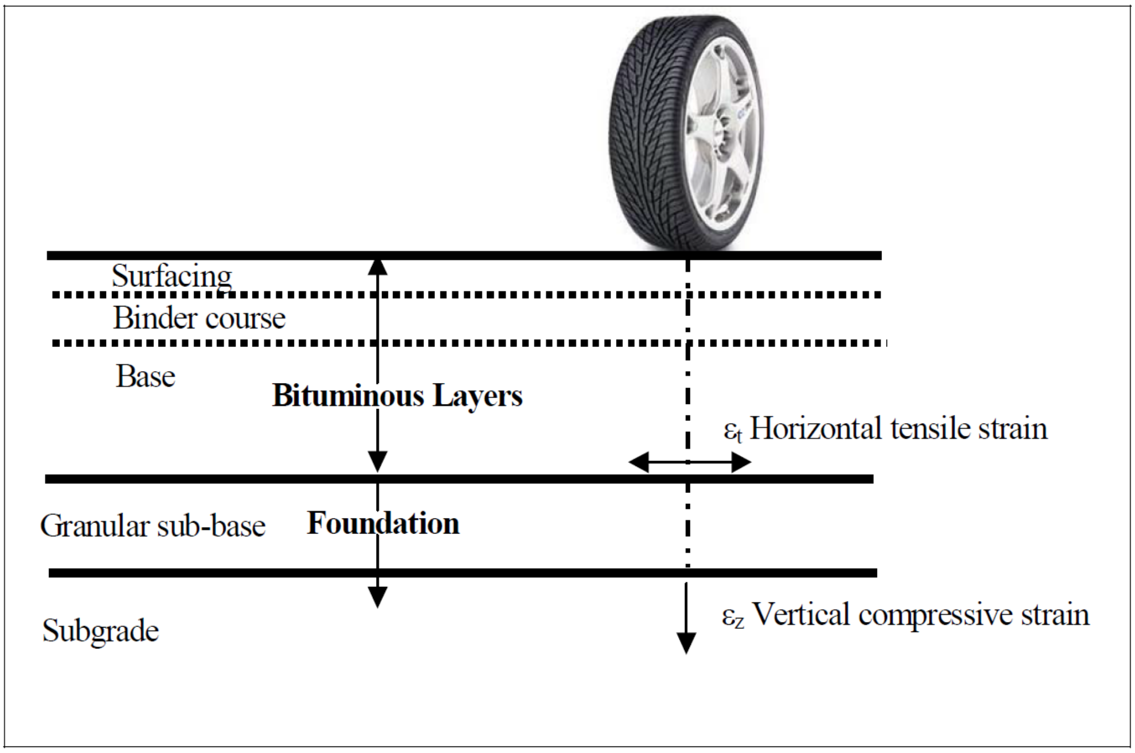


Figure 1.19: Typical Spanish flexible pavement structure

- High elastic stiffness to ensure good load spreading ability
- High fatigue strength to prevent the initiation and propagation of cracks due to repeated traffic load and due to environmental variation, i.e. temperature.
- High resistance to permanent deformation to prevent surface rutting.
- Adequate skid resistance in wet weather as well as a comfortable vehicle ride.

In order to design and evaluate road pavements it is necessary to have an understanding of their failure mechanism. The two main failure mechanisms for analytical pavement designs are illustrated in Figure 1.19. The maximum tensile strain at the bottom of the bituminous layer, which generally reflects the fatigue criteria and the maximum compressive strain at the top of subgrade that reflects permanent deformation criteria.

1.7.1. Hot Mix Asphalt

Hot Mix Asphalt (HMA) are the bound layers of flexible pavement structure and they are essentially made up of various kinds of aggregates in appropriate size combinations and different types of asphalt binders (Asphalt Institute, 2001).

The largest use of bitumen is in the production of Hot Mix Asphalt for construction of flexible pavements. By applying heat to the bitumen, it can be liquefied for mixing with mineral aggregates; it adheres to aggregate particles and binds them to form HMA. After cooling to ambient temperature, with bitumen’s excellent adhesive and waterproofing characteristics, HMA become a very strong and durable paving material which can sustain heavy traffic loads.

This type of asphalt mixture is referred to as HMA mainly because of an elevated temperature range of 135 °C to 170 °C required to plant produce the mixture. The HMA mixture usually consists of 94 to 96 percent of mineral aggregates and 4 to 6 percent of asphalt cement by weight of the mixture.

1.7.1.1. Binder

Bituminous binders form another important component of asphalt mixes. The binder content is a key mixture design parameter. It is known that the amount of binder in the mixture affects the durability and performance of the mixture. Most of the studies on the effect of binder on permanent deformation response of mixtures found in the literature centred on the effect of binder type (or grade) rather than the binder content. However, the studies that considered the effect of binder content found that it has significant influence on resistance to permanent deformation of mixtures. Specifications are put in place for the selection of the correct grade of asphalt based on environment, traffic, and the desired reliability factor (Asphalt Institute, 2001; Ontario Provincial Standard Specification, 2007).

1.7.1.2. Aggregates

Aggregate represents a major portion of asphalt concrete and it is responsible for the strength and toughness of the material. The physical properties of aggregates significantly affect the performance of asphalt pavement in service. In order to design asphalt concrete mixes properly, one has to understand the basic properties of aggregates, interactions between aggregates and binders, and the effect of different aggregate characteristics on the performance of asphalt mixtures. The Strategic Highway Research Program (SHRP) divided aggregate properties into two parts: consensus properties and source properties. Consensus properties include aggregate gradation, coarse aggregate angularity, fine aggregate angularity, flat and elongated particles and clay content. Source properties include toughness, soundness, and deleterious materials. All of these properties affect the performance of asphalt mixes in one way or another, but many authors have singled out aggregate gradation, aggregate angularity, and filler content as having significant influence on the rutting resistance of asphalt concrete (Asphalt Institute, 2001).

1.7.2. HMA for Wearing Courses

Wearing course is the top layer of the pavement and it is directly exposed to traffic and environmental forces (Transportation research board committee, 2011).

Wearing course provides characteristics such as friction, smoothness, noise control, rut and shoving resistance, and drainage. In addition, it serves to prevent the entrance of excessive quantities of surface water into the underlying HMA layers, bases, and subgrade (Garcia et al., 2001).

1.7.2.1. Asphalt Concrete

Asphalt concrete (AC) is designed to resist rutting, fatigue, low temperatures cracking and other distresses. The serious distresses associated with asphalt pavements are cracking, which occurs at intermediate and low temperatures, and permanent deformation, which occurs at high temperatures. These distresses reduce the services life of the pavement and elevate the maintenance costs (Hamed , 2010).

Bitumen binds the aggregate particles together, enhancing the stability of the mixture and providing resistance to deformation under induced tensile, compressive, and shear stresses. The performance of asphalt mixture is a function of asphalt cement, aggregate, and its volumetric properties. In recent years, there has been a rapid increase in using additives in asphalt concrete mixtures to improve its properties.

1.7.2.2. Very Thin Layer Asphalt Concrete (Béton Bitumineux Mince)

A very thin asphalt surfacing, made as an asphalt mixture by hot process, is a bituminous layer that improves the existing properties of pavement structure in terms of strength and deformability, while simultaneously it is less than 50 mm in thickness (Nicholls, at al. 2006). According to the French standard, a very thin asphalt surfacing (asphalt mixture label: BBTM – béton bitumineux très mince) is the layer 20-25 mm in thickness, with the absolute minimum of 15 mm at each point of the layer (AFNOR, 1992). In maintenance procedures, it is used as a layer of the pavement structure, whereas in rehabilitation procedures it is referred to as the layer for coating the existing surfacing for better separation of functions between the new surfacing and the existing one.

The thin asphalt surfacing extends the lifespan of pavement structures damaged by rutting, mesh and thermal cracks, and affected by material fatigue under the traffic load and temperature changes (Gilbert et al. 2004). It contributes to the aesthetic appearance of the final layer of the pavement structure and, while not being a structural layer, it contributes to the strength and water resistance, ride comfort, and noise reduction (Gilbert et al. 2004; Cooley et al., 2002). Numerous positive international examples, in which this type of asphalt surfacing is used for wearing layers of rehabilitated or maintained roads, testify to their applicability regardless of climatic or geographic position.

1.7.2.3. Stone Mastic Asphalt

Stone matrix asphalt (SMA) is a gap-graded asphalt mixture that has gained popularity worldwide. SMA was first developed in Germany during the mid-1960s to provide maximum resistance to rutting caused by the studded tyres on road (Brown et al. 1993). Earlier in the 1990s, SMA technology was widely used in the United States; however, most researchers' reports highlighted the mixtures' great possibility in rutting resistance but ignored any potential fatigue resistance of SMA (Ratnasamy et al., 2005–2010). Due to the nature of SMA mixes (gap-graded) and the relatively large proportion of asphalt content, stabilization is required to inhibit drain down of bitumen. These requirements can be achieved by adding fibre or polymer modifier, since commercial polymer is not economical in terms of usage (Mahrez, 2008); therefore using waste materials such as crumb tyre rubber in the asphalt mixture has been found to be more economical and environment-friendly. The use of crumb rubber modified bitumen binder seems to enhance the fatigue resistance, as illustrated in a number of studies.

Since there are only a limited number of studies that investigate the fatigue life of SMA mixtures using bitumen modified with waste materials, thus the main aim of the current study is to investigate the fatigue properties of SMA mixtures reinforced with waste tyre rubber.

Chapter II: EXPERIMENTAL

This chapter describes a more detailed insight of the materials and procedures (i.e., plans and methods) used throughout this research process. The information presented contains details on materials (e.g., asphalt binders, aggregates, crumb tyre rubber and polymeric additives), experimental plans and the test methods employed in this research work. All the materials used in this study were supplied or provided by Repsol S.A.

2.1. MATERIALS

The first step of the experimental work explained in this chapter focuses on materials. The following chapters describe all types of bitumen, rubber, polymers, and aggregates used.

2.1.1. Bitumen

Three different binders were used as base materials in this study: two neat bitumen samples, conventional bitumen 50/70 and 70/100, and crumb rubber modified bitumen.

2.1.1.1. NEAT BITUMEN

Conventional bitumen 50/70 was used as reference for the mixtures characterization, while the conventional bitumen 70/100 as reference for binder study. The physical and chemical properties of both bitumen are presented in Table 2.1.

Table 2.1. Physical and chemical properties neat bitumen.

Test	Units	Standard	B 50/70	B 70/100
Penetration (25°C, 100 gr, 5s)	0.1 mm	UNE-EN 1426	56	75
Softening point	°C	UNE-EN 1427	49	46
Penetration Index	-	UNE-EN 12591	-1.2	-1.3
Elastic Recovery at 25ºC	%	UNE-EN 13398	13	13
Fraass breaking point	°C	UNE-EN 13399	-10	-10

In order to minimize any variability in the characteristics of Crumb Tyred Rubber modified bitumen, CTR was obtained at industrial scale from the same batch of a Repsol Refinery.

2.1.2. Rubber

The crumb rubber used in this work was produced by the cryogenic process with maximum particle size 0.5 mm. Crumb tyre rubber NC 0-0,5 for the binder modification was supplied by Repsol S.A. (Spain). The crumb rubber gradation is shown in Figure 2.1. Its technical characteristics are resumed in the following Table 2.2, with the thermogravimetric analysis, both provided by the supplier (Repsol S.A.).

Table 2.2. Technical characteristics of crumb rubber

Grinding	Ambient
Weight (kg/dm^3)	1.15
Density (kg/m^3)	550
Color	Black
Rubber (%)	± 50
Carbon Black (%)	± 32
Acetone Exract (%)	± 12
Ash (%)	± 4

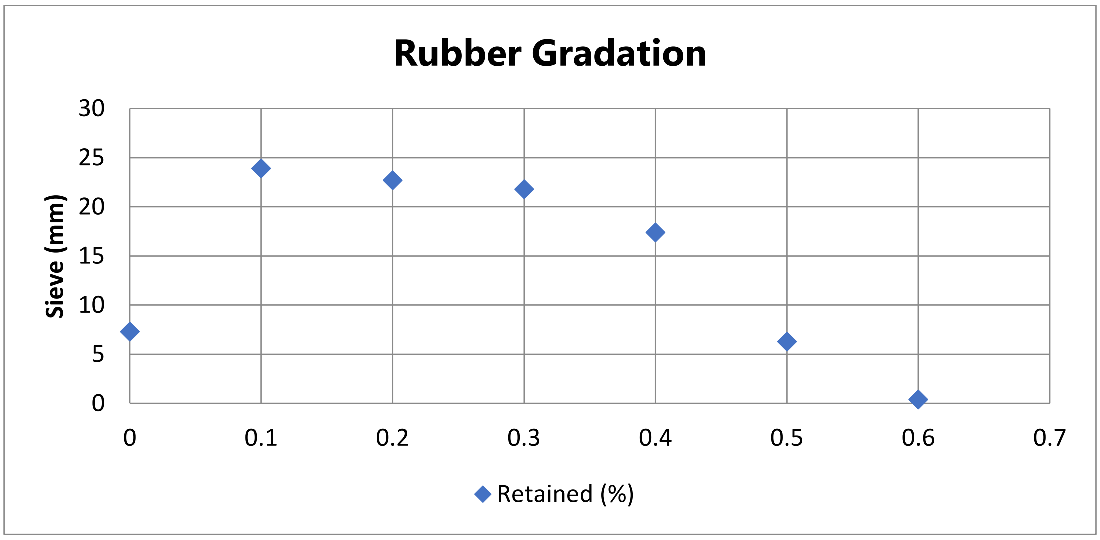


Figure 2.1. Gradation of the crumb rubber

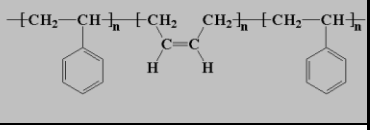
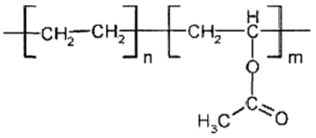
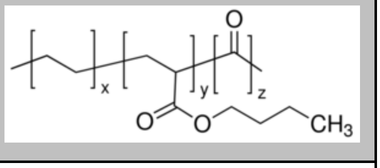
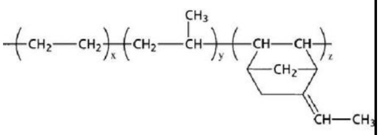
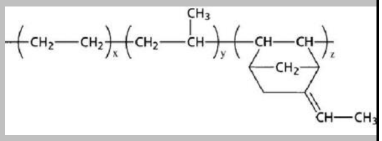
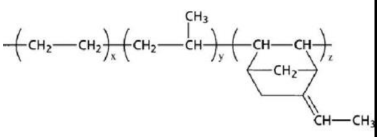
2.1.3. Polymers for bitumen

The copolymers used to formulate the so-called Hybrid Systems (HS), provided for different suppliers with confidentiality agreement with Repsol S.A., were styrene-butyl-styrene (SBS), typically used in the paving industry, ethylene-vinyl-acrylate (EVA), three different ethylene-propylene-diene-monomers (EPDM), two propylene-based elastomers (PBE), two types of ethyl-methyl-acrylate (EMA) and a polyolefin mixture for asphalt modification. Selected physiochemical characteristics of every polymer used are summarized in Table 2.3 and Table 2.4.

Table 2.3. Physiochemical characteristics of no-reactive polymers

Name	**Commercial Name**	**Supplier Company**	**Composition**
PBE 1	Vistamaxx 3000	Exxon Mobile	Ethylen Content [wt%] 11.0 ± 1.0
PBE 2	Vistamaxx 6202	Exxon Mobile	Ethylen Content [wt%] 15.0 ± 1.0
EMA 1	Exxelor 1202	Exxon Mobile	Maleic Anhydride Graft content: (0.5-1%w)
EMA 2	Exxelor 1840	Exxon Mobile	Maleic Anhydride Graft content: (0.2-0.5%w)
Rheopave	Xp10	LeHigh Technologies	Polyolefin Mixture with polyglicidilmethacrylate

Table 2.4. Physiochemical characteristics of reactive polymers

Pristine Polymer	**Sructure**	**Flow properties**	**Composition (wt.%)**	**Chemical Structure**
SBS	Radial structure	1 (B) (200ºC, 5kg)	Polystyrene: 23	
EVA	Copolymer	25 (B) (190ºC, 2.16kg)	Vinil Acetate: 28 Ethylene: 72	
EBA	Copolymer	7 (B) (190ºC, 2.16kg)	Butil Acrilate: 17 Ethylene: 83	
EPDMa	Copolymer Metallocene catalysts Narrow MWD	1 (B) (190ºC, 2.16kg) 17 (C)	Ethylen: 72	
EPDMb	Terpolymer, with ENB (A) Bimodal MWD Metallocene catalysts	60 (C)	Ethylene: 73 ENB: 5	
EPDMc	Copolymer Ziegler-Natta catalyst	44 (C)	Ethylene: 72	

2.3. MATERIALS TESTING

A comprehensive laboratory evaluation was conducted on modified binders. A suite of mechanistic and simulative tests was performed to study the behaviour of bitumen under various loading and environmental conditions. This section provides a description of the test methods and procedures performed in order to characterize the materials studied in this research.

2.3.1. Technological tests

This section details the different test performed in order to assess the properties of bituminous materials. In the Table 2.6 are summarized the test according to the standards and the laboratory devices.

Table 2.6. Technological test's standards and laboratory devices.

Test	Standard	Device
Penetration	UNE-EN 1426	Petrotest PNR12 (Germany)
Softening point	UNE-EN 1427	Herzog Walter GmbH (Germany)
Penetration Index	UNE-EN 12591	
Force ductility test, at 5°C	UNE-EN 13589	Mecanica Cientifica (Spain)
Elastic Recovery at 25ºC	UNE-EN 13398	Mecanica Cientifica (Spain)
Fraass breaking point	UNE-EN 12593	Petrotest BPA 5 (Germany)
Polymers dispersion on bitumen. Microscopy	UNE-EN 13632	Leica DM 2500 (Germany)
Storage stability at 180ºC	UNE-EN 13399	Toothpaste tubes
Multi Stress Creep Recovery (MSCR)	AASHTO T 350_14	DSR Rheometer 302, Anton Paar (Austria)

2.3.1.1. Penetration test

The test is a measure of consistency at medium in-service temperature (25 ºC), according to the standard EN 1426. It was performed by allowing a standard loaded needle of specified dimensions, which is loaded to 100 g to penetrate vertically into the material for a period of 5 seconds. Penetration was measured by the distance the needle sinks into the bitumen, in units of 1/10 mm. Three or more measurements were registered for each binder sample and the average value was considered.

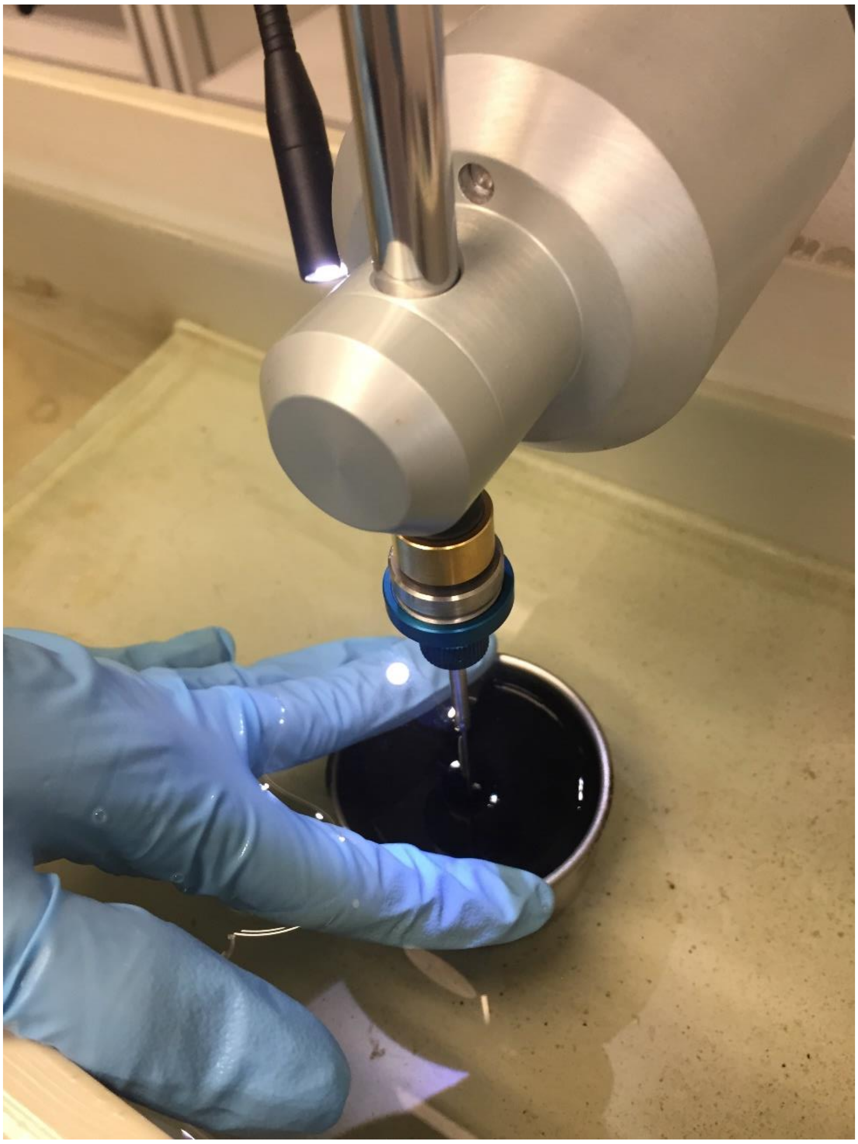


Figure 2.4. Penetration test

2.3.1.2. Ring & Ball softening point test

Ring & Ball softening point test is a method to determine bitumen consistency at high in-service temperatures. The standardized procedure for this test can be found in UNE-EN 1427:2007. The test is conducted by using Ring and Ball apparatus. A brass ring containing test sample of bitumen is suspended in liquid like water or glycerine at a given temperature. A steel ball is placed upon the bitumen sample and the liquid medium is heated at a rate of 5° C per minute. Temperature is noted when the softened bitumen touches the metal plate which is at a specified distance below. Generally, higher softening point indicates lower temperature susceptibility and is preferred in hot climates.

2.3.1.4. Fraass breaking point

The scope of this test is to determine the temperature at which the binder tends to break rather than to flow when stressed. A thin steel flat steel plaque, coated with the bitumen sample, is flexed under specified conditions at a descending series of temperature. The Fraass breaking-point is the temperature at which the first cracks appear in the coating. According to the standard EN 13399, the amount of bitumen on the steel plaque has to be 410 ±10 mg, the cooling rate is 1 ºC/min and the flection starts at a temperature 10 ºC higher than the expected Fraass temperature.

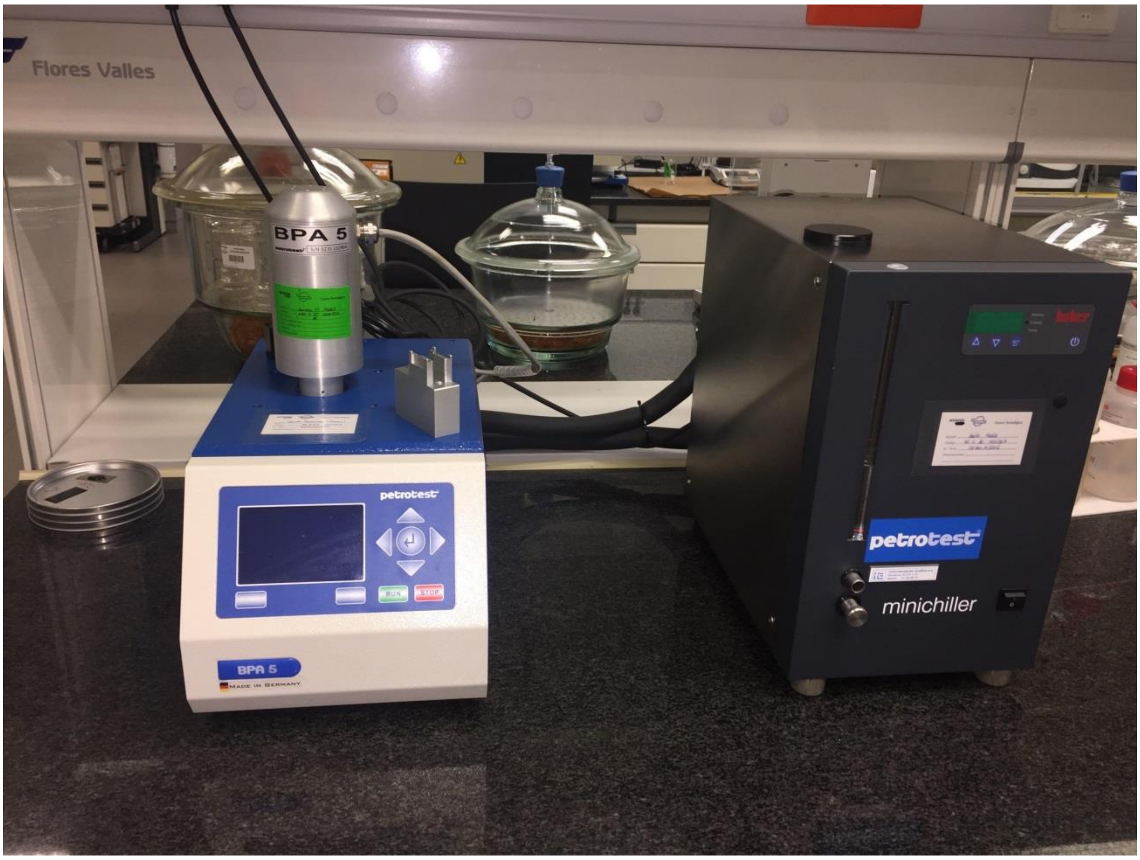


Figure 2.5. Fraass breaking point test

2.3.1.5. Force-ductility

The Force Ductility test measures the tensile properties of polymer modified asphalt binders. The standard used in this study for the force-ductility test was EN 13589:2008. According to this standard, the test sample must be stretched in a ductilometer at 5 ºC and at consistent speed of 5 mm/min until it breaks or until it reaches 1,333% elongation (400 mm). The result of the force-ductility test is a plot of force (stress) vs. distance (strain). The total area under the resulting force-distance curve is used to represent the cohesive energy (Read and Whiteoak, 2003). This area can differentiate between bitumens. Performance can be measured through interpreting the results of the deformation energy ratio, maximum stress/force, modulus, the elastic phase (or the area under the curve before the initial primary peak), the total area under the stress-strain curve and/or the total ductility until specimen rupture.

2.3.1.6. Elastic recovery

Elastic recovery (ER) is the degree to which a substance recovers to its original shape after release of stress. A certain degree of ER is desirable in pavement to avoid permanent deformation. The bitumen sample is heated and poured in the mould assembly placed on a plate. These samples with moulds are cooled in the air and then in water bath at 25 °C temperature (EN 13398). The excess bitumen is cut and the surface is levelled using a hot knife. Then the mould with assembly containing sample is kept in water bath of the ductility machine for about 90 minutes. The sides of the moulds are removed, the clips are hooked on the machine and the machine is operated. The distance up to the point of breaking of thread is the elastic recovery value which is reported in cm.

2.3.1.7. Storage stability

In order to evaluate quality of dispersion of polymer and rubber into the bituminous base, storage stability tests were performed using aluminium toothpaste tubes (32 mm in diameter and 160 mm in height) filled with HSs or CTR70, at 180ºC for 72 h, according to the UNE-EN 13399. Finally, the tube was cut into three equal sections and the storage stability value was determined by the difference of softening point temperatures of the top and the bottom fractions.

2.3.2. Thermal analysis characterization and microscopy

All the binders were characterized trough thermal analysis by two different techniques which will following described. In addition, the quality of dispersion of additives and rubber was evaluated with fluorescence microscopy.

2.3.2.1. Microscopic fluorescence

The morphology of the samples and the polymer dispersion were evaluated by means of fluorescence microscopy observations in accordance with UNE-EN 13632 using a Leica DM 2500 microscope (Germany) with a 400X magnification at room temperature. Fluorescence microscopy reveals a polymer rich phase and bitumen rich phase. The bituminous phase is black in the image. The polymer phase is yellow if printed in colour and shades of grey if viewed in black and white. The fluorescence microscope differs from a normal light microscope because two filters and a dichromatic mirror are attached to the fluorescence microscope. The two filters and dichromatic mirror are part of a set that changes the source light to the excitation frequency and allows the fluorescence emissions to go to the eyepiece (Slavik, 1996).

Figure 2.6. Leica DM 2500 microscope

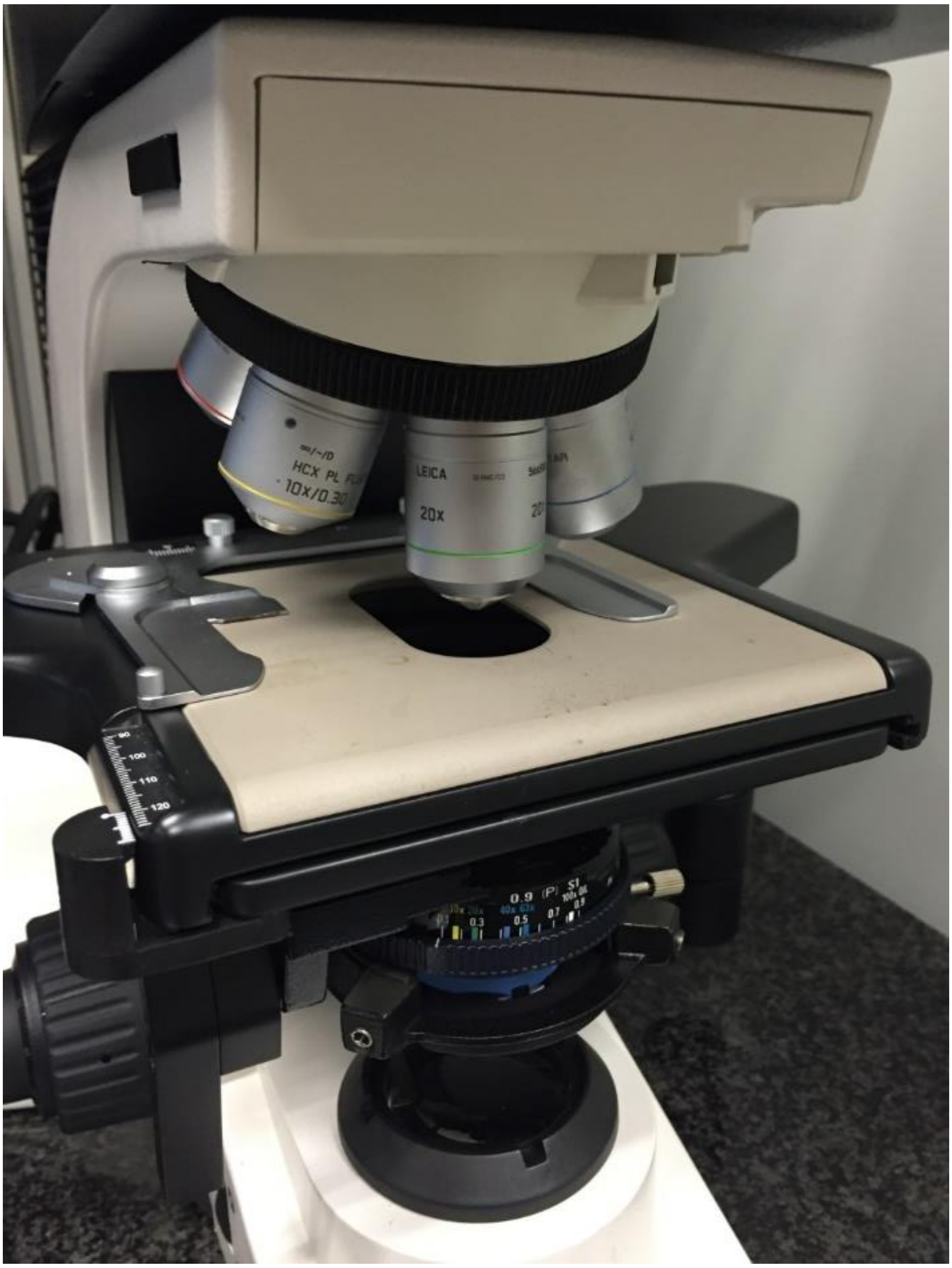


Figure 2.7. Fluorescence microscopy observations

2.3.3.5. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures the temperatures and the heat flows associated with transitions in materials as a function of time and temperature. This kind of analysis provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity.

In this work modulated differential scanning calorimetry (MDSC) was carried out with a DSC-Q100 calorimeter (TA Instruments, USA), using 5–10 mg samples sealed in hermetic aluminium pans. The sample was purged with dry nitrogen gas at a flow rate of 50 ml/min, to avoid any condensation of moisture. In order to provide the same recent thermal history, all the modified binders were heated for 5 min at 150ºC and placed into hermetic aluminium pans for 24 h at room temperature before measurement.

During the MDSC samples were quench-cooled to −80 ºC, kept for 5 min at this temperature to reach the equilibrium, and, finally, heated up to 120 ºC, at a heating rate of 5°C/min with an oscillation period of 60 s and amplitude of ±0.50°C.

2.3.3.7. Thermogravimetry analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique for measuring the amount and rate of change in sample mass as a function of temperature and time. It is used to characterize any material that exhibits weight loss or phase changes as a result of decomposition, dehydration and oxidation. Thermal degradation studies were performed on a TA Instruments 500 thermogravimetric analyzer using 10.0 ± 0.5 mg samples to eliminate any sample size effects.

The initial purge gas, Nitrogen (N_2), flow rate to the TGA was set at 40 mL/min from 40 °C to 550°C. Sample temperature was allowed to equilibrate at 40°C where isothermal conditions were maintained for 3 min. At this point the purge gas was changed to air with the flow rate to the TGA set at 40 mL/min and the sample temperature was increased to 750°C at a heating rate of 20 °C/min and held in isothermal conditions for an additional 5 min.

Finally, the purge atmosphere was changed to N_2 and heating continued until a constant weight was achieved at 750°C.

2.3.3. Rheological characterization

Rheological properties of a bitumen system are determined by measuring its viscosity at different rates of shear for a given temperature, shear stress and time (Loeber, et al., 1998). The measures can be done with stead-state tests or with dynamic tests.

The viscous flow behaviour and the linear viscoelastic properties of bitumen were studied through different types of equipement: Dynamic Shear Rheometer (DSR-Physica MCR302, Anton Paar, Austria) for the dynamic test and the Brookfield Viscometer DV-II+Pro for the stead-state test.

2.3.3.1. Viscosity

Viscosity measurements were performed in rotational viscometer (Brookfield Viscometer DV-II+), changing the shear rate (10, 20, 50 and 100 rpm) and the temperature (135, 150 and 180 °C). Three readings of viscosity were made to each combination (shear rate and temperature). The spindle SC4-21 was used for all the binders, as specified by Asphalt Institute (1994).

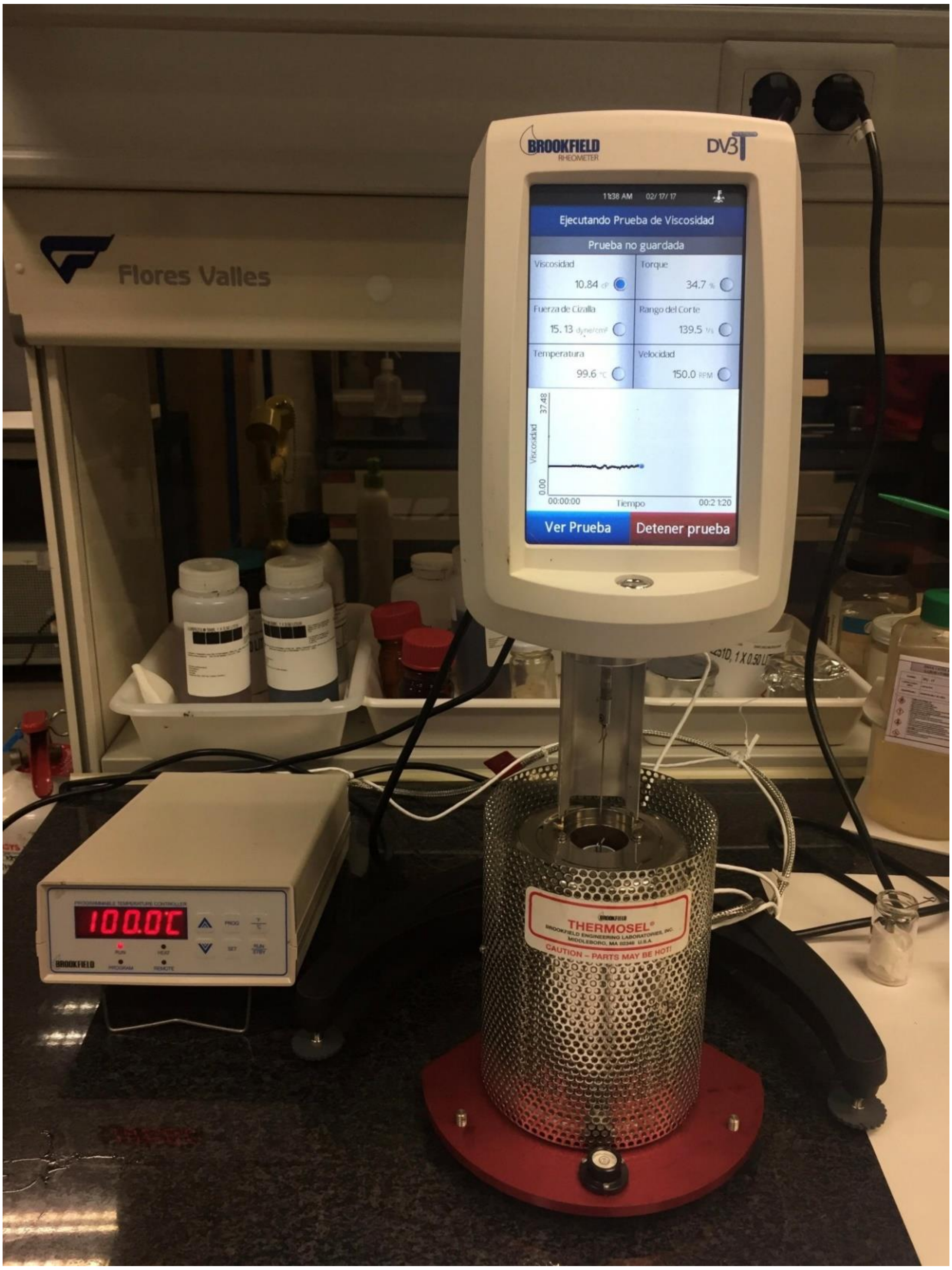


Figure 2.8. Brookfield Viscometer

2.3.3.2. Temperature and Frequency sweep

Frequency sweep tests, at different temperatures (40, 60 and 80ºC), within the linear viscoelasticity region were performed, over a range from 0.1 up to 10 Hz using smooth plate-and-plate geometry (25 mm diameter, 1–2 mm gap). Dynamic temperature sweep tests, at 1% strain, using a heating rate of 1 °C min−1 and 10 rad s−1 (AASHTO TP5 [26] were carried out in the range of temperature 40–100ºC.

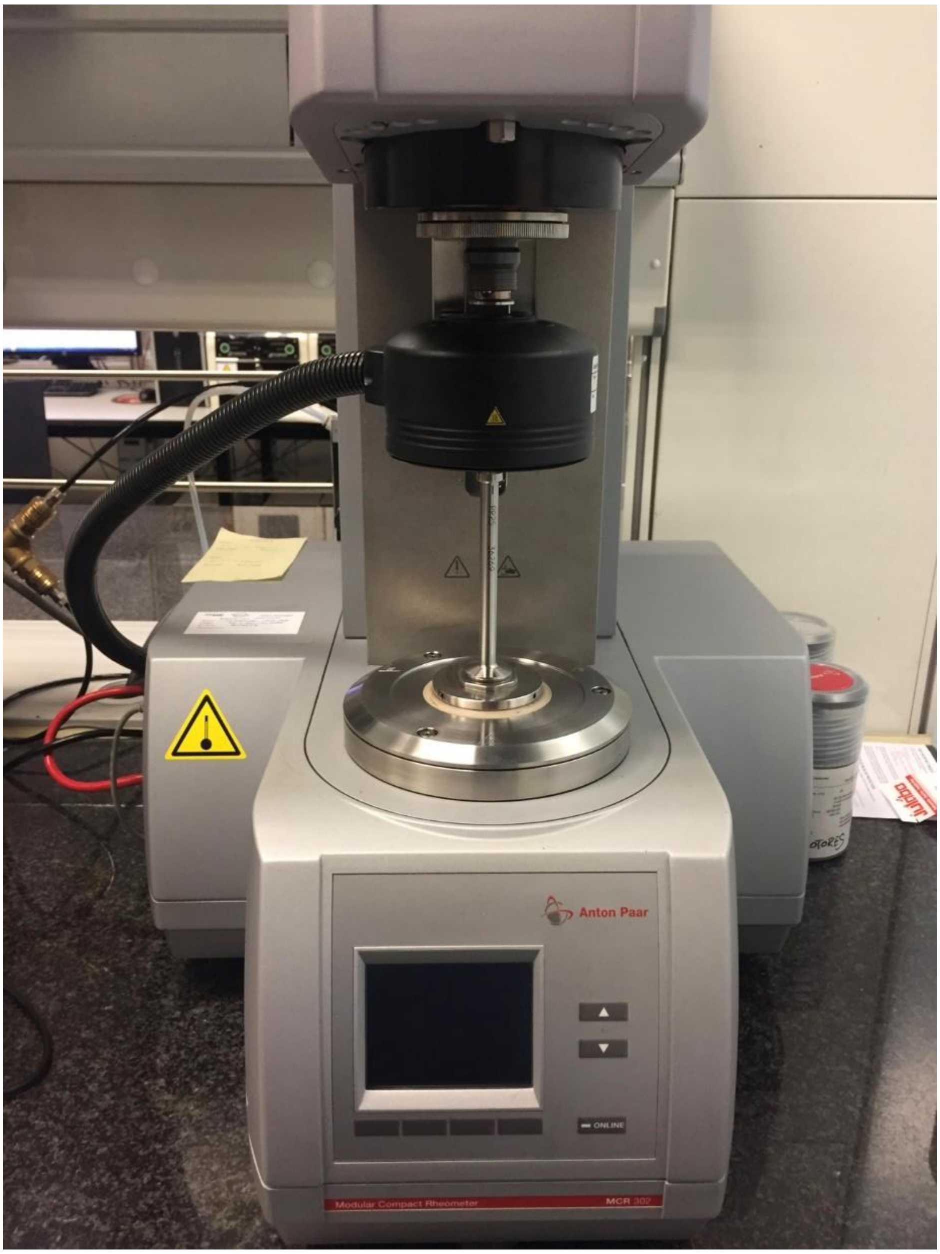


Figure 2.9. Dynamic temperature sweep tests

2.3.3.3 Multi Stress Creep Recovery Test

Multi stress creep recovery tests (MSCR) were conducted in accordance with the EN 16659 standard. The MSCR test is performed using a Dynamic Shear Rheometer (DSR), with parallel plates of 25 mm diameter and a gap of 1 mm. The binder specimen is subjected to series of ten creep/recovery cycles, with a 1 second creep period followed by a 9 seconds recovery period. This test was carried out at temperature of 60° C, which can be considered a typical maximum temperature expectable in pavement. The test is performed at a low stress level of 0.1 kPa, followed by a stress level of 3.2 kPa.

2.3.3.4. Black Diagram

Black Diagram consists in a graph of complex modulus obtained from a dynamic test versus phase angles. The frequencies and temperatures are eliminated from the plot, which allows all the dynamic data to be presented in one plot without the need to perform the time-temperature superposition principle (TTSP) manipulations on the raw dynamic shear data. This plot is very useful for presenting the effect of ageing or modification of bitumen. Black diagrams were studied for all the binders comparing the behaviours between the different HS and the neat bitumen.

Chapter III: BINDERS RESULT ANALYSIS

This section portrays all the results of binder characterization. The analysis of results is divided in no-reactive and reactive polymer modified binder behaviour. The skeleton of testing covers was chosen keeping in mind the end goal to research that impact of hybrid system in the bitumen properties subjected to distinctive loading parameters. The rheological properties of the different binders were portrayed utilizing dynamic shear rheometer over wide ranges of temperatures and frequencies. In this study both all types of hybrid systems designed were characterized and a summary of all results introduced underneath in tables and graphical structure.

3.1. NON-REACTIVE POLYMER MODIFIED HYBRID SYSTEMS

3.1.1 Mechanical and Technological Characteristics

Table 3.1 gathers conventional test results (penetration grade, ring and ball softening temperature, penetration index values, elastic recovery at 25 ºC, and Fraass breaking point) typically employed by the paving industry according to the European Standards, for the base rubberised bitumen (CTR70), for the resulting HSs and, for the sake of comparison, for a neat bitumen of similar penetration than CTR70. In general, this table points out some well-known effects of bitumen modification with crumb tyre rubber.

Table 3.1. Convention test results of bitumen

	Unit	HS-SBS	HS-EVA	HS-EBA	HS-EPDMa	HS-EPDMb	HS-EPDMc	CTR70	70/100
Penetration	0.1mm	54	69	61	58	53	52	70	75
Softening Point ($T_{R\&B}$)	ºC	75	58	65	58	57	60	51	46
Penetration Index	-	3.8	1.4	2.6	1.0	0.6	1.1	0.1	-1.3
Elastic Recovery, 25°C	%	93	63	60	57	65	63	61	13
Fraass Point	°C	-25	-21	-19	-15	-15	-18	-20	-10
Dif. of $T_{R\&B}$ (Stability)	°C	4.3	1.4	7.5	1.7	1.8	2.1	10	
Cohesive Energy	J/cm^2	3.165	3.232	3.202	1.743	2.949	1.721	2.702	0.007

Thus, by comparison with the neat bitumen (70/100), the rubberised bitumen (CTR70) presents a softening temperature 5 °C higher than the reference and an elastic recovery four times larger, giving clear indications of a higher elastic character and so, an improvement of the high in-service temperature behaviour. The greater and positive values of the penetration index point out the expected lower temperature susceptibility of the rubberised bitumen. Finally, as the Fraass point is 10 °C below 70/100, the brittleness of the CTR70 is beneficially lower than the breaking point of a comparable conventional bitumen (Piłat, 2011). Unfortunately, the large difference between the ring and ball softening points of the top and bottom fraction after the storage stability test discloses the mentioned instability of the rubberised bitumen as a consequence of the settling of undissolved rubber particles.

Aiming to mainly improve the high temperature storage stability and, secondarily, the in-service properties of the binder, Hybrid Systems (HSs) were prepared by blending selected polymers with CTR70 and further curing with sulphur. According to the results presented in Table 3.2, all HSs, with the exception of HS-EBA, present a notable improvement in storage stability since differences in softening point temperatures remain below 5 °C, which is the limit value to meet the storage stability requirement of EN14023.

Table 3.2. Technological properties for the bituminous binders studied.

	Unit	**HS-SBS**	**HS-EVA**	**HS-EBA**	**HS-EPDMa**	**HS-EPDMb**	**HS-EPDMc**	**CTR 70**	**70/100**
Penetration	0.1mm	54	69	61	58	53	52	70	75
Softening Point ($T_{R\&B}$)	°C	75	58	65	58	57	60	51	46
Penetration Index	-	3.8	1.4	2.6	1.0	0.6	1.1	0.1	-1.3
Elastic Recovery, 25°C	%	93	63	60	57	65	63	61	13
Fraass point	°C	-25	-21	-19	-15	-15	-18	-20	-10
Dif. of $T_{R\&B}$ (Stability)	°C	4.3	1.4	7.5	1.7	1.8	2.1	10	
Cohesive Energy	J/cm^2	3.165	3.232	3.202	1.743	2.949	1.721	2.702	0.007

Table 3.2 also reveals that the addition of 3 wt% of a second polymeric modifier to the rubberised bitumen further improves all technological properties because, on the one hand, penetration is reduced and, on the other hand, softening point, elastic recovery and penetration index are remarkably

increased. However, only HS-EVA and, especially, HS-SBS are able to improve the low- temperature flexibility as pointed out by the shifting of the Fraass temperature to lower values. In this sense, hybrid modification with all EPDMs tested seems to worsen the low temperature behaviour, since the ''Fraass'' brittle fractures happen at higher temperatures compared to the base rubberised bitumen.

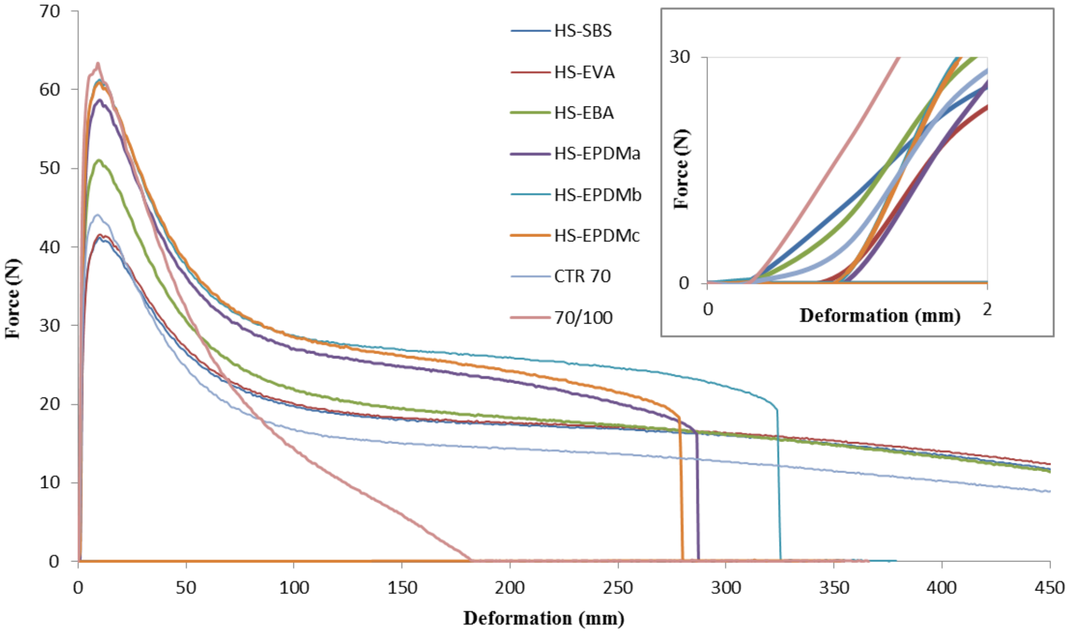


Figure 3.1. Force ductility curves, at 5ºC, for the studied binders.

Force Ductility Tests are not only useful to determine the cohesive energy but also provide more detail about the mechanical behaviour and the effect of modifiers on elongation and failure of bitumen. In this regard, Fig. 4.1 shows that Force elongation curves of all HSs exhibit the typical ductile profile of modified binders. At small elongation ratio, force is linear with elongation, corresponding to the elastic region (inset in Figure 3.1). Even though some authors claim that, in this region, stress development is mainly due to bitumen properties, while the modifier's contribution is very small (Shuler, 1987), by contrast, according to the inset in Figure 3.1, it can be deduced that all EPDMs yield larger elastic modulus compared to the other polymers. All samples reach the maximum force (yield point) early in the elongation process, at around 100 mm elongation, and then begin to decline, due to flow of the binder up the breaking point.

The highest maximum force load is showed by HS-EPDMs and neat bitumen, next a second group of CTR70 and HS-EBA, while the lowest values correspond to HS-EVA and HS-SBS. As shown by these results, EPDM copolymers give rise to stiffer, but less cohesive materials, since they break clearly before the required final length of 400 mm.

Regarding the rubberised bitumen, it is commonly reported in the literature that test specimens present a premature rupture during the elongation process, as a consequence of the heterogeneity of the rubber particles, which act as breaking points (Rodríguez-Alloza, 2013). Nevertheless, here, CTR70 reaches an ultimate elongation very close to the required limit of 400 mm (Figure 3.1) and presents a high cohesive energy clearly higher than 2 J/cm2 (Table 3.2), which is a value typically required for polymer modified bitumen. This result hints that the homogeneity of the rubberised bitumen, used as base for HSs, has been improved by the digestion/dispersion of rubber particles during processing.

According to the main goals of this research, as shown in Table 3.2, it noteworthy that all HSs (except HS-EBA) present an improved high temperature storage stability fulfilling the ring and ball softening point criterion (ΔTR&B<5ºC). Consequently, as it will be discussed in the following sections, the combined modification by both, CTR and polymeric additives may yield to positive and complementary synergic interactions.

3.1.2 Rheological characterization

One of the most significant aspects of the rheological behaviour of bitumen is its dependence on temperature. Hence, temperature sweep tests in oscillatory shear were firstly performed on all samples, showing, in Figure 3.2, the evolution of the complex shear modulus and loss tangent with temperature.

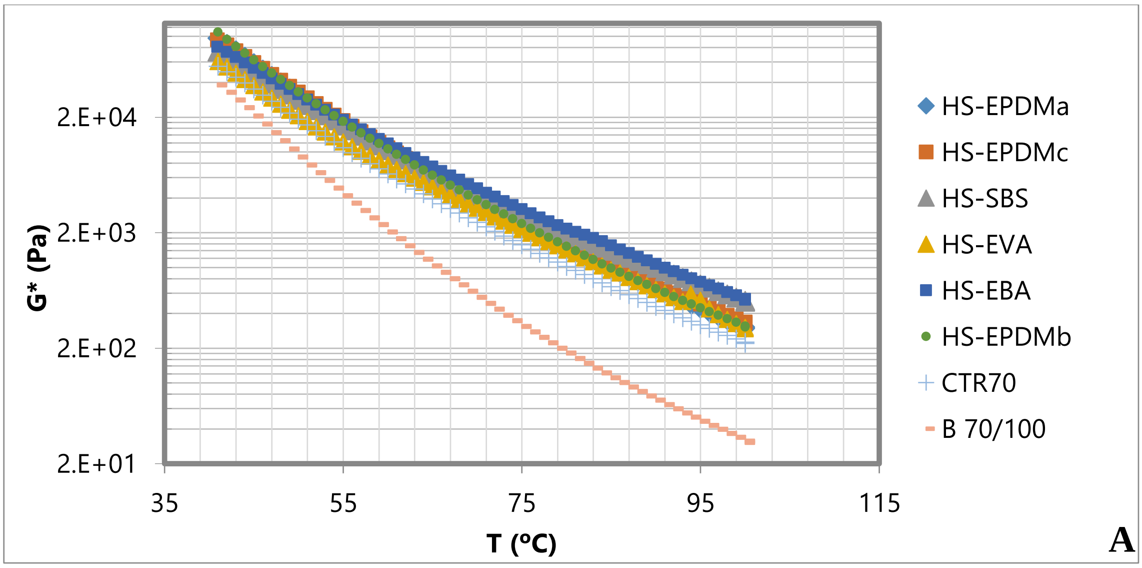


Figure 3.2a. Evolution of complex shear modulus with temperature, at 10 rad/s, for the studied systems.

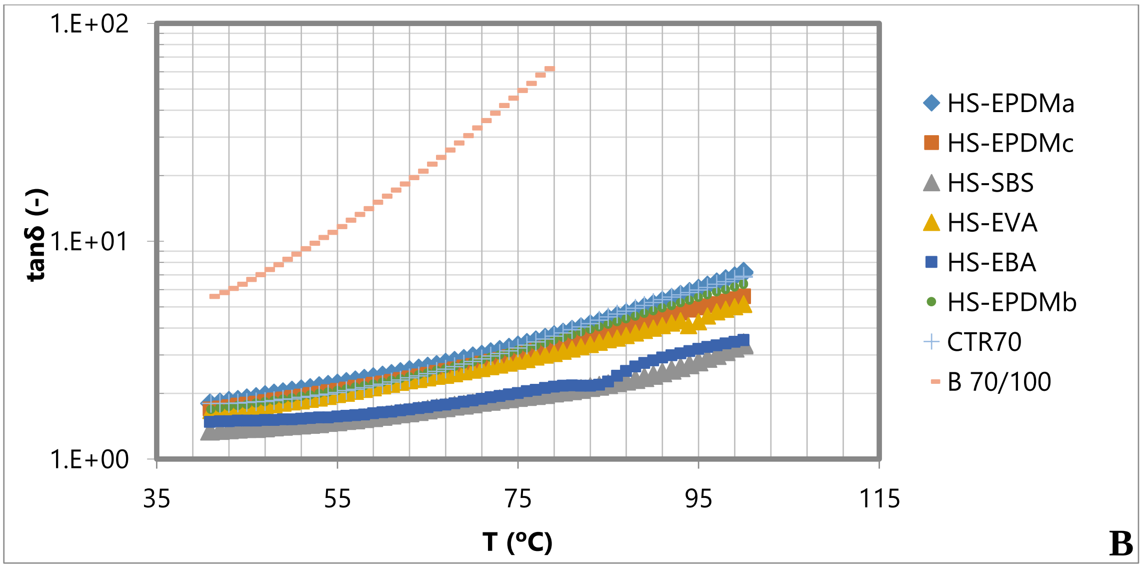


Figure 3.2b. Evolution of loss tangent with temperature, at 10 rad/s, for the studied systems.

As can be seen, B70/100 presents the typical evolution of the viscoelastic functions of unmodified bitumen, characterised by a steady decrease of G* with temperature, whereas loss tangent is progressively increased. In addition, this neat bitumen presents the expected prevailing viscous behaviour, with tan $\delta > 1$, over the entire temperature interval tested and the absence of the "plateau" region. Therefore, a continuous transition from the glassy to the Newtonian region takes place by increasing temperature.

Even though, the rubberised bitumen (CTR70) presents similar penetration than the reference neat bitumen, the addition and processing of rubber particles remarkability modifies rheological properties, in the whole temperature range, yielding a large increase in complex modulus and a drop in loss tangent.

Regarding HSs, in general, the addition of any of the polymeric modifiers to the rubberised bitumen, further enhances the linear viscoelastic response, but the magnitude of the improvement depends on the polymer type and the testing temperature. In order to achieve a comparative analysis of the different polymers, loss tangent is chosen because of its greater sensitivity to modification changes. Thus, according to the results portrayed in Fig. 4.2B, EBA and especially SBS, yield the greatest ability to modify the rheological response.

In addition, the slope of the loss tangent or complex modulus vs. temperature can be considered as a measure of material thermal susceptibility over the temperature range studied. As can be seen in Figure 3.2, the observed flattening in both curves for HSs, points out a reduction in binder temperature susceptibility in the whole temperature window and, consequently, better thermal resistance is expected for the resulting pavement. Finally, it is worth to mention that, as appreciated in Figure 3.2B, HS-EBA displays a distinctive feature illustrated by a shoulder in loss tangent at about 80ºC. As it will be discussed later, this is attributed to the melting of an EBA-rich phase inside the bituminous system, which contributes in a greater extent to the total rheological behaviour.

More detailed information can be deduced by analysing the frequency sweep tests at selected high in-service temperatures (Figures 4.3 and 4.4, at 40, 60 and 80 ºC) for neat bitumen, CTR70 and HS blends.

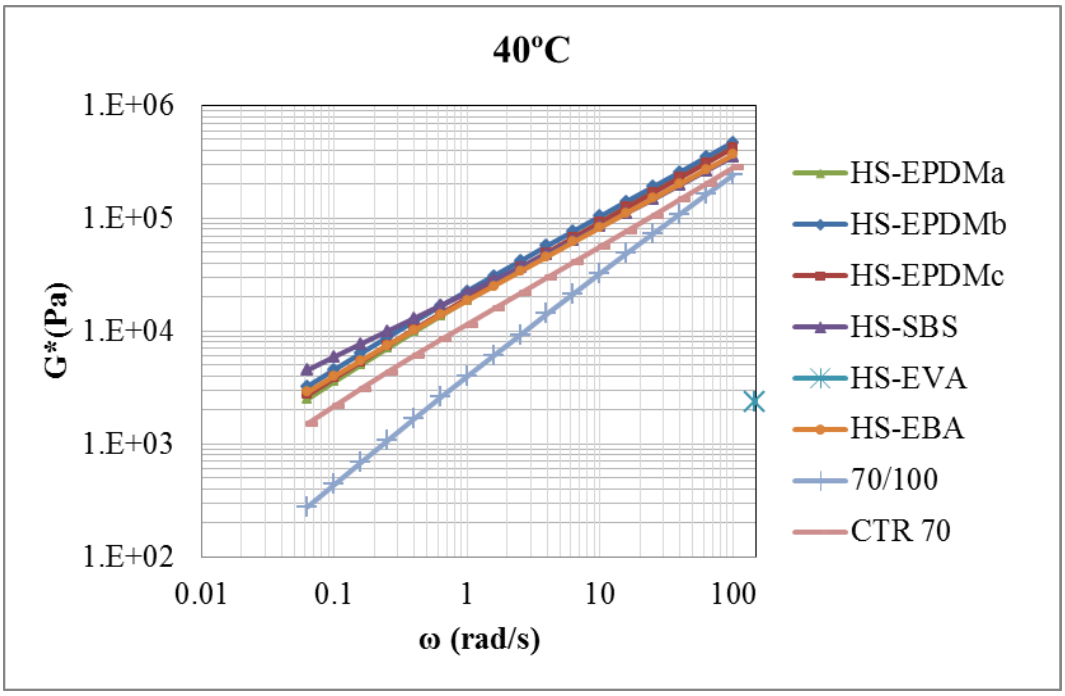


Fig. 4.3a

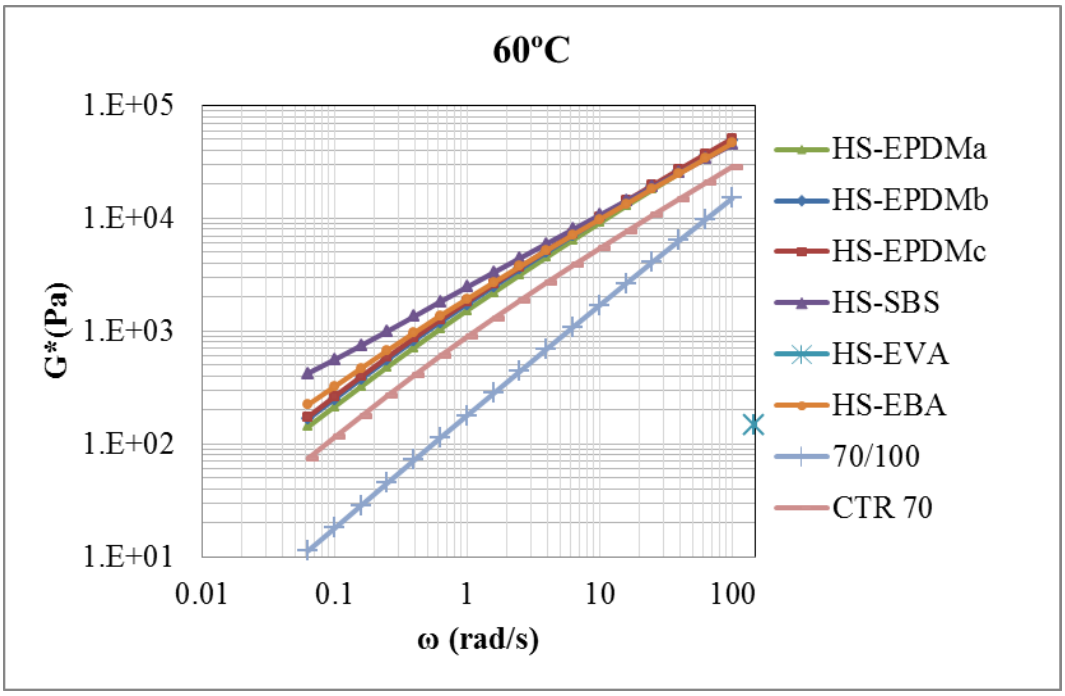


Fig. 4.3b

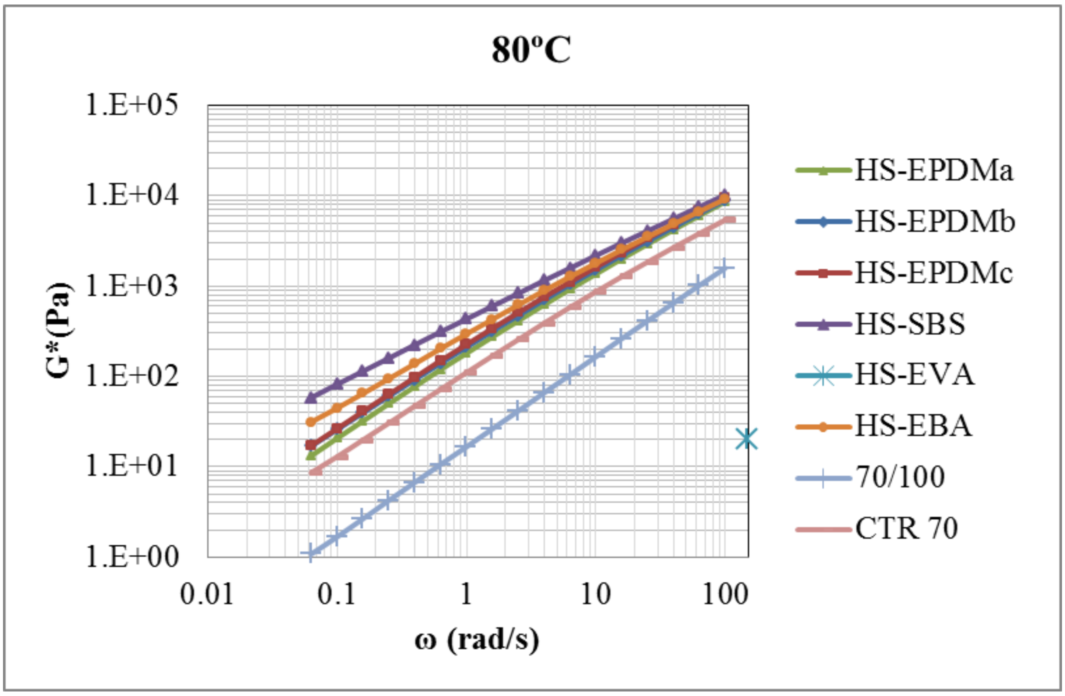


Fig. 4.3c

All samples are characterised by a steady increase of G* with frequency and a predominately viscous character (tanδ>1). In general, as temperature rises and frequency decreases the improvement degree, of the polymer addition, is more pronounced, reaching differences of more than one order of magnitude for the complex shear modulus. In addition, whereas neat bitumen reaches the terminal region at 60 and 80ºC, (as evidence by G* slopes of -1) HSs present flattened slopes and, consequently, the Newtonian region is shifted towards lower frequencies.

As a result, according to the obtained rheological results a sequence of capability of modification of polymeric additive of rubberized bitumen may be established as follows: SBS>EBA>EVA>EPDMs, which is in general in agreement with the technological tests.

Finally, it is important to underline that, at 80ºC, as modification is more effective, HSs tend to develop a critical gel, characterised by loss tangent values close to 1 and almost independent of frequency (Navarro, 2005).

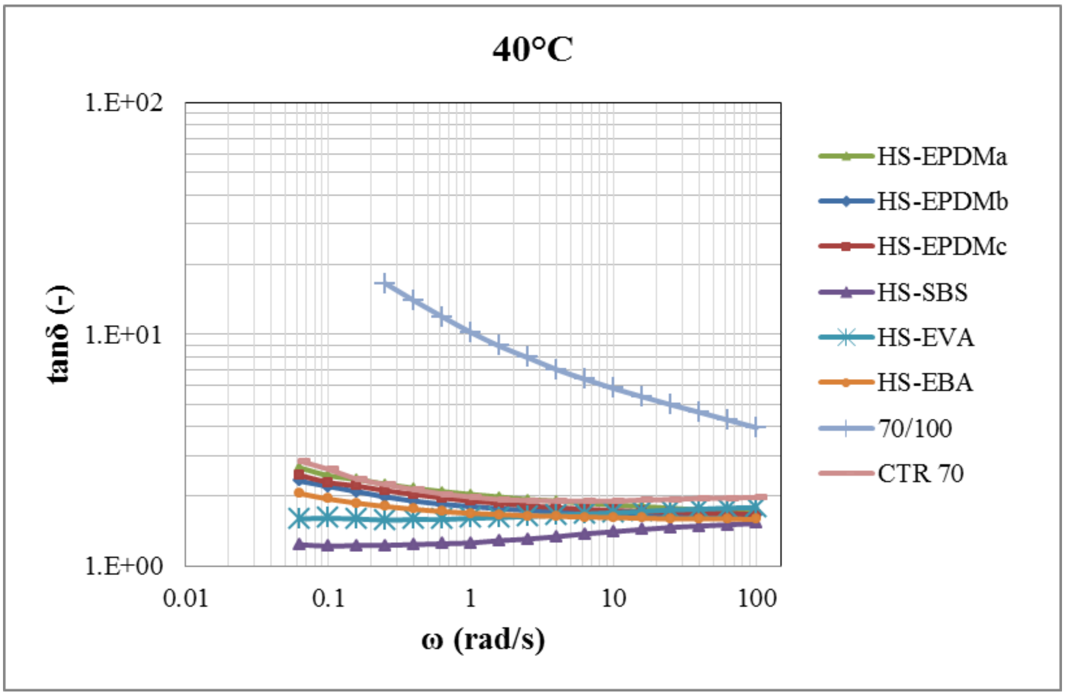


Fig. 4.4a

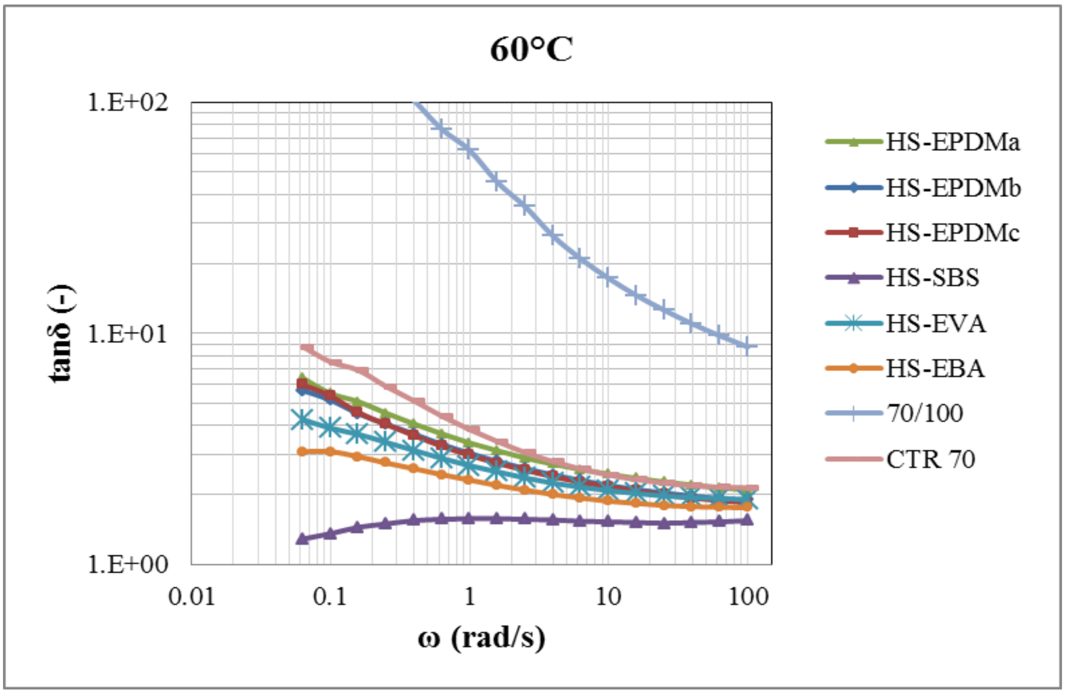


Fig. 4.4b

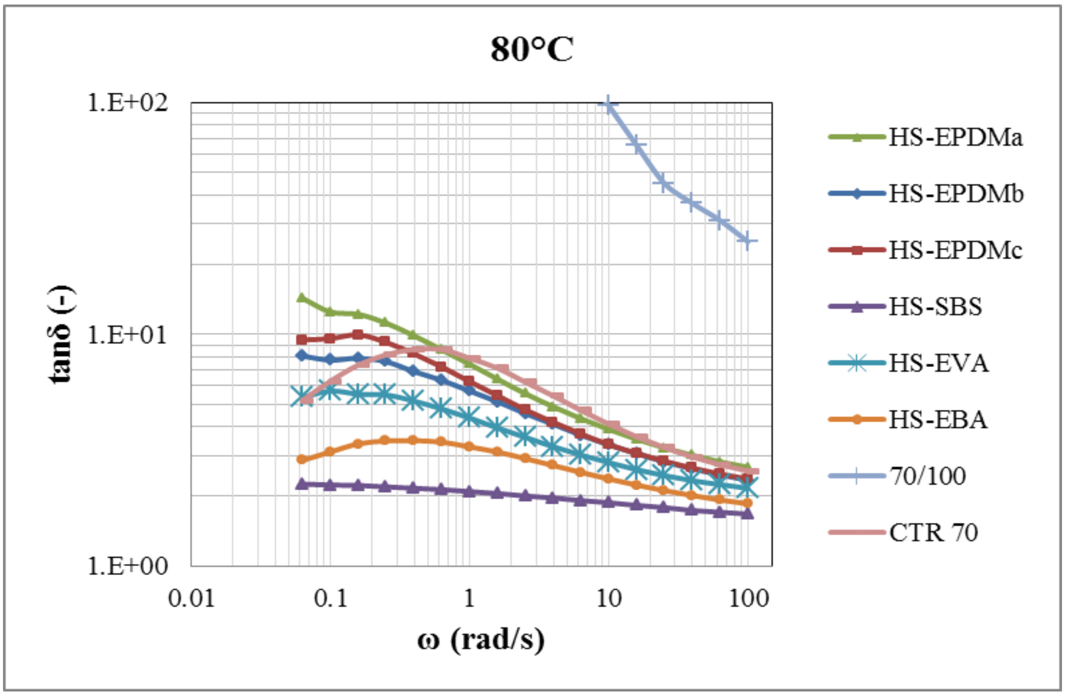


Fig. 4.4c

Finally, as a drop in the loss tangent values correlates to improved global elasticity characteristics and, the increased complex modulus means better total resistance to deformation when the bitumen is subjected to shear loading, it may be concluded that the high in-service properties of HSs undergo a notable improvement (Airey, 2003). Therefore, a significant improvement of the rutting resistance of the resulting pavement is expected at these temperatures.

A different approach to analyse the linear viscoelastic behaviour in a wide temperature range is by means of the Black diagrams, i.e. phase angle (δ) vs. complex shear modulus (Figure 3.5). For a better visualisation, data have been split in two plots (Figure 3.5A and 4.5B) and neat bitumen and CTR70 were included in both Figures for comparison purposes. These plots have been widely used not only for verifying the time–temperature superposition principle in bituminous systems, but also for evaluating the topological structures, given its sensitivity to structural or compositional changes.

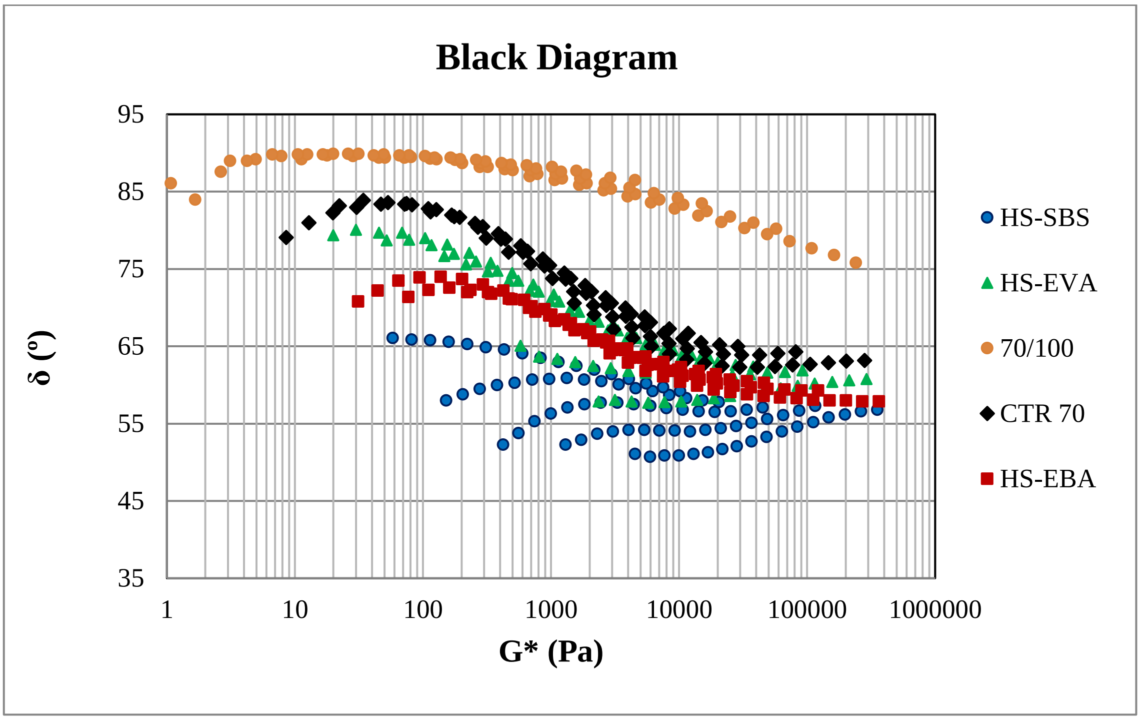


Fig. 4.5a

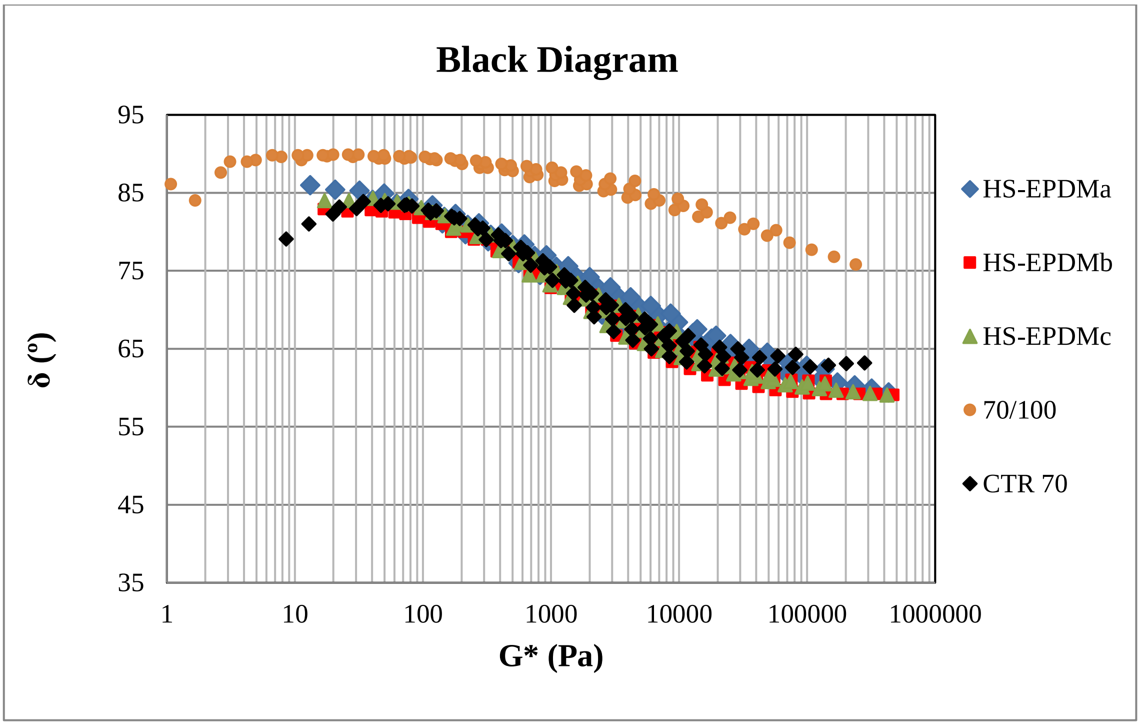


Fig. 4.5b

As shown in Figure 3.5, B70/10 displays the well-known pattern of neat bitumen, consisting in a wide Newtonian viscous flow region (at G*<100 Pa) followed by a steady decrease of the phase angle. In addition, given that all isothermal frequency data merge into a single common curve, the Time-Temperature-Superposition Principle holds, at least, empirically for B70/100.

The addition of CTR/polymer gives rise to a markedly different behaviour since isothermal curves either do not completely overlap (CTR70, HS-EBA and HS-EPDMs), or are clearly dispersed and, therefore, not superimposable (HS-EVA and HS-SBS). This thermo-rheological complexity is indicative of rheological moduli having non-uniform temperature dependence, which is characteristic of multiphase systems. Consequently, these outcomes point out the multiphasic nature of the binder in which non-dissolved CRT particles and polymer phases exert a remarkable influence.

The presence of CTR yields lower values of phase angle curves, which are further decreased by the contribution of the polymeric phase, a fact that points out the above-mentioned enhancement in the elastic response, especially in the case of SBS, EVA and EBA. In addition, a very interesting feature is revealed by the appearance of a shuttle phase angle maximum observed for CTR70 and HSs, in the low modulus range (i. e. high temperature) which is attributed to relaxation processes inside the new polymer-rich phase developed inside the bituminous system. Finally, it is important to underline that, once again, the most significant modification is observed for the binder with the SBS.

As it was previously commented, the information reported by the rheological measurements seems to indicate a better resistance to rutting problems in the resulting pavement. However, it has been recently reported that the use of parameters based on linear viscoelastic functions result to be inadequate in rating polymer-modified binders, because of its bad correlation with field rutting measurements. This is mainly attributed to the fact that this type of failure happens out of the linear viscoelastic region, due to high stresses needed to produce irreversible deformations. Thus, lately, the repeated creep and recovery tests (MSCR) have been used to better evaluate the binder potential to undergo permanent deformations. MSCR consists of 10 cycles of 1 s creep followed by 9 s recovery, at two consecutive stress levels (0.1 and 3.2 kPa) and allows for characterising the recovery and non-recovery properties of the binder. Thus, taking into account that permanent deformations in the top layer of pavements are related to accumulation of irreversible strain due to repeated traffic loads, MSCR test is expected to better simulate these field conditions.

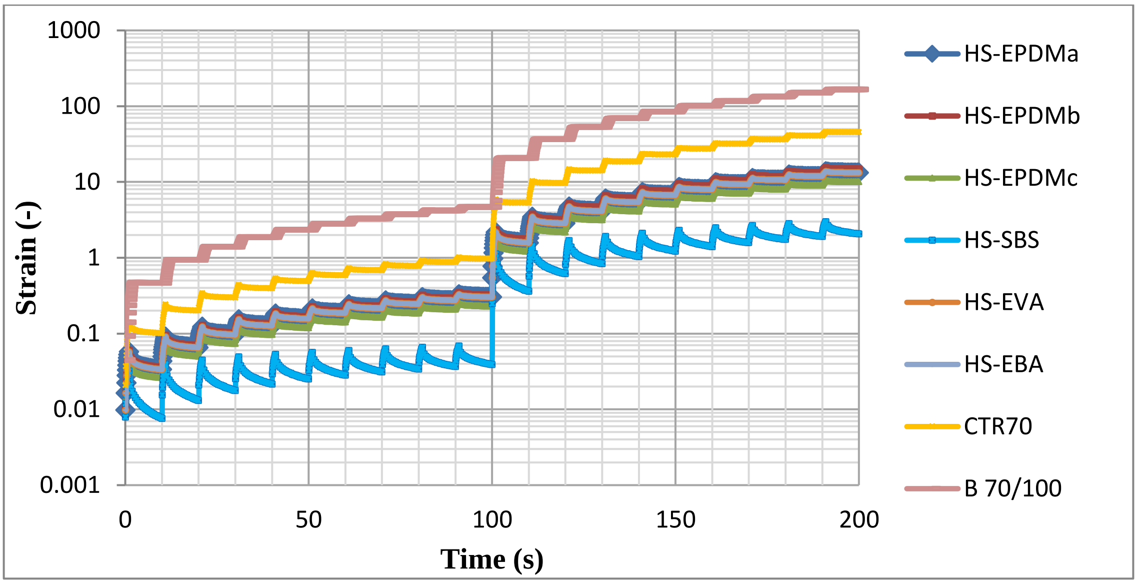


Fig. 4.6

Figure 3.6, which portrays the results of MSCR tests performed at 60ºC for all the studied systems, points out different patterns, depending on the modification achieved. Thus, neat bitumen presents a viscous Newtonian response (staircase pattern), characterised by large cumulative strain and almost insignificant strain recovery during unloading. In the case of CTR70, the presence of elastic rubber particles yields changes in the recovery cycle leading to delayed elastic strain recoveries. However, the combined effect of both polymer and CTR produces the most remarkable modification in the creep recovery profile, leading to notable non-linear response, as accumulated compliances in every 10 cycle’s interval appreciably changes and become stress dependent (Khadivar, 2013). Thus, the strain recovery increases, especially for HS-SBS, leading to saw tooth shape profile, which is characteristic of highly elastic binders.

In addition, it is worth mentioning that the cumulative strain of neat binder is significantly higher than the corresponding to modified binders, and a, pointing out its improper resistance to rutting.

In order to quantify the previous mentioned effects, two main average parameters can be stablished from MSCR test from every loading set of 10 cycles, the non-recoverable creep compliance (Jnr) and the percent of elastic recovery (%R) which are useful to characterise the delayed viscoelastic response. The percent of elastic recovery (%R) can be considered an indirect assessment of the elastic response and the change in elasticity at two different stress levels (0.1 kPa and 3.2 kPa), at the chosen temperature of 60ºC which can be considered a typical maximum expectable pavement temperature.

In addition, since the non-recoverable compliance can be considered a way of determining the amount of dissipated energy during the recovery cycles it provides information about the feasibility of modified bitumen to undergo permanent deformation under repeated loads. Consequently, both parameters provide complementary information about high in-service temperature behaviour.

In general, the results reported in Table 3.3 are in line with those deduced from the linear viscoelastic properties because similar trends are noticed in the ability of HSs to enhance binder properties. Once again, HS-SBS presents by far the lowest sensitivity to rutting, displaying percentage of recovery higher that 80%.

Finally, the stress sensitivity, measured as differences in compliance and recovery, are also strongly reduced with the modification procedures.

Table 3.3 Non-recoverable creep compliance (J_{nr}) and the percent of elastic recovery (%R) obtained from MSCR tests.

	%R		**J_{nr} (kPa^{-1})**	
	0.1 kPa	**3.2 kPa**	**0.1 kPa**	**3.2 kPa**
HS-SBS	87.7	81.2	0.039	0.063
HS-EVA	57.9	28.3	0.263	0.561
HS-EBA	71.3	53.0	0.081	0.142
HS-EPDMa	46.6	32.2	0.304	0.406
HS-EPDMb	45.9	29.0	0.325	0.455
HS-EPDMc	49.6	36.0	0.232	0.308
B 70/100	0.7	0.0	4.720	5.071
CTR 70	30.7	10.6	0.976	1.398

3.1.3 Thermal behaviour and microstructure

A literature review shows that some studies have been carried out on the combined use of CTR and another polymeric material, mainly SBS (Gonzalez, 2010) or Polyolefins (Yan, 2015), leading to enhanced properties as a consequence of the individual contribution of each of the modifiers.

However, the interest of the so-called hybrid systems not only lies on the solely use of both modifiers but also tries to promote physicochemical interactions among all constituent. In this paper, this goal is intended to be achieved by the use of sulphur and a vulcanization accelerator (ZnO). In this sense, it has been reported the formation of C-S bonds that links sulphur and some bituminous compounds and, additionally, crosslinks between sulphur and tyre rubber particles (NF, 2008). In this sense, given the high storage instability of CTR 70 (Table 3.2) the latter chemical interactions would not have been developed in a great extent.

For the sake of comparison, all blends presented here (even CTR70) have been submitted to the same protocol of sulphur addition and curing conditions. Consequently, the differences observed can be attributed to the polymeric additive and its interaction with bitumen and tyre rubber.

The obtained technical and thermomechanical results can be explained on a microstructural basis by the development of a complex multiphasic systems composed of: the remaining dispersed tyre rubber particles swollen by certain maltenic compounds; a polymer-rich phase which also may have absorbed light compounds; and the remaining asphaltene-rich phase which include dissolved or disintegrated rubber chains.

Aiming to gain a deeper insight on the HS microstructure modulated scanning calorimetry tests (MDSC) were performed on both pristine polymers and the resulting HSs. Figure 7A and B display the heat flow curves for neat polymers (7A) and HSs (HSs) and allows for analysing mainly the evolution of polymer-rich phase, whereas the non-reversing component of the heat flow (Figure 7C) provides information about minor transitions associated to the bituminous rich phase.

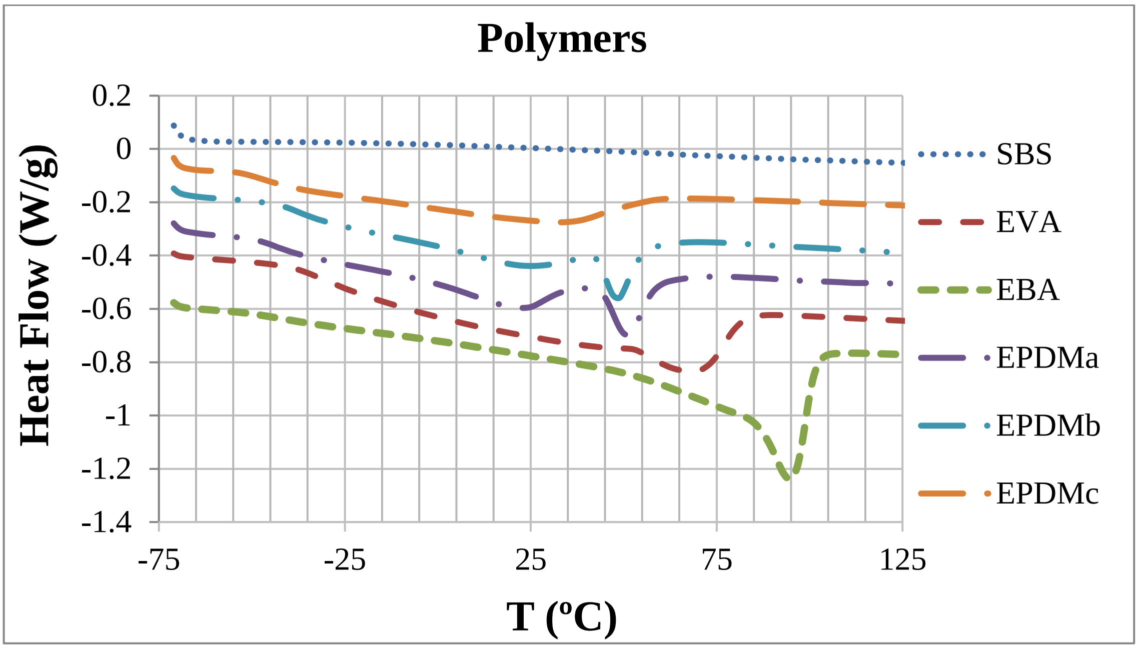


Fig. 4.7a. Total heat flow curves for neat polymers, obtained from MDSC experiments.

Figure 3.7A points out the diverse thermal behaviour of the copolymers used derived from their amorphous (SBS) or semicrystalline nature (EVA, EBA, EPDMs). Thus, SBS is an amorphous thermoplastic elastomer that does not show any relevant peak in the total heat flow diagram, whereas the rest of the samples present characteristic melting peaks of their crystalline fraction. The presence of melting peaks in these ethylene copolymers (EVA, EBA EPDMs) points out that their ethylene sequences are long enough to be able to crystallize. Even though, the crystalline properties depend on a large number of factors as, the monomer type and content, average molecular weight, and distribution of molecular weight, etc., in general both melting temperature and enthalpy are reduced as comonomer concentration increases.

EVA polymer is characterised by a broad shoulder followed by a single endothermic peak, centred at 68.9 ºC, as it has been reported by other authors for EVAs containing similar vinyl acetate content (Yuliestyan, 2016). These endothermic events are attributed to the melting of the crystalline lamellar structures of the copolymer, more precisely of small and imperfect crystallites (shoulder) and of regular crystallites (main peak) (Haddadi, 2008).

In the case of EBA, a similar pattern of multiple endotherms (with a main peak centred at 94.7 ºC) is also observed suggesting a segregation of the crystalline phase, probably due to the existence of different crystalline species by the presence of fractions of different acrylate content in the copolymers (Feller, 2001). Thus, the acrylate comonomers are considered as defects toward crystallization and result rejected from the crystals, leading to a decrease in the lamella thickness, causing a decrease in the melting temperature compared to polyethylene homopolymers.

Table 3.4: Melting temperatures and enthalpies, and crystalline fraction obtained from MDSC tests.

Samples	**T_m [ºC]**	**ΔH_m [J/g]**	**χ_c [%]**
EVA	68.9	61.7	21.1
EBA	94.7	80. 3	27.4
EPDMa	18.10/50.50	19.97	6.8
EPDMb	23.80/48.75	13.8	4.7
EPDMc	31.7	26.9	9.2
HS-EVA	49.1	1.186	13.5
HS-EBA	80.5	1.369	15.6
HS- EPDMc	23	0.082	0.93

The DSC analysis of EPDMc shows only a single very broad peak whereas EPDMa and EPDMb present two endothermic peaks at temperatures detailed in Table 3.4, (extended over similar temperature range). This is associated to the melting of the ethylene segments of different molecular weight, which selectively crystallize out, which is in agreement with results reported in the literature (Feller, 2001).

The approximate crystalline fraction (χ) for all copolymers has been determined by dividing the area of the melting peak by the fusion enthalpy of a perfect crystal of polyethylene (293 J/g). In line with literature, EBA and EVA present relatively high crystalline fractions (>20%) whereas all EPDMs have a lower crystallinity, especially for EPDMb in which the presence of ENB (ethylidene-2-norbornene) groups hinders the ordering process resulting in the lowest crystallinity.

In order to explore the compatibility between bitumen and the polymers used, Figure 7B and Table 3.4 report the results of the MDSC tests carried out on HSs.

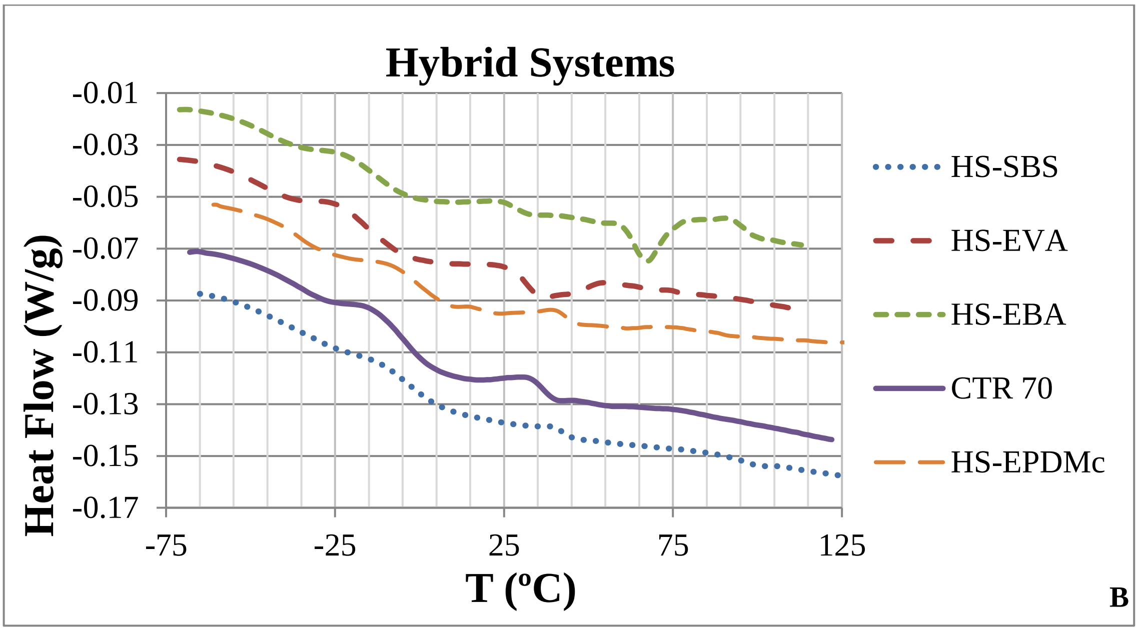


Figure 3.7b. Total heat flow curves for HSs, and (C) non-reversing heat flow curves for HSs, obtained from MDSC experiments.

In this regard, it is important to underline that, as CTR70 presents a number of minor thermal events that will be disused below, the corresponding melting peaks of the polymer fraction are identified as new peaks compared to the reference of this sample. According to this, for the sake of comparison, the crystallinity of the polymer-rich phase gathered in Table 5 is obtained from melting enthalpy of HSs multiplied by a factor of 100/3 to take into account the polymer concentration. The obtained results point out the partial compatibility of bitumen compounds with EVA and EBA crystalline fraction, because the HSs present a notable melting point depression and a reduction of around 30% of the crystallinity. This effect is attributed to the swelling of polymer-rich fraction by bitumen light component able to disrupt the crystalline part, making crystallites with a smaller size distribution. This effect is particularly significant for all HS-EPDMs which are characterised by a complete or almost complete disappearance of the crystalline phase, although it must be noted that EPDMs have the lowest crystallinity.

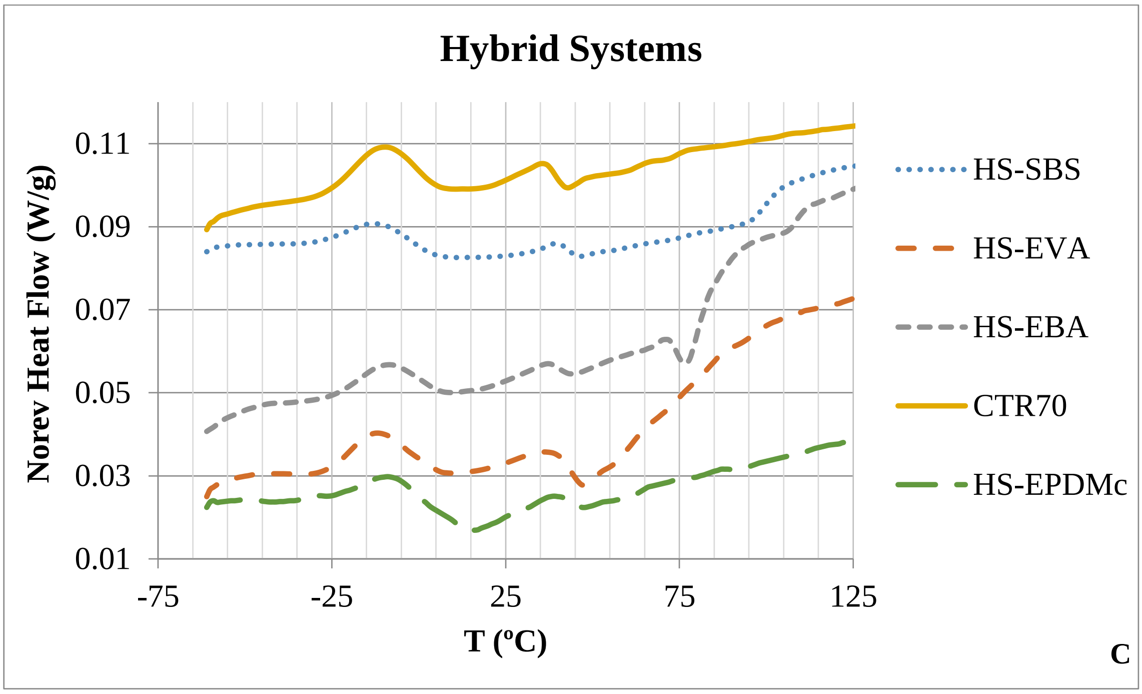


Figure 3.7c. Total heat flow curves for HSs and non-reversing heat flow curves for HSs, obtained from MDSC experiments.

Shuttle transitions associated to any of the phases present inside HSs, and especially for the bituminous fraction, can also be analysed by using the non-reversing heat flow curves in Figure 3.7C. As it has been widely described in the literature, the below reported thermal events are associated to different bitumen phases or structures, as a consequence of time-dependents ordering processes that occurs when bitumen is quenched from the melt. Thus, the broad endothermic background, approximately extended from -50 to 100ºC, is mainly due to the melting of ordered simple aromatic mesophasic structures and, in a minor extent, to crystallized saturates. In addition, two exotherms, at -15 and 40 ºC for CTR70, are clearly noticed, related to the cold crystallization of low and high molecular weight segments, respectively, of saturated and aromatic compounds. Finally, the later event is followed by a subtle endotherm located at around 50 ºC, resulting from the disordering of large structures, found in resin and asphaltene fractions, which slowly diffuse to form a mesophase upon annealing.

Additional endotherms appear for some HSs, related not to the bituminous phase but the polymer rich one, due to the melting of crystalline polymer fractions at the temperatures reported in Table 3.4. By comparing the non-reversing flow curves of CTR70 with those of HSs, similar qualitative results may be drawn, since the magnitude of those reported bituminous thermal events are clearly lessened. As a result, the presence of an additional polymer-rich phase hinders the ordering of bitumen phases in HSs because, on the one hand, dampens the cold crystallization of crystallizable alkanes and alkyl aromatics (responsible of the appearance of the exotherms) and, on the other hand, reduces the mesophasic ordering of the asphaltenes (endotherm at around 50ºC).

From a microstructural point of view, HS are complex ternary systems, where the polymer preferably interacts with maltenes, absorbing light molecules. For non-dissolved rubber, this process yields swollen elastic particles suspended in a low viscosity medium, leading to the observed improvement of the thermorheological behaviour of CTR70. For the added polymer, as a consequence of its partial thermodynamic compatibility with some bitumen compounds, the swelling gives rise to the development of a polymer-rich phase. With this regard, fluorescence microscopy has been used to analyse the morphology of samples, to characterize their state of dispersion, and to determine the nature of the continuous and discontinuous phases (Figure 3.8).

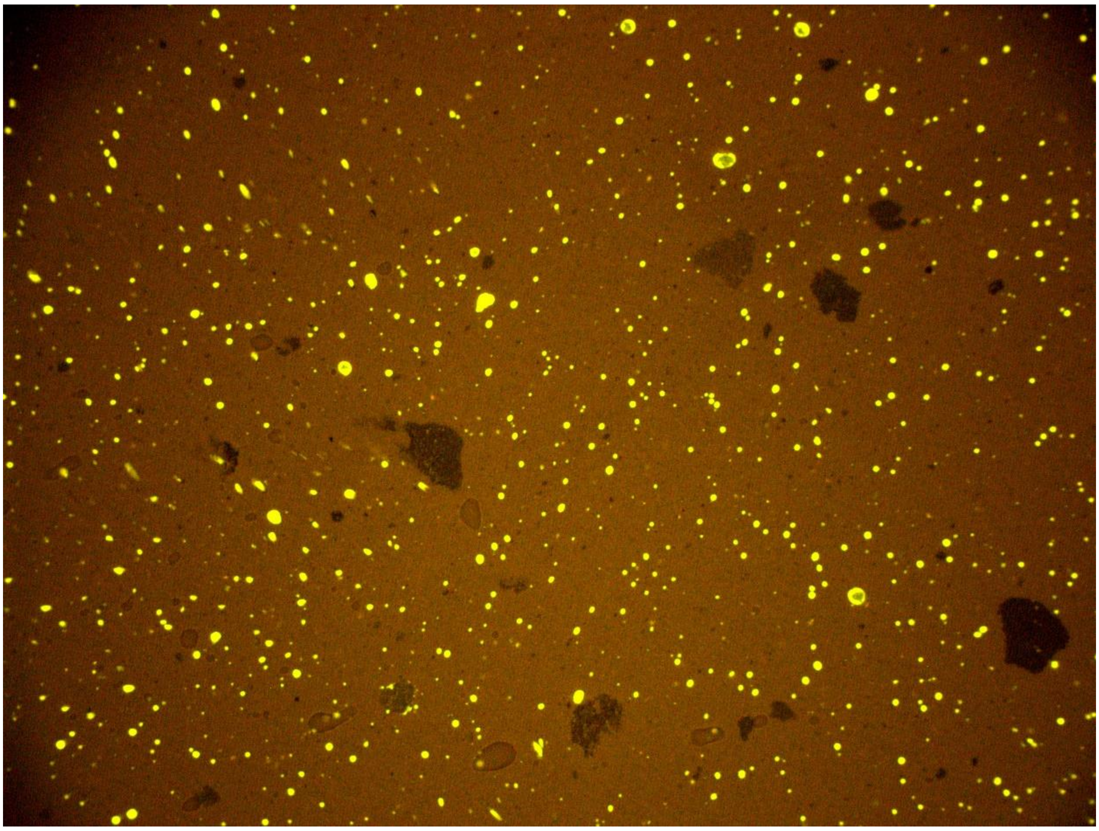


Fig. 4.8a. Fluorescent optical microscopy images for samples CTR70

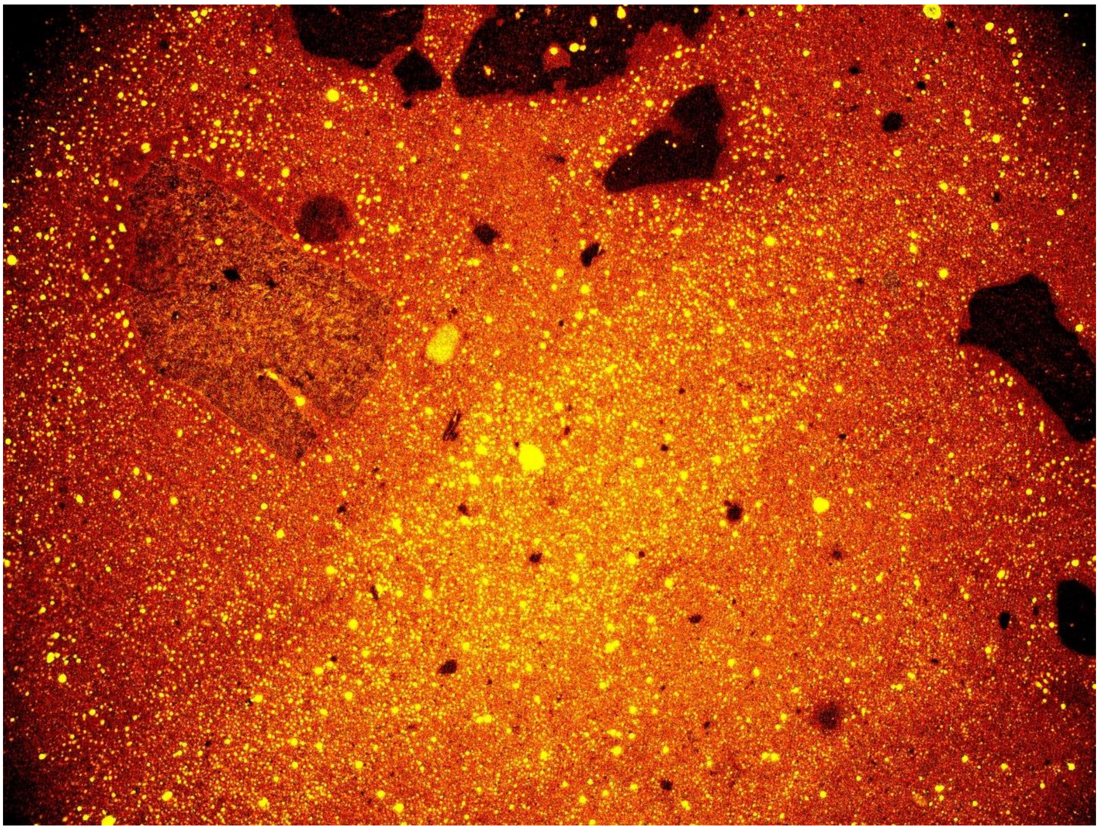


Fig. 4.8b. Fluorescent optical microscopy images for samples HS-EBA

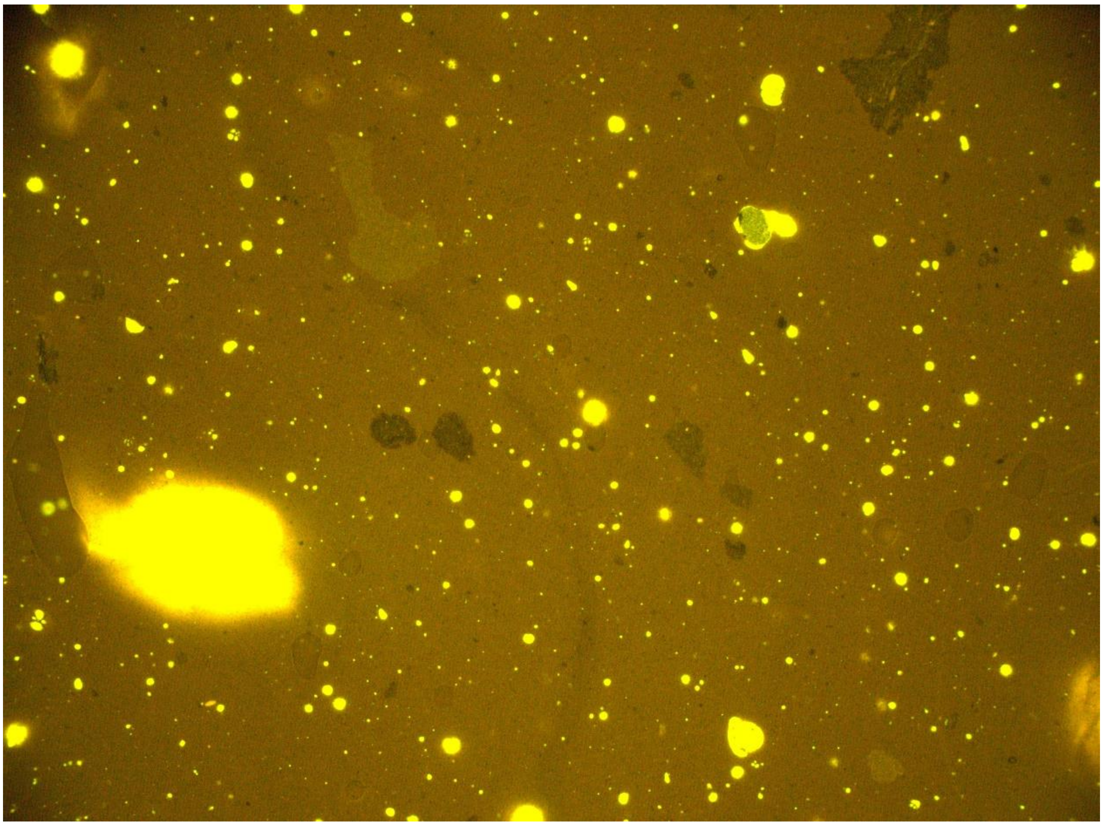


Fig. 4.8c. Fluorescent optical microscopy images for samples HS-EPDMb

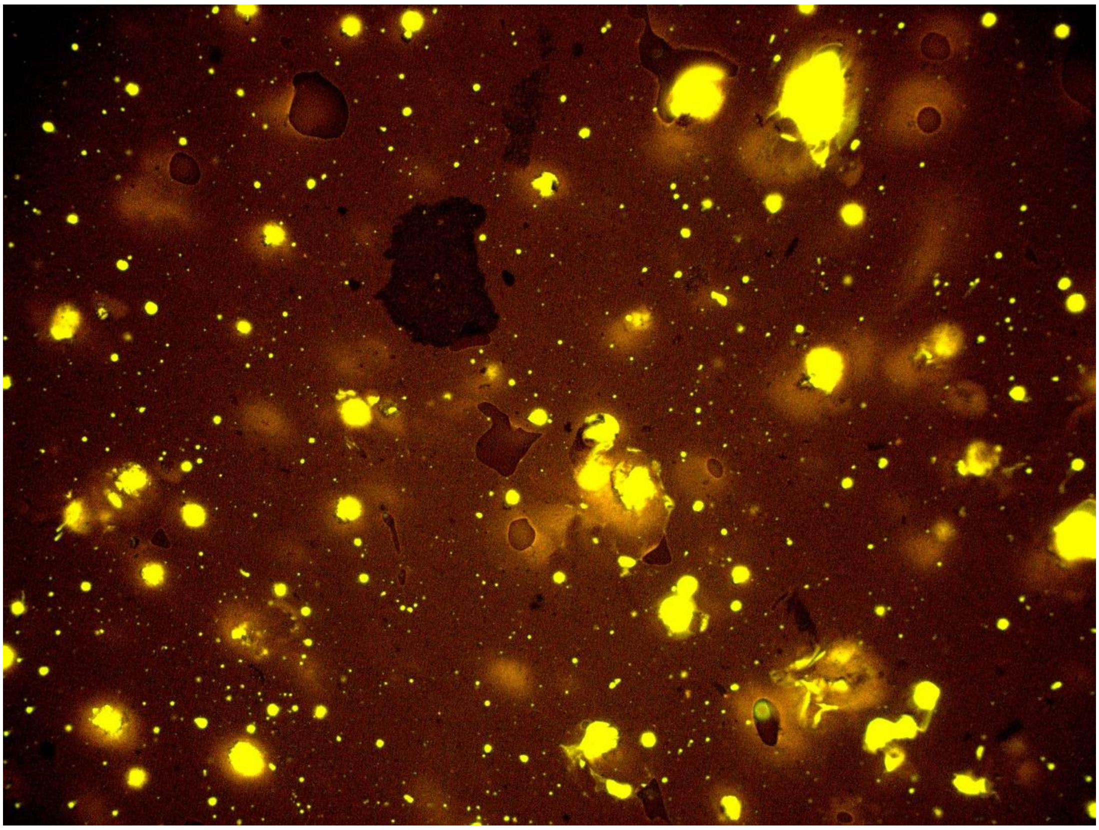


Fig. 4.8d. Fluorescent optical microscopy images for samples HS-EPDMc

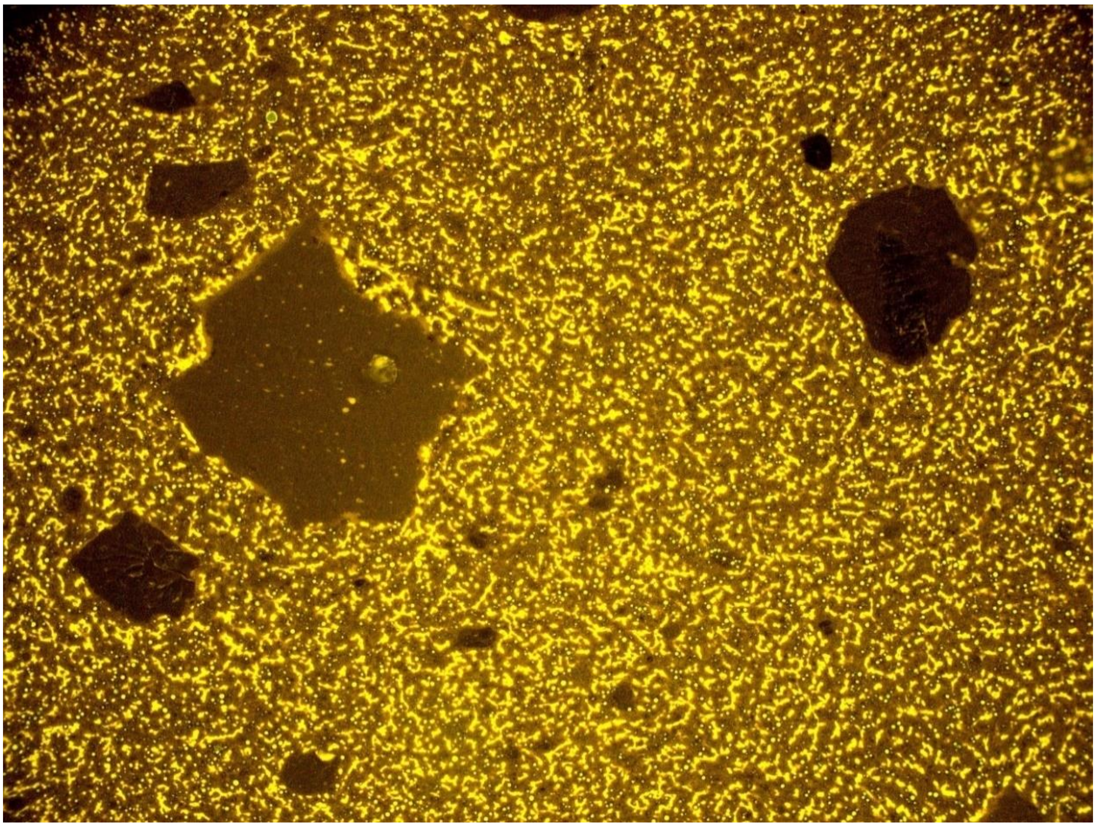


Fig. 4.8e. Fluorescent optical microscopy images for samples HS-SBS.

On this regard, even though bitumen contains compounds able to produce fluourescence (mainly resins and aromatic), due to the mixing among all bituminous fractions, micrographs of the reference neat bitumen only reveal an homogenous pattern (data not shown). However, the fluorescent image of the rubberised bitumen (CTR70) points out some interesting features. Thus, the presence of irregular shaped non-digested rubber particles is clearly noticed, but at a relative proportion lower than the corresponding to the tyre rubber added (10 wt.%), a fact that corroborates the digestion/disgregation of the crosslinked tyre rubber. Moreover, it is noteworthy the appearance of new lightly toned regions, uniformly dispersed forming droplets of small diameter. Since this new phase is not visible in neat bitumen, most probably, it can be attributed to devulcanized/depolymerized rubber chains, swelled by some bitumen fluorescent compounds.

Regarding HSs, two very different patterns can be distinguished. Hence, HS containing polyolefin copolymers (EVA, EBA and EPDMs, Figures 4.8B-D) give rise to the development of a multiphase system, containing a new disperse polymer-rich phase (which fluoresce) inside a continuous asphaltene rich-phase (which appear black in the picture), where non-dissolved solid rubber particles and devulcanized/depolymerized rubber are also included. Therefore, the reported thermomechanical behaviour is influenced by the individual contribution of the different phases and the interactions among them. In this sense, the better performance of HS-EBA could be attributed to the finer distribution of the polymer-rich phase (Figure 3.8B).

Furthermore, once again the partial compatibility of bitumen compounds with the copolymers is pointed out because the swollen polymer rich region occupies a volumetric fraction far greater than that of the polymer in the blend.

By contrast, HS-SBS displays a different feature characterised by interconnected polymer-rich zones, forming a continuous three dimensional network structure in which both, asphaltene-rich phase and rubber particles, are dispersed. This is a consequence of the chemical cross-linking of the swollen SBS and is considered the main cause behind the superior performance of this sample. Thus, carbon–carbon double bonds of polybutadiene chains in SBS molecules were crosslinked by sulphur during the processing leading to the formation of the chemical network.

Consequently, the thermomechanical behaviour is improved in the whole experimental interval, increasing the flexibility at low temperatures and enhancing the viscosity and elasticity at high temperatures. In addition, this may also explain the improved high-temperature storage stability, because the three dimensional structure can effectively interact with the non-digested rubber particles by either specifically binding to or physically entrapping them, preventing or reducing their settling.

Finally, it is worth mentioning that, even though EPDM-b copolymer presents double bonds (in the side group ENB) able to be vulcanized, the observed microscopy pattern does not reveal a network structure but a dispersed polymeric phase. This result is probably related to the lower double bond content in EPDM-c compared to SBS, which provokes that the vulcanizing sulphur reaction is not so effective.

3.2. REACTIVE-POLYMER MODIFIED HYBRID SYSTEMS

3.2.1 Materials

Different ethylene-based copolymers, provided by Repsol S. A., were used to formulate HSs. Melt flow rates, at 230ºC, and polymer composition were gathered in Table 3.5. PBEa and PBEb are non-reactive propylene-based elastomers formed by isotactic propylene repeat units with random ethylene blocks, produced using metallocene catalyst technology, and with 11.0 and 15.0 wt.% of ethylene content, respectively. EMAa and EMAb are fully saturated ethylene-co-1-octene copolymers functionalized by reactive extrusion with maleic anhydride, containing 0.85 and 0.35 wt.% of pendant succinic anhydride groups respectively. Finally, RPO is a reactive polyolefin composed of a mixture of isotactic polypropylene, ethylene vinyl acetate copolymer (EVA), polyethylene wax and poly glycidylmethacrylate (5 wt.%).

Table 3.5. Melt flow rates, at 230ºC, and polymer composition of the ethylene-based polymers used.

Name	**Description**	**MFR$^{(A)}$**	**Composition**
PBEa	ethylene–propylene elastomer	8	Ethylene 11.0 wt.%
PBEb	ethylene–propylene elastomer	20	Ethylene 15.0 wt.%
EMAa	ethylene-co-1-octene copolymer functionalized with maleic anhydride	17	Maleic Anhydride 0.85% wt.%
EMAb	ethylene-co-1-octene copolymer functionalized with maleic anhydride	8	Maleic Anhydride 0.35 wt.% Octene: (28 wt.%)
RPO	Mixture: Isotactic polypropylene, EVA, polyethylene wax and poly glycidylmethacrylate	-	Poly (glycidyl methacrylate) 5 wt.%

3.2.2 Sample preparation

Ternary blends, called here Hybrid Systems (HSs), were prepared by hot mixing the base rubberised binder (CTR70) with 3 wt.% of the e polymers (with the exception of RPO), following the procedure described below. Since the sample formulated with 3 wt.% reactive polyolefin (HS-RPO) tends to form a strong gel that cannot be used for paving applications, RPO concentration in HS-RPO was limited to 2 wt.%.

Firstly, the base CTR70 was obtained mixing 10 wt.% CTR at 180ºC, with a soft bitumen to achieve a penetration of 70 dmm, at pilot plant scale, using an in-line high shear homogenizer rotor-stator IKA-WERKE Process-Pilot 2000/4-HT equipped with a Dispax Modulus. Next, Hybrid Systems (HSs), were prepared by adding the second polymer modifier, at 180ºC, in a high shear mixer Silverson L4RT for 2 hours and, then, cured in an oven at 160ºC for 24 h, in order to complete the chemical reactions.

3.2.3 Technological characterization and storage stability

In order to make a quick comparison of the performance of all modified bitumens, the results of selected technological tests, according to EN 14023, are presented in Table 3.6.

Table 3.6. Technological properties for the bituminous binders studied.

Property	unit	HS-PBEa	HS-PBEb	HS-EMAa	HS-EMAb	HS-RPO	CTR 70	B 70/100
Penetration	0.1 mm	60	61	63	63	54	70	75
Softening Point, $T_{R\&B}$	°C	56	56	68	63	63	51	46
Penetration Index	-	0.6	0.6	3.2	2.3	0.5	0.1	-1.3
Fraass Point	°C	-18	-25	-21	-19	-20	-20	-10
Elastic Recovery at 25°C	%	64	61	62	61	60	61	13
Dif. of $T_{R\&B}$ (Stability)	°C	2.1	4.3	1.4	7.5	1.2	10	0
Cohesive Energy	J/cm^2	3.088	3.636	3.923	3.075	2.019	2.702	0.007

By comparing CTR70 with a model neat bitumen of similar penetration range (B70/100) the expected positive effects of CTR are revealed: higher softening point (5ºC), improved elasticity (much larger elastic recovery), enhanced low temperature flexibility (reduction of 10ºC in Fraass breaking point) and lower temperature susceptibility (greater and positive values of the penetration index) (Navarro et al., 2010; Yan et al., 2015). Unfortunately, Table 3.6 also discloses the poor high temperature storage stability of CTR70, as may be easily deduced from the difference of 10ºC between the softening point at the top and bottom sections of the settling tube, which noticeably exceeds the limit of 5ºC established by EN 13399. This well-known phenomenon results from the settling of non-dissolved rubber particles during hot storage and represents one of the main drawbacks that limits the use of rubberised bitumens by the industry (Lo Presti, 2013; Navarro et al., 2005).

In this sense, according to the results presented in Table 3.6, it is clear that all ethylene copolymers used in this study lead to a notable improvement in hot storage stability in such a way that, with the exception of HS-EMAb, these binders fulfil the stability requirement stabilised by the European standard EN 13399. Furthermore, Table 3.6 also points out that technological properties such as penetration, softening point and cohesive energy are greatly improved after the addition of the ethylene copolymer, whereas Fraass breaking point and elastic recovery remain almost unaffected. This former result is considered satisfactory since low-temperature properties and elastic recovery are often deteriorated after modification with ethylene-based polymers (Senise et al., 2017). This outcome is in line with force-ductility tests, at 5ºC, reported in Figure 3.9 while most of HS (with the exception of HS-PBEa) give rise to elongations larger than the required 400 mm stabilised by EN13703 and, therefore, improve the observed behaviour for the base rubberised bitumen which breaks before reaching this length.

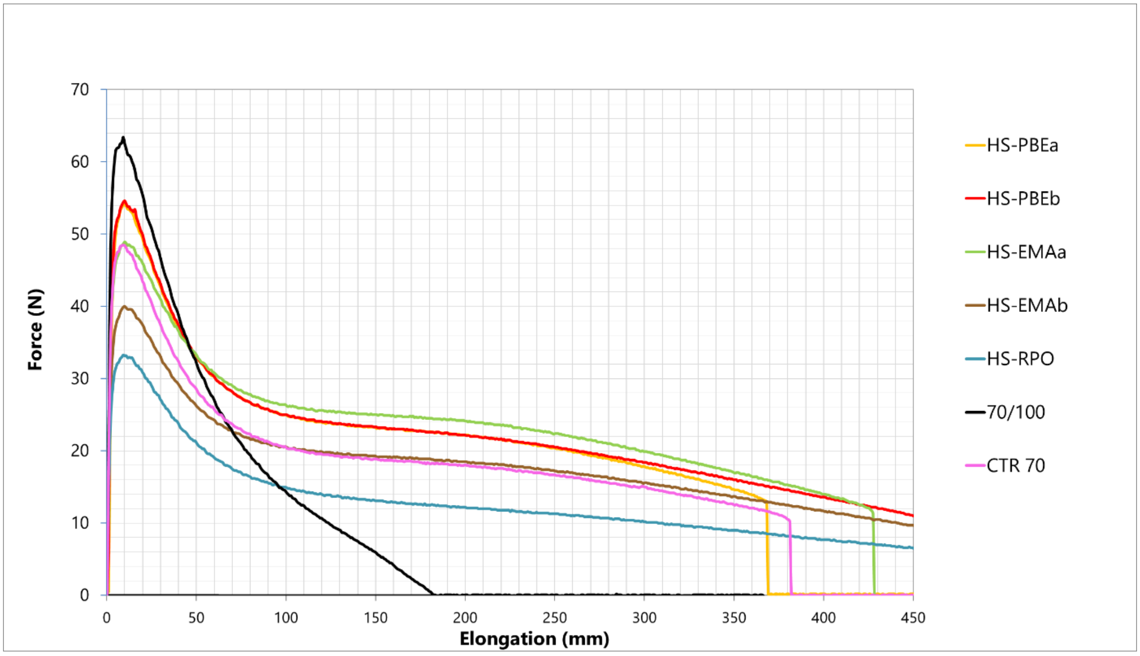


Fig. 4.9. Force ductility curves, at 5ºC, for the studied binders

As expected, all systems exhibit a ductile-like behaviour characterised by sharp peak (yield point) early in the elongation process followed by a smooth decrease during the plastic deformation period until the rupture point. Even though neat bitumen presents the highest maximum at the yield, the force declines sharply and breaks very rapidly after the yield drop. Surprisingly, despite CTR70 does not strictly fulfil the breaking criteria, its force-ductility behaviour is very close to the hybrid systems and, in addition, its cohesive energy (Table 3.6) is clearly above the values typically required for a polymer modified bitumen (at least 2 J·cm-2). Therefore, taking into account that remaining CTR particles usually act as crack initiators yielding to premature breakage during elongation, this result hints an enhanced digestion of CTR and, therefore, a better homogeneity of the rubberised bitumen. In general, according to Figure 3.9 and Table 3.6, no direct correlation between the type of polymer and force ductility results can be established, although HS-PBEb and HS-EMAa show the best results in terms of stiffness and cohesion energy.

Figure 3.10 gathers Brookfield viscosity data at 135, 150 and 180ºC, which are of a particular interest for mixing and compaction operations.

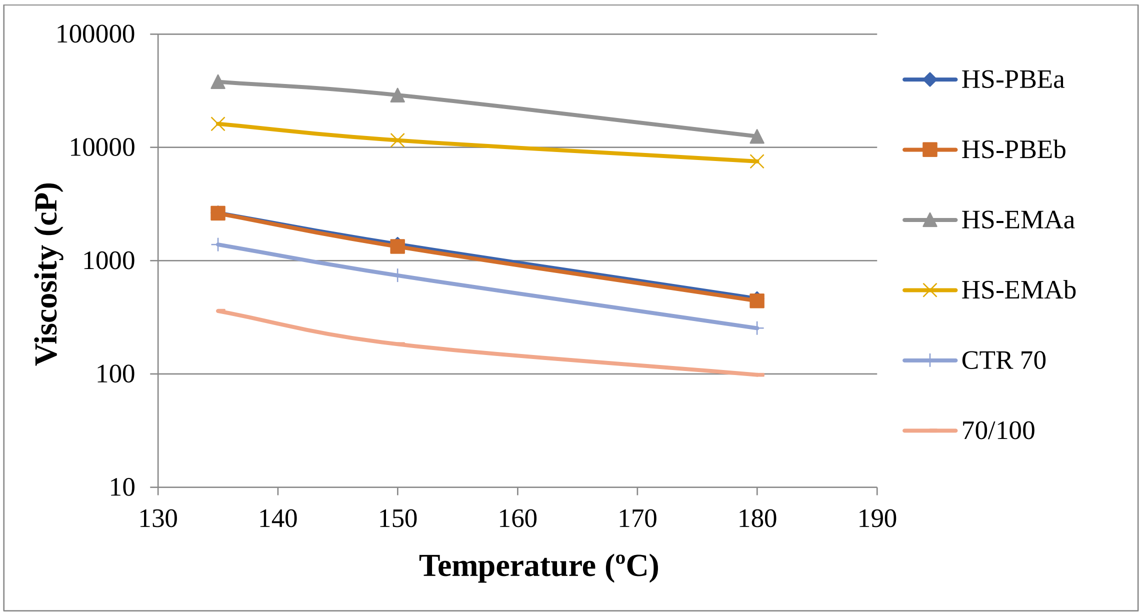


Fig. 4.10. Evolution of Brookfield viscosities with temperature for the studied binders.

By comparing neat bitumen with CTR70 it is clear that CTR addition gives rise to an increase in binder viscosity, mainly attributed to the presence of non-dissolved rubber particles (Navarro et al., 2004). Further polymer modification to form HSs yields an additional increase in viscosity that is dependent on the type of polymer used. Thus, while HS-PBEs only present a slight rise, HS-EMAs undergo a remarkable increase in high temperature viscosities, particularly for HS-EMAa. Therefore, all reactive systems (HS-EMAs) fail to meet the Superpave criterion that requires a maximum viscosity limit of 3000 cP at 135ºC, in order to ensure bitumen fluidity for pumping during delivery and workability in plant operations (Yan et al., 2015). This result hints that, as consequence of chemical processes, EMA polymers develop a polymeric structure able to resist high temperatures. However, since this requirement was developed for Newtonian bitumen it is not strictly applicable to shear-thinning materials like rubberised bitumen and hence, this criterion may be violated if the asphalt can be pumped and mixed at safe temperatures i.e. high shear rates (Navarro et al., 2005).

3.2.4 Rheological characterization

The effect rubber and polymeric modifiers on the performance of binders over a wide range of temperatures can be easily analysed by means of the dynamic shear temperature sweeps (Figure 3.11).

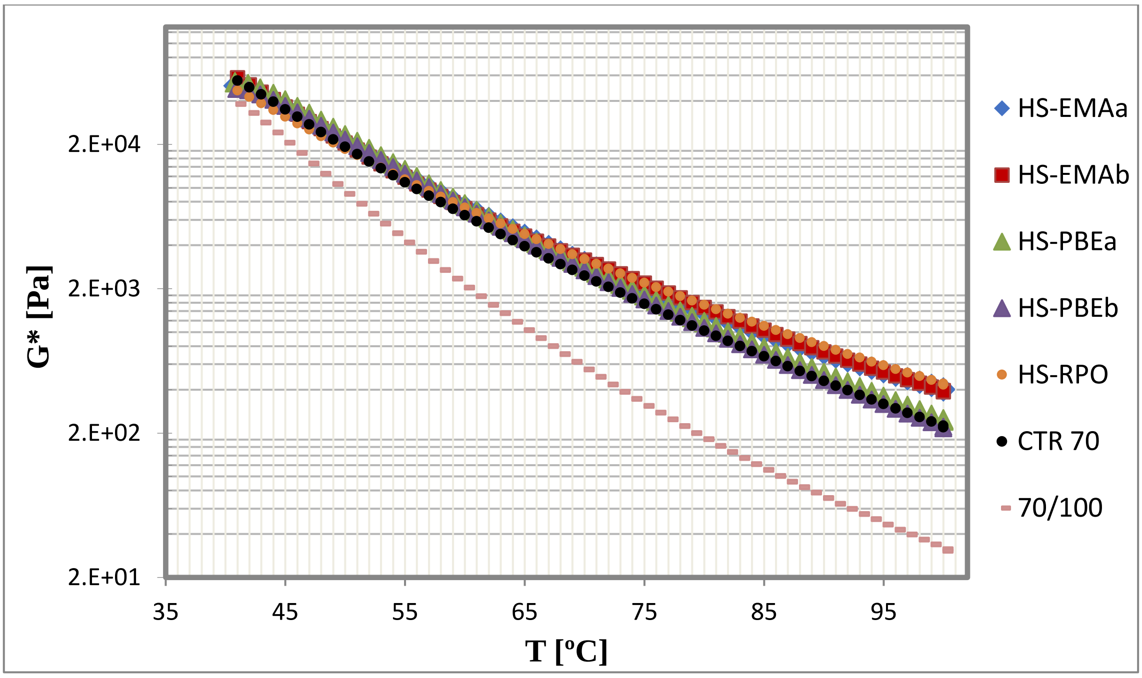


Fig. 4.11a. Evolution of complex shear modulus with temperature, at 10 rad/s, for the studied systems.

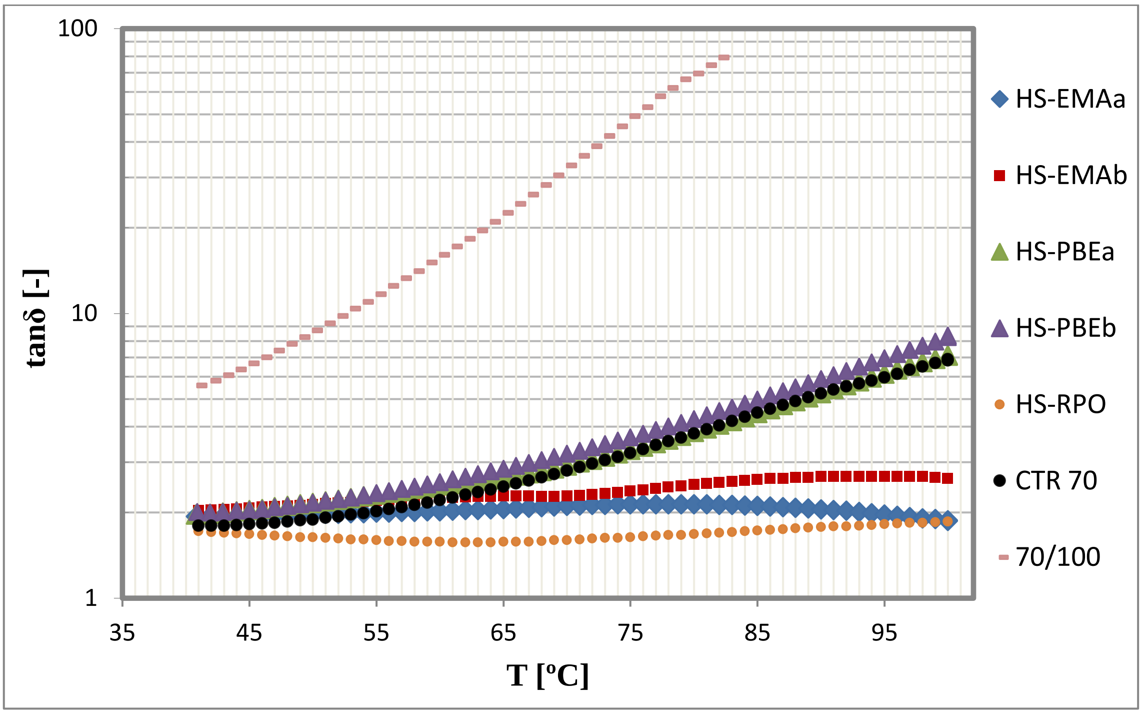


Fig. 4.11b. Evolution of loss tangent with temperature, at 10 rad/s, for the studied systems.

As expected, complex shear modulus undergoes a continuous decrease with testing temperature, from 30 to 100 °C, for all samples (Figure 3.11A). Hybrid modification causes a remarkable increase in G*, more evident as temperature is raised, when compared to the reference neat bitumen. As the complex modulus is correlated with the stiffness of the sample, this result points out a better performance in the intermediate and high in-service temperature range and presumably a superior resistance to permanent deformation as well (Navarro et al., 2010; Yan et al., 2015). In addition, an enhancement in the temperature susceptibility is also displayed, as deduced from a decreased value of the average slope of G* and tanδ vs. temperature (Figures 4.11A and 4.11B), within the testing interval. Consequently, a better thermal resistance is expected for the resulting pavement (Navarro et al., 2010).

In addition, as loss tangent presents greater sensitivity to modification changes, Figure 3.11B may be used to quantify the contribution of every polymer to the global rheological response of the HS, in the sense that, the lower the values of tanδ, the better the modification effect is.

Finally, Figure 3.11B also allows distinguishing two types of rheological behaviours after polymer addition. On the one hand, CTR70 and HS-PBEs present curves with similar qualitative evolution with temperature than neat bitumen, characterised by a continuous increase of the loss tangent, a prevailing viscous behaviour (tan $\delta>1$) and the absence of the "plateau" region, over the entire temperature interval tested. Hence, a gradual transition from the glassy to the Newtonian region is a distinctive characteristic of these non-reactive systems. On the other hand, for reactive systems (HS-EMAs and HS-RPO), loss tangent curves become virtually independent of temperature reaching values close to 1, which is the typical response of a critical gel (Navarro et al., 2010).

The used frequency (10 rad/s) in accordance with Superpave specifications was chosen by performance criteria because it simulates the deformation rate caused by a car passing at 60 km/h. However, from a rheological point of view, this value is considered relatively high and may mask differences among samples. In this sense, frequency sweep tests, at selected constant temperatures (40, 60 and 80ºC) were also performed in order to provide a deeper insight into structural effects of crumb rubber and polymers. Figure 3.12 points out the typical evolution of G* of bituminous materials at high temperatures (at 40, 60 and 80 ºC), characterised by a steady increase of G* with frequency.

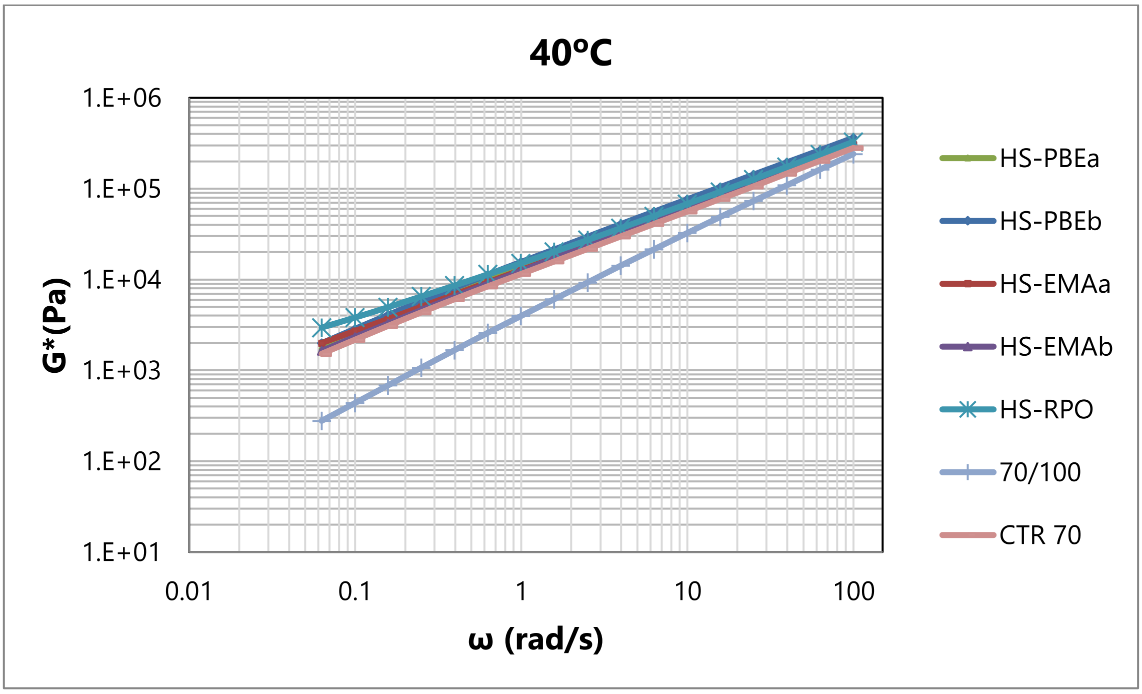


Figure 3.12a. Evolution of the complex shear modulus with frequency, for the studied systems at 40ºC.

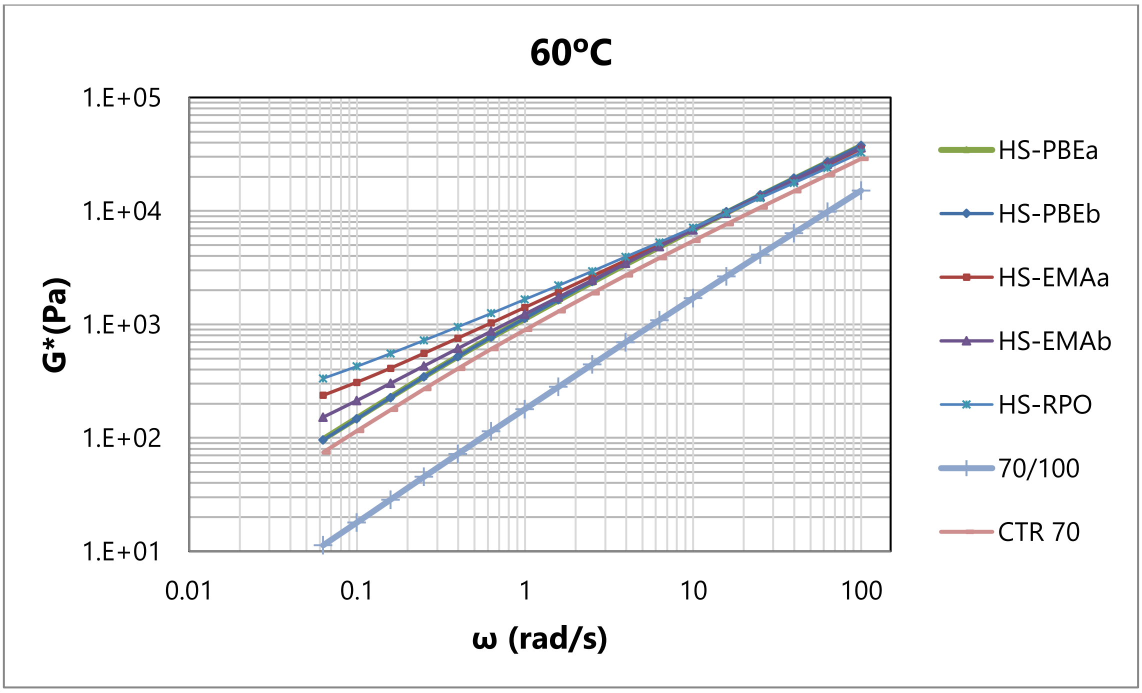


Figure 3.12b. Evolution of the complex shear modulus with frequency, for the studied systems at 60ºC.

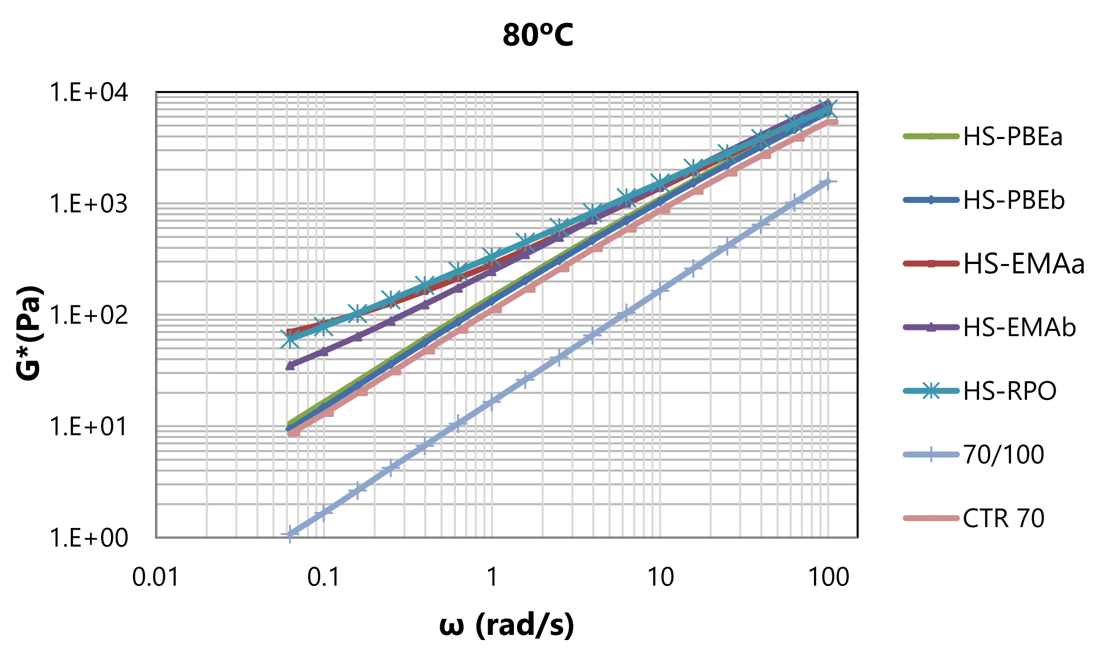


Figure 3.12c. Evolution of the complex shear modulus with frequency, for the studied systems at 80°C.

As testing temperature rises and frequency lowers differences among samples become more apparent, pointing out the effects caused by ethylene copolymers. It is important to note that, once again, two distinctive behaviours are revealed. Thus, the group of the non-reactive samples (neat bitumen, CTR70 and HS-PBEs) is characterised by a predominant viscous character, which is intensified as temperature rises, showing a tendency to reach the flow region of the mechanical spectrum, at low frequencies. On the contrary, reactive HSs, undergo a flattening on complex shear modulus curves and develop a plateau in the loss tangent, confirming the previously mentioned critical gel-like behaviour.

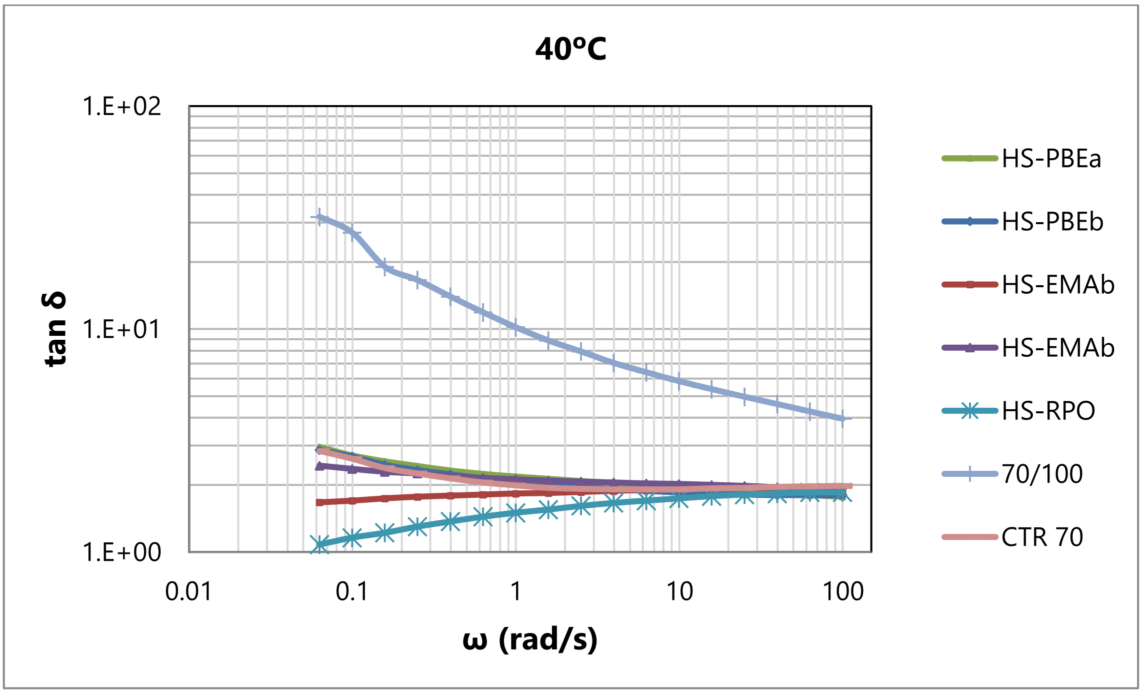


Figure 3.13a. Evolution of the loss tangent with frequency, for the studied systems at 40ºC.

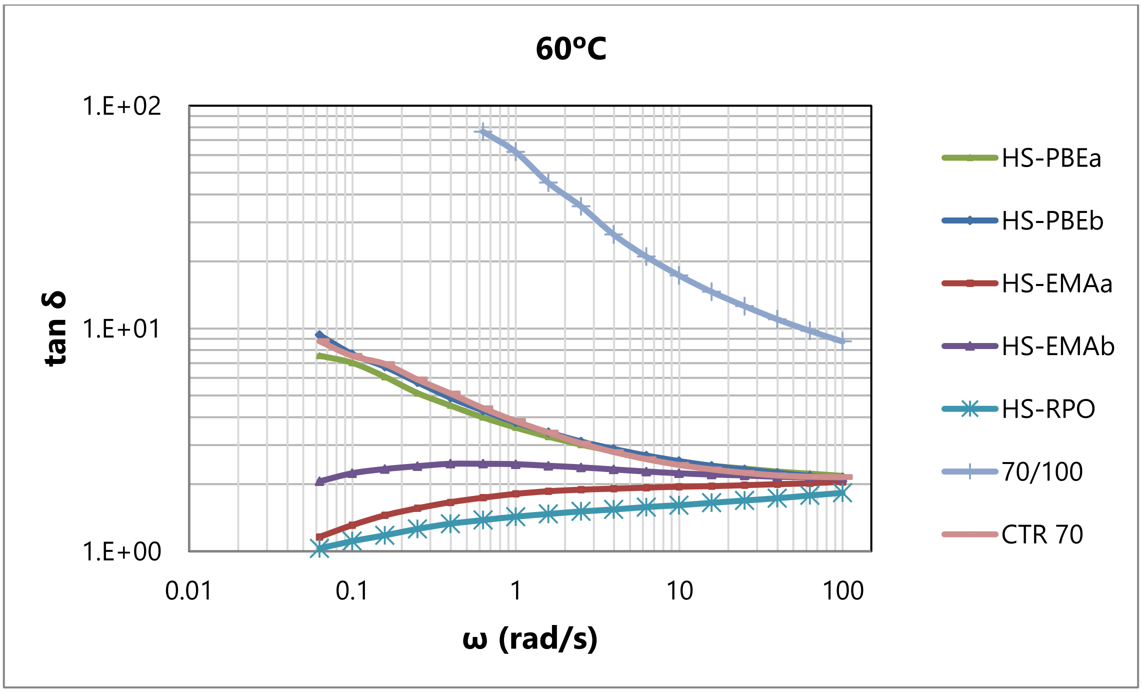


Figure 3.13b. Evolution of the loss tangent with frequency, for the studied systems at 60ºC.

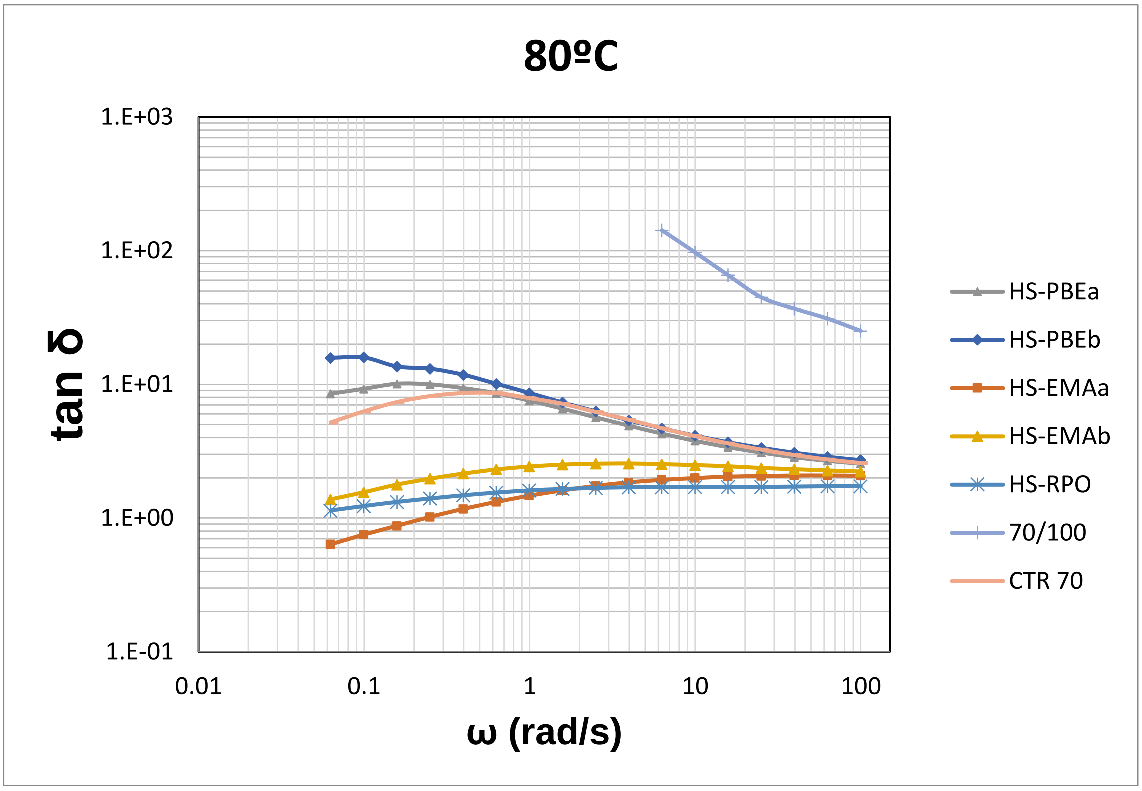


Figure 3.13c. Evolution of the loss tangent with frequency, for the studied systems at 80°C.

Taking into account that loss tangent is inversely proportional to the overall elasticity of the sample, Figure 3.13 allows to rank samples with respect to the modification potential of the polymers used (PBEb≈PBEa<<EMAb<EMAa<RPO).

The observed change in the thermomechanical response is more clearly evidenced by the so-called Black diagrams (δ vs. G*, see Figure 3.14), where non-reactive (A) and reactive HSs (A) are portrayed separately with B70/100 and CTR70 as references. These graphs have been widely employed for modified bitumens not only for verifying the time–temperature superposition principle, but also for evaluating the topological structures, given its sensitivity to structural or compositional changes (Senise et al., 2017).

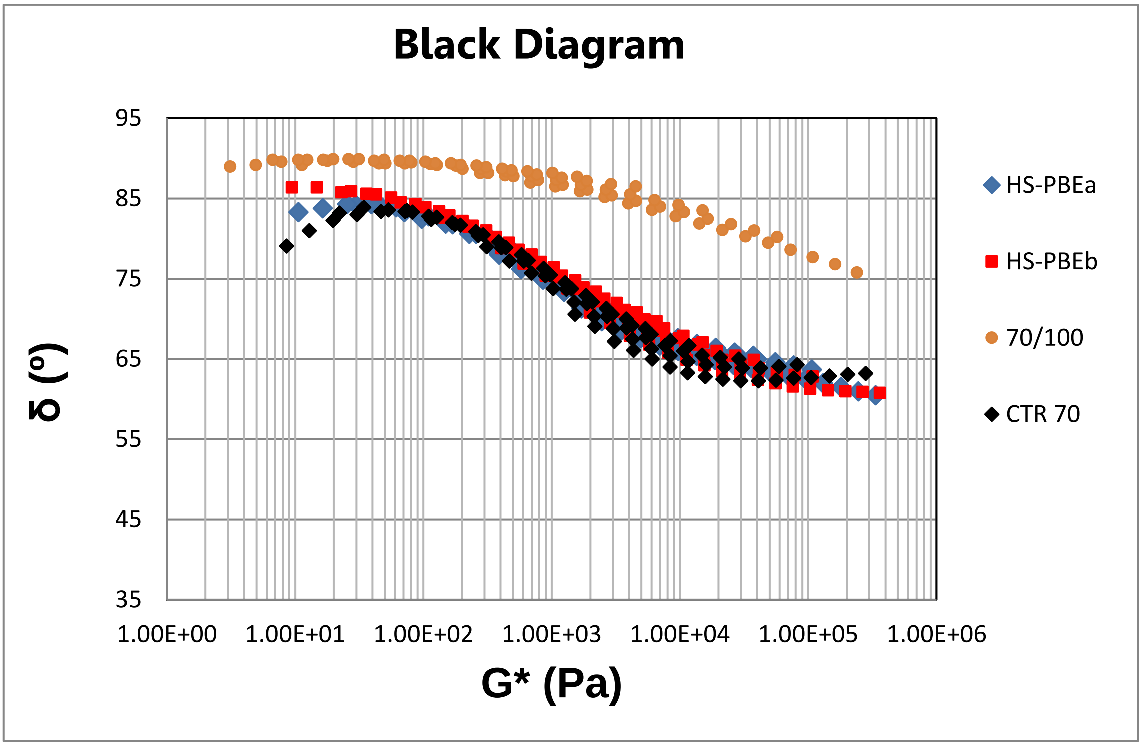


Figure 3.14a. Black Diagrams for reactive HSs. Neat bitumen (70/100) and the rubberised binder CTR70 have been included for comparison.

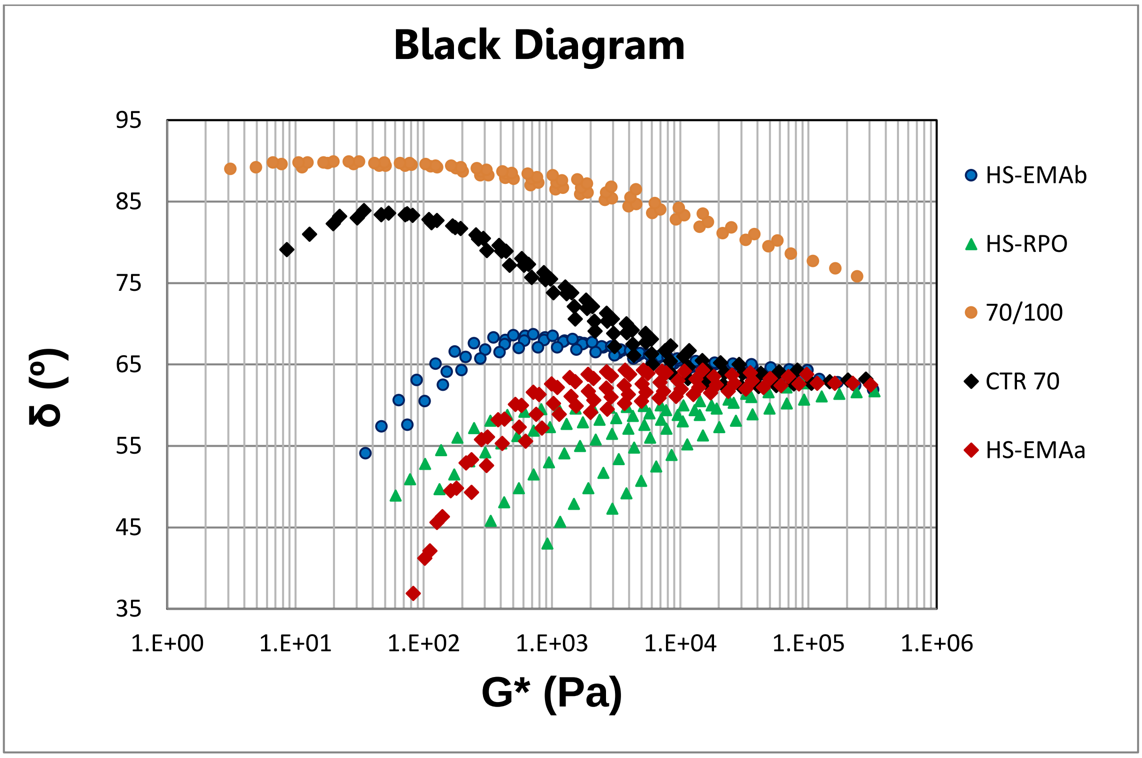


Figure 3.14b. Black Diagrams for non-reactive HSs. Neat bitumen (70/100) and the rubberised binder CTR70 have been included for comparison.

As may be shown in Figure 3.14A, whereas neat bitumen presents nicely superposed curves and a transition to a wide Newtonian region (δ = 90º), non-reactive systems present curves which are not completely overlapped, with a notable modification of the rheological behaviour. Thus, phase angle is shifted downward, tending to develop a plateau of the phase angle as G* increases. This fact that points out an enhancement in elasticity and appears to indicate structural changes in binder microstructure.

The modification in the rheological behaviour is even more apparent for reactive HSs, as can be illustrated in Figure 3.14B. These curves develop a subtle maximum of δ in the low G* region and tend to flatten at higher values. In addition, as modification is more intense, isothermal curves do not overlap at all, pointing out a thermorheologically complex behaviour. This outcome is attributed to the different temperature dependences of the relaxation times of the dispersed phases that are expected to be developed: non-dissolved rubber particles and polymer-rich phase (Navarro et al., 2005; Senise et al., 2017). Consequently, these results reveal the multiphasic nature of the HSs in which non-dissolved CTR particles and polymer phases exert a remarkable influence.

It is important to note that, HSs present a remarkable improvement in binder elasticity, as may be deduced from the linear viscoelastic behaviour, which is usually related a better in-service performance. However, taking into account that distresses like pavement rutting take place at stresses larger than those of the lineal viscoelastic range, these functions cannot fully account for the performance characteristics of modified binders and may be inadequate in rating polymer-modified binder (Senise et al., 2017).

With this aim, the multiple stress creep recovery test (MSCR, UNE-EN 16659) has been proposed to evaluate how prone to permanent deformations a binder is.

MSCR characterises the recovery and non-recovery properties of the bitumen by means of 10 cycles of 1 s creep followed by 9 s recovery, at two consecutive stress levels (0.1 and 3.2 kPa). The chosen temperature was 60ºC because this value is typically considered the maximum expectable pavement temperature in southern European countries. Taking into account that, irreversible deformations of asphalt mixes are highly dependent on the stress levels, rutting itself is a non-linear viscoelastic phenomenon and, therefore, MSCR test is considered a better method in evaluating the rutting resistance.

As shown in Figure 3.15, neat bitumen undergoes large strains and small magnitudes of strain recoveries, forming a staircase pattern, typical of a viscous Newtonian response.

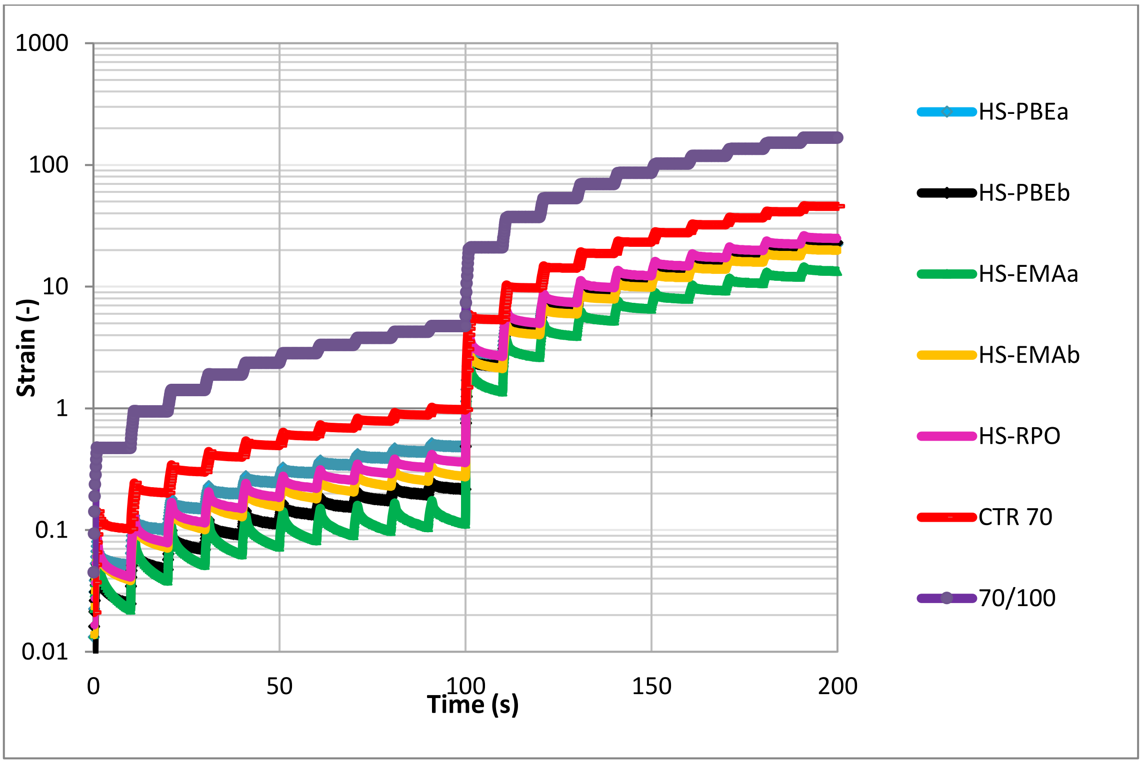


Figure 3.15. MSCR test results at stress levels of 0.1 (< 100 s) and 3.2 kPa (> 100 s) for the studied systems.

The improved elasticity reported previously for the rubberised bitumen (CTR70) and, especially for HSs, give rise to a notable modification in strain profiles on

MSCR. Thus, in every cycle, delayed elastic strain recoveries are clearly pointed out leading to a remarkable non-linear response, because accumulated compliances become stress dependent (Senise et al., 2017).

In addition, it is important to underline that, strain recoveries result clearly increased, in particular for reactive HSs, in such a way that a saw tooth shape profile is disclosed, which is associated to highly modified bitumen with enhanced elastic response. Again, the synergistic effect of non-dissolved CTR particles and the second polymeric phase seems to be the responsible for the remarkable modification in the creep recovery profile. Regarding the in-service issues, it is worth mentioning that the reduced cumulative strains for HSs would lead to a better rutting resistance of the pavement.

In addition, MSCR test allows to obtain two important average parameters from every set of 10 cycles, the non-recoverable creep compliance (Jnr) and the percent of elastic recovery (%R), which can be employed to characterise the creep response at the selected stress levels (0.1 kPa and 3.2 kPa). The percent of elastic recovery (%R) quantifies the elastic character of the material, whereas the non-recoverable compliance (Jnr) measures the amount of dissipated energy during the recovery cycles and, therefore, gives indications of the proneness of asphalt mixtures to undergo permanent deformation damages. Consequently, both parameters enable a quantitative analysis of MSCR results (Table 3.7).

Table 1.7. Non-recoverable creep compliance (J_{nr}) , the percent of elastic recovery (%R) and minimum %R obtained from MSCR tests.

	Non-Recoverable Creep Compliance J_{nr}(kPa^{-1})		**% Recovery (%R)**		**Minimum %R 3.2 kPa** $= 29.37 J_{nr\,3.2kPa}^{-0.263}$
	0.1 kPa	**3.2 kPa**	**0.1 kPa**	**3.2 kPa**	**3.2 kPa**
HS-PBEa	0.510	0.718	39.6	21.3	32.0
HS-PBEb	0.216	0.709	58.4	18.5	32.2
HS-EMAa	0.112	0.415	83.8	44.3	37.0
HS-EMAb	0.275	0.613	64.8	28.9	33.4
HS-RPO	0.360	0.767	60.0	35.1	31.5
B 70/100	4.720	5.071	0.7	0	-
CTR-70	0.976	1.398	30.7	10.6	26.9

In general, all reactive HSs and especially HS-EMAa, exhibit the largest %R and the lowest Jnr values in magnitude, at each of the applied test stresses, pointing out a good elastomeric behaviour and a lower rutting susceptibility. In this regard AASHTO M 332, (AASHTO M 332, 2014) introduced a new method to classify binders in terms of their elasticity by means of an exponential function of non–recoverable creep compliance, at the cycle of 3.2 kPa:

$$\%R_{3.2kPa} > 29.37 J_{nr\,3.2kPa}^{-0.263}$$

Therefore, bitumens with a percent of elastic recovery greater than this limit are expected to have good elastomeric behaviour (Gama et al., 2018). Consequently, according to this criterion, HS-EMAa and HS-RPO present the best performance under rutting conditions. However, it must be noted, that this condition only provides a pass or fail criterion and does not allow a quantitative evaluation, because the calculated compliance parameter is calculated from Jnr, 3.2kPa which changes from binder to binder (Gama et al., 2018).

3.2.5 Correlation of properties with microstructure: optical microscopy

From the presented results, it is clear that different improvement degrees are pointed out after the modification of the rubberised bitumen, depending on the type of polymer used. The thermomechanical behaviour of HSs could be explained by the formation of a complex multiphasic system composed of different polymeric phases, as may be supported by fluorescent microscopy (Navarro et al., 2010).

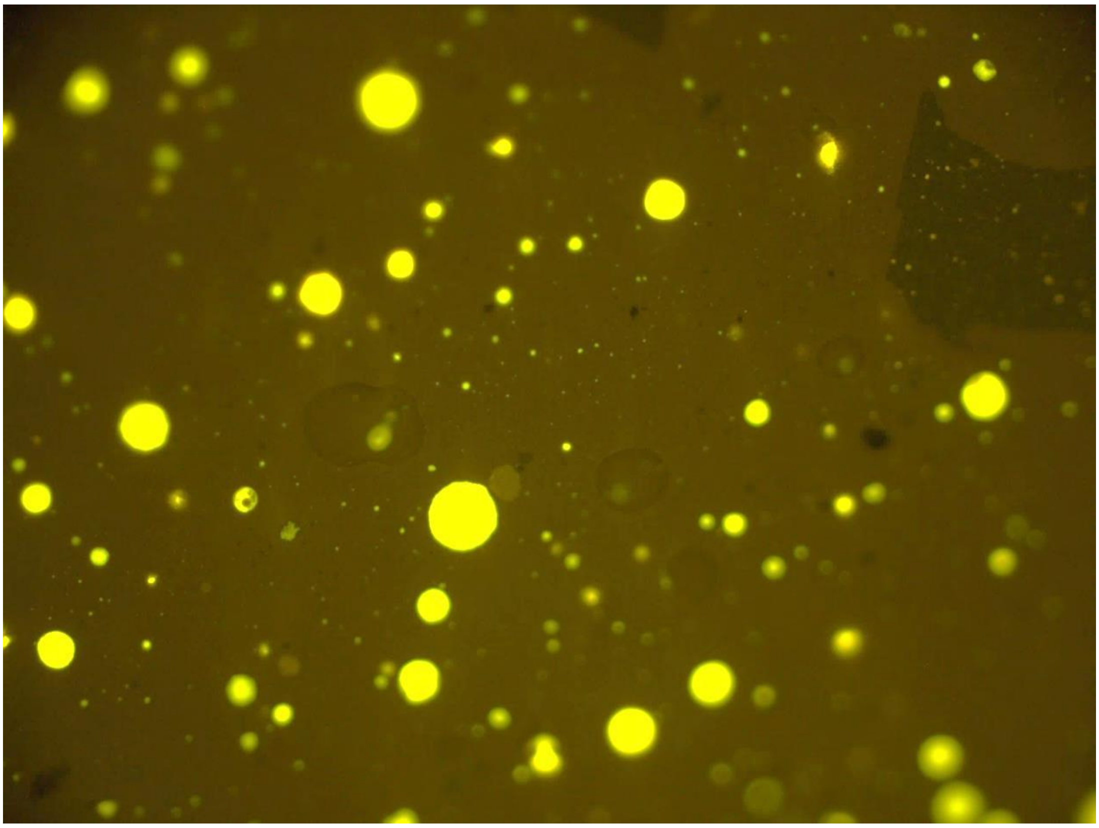


Fig. 4.16a. HS-PBEa

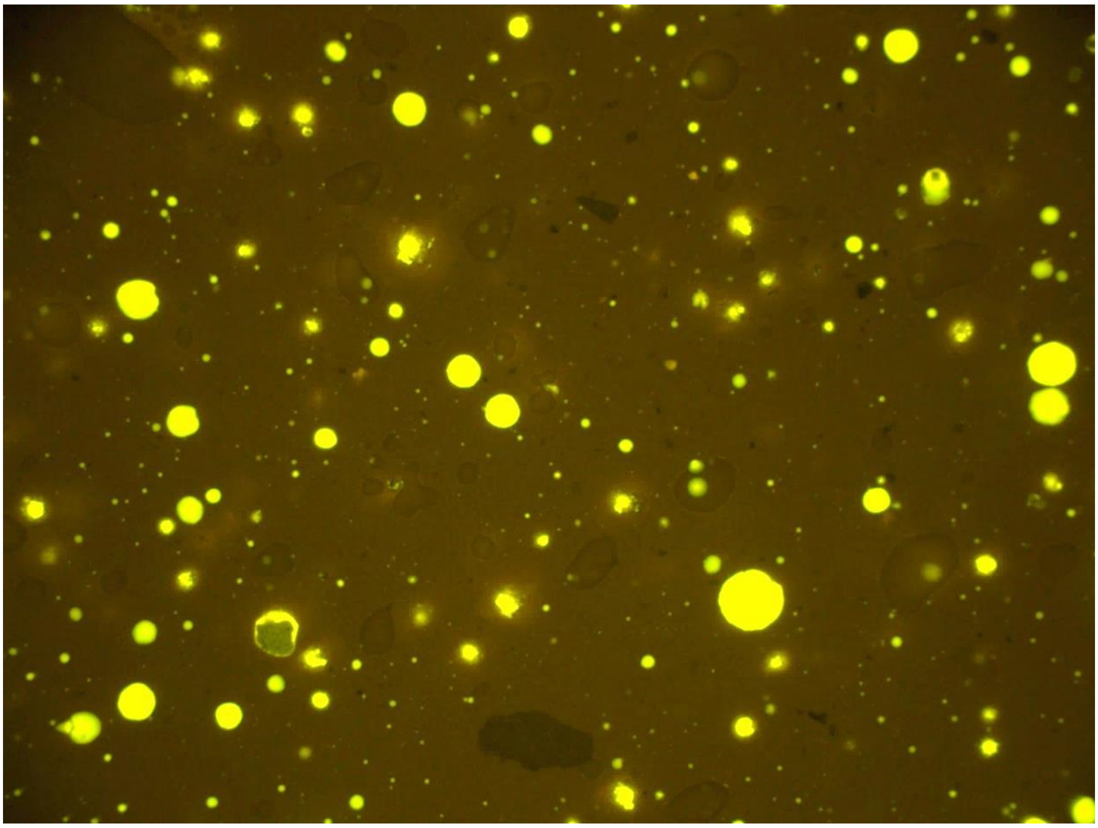


Fig. 4.16b. HS-PBEb

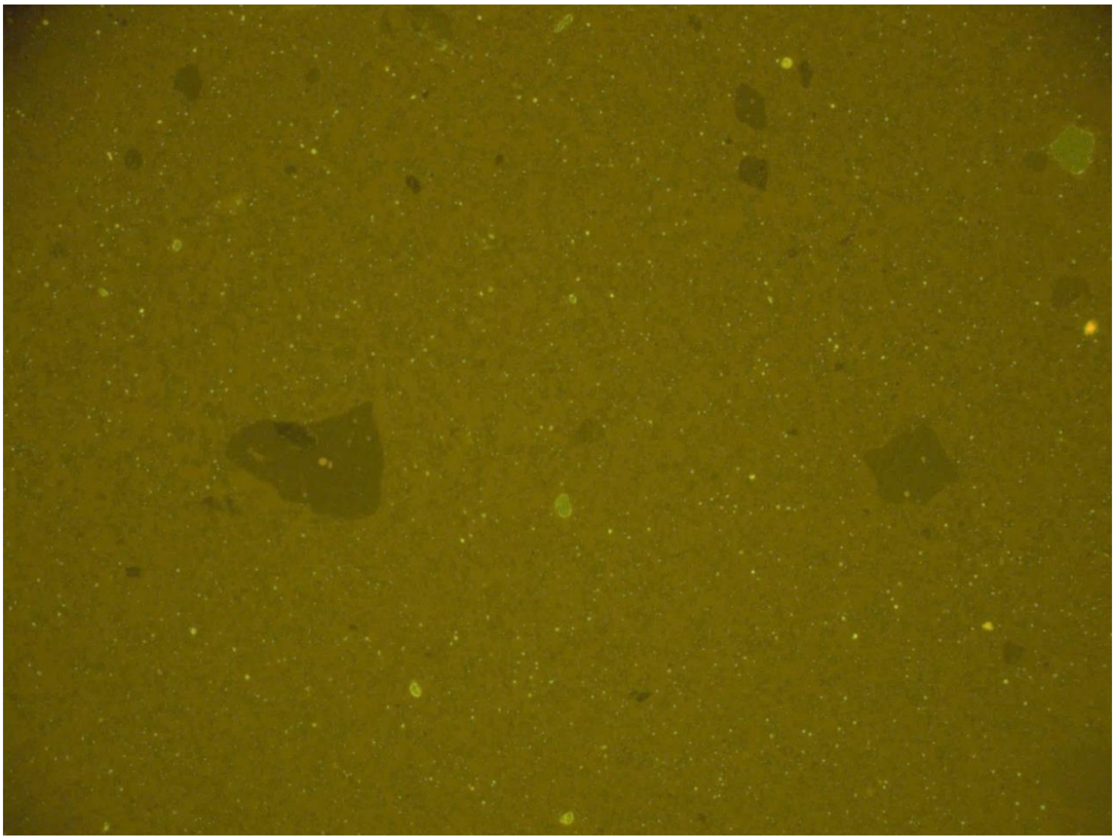


Fig. 4.16c. HS-EMAa

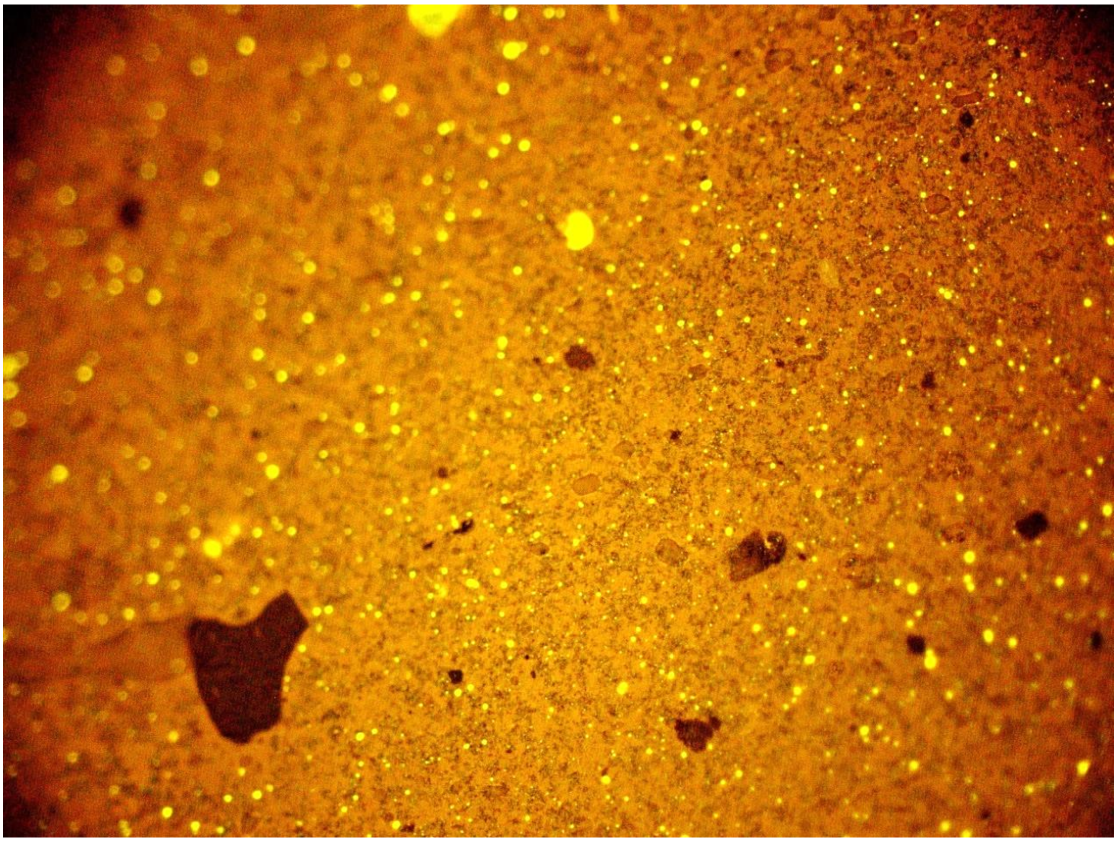


Fig. 4.16d. HS-EMAb

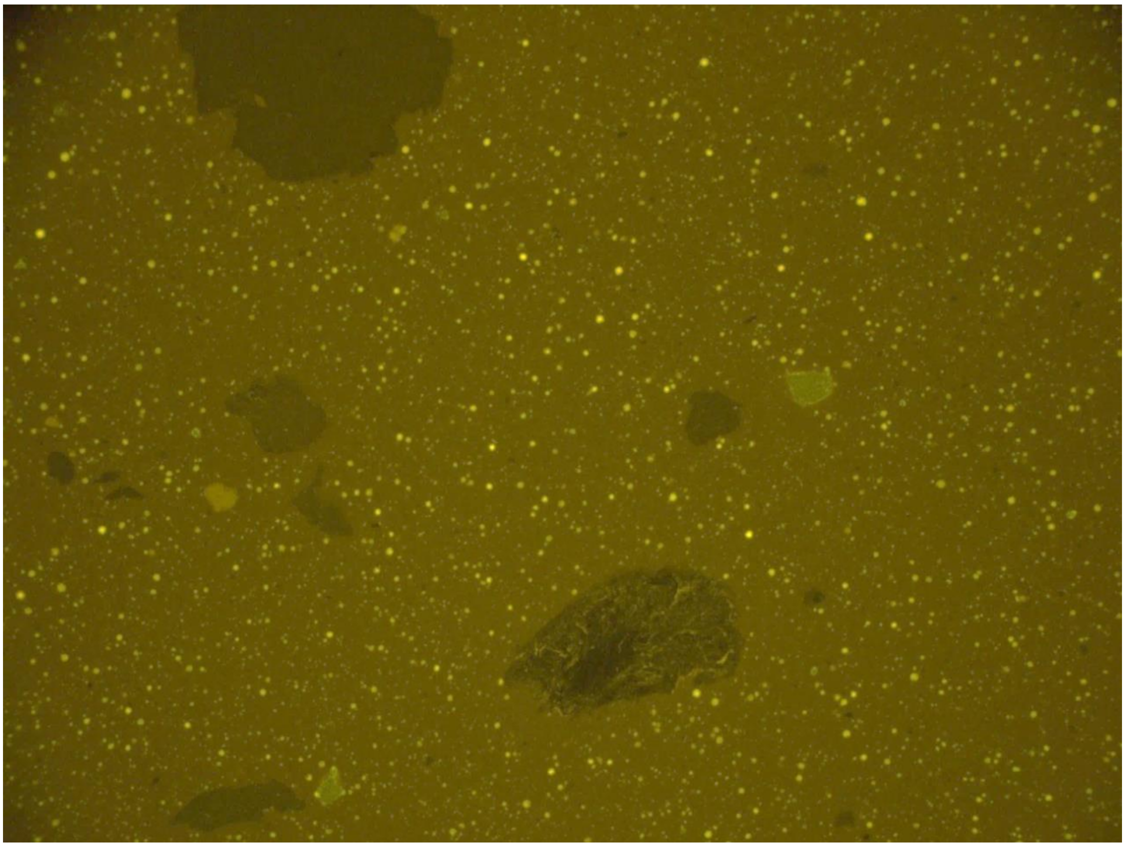


Fig. 4.16e. HS-Polyolefin

On the one hand, all HSs presented in Figure 3.16 show the presence of non-dissolved CTR particles of different sizes, resulting from the disintegration of the original rubber. As it has been widely reported (Navarro et al., 2007; Navarro et al., 2010) these elastic particles together with the dissolved rubber chains give rise to the observed improvement for CTR70. It is noteworthy that the presence of these particles, far from acting as cracking promoters of the asphalt, contribute to the improvement of the low-temperature properties, as evidenced by the lower Fraass Point compared to a neat bitumen (Table 3.6) (Navarro et al., 2010).

Table 3.6. Technological properties for the bituminous binders studied.

Property	unit	HS-PBEa	HS-PBEb	HS-EMAa	HS-EMAb	HS-RPO	CTR 70	B 70/100
Penetration	0.1 mm	60	61	63	63	54	70	75
Softening Point, $T_{R\&B}$	°C	56	56	68	63	63	51	46
Penetration Index	-	0.6	0.6	3.2	2.3	0.5	0.1	-1.3
Fraass Point	°C	-18	-25	-21	-19	-20	-20	-10
Elastic Recovery at 25°C	%	64	61	62	61	60	61	13
Dif. of $T_{R\&B}$ (Stability)	°C	2.1	4.3	1.4	7.5	1.2	10	0
Cohesive Energy	J/cm^2	3.088	3.636	3.923	3.075	2.019	2.702	0.007

On the other hand, Figure 3.16 also displays the existence of dispersed light-toned regions, pointing out the presence of a polymer-rich phase for all HSs. However, different proportions and phase distributions of the polymer rich phases are clearly distinguished. On the one hand, physical HSs (HS-PBEa and HS-PBEb) present spherical droplets randomly distributed in the asphaltene-rich phase, covering a surface fraction of roughly 8%, greater than that of the polymer concentration in the blend (3 wt.%.). This fact confirms the polymer swelling by maltenic oils and reveals their partial compatibility, which is required to improve the performance (Navarro et al., 2010; Polacco et al., 2015). Thus, for physical HSs, a multiphasic structure is formed by two dispersed phases (non-dissolved CTR particles and polymer-rich droplets) within a continuous asphaltene-rich phase, since asphaltenes are more reluctant to polymer swelling [30]. Therefore, the synergistic contribution of these phases would explain the reported rheological and technological results (Senise et al., 2017).

On the other hand, in the case of reactive HSs, even though a fluorescent dispersed polymer-rich phase is also recognisable, the morphologies are deeply different. Thus, the surface fractions of the light regions are clearly below the proportion of added polymer (3 wt.% for HS-EMAs and 2 wt.% for HS-RPO) and microphases present smaller sizes than those of physical HSs. It is well known that if a polymer is physically dissolved in the bituminous matrix, then its original structure is lost during mixing and the macroscopic properties would not be transferred to the modified bitumen (Polacco et al., 2015). According to this, the observed morphologies of reactive HSs cannot explain the strong variation of their rheological behaviour. Therefore, although the presence of both polymer-droplets and non-dissolved CTR particles would partially contribute to enhance the rheological behaviour, the main origin of the modification seems to be caused by chemical changes that happens at a much lower scale. Thus, new chemical structures, undetectable by optical microscopy, are developed in reactive HSs by forming chemical bonds between polymer molecules and some bituminous compounds.

As regards HS-EMAs, since these samples were formulated using a maleated copolymer, the reported behaviour can be explained on the basis of the chemistry of reactive pendant groups (free succinic anhydride). It is well known that cyclic anhydrides easily react with hydroxyl and amine groups giving rise to ester and amide bonds, respectively, in a ring opening reaction (BraüerS et al., 2007). Therefore, as such groups are abundant in bitumen (Mohammadi et al., 2017), succinylation reactions are expected to happen, linking copolymer chains covalently to some polar bituminous compounds (resins and asphaltenes). Therefore, new complex chemical structures are developed, leading to structural arrangements at a molecular scale and conferring the reported enhancement of in-service properties. According to this, the observed critical gel-like behaviour is then attributed to the formation a chemical network. This assumption is consistent with the copolymer composition and it would explain why EMAa is a more effective than EMAb for modification. Thus, the higher proportion of succinic grafted groups in EMAa leads to a superior reactivity and, therefore, modification capacity, despite presenting a higher MFR i.e. lower polymer melt viscosity (Table 3.5) (Yousefi, 2003).

Finally, regarding the reactive polyolefin HS-RPO, again, the improvement should be attributed to chemical interactions between RPO and bitumen compounds (Wang et al., 2016; Polacco et al., 2004). In fact, it has been reported that the presence grafted glycidyl methacrylate groups in olefin copolymers exerts a compatibilizing role with certain bitumen molecules (Polacco et al., 2005; Jun et al., 2008). Therefore, according to the epoxy chemistry, it is believed that oxiranic rings react with polar nucleophilic bitumen molecules, allowing an improvement of the miscibility between them, a fact that would explain the reported morphology (Polacco et al., 2004). Thus, as it has been reported in the bibliography, a ring-open reaction happens between the epoxy group and functional carboxylic acid or hydroxyls groups of polar molecules in bitumen to form ester or ether bonds respectively leading to formation of a network structure (Jun et al., 2008).

Taking into account that complex bituminous molecules are grouped forming a micellar structure containing more than one nucleophilic group, a chemical network structure may be built-up by reaction with the grafted groups of the olefinic chains of EMAs and RPO. Therefore, the consolidation of the three dimensional structure would explain the reported critical gel behaviour and the improved hot storage stability. Thus, the formed network would interact with the non-digested CTR particles probably by entrapping them by physical means hindering the settling of particles (Senise et al., 2017).

3.2.6 Correlation of properties with microstructure: MDSC characterisation

MDSC tests were performed to provide structural information about crystalline and amorphous phases of the polymers and their compatibility and interaction with bitumen compounds (Navarro et al., 2010).

DSC curves of pristine PBEs, presented in Figure 3.17, point out a similar qualitative pattern characteristic of semi-crystalline ethylene/propylene copolymers, showing a clear glass transition (at -24.1 for PBEa and -27.7ºC for PBEb) followed by a cold crystallization and a single melting process (see Table 5).

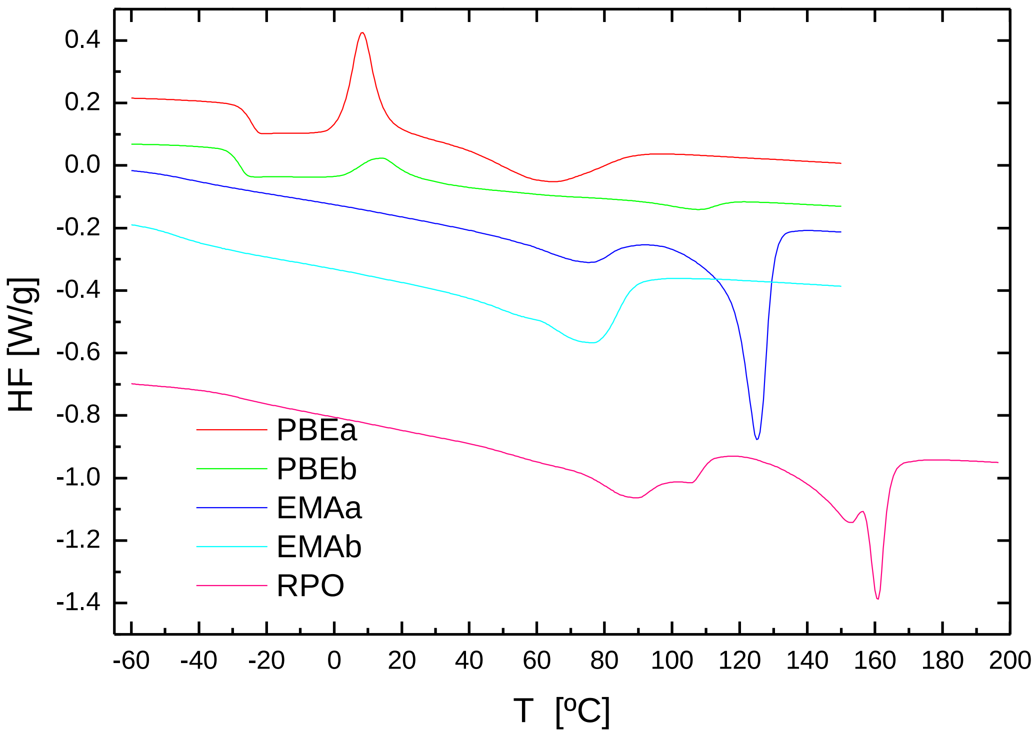


Fig. 4.17. Total heat flow curves for neat polymers obtained from MDSC experiments

Surprisingly, despite its high polypropylene content (Table 3.5), the melting pattern deviate from that of this homopolymer (with a melting process at around 163ºC) showing melting endothermal peaks at a much lower temperatures. This result is attributed the inclusion of ethylene comonomer in propylene backbone that interferes the crystallization process and shifts the melting temperature to lower values, (Mathot et al., 2002).

Regarding EMA copolymers, Figure 3.17 shows the presence of one (EMAb) or two (EMAa) melting peaks. The origin of this distinct behaviour cannot be precisely determined based solely on DSC results, because more experimental techniques are necessary to determine the nature of crystalline phases. However, according to bibliography, the presence of an extra melting peak may happen in commercial ethylene-octene and ethylene-butene copolymers, reflecting two crystal populations with different thermal stability, and could be indicative of the presence of polymer fractions with different comonomer content in EMAa (Rabiej et al., 2004).

Finally, since RPO is a complex reactive polyolefin mixture, its DCS thermogram shows a multiple-peak pattern corresponding to the melting process of the crystalline fractions of its constituents, isotactic polypropylene, ethylene vinyl acetate copolymer and polyethylene wax.

By contrast, total heat flow curves of the HSs presented in Figure 3.18 display multiple thermal events resulting from both bituminous and polymer-rich phases.

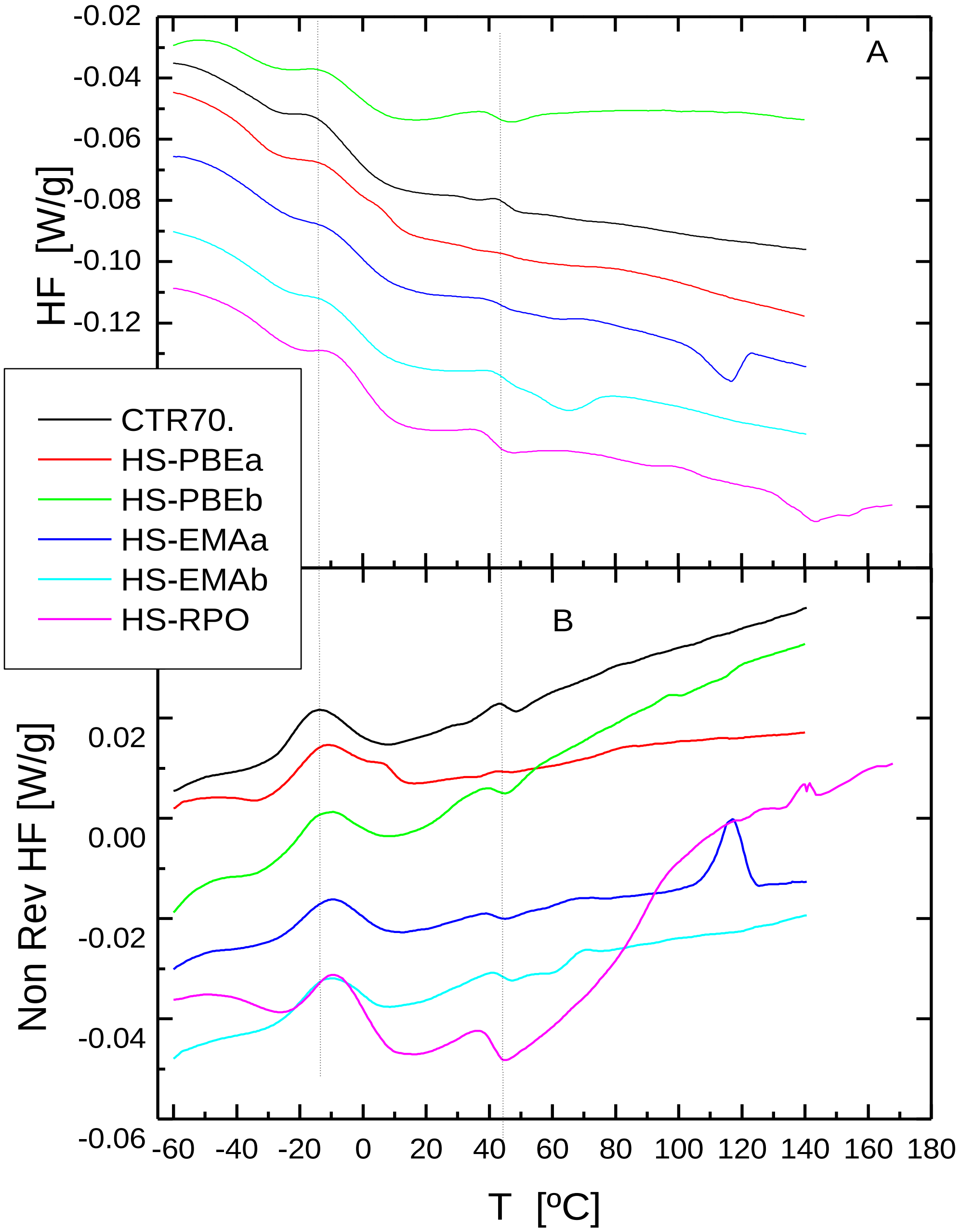


Figure 3.18. (A) Total heat flow curves and (B) non-reversing heat flow curves for HSs and CTR70, obtained from MDSC experiments

Firstly, by comparing DSC curves of neat polymers and their corresponding HSs, a compatibility analysis of the crystalline fraction with bitumen can be performed. The degree of crystallinity of the polymer phase was calculated from the melting enthalpies of HSs weighted by its mass fraction, divided by 293 J/g for the heat of fusion of 100% crystalline polyethylene (Table 3.9).

Table 3.9. Melting temperatures and enthalpies, and crystalline fraction (χ_c) obtained from MDSC tests.

Samples	T_m [°C]	ΔH_m [J/g]	χ_c[%]
PBEa	64.1	14.2	4.8
HS-PBEa	55.8	0.30	3.4
PBEb	107.5	2.79	1.0
HS-PBEb	100.8	0.0113	0.1
EMAa	75.2/125.3	47.2	16.1
HS-EMAa	116.7	1.19	13.5
EMAb	75.9	75.9	25.9
HS-EMAb	1.73	64.2	19.7
RPO	89.5/105.0/ 153.5/160.0	51.6	17.6
HS-RPO (2%)	52.0/98.8/106/143	0.94	16.0

In the case of non-reactive polymers, Table 3.9 and Figure 3.18 point out a lowering of the melting point (8.3°C for PBEa and 6.7°C for PBEb) and a reduction of crystallinity, due to the migration of maltenic molecules to the polymer crystalline regions. However, taking into account their low crystallinity (compared to the homopolymers) this result does not completely explain the reported enhancement in the rheological behaviour of HS-PBEs since conventional polyolefins usually show poor compatibility with bitumen. In fact, the metallocene catalysis polymerization method used for producing PBEs, seems to be behind the moderate compatibility that allows the inter diffusion phenomena that leads to the swollen polymer-rich phase observed in Figure 3.18A and 4.18B. Thus, the structure of these metallocene-based polyolefins (polydispersity and degree of short-chain branching) favours a better dispersion in the bituminous matrix and improves the in-service properties (Polacco et al., 2004; Polacco et al, 2015).

On the other hand, the used reactive polymers and their corresponding modified bitumens display a much higher crystalline fraction than PBEs and HSs (HS-EMAa, HS-EMAa and HS-RPO). Similarly, these systems are characterised by a melting point depression and small reduction in χc as well. In spite of this, the observed micromorphologies (Figure 3.16C-E) does not seem to reflect this outcome because of the small proportion of light toned regions. However, as micrographs show a lower population of smaller fluorescence drops, this result hints lower crystallite sizes and improved dispersion of the copolymer. This outcome, together with the improved reactive compatibility suggests that the chemical network will also include submicron crystalline domains via covalent chemical bridges between macromolecules. Consequently, this more complex morphology, invisible by optical microscope, would be responsible of the enhancement in the thermomechanical behaviour.

On the other hand, total heat flow (major events) and non-reversing heat flow (minor transitions) curves in Figure 3.18 curves disclose changes induced in the rubberised bitumen microstructure by the addition of the polyolefin copolymer. Thus, total heat flow curves of HSs are result of the contribution of polymer-rich phase, asphaltene-rich phase and remaining CTR particles (Navarro et al., 2010). As it was previously discussed, the polymer-rich phase causes the endothermal melting thermal events. By contrast, rubberised bitumen presents several overlapping thermal effects as a consequence of the developed structures, due to time-dependents ordering processes that happens when bitumen is quenched from the melt (Navarro et al, 2005; Senise et al., 2017; Polacco et al., 2015). These shuttle transitions can be analysed in a better way by using the non-reversing component of heat flow (Figure 3.18B) (Senise et al., 2017; Polacco et al., 2015). First of all, the broad endothermic background observed from -50 to 100ºC, has been mainly attributed to the melting of ordered mesophasic structures developed by simple aromatic bituminous compounds and, in a lower degree, to crystallized saturates. In addition, low and high molecular weight segments of saturated and aromatic compounds undergo the two cold crystallization peaks placed at around -15 and 40 ºC, respectively. Additional cold crystallization exothermic peaks, associated to polymer phases, appear for some samples: HS-PBEa (~6ºC) and HS-EMAa and b (~117 and 71ºC respectively). Furthermore, a minor endotherm can be viewed approximately at around 50 ºC, associated to larger mesophasic structures, found in resin and asphaltene fractions. Although the complex nature of HSs makes difficult a structural analysis, in general, as all these events undergo a modification in their intensities and positions, it can be interpreted as a proof on interaction of bitumen molecules with the added polymer (Navarro et al., 2007; Senise et al., 2017; Navarro et al., 2010; Polacco et al., 2005).

Conclusion

In this thesis it has been updated and made a complete research of all the state of art regarding to the modified bitumen with rubber and polymers process. Basic concepts of bitumen have been described, studying its structure and composition. Rheology behavior applied to complex mixtures (hybrid systems), both rubber and polymer modified bitumen, has been explained and represented all the data for a better understanding.

From all the possible hybrid systems it has been chosen those which has competitive technical advantages and better fits to the Industrial sector needs.

In the first stage of the research, Hybrid Systems (HSs) were formulated by the addition of selected polymers (SBS, EBA, EBA and EPDMs) to a model rubberised bitumen (10 wt.% CTR) and cured with sulphur and ZnO. Crumb Tire Rubber (CTR) modification of bitumen has been extensively proven that exerts a notable improvement the in-service properties and therefore, the resulting pavement would present better in-service properties. Thus, it is expected a higher rutting resistance, lower tendency to low-temperature cracking and reduced sensibility to temperature changes.

The data acquired shows an improvement in HSs as a result of the development of a multiphasic system composed of: a polymer-rich phase, an asphaltene rich-phase, non-dissolved solid rubber particles and digested rubber. Physicochemical interactions and synergistic effects among the different phases also play an important role, reducing or preventing a large-scale phase separation, leading to better high temperature storage stability.

The capability of modification of the polymeric additives were established as follows: SBS>EBA>EVA>EPDMs. The Hybrid System containing SBS (HS-SBS) presents, by far, the best overall performance due to the development a continuous SBS-rich phase as a consequence crosslinking reaction of polybutadiene double bonds with sulphur, which further interacts with the non-digested rubber particles by either specifically binding to or physically entrapping them.

Furthermore, a second batch of polymers have been studied to analyze Hybrid Systems. Non-reactive HSs (HS-PBEa and HS-PBEb), which were formulated with two semi-crystalline ethylene/propylene based elastomers, yield stable binders with improved in-service properties without deteriorating low temperature flexibility. Reactive HSs (HS-EMAa, HS-EMAb and HS-RPO) use ethylene-based polymers containing functional groups (pendant succinic anhydride in EMAa and EMAb; and epoxy groups in RPO) that react with bitumen polar molecules, leading to a much higher degree of improvement than PBEs.

From a structural point of view, the enhancement in the thermomechanical response is consequence of the development of a complex multiphasic system composed of: non-dissolved CTR particles, a swollen polymer-rich phase and an asphaltene rich-phase. Physicochemical interactions and the synergistic effect among these phases contribute to the improved bulk properties and favour heat storage stability.

The obtained results allow to rank samples with respect to the capability of modification of the ethylene polymer as follows PBEb≈PBEa<<EMAb<EMAa<RPO.

In this investigation, Hybris Systems seems to be a proper alternative to achieve hot storage stability and to improve binder quality. Therefore, the resulting pavement presents a higher mechanical performances and better thermal properties.

This thesis among other future researches would allow to improve the current technological performance in the Industry, meeting sustainability needs with the least environmental and economic cost. Synergies between Asphalt pavements companies and government policies must agree in order to develop new products to address environmental in asphalt production.

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