DEFORMATION AND RECOVERY BEHAVIOUR OF THERMOPLASTIC VULCANISATES

by

ROHAIDAH ABD.RAHIM

A Master's Thesis submitted in
partial fulfilment of the requirements
for the award Master of Philosophy
of Loughborough University.

April 2007

Director of research : **Professor Doug Hourston**
Supervisors : **Dr Jane Clarke,**
Institute of Polymer Technology & Materials Engineering
Dr Andrew Tinker, Tun Abdul Razak Research Centre
Dr Stuart Cook, Tun Abdul Razak Research Centre

ACKNOWLEDGEMENTS

I am deeply indebted to a large number of individuals for their help and encouragement throughout this work.

I would first like to thank Dr Jane Clarke for her continual interest in my work, for her guidance and a valuable source of ideas. I wish to express my sincere gratitude to Dr. Andrew Tinker and Dr Stuart Cook for their supervision, continual guidance, tremendous help, and unfailing encouragement throughout this work. I also wish to thank all TARRC staffs for their kind assistance and valuable discussions in some aspects of the experimental work.

I also wish to thank to Director General of Malaysian Rubber Board (MRB), Dato' Dr Kamarul Baharin Basir, Deputy Director General (Research & Development), Dr Mohd Akhbar Md. Said, Director of Technology and Engineering Division, Dr Alias Othman, Head of Advanced Rubber Technology Unit, Dr M. Aris Ahmad for giving me this opportunity to gain new knowledge. Financial support from Malaysian Rubber Board, is gratefully acknowledged.

I would also wish to express my gratitude to my colleagues at Malaysian Rubber Board (MRB), Malaysia, Tun Abdul Razak Research Centre (TARRC), Brickendonbury, Institute Polymer Technology, Materials and Engineering (IPTME), University of Loughborough, for their friendly help, suggestions and support. Thanks to all my friends that I met during my stay here for their kindly support and making my stay here a wonderful experience.

Finally, I would like to express my never-ending gratitude to my family especially my lovely father and mother, brothers, sisters and other family members for their continuous support, encouragement and tireless patience throughout this study.

Rohaidah Abd.Rahim

ABSTRACT

The purpose of this study was to identify key elements in the microstructure of thermoplastic vulcanisates (TPVs) in order to understand better the deformation and recovery characteristics of thermoplastic vulcanisate blends. Thermoplastic vulcanisates based on natural rubber and a thermoplastic (polypropylene) were studied. The rubber was dynamically crosslinked during melt-blending and test specimens were produced by injection moulding and extrusion. Morphological analysis and tensile stress-strain studies were used to investigate the effect of composition, processing and microstructure on the deformation and recovery behaviour of thermoplastic vulcanisate blends. Solvent extraction and electron microscopic analysis revealed that the TPVs had a co-continuous morphology. The PP phase consisted of relatively large domains (1.0 to 7.0 μm) joined by thinner ligaments. The NR/PP TPV exhibited similar trends in deformation and recovery behaviour to commercial TPVs. Properties were dependent on the NR/PP ratio of the TPVs with the modulus values increasing with PP content, due to the greater stiffness of the PP. Good recovery behaviour, which improves with increased NR content, is largely attributed to the elasticity of the crosslinked elastomer phase. The TPVs exhibited stress softening behaviour, which is believed to be mostly due to a permanent alteration of the thermoplastic phase of the blend, probably by either breaking or stretching the PP ligaments beyond their yield point. Understanding the relationship between morphology and physical properties helps to identify routes to improved TPV performance.

TABLE OF CONTENTS

CHAPTER 1 : INTRODUCTION

CHAPTER 2 : LITERATURE REVIEW

CHAPTER 3 : EXPERIMENTAL

CHAPTER 4 : RESULTS AND DISCUSSION

CHAPTER 5 : CONCLUSIONS AND FUTURE WORK

FIGURES

TABLES

APPENDIX

CHAPTER 1

INTRODUCTION

1.1 Background and industrial justification

Elastomer-thermoplastic blends have become technologically useful as thermoplastic elastomers (TPEs) over the past 30 years. They have many of the key properties of elastomers, but they are processed as thermoplastics. They do not need to be vulcanised during fabrication into end-use parts. Thus, they offer a substantial economic advantage in respect to the fabrication of finished parts.

Global demand for thermoplastic elastomers (TPEs) is expected to increase by 6.2 percent per year through to 2009[1-2], expanding to 3.1 million metric tons. The global TPE sales will remain focused in the US, Japan and Western Europe. However, the growth prospects will be strongest in a developing countries such as India and China (the worlds largest TPE market in terms of metric tons)[3]. The higher market for global TPE will remain concentrate in copolyester elastomers (COPEs) and thermoplastic vulcanisates (TPVs). However, many developing countries, particularly in Asia, are rapidly expanding their positions in TPEs, initially focusing on low-cost styrenic block copolymers (SBCs) due to their existing positions in styrene-butadiene and polybutadiene rubber, but also diversifying into compounded thermoplastic polyolefins (TPOs) and thermoplastic polyurethanes (TPUs)[1-2].

The Freedonia Market Research, a leading international study/database company, in November 2005[1-2] reported that motor vehicles would remain the largest market for TPEs at the global level especially for exterior (e.g., body seals) and interior (e.g., instrument and door panel skins) products applications at the expense polyvinyl chloride (PVC) and ethylene-propylene diene monomer (EPDM). Although all major generic types of TPEs are gaining new motor vehicle applications, the TPOs will remain the largest volume segment contribute to the industry. The smaller consumer will be primarily attributable to expanding uses in footwear industry, sporting goods sector and personal care goods will remain the fastest growing market for TPEs through 2009, where TPEs will benefit from the continued displacement of traditional materials such as thermoset rubber and thermoplastics (particularly PVC)[2].

The early development of thermoplastic elastomers was encouraged by industrial interest in elastomers with hardness and stiffness intermediate between those of traditional resilient rubbers and harder materials such as ebonite and thermoplastic resins. This type of polymer is particularly in demand in the car industry for use as sight shields, soft fronts, rear ends, rubbing strips and bumpers.

Thermoplastic vulcanisates are a type of TPE with particularly good elastic properties. TPVs are dynamically vulcanised blends of thermoplastic and elastomer.

The purpose of this study is to identify key elements in the microstructure of TPVs that might explain more about the deformation and recovery characteristics of thermoplastic vulcanisate blends. Understanding the relationship between the morphology and properties will help to give ideas of how to modify morphology and hence, get the required end properties of the TPVs.

1.2 Current issues concerning the morphology of thermoplastic vulcanisates

The effect of microstructure on properties of thermoplastic vulcanisates is particularly problematic. The question arises as to why dynamic vulcanisates can recover elastically from highly deformed states, even though the matrix consists of a ductile thermoplastic polymer.

In early studies, it was proposed that the morphology of thermoplastic vulcanisates consists of a dispersed rubber particle in a hard, continuous matrix of thermoplastic, simply to be consistent with the flow behaviour of the melt. A lot of researchers have prepared TPVs using both pre-vulcanised rubber particles and by using dynamic vulcanisation. The use of fine pre-vulcanised rubber particles improved the thermoplastic processability[4-6] of the blend but dynamically vulcanised blends had better physical properties[7-8]. Later, it was found that a variety of morphologies could be obtained depending on the polymer ratios and processing conditions. The morphologies range from dispersed rubber particles in a thermoplastic matrix to co-continuous phases of a rubber and thermoplastic[8-14].

1.3 Aims and scope of research

It is assumed that the microstructure of thermoplastic vulcanisates affects the physical properties, such as the tensile strength, the hardness, the modulus and the deformation and recovery properties. This area needs more understanding and knowledge.

The overall objective of this research is to understand better the microstructure of thermoplastic vulcanisates and the degree to which microstructure affects, and can be used to control, the properties of the materials. Furthermore, a particular objective is to find a way to improve the deformation and recovery characteristics of thermoplastic vulcanisates.

In this study, the effect of dynamic vulcanisation, natural rubber to polypropylene ratio, orientation, annealing on physical properties and deformation behaviour is investigated. To do this, tensile stress-strain, cyclic tensile stress-strain, compression set and tension set experiments were carried out and the morphology was analysed by scanning electron microscopy (SEM), scanning [transmission] electron microscopy S[T]EM, solvent extraction and etching technique.

This study is based on natural rubber/polypropylene thermoplastic vulcanisate blends. The study was further extended by comparing the physical properties and the deformation behaviour with commercial TPV based on EPDM/PP blends with a similar hardness to better understand the deformation and recovery behaviour of thermoplastic vulcanisates.

References

1. Abstract from World Thermoplastic Elastomer to 2009-Market size, market share, market leaders, demand forecast sales, company profiles, Market Research Industry Trends. http:www. Bharatbook.com/bookdetail. asp?bookid=8192&publisher= (accessed on 15 May 2006).

2. World Thermoplastic Elastomers : Industry Research Report-published by Freedonia group. http:www. mindbranch.com/Thermoplastic-Elastomers-R154-1523/ (accessed on 15 May 2006).

3. Study details China TPE market, Modern Plastics, Aug 31st, 2006. The Global Plastics Magazine http://modplas.com/inc/mparticle.php?section=E-Weekly&thefilename=eweekly08012006_07 (accessed on 14 Jan, 2007).

4. W. K. Fischer (1973) Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic, US 3758643 (to Uniroyal, Inc.).

5. A. Y. Coran, B. Das and R. P. Patel (1978) Thermoplastic vulcanisates of olefin rubber and polyolefin resin, US 4130535 (to Monsanto Co.).

6. A. Y. Coran and R. P. Patel (1980) Rubber-thermoplastic compositions. Part 1. EPDM-polypropylene thermoplastic vulcanisates, *Rubb. Chem. Technol.* **53**, pp. 141-150.

7. A. M. Gessler and W. H .Haslett (1962) Process for preparing a vulcanised blend of crystalline polypropylene and chlorinated butyl rubber, US 3037954 (to Esso Research and Engineering).

8. M. A. L-. Manchado, M. Arroyo and J. M. Kenny (2003) New development in dynamically cured PP-EPDM blends, *Rubb. Chem. Technol.* **74**, pp.211-220.

9. D. J. Elliot and A. J. Tinker (1988) "Chapter 9. Blends of natural rubber with thermoplastic" in "Natural Rubber Science and Technology (Ed., A.D. Robert)". Oxford University Press, Oxford, pp. 327-357.

10. C. L. Riddiford and A. J. Tinker (1990) TPENR, a new oil-resistant thermoplastic elastomer. Presented at a meeting of the Rubber Division, American Chemical Society, Washington DC. Paper no. 33.

11. A. -S. Sabet and R. Patel (1991) Morphology of elastomeric alloys, *Rubb. Chem. Technol.* **64**, pp. 769-779.

12. S. Cook, R. T. Davies, J. Patel, K. M. E. Lawrence and G. Sica (2003) Morphological studies of thermoplastic vulcanisates. Int. Rubb. Conf. 2003, Nurnberg.

13. J. Orderkerk and G. Groeninckx (2002) Morphology development by reactive compatibilisation and dynamic vulcanisation of nylon6/EPDM blends with a high rubber fraction, *Polymer* **43**, pp. 2219-2228.

14. S. Danesi and R.S. Porter (1978) Blends of isotactic polypropylene an ethylene-propylene rubbers: rheology, morphology and mechanics, *Polymer* **19**, pp. 448-457.

CHAPTER 2

LITERATURE REVIEW

2.1 Thermoplastic elastomers

Polymer blending is a widely practised method of modifying the properties of polymers[1-6]. Blends of various polymers, often intended for specific applications, are commercially available[4-5]. Among them are blends of thermoplastic and elastomeric materials, which combine some of the properties of conventional elastomers and thermoplastics. There are a very large number of possible thermoplastic-elastomer blends[7-13] because of the wide variety of commercially available elastomers and thermoplastics. The range of proportions over which they can be blended means that a wide range of mechanical properties can be obtained. At one end of the range, with a high thermoplastic content, the material is semi-rigid and is known as a rubber modified plastic. At the other end of the range, with high elastomer content, the soft, flexible and elastic materials are known as thermoplastic elastomers (TPEs). TPEs have a rapidly growing market[15-17], with applications including 'soft touch' aesthetic materials, automotive components, vibration or noise damping components, food containers, medical devices, sheeting goods, wire and cable covering, footwear and adhesives[18-21].

The characteristic advantage of TPE materials is that they exhibit the properties of vulcanised rubber at room temperature and thermoplastic processability at elevated-temperatures. This means that they have some of the flexibility and resilience of thermoset rubbers at service temperatures but can be processed using thermoplastic processing equipment. The great advantage of being able to use thermoplastic production processes is that they are simple, quick and have a high throughput compared to conventional thermoset rubber processes. A further advantage of TPEs is that material waste is reduced since scrap can be recycled with only marginal effect on the properties[6,22-26]. This can be seen as a big advantage compared with traditional rubber, which is relatively difficult to recycle and usually leads to inferior products. The disposal of used thermoset rubber products has also become an ecological problem in developed countries. The continued trend toward recycling, particularly in the United States and in Western European countries such as Germany and the Netherlands, is likely to accelerate the substitution of thermoset rubber with TPEs in the future. A lot of research has also been carried out to make TPEs by blending thermoplastics, especially polypropylene with scrap thermoset rubber such as ethylene-propylene-diene rubber (EPDM), styrene-butadiene rubber (SBR) and NR/SBR blend families[25,27-29].

2.1.1 Classification of TPEs

Thermoplastic Elastomers (TPEs) can be classified according to their chemistry and morphology as follows[30] :

A. Block copolymers :
   1. Styrenic block copolymers (SBCs)
   2. Thermoplastic copolyesters (COPEs)
   3. Thermoplastic polyurethanes (TPUs)
   4. Thermoplastic polyamides (TPAs)

B. Blends :
   1. Thermoplastic polyolefins (TPOs)
      a. Ethylene propylene diene rubber/polyolefins (EPDM/POs)
      b. Natural rubber/polyolefins (NR/POs)
   2. Nitrile rubber/polyvinyl chloride (NBR/PVC)

C. Elastomeric alloys (EAs)
   1. Thermoplastic vulcanisates (TPVs)
      a. EPDM rubber/polyolefins
      b. Natural rubber/polyolefins
      c. Nitrile rubber/polyolefins
      d. Butyl rubber/polyolefins
   2. Melt-processable rubber (MPR)

D. Ionomers
   1. Sulfonated EPDM rubber (S-EPDM)
   2. Zn or Na salt of ethylene acrylic acids

E. Miscellaneous

A number of other polymers have the characteristics of TPEs and some are available commercially, such as 1,2-polybutadiene, trans- polyisoprene, modified polyethylene (e.g., ethylene vinyl acetate).

2.2 Dynamic vulcanisation

Thermoplastic vulcanisates (TPVs) are a special class of TPE blends with particularly good elastic behaviour. In TPVs, the elastomer domains are crosslinked, promoting elasticity (the ability of the blend composition to retract forcibly from a large deformation)[31-32].

TPVs are normally prepared by dynamic vulcanisation (DV). Dynamic vulcanisaion[33-34] involves vulcanisation of a suitable reactive rubbery polymer during melt-mixing with a thermoplastic polymer under high shear[35-36]. The processing temperature must be above the melting point of the thermoplastic and sufficiently high to activate and complete vulcanisation of the elastomer in a short time. Any crosslinking system can be used as long as it does not alter the characteristics of the thermoplastic phase. Crosslinking systems include : sulphur[37], phenolic resin[38-40], a peroxide[41-45], metal oxides, metal salts, amines, quinone dioxime[46-49] or a third monomer[37,50-51].

The dynamic vulcanisation process was invented by Gessler and Haslett [3] who prepared a dynamically vulcanised TPV by blending chlorinated butyl rubber with PP. The process was further developed by Fisher[52], Sabet, Puydak and Rader[53] and Coran *et al.*[37,54]. In the early studies, internal mixers like Banbury mixers were used for dynamic vulcanisation. Recently, twin screw extruders seem to be mainly used, because a continuous process is more suitable for commercial production[36,55].

TPV materials can be processed by the same methods as used for conventional thermoplastic materials such as extrusion, injection and blow moulding[56-57]. Extrusion can be used to manufacture a variety of TPV shapes such as tubing, hose, sheet and complex profiles. Co-extrusion of TPV with a thermoplastic or another TPV is possible by combining two-extruders[58-59]. Together with co-injection moulding, these are cost-effective processes by which dual functionality can be produced in a product, for example soft TPV can be used as a sealing surface and a rigid hard plastic can act as a support[30]. TPVs can be moulded in the same type of injection moulding machine as is used for conventional thermoplastics. The operating temperature for processing normally lies in the range of 180°C to 250°C. This is above the melting point of the thermoplastic in the TPV, to allow adequate mould packing and minimum shrinkage. The injection pressure, screw speed, back pressure, mould temperature and cycle time will vary depending on the different hardness of the TPV materials. Thermoforming is another process that can be used for TPV, which is fast and has low production costs. The technique has been applied in forming extruded profiles, tubing and sheeting with a thin solid skin over closed cell interior foam[60-61]. One of the processes that cannot be used in conventional thermoset rubber, but is available for TPV, is blow moulding. This process allows the production of thin walled end products[56,62-63].

2.3 Composition of thermoplastic vulcanisates (TPVs)

TPV materials consist of a two-phase system: elastomer (soft phase) and thermoplastic (hard phase)[64]. Commonly, TPV is recognized as a dispersion of rubber particles in a continuous thermoplastic matrix. This hard phase is responsible for the integrity and strength of the TPV and also its ability to be processed. When the hard phase melts, the material will flow and gives the TPVs their ability to be processed. On cooling, the hard phase solidifies and the TPVs regain their strength[65]. The hard phase acts in a similar manner to the sulphur crosslinks in conventional vulcanised rubbers and can be called physical crosslinking[64]. Since TPVs are phase separated systems, TPVs show many of the characteristics of the individual polymers that constitute the phases. For example, each phase has its own glass transition temperature, T_g or crystal melting point, T_m, (if it is crystalline) and these in turn determine the temperatures at which the TPV goes through transitions in its physical properties. Other properties of the

TPVs are also strongly influenced by the properties of the individual phases. For this reason, the structure and properties of thermoplastics and elastomers that are likely to have the greatest influence on TPV behaviour are discussed separately in the following two sections. Apart from properties of the individual phases, TPV properties are strongly affected by a further three factors; the thermoplastic: elastomer interface, phase morphology and other additives. These factors are discussed in subsequent sections.

2.4 Structure and properties of thermoplastics

In terms of microstructure, thermoplastics can be divided into amorphous and semi-crystalline sub-groups[60,66] The amorphous thermoplastics behave as stiff, brittle solids (glassy) up to a glass transition temperature, T_g. Above the T_g, they become rubbery and with further increase in themperature the viscosity falls gradually. Amorphous thermoplastics include polycarbonate, polystyrene, ABS (acrylonitrile-butadiene-styrene) and SAN (styrene-acrylonitrile).

Semi-crystalline thermoplastics consist of two phases: an amorphous phase and a crystalline phase. The amorphous phase is similar to the amorphous thermoplastics described above, and has a Tg associated with it. The crystalline regions have a melting temperature T_m at which the crystalline structure breaks down and becomes disordered. Semi-crystalline polymers include acetal, nylon, polyethylene, polypropylene and polyester. The crystalline regions are joined by non-crystalline or amorphous zones (Figure 2.1). Semi-crystallinity is a desirable property for most plastics because they combine the strength of crystalline polymers with the flexibility of amorphous ones (above their Tg). Semi-crystalline polymers can be tough with an ability to bend without breaking. When crystals are formed from the melt, chain entanglements are extremely important. In this case the solid is irregular with polymer chains meandering in and out of ordered crystalline portions. Figure 2.1 shows the crystalline region in lamellae and the amorphous region outside the lamellae[67].

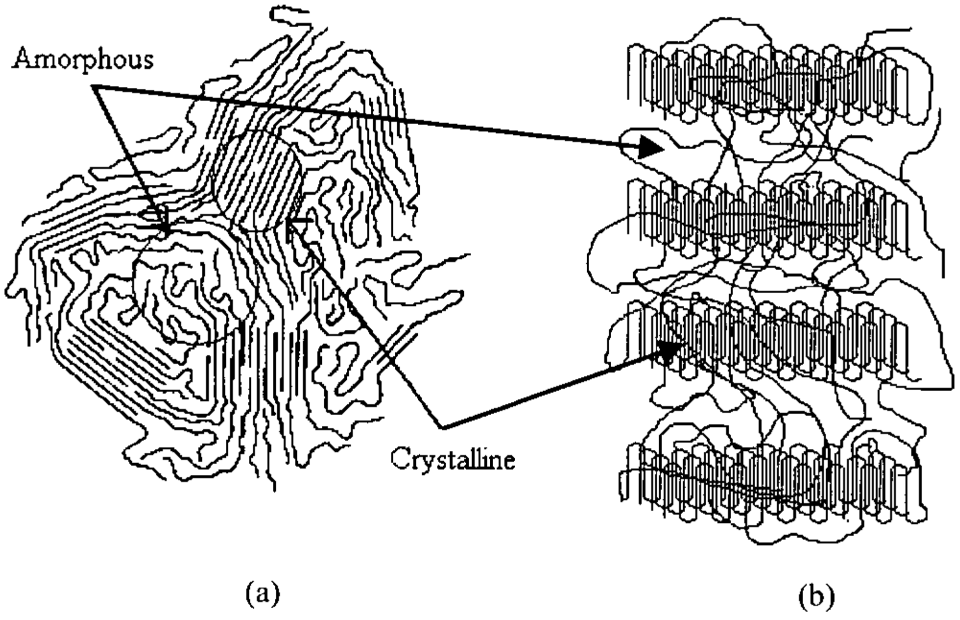


Figure 2.1 (a) Two dimensional representation of molecules in a semi crystalline polymer (fringed micelle theory)[68-69] and (b) semi-crystalline polymer[67].

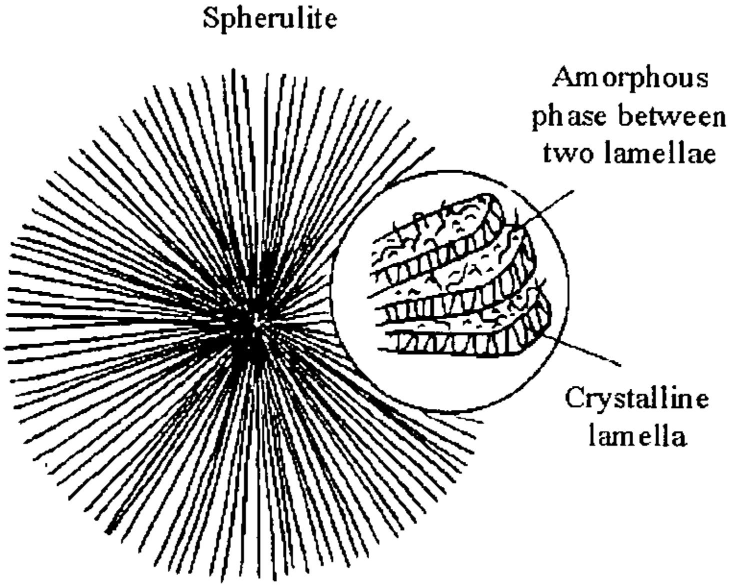


Figure 2.2 Schematic structure of a spherulite[70].

Many semi-crystalline polymers in bulk form have a spherulitic structure (Figure 2.2). Lamella crystals grow from the centre of the spherulite. The enlarged part of the diagram shows several lamellae and an amorphous region in between lamellae. The molecular chains in the amorphous region are of four types[70-71]; 1. tails, with one end in the lamella and one free end, 2. loops, which start and end in the same lamella, 3. bridges (tie molecules) which join up two lamellae and 4. floating molecules which are unattached to any lamella. The tie chains contribute to the mechanism of elastic and plastic deformation of semi-crystalline polymers[70,72].

2.4.1 Polypropylene

The increasing market demand for moderately priced, recyclable engineering plastics has made polypropylene (PP) an attractive polymer for numerous applications. PP is available in a wide variety of melt flow indices (MFI) and can be processed by virtually all methods, including injection moulding, extrusion, blow molding and thermoforming make it easy to be recycled. PP was added into elastomer as rubber toughened to improving the fracture toughness[73]. PP[74] is also commonly used as the thermoplastic phase in TPVs and has been selected for the current study. PP is widely used in many market applications ranging from automotive parts to carpets, and from food packaging to consumer products. The versatility of this plastic has led to its distinction of having the highest growth rate of any commodity thermoplastic[75]. Typical practical characteristics of PP are shown in Figure 2.3.

PP is a semi-crystalline polymer[42,76]. To understand the relationship between microstructure and physical properties of semi-crystalline materials it is necessary to consider the level of order present. Important aspects include; the bonding in the crystal unit cell, the size and shape of lamellar crystals, the microstructure of spherulites, and particularly the overall crystallinity.

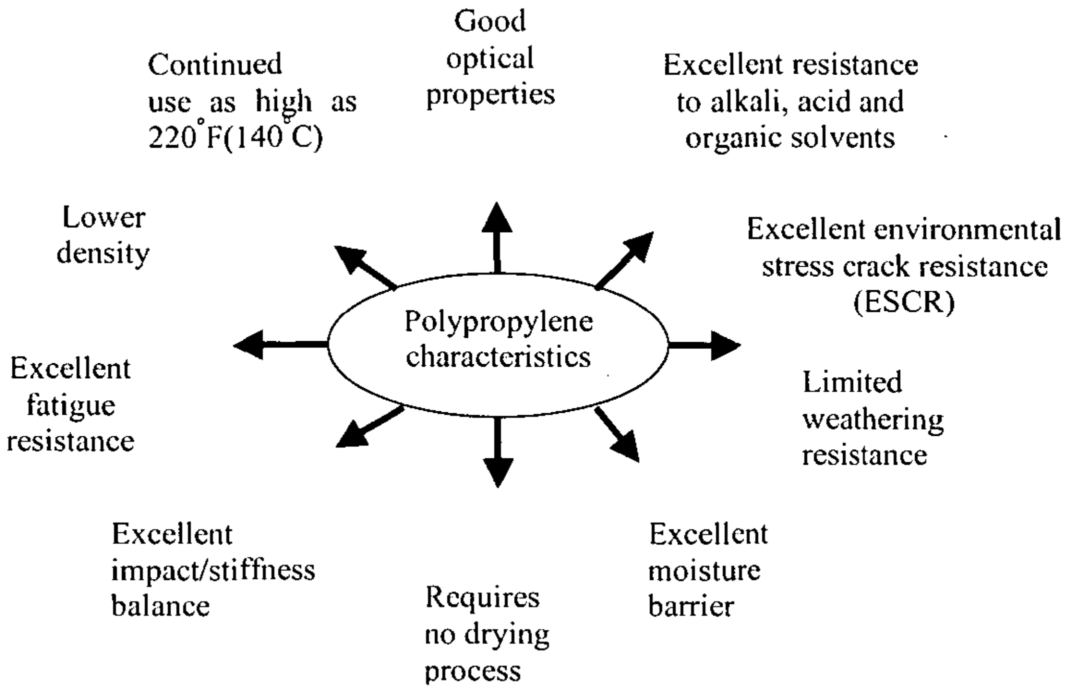
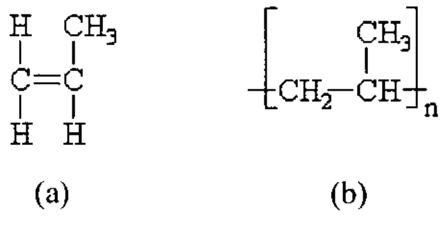


Figure 2.3 Typical characteristics of polypropylene[77].

Crystallinity refers to the proportion of crystals present and is dependent on the particular stereoisomer of PP and the processing conditions. The basic structural unit of PP is shown in Figure 2.4[78].



$$\mathrm{H_2C{=}CH{-}CH_3} \qquad \left[\mathrm{CH_2{-}CH(CH_3)}\right]_n$$

(a) (b)

Figure 2.4 (a) monomer-propylene and (b) polymer-polypropylene structure.

The PP molecule can exist in different configurations : atactic, isotactic and syndiotactic (Figure 2.5). Most commercially available PP is highly isotactic and contains only a few percent of atactic material[79]. The isotactic configuration means that all the methyl groups are on the same side of the chain as shown in Figure 2.5(a). In an atactic configuration the methyl groups are placed randomly on both sides of the chain. For the syndiotactic configuration, the methyl group is arranged in a regularly alternating pattern on either side of the polymer backbone. Stereochemistry can have an important effect on chain packing. The atactic PP is a somewhat rubbery material whereas isotactic PP (iPP) is potentially highly crystalline, and also stiff due to the regular chains can pack closely together. Isotactic PP has a melting point of 160°C. Atactic PP, on the other hand is a soft noncrystalline polymer with a melting point of only 75°C[80].

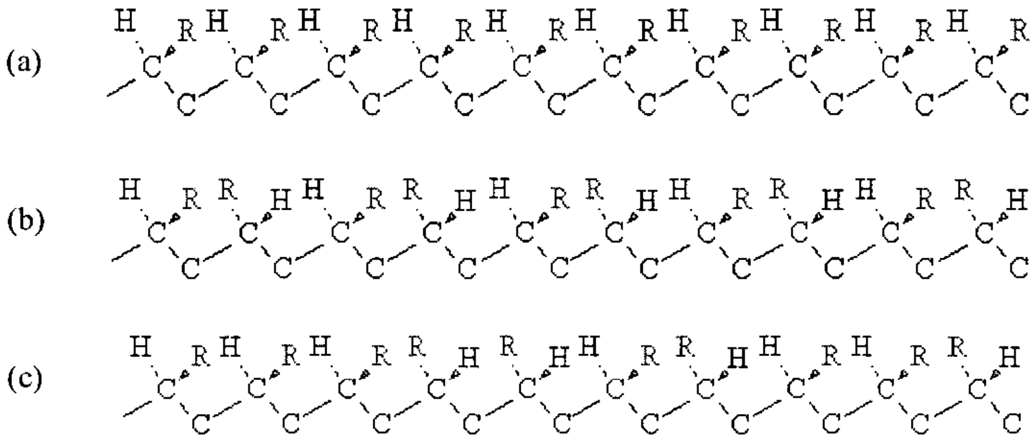


Figure 2.5 (a) Isotactic polypropylene, (b) syndiotactic polypropylene and (c) atactic polypropylene[78].

In order to understand the relationship between microstructure and physical properties of semi-crystalline materials it is necessary to consider, the level of order present. Important aspects include; the bonding in the crystal unit cell, the size and shape of lamellar crystals, the microstructure of spherulites, and particularly the overall crystallinity.

Crystallinity influences many of the polymer properties such as hardness, modulus, tensile strength, stiffness and melting behaviour. The room temperature stiffness, or modulus of the PP is directly related to the level of crystallinity, since the crystal phase is much stiffer than the amorphous phase at temperatures above the glass transition temperature (T_g) of the amorphous phase (T_g of about 0°C). As degree of crystallinity increases, so do the modulus, yield and tensile strength, hardness and softening point. Percent crystallinity of polymer can be determined by using DSC and X-ray diffraction.

2.4.2 Deformation of semi-crystalline polymer

The stress-strain behaviour of polymers can be categorised into several classes of behaviour; brittle, ductile (with and without necking) and elastomeric. Figure 2.6 shows the curves that correspond to these mechanisms[81]. A stiff, strong, brittle material shows a large initial slope and fails with little strain. A softer and tougher material (ductile), on the other hand, shows a lower initial slope but longer elongation at break. Semi-crystalline polymers such as PP show a ductile response, with necking behaviour. The area under the curve is a measure of the amount if energy required to break the material. The greater that area, the tougher the material, and the greater the amount of energy required to break it.

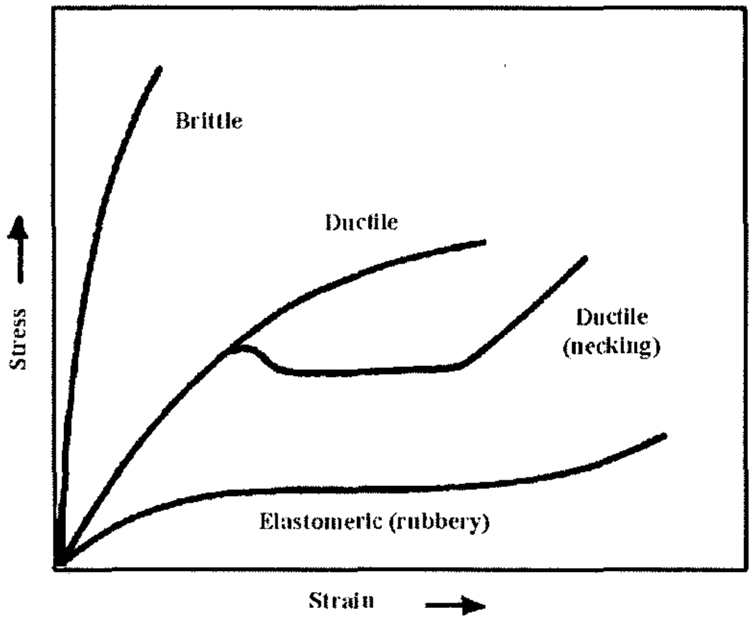


Figure 2.6 Polymer behaviour shown by tensile stress curves[81].

A typical stress-strain curves of semi-crystalline polymers are shown in Figure 2.7. Being composed of crystalline lamellae and entangled amorphous polymeric chains in between, semicrystalline polymers always show a complicated deformation behavior under tensile deformation[81-83]. The process of tensile deformation was found to exhibit several regimes: intralamellar slipping of crystalline blocks occurs at small deformation whereas a stress-induced crystalline block disaggregation-recrystallisation process occurs at a strain larger than the yield strain. The strain at this transition point is related to the interplay between the amorphous entanglement density and the stability of crystal blocks. It is emphasised that tie molecules, which connect adjacent lamellae, are of lesser importance with respect to the deformational behaviour. The amorphous regions greatly influence the deformation behavior of semi-crystalline thermoplastics when subjected to low loads (elastic deformation). The crystalline regions become more significant only when subjected to high loads, whereas at high extension, fibrillation occurs and crystal cleavage processes predominate[84].

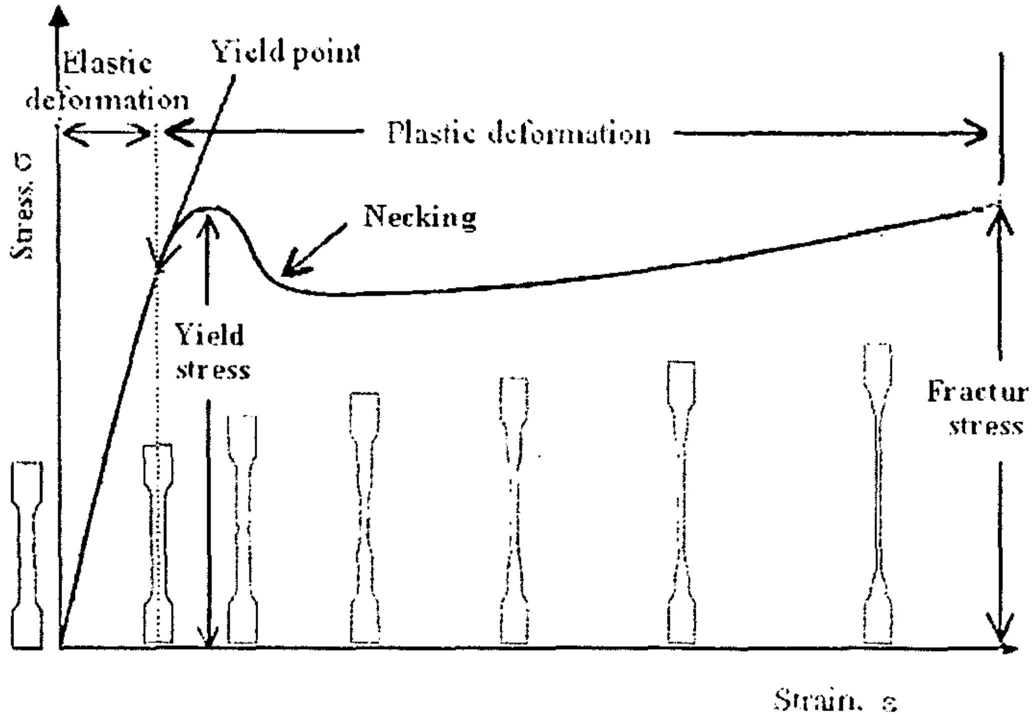


Figure 2.7 Nominal stress-strain relationship for a thermoplastic which undergoes yield and cold drawing[82,85].

The yield stress defines the maximum upper stress limitation for any thermoplastics material which is expected to fail in a ductile manner. At the yield point, molecular chain segments are able to slip past each other[86]. This is the first point at which the specimen yields, where the specimen's cross-sectional area begins to decrease (neckdown) significantly, or an increase in strain occurs without an increase in stress[81]. The macroscopic deformation of PP involves necking. The neck gets stronger since the deformation aligns the chains and increases local strength in the neck region (up to 2 – 5 times). Although the level of stress is greater in the neck, due to the smaller cross-sectional area, the strengthening mechanism leads to the neck extending with further increase in strain, rather than breaking (Figure 2.8). This phenomenon is also known as cold drawing.

Figure 2.8 Necking and cold drawing in tensile test pieces of polypropylene[85].

The ultimate tensile strength is the maximum stress a material can withstand before failing. Elongation at break is the strain, or the percent change in length at failure. At the maximum stress, the polymer molecules experience a highly strained or "chain-extended" crystalline morphology that forms during cold-drawing. Although the strength and stiffness properties parallel to the elongation direction have been enhanced, adjacent molecules of parallel chains are generally held only by secondary bond forces. The longitudinal fibrillation causes ultimate fracture when the material in the remaining cross-section is unable to support the applied load[86].

In the following paragraphs a more detailed explanation is given of the microscructural changes that are responsible for the observed deformation behaviour described above. The deformation of semi-crystalline polymers involves the elongation of the amorphous phases and the alignment of the crystalline phase as shown in Figure 2.9 also named plastic deformation. The schematic deformation of thermoplastic materials can be illustrated as follows. (a) Initial stage - two adjacent chain folded lamellae and interlamellar amorphous materials before deformation, (b) Deformation of the amorphous area-elongation of amorphous tie chains during the first stage of deformation, (c) Rotation of the crystalline lamellae-tilting of lamellar chain folds during the second stage, (d) Separation of into individual crystalline block segments during third stage, and (e) Formation of individual micro-fibrils -orientation of block segments and tie chains with tensile axis is the final deformation stage[87-90].

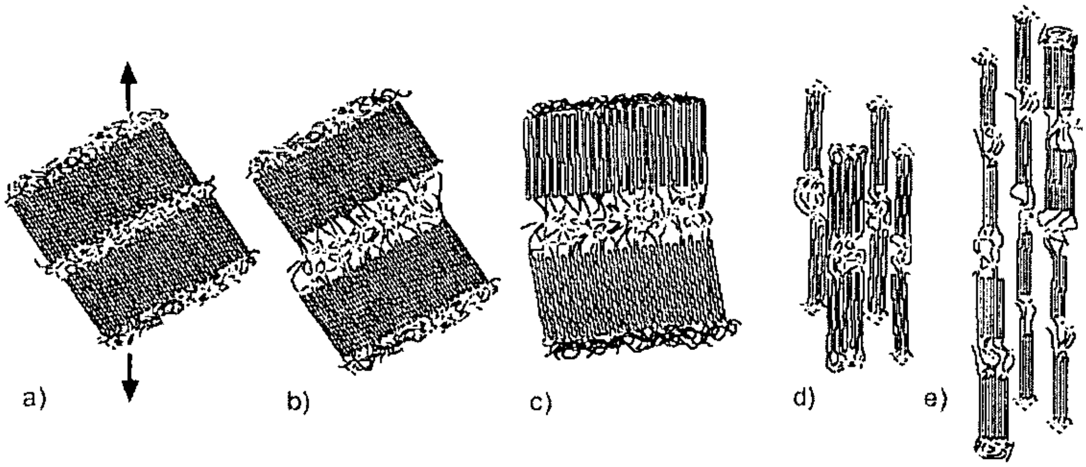


Figure 2.9 Schematic deformation of semi-crystalline polymer[82,87,91].

At high extensions, the transition of lamella structure to macro-fibril structure orientated in the direction of strain is shown in Figure 2.10. The chains within the crystalline segments that were originally perpendicular to the direction of elongation have become completely reoriented. Individual segments of the crystallites are separated at locations of weakness allowing the chains to rotate and become situated in the main shear stress direction. In position (b), the chains begin to slide and shift. Individual chain segments in (c), with a larger number of entangled chains are developed. The locally confined deformation regions within areas (b) and (c) are accompanied by a substantial rise in the temperature that further facilitates chain relocation during the reorientation processes.

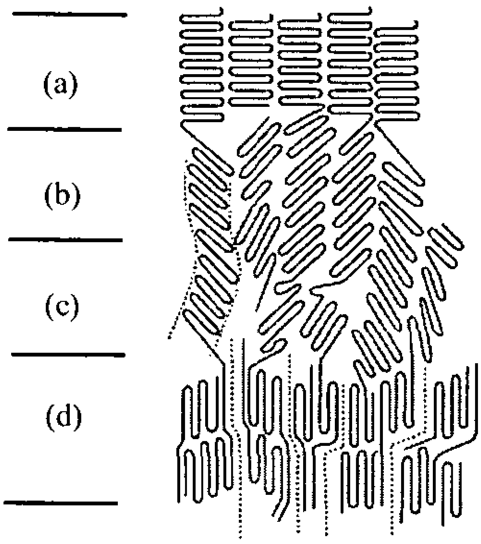


Figure 2.10 Relocation of lamellae when drawing in crystals to form a macro-fibril (a) original lamellae structure (b) rotation and shifting of the lamellae (c) formation of individual crystalline segments and (d) assembly of segments to form macro-fibrils[82].

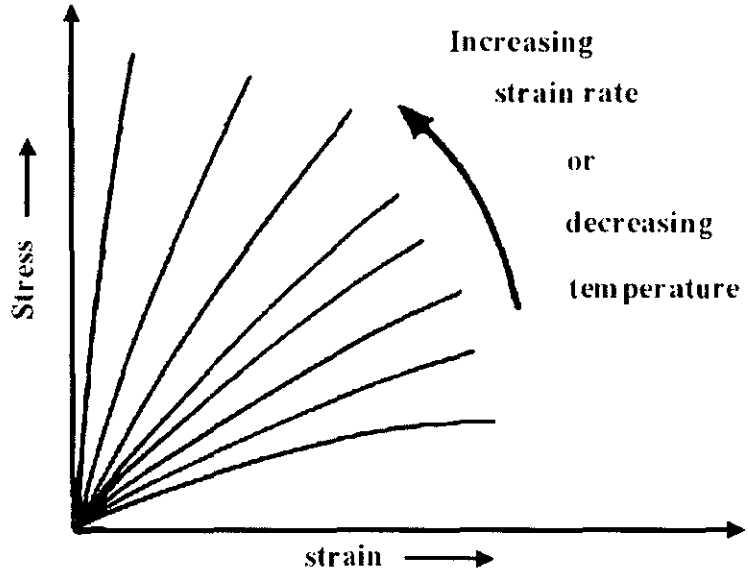


Figure 2.11 Effect of strain rate and temperature on stress-strain curves[81].

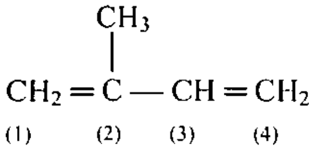
Another very important aspect of deformation behaviour of polymers is that their viscoelastic behaviour causes their stress-strain behaviour to be dependent on deformation rate. Temperature and strain rate have opposite effects. Increasing the strain rate (or decreasing the temperature) will lead to higher stress levels, but a lower value of strain at break (Figure 2.11). At a high strain rate, there may not be a sufficient time for rotation bonds to occur, and instead of the amorphous areas becoming orientated and converted to crystalline phase they may be broken. Hence, at higher strain rates the test pieces failure at lower strain[81,92].

2.5 Structure and properties of elastomers

An elastomer is a material that at room temperature can be stretched repeatedly to at least twice its original length and, immediately upon release of the stress, returns with force to its approximate original length. This definition is one criterion by which plastics are distinguished from elastomers or rubbers. Two commercially important elastomers used in conventional thermoset rubber compounds are natural rubber and EPDM. These two rubbers are described in the following two sections.

2.5.1 Natural rubber (NR)

Natural rubber (NR)[93-94] is represented by the formula $(C_5H_8)n$ in which the C_5H_8 unit is structurally related to isoprene. In natural rubber, essentially all the isoprene units are linked together at carbon atoms 1 and 4 in a head-to-tail arrangement (Figure 2.12).



$$\underset{(1)}{CH_2}=\underset{(2)}{\overset{\overset{CH_3}{|}}{C}}-\underset{(3)}{CH}=\underset{(4)}{CH_2}$$

Figure 2.12 Isoprene monomer.

This segment of the polyisoprene chain can have four different isomers (Figure 2.13). The difference in properties between the cis- and trans-isomers is apparent in naturally-occurring polyisoprenes[95]. *Gutta percha* is predominantly *trans*-1,4-polyisoprene, having a regular structure that allows close-packing of chains and hence, crystallization, making it hard and rigid. Whereas, natural rubber is *cis*-

1,4-polyisoprene (Figure 2.14) which does not allow close-packing of chains, is not crystalline in a relaxed state or at normal service temperatures and is an amorphous rubbery material. However, the regularity of microstructure plays an important part in determining some of the most characteristic properties of natural rubber, such as its extremely high tensile strength[97]. The amorphous mass of coiled and kinked chains readily allows motion of its molecular chains making it extremely flexible.

(1)Cis-1,4-addition (2) trans-1,4-addition

(3) 1,2-addition (4) 3,4-addition

Figure 2.13 Polyisoprene structure[96].

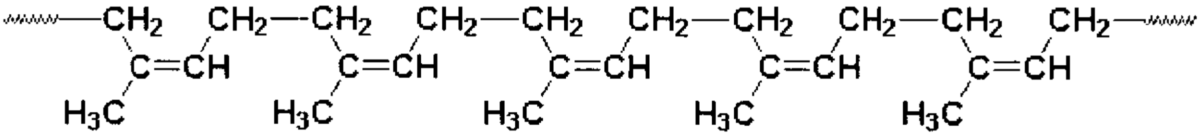


Figure 2.14 Cis-1,4-polyisoprene[93].

The long chain structure of natural rubber allows it to spring back into shape when it is compressed or stretched. However, under increasing tensile load, the structure of rubber changes as the bonds straighten and the chains become elongated. As more and more stress is applied to the structure of rubber, crystallinity is achieved. This phenomenon is known as strain-induced crystallization. The increase in crystallinity causes greater strength, increased hardness, and increased rigidity in the rubber.

The problem with using natural rubber in its raw state for technical applications is that it is too soft and is prone to degrade when exposed to UV light, oxygen or heat. In order to make it more useful as a material, modifiers and fillers are added and other processing techniques are applied to improve the strength, rigidity, and hardness of the rubber. Vulcanisation is the process of applying cross-links to the chains in natural rubber in order to make it stronger and more elastic.

2.5.2 Ethylene propylene diene rubber (EPDM)

The characteristics of NR (very good elasticity, expansion, good cold-flexibility, tensile strength, poor heat resistance) cannot be adapted or manipulated. However, with a synthetic product, scientists can select, adapt and modify the base products to control the molecular structure, and influence their properties. The result of such manipulation means that synthetic rubber can be made to measure, with characteristics precisely adapted to a specific use and its particular requirements. The most common TPV commercially available based on synthetic rubber is based on ethylene propylene diene rubber (EPDM).

Homopolymers of ethylene and propylene, i.e. polyethylene and isotactic polypropylene are semi-crystalline non-elastomeric materials (thermoplastic). Random polymerisation of ethylene with propylene, or copolymerisation of these two monomers with a conjugated diene gives non-crystalline copolymers (EPR) which are in a rubber-like state at room temperature[97]. The percentage of ethylene and propylene repeat unit is one of the factors determining the properties of the copolymers (reported values are in a range 45/55 to 75/25 ethylene and propylene, respectively[98]. Since neither ethylene nor propylene repeat units consist of unsaturation (C=C), The copolymers do not contain double bonds (are saturated) and this makes them resistant to ozone, weathering and heat aging, compared to natural rubber. However, the lack of double bonds does not allow them to undergo conventional vulcanisation with a sulphur based system.

The EPDM structure is shown in Figure 2.15.

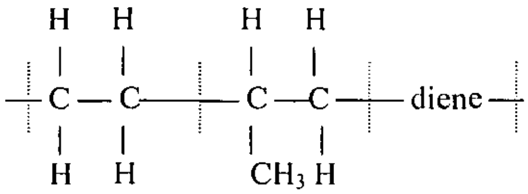
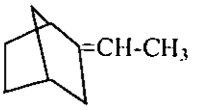
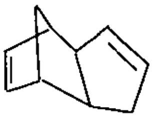


Figure 2.15 EPDM structure[97].

The incorporation of a small fraction of a third monomer such as ethylidence norbornene (ENB), 1,4-hexadiene (HD) and dicyclopentadiene (DCPD) introduce unsaturation (diene) in EPDM allows conventional vulcanisation[99]. These characteristics are summarised in Table 2.1. Each diene has a different tendency for introducing long chain branching (LCB) or polymer side chains that influence processing and rates of vulcanisation by sulfur or peroxide cures. The unsaturation in EPDM is localised in side substituents, so the molecular backbone is still fully saturated and internally resistant to degradation[97]. This enables the EPDM to retain the ozone and weathering resistance and good heat aging of EPR rubbers[100]. EPDM can therefore be used anywhere that these special characteristics are required e.g. windows and door seals in the automobile industry, waterproofing of flat roofs, garden roofs, ponds, basins of purification plants and sealing of acid containers. The weathering resistance also makes EPDM the most widely used elastomer in TPVs. The limitations of EPDM are mostly associated with low resistance to oils and fuels, poor adhesion to many substrates or internal reinforcement, and generally low compatibility with other rubbers.

The processing, vulcanisation and physical properties of ethylene-propylene elastomers are largely controlled by the characteristics of ethylene content, diene content, molecular weight (or Mooney viscosity) and molecular weight distribution (MWD). For example, decreasing ethylene content decreases crystallinity and associated properties such as hardness and modulus[98].

Table 2.1 Cure-site diene termonomers in ethylene-propylene elastomers[99-100].

Name	Structure	Characteristics	Branching
5-ethylidene-2-norbornene (ENB)		Fast cure Good tensile strength Good compression set	Low to moderate
1,4-hexdiene (HD)	$CH_2=CH-CH_2-CH=CH-CH_3$	Best compression set Normal cure rate Scorch-safe	none
Dicyclopentadiene (DCPD)		Low cost Slow sulphur cure Good compression set	high

2.5.3 Peroxide cure vulcanisation

The vulcanisation of unsaturated rubber by organic peroxide is illustrated by the following sequence of reaction[102-104] (Figure 2.16). The first step in the crosslinking reaction is the homolytic cleavage of a peroxide molecule to form two free radicals (1). These free radicals then typically extract hydrogen from the polymer chain (2). The polymer radicals then react with other polymer segments of polymer chain to form carbon-to-carbon crosslinks(3).

(1) $ROOR \xrightarrow{\Delta} 2RO^{\cdot}$ Peroxide decomposition

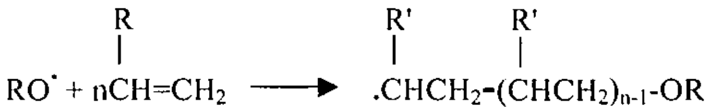
(2) $RO^{\cdot} + PH \rightarrow ROH + P^{\cdot}$ H abstraction

(3) $2P^{\cdot} \rightarrow P\text{-}P$ Formation of crosslink

where PH represents the rubber molecule

Figure 2.16 Mechanism of free radical of peroxide crosslinking.

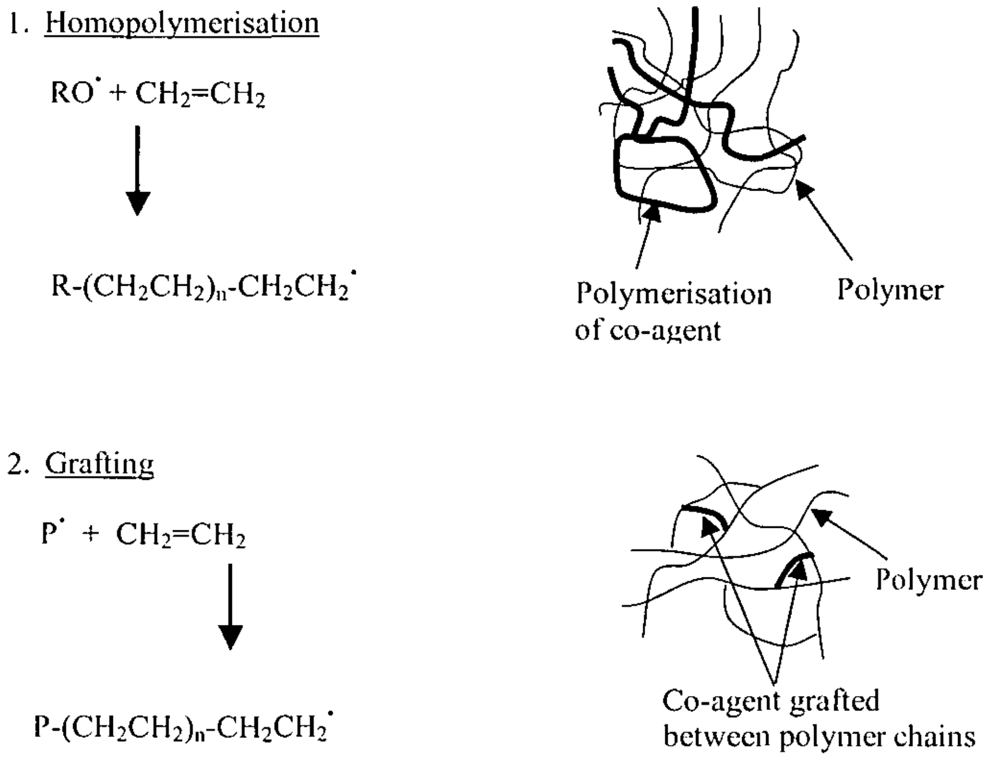
Co-agents are used with peroxide to increase the efficiency of cure, i.e. to give more crosslinks. The peroxide is usually incorporating to initiate the reaction (Figure 2.17)[104-105].



$$RO^{\bullet} + n\overset{\displaystyle R}{\overset{|}{C}}H{=}CH_2 \longrightarrow .\overset{\displaystyle R'}{\overset{|}{C}}HCH_2\text{-}(\overset{\displaystyle R'}{\overset{|}{C}}HCH_2)_{n-1}\text{-}OR$$

$RO^{\bullet}$ initiates polymerisation

Figure 2.17 Possible mechanism for co-agent response[104-105].



1. Homopolymerisation

$$RO^{\bullet} + CH_2{=}CH_2 \downarrow R\text{-}(CH_2CH_2)_n\text{-}CH_2CH_2^{\bullet}$$

2. Grafting

$$P^{\bullet} + CH_2{=}CH_2 \downarrow P\text{-}(CH_2CH_2)_n\text{-}CH_2CH_2^{\bullet}$$

$CH_2{=}CH_2$ represents the co-agent

Figure 2.18 Possible mechanisms of co-agent reactions during vulcanisation[102-103].

There are two possible mechanisms for co-agent cures (Figure 2.18)[103-104]. An interpenetrating network can be produced if the co-agent homopolymerises during polymer crosslinking. Also, the co-agent can form a grafted chain on the polymer backbone. This will occur if the radical on a polymer chain initiates polymerisation of the co-agent, or the original alkoxy radical initiates polymerisation of the co-agent and the terminal radical of the polymerised co-agent couples with a polymer radical.

2.5.4 Deformation of rubber

Natural rubber can be categorised as a hyperelastic material. This is due to the ability of the rubber to be deformed elastically under quite small stresses to a very large extension. Natural rubber is an elastomeric material and its ability to crystallize at large deformations (strain-induced crystallization) results in an extraordinary toughness. Tosaka *et al.*[106-107] proposed a model for strain-induced crystallisation in natural rubber as shown in Figures 2.19[106] and 2.20[107]. The heterogeneity of the crosslink distribution in vulcanised rubber results in inhomogeneous arrangements of phases in stretched rubber[108-111]. This is due to short chains being highly extended, while most of the chains remain in the almost randomly coiled state. This hypothesis is supported by a pulsed NMR study of stretched rubber samples, which showed that the lower molecular weight chains between network points facilitated deformation-induced crystallisation at the same strain when compared to higher molecular weight chains between network points[112]. Therefore, crystallisation must be initiated in the dense network region having shorter molecular weight chains between the network bridges. The dense network regions should become harder by deformation because of the crystallites.

The structures in the strain-crystallised rubber include highly oriented micro-fibrillar structure (composed of crystallites and probably vulcanisation bridges) with oriented amorphous chains and random coil amorphous chains (connected with each other by vulcanisation-network points) as the major matrix. The micro-fibrillar structure should function as a stronger network point than the single chemical bonds in the pure chemical network structure. Although strain-induced crystallisation itself does not increase the stress (it actually decreases the stress slightly), the crystallisation creates the micro-fibrillar network structure that is able to increase the elongation at break, since the stronger network points can endure the high strain. As a result, the tensile strength is increased. The network points may have two opposite effects on strain-induced crystallisation during different stages of stretching. First, the vulcanisation points can enhance molecular orientation of chains in the vicinity of network points under deformation, thus inducing crystallisation of polymer chains. Second, these points may also hinder the growth of a crystalline structure.

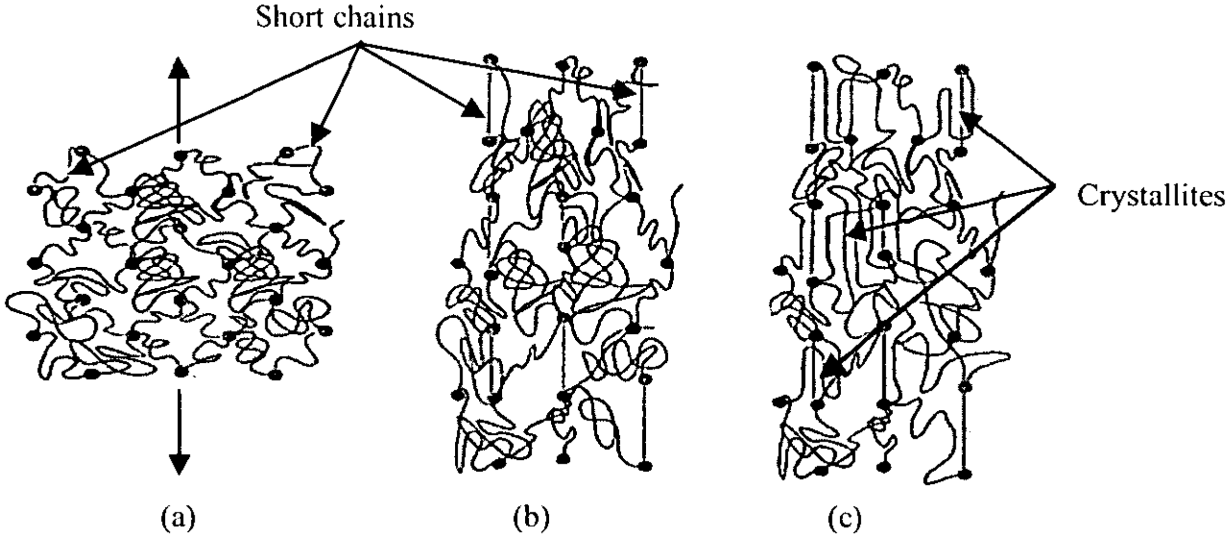


Figure 2.19 A model of the strain induced crystallization in vulcanised NR. Filled circles represent crosslink (a) before deformation, (b) after deformation. Short chains are fully stretched and (c) crystallite are grown from the stretched chains[106].

A clear schematic diagram of deformed natural rubber is also illustrated in Figure 2.20; A. micro-fibrillar structure (crystallite and vulcanisation network point), B. oriented amorphous, C. un-oriented amorphous, D. vulcanisation bridge (network point).

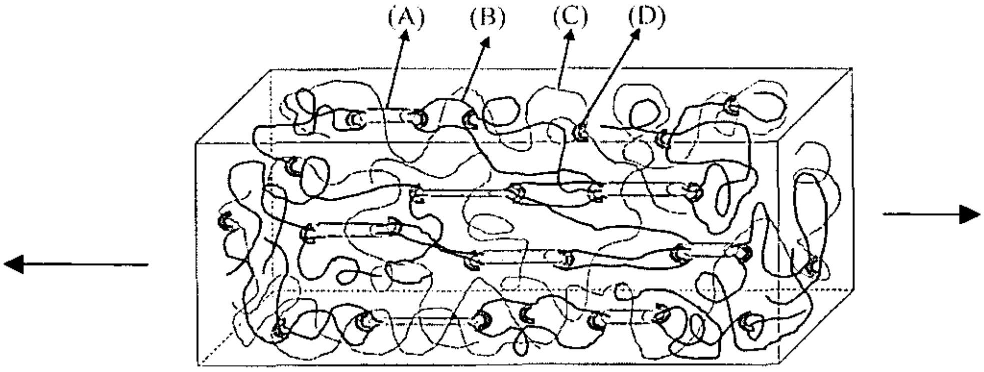


Figure 2.20 The schematic diagram of deformed vulcanised rubber[107].

Another important factor in the dynamic deformation of elastomeric materials is that their mechanical behaviour is often altered to some degree after an initial loading, as shown in Figure 2.21[113]. The stress-strain behaviour is observed to be softer (more compliance) during deformation after the initial loading excursion of the first cycle. There is a reduction in the stress measured at a given deflection and hence, the phenomenon is often referred to as 'stress-softening' or the 'Mullins effect'.

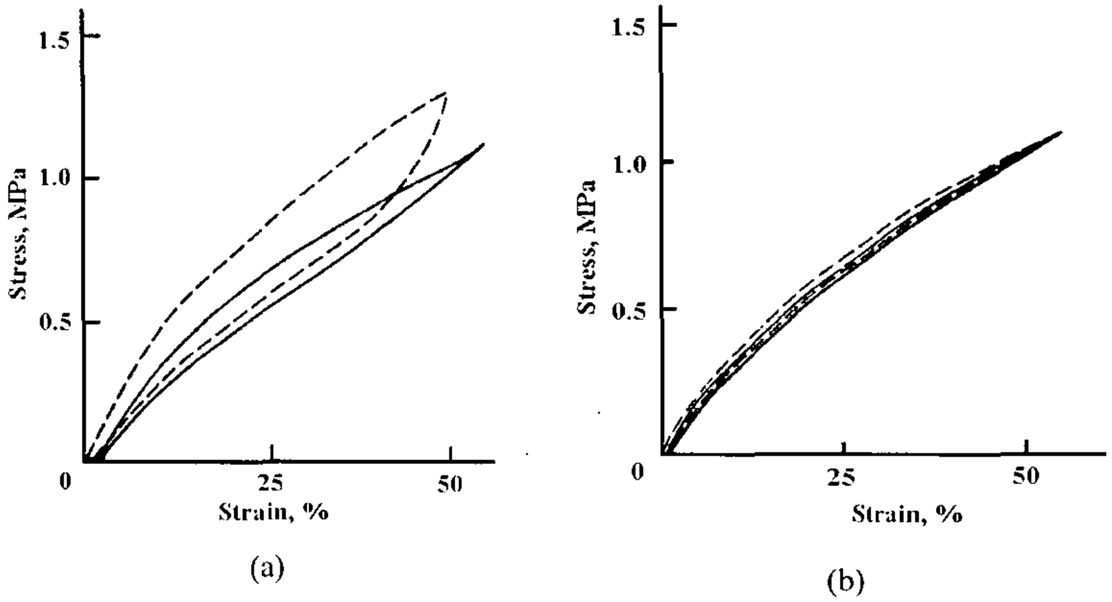


Figure 2.21 Cyclic behaviour of vulcanisates natural rubber containing 50 parts of (a) black filler and (b) white filler. The broken lines represent the first cycle of each test. The full lines represent after the ten cycles[113].

The 'stress softening' behaviour occurred in unfilled and filled rubber[114-118]. However, normally it is associated with filled vulcanisates, particularly those containing reinforcing fillers[113,119]. The 'stress softening' theories are based on two concepts[119]. The first theory is based on work by Blanchard, Parkinson[120] and Bueche works[121-122]. They proposed that the softening is due to breakdown or loosening of some of rubber-filler attachments[121-122], strain-induced relative motion of carbon black and rubber[123] and in some cases local separation of carbon black particles and rubber[124]. The second theory is based on work by

Mullins and Tobin[114-115], Harwood *et al.*[116], Harwood and Payne[117-118] and Mullins[125] works. They considered that stretching produces a quasi-irreversible rearrangement of molecular networks due to non-affine deformation in which the network junctions are displaced from their initial state. They proposed that this produces some form or rearrangement of hard and soft domains in the elastomeric phase that acts to increase the effective volume fraction of soft domain.

The greatest difference in shape of the stress-strain curves is observed between extension cycles one and two, but, more similar behaviour is shown by the subsequent cycles. Subsequent cycles produce successively smaller changes, so that most of the softening occurs in the first few cycles.

2.6 The thermoplastic:elastomer interface

Apart from the influence of the properties of the individual thermoplastic and elastomer phases, the behaviour of TPVs are strongly affected by the nature of the interface between them.

The interfacial region between the hard and soft elements is often considered as a separate phase (interphase) and can be substantially different from the bulk of the material. TPVs demonstrate a synergistic interaction between two polymers to give properties better than those of simple blends. It is proposed that the interaction can be brought about in a semi-crystalline thermoplastic and soft elastomer system by crosslinking the elastomer and generating well dispersed rubbery regions in a continuous thermoplastic matrix without the need for compatibilisers. However, by incorporation of N,N'-metaphenylene dimaleimide (HVA-2) in NR/PP blends, the interfacial adhesion between the disperse NR phase and the PP phase can be improved by introducing a low degree of crosslinking between the rubber and PP phases[126-129]. HVA-2 was found to be an effective crosslinking agent in the presence of a radical activator like an organic peroxide and the crosslinks formed are heat stable[130-131]. It was proposed that the HVA-2 crosslinks the NR phase and forms block or graft copolymers at the PP and NR interface[132]. It was also shown that the morphology of an NBR/PP blend could be controlled by adding block copolymers comprising compatibilising segments of both polymers[133]. There is a possibility that the interface of NR/PP blends could be observed in detail by a network visualisation technique[134].

2.7 TPV phase morphology

Phase morphology has an important influence on the properties of polymers blends, including TPVs. Morphological analysis can be studied by using light microscopy, scanning electron microscopy, transmission electron microscopy and scanning (transmission) electron microscopy or solvent extraction.

TPV consists of two phases system which one phase is hard and solid at room temperature while another phase is an elastomer[64]. Most work on TPV phase morphology proposes a dispersed rubber phase in a hard, continuous matrix of thermoplastic, simply to explain the flow behaviour of the melt. However, some researchers have observed a co-continuous phase of rubber and thermoplastic[135-138] in TPVs. The rubber phase can exist in continuous phase. As crosslinking proceeds the viscosity of the rubber phase increases, causing less viscous PP to form a continuous phase even at low volume fraction of plastic phase[139].

Sabet *et al.*[53] reported that the morphology of an uncrosslinked blend can be that of EPDM particles dispersed in PP, or two co-continuous phases, or PP particles dispersed in an EPDM matrix, depending on the rubber to thermoplastic ratio. At a high ratio of rubber to thermoplastic, such as 80/20, it was proposed that the thermoplastic is as a minor component and appears as dispersed particles in the EPDM matrix, before vulcanisation. During dynamic vulcanisation of such a blend, the polymer is suggested to undergo a phase inversion to maintain the thermoplasticity of the blend. At the early stage of vulcanisation, two co-continuous phases will appear. However, as crosslinking of the rubber phase progresses, shear during mixing was believed to create elongated rubber phases which were then broken down into elastomer droplets. As these elastomer droplets are forming, the PP becomes the continuous phase[53].

Riddiford and Tinker[140], Cook *et al.*[136-137] demonstrated the co-continuous phase morphology of TPVs based on NR and PP blends, by extraction of the polypropylene phase to leave the rubber phase as a self-supporting three-dimensional structure. It was proposed that at higher rubber contents, the rubber phase is essentially continuous, whilst at lower rubber contents the rubber forms discrete particles. Studies of binary nylon6/rubber blends with 50 and 60 weight percent of EPDM showed that the TPVs exhibit co-continuous morphologies[138]. On the other hand, Goharpey *et al.*[141]claimed that at a 60/40 (w/w) EPDM/PP ratios, two-phase morphologies were observed for uncured blends. The quick cooling of the samples prevented the coalescence and agglomeration of the dispersed rubber particles. A two-phase morphology, with the rubber particles dispersed throughout the PP matrix, was observed for the uncured but frozen samples, whereas unfrozen blend samples showed a co-continuous morphology in the uncured state. While the TPV showed crosslinked rubber particles finely distributed through out the continuous PP matrix.

2.8 Deformation and recovery behaviour of TPVs

The elastic behaviour of TPVs cannot be understood only from the blend morphology. The continuous phase, being a semi-crystalline polymer, is only elastic when the applied deformation remains small (below yield point). There will be almost no recovery after the yield strain is passed. One would expect that the deformation behaviour of a TPV is similar to that of its continuous phase. However, these materials display a high elasticity although the hard matrix phase consists of a thermoplastic polymer which is expected to deform plastically[142].

Several models have been proposed to describe the deformation of EPDM/PP TPV based on the phase morphology of the TPV as a distribution of rubber particles in a thermoplastic matrix. Kikuchi *et al.*[143-144], used finite element analysis on a two-dimensional model of particles in a matrix. The elastic behaviour is due to 30% of the PP phase acting as a glue between the rubber particles during stretching, while the remaining PP is deformed beyond its yield point. The adhesion links the rubber particles together in a continuous network that supports the elastomeric behaviour in the TPV. By contrast, Kawabata *et al.*[152] proposed that the adhesion between the rubber particles in a thermoplastic matrix is weak and a large numbers of voids are formed during deformation of the TPV. Yang *et al.*[145] used X-ray diffraction (WAXD) to study the orientation of crystalline regions in the PP phase during deformation and relaxation. It was suggested that PP had been occluded in the rubber phase. The PP crystalline regions in TPV are smaller than those in bulk PP. That is, the occluded rubber in the PP phase may play the role of an impurity and lead to the formation of smaller crystallites. The smaller crystallites suffer less plastic deformation and rather play the role of tie molecules, to provide the elastic properties of the PP matrix.

Spectroscopy, in combination with tensile stress-strain measurements[142,146-148] were used to understand the elastic behaviour of the TPVs. Huy *et al.*[146] studied the deformation of EPDM/PP by using polarized infrared spectroscopy. The research supports the idea that the ability of the TPVs to recovery elastically is due to the recoverable deformation of highly cured, highly dispersed rubber phase and its influence on the crystalline structure of a continuous PP phase. The authors found that the PP phase was less orientated than the EPDM phase in the TPV. Soliman *et al.*[147] proposed a model for the deformation behaviour of TPV that suggests that only a small fraction of PP orients and that this inhomogeneous deformation leads to a high recoverability. Finite element method[148] analysis of a PBT/rubber thermoplastic elastomer blend revealed that there are two key mechanisms of strain recovery in TPE. Firstly, the low stress evolved in the PBT matrix during bulk deformation, especially in the ligament matrix between rubber 'particles' in the stretching direction, is locally preserved within an elastic limit and so the PBT acts as an in situ formed adhesive for interconnecting the rubber 'particles'. Secondly, the volumetric strain of rubber 'particles' with high Poisson's ratio provides the contractile stress to heal the plastically deformed PBT phase outside the ligament matrix. Their mechanism was supported by polarized FT-Raman spectroscopy in terms of the peak shift caused by chain distortion, its anisotropy, and the gauche-to-trans transformation associated with plastic deformation. Atomic force microscopy[153] studied shows that the process of lamellar rearrangement on TPE samples before and after deformation. The AFM image of the sample before deformation exhibited the existence of a lamellar structure in the spherulitic arrangement without preferred orientation. After deformation, clearly showed an oriented lamellar structure having the lamellae to the stretching direction[153].

The ability of TPV to recover its shape after deformation is an important property for many applications such as weather strip and door seals. Measurement of compression set has become standardised and is able to determine this characteristic reasonably simply and accurately and has thus been widely used. However, to determine the deformation at different strain rates or at high extension, a tensile stress-strain measurement is more appropriate. In order for the TPV to show good elasticity, the following conditions are necessary: Firstly, within the two phases structure there must be an interphase that provides a high degree of adhesion between the phases. Secondly, the rubber phase also must be crosslinked to behave elastically. Thirdly, the rubber phase must be small enough that it can be deformed by relatively thin PP ligaments. And finally, the crystalline structure in the thermoplastic should be modified by the rubber particle to produce an elastic plastic phase[149].

Typical cyclic tensile stress-strain and recovery behaviour of soft TPVs is shown in Figure 2.22. The stress-strain curve of TPVs is intermediate between that of the ductile plastic and the elastomer . The cyclic deformation and recovery behaviour is similar to that of a low crystallinity, semi-crystalline[150] above its Tg and also similar to ordinary black filled vulcanisates.

If a series of repeated extension-retraction cycles are applied to a TPV, the TPV becomes progressively softer on each loading cycle, that is, it undergoes stress softening. As can be seen in Figure 2.22, there is a large difference in curve shape between extension cycles one and two, but, more similar behaviour shown by cycles 2 and the subsequent cycles. The area of the 'hysteresis loop' is proportional to the energy dissipated when the system goes through a cycle; this represents a considerable energy loss[151]. A large amount of energy is lost in cycle one, but there is a much smaller energy loss in the subsequent cycles. The difference between cycle one and cycle two is due to local destruction of the virgin structure of crystalline thermoplastic region of the TPV[152].

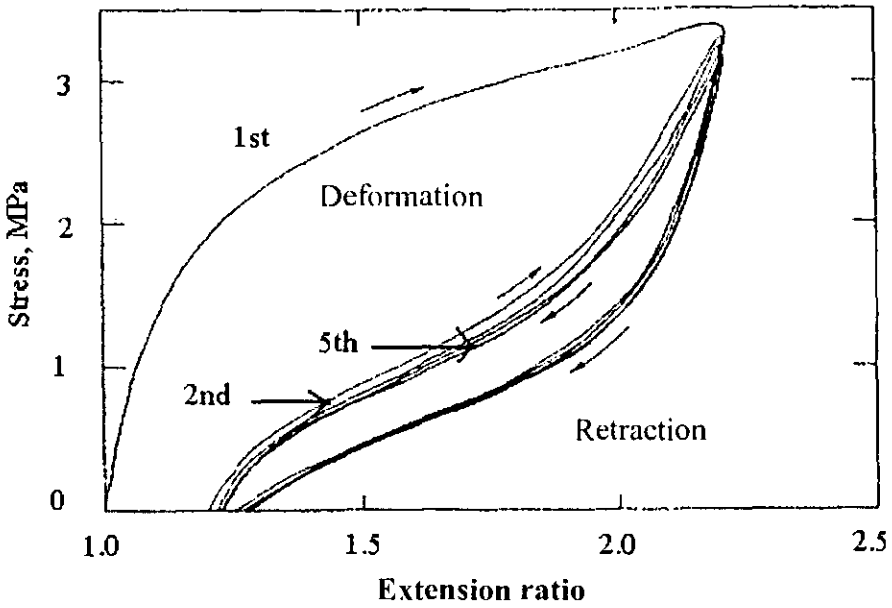


Figure 2.22 The tensile cycle stress-strain behaviour of the TPV based on EPDM/PP blends[152].

Toki *et al.*[153-154] proposed a schematic model of deformation on cycle one of a TPE is the study was based on tensile stress-strain and wide angle X-ray diffraction (WAXD) synchrotron techniques (Figure 2.23). The TPE is composed of the hard phase (propylene) and the soft phase (ethylene-propylene amorphous chains). The matrix is ethylene-propylene rubber and the island is composed of crystalline lamella stacks and tie molecules. Before deformation (A), the folded lamella crystalline structure is oriented randomly. During extension at low strain (B), original crystallites are destroyed, new induced crystallites created and thin lamella stacks developed simultaneously. At the maximum strain (C), all induced crystalline fiber axes are aligned to the stretching direction and lamella stacks are perpendicular to the stretching direction. Amorphous molecules are also oriented to the stretching direction. During retraction back to stress 0 (D), induced crystallites remain oriented to the stretching direction. However the fiber axis of the crystallites and lamella stacks are tilted slightly.

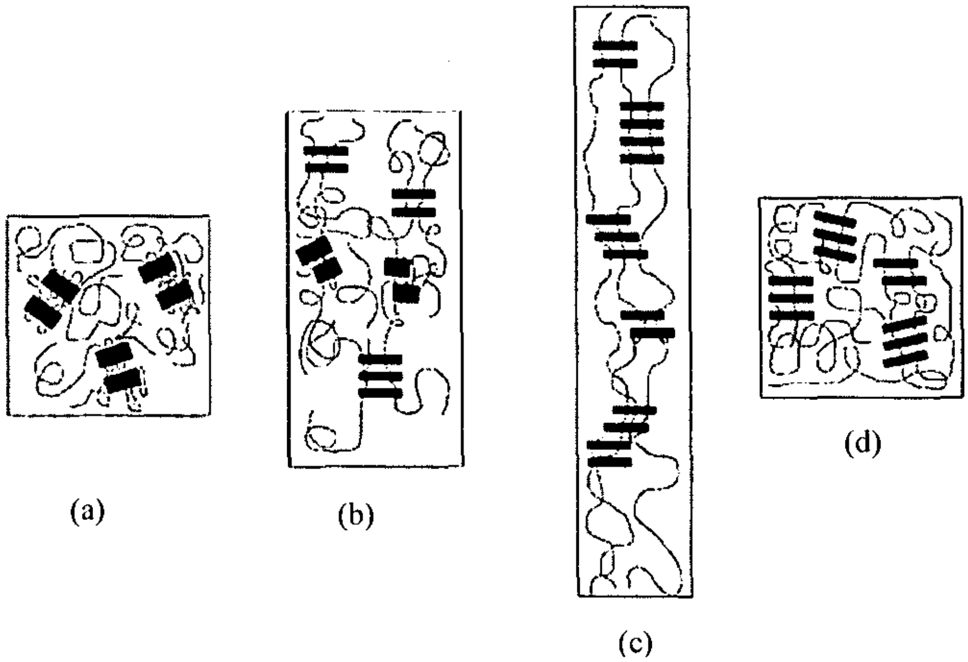


Figure 2.23 Schematic diagrams of permanent set mechanism during deformation and retraction in the first cycle : (a) before deformation, (b) during extension below permanent set strain, (c) during extension at strains larger than permanent set and (d) during retraction to zero stress[153-154].

While in the second cycle, the crystalline network topology can be considered 'permanent set'. In this network, the strain-induced crystallites are oriented along the stretching direction with a slight tilt angle. During stretching, the crystalline fraction slightly increases with strain and the crystallites orient along the stretching direction completely. During retraction, the crystalline fraction slightly decreases with strain and the crystallites relax to form a small tilt angle to the stretching direction. The procedure is reversible, therefore, it shows an elastic behavior similar to that of vulcanised rubber.

The stress softening effect on EPDM/PP TPV was studied by Boyce *et al.*[155-157]. They considered softening to be reorganisation of the crosslinked rubber 'particles'/ thermoplastic matrix microstructural configuration, due to plastic stretching of interparticle ligaments during the initial cycle. This is followed by ligament bending and rotation during retraction. The new microstructural configuration that exists after the first cycle of deformation and retraction, favours bending and rotation of the (now thinned) thermoplastic ligaments (as opposed to plastic deformation of the ligaments). Hence, during re-deformation; the ligament bending and rotation occur under low stress levels which results in the more compliant response[157]. The TPV exhibits rubber-like elastic behaviour at low extension, while the elastic deformation is superimposed by an irreversible plastic deformation at high extension[158].

2.9 Flow behaviour of co-continuous blends

It has been proposed that regardless of whether the crosslinked rubber phase is continuous or discrete, the materials have similar melt flow behaviour[140]. This is surprising since it does not seem reasonable that a continuous, crosslinked elastomer phase is capable of flowing. The apparent inconsistency is explained in the following way. During the injection moulding process, it is assumed that a PP 'rich' surface layer results in plug type flow with most shearing occurring in the low viscosity PP layer next to the cavity wall[159-161]. It was found that there was a very thin PP surface layer solidified on the outside surface of a TPV formed in a tubular blow moulding process[160]. The hypothesis implies that there must be very great elastic deformation of the rubber phase during flow unless there is substantial fragmentation of the elastomer phase structure.

2.10 Non-polymeric components of thermoplastic vulcanisates

The characteristics of thermoplastic vulcanisates can be changed by using non-polymeric additives. Plasticisers, processing aids, fillers, additives, etc., normally used in thermoset rubber compounds are suitable additives that can be incorporated for specific property modification of TPVs.

2.10.1 Fillers

A number of commonly available reinforcing and non-reinforcing fillers find use in thermoplastic elastomers. Material such as calcium carbonate, talc and fibreglass are often used to enhance specific physical properties, or as a means of reducing overall raw material cost. White fillers are added in order to reduce compounding cost, while a low level of carbon black is added generally as a colorant and to provide UV resistance. However, one exception is the use of relatively high levels of semi-conductive black in wire and cable formulations and other applications requiring a semi-conductive thermoplastic compound. The addition of fillers has little effect on hardness, stiffness and strength, though extensibility is reduced. Filler is incorporated in the elastomer phase and has the effect of both stiffening the elastomer and increasing the volume of its phase. It also reduces the thermoplasticity and therefore reduces the fabricability. To obtain the full benefit of filler, plasticisers can be used to regain both thermoplasticity and extensibility[162].

2.10.2 Plasticisers

Plasticisation will increase the free volume of TPV phase. A correct plasticiser-polymer compatibility of a two polymers is important to form a homogeneous mixture during processing and, once cured, the plasticiser will remain in the compound upon cooling and resting at low temperature, do not exude from the product when exposed to a bright sun for an entire year[163,165].To achieve a high degree of plasticiser compatibility, it is generally necessary that the plasticiser and polymer have approximately the same polarity[163], normally requires solubility parameter (δ) values that do not differ by more than +/-1.5 (cal./cc).

The oil and ester plasticiser oils have been extensively used in thermoset rubber technology for many years. In rubber blends and TPEs the use of suitable mineral oils have proved to be a valuable way of enhancing the compatibility of the two polymers[163-168]. The incorporation of oil plasticiser also to decrease modulus and increase flexibility, workability and distensibility of the polymer[53,169-171]. Large amounts of oil are included in the formulations, mainly acts as processing aid. It was recognized that the presence of a high level of paraffinic oil allowed the preparation of soft, processable TPVs without affect the ability of the TPE to shrink back from highly deformed states[145,172]. Platicisation involves either by plasticising or by diluting the crosslinked rubber[53,170,173].

There are three types of process oil avilable[168,174];

1. Paraffinic. High levels of isoparaffinic molecules. Lower odour and more oxidative stability than napthenic and aromatic oils. Levels of monoaromatics similar to those of the aromatic oils, but mich lower levels of multi-ring aromatics than aromatic process oil.
2. Napthenic. Higher level of saturated rings than aromatic and paraffinic process oils. Similar odour to paraffinic process oil. But the colour is lighter than paraffinic.
3. Aromatic. High levels of unsaturated single- and multiple- ring compounds, higher odour, lower oxidation stability and higher reactivity than paraffinic oils.

In the melt, the oil partitions between the phases and greatly lowers the viscosity, resulting in very good injection moulding and extrusion characteristics. It was found that an introduction of oil into the elastomeric phase of iPP/EPDM rubber resulted in an improvement in its rheological properties and also altered the structure of the interfacial layer[175]. On crystallisation of the thermoplastic, the oil is believed to be absorbed by the amorphous rubber phase and is not rejected to the material's surface. This is particularly useful when using a phenolic resin curative in a TPV based on EPDM/PP blends. Plasticisers can either increase or decrease ultimate elongation whereas the tensile strength generally decreases with the incorporation of plasticiser.

Ester plasticiser been used in circumstances where petroleum oils may be unsuitable, e.g. because of incompatibility with the polymer[166-167] or to provide excellent low temperature end properties of the TPV[163]. Increasing a free volume phase of a polymer consequently lowering the glass transition temperature, Tg. PP in its isotactic and syndiotactic forms can become very brittle at low temperature due to its inherent crystallinity and relatively high Tg. Based on work done by Ellul[171], it was discovered that certain 'non-polar' aliphatic esters, in particular monomeric tallates and sebacates, can effect a large depression in Tg of the PP amorphous component. In this work, the plasticiser was distributed equally in the polypropylene and the vulcanised EPDM phases. The data also indicate that only the amorphous region of the PP is plasticised, while the crystalline region remains essentially intact. This is an extremely important finding, because it implies that semi-crystalline polymers can be successfully plasticised with certain aliphatic esters without much detraction of elevated temperature performance. Elastomers plasticised with low polarity polymer modifiers (LPPMs) exhibited a combination of high tensile strength and hardness, with excellent low temperature properties. Ester plasticisers modify polymers or provide softening of the polymer, lower modulus, lower tensile strength, increased elongation, increased flexibility, lower glass transition, increased tear strength, increased temperature range of usefulness, increased cohesion, modified frictional character, improved surface appearance and increased static charge. Such properties can have importance in applications such as v-belts, radiator hoses, automotive insulation, seals and gaskets[163].

2.10.3 Other Additives

Others additives such as antioxidants, flame retarders, pigments and deodorants can be added to the compound. Antioxidants can be added in order to improve the heat and ozone resistance of thermoplastic vulcanisates. However, the PP itself protects the rubber phase from ozone and TPVs can be mixed without antiozonant. Processing aid such as calcium and zinc stearate used in formulations to impart improved handling, or superior release characteristic from hot metal parts during mixing and processing. These aids are particularly valuable when batch mixing low melt-viscosity or sticky. The addition of these materials results in 'cleaner drop' upon discharge from an internal mixer, as well as improved mill release characteristics. Process aids such as compatibilisers can improve the compatibility between the elastomer and the thermoplastic phases, with a consequent improvement in properties.

2.11 Types of TPV

2.11.1 TPV based on ethylene propylene diene rubber

A thermoplastic blend of partially cured mono-olefin copolymer rubber (EPM or EPDM) with a polyolefin resin (such as polypropylene) was patented by Fischer[52] in 1971. Fischer's work on EPDM/PP blends employing a peroxide system concludes that the maximum cure state of the elastomer phase needs to be controlled by limiting the amount of peroxide, in order to maintain the thermoplastic processability of the blend[31]. Fischer's work on EPDM/PP blends employing a peroxide system[31] concluded that, due to PP breakdown by the peroxide rubber curative, the TPV produced did not achieve their full property potential. For a TPV cured with a phenolic resin curing system containing a halogen donor. Sabet *et al.*[176] claimed that better compression set and oil resistance were obtained than with a similar composition cured with sulphur curative. However, the phenolic resin system required a longer cure time and was not suitable for commercial exploitation.

Uniroyal Chemical Company developed and patented and introduced in 1971 represent the first commercial EPDM/PP known as TPR[177]. The field of thermoplastic vulcanisates based on EPDM was expanded by studies and patents published by Coran *et al.*[54,178-179]. These publications were followed by the introduction of a commercial TPV, Santoprene™ by the Monsanto Company in 1981. Santoprene™ TPV differentiates itself from TPR primarily due to the higher degree of crosslink densitiey and relatively smaller particle size of its elastomeric component (EPDM). Coran's work is based on two methods: 1) by introducing partially or fully cured rubber particles of different size followed by melt-blending with the thermoplastic resin or 2) by using a dynamically vulcanised system. Most studies have employed the first technique. The use of fully cured particles exhibits better physical properties, but still retains thermoplastic reprocessability[180]. However, the degree of curing needs to be controlled in order to have better processability. On the other hand, Coran *et al.*[174] found that the physical properties improve when dynamic vulcanisation is continued to achieve a high rubber cure state. This is attributed to the presence of very small rubber particles (less than 50μm in diameter) dispersed in a thermoplastic matrix. In this way an EPDM/PP thermoplastic rubber material based on a sulphur cured system with good strength, high temperature mechanical properties, good fatigue and compression set has been produced. Coran and Patel[174], and Miguel *et al.*[181] also declared that thermoplastic vulcanisates, which consist of a fully cured dynamically vulcanised EPDM, can be fabricable as a thermoplastic if the proportions of rubber and thermoplastic resin are correct. The authors demonstrated that mechanical properties could be improved by using the dynamic vulcanisation process.

EPDM based TPVs are the most widely available of all commercial TPVs. They produce soft to hard materials, where the hardness ranges from 15 Shore A to 50 Shore D. They offer a constant service temperature range from -60°C to + 135°C (-81°F to +275°F) with no cracking or tackiness. They have excellent heat aging, resistance to cut growth while flexing, high tear strength and superior resistance to fatigue, and good resistance to many acids, bases and aqueous solutions. They are used in many automotive and non-automotive applications such as over moulded grips, handles, soft touch features, bumpers, seals, gaskets, grommets, bellows, knobs, foot pads, pedals, cases, housings, sporting equipment and many, many more types of applications[182].

Leading EPDM/PP suppliers today[183] include ExxonMobile Chemical/Advanced Elastomer Systems (Santoprene™), Mitsui (Milastomer®), Sumitomo (Sumitomo TPE), and DSM Copolymer (Sarlink®).

2.11.2 TPVs based on natural rubber

NR/PP TPV blends have two distinct advantages over other thermoplastic vulcanizates; they are made from relatively low cost materials and they have low densities[184]. Several methods of making thermoplastic vulcanisates from natural rubber (NR/PP TPV) have been studied at the Malaysian Rubber Producers' Research Association (MRPRA), now recognized as Tun Abdul Razak Research Centre (TARRC), Brickendonbury Hertford, UK[42]. This includes the formation of thermally labile crosslinks and the preparation of graft copolymers with carefully tailored architectures. However, it has transpired that blends of NR with thermoplastic resin, studied since 1975, are more economic, lighter materials, providing a simpler and more viable route to a thermoplastic elastomer. In addition, it provides a new perspective on uses of NR. Not only can NR/PP TPV replace vulcanised rubber in a number of applications, but it can also supply a demand for suitable materials used in lightweight moulded components.

The original impetus for the development of NR/polyolefin blends came from considerable industrial interest in materials with a modulus intermediate between those of conventional elastomers and harder materials such as ebonite and thermoplastic.

Tinker[23], Campbell *et al.*[42,185-188] have developed TPVs based on natural rubber and polyolefins. The materials range from soft TPV to semi-rigid materials such as rubber modified PP. A good recovery TPV[189-190] and co-continuous phase morphology[136-138,179] have been observed.

Gelling and Tinker[24] proposed that the properties of NRTPV depend on their blend composition, blend morphology and the degree to which the NR phase is crosslinked. At low NR contents, the materials are rubber-toughened forms of PP. It is only the softer grades with high NR contents that can be classed as thermoplastic vulcanisates. The elastomeric forms of NR/PP TPVs have high strength and good recovery[24,191]. This good strength may relate to the NR phase undergoing strain induced crystallisation[183]. The resistance to heat ageing is better than that of general purpose rubber vulcanisates, the ozone resistance is excellent[24,186] and can be recycled up to five times with little loss in properties[24]. In general, NR/PP TPV can be used in applications not requiring the superior strength and elasticity of vulcanised rubber, such as footwear, sports goods, glazing seals and some types of hose, bellows and mountings[183].

A TPV based on ENR and PP is TPENR and this was also invented at MRPRA, Brickendonbury, UK[192]. ENR is a modified natural rubber[193-195] in which a portion of the double bonds are converted to epoxide by reaction with peroxy acid or hydrogen peroxide/ formic acid systems. Such modification of the natural rubber gives an elastomer with good strength properties and increases the resistance to hydrocarbon oil, increases damping properties, lowers air permeability and gives better heat resistance[196-198]. Hence, the TPV based on ENR exhibits good oil resistance, mechanical and environmental properties. A transition in phase morphology is seen depending on polymer ratio. At higher rubber contents, the rubber phase is continuous whilst at lower rubber contents the rubber forms discrete particles.

2.11.3 TPVs based on nitrile rubber

Hot-oil resistant thermoplastic elastomers from blends of nitrile rubber (NBR) with polyethylene and polypropylene have been developed by Coran and Patel[133]. Some research has also been done on nitrile rubber/nylon blend. A TPV based on nitrile rubber/polyolefin such as NBR/PP requires a compatibiliser to give a sufficient dispersion of rubber in the PP[199]. Production of a block copolymer from the two incompatible polymers would be one way of achieving compatibilisation[200]. The block copolymers act as a surfactants to reduce the interfacial tension between the phases and stabilize the emulsion of the homopolymers PP[194]. A commercial nitrile rubber/polyolefin available in the market is called Geolast® produced by Exxon Mobile Corporation. It is suitable in applications requiring enhanced oil resistance that meets or exceeds that of nitrile rubber and epichlorohydrin. These polymers are aimed at the automotive, domestic appliance, fluid power and industrial hose industries, seals and gasket applications where oil resistance is required.

2.11.4 TPVs based on butyl rubber

A dynamically crosslinked blends of butyl rubber with polyethylene and polypropylene has been studied by Coran *et al.*[201-202]. A commercial based on butyl/PP TPV, called Trefsin™ is ideal for medical, industrial and consumer goods that require the low to moisture, air and oxygen[203] Hydro-Flex® Waterstop based on a butyl/PP TPV is a preformed hydrophilic adhesive designed to swell in the presence of water providing a watertight seal in cold joints on concrete structures, allowing it to penetrate into poorly consolidated concrete surfaces.

Other TPVs available in the market such as zeotherm® (based on polyacylate elastomer and polyamide)[204], thermoplastic silicone vulcanisate, TPSiV™ (based on silicone rubber/polyamide or polyurethane)[205] and Uniprene® XL (hydrogenated SBC rubber/PP)[206] produced by Zeon Chemical LP, Dow Corning Company and Teknor Apex, respectively. Freedonia group examined the market environment, details industry structure and market share, and profiles 40 leading competitors of TPE include Kraton Polymers, Advanced Elastomer Systems, Solvay, DuPont, Atofina, Noveon, Celanese, Dexco Polymers, and Eni was reported[207].

References

1. D.R. Paul and S. Newman (1978) "Polymer blends, Vol. 1". Academic Press, New York and London.

2. D.R. Paul and S. Newman (1978) "Polymer blends, Vol. 2". Academic Press, New York and London.

3. L.A. Utracki (2002) "Polymer blends handbook, Vol. 1 and 2". Kluwer Academic Publishers, Dordrecht.

4. L.A Utracki (1998) "Commercial polymer blends". Chapman & Hall, London.

5. F.M. Sweeney (1988) Polymer blends and alloys : guidebook to commercial products, Technomic Pub Co., Lancaster.

6. D.R. Paul and C.B. Bucknal (2000) "Polymer blends: formulation, Vol. 1". John Wiley & Sons, Inc. New York Chichester Weinheim Brisbane Singapore Toronto.

7. J.R. Dunn (1976) Blends of elastomers and thermoplastics- a review, *Rubb. Chem. Technol.* **49**, pp. 978-991.

8. P.J. Cornish and B.D. Powell (1974) Elastomer blends, *Rubb. Chem. Technol.* **47**, pp. 481-510.

9. N.R. Legge, G. Holden and H.E. Schroeder (1987) Thermoplastic elastomers A comprehensive review. Hanser Publishers, Munich Vienna New York.

10. A.Y. Coran (1988) "Chapter 8. Thermoplastic rubber-plastic blends" in "Handbook of Elastomers – New Development and Technology (Eds., A.K.Bhowmick and L.H. Stephens)". Marcel Dekker, New York. pp. 247-312.

11. S.K. De and A.N. Bhowmick (1990) Thermoplastic elastomers from rubber-plastic blends. Ellis Horwood, New York London Toronto Sydney Tokyo Singapore.

12. A.Y. Coran (1990) "Chapter 10. Thermoplastic elastomeric rubber-plastic blends" in "Thermoplastic Elastomers from Rubber-Plastic Blends (Eds., S.K.De and A.K.Bhowmick)". Ellias Horwood Ltd., Chichester, pp. 265-320.

13. N.R. Legge (1989) Thermoplastic elastomers – three decades of progress, *Rubb. Chem. Technol.* **62**, p.543.

14. R. Ranalli (1982) "Ethylene rubber-polypropylene blends" in " Development in T-3 (Eds., A. Whelan and K.S. Lee)". Applied Science, London.

15. Abstract from World Thermoplastic Elastomer (December 2003) Freedonia Group Incorporated Market Research Report (International study/database company).

16. World Thermoplastic Elastomers : Industry Research Report-published by Freedonia group. http:www. mindbranch.com/Thermoplastic-Elastomers-R154-1523/ (accessed on 15 May 2006).

17. Abstract from World Thermoplastic Elastomer to 2009-Market size, market share, market leaders, demand forecast sales, company profiles, Market Research Industry Trends. http:www. Bharatbook.com/bookdetail.asp?bookid=8192 &publisher= (accessed on 15 May 2006).

18. M. Shetty and W. Ripple (2005) Innovative TPE overmoulding : trends, materials selection criteria and part design . Online seminar organised by GLS on 26 June 2005 (www.glscorp.com).

19. G. Mottershead (2002) Moving the rubber industry into the plastic world, GCP elastomeric Inc., Asia Rubber Market, Kuala Lumpur.

20. J.J. Gordon and M.A. Lemieux (1998) Thermoplastic elastomers for automotive applications – past, present and future. Presented at a meeting of the Rubb. Div., ACS, Nashville, Tennessee, paper no. 90.

21. D. Shaw (2002) TPEs set for growth in automotive sector, *Eur. Rubb. J.* **184**, p. 16.

22. A.J. Tinker, R.D. Icenogle & I. Whittle (1988) Thermoplastic NR opens TPEs to new uses, *Rubb. Plast. News*, pp. 80-81.

23. A.J.Tinker (1987) Thermoplastic natural rubber blends – update. *NR Technol.* **18**, pp. 30-34.

24. I.R. Gelling and A.J. Tinker (1988) Thermoplastic natural rubber, performance and applications. Proceeding International Rubber Conference 1988.

25. R.S. Rajeev and S.K. De (2004) Thermoplastic elastomers based on waste rubber and plastics, *Rubb. Chem. Technol.* **77**, p. 569-578.

26. Y. Tanaka, T. Watanabe, T. Okita, M. Matsushita, H. Okamoto, K. Fukumori, N. Suzuki and Y. Suzuki (2004) The technology to produce thermoplastic elastomer based on waste rubber. SAE Transactions: Journal of Materials & Manufacturing. Vol. 112, pp. 495-500.

27. A.Y. Coran and F. Howard (1999) Thermoplastic rubbery compositions, US 5889119 (to The University of Akron).

28. C. R. Pillai and C. H. Chandra (2001) Process for preparing thermoplastic rubbers from vulcanised rubber scrap materials and olefinic plastic, US 6313183.

29. Technical Report 36 (2001) Process development of scrap rubber/thermoplastic blends. Chelsea Center for Recycling and Economic Development, University of Massachusetts Lowell.

30. N.K. Dutta, A.K. Bhowmick and N. R. Choudhury (1997) "Chapter 15. Thermoplastic elastomer" in "Handbook of Thermoplastics (Ed, O. Olabisi)". Marcel Dekker, Inc., New York: Basel : Hong Kong , p. 351.

31. W.K. Fischer (1974) Dynamically partially cured thermoplastic blend of monoolefin copolymer rubber and polyolefin plastic, US 3806558 (to. Uniroyal, Inc.).

32. A.Y. Coran and R.Patel (1980) Rubber-thermoplastic composition Part 1. EPDM-polypropylene thermoplastic vulcanisate, *Rubb. Chem. Technol.* **53**, pp. 141.

33. T. Abraham and M. Colleen (2004) Chapter 5. "Thermoplastic elastomers" in "Rubber Compounding Chemistry and Applications" (Ed. B.Rodgers). Marcel Dekker , Inc., New York Basel, p.198.

34. A.M. Gessler and W.H. Haslett (1962) Process for preparing a vulcanised blend of crystalline polypropylene and chlorinated butyl rubber, US 3037954 (to Esso Research and Engineering).

35. S.A.-Sabet and K.-S. Shen (1986) Process for preparation of thermoplastic elastomers, US 4594390 (to Monsanto Co.).

36. D.R. Hazelton, R.C. Puydak and D.A. Booth (1986) Dynamically cured thermoplastic olefin polymers, US 4607074 (to Exxon Research & Engineering Co.).

37. A.Y. Coran and R.P. Patel (1978) Thermoplastic compositions of high unsaturation diene rubber and polyolefin resin, US 4104210 (to Monsanto Co.).

38. Y.L. Wang (1984) Process for preparing elastoplastic compositions, US 4480074 (to Monsanto Co.).

39. A.Y. Coran and S. A.-Sabet, (2002) Thermoplastic vulcanisates and process for making the same, US 6437030 (to Advanced Elastomer Systems, L.P.).

40. A.O. Dozeman, P. Gijsman, H.A.J. Schepers and W.A.M. Debets (2000) Process for the preparation of a thermoplastic elastomer, US 6051681 (to DSM N.V. Heerlen, NL).

41. W.K. Fisher (1984) Dynamically partially cured thermoplastic bends of mono olefin copolymer rubber and polyolefine plastics, US RE 31518 (to Uniroyal, Inc.).

42. D.J. Elliot and A.J. Tinker (1988) "Chapter 9. Blends of natural rubber with thermoplastic" in "Natural Rubber Science and Technology (Ed., A.D.Robert)". Oxford University Press, Oxford, pp. 327-357.

43. J.D. Umpleby (1989) Process for preparation of thermoplastic elastomers, US 4803244 (to Union Carbide Corporation).

44. T. Mitsuno, H. Shinonaga and A. Daimon (1990) Thermoplastic elastomer composition, US 4946896 (to Sumitomo Chemical Company, Ltd.).

45. E. Aldrovandi, N. Luca, P. Patriziai, A.G. Gian and L. Roger (1996) Vulcanised polyolefinic plastoelastomer composition and process for its preparation, US 5523356 (to Enichem Elastomeri S.r.l).

46. S. Danesi, S. Forti and M. Manica (1983) Process for preparing polyolefinic elastomeric composition by dynamic vulcanisation, US 4477631 (to Montedison S.p.A. Milan, Italy).

47. J.V. Jeffrey (1991) Thermoplastic elastomeric elastomeric compositions and method for their preparation, US 6013729 (to Sumitomo Bakelite Co., Ltd.).

48. C.Y. Thomas, C.P. Robert, W.D. Charles (1991) Dynamically cured thermoplastic olefin polymers and process for producing the same, US 5051477 (to Advanced Elastomer Systems, L. P).

49. A. Manoj, K. Christopher, G.W. Lawson and V. Rajesh (2004) Thermoplastic elastomer composition , US 7015284 (to The Goodyear Tire & Rubber Company, GLS Corporation).

50. U. Eisele, D. Jache, L. Mott and K.-H. Schabel (1988) Thermoplastic elastomers, US 4747149 (to Bayer).

51. M. Takimoto, J. Takeuchi and Y. Yamazaki, (1987) Thermoplastic olefin elastomers, US 4713419 (to Toyoda Gosei Co.).

52. W.K. Fischer (1973) Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic, US 3758643 (to Uniroyal, Inc.).

53. S.A.-Sabet, R.C. Puydak and C.P. Rader (1996) Dynamically vulcanised thermoplastic elastomers, *Rubb. Chem. Technol.* **69**, p. 476.

54. A.Y. Coran (1978) "Chapter 7. Thermoplastic elastomers based on elastomer-thermoplastic blends dynamically vulcanised" in "Thermoplastic Elastomers A Comprehensive Review (Eds., N.R. Legge,H.F. Holden, and H.E Schroeder)". Hansers Publishers, Munich, p. 135.

55. H. Ocker (1978) Screw extruder for continuously processing and degassing of elastomers and polymers having a viscosity of more than 1000 poise, US 4107787 (to Werner & Pfleiderer).

56. P. Dufton (2001) "Chapter 7. Processing, machinery and other factors" in "Thermoplastic Elastomers". A Rapra Industry Analysis Report RAPRA Technology Limited, Shawbury.

57. K.E.Kear (2003)Developments in thermoplastic elastomers, RAPRA Review Report **14**, report 166.

58. TPE/PP or TPE/TPE co-extrusion. Elastomer products limited http://www.elastomer.co.nz/dgs/dgs_coextrusion.html (accessed on 12Dec 2006).

59. J.C. Stebnicki and T.R. Buchholz (2006) Composite article having thermoplastic elastomer region on thermoplastic substrate, US 7132167 (to Rexnord Corporation).

60. K. D. Naba, A.K. Bhowmick and N.R. Choudhury (1997) "Chapter 15. Thermoplastic elastomer" in "Handbook of Thermoplastics (Ed., O. Olabisi)". Marcel Dekker, Inc. New York, p. 371.

61. C. Thomas and A. Hill (1998) Material properties of TPE sponge profiles, TPE 98 New opportunities for thermoplastic elastomers, Official conference proceedings 98. RAPRA Technology Ltd., Westminster London.

62. J.G. D'auteuil, D.E. Peterson, C.P. Rader (1989) Blow molding of thermoplastic elastomers : a major opportunity for the plastics processor, *J. Elastomers Plast.* **21**, pp. 256-274.

63. J.G.D. Auteuil, D.E. Peterson and C.P. Rader (1989) Blow moulding of thermoplastic elastomer : a major opportunity for the plastic processors. ANTEC'89, 47th. Annual Tech. Conf. of SPE, New York, p. 1740.

64. G. Holden (1987) "Chapter 13. Applications of thermoplastic elastomers" in "Themoplastic Elastomers A Comprehensive Review" (Eds., N.R. Legge, G. Holden and H.E. Schroeder). Hanser Publishers, New York.

65. Electronic Development Labs, Inc. Dictionary (http://www.edl-inc.com/Engineering%20data/Plastic%20dictionary.htm) (accessed on 23 Jan. 2004).

66. N.J. Mills (1993) "Chapter 1. Molecular structures and manufacture of polymers" in "Plastics Microstructure and Engineering Applications (Eds.,R.W.K. Honeycombe and P.Hancock)". Edward Arnold, London Melbourne Auckland, pp. 2-3.

67. E. Brown (2002) "Chapter 2.The characterisation of polymer" in "Optical Characterization of Domain Growth in Polymer Systems, Dissertation for the MSc in Software Systems Technology". Department of Computer Science, University of Sheffield.

68. W. M. D Bryant (1947) Polythene fine structure, *J. Polym. Sci.* **2**, pp. 547-64.

69. Polymer morphology . Crystallinity http://plc.cwru.edu/tutorial/enhanced/files/polymers/orient/orient.htm. (accessed on 8 April 2004).

70. R.S. Stein and A.V. Tobolsky (1974) "Crystallinity in polymers" in "Polymer Science and Materials (Eds., A.V. Tobolsky and H.F. Mark)". John Wiley and Sons, Inc., New York London Sydney Toronto, pp. 161-187.

71. N. Severin (2003) "Chapter 3. MD simulation of polyethylene/isotactic polypropylene (PE/iPP) interfaces" in "Molecular Dynamics Simulations of Polymers and Micelles at Interfaces" Dissertation http://edoc.hu-berlin.de/dissertationen/physik/severin-nikolai/HTML/severin-ch3.html (accessed on 5 Nov. 2003).

72. C.A. Cooper, B.C. Gates, R.L. McCullough and J.C. Seferis (1982) The influence of draw-induced structural changes on the activity of a semi-crystalline polymer – support catalyst, *J. Appl. Polym. Sci.* **20**, pp. 173-189.

74. J.A. Brydson (1982) "Chapter 11. Aliphatic polyolefins other than polyethylene and diene rubbers" in "Plastics Materials, 4th. Ed.". Butterworth Scientific, London, pp. 225-243.

75. P. Jacoby. Nucleation and Clarity in Polypropylene (accessed on 22 Nov. 2004) (http://www.mayzo.com/Paper/NucleClarityinPE.pdf).

76. W.K. Fischer (1973) Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic, US 3758643 (to Uniroyal, Inc.).

77. Polypropylene, Dow Company http://www.dow.com/polyolefins/about/pptechctr/primer/fig_tab/typ.htm (accessed on 23 Jan. 2004).

78. J.A. Brydson (1982) "Plastics materials". Butterworth scientific, London Boston Durban Singapore Sydney Toronto Wellington, p.63.

79. H.P. Frank (1969) "Chapter 4. Polypropylene properties" in "Polypropylene". Macdonald Technical & Scientific, London, Pg. 47.

80. Polymer chemistry. Stereochemistry. http://www.lasalle.edu/academ/chem/ms/polymersRus/Resources/Stereochem.htm(accessed on 14 Jan., 2007).

81. M.A. Meyers and K.K. Chawla (1999)"Chapter 3. Plasticity" in "Mechanical Behaviour of Materials". Prentice Hall Int. (UK) Ltd., Upper Saddle River, New Jersey, pp. 111-146.

82. Mechanical behaviour https://www.hansergardner.com/sample/1-56990-310-7.pdf (accessed on 3 Jan 2007).

83. Y. Men, J. Rieger and G. Strobl (2003) Role of the entangled amorphous network in tensile deformation of semi-crystalline polymers, *Phys. Rev Lett.* 91, pages 095502.

84. R.J. Samuels (1968) Quantitative characterization of deformation in draw polypropylene films, *J. Polym. Sci. Part A-2* **6**, pp. 1101.

85. Introduction to materials science, Chapter 16. Applications and processing of polymers. http://www.people.virginia.edu/~lz2n/mse209/Chapter16.pdf (accessed on 8 Aug. 2004).

86. A.W. Birley, B. Haworth and J. Batchelor (1992) "Chapter 6. Mechanical properties-deformation" in "Physics of Plastics Processing, Properties and Materials Engineering)". Hanser Publishers, Munich Vienna New York Barcelona, pp. 283-284.

87. J.M. Schulz (1974) Polymer Materials Science, Pretice-Hall, Englewood Cliffs, New Jersey. pp.500-501

88. Advanced material. Lecture 3- Polymer structure. (http://www.cmse.ed.ac.uk/AdvMat45/Lecture3_Polymer%20Structure.pdf (accessed on 8 August. 2004).

89. A.J.Perlin (1971) Molecular model of drawing polyethylene and polypropylene, *J. Mater. Sci.* **6**, pp. 490-508.

90. A. Dasari, S.J.Duncan and R.D.K. Misra (2002) Atomic force microscopy of scratch damage in polypropylene, *Mater. Sci. Technol.* **18**, pp.1227-1234.

91. C.A. Cooper (1982) The influence of draw-induced structural changes on the activity of a semi-crystalline polymer supported catalyst, *J. Appl. Polym. Sci.* **20**, pp. 173-189.

92. C.A. Daniels (1989) Polymers : structure and properties, Technomic Pub. Co. Lancaster, pp. 43-55.

93. E.G. Cockbain (1961) "Chapter 1. Natural and synthetic lattices" in "The Applied Science of Rubber (Ed., W.J.S. Naunton)". Edward Arnold (Publishers) Ltd., London, p.3.

94. G.F. Bloomfield (1961) "Chapter 11. Chemistry and structure of natural rubber" in "The Applied Science of Rubber (Ed., W.J.S.Naunton)". Edward Arnold (Publishers) Ltd., London, p.61.

95. R. J. Young and P.A. Lovell (1991) "Introduction to Polymers". Chapman & Hall, London, p. 88.

96. Polymer Chemistry.Isomerism http://pcol.ch.iup.edu/Polymers/Resources/Isomerism.htm. (accessed on 22 March. 2004).

97. B. Meissner, M. Schatz and V. Brajko (1989) " Chapter 4. Synthetic rubbers" in "Elastomer and Rubber Compounding Materials: Manufacture, Properties and Applications (Ed.,I.Franta)". Elsevier, Amsterdam Oxford New York Tokyo, p. 78.

98. D.J. Synnott, D.F. Shaeidan and E.G. Kontos (1990) "Chapter 5. EPDM-polypropylene blends" in "Thermoplastic Elastomers from Rubber-plastics Blends, (Ed.s, S.K.De and A.N. Bhowmick)". Ellis Horwood Ltd., New York London Toronto Sydney Tokyo Singapore, pp. 130-158.

99. G.V. Strate (1986) "Ethylene propylene elastomers" in "Encyclopedia of Polymer Science and Engineering (Eds., H.F.Mark, N.M. Bikales, C.G. Overberger, G. Menges and J.I. Kroschwitz), Vol. 6". A wiley-Interscience Pub., John Wiley & Sons, New York Chichester Brisbane Toronto Singapore, p.524

100. J.- M. Charrier (1990) "Chapter 3. Classes of polymeric materials" in "Polymeric Materials and Processing : Plastic Elastomer and Composites". Hanser Publishers, Munich Vienna New York , p. 203-204.

101. Website : www.iisrp.com/WebPolymers/10EPDMSept11.pdf (accessed on 12 Sept. 2005).

102. A.Y. Coran (1994) "Chapter 7. Vulcanisation" in "Science and Technology of Rubber, 2nd. ed. (Eds., J.E.Mark, B.Erman and F.R.Eirich)". Academic Press, San Diego New York Boston Sydney Tokyo Toronto, p. 375.

103. J.B. Class (1998) A review of fundamentals of crosslinking with peroxides. Presented at a meeting of the Rubb. Div., ACS, Indianapolis, Indiana. Paper no. 1.

104. P. Kovacic (1997) Peroxide vulcanisation of elastomers, *Rubb. Chem. Technol.* **74**, pp. 452-492.

105. P. Kovacic and P.W. Hein (1962) Crosslinking of polymers with dimaleimides. I, *Rubb. Chem. Technol.* **35**, 520-527.

106. M. Tosaka, S. Murakami, S. Poompradub, S. Kohjiya, Y. Ikeda, S. Toki, I. Sics and B. S. Hsiao (2004) Orientation and crystallization of natural rubber network as revealed by WAXD using synchrotron radiation, *Macromol.* **37**, pp. 3299-3309.

107. S. Toki, M. Tosaka, S. Kohjiya, S. Poompradub, Y. Ikeda and A.H. Tsou (2000) Strain-induced molecular orientation and crystallisation in natural rubber and synthetic rubber under uniaxial deformation by in-situ synchrotron X-ray study, *Rubb. Chem. Technol.* **77**, pp. 317 – 335.

108. D. Göritz and R. Grassler (1987) Melting temperatures as a function of the strain of oriented polymer networks, *Rubb. Chem. Technol.* **60**, pp. 217 – 226.

109. W. F. Reichert and D. Göritz (1992) Gas adsorption at uniaxial deformation of filled natural rubber, *Rubb. Chem. Technol.* **66**, pp.1-13.

110. S. Toki, I. Sics, S. Ran, L. Liu, B.S. Hsiao (2002) New insights into structural developments in natural rubber during uniaxial deformation by *in-situ* synchrotron x-ray diffraction, *Macromol.* **35**, pp. 6578-6584.

111. S. Toki, I. Sics, S. Ran, L. Liu, B. S. Hsiao, S. Murakami, K. Senoo and S. Kohjiya (2003) Molecular orientation and structural development in vulcanised polyisoprene rubbers during uniaxial deformation by in situ synchrotron X-ray diffraction, *Polymer* **44**, pp. 6003-6011.

112. T. Nishi and T. Chikaraishi (1981) *J. Macromol. Sci. Phys.* **B19**, 445-457 (1981).

113. P.B. Lindley (1992) Engineering design with natural rubber (revised by K.N.G. Fuller and A. Muhr). The Malaysian Rubber Producers' Research Association, NR Technical bulletins, ISSN 0956-3856, pp. 6-7.

114. L. Mullins and A.R. Payne (1957) Theoretical model for the elastic behaviour of filler-reinforced vulcanised rubber, *Rubb. Chem. Techol.* **30**, pp.555-571.

115. L. Mullins and N.R. Tobin (1965) Stress softening in rubber vulcanizates. Part I. Use of a strain amplification factor to describe the elastic behavior of filler-reinforced vulcanised rubber, *J. Appl. Polym. Sci.* **9**, pp. 2933-3010.

116. J. A. C. Harwood, L. Mullins, A. R. Payne (1965) Stress softening in natural rubber vulcanizates. Part II. Stress softening effects in pure gum and filler loaded rubbers, *J. Appl. Polym. Sci.* **9**, pp. 3011-3021.

117. J. A. C. Harwood and A. R. Payne (1966) Stress softening in natural rubber vulcanisates. Part IV. Unfilled vulcanisates, *J. Appl. Polym. Sci.* **10**, pp. 1203-1211.

118. J. A. C. Harwood, A. R. Payne (1966) Stress softening in natural rubber vulcanisates. Part III. Carbon black-filled vulcanisates, *J. Appl. Polym. Sci.* **10**, pp. 315-324.

119. H.J. Qi and M.C. Boyce (2004) Constitutive model for stretch-induced softening of the stress-stretch behaviour of elastomeric material, *J. Mech. Phys. Solids* **52**, pp. 2187-2205.

120. J.S. Blanchard and D. Parkinson (1952) Breakage of carbon-rubber network by applied stress, *Ind. Eng. Chem.* **44**, p. 799.

121. F. Bueche (1960) Molecular basis for Mullins effect, *J. Appl. Polym. Sci.* **4**, pp. 107-114.

122. F. Bueche (1961) Mullins effect and rubber-filler interaction, *J. Appl. Polym. Sci.* **5**, pp. 271-227.

123. E.M. Dannenberg (1974) The effects of surface chemical interaction on the properties of filler-reinforced rubbers, *Rubb. Chem. Techol.* **48**, pp.410-444.

124. Z. Rigbi (1980) Reinforcement of rubber by carbon black, *Adv. Polym. Sci.* **36**, pp. 21-68.

125. L. Mullins (1969) Softening of rubber by deformation, *Rubb. Chem.Techol.* **42**, pp. 339-362.

126. P. Kovacic and R.W. Hein (1956) *J. Amer. Chem. Soc.* **81**, pp.1187.

127. D.J. Elliot (1986) Influence of crosslinking agents and interfacial adhesion promoters on the properties of natural rubber – polypropylene blends. Int. Conf. on Rubber and rubber-like materials, Jamshedpur, India (Ed., S.K.De). Kharagpur : India Institute of Technology.

128. T. Inoue (1994) Selective crosslinking in polymer blends. I. Novel selective crosslink systems for polypropylene/unsaturated elastomer blends, *Polymer* **54**, pp. 709-712.

129. H. I. Halimatuddahliana and H.M. Akil (2005) The effect of HVA-2 addition on the properties of PP-EPDM-NR ternary blends, *J. Elas. Plast.*. **37**, pp. 55-72.

130. A. Hassan, M.U. Wahit and C.Y. Chee (2002) Mechanical and morphological properties of PP/NR/LLDPE ternary blend-effect of HVA-2, *Polymer* **22**, pp. 281-290.

131. S. Norzalia, H. Hanim and M.Y. Ahmad Fuad (1994) The effect of addition of bismaleimide and maleated PP wax on the crystallisation and mechanical properties of PP/NR blends, *Plast. Rubb. Comp. Process. Appl.* **22**, pp. 185-193.

132. A.J. Tinker (1995) Interfacial adhesion in polymer blends. Elastomer and Rubber Technology (Eds., R.E. Singler and C.A.Byrne). Sagamore Army Materials Research Conference Proceedings Lake Luzerne, New York.

133. A.Y. Coran and R.P. Patel (1983) Rubber-thermoplastic compositions. Part VIII. Nitrile polyolefin blends with technological compatibilisation, *Rubb. Chem. Techol.* **56**, pp.1045-1060.

134. P.E.F. Cudby, J. Patel and A.J. Tinker (1992) Application of new techniques to the characterisation of dynamically vulcanised thermoplastic elastomers. Paper presented at a meeting of the Rubb. Div., ACS, Nashville, Tennessee. Paper no. 67.

135. S.A.-Sabet and R. Patel (1991) Morphology of elastomeric alloys, *Rubb. Chem. Technol.* **64**, pp. 769-779.

136. S. Cook, N.A. Jones, J. Patel and A.J. Tinker (2001) Fatigue properties of thermoplastic elastomers. Int. Rubber Conference 2001, Birmingham.

137. S. Cook, R.T. Davies, J. Patel, K.M.E. Lawrence and G.Sica (2003) Morphological studies of thermoplastic vulcanisates. Int. Rubb. Conf. 2003, Nurnberg.

138. J. Orderkerk and G. Groeninckx (2002) Morphology development by reactive compatibilisation and dynamic vulcanisation of nylon6/EPDM blends with a high rubber fraction, *Polymer* **43**, pp. 2219-2228.

139. E.N. Kresge (1978) "Rubbery thermoplastic blends" in "Rubber Blends (Eds, D.R. Paul and S. Newman) Vol. 2". Academic Press, New York London.

140. C.L. Riddiford and A.J. Tinker (1990) TPENR, A new oil-resistant thermoplastic elastomer. Presented at a meeting of the Rubb. Div., ACS, Washington DC, Paper 33.

141. F. Goharpey, A.A. Katbab and H. Nazockdas (1995) Mechanism of morphology development in dynamically cured EPDM/PP TPEs. I. Effects of state of cure, *J. Appl. Polym. Sci.* **81**, pp. 2531-2544.

142. J. Oderkerk and G. Groeninckx and M. Soliman (2002) Investigation of the deformation and recovery behaviour of nylon-6/rubber thermoplastic vulcanisates on the molecular level by infrared-strain recovery measurements, *Macromol.* **35**, pp. 3946-3954.

143. Y. Kikuchi, T. Fukui, T. Okada and T. Kikuchi (1991) Elastic-plastic analysis of the deformation mechanism of PP-EPDM thermoplastic elastomer : origin of rubber elasticity, *Polym. Eng. Sci.* **31**, pp. 1029-1032.

144. Y. Kikuchi, T. Fukui, T. Okada and T. Kikuchi (1992) Origin of rubber elasticity in thermoplastic elastomers consisting of crosslinked rubber

particles and ductile matrix. *J. Appl. Polym. Sci: Appl. Polym. Symp.* **50**, pp. 261-271.

145. Y. Yang, I. Chiba, H. Saito and T. Inoue (1998) Physical characterization of a polyolefinic thermoplastic elastomer, *Polymer* **39**, 3365-3372.

146. T.A. Huy, T.Luepke, H.-J. Radusch (2001) Characterization of the deformation behavior of dynamic vulcanisates by FTIR spectroscopy, *J. Appl. Polym. Sci.* **80**, pp. 148-158.

147. M. Soliman, M. van Dijk and M. van Es (1998) Deformation mechanism of thermoplastic vulcanisates investigated by combined FTIR- and stress-strain measurements. Proceeding of the American Chemical Society Division of Polymeric Materials : Science and Engineering. Boston Massachusetts. Vol. 79.

148. T. Aoyama, A.J. Carlos, H. Saito, T. Inoeu and Y. Niitsu (1999) Strain recovery mechanismof PBT/rubber thermoplastic elastomer, *Polymer* 40, pp.3657-3663.

149. A.Y Coran and R. P. Patel (1995) "Chapter 6. Thermoplastic elastomers by blending and dynamic vulcanization" in "Polypropylene Structure, Blends and Composites: Copolymers and Blends, (Ed., J. K.-Kocsis) **Vol. 2"**, Chapman and Hall.

150. D. Puett, K.J. Smith and A. Ciferri (1965) Elasticity of semi-crystalline polymers, *J. Physc. Sci.* **69**, pp. 144.

151. N.R. Choudhury and A.K. Bhowmick (1989) Hysterisis of thermoplastic vulcanisates, *Plast. Rubb. Procces. Appl.* **11**, pp. 185-188.

152. S. Kawabata, S. Kitawaki, H. Arisawa, Y.Yamashita and X.Guo (1992) Deformation mechanism and microstructure of thermoplastic elastomer

estimated on the basis of its mechanical behaviour under finite deformation, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **50**, pp. 248.

153. S. Toki, I. Sics, C. Burger, D. Fang, L. Liu, B.S. Hsiao, S. Data and A.H. Tsou (2006) Structure evolution during cyclic deformation of an elastic propylene-based ethylene-propylene copolymer, *Macromol.* **39**, pp. 3588-3597.

154. S. Toki, I B.S. Hsiao, S. Kohjiya, M. Tosaka, A.H. Tsou and S. Data and (2006) Synchrotron X–ray studies of vulcanized rubbers and thermoplastic elastomers, *Rubb. Chem. Technol.* **79**, pp. 460-487.

155. M.C. Boyce, K. Kear, S. Socrate and K. Shaw (2001) Deformation of thermoplastic vulcanisates, *J. Mech. Phys. Solids* **49**, pp. 1073-1098.

156. M.C. Boyce, S. Socrate, K. Kear, O.C. Yeh and K. Shaw (2001) Micromechanisms of deformation and recovery in thermoplastic vulcanisates, *J. Mech. Phys. Solids* **49**, pp. 1323-1342.

157. M.C. Boyce, O.C. Yeh, S. Socrate, K. Kear and K. Shaw (2001) Micromechanisms of cyclic softening in thermoplastic vulcanisates, *J. Mech. Phys. Solids* **49**, pp. 1343-1360.

158. C.G. Reid, K.G. Cai, H. Tran and N. Vennemann (2004) Polyolefine TPV for automotive interior applications, *Ksuts. Gummi Kunsts.* 57, pp. 227-234.

159. A.J. Tinker (2005) MPG seminar, Manchester (TARRC unpublished paper).

160. M.D. Wang and M. Cakmak (2001) Basic studies on development of structure hierarchy in tubular film blown dynamically vulcanised PP/EPDM blend, *Rubb. Chem. Techol.* **74**, pp. 761 -777.

161. M. Cakmak and S.W. Cronin (2000) The effect of composition and processing conditions on the structure development in injection moulded dynamically vulcanised PP/EPDM blends, *Rubb. Chem. Techol.* **73**, pp. 753-778.

162. N.R. Choudhury, P.P. De and A.K. Bhowmick (1990) "Chapter 3. Thermoplastic elastomeric natural rubber-polyethylene blends" in Thermoplastic Elastomers from Rubber-Plastic Blends (Eds., S.K.De and A.K.Bhowmick)". Ellias Horwood Ltd., New York London Toronto Sydney Tokyo Singapore, pp. 71-101.

163. Modifiers for low polarity polymers, ester plasticiser - http://www.thefreelibrary.com/Modifiers+for+low+polarity+polymers-a0131690381 (1 April, 2007).

164. E.N. Kresge (1991) Polyolefin thermoplastic elastomer blends, *Rubb. Chem. Techol.* **64**, pp. 469-480.

165. H.E. Sheemy (1999 Thermoplastic elastomers and mineral oils, *Kauts. Gummi Kunst.* **52**, pp. 586-587.

166. T.C. Erderly, J.J. Chludzinski, A.H. Dekmezian, A.A. Montagna, D.G. Peiffer, D.M. Ellul, D.R. Hazelton, B.M. Rosenbaum (2001) Thermoplastic elastomer compositions having improved processing properties, US 6297301 (to ExxonMobil Chemical and Advanced Customer Systems).

167. K. Venkataswamy and A.M. Person (2002) Olefinic slip-coating for automotive weatherseals, US 6368700 (Advanced Elastomer Systems, L.P.).

168. C.M. Blow and C. Hepburn (1982) Rubber Technology Manufacture, 2nd. eds., Butterworths, London, p. 233.

169. H.G. Moneypenny, K.-H. Menting and F.M. Gragg (2004)"Chapter 8. General compounding" in "Rubber Compounding Chemistry and Applications (Ed., B. Rodger)". Marcel Dekker , New York, pp. 394-415.

170. A.Y. Coran and R. Patel (1982) Polymer blends, US 4338413 (to Monsanto Co.).

171. M.D. Ellul MD (1998) Plasticisation of polyolefin elastomers, semi-crystalline plastics and blends crosslinked in situ during melt-mixing, *Rubb. Chem. Technol.* **71**, pp.244–76.

172. A. M. Gessler and E.N. Kresge (1979) Elastomer blends, US 4132698 (to Esso Research and Engineering).

173. M. Mariano, J.P. Tomba, J.M. Carella and M.I. G.-Mitre (2004) Physical characterization of commercial polyolefinic thermoplastic elastomers, *Eur. Polym. J.* **40**, pp. 2757-2766.

174. F.M. McMillan (1959) 'Chapter 7. Rubber, plasticisers, softeners and extender' in 'Introduction to Rubber Technology, (ed., M. Morton)', Reinhold Publishing Corp. New York, pp. 151-171.

175. A.O. Baranov, N.A. Erina, S.A. Kuptsov, T.I. Medintseva and E.V. Prut (2003) Interphase layer formation in isotactic polypropylene/ethylene-propylene rubber blends, *J. Appl. Polym. Sci.* **89**, pp. 249-257.

176. S.A-. Sabet and M.A. Fath (1982). Thermoplastic elastomeric blends of olefin rubber and polyolefin resin, US 4311628 (to Monsanto Co.).

177. Plastic Technology online article. No. 20 Thermoplastic Elastomers. http://www.ptonline.com/articles/200510fa21.html (accessd on 12 Jan 2007).

178. A.Y. Coran, B. Das and R.P. Patel (1978) Thermoplastic vulcanisates of olefin rubber and polyolefin resin, US 4130535 (to Monsanto Co.).

179. A.Y Coran and R.P. Patel (1978) Thermoplastic compositions of high unsaturation diene rubber and polyolefin resin, US 4104210 (to Monsanto Co.).

180. R.C. Puydak, D.R. Hazelton, B.A. Graham, R. Dharmarajan and R. Narayanaswami (1992) Dynamically vulcanized alloys having improved stiffness/impact balance US 5100947 (to Advanced Elastomer Systems).

181. M.A.L-. Manchado, M. Arroyo and J.M. Kenny (2003) New development in dynamically cured PP-EPDM blends, *Rubb. Chem. Technol.* **74**, pp.211-220.

182. P. Dufton (2001) "Chapter 13. The supply and demand for thermoplastic elastomers" in "Thermoplastic Elastomers. A Rapra Industry Analysis Report", Rapra Technology Ltd., Shawbury, pp. 129-144.

183. T. Abraham and C. McMaham (2004) Fundamentals of thermoplastic elastomers produced by dynamic vulcanisation. Presented at a meeting of the Rubb. Div., ACS, 165th Spring Technical Meeting, Grand Rapids, Michigan.

184. S.A. -Malaika and E.J. Amir (1986) Thermoplastic elastomer I. Effect of processing variables on tensile properties of natural rubber/polypropylene blends, *J. Nat. Rubb. Res.* **1**, pp. 104-121.

185. D.S. Campbell, D.J. Elliot and M.A. Wheelans (1978) Thermoplastic natural rubber blends, *NR Technol.* **9**, pp. 21-31.

186. D.J. Elliot (1981) Developments with thermoplastic rubber blends, *NR Technol.* **12**, pp. 59-67.

187. D.J. Elliot (1986) Some properties and prospects of thermoplastic natural rubber blends. *Kauts. Gummi Kunsts.* Vol. 39(No.7), 621-624, 1986.

188. D.J. Elliot (1990) "Chapter 4. Natural rubber-polypropylene blends" in Thermoplastic Elastomers from Rubber-Plastic Blends (Eds., S.K. De and A.K. Bhowmick)". Ellias Horwood Ltd., New York London Toronto Sydney Tokyo Singapore, pp. 102-129.

189. S. Cook, P.S. Brown, C.D. Forge, G. Sica and A.J. Tinker (2003) A new TPV with excellent recovery performance. Conf. Proc. of TPE 2003, Brussels Belgium, Paper 11.

190. S. Cook, J. Patel and A.J. Tinker (2005) Natural rubber based TPVs for improved performance. Conf. Proc. of TPE 2005, Berlin Germany, Paper 10.

191. I.R. Gelling (1989) Thermoplastic and epoxidised natural rubbers meet strength demands, *Elastomerics* **121,** pp. 18-21.

192. I.R. Gelling, A.J. Tinker and C.L. Riddiford (1988) Elastomeric compositions, US 4769416 (to Malaysian Rubber Producers' Research Association).

193. K.F. Gazeley, A.D.T. Gorton and T.D. Pendle (1988) "Chapter 3. Latex concentrates: properties and composition" in "Natural Rubber Science and Technology (Ed., A.D.Roberts)". Oxford University Press, Oxford, pp 91.

194. I.R Gelling and M. Porter (1988) "Chapter 10. Chemical modification of natural rubber" in "Natural Rubber Science and Technology (Ed., A.D.Roberts)". Oxford University Press, Oxford, pp 419-425.

195. I.R. Gelling (1984) Thermoplastic and epoxidized natural rubber. Paper presented at the 125th meeting of the Rubb. Div., ACS, Indianapolis, pp 67-85.

196. I.R.Gelling (1987) Epoxidized natural rubber, *NR Technol.* **18**, pp. 21-29.

197. P. Dufton (2001) "Chapter 4. Material developments, products and trends" in "Thermoplastic Elastomers". A Rapra Industry Analysis Report RAPRA Technology Limited, Shawbury.

198. P.W. Milner (1987) "Chapter 2. Advances in nitrile rubber" in "Developments in Rubber Technology-4 (Eds., A.Whelan and K.S.Lee)". Elsevier Applied Science, London and New York, p. 71.

199. S. Thomas and S.K. De (1990) "Chapter 8. Thermoplastic elastomers from miscellaneous rubber-plastic blends" in Thermoplastic Elastomers from Rubber-Plastic Blends (Eds., S.K.De and A.K.Bhowmick)". Ellias Horwood Ltd., New York London Toronto Sydney Tokyo Singapore, pp. 233-263.

200. Santoprene product website http://www.santoprene.com/site/products/3308.html (accessed on 24 July 2004),

201. A.Y. Coran and R.P. Patel (1978) Elastoplastic compositions of butyl rubber and polyolefin resin, US 4138534 (to Monsanto co.).

202. A.Y Coran, R.P. Patel and D.Williams (1982) Rubber-thermoplastic compositions. Part v. Selecting polymers for thermoplastic vulcanizates, *Rubb. Chem. Technol.* 55. pp. 116.

203. Trefsin® 3201-85 W305 Thermoplastic Rubber, Advanced Elastomer Systems http://www.matweb.com/search/SpecificMaterialText.asp?bassnum=PADW55. (accessed on 3 March, 2007).

204. Zeotherm®. Thermoplastic vulcanisates with incredible heat and oil resistance, Zeon Chemical LP brochure, http://www.zeonchemicals.com/zeotherm.aspx (accessed on 5 April, 2007).

205. TPSiV™ , Dow Corning Company brochure, http://www.multibase.com/tpsiv.htm (accessed on 5 April, 2007).

206. Uniprene®. Unique TPVs providing the look and feel of rubber with the processing ease of TPOs, Texnor Apex Thermoplastic Elastomer Division brochure, http://www.teknorapex.com/ftp/TPE/Uniprene/UnipreneBrochure.pdf (accessed on 5 April 2007).

207. Thermoplastic Elastomers - Market Research, Market Share, Market Size, Sales, Demand Forecast, Market Leaders, Company Profiles, Industry Trends, Thermoplastic Elastomers to 2007, Freedonia group.

CHAPTER 3
EXPERIMENTAL

3.1 Materials

The main materials in the thermoplastic rubber vulcanisates employed in this research consist of an elastomer based on natural rubber (NR) and the thermoplastic, polypropylene (PP). Standard Malaysian Rubber grade that has Mooney ML 1+4 (100°C) viscosities of 60±5 (SMR CV60)[1-2] was chosen for its cleanliness and good-batch-to-batch reproducibility of viscosity. Commercial homopolymer polypropylene with low melt flow was chosen for a good fabrication processability through injection moulding and extrusion. The ingredients, functions and the name of suppliers of TPV raw materials are shown in Table 3.1.

In order to avoid any inconsistencies within and between compounds, the same bale of rubber was used throughout the investigation. In the early stages of the study, unvulcanised NR/PP blends and highly vulcanised NRTPVs based on NR/PP ratios of 60/40 and 70/30 were selected. The unvulcanised NR and PP blends were also based on NR/PP ratios of 60/40 and 70/30, and were coded NR60/PP40 blend and NR70/PP30 blend, respectively. The vulcanised NRTPVs were coded as NR60/PP40 TPV(HP) and NR70/PP30 TPV(HP), based on NR/PP ratios of 60/40 and 70/30, respectively. The HP refers to the relatively high concentration of peroxide level in the blends (0.36php). NRTPVs with NR/PP blend ratios of 70/30, 75/25 and 80/20, with low level of peroxide (and hence low level of crosslinking) were also investigated. The NRTPVs were coded as NR70/PP30 TPV(LP), NR75/PP25 TPV(LP) and NR80/PP20 TPV(LP). Table 3.2 shows the formulations of the NR/PP blends and TPVs mixed in this research.

Table 3.1 Ingredients of unvulcanised NR/PP blends and TPVs.

Ingredients	Function	Name of supplier
Natural Rubber, SMR CV 60	Elastomeric polymer	Malaysian Rubber Board, Malaysia
Polypropylene, Mosten 58.412 (MFI 3.5 g/10min, 230°C/2.16kg)	Thermoplastic polymer	Chemopetrol, Czech Republic
HVA-2 MB, *N,N'*-m-phenylenebismaleimide masterbatch in PP (1:2 ratio)	Co-agent	Teknor Apex Company, Pawtucket, Rhode Island, USA
DIPP, Di(tert-butyl peroxyisopropyl)benzene (98%)	Peroxide	Akzo Nobel, Polymer Chemicals, The Netherlands
ConoPure ™ 12P	Naphthenic process oil	SIP Ltd., London, UK
Irganox 1010, Tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane or Pentaerthrityl tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]	Antioxidant (polyolefins)	Akzo Nobel, Polymer Chemicals, The Netherlands
Flectol H, 1,2-dihydro-2,2, 4trimethylquinoline	Antioxidant	Akzo Nobel, Polymer Chemicals, The Netherlands
Arbestab Z, Zinc diisononyl dithiocarbamate	Antioxidant (thermoplastic)	Robinson Brothers

Table 3.2 Basic formulation of unvulcanised NR/PP blends and TPVs.

Blends Ingredients	Formulation parts per hundred polymer by weight (php)						
	Unvulcanised NR60/ PP40 blend	Unvulcanised NR70/ PP30 blend	NR60/PP40 TPV(HP)	NR70/PP30 TPV (HP)	NR70/PP30 TPV (LP)	NR75/PP25 TPV (LP)	NR80/PP20 TPV (LP)
Natural rubber	60	70	60	70	70	75	80
Polypropylene	40	30	25.94	25.27	25.27	19.93	14.59
HVA-2 MB	-	-	6.08	7.10	7.10	7.61	8.11
Peroxide *	-	-	0.36	0.36	0.036	0.036	0.036

* prepared as 10% solution in process oil

NRTPV with an NR/PP blend ratio of 75/25 was also prepared with an addition of process oil and antioxidants (plasticised NR75/PP25 TPV or coded as NR75/PP25 TPV, see Table 3.3). The blend ratios and an addition of process oil (plasticiser) were selected in order to produce soft TPV materials similar to commercial TPVs available in market. An NR compound was also prepared to correspond as closely as possible to the NR phase of the TPV. The NR compound formulation is shown in Table 3.3.

Table 3.3 Plasticised NR75/PP25 TPVs and NR compounds formulation.

	Formulation parts per hundred polymer by weight (php)	
	NR75/PP25 TPV	NR compound
Natural rubber	75	100
Polypropylene	25	
HVA-2 MB	7.65	
Irganox 1010	0.5	
Flectol H	0.5	
Peroxide (DIPP)	0.09**	0.09
Process oil	50.0	
Arbestab Z	1.0	

** prepared as 10% solution in process oil

3.2 Preparation of thermoplastic vulcanisates and unvulcanised blends

The TPVs and blends shown in Table 3.2 were prepared in a Brabender Plasticorder 2000-6 with a capacity of 390 ml. Before blending the Brabender mixing chamber was warmed to 150°C±10°C by mixing a 275 g sample of PP. A starting temperature of 145°C±5°C and a rotor speed of 100 rpm (revolutions per minute) was applied to all mixes. The melt mixing was carried out for 5 minutes. The peroxide, used as the crosslinking agent, was first dissolved in process oil in order to prevent premature crosslinking and to achieve a better dispersion of the curative in the compound. The peroxide was prepared by dissolving a 2 g of peroxide in 18 g of process oil. The mixture was allowed to dissolve by warming in an air oven at a temperature of 40°C±5°C. The mixing cycle adopted in preparing the TPV materials shown in Table 3.2 are summarised below.

0 min. - Add polymers, co-agent, peroxide
5 min. - Discharge

The NR/PP blends shown in Table 3.2 were prepared without addition of co-agent and peroxide in the formulation. The blends was mixed for 3 minutes.

The TPV formulation shown in Table 3.3 was mixed in a 00C Banbury with a capacity of 4300ml and a starting rotor speed of 70 rpm (fill factor 0.86). The mixing cycle and conditions are summarised as below.

0 min - Add polymers, co-agent, peroxide and antioxidant
At 150°C - Add 1/3 of process oil
After dynamic vulcanisation** - Add 1/6 of process oil (with Arbestab Z)
- Add 1/6 of process oil in each of 3 steps

* see section 2.2 for explanation of dynamic vulcanisation

Rubber compound was prepared by mixing on a Bridge two-roll mill (12″ x 6″) at 70°C±5°C by having the rolls rotating at uneven speed with ratio 1:1.4 and at the back roll rotating at 31rev/min. The natural rubber was masticated and mixed with addition of peroxide. The mixing was completed after about 15 minutes.

3.3 Preparation of test specimens

Immediately after mixing, the NR/PP and TPV blends were sheeted on a Bridge two-roll mill (12″ x 6″) at 70°C±5°C, while the compound was still hot, and then allowed to cool in the form of a 2 - 4 mm thick slab. The sheets were cut into smaller pieces and granulated by using a Blackfriars small granulator (junior rotary cutter no. 51/38). The granules were dried for about 2 hours at 80°C in air oven, and then injection moulded or extruded.

3.3.1 Injection moulding

Granules of thermoplastic vulcanisates and unvulcanised blends were moulded using an Arburg 220-90-350 Injection Moulding machine. The conditions adopted for the moulded samples of 2 mm thick sheets and 6 mm thick plaques are as shown in Table 3.4.

Table 3.4 Injection moulding conditions with the Arbug 22- 90-350 machine.

	2 mm (unvulcanised)	2 mm (vulcanised)	6 mm (vulcanised)
Barrel temperatures,			
Rear (feed) end	170°C±5°C	170°C±5°C	170°C±5°C
Centre zone	180°C±5°C	180°C±5°C	180°C±5°C
Front zone	190°C±5°C	190°C±5°C	190°C±5°C
Nozzle	190°C±5°C	190°C±5°C	190°C±5°C
Back pressure, p5, bar	40	60	60
Screw speed, v5, rpm	80	80	80
Mould dimensions, mm	112.5 x 112.5 x 2	112.5 x 112.5 x 2	110 x 60 x 6
Mould volume, cm^3	25	25	39.37
Mould temperature, °C	30 – 60	30 – 60	30 – 60
Speed, Volume in % of max			
1st Clamp closing speed, v1	70	50	50
2nd Clamp closing speed, v2	30	30	30
1st Injection speed, v3	70	70	70
2nd Injection speed, v4	60	60	60
1st Clamp opening speed, v6	60	70	70
2nd Clamp opening speed, v7	20	20	20
Pressure in % of line pressure			
1st Injection pressure stage, p2	51-54	27-35	34-37
2nd Injection pressure stage, p3	50-53	24-33	29-34
3rd Injection pressure stage, p4	49-51	19-23	25-27
Cycle times : Limit time for mould protection,	Seconds	Seconds	Seconds
Clamp unit close time, t7	2.0	2.0	2.0
Injection delay; to start screw forward, t8	1.0	1.0	1.0
1st injection pressure time, t2	2.6	2.2	1.2
2nd injection pressure time, t3	2.4	2.4	3.4
3rd injection pressure time, t4	2.2	1.2	2.2
Cooling time , t5	4.5	3.5	2.5
Clamp unit open time, t6	1.5	1.5	1.5
Total	15.2	13.8	13.8

3.3.2 Extrusion

Granules of TPV were processed using a single screw 20 mm Baughan extruder 25:1 LD, to extrude tape of profile 10 mm x 2 mm. The extrusion conditions were stated in Table 3.5.

Table 3.5 Extrusion conditions with the Baughan 20 mm extruder for a 10 mm x 2 mm thick profile.

Screw speed	-	60 rpm
Feed zone	-	170°C±5°C
Transfer zone	-	180°C±5°C
Metering zone	-	190°C±5°C
Die	-	190°C±5°C

The basic physical properties of the extrudates were compared with injection moulded sheets.

3.3.3 Compression moulding

The NR compound sheets were prepared by compression moulding by using a Bradley and Turton hot press (9″ x 9″ platen) at a temperature of 100°C±5°C for 15 minutes. Then the hot platen was transferred to a Dixon and Letchworth electrical press (14″ x 14″ platen) at a temperature of 190°C±5°C for 10 minutes. The cure times chosen was based on a t_{90} value of Rheometer MDR 2000 curemeter at 190°C (approximately 3 times half-life of DIPP at 190°C). Dumb-bell test pieces were cut from the moulded sheets for tensile and cyclic stress-strain test.

3.4 Sample preparation for morphological characterisation

3.4.1 Thin sections from injection moulded sheet

Scanning [transmission] electron microscopy (S[T]EM) was used to observe phase morphology of thermoplastic/rubber blends. The orientation of phases in the injection moulded sheets of unvulcanised NR70/PP30 blend and NR70/PP30 TPV (HP) were studied in two regions, 1 and 2 (Figure 3.1a).

Two sections were cut from region 1. First, samples were cut from the sheet in order to have sections that orientated in the plane of YZ (parallel to the direction of flow). Second, samples were cut from the sheet in order to have sections in the plane of flow (XZ plane) (Figure 3.1a and 3.1b). Two types of sample were cut from XZ plane, near a surface of the injection moulded sheet and deeper into the sheet. In region 2, samples were cut from the sheet in order to have sections that orientated in the XY plane (perpendicular to the direction of flow).

The preparation of S[T]EM samples involved the preparation of a thin film of the material less than 150 nm thick. Sections of the NR70/PP30 TPV (HP) and NR70/PP30 blend were cut using a RMC MT7000 ultra-microtome with a 45° glass knife, equipped with a liquid nitrogen cooling system at a temperature of approximately −110°C. Then, the cut NR70/PP30 TPV (HP) sections were collected with the aid of ethanol and mounted onto nickel grids. However, the sections of unvulcanised materials such as unvulcanised NR70/PP30 blend are sensitive to water. Therefore cyro-ultramicrotomy of these materials were carried out under dry condition and no liquids were used to collect the sections. The thin sections were allowed to warm to room temperature in dry conditions under a stream of nitrogen gas. Then, the sections were stained in osmium tetroxide (OsO_4) vapour in a fume cupboard for one hour. Later, the sections were observed in a Hitachi S2700 scanning electron microscope.

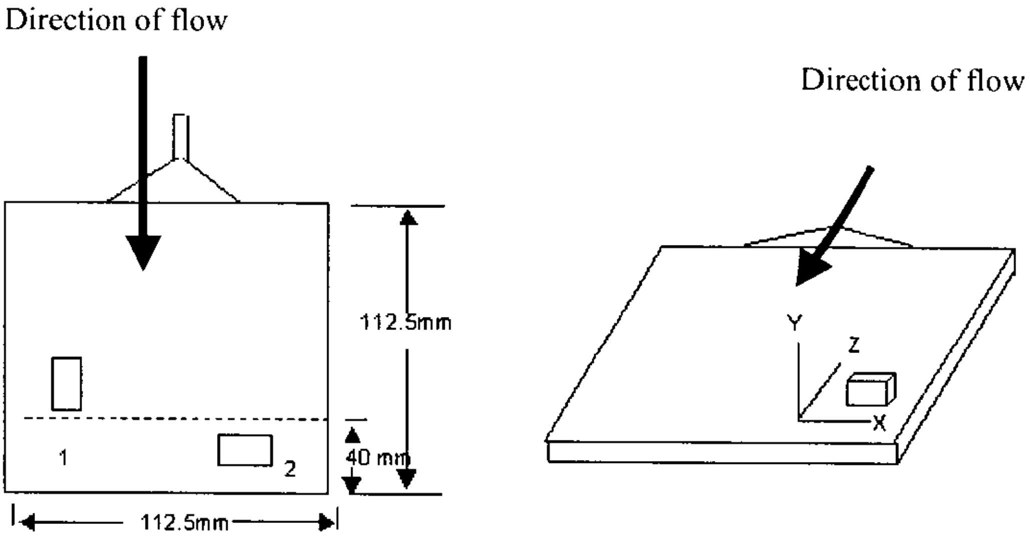


Figure 3.1 (a) Plan view of injection moulded sheet and (b) Three-dimensional view of injection moulded sheet.

3.4.2 Partial extraction of natural rubber (NR)

Extraction of NR from unvulcanised NR60/PP40 blends for scanning electron microscopy (SEM) study was done in a similar manner to that described in 3.4.1. The sample used was approximately (50 x 15 x 2) mm in size and weighting about 1.5g cut from an injection moulded sheet as seen in Figure 3.2. A gentle extraction was performed using tetrahydrofuran (THF) over a period of 180 hrs.

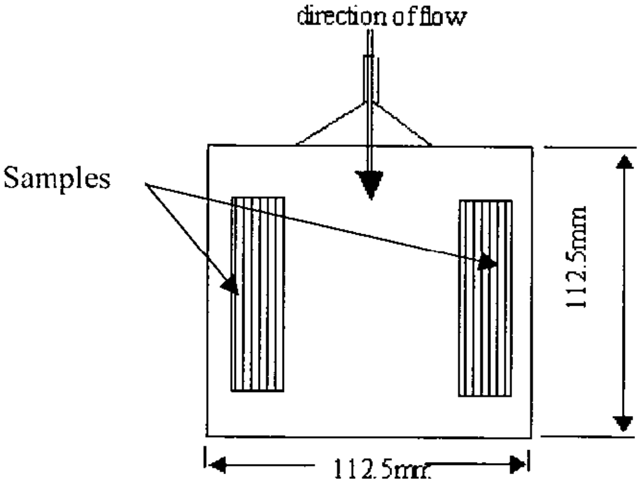


Figure 3.2 Sample for extraction of unvulcanised NR60/PP40 blend.

The "fresh surfaces" of extracted samples were prepared by peeling apart several layers of the sample in order to provide newly exposed surfaces for subsequent S[T]EM analysis.

3.4.3 Etching with chromic acid

Etched NR75/PP25 TPV samples were prepared by exposing the injection moulded or extruded samples to chromic acid (98% concentration) at room temperature in a fume cupboard. The samples were cut from injection moulded sheets or extruded strip approximately (50 x 10 x 2) mm in size. Then the samples were brushed with, or soaked in chromic acid for between 2 to 6 hours. A fresh chromic acid was used for every one hour until the process was completed. The completely etched samples were washed under warm running water at temperature of about 35°C±5°C for about 3 hours and then dried in an air oven overnight at temperature of 40°C±5°C. The dried samples were then examined by SEM.

3.4.4 Sample preparation for scanning electron microscopy

The preparation of SEM samples involved cutting of cross-sections through the samples with a fresh razor blade and mounting on an SEM stub.

The fracture surface or etched test pieces were taken from selected dumb-bell fracture or etched samples. Then the samples were mounted on the SEM stub. The samples were then coated with a layer of evaporated carbon (to prevent them charging up in the electron beam) and examined by SEM.

3.5 Morphological characterisation

Scanning Transmission Electron Microscopy (S[T]EM) is a technique that allows imaging thicker of sections and is a relatively rapid technique for observing phase morphology at a medium resolution[3]. The morphological study of TPVs was carried out using a standard Hitachi S-2700 scanning electron microscope

(SEM) with specially fabricated mounts that can perform in scanning/transmission mode[4].

3.6 Solvent extraction

Extraction of individual phases from blends and TPVs was used to investigate morphology, particularly whether the remaining phase after extraction was continuous or discrete. Extraction of polypropylene or unvulcanised NR was performed using a soxhlet reflux apparatus as shown in Figure 3.3.

3.6.1 Extraction of unvulcanised rubber

Extraction of NR from unvulcanised NR/PP blends was achieved by refluxing solvent using a modified soxhlet extraction procedure. Typically, the sample used was approximately (10 x 10 x 2) mm in size and weighing about 0.2g, cut from an injection moulded sheet. The sample was placed in an aluminium gauze basket (10mesh) suspended by wire from the condenser so that the basket was located in a region of refluxing solvent vapour (1). For a period of 72 hours, condensed hot solvent (2) was directed to flow down the wire (3) to the suspended mesh basket and wash over the swollen sample, thus dissolving and extracting material. The dissolved material was then carried away by the solvent to the solvent receiving flask (4). It should be noted that it was important to prevent drips of condensed solvent from dripping directly on the sample which, when highly swollen in hot solvent, was very fragile and easy eroded. Extraction was performed using a number of different solvents; ethyl acetate, chloroform, cyclohexanone and toluene, the latter being the most effective.

3.6.2 Extraction of polypropylene

Extraction of PP from TPV material was achieved in a similar manner to that described for the extraction of unvulcanised rubber from unvulcanised NR/PP blends. However, the extraction was performed using xylene for a period of 2 hours.

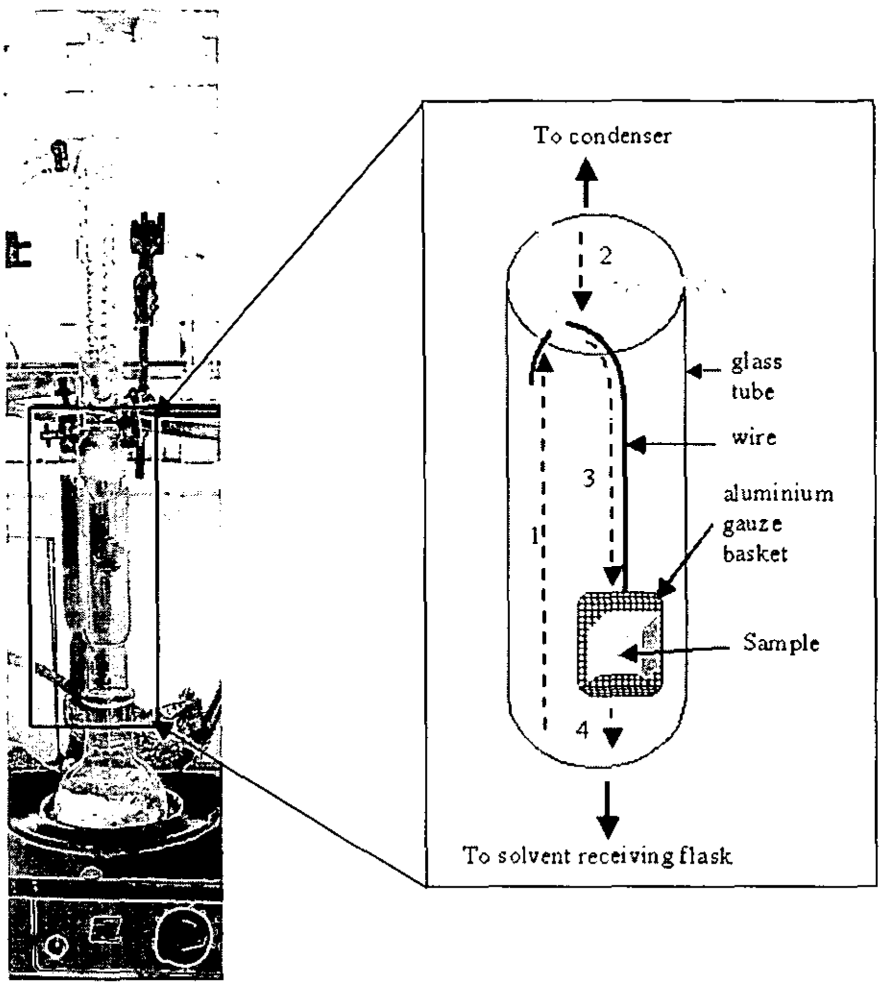


Figure 3.3 Soxhlet reflux apparatus.

3.7 Physical/mechanical properties

3.7.1 Hardness (ASTM 2240)[5]

Hardness is a simple, inexpensive and fast test used to identify the relative stiffness of elastomeric materials used throughout the rubber industry. Hardness measures the resistance to deformation when a force is applied to a rigid indentor. This gives a rough measurement of the modulus of the materials at a small deformation (strain)[6]. Although the measurement may not relate well to end product applications, it is a quick and simple method of detecting differences in cured compound properties.

Hardness values obtained can be Shore A and D type or international rubber hardness degrees (IRHD). The Shore A scale corresponds approximately to the IRHD scale and the Shore D scale can conveniently be used for hard rubber above about 90 IRHD[7].

In this study, the hardness test was carried out using a modified durometer Shore A and tested according to ASTM 2240 for determining indentation hardness of materials including thermoplastic elastomers. A triple ply of 2 mm sheets was first placed on a hard flat surface. The indentor for the instrument was then pressed into the sheet making sure that it was parallel to the surface. Each measurement was recorded after 5 seconds of firm contact with the specimen at a temperature of 23°C±2°C.

3.7.2 **Tensile stress-strain** (BS 903:Part A2:1995 ISO 37:1994)[8]

Tensile tests are one of the most commonly performed tests to measure strength and stiffness of polymer materials. Figure 3.4 shows a standard dumb-bell test piece.

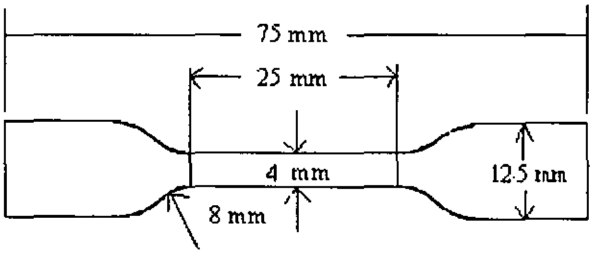


Figure 3.4 Dumb-bell test pieces (Type 2).

Tensile properties of an injection moulded sheet can be strongly affected the flow orientation of the sample. For this reason, samples were cut at right angles to each other with respect to the main direction of flow. The samples referred to as parallel (||) were cut parallel to the main direction of flow. The samples referred to as perpendicular (⊥) were cut perpendicular to the main direction of flow (Figure 3.5). For extrudate tape, samples were cut parallel to the main direction of flow only, because the strip was too narrow for perpendicular samples to be cut. The extrudate was tested as a comparison with injection moulded test pieces.

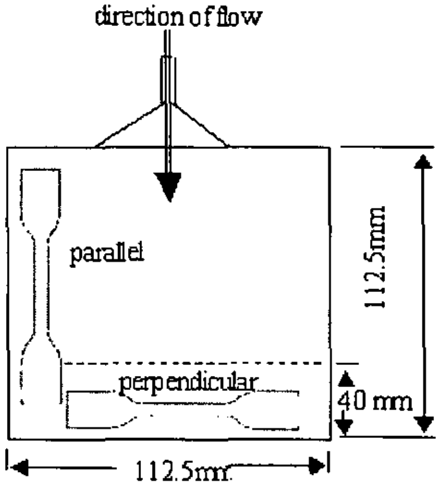


Figure 3.5 Parallel and perpendicular from main direction of flow of dumb-bell test pieces.

In a tensile test a standard dumb-bell type test piece of known cross-sectional area is stretched until it breaks. The force is recorded and then converted to stress by dividing by the unstrained cross-sectional area of the gauge length. The length of a gauged portion of uniform cross-section is also recorded as the original length. Increase in length of the gauged portion during testing is measured and converted to percent elongation by dividing by the original length and multiplying by one hundred. Elongation at break is defined as the % elongation at breaking point. The modulus is used as a measure of the stiffness[9]. The modulus is measured as the stress required to extend the rubber by a stated percentage of its original length, for example, 100% modulus is the stress at 100% elongation.

All tensile testing was performed at a strain rate of 500 mm/min unless stated. In addition, some materials were also tested at 20 mm/min and PP was also tested at strain rates of 5 mm/min and 50 mm/min.

Annealing was carried out on selected samples in order to see the effect of crystallinity on TPV materials. Dumb-bell samples were exposed to the temperature of 150°C±5°C (polypropylene softening point) for 30 minutes, and then slowly cooled to room temperature at rate of 0.6°C/min. The samples were conditioned at least 16 hours at the testing temperature (23°C±2°C) before being tested.

3.7.3 Compression set (ISO 815:1991)[E][10]

Recovery behaviour of NR75/PP25 TPV, Santoprene™ 101-55 and Sarlink® 3160B is measured by compression set. Compression set is the permanent deformation remaining after release of compressive stress. Compression set is expressed as a percentage of the original deflection. The compression set value is measure according to the equation 3.1.

$$\text{Compression set, \%} = \left[\frac{t_o - t_i}{t_o - t_n}\right] \times 100 \qquad (3.1)$$

where

t_o is the original thickness of the cylindrical disk, mm

t_i is the final thickness of the cylindrical disk, mm

t_n is the thickness of the space bars used between the supporting plate, mm

Test pieces used comprised of a cylindrical disks cut from a plaque of the testing material. The cylindrical disk used for testing are a 13.0 mm +/- 0. 2mm in diameter and 6.0 mm +/- 0.2 mm in thickness. A cylindrical disks were cut from eight different areas; A to H (Figure 3.9) of 6mm plaque in order to check a reproducibility of the compression set value.

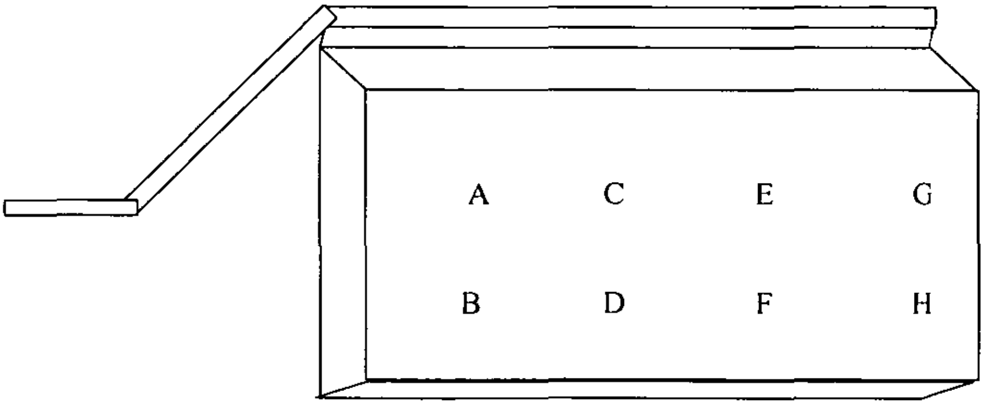


Figure 3.6 Six mm plaque for compression test disk.

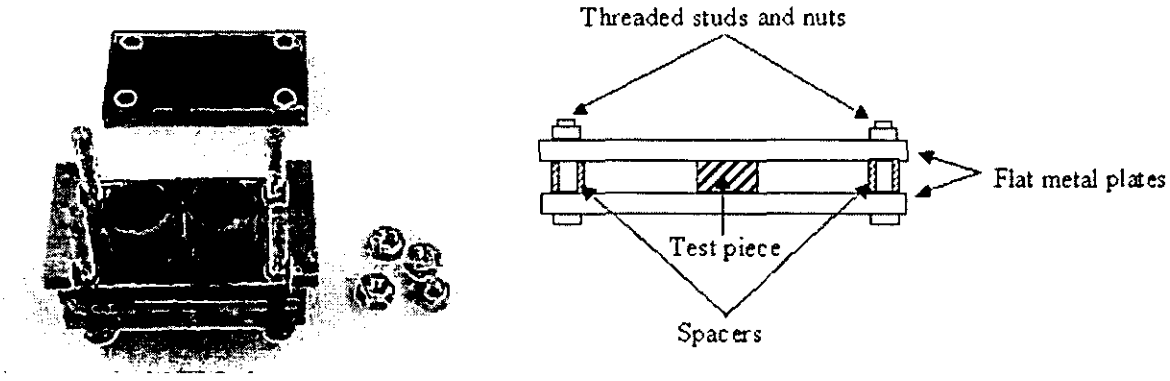


Figure 3.7 Compression set apparatus.

Compression set was measured using TARRC internal compression set apparatus. The apparatus and test-piece are shown schematically in Figure 3.7. The original thickness of each original specimen was measured. Several test pieces were then placed between the spacers in the compression device. The test pieces were compressed to 25% of their original height, using spacers to accurately set the compression. Within two hours of assembly, the compression apparatus placed in an oven at a specified temperature as shown in Table 3.7. After removing the apparatus from the oven, the test pieces were removed from the apparatus and allowed to cool for 30 minutes before measuring their final thickness (t_i). Median values of five measurements were recorded.

Table 3.6 Compression set test conditions.

Duration time	Temperatures, °C		
	23°C	70°C	100°C
24hs	√	√	√
170hrs	√	√	√

3.7.4 Tension set (ISO 2285: 1988)[11]

Tension set is a quick test to identify recovery properties of materials. It is measured as the remaining strain after a material has been stretched and allowed to retract. Figure 3.8 shows a standard tension set test piece according to ISO 2285:1988.

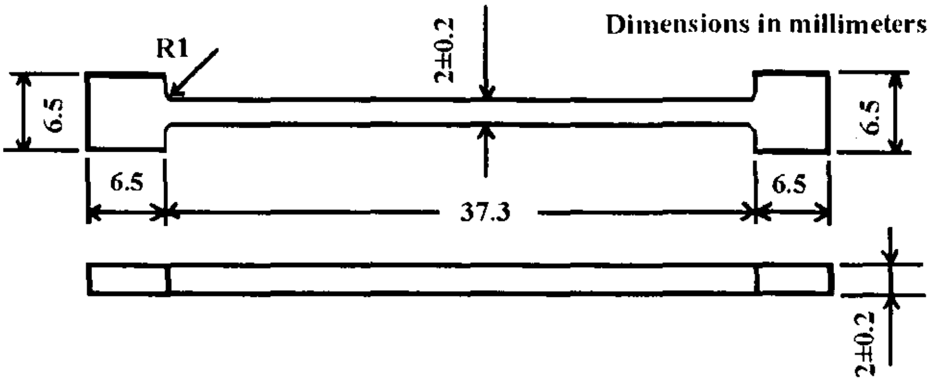


Figure 3.8 Tension set test piece.

Test tension set value is measure according to the equation 3.2.

$$\text{Tension set,\%} = \left[\frac{L_l - L_o}{L_s - L_o}\right] \times 100 \tag{3.2}$$

where

L_o is the original unstrained reference length, mm

L_s is the strained reference length, mm

L_l is the reference length after recovery, mm

Tension set was measured using a Wallace tension set apparatus. Sets of samples were cut from injection moulded sheets, parallel and perpendicular to the main direction of flow. The extrudate was cut parallel to the extrusion direction. Test pieces were extended to 100% elongation at a temperature of 23°C±2°C and at a rate of 5mm/second. The samples were held at 100% elongation for 10 minutes and then the sample removed from the apparatus and allowed to relax for 10 minutes. After relaxation, the length was measured (Ls). Median values of five measurements were recorded.

3.7.5 Recovery

Short term recovery behaviour of bulk PP, NR compound, NR75/PP25 TPV, Santoprene™ 101-55 and Sarlink® 3160B were studied by measuring the changing in length with time of 'bongo' test pieces. Three samples for each materials were tested and all test results of the same materials showed good reproducibility. For comparison purposes, for each material, a median value was selected in each case to represent all the tested samples. All results reported in this section were tested stretching parallel to the main direction of flow of 2mm injection moulded sheets. Figure 3.9 shows a 'bongo' test piece used in the recovery and cyclic tensile stress-strain test. 'Bongo' test pieces of injection moulded sheets was strained at strain rate of 500mm/min up to 30% extension. After the sample reached 30% extension, the sample is released and its 'set' was measured. The change in length with time due to set was recorded for 15 days.

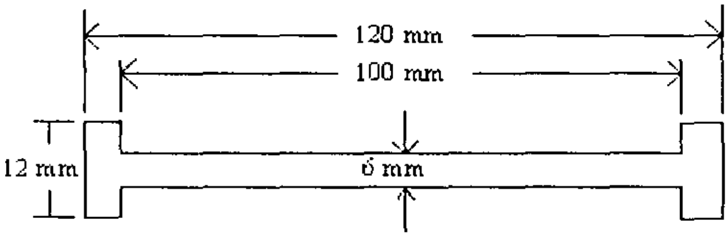


Figure 3.9 'Bongo' test pieces.

The set is calculated according to the following equation :

$$\text{'Set', \%} = \left[\frac{hr - h_o}{h_o}\right] \times 100 \tag{3.3}$$

where

hr is a length of the sample after 30% of strain

h_o is initial length of the sample

3.7.6 Cyclic tensile stress-strain

Cyclic tensile stress-strain is one of the techniques to measure a deformation and recovery behaviour. In cyclic tensile stress-strain tests, the deformation and recovery behaviour of bulk PP, NR compound, NR75/PP25 TPV, Santoprene™ 101-55 and Sarlink® 3160B were compared using an Instron 5500R with Merlin cyclic loading software at a temperature of 23°C±2°C.

The 'Bongo' test pieces (Figure 3.9) were strained from an initial length of 100 mm at a rate of 500 mm/min up to 60% strain, then the strain was reversed at the same strain rate, until zero strain was reached. The cycle was repeated for another four cycles. Three samples cut from injection moulded sheets, parallel and perpendicular to the main direction of flow were tested.

The cyclic tensile stress-strain was also performed on THF extracted sample. The 'Bongo' test pieces were cut from THF extracted sample and strained from an initial length of 50 mm at a strain rate of 20 mm/min up to 15% strain, then the strain was reversed at the same strain rate, until zero strain was reached. The cycle was repeated for another four cycles.

3.7.6.1 Pre-strain

The 2mm extrude strips were strained from an initial length of 250 mm at a strain rate of 500 mm/min up to 100% strain, then the strain was released, until zero strain was reached. 'Bongo' test pieces were cut from the strips and cyclic tensile stress-strain was tested according to the required recovery time.

3.7.6.2 Cyclic behaviour with increasing amplitude

The effect of pre-strain and progressive increasing strain was performed in NR75/PP25 TPV and Sarlink® 3160B TPV materials. The effect of progressive increasing strain were studied at a strain rate of 20 mm/min and the sample was strained sequentially from 0% to 10%, 0% to 40%, 0% to 60%, 0% to 80% and 0% to 100% extension.

3.7.6.3 Relaxation time

Three ‘bongo’ test pieces cut from strained extrude strip was tested to see the effect of relaxation time on recovery behaviour. The ‘bongo’ test pieces was strained from an initial length of 100 mm at a strain rate of 20 mm/min or 500 mm/min up to 5% or 100% or 200% strain, and then the strain was reversed at the same strain rate, until zero strain was reached. The cyclic tensile stress-strain was also carried out after relaxation time of 30 minutes, 24 hours, 7 days, 14 days and 4 months.

References

1. Viscosity-stabilised Standard Malaysian Rubbers(1970) SMR Bulletin No.8. Rubber Research Institute of Malaya.

2. Natural rubber technical information sheet D61(1979). The Malaysian Rubber Producers' Research Association, Tun Abdul Razak Laboratory.

3. P. Cudby (1988) " Chapter 3. Characterization of vulcanised blends by microscopy" in "Blends of Natural Rubber. Novel Techniques for Blending with Speciality Polymers (Eds. A.J. Tinker and K.J. Jones, 1st ed)". Chapman & Hall, London.

4. P. Cudby and B.A. Gilbey (1995) Scanning transmission imaging of elastomer blends using an unmodified conventional scanning electron microscope, *Rubb. Chem Technol.* **68**, pp. 342-350.

5. ASTM D 2240-03(2003) Standard test method for rubber Pproperty – Durometer hardness, Annual Book of ASTM Standards, Vol. 09.01. American Society for Testing and Materials, West Conshohocken, PA.

6. L.R.G. Treloar(1975) "The Physics of Rubber Elasticity, 3rd edition". Clarendon press, Oxford.

7. R.P.Brown (1986) "Chapter 3. Short-term stress and strain properties" in Physical Testing of Rubber, 2nd. ed.". Elsevier Applied Science Publishers Ltd., London and New York.

8. BS 903:Part A2:1995 ISO 37 : 1994 (1995) Physical testing of rubber. Part A2. Method for determination of tensile stress-strain properties, BSI standard.

9. R. Houwink (1948) "Chapter 6. Mechanical properties" in Elastomers and Plastomers, their Chemistry, Physics and Technology, Vol. 3 Testing and

Analysis: Tabulation of Properties. Elsevier Publishing Co. Inc,. New York Amsterdam London Brussels.

10. ISO 815:1991(E) (1991) Rubber, vulcanised or thermoplastic – Determination of compression set at ambient, elevated or low temperatures 3rd. ed.. International Organization for standardization.

11. ISO 2285:1988 (1988) Rubber, vulcanised or thermoplastic – Determination of tension set at normal and high temperatures 3rd. ed.. International organization for standardization.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter brings together all the results from the practical work described in chapter 3. It is divided into sections: sample preparation, morphology characterisation and deformation behaviour.

4.1 Sample preparation of unvulcanised blends and TPVs

4.1.1 Melt-mixing

The unvulcanised NR/PP blends and TPVs based on NR (LP and HP) were prepared without addition of filler and process oil (except for a small amount in the peroxide solution). This basic formulation was applied in order to produce as simple a system as possible. The purpose was to eliminate the effect of other additives normally found in TPVs to enable behaviour of the materials to be characterised in terms of the NR and PP phases and the interactions between them. By contrast, the NR75/PP25 TPV was prepared with addition of process oil and antioxidants to produce a soft, easily processed material like the commercially available TPVs; Santoprene™ 101-55 TPV and Sarlink® 3160B TPV.

The mixing procedure is a critical part of the preparation of TPV materials. The materials described here were prepared in an internal mixer (refer to Section 3.2). Typical mixing torque and batch temperature curves for the unvulcanised NR/PP blends and NR/PP TPVs are shown in Figures 4.1 to 4.3. The curves were plotted based on the original value.

Figure 4.1 shows the variation of mixing torque and batch temperature curves during melt-mixing of the unvulcanised NR/PP blend in the Brabender Plasticorder PL2006 internal mixer. The mixing process can be divided into stages as follows:

against the rotors. Following this initial peak there is a decrease in torque and an increase in temperature. The rubber and PP are warmed by the mixing chamber reducing the viscosity of the NR. The shearing of the NR in particular will also result in mastication and shear heating that results in a further decrease in viscosity and hence, torque. The temperature is lower than the melting point of PP, so that it behaves more as a filler in the NR, contributing to a relatively high viscosity of the mixture and hence, the relatively high torque measured in this stage.

B. The relatively rapid decrease in torque in this stage is due to melting of the PP which is then blended into the NR, resulting in a relatively low viscosity blend. The temperature increase is very slow in this stage, partly due to the heat absorbed in the melting of the PP.

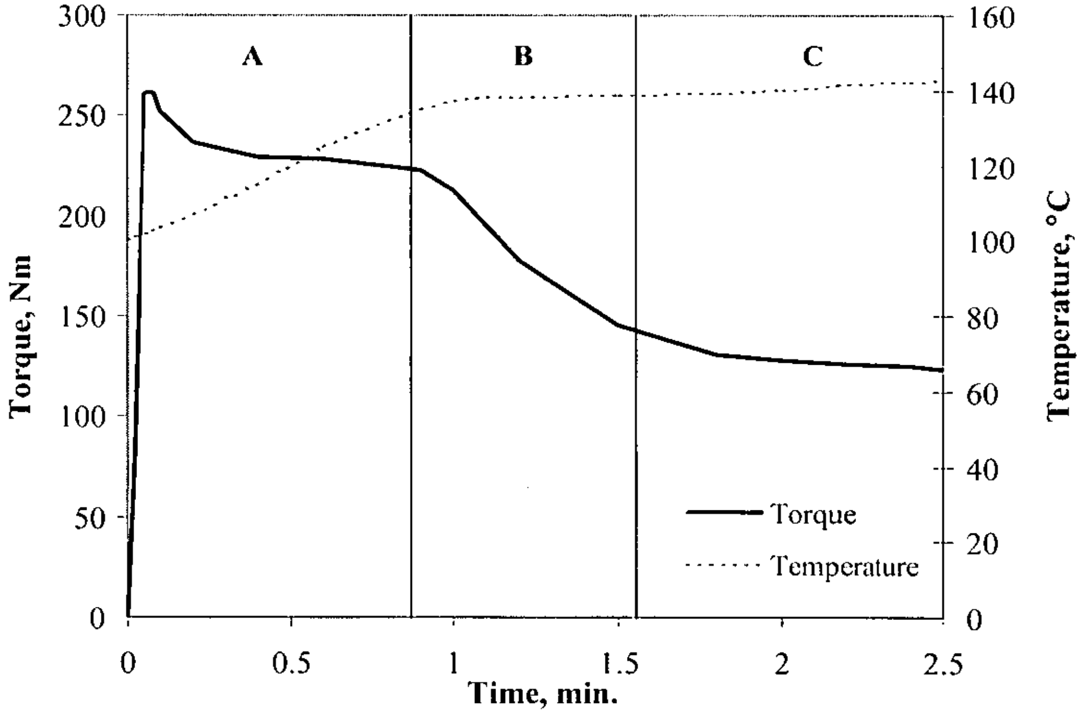


Figure 4.1 Variation of mixing torque and batch temperature with mixing time of unvulcanised NR60/PP40 blend in the Brabender Plasticorder.

C. After 1.5 minutes mixing, the torque decreases only slightly and the temperature rises only very slowly because the low viscosity of the blend will not result in much shear heating. The mixing was stopped after 2.5 minutes where the torque levelled off that indicating that the mixing was stabilised.

Figure 4.2 shows the typical torque and temperature curves during melt-mixing of NR/PP TPV in Brabender Plasticorder PL 2006 internal mixer. The stages of the mixing processes are described below :

Stages A and B are similar to those observed for the unvulcanised blends (Figure 4.1)

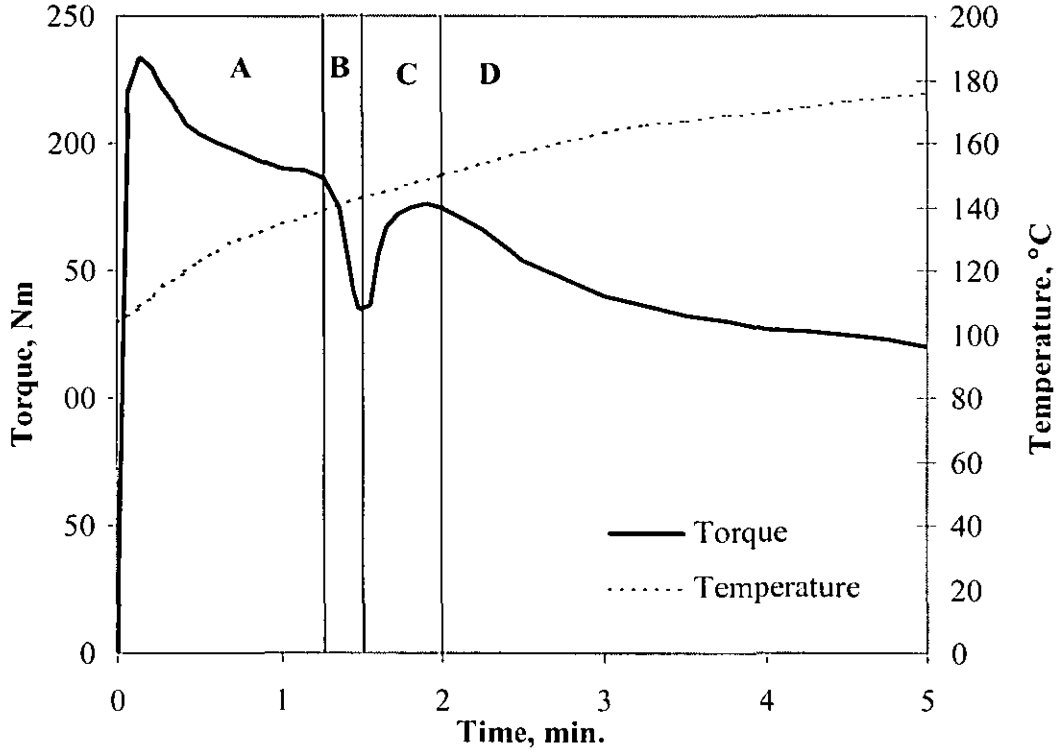


Figure 4.2 Variation of mixing torque and batch temperature with mixing time of NR60/PP40 TPV in the Brabender Plasticorder.

C. After 1.5 minutes mixing, there was a substantial increase in torque with increasing mixing time. This is due to dynamic vulcanisation inside the rubber phase leading to greater resistance to rotor rotation. The dynamic vulcanisation peak immediately follows the dip in torque due to melting of the PP, suggesting that at this temperature the decomposition of the peroxide occurs at a sufficiently high rate to cause substantial crosslinking in the NR.

D. There is a slight decrease in torque in this stage suggesting that the dynamic vulcanisation is complete. Shear heating alone could be responsible for the continued temperature rise and consequent decrease in torque. Mixing was stopped after 5 min. when it was clear from the mixing traces that the dynamic vulcanisation and blending processes were complete.

Figure 4.3 shows the typical torque and temperature curves during melt-mixing of the plasticised NR75/PP25 TPV or stated as NR75/PP25 TPV in a 00C Banbury internal mixer. The stages of the mixing processes are described below:

A. This stage is similar to those described previously except that a third of the process oil was added when the mixing temperature reached 150°C, in order to control the temperature and to prevent degradation of NR during the mixing. The addition of oil causes a dramatic decrease in torque and temperature. The decrease in torque is initially due to slippage but once the oil is incorporated into the rubber the torque rises sharply again. The temperature continues to rise due to shear heating until the melt temperature of the PP is reached.

B. The dip in torque due to melting of the PP is observed in the Banbury as in the Plasticorder, although it happens at a higher temperature (about 167°C). This may be due to differences in temperature distribution within the batch in the different mixers.

C. An increase in torque due to dynamic vulcanisation is observed as for the TPV mixed in the Plasticorder.

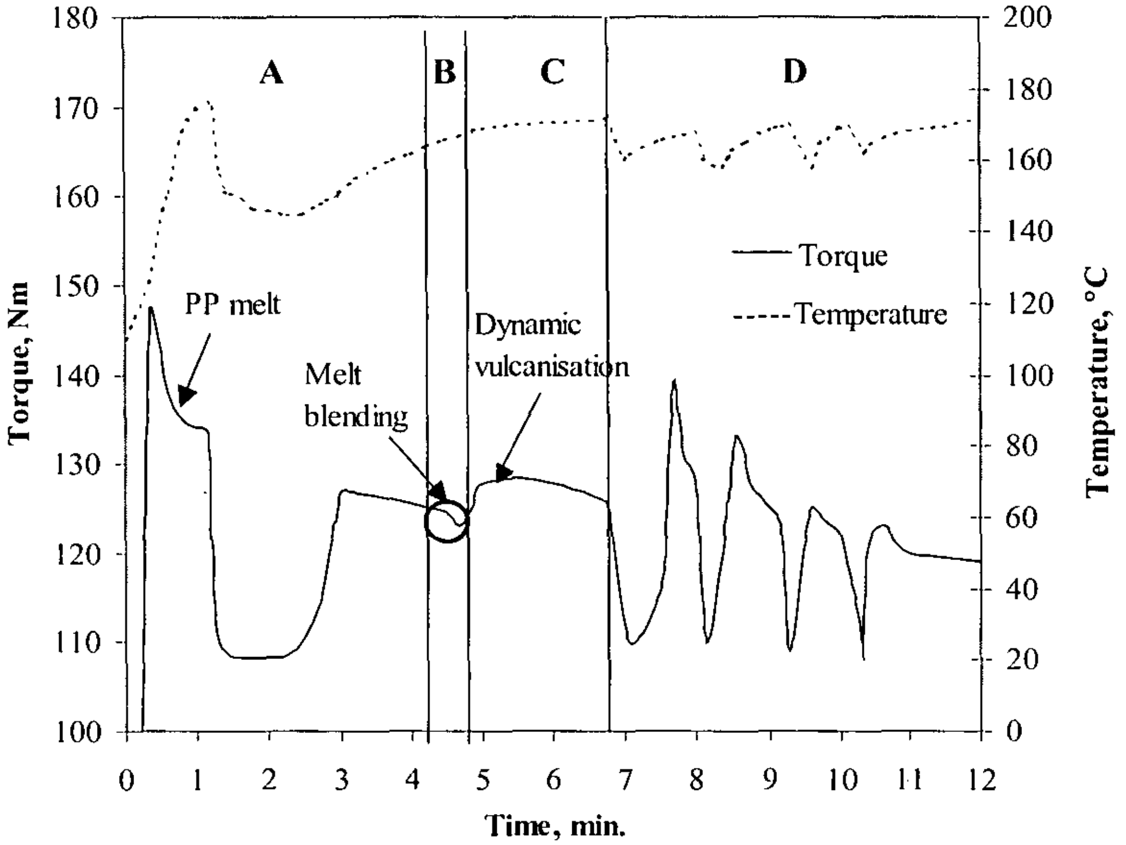


Figure 4.3 Variation of mixing toque and batch temperature with mixing time of NR75/PP25 TPV in the 00C Banbury.

D. After the dynamic vulcanisation was complete, 1/6 of the process oil with antioxidant (Arbestab Z) was added. Then, the remaining process oil was added in 3 steps to cool the materials and avoid NR and PP degradation while ensuring the material was well-mixed. During the addition of process oil, the torque initially decreases due to slippage but then increases to a higher level than that observed at the end of stage C. The increase in torque following oil addition seems surprising but is presumably due to an increase in viscosity due to the decrease in batch temperature. With further oil addition the torque gradually decreases, due to reduction in viscosity and the temperature tends to level out. As the torque deceases to a stable level it is assumed that the mixing was complete.

4.1.2 Sample preparation

The NR/PP TPV (HP) materials produced had a high viscosity and required a high injection pressure to be injection moulded. On the other hand, the unvulcanised NR/PP blends were very low viscosity and also slightly sticky, making them difficult to injection mould. The unvulcanised blends were liable to distortion due to non-uniform shrinkage[1] and had an uneven surface, which also slightly reduced the accuracy of measurements such as hardness and thickness. The NR75/PP25 TPV and commercial TPV materials were intermediate in viscosity between the NR/PP TPV (HP) and unvulcanised blends and so were much easier to injection mould and extrude.

The extruded NR75/PP25 TPV had a smooth surface finish showing that the addition of plasticiser improved the processing characteristics of the TPV significantly.

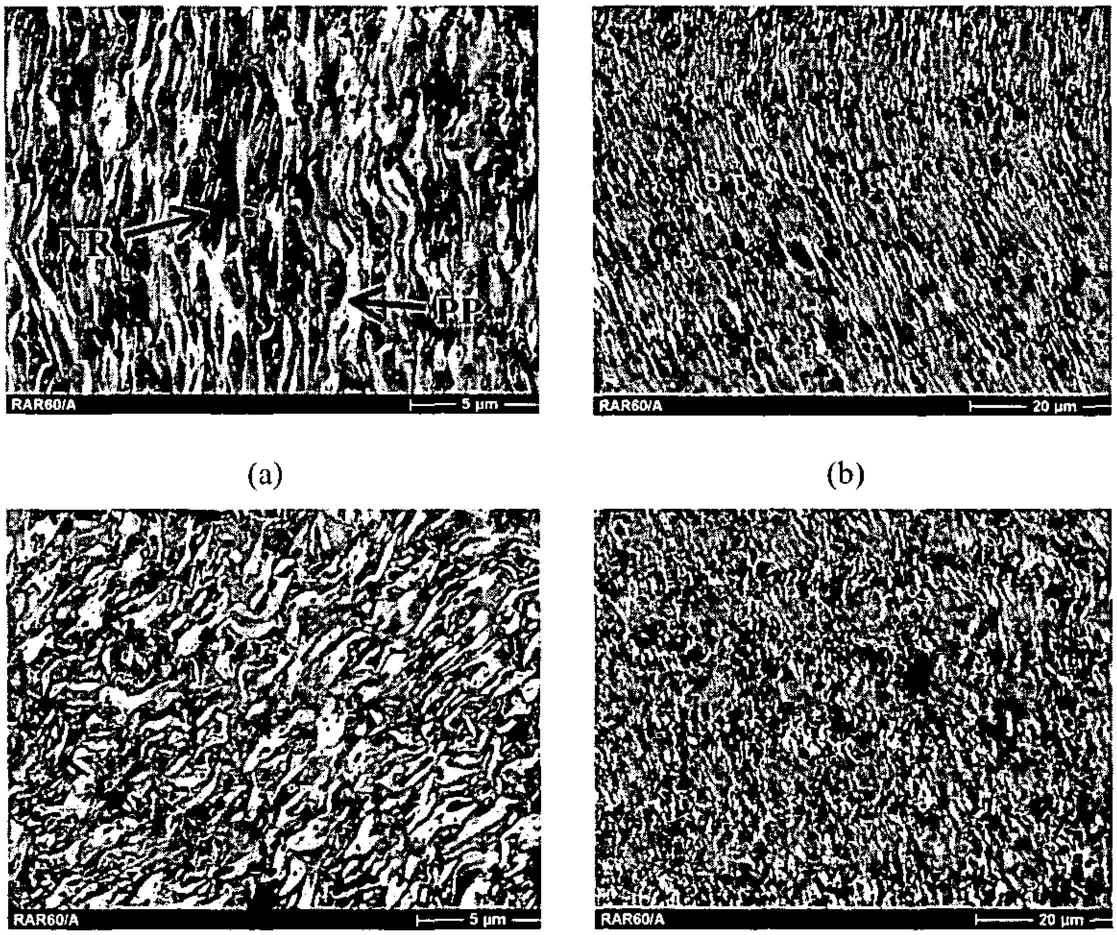
4.2 Characterisation of phase morphology of unvulcanised and vulcanised blends

The phase morphology of unvulcanised NR/PP blends and TPVs was investigated by S[T]EM and SEM. Both NR and PP phases can be identified in micrographs produced using these techniques but experience is needed to analyse and to interpret fully what is observed. In this study the unvulcanised NR70/PP30 blend, NR70/PP30 TPV(HP) and NR75/PP25 TPV were selected for examination.

4.2.1 Phase morphology of the unvulcanised NR70/PP30 blend

The phase morphology of unvulcanised NR70/PP30 and NR70/PP30 TPV (HP) blends were studied in two regions (1 and 2) of a injection moulded sheet by using S[T]EM. The sections were cut in the YZ plane (parallel to the direction of flow) in region 1 and in the XY plane (perpendicular to the direction of flow) in region 2 (see Figures 3.1a and 1b). Staining of the sections with osmium tetroxide resulted in excellent contrast between the two phases of the blends. Because of higher unsaturation, and hence greater stainability, the NR phase appeared much darker in the electron micrographs than the PP phase[2-3].

The phase morphology of the unvulcanised NR70/PP30 blend in the YZ plane is shown in Figures 4.4a to 4.4d. The micrographs are taken as an illustration of morphology parallel to the main direction of flow. The phase morphology in this sample is generally fine, with domains about 0.5μm width. Some regions of NR (dark) can be seen within the PP phases (light). As can been seen in the micrographs, the NR phase looks continuous, but it is not clear whether the PP phase is also continuous or is discrete.

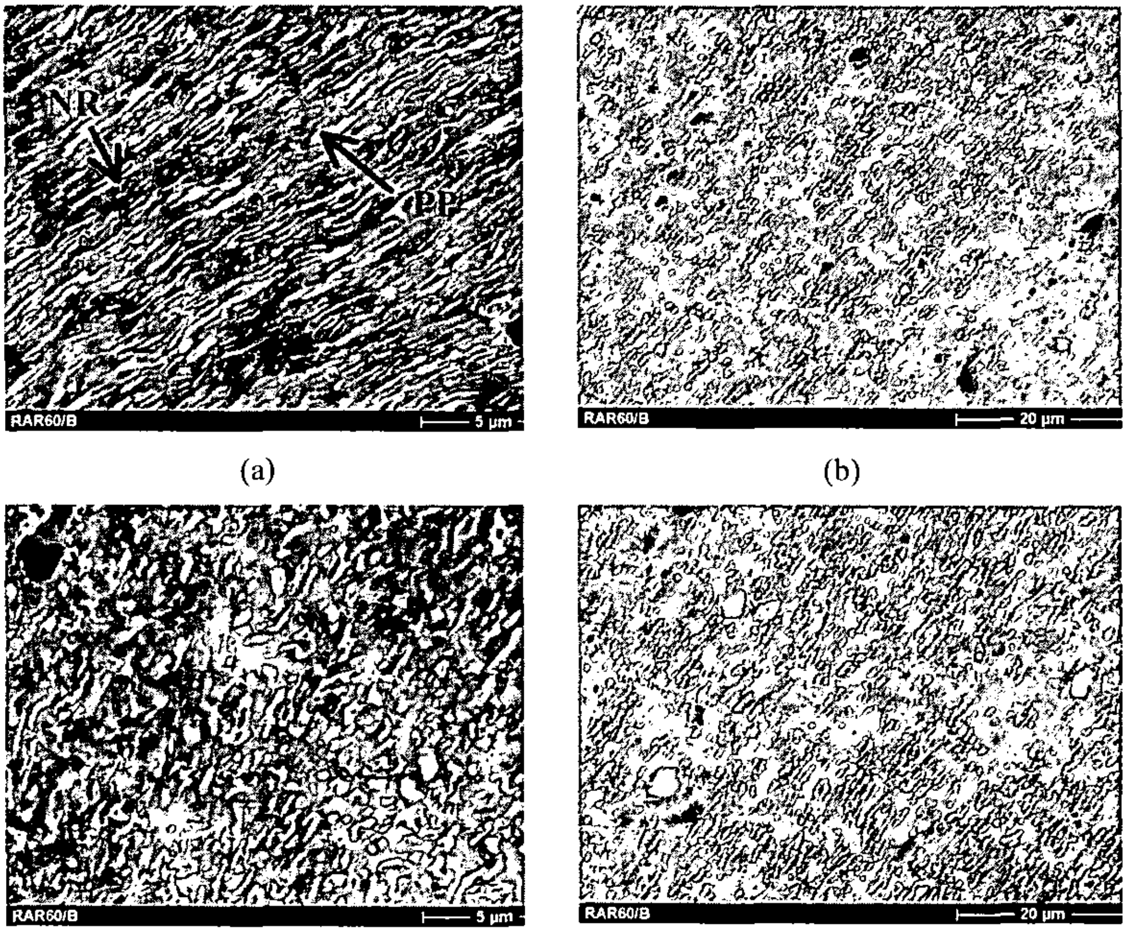


(a) (b)

(c) (d)

Figure 4.4 S[T]EM micrographs of OsO_4 stained unvulcanised NR70/PP30 blend in the YZ plane.

The phase morphology of the unvulcanised NR70/PP30 blend in the XY plane is shown in Figures 4.5a to 4.5d. The micrographs are taken as an illustration of the morphology perpendicular to the main direction of flow. The morphology is similar to that in the YZ plane where the NR phase displays a continuous morphology. The PP phase looks continuous, but it still can be questioned whether it is continuous or discrete because of the two-dimensional nature of the image. Most sections show oriented morphology but Figure 4.5c displays disordered phase morphology where the PP domains exhibit regions that are more rounded in shape, which might be expected from a cross-section through the main direction of flow.



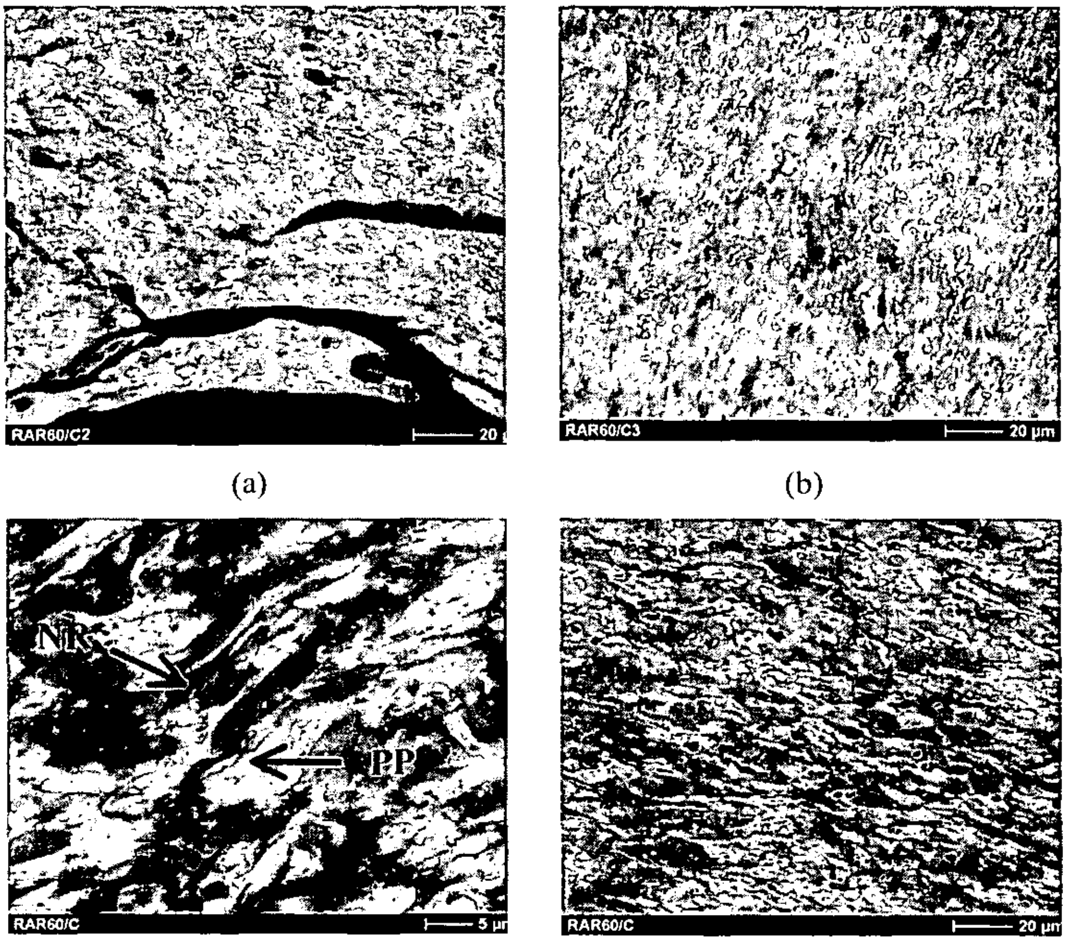
(a) (b)

(c) (d)

Figure 4.5 S[T]EM micrographs of OsO_4 stained of unvulcanised NR70/PP30. blend in XY plane.

Sections in the YZ and XZ plane show little difference in morphology between the the parallel and perpendicular direction of flow. Therefore, the morphology appears to be generally laminar rather than linear, while the areas of disordered morphology may be due to differences in depth from the surface or uneven flow behaviour. The effect of depth from the sample surface on morphology was investigated by examining sections cut in the XZ plane (Figure 4.6).

Figures 4.6a and 4.6b are images of the unvulcanised NR70/PP30 near the surface, whereas Figures 4.6c and 4.6d are images deep in the sample sheets. Images taken from deep in the sheet show larger PP areas than are seen close to the surface, but they appear to contain some streaks and spots of NR within them.



(a) (b)

(c) (d)

Figure 4.6 S[T]EM micrographs of OsO_4 stained of unvulcanised NR70/PP30 blend in XZ plane.

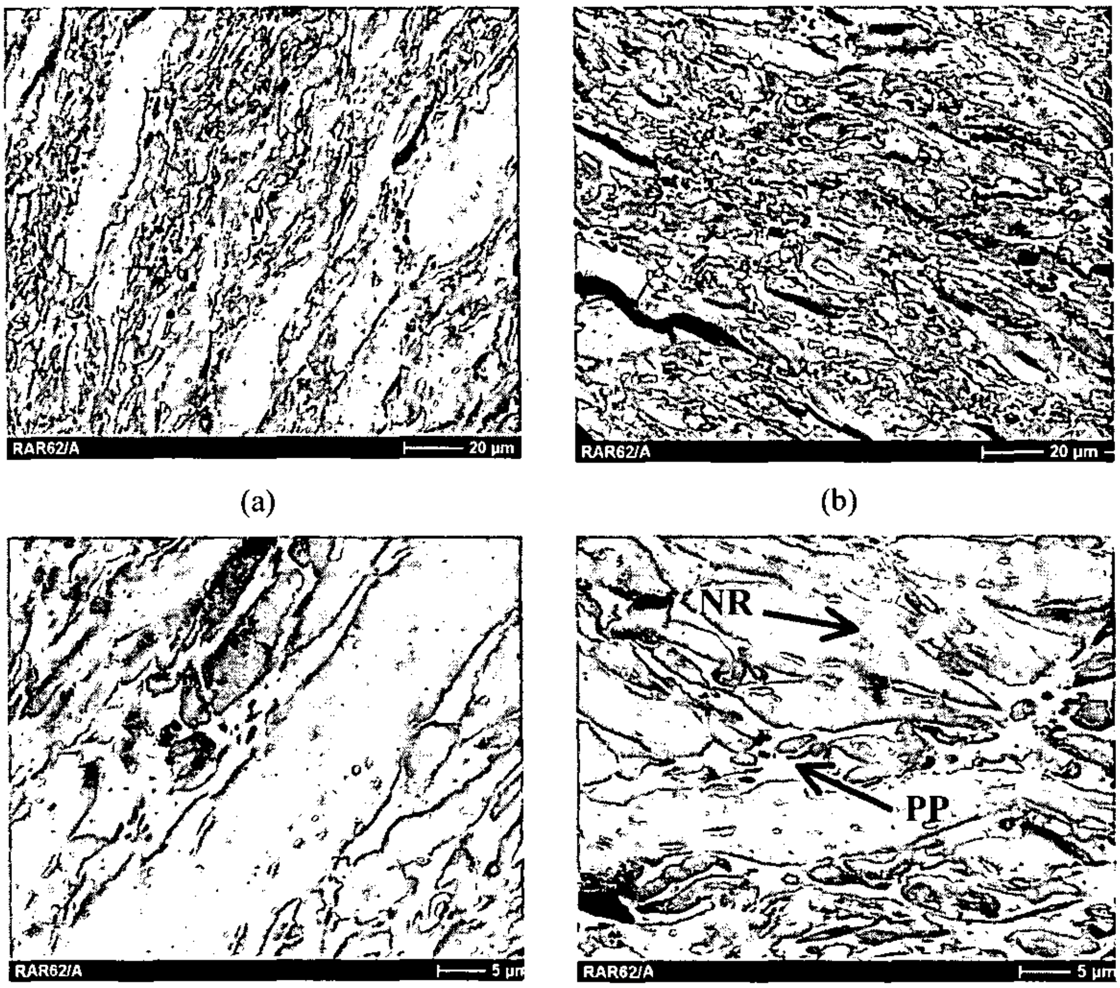
The high magnification image in Figures 4.6 shows a coarser morphology than those for sections cut across the plane of flow (Figures 4.4a, 4.4b, 4.5a and 4.5b) In sections cut in the XZ plane, the areas of PP are larger, but less distinct than in sections taken from the YZ and XY plane. The effect might be caused by the sections in the XZ plane being slightly thicker than sections in the YZ and XY plane. However, it looks as if the PP phase in the section from the XZ plane is darkened by streaks, spots or thin layers of occluded NR. It can be suggested that the polymer phases are laminar, parallel with the XZ plane in the sample sheet. Sections, which are cut parallel to this plane (i.e XZ plane), might therefore include very thin layers of both NR and PP on top of each other.

4.2.2 Phase morphology of the NR70/PP30 TPV (HP)

The ideal morphology of a TPV is a fine dispersion of the elastomer in a relatively small amount of the thermoplastic polymer. Dynamic vulcanisation may produce such a fine dispersion. The well recognized phase morphology of dynamically vulcanised blends is discrete rubber particles in a continuous PP phase, on the basis of microscopy studies. However, some researchers proposed that a TPV with a high fraction of rubber demonstrates a co-continuous phase at the early stages of mixing, but changes to discrete rubber particles in a continuous thermoplastic phase at the end of mixing[3]. On the other hand, some TPV studies show that the high fraction of rubber displays a continuous phase morphology after mixing[4-6].

In the current study, the unvulcanised NR70/PP30 blend shows a fine morphology of NR and PP phases (as described in the previous section). However, the NR70/PP30 TPV (HP) generally shows a coarser phase morphology than the unvulcanised NR70/PP30 blend (Figures 4.7 to 4.9).

The phase morphology of NR70/PP30 TPV(HP) shown in Figures 4.7 a to 4.7d, is for sections in the YZ plane. The images display the morphology of the sample in the main direction of flow. As can be seen in Figures 4.7a and 4.7b, it appears that the PP phase (light) is aligned or elongated within an elastomer phase (dark) that is somewhat orientated in the direction of flow. However, the crosslinked elastomer phase displays irregular shapes and sizes and shows less orientation than in the unvulcanised NR70/PP30 blend (Figures 4.4 and 4.5).

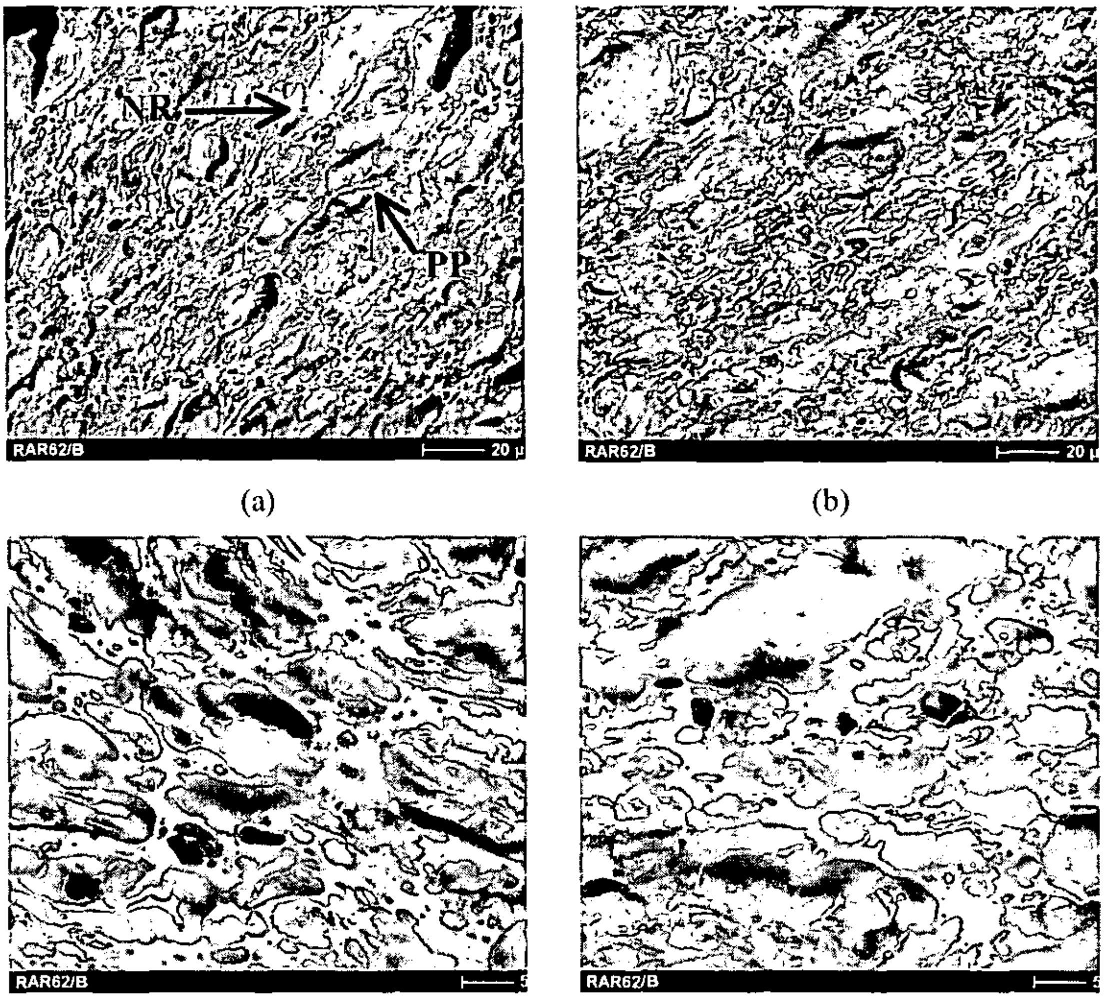


(a) (b)

(c) (d)

Figure 4.7 S[T]EM micrographs of OsO_4 stained of NR70/PP30 TPV(HP) in YZ plane.

The phase morphology of NR70/PP30 TPV(HP) in the XY plane is shown in Figures 4.8 to 4.8d. These images show a slight difference in phase morphology compared with images of sections from the same materials cut in the YZ plane. The XY plane is a cross-section through the direction of flow and displays an irregular phase morphology. Hence, there seems to be slightly more orientation of the polymer phases in the YZ plane than in the XY plane.

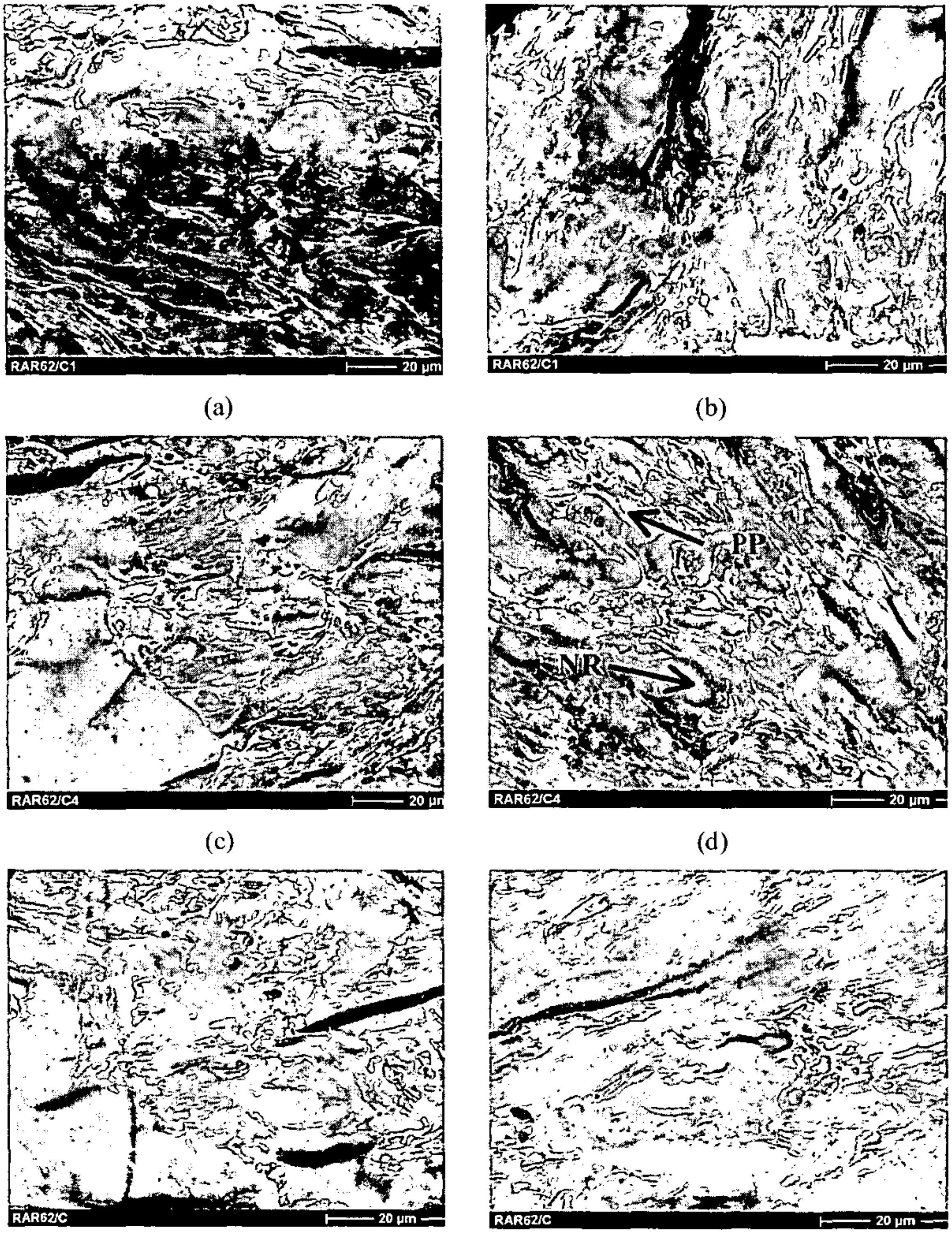


(a) (b)

(c) (d)

Figure 4.8 S[T]EM micrographs of OsO_4 stained of NR70/PP30 TPV(HP) in XY plane.

The phase morphology of NR70/PP30 TPV(HP) shown in the XZ plane shown in Figures 4.9 a to 4.9h. Figures 4.9a to 4.9d represent micrographs of the NR70/PP30 TPV(HP) near the surface, whereas Figures 4.9g and 4.9h represent micrographs deep within the sheet. Both phases near the surface demonstrate a continuous morphology with a chaotic phase orientation. In the sections taken from deeper in the sheet, images display more orientation than those close to the surface. Images of sections in the XZ plane do not clearly represent changes in phase morphology with depth from surface since no depth control was applied.

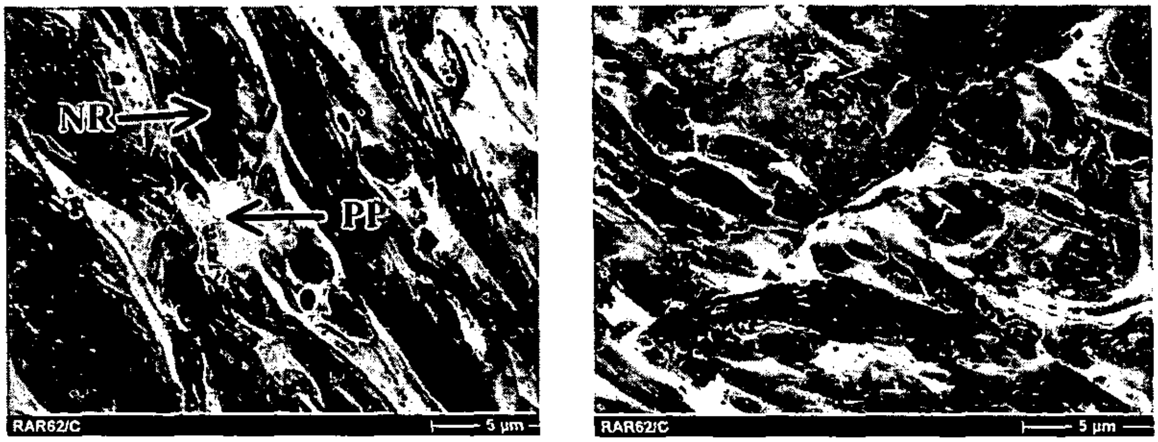


(a) (b)

(c) (d)

(e) (f)

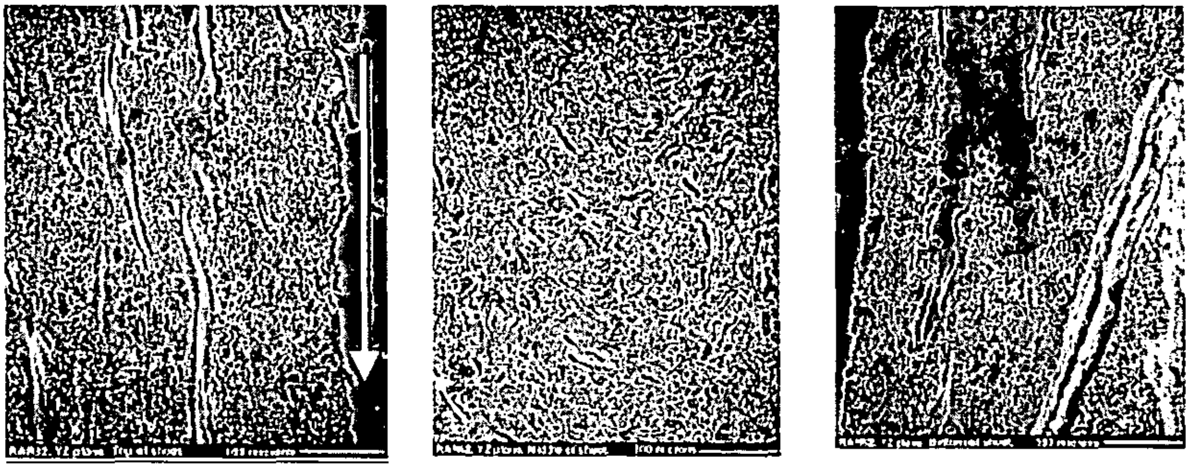
Figure 4.9 S[T]EM micrographs of OsO_4 stained of NR70/PP30 TPV(HP) in XZ plane.



(g) (h)

Figure 4.9 S[T]EM micrographs of OsO_4 stained of NR70/PP30 TPV(HP) in XZ plane (cont.).

In order to confirm the different phase morphology observed in the sample at different depths from the surface, sections cut in the XZ plane from vulcanised NR70/PP30 TPV(HP) were examined. Figures 4.10a and 10c represent images of the NR70/PP30 TPV(HP) near the surface (top and bottom), whereas Figure 4.10b represents an image in the middle of the sheet. The direction of flow is from the top to the bottom of the images. The materials were flow forward through the gate by injection pressure. The materials were deformed before enter the gate. After pass through the gate, the materials near the surface (Figures 4.9a and 4.9c) recover more orientated to the main direction of flow than the materials in the middle due to their lower viscosity.



(a) near surface of sheet (b) middle of sheet (c) near bottom of sheet

Figure 4.10 Light microscopy of NR70/PP30 TPV(HP) in XZ plane.

Using information from all the micrograph images, a schematic morphology of the NR70/PP30 TPV was developed. Figure 4.11 shows the schematic morphology of co-continuous NR70/PP30 TPV when microtomed perpendicular and parallel to the main direction of flow. The dark phase represents the NR phase whereas the light phase represents the PP phase. This model of the morphology explains why some of the micrographs show more orientation than others.

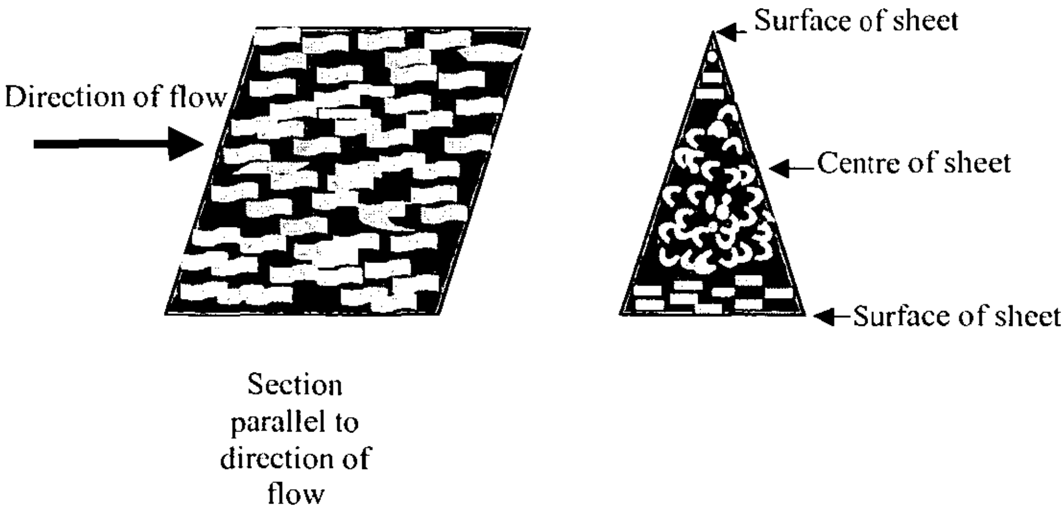
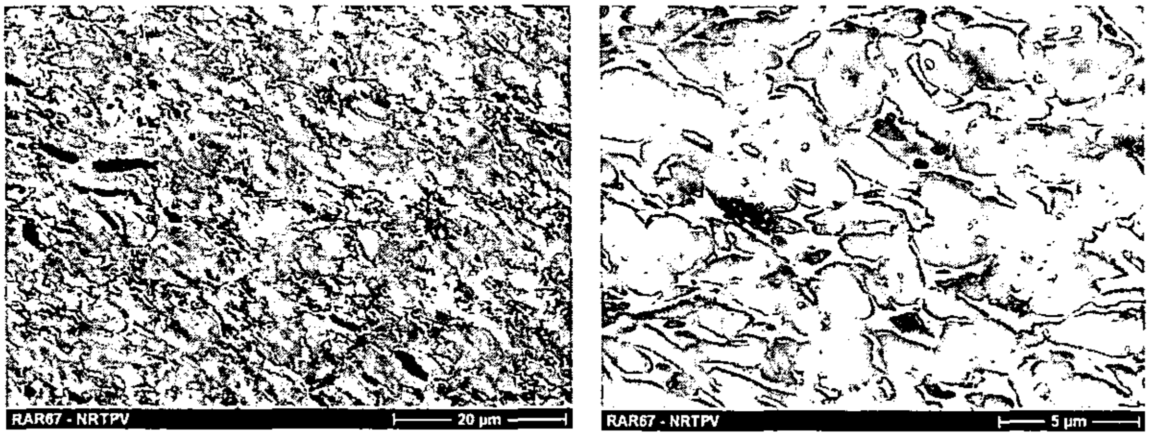


Figure 4.11 Schematic morphology of NR/PPTPV material.

In summary, the NR70/PP30 TPV(HP) appears to display continuous morphology of NR and PP phases. During the melt-mixing process, prior to dynamic vulcanisation, the elastomeric phase is dispersed into the molten thermoplastic phase. Progressive crosslinking during dynamic vulcanisation increasingly restricts further dispersion of the NR phase. However, because the NR phase is present in a larger proportion than the PP, there is the possibility of physical interaction between regions of crosslinked NR to give an apparently continuous NR phase within the PP phase.

4.2.3 Phase morphology of the NR75/PP25 TPV

Thin sections of NR75/PP25 TPV were examined to compare the morphology to that of the unvulcanised NR/PP blends and simple TPV materials described in the preceding sections. As can be seen in Figures 4.12a and 4.12b, the NR75/PP25 TPV has a finer and more homogeneous phase morphology than the blends and TPVs discussed in the earlier sections. The improvement of morphology is probably due to the addition of process oil to the NR75/PP25 TPV. The process oil is likely to be preferentially absorbed into the NR phase, reducing its viscosity to a level closer to that of the PP. Polymers of more similar viscosity are able to blend more thoroughly together, giving a finer morphology .



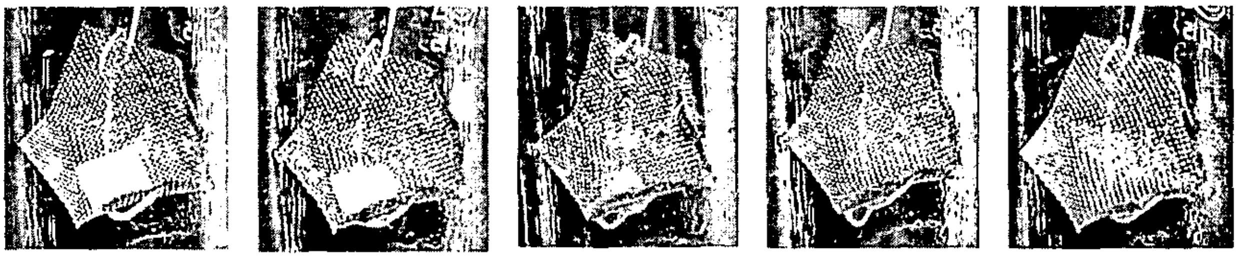
(a) (b)

Figure 4.12 S[T]EM micrographs of OsO_4 stained of NR75/PP25 TPV.

Micrographs showing phase morphology are however, limited in what they show, being a 2-dimensional image of a 3-dimensional structure. Information in the planes above and below the image plane is not provided. In particular, a phase which appears discrete in a 2D image may be co-continuous in 3D. Solvent extraction can be used as a tool to investigate the continuous nature of phases.

4.2.4 Extraction of polypropylene from TPVs

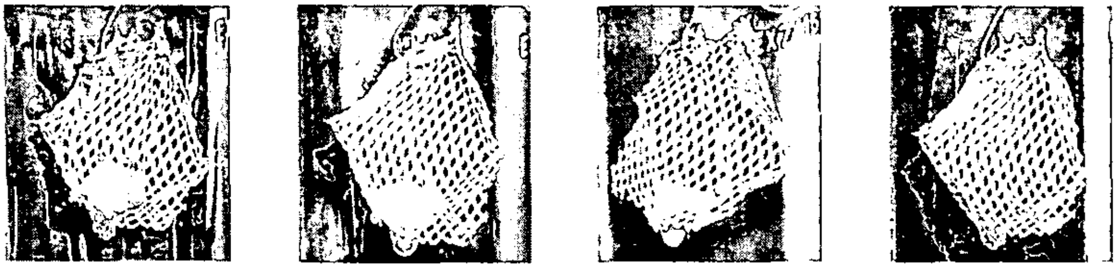
NRTPV materials were refluxed in xylene vapour using a soxhlet system in order to verify the phase morphology of TPV materials. Hot xylene is effective in removing the PP phase from TPVs based on NR/PP[4] and EPDM/PP blends. It was suggested that a minimum time of two hours should essentially completely extract PP from the TPV[5-6]. To confirm this, a piece of injection moulded PP was refluxed under similar conditions. The sample was softened and then completely dissolved in refluxing xylene vapour in 35 minutes as illustrated in Figure 4.13.



0 minutes 7 minutes 15 minutes 30 minutes 35 minutes

Figure 4.13 Extraction of polypropylene by hot-xylene.

A similar observation was also made for the unvulcanised NR/PP blends (Figures 4.14 and 4.15), where all of the unvulcanised NR and PP was completely removed in 35 minutes. The experiment confirmed that both unvulcanised NR and PP would be removed during refluxing with hot xylene.



0 minutes 7 minutes 15 minutes 30 minutes

Figure 4.14 Extraction of unvulcanised NR60/PP40 blend by hot-xylene.

0 minutes 7 minutes 15 minutes 30 minutes

Figure 4.15 Extraction of unvulcanised NR70/PP30 blend by hot-xylene.

0 minutes 7 minutes 15 minutes 30 minutes 2 hours

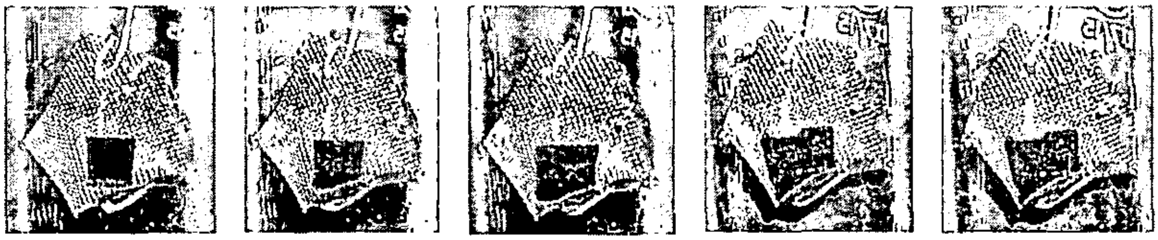
Figure 4.16 Extraction of NR60/PP40 TPV (HP) by hot-xylene.

0 minutes 7 minutes 15 minutes 30 minutes 2 hours

Figure 4.17 Extraction of NR70/PP30 TPV(HP) by hot-xylene.

The same size and shape pieces of injection moulded NR60/PP40 TPV(HP) and NR70/PP30 TPV(HP) were exposed to similar conditions as mentioned above. Even though the PP phase in the vulcanised NRTPV materials was removed, the integrity of each of swollen sample was clearly maintained and is typically illustrated in Figures 4.16 and 4.17. This indicates that the NR/PP TPV has a continuous rubber phase similar to that of a TPV based on EPDM/PP blends[7]. As expected, unvulcanised NR60/PP40 TPV(HP) did not have as good an integrity as NR70/PP30 TPV(HP), since the former has a higher proportion of PP. Although a change in shape indicates that some of the rubber phase structure has collapsed after removal of the polypropylene phase, the highly swollen sample is still in one piece, showing that the rubber phase is continuous, even at this lower rubber volume fraction.

In order to compare the phase morphology of the NR/PP TPVs to a commercial TPV based on EPDM/PP blends, a sample of Santoprene™ 101-80 was extracted. Santoprene™ 101-80 was selected since it has a similar hardness to the TPVs(HP) (refer to Tables 4.2 and 4.3). Figure 4.18 illustrates that after the removal of PP, the remaining highly swollen sample also kept its original shape. This suggests that the rubber phase in Santoprene™ 101-80 is also continuous.



0 minutes 7 minutes 15 minutes 30 minutes 2 hours

Figure 4.18 Extraction of Santoprene™ 101-80 with hot-xylene.

4.2.5 Extraction of rubber from unvulcanised NR/PP blends

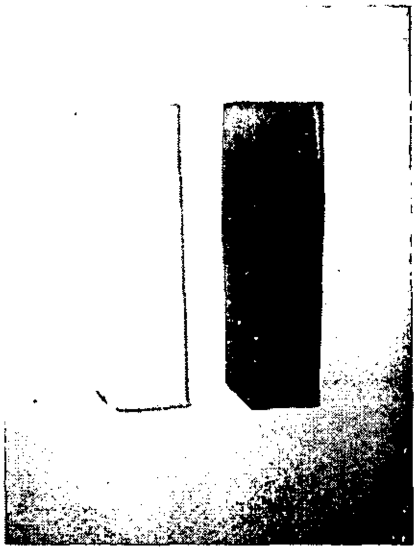
If the NR phase of the TPV could be extracted and the PP retains its integrity, the PP phase could be said to be continuous. However, the crosslinked NR phase of the TPV cannot be extracted, the rubber phase can only be extracted from unvulcanised NR/PP blends. It is assumed that if the PP phase is continuous in the unvulcanised blends it is also continuous in the TPVs where it shows a similar morphology under SEM.

Samples of unvulcanised NR60/PP40 blends (injection moulded) were refluxed in solvent vapour using a soxhlet system in order to investigate the phase morphology of the PP. The percentage extraction by four types of solvent in 72 hours is displayed in Table 4.1. As can be seen, toluene is the best solvent to extract NR. However, toluene extracted more than 60%, which could be explained by toluene also extracting a small amount of low molecular weight PP. To prevent extraction of the PP, a more gentle extraction was applied using tetrahydrofuran (THF), which left a very small amount of the NR in the sample.

Table 4.1 Percentage extraction of rubber in unvulcanised NR60/PP40 blend.

Solvents	Extraction, %	Extraction time, hours
Toluene	61	72
Tetrahydrofuran	58	120
Chloroform	53	72
Cyclohexanone	53	72
Ethyl Acetate	33	72

Figure 4.19 shows that the white extracted sample showed a decrease in thickness and a slight changed in the shape, but retains its integrity. This result indicates that the PP has continuous phase morphology in the unvulcanised NR/PP blend. The THF extracted sample shows a "laminate" appearance, which might have developed during the injection moulding process.

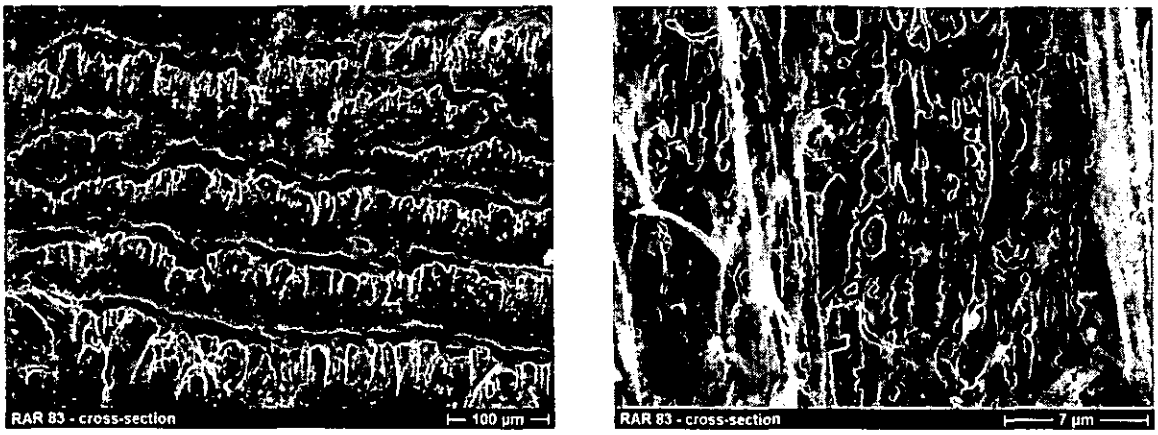


(a) (b)

Figure 4.19 Unvulcanised NR60/PP40 blend (a) THF extracted and (b) unextracted.

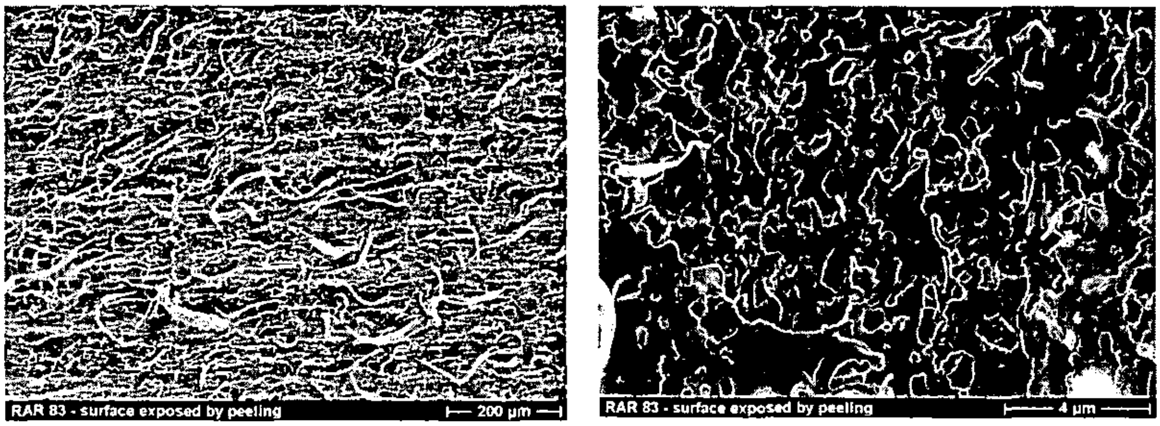
A cross-section of a THF extracted, unvulcanised NR/PP sample is shown in Figure 4.20. The section is cut from an injection moulded sheet, perpendicular to the main direction of flow. The micrographs show discontinuous layers of PP (Figure 4.20a) separated and held together by thin strands of PP (Figure 4.20b). Figure 4.21a shows a micrograph of a "fresh surface" produced after peeling apart the layers, breaking some of the thin strands of PP. Figure 4.21b shows the morphology of the PP phase in between the layers of PP in the unvulcanised NR/PP blend. The micrographs show that the PP phase in the unvulcanised NR/PP blend has a continuous, partly laminar and partly fibrous morphology.

Taken all together the S[T]EM images of the unvulcanised NR/PP samples shown in Section 4.2.1 suggest a generally laminar or lenticular type morphology which is consistent with the images of the section through the extracted sample (Figure 4.21).



(a) (b)

Figure 4.20 Cross-section of a "fresh surface" peeled unvulcanised NR60/PP40 blend.



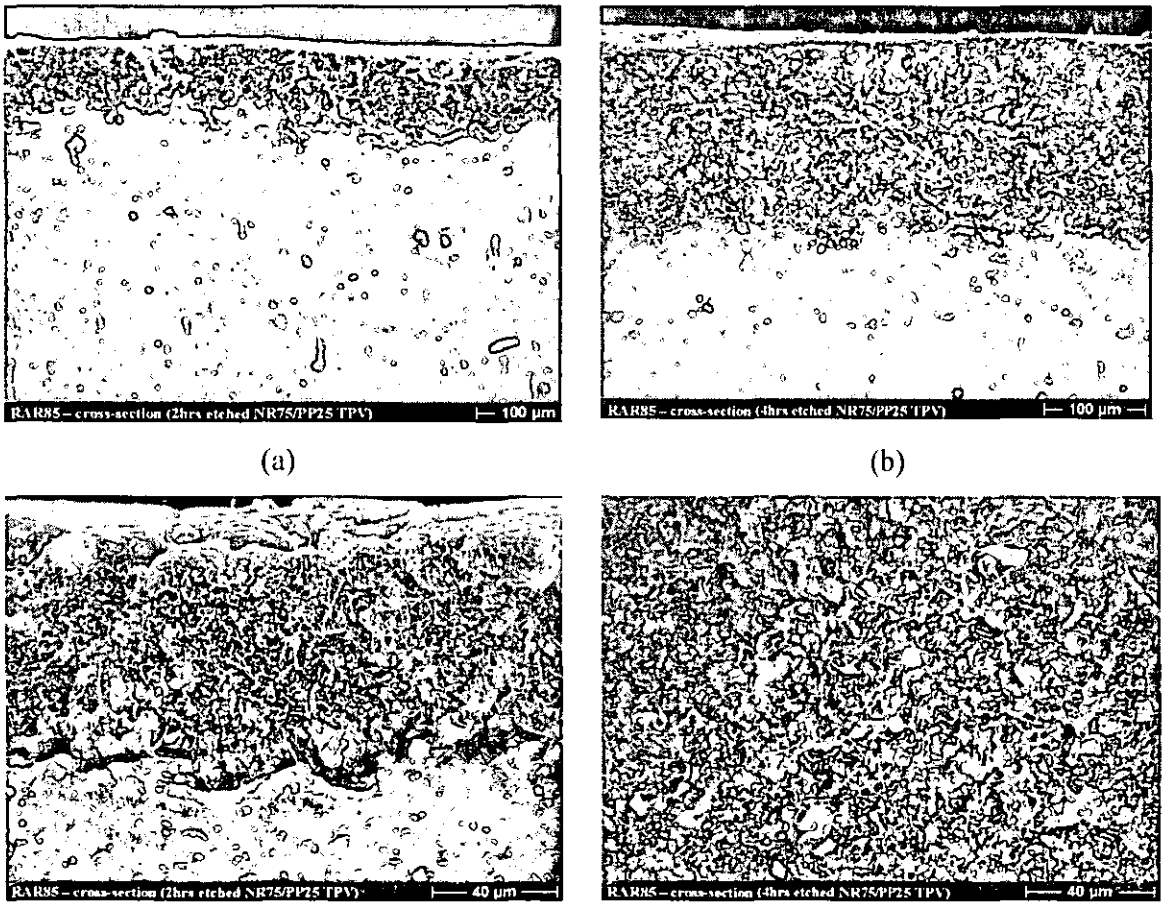
(a) (b)

Figure 4.21 A "fresh surface" of peeled unvulcanised NR60/PP40 blend.

4.2.6 Etching of crosslinked rubber from TPV

In order to demonstrate better the 3-dimensional structure of TPVs, chemical etching was carried out. The etching technique was applied since the crosslinked NR cannot be solvent extracted and it is possible that the unvulcanised blends discussed in the previous section have a different morphology than the TPVs.

An extruded tape of NR75/PP25 TPV was investigated in this work because the extruder gives a simpler flow pattern than injection moulding and will result in a more consistent orientation of morphology. Figures 4.22a to 4.22c show micrographs of a cross-section of the NR75/PP25 TPV that has been etched by concentrated chromic acid for either two hours (Figures 4.22a to 4.22d) or four hours (Figures 4.22b and 4.22d). It is clearly seen that the two hours addition of etching is sufficient to get a clearer image of the morphology. However, by increasing the etching time from two to four hours, the etched thickness is increased and reveals a 3-dimensional image of the etched sample. The NR phase has been oxidised by the acid leaving holes and giving the appearance of a PP foam structure.

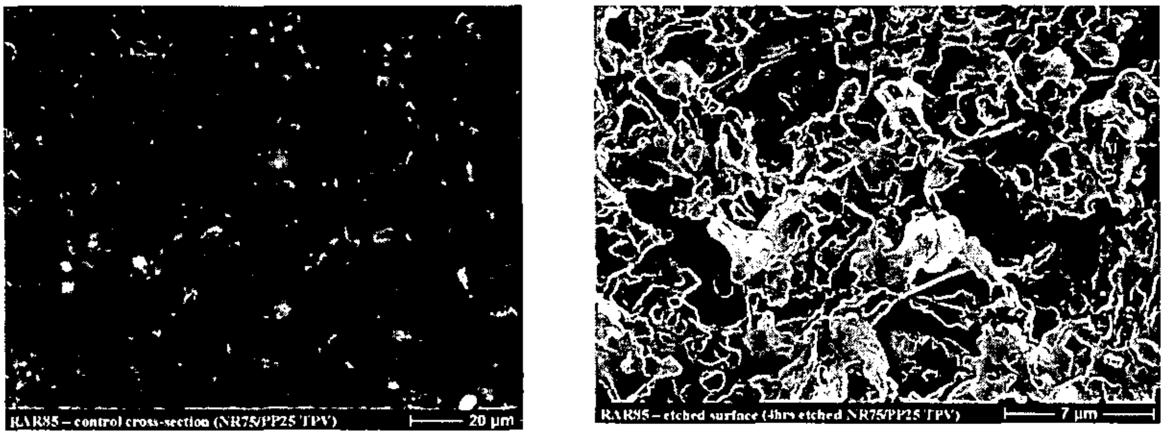


(a) (b)

(c) (d)

Figure 4.22 SEM micrographs of cross-section concentrated chromic acid etched of NR75/PP25 TPV.

Figure 4.23b shows the effect of surface etching using concentrated chromic acid of NR75/PP25 TPV compared with unetched images (Figure 4.23a). The micrographs of the etched samples show a 3-D morphology which indicates a continuous PP phase, while the interconnectedness of the voids suggests a continuous NR phase as well.



(a) (b)

Figure 4.23 SEM micrographs of surface unetched and concentrated chromic acid etched of NR75/PP25 TPV.

The results from solvent extraction and chemical etching experiments strongly suggest that the phase morphology of the NR/PP TPV produced is co-continuous.

There are similarities in morphology, particularly at a small scale (10-50 μm), between the morphology of the PP phase in the unvulcanised blends (Figure 4.22) and the TPVs (Figure 4.23). However, at a larger scale (100-500 μm) the morphology of the unvulcanised blend appears rather more laminar than that of the TPV. The more laminar morphology is probably due to the presence of larger NR phases in the unvulcanised blend, which are destroyed during dynamic vulcanisation of the TPV.

4.3 Deformation behaviour

4.3.1 Hardness

The hardness values of injection moulded sheets of unvulcanised NR/PP blends, NR/PP TPVs and commercial TPVs based on EPDM are shown in Tables 4.2 to 4.4. As can be seen, NR/PP TPVs have a higher hardness value than do the unvulcanised NR/PP blends. The effect is particularly clearly seen in blends containing a relatively high proportion of NR. Both NR60/PP40 TPV(HP) and NR70/PP30 TPV(HP) show a three point increase compared with the equivalent unvulcanised NR/PP blends. An increase in hardness of unvulcanised NR/PP blends by introduction of crosslinking in the rubber phase has also been reported in the literature[8-9]. Hardness also increases with increased in polypropylene (PP) content as can bee seen in Table 4.2. The NR60/PP40 TPVs (LP) has a higher hardness than NR80/PP20 TPV(LP), indicating that PP has an important role in contributing to increased hardness. Hence, hardness is increased by both dynamic vulcanisation and by an increase in PP content.

Commercial TPVs based on EPDM/PP, Santoprene™ 101-80 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160 B TPV were chosen to compare with the physical properties of the materials produced in this study. These materials were selected because they were similar in hardness to the experimental NR/PP TPVs. Sarlink™ 3160 B TPV has a higher hardness than NR75/PP25 TPV and Santoprene™ 101-55 TPV. Table 4.3 shows that the measured hardness of Santoprene™ 101-80 TPV (91 Shore A), Santoprene™ 101-55 TPV (60 Shore A) and Sarlink® 3160 B TPV (76 Shore A) are however, greater than that given in the specification (80 Shore A and 55 Shore A and 62 Shore A)[10-12]. It is known that the hardness measured for plied sheets may be higher than the hardness for a single sheet of the same thickness[13], as a result of PP 'rich'[10,12-14] material occurring at the moulded surfaces[13-20]. In addition, different mould cavities can also produce different flow behaviour, which can affect properties.

4.3.2 Tensile strength

All samples for tensile testing were tested at the standard extension rate for rubber, 500mm/min, unless stated otherwise. The stress at 50% extension (M50) and stress at 100% extension (M100), tensile strength (TS) and extension at break (EB) were measured for test pieces cut parallel(||) and perpendicular(⊥) to the main direction of flow.

Dynamic vulcanisation increases the tensile stiffness and strength of the unvulcanised NR/PP blends. Similar results have been reported in the literature where dynamic vulcanisation has been shown to increase hardness, modulus, strength and recovery properties of TPVs[21-23]. It was observed that the effects are particularly marked in blends containing more than 65% of NR[24].

Table 4.2 Hardness and tensile properties of injection moulded samples of unvulcanised NR/PP blends and NR/PP TPVs.

Property	Unvulcanised NR60/PP40 blend	Unvulcanised NR70/PP30 blend	NR70/PP30 TPV (LP)	NR75/PP25 TPV (LP)	NR80/PP20 TPV (LP)	NR60/PP40 TPV (HP)	NR70/PP30 TPV (HP)
Hardness, 5s,shore A*	93	90	88	82	76	96	93
M50, MPa							
∥	8.9±0.2	7.1±0.1	7.0±0.4	5.7±0.6	5.8±0.3	11.3±0.1	9.2±0.5
⊥	7.4±0.1	5.2±0.1	4.1±0.2	3.0±0.2	2.5±0.2	7.8±0.1	5.5±0.1
M100, MPa							
∥	9.2±0.2	7.0±0.6	8.51±0.5	7.3±0.7	7.8±0.3	12.7±0.2	11.5±0.6
⊥	7.4±0.1	5.5±0.1	5.1±0.3	4.0±0.2	3.5±0.2	8.8±0.1	6.6±0.1
TS, MPa							
∥	9.5±0.2	7.7±0.4	13.9±1.3	9.0±0.9	9.9±0.8	15.2±0.2	13.4±0.9
⊥	9.6±0.2	7.5±0.1	17.7±1.3	11.4±1.3	10.5±1.2	17.7±0.1	16.5±0.7
EB, %							
∥	171±34	166±38	181±25	159±5	161±16	229±39	158±13
⊥	458±107	478±18	456±15	445±33	422±35	426±9	399±20

*median value of 5 samples

Two ways have been suggested in which dynamic vulcanisation has this effect on properties. Firstly, crosslinking of the elastomer phase with peroxide increases its modulus and makes it stronger and more resilient[25-26]. Secondly, both NR and PP undergo chain scission during mastication to give polymeric radicals, with the possibility of combination of dissimilar polymer radicals to give a 'copolymer'. The effect of peroxide concentration on properties will be discussed in more detail in a later section (section 4.3.3.5)

The tensile properties of NR75/PP25 TPV and commercial TPV based on EPDM rubber : Santoprene™ 101-80 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160 B TPV are shown in Table 4.3. Santoprene™ 101-80 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160 B TPV s how fairly similar tensile properties to those stated in the specification[10-12].

Table 4.3 Hardness and tensile properties of injection moulded samples of NR75/PP25 TPV and TPV based on EPDM/PP blends.

Property		NR75/PP25 TPV	Santoprene™ 101-80 TPV[spec]	Santoprene™ 101-55 TPV [spec]	Sarlink® 3160 B TPV[spec]
Hardness, 5s, Shore A, plied 2mm sheets		62	91[80]	60[55]	79[62]
M50, MPa	∥	2.3±0.1	6.1±0.4	2.2±0.1	3.3±0.1
	⊥	1.4±0.1	4.4±0.3	1.3±0.1	1.9±0.1
M100, MPa	∥	3.0±0.1	6.9±0.3	3.0±0.1	4.1±0.1[3.8]
	⊥	2.0±0.1	5.0±0.2[4.6]	2.0±0.1[2.0]	2.5±0.1[2.3]
TS, MPa	∥	5.1±0.1	10.3±0.2	3.4±0.1	5.8±0.1[5.4]
	⊥	6.5±0.5	12.2±0.4[11.3]	3.5±0.6 [4.4]	7.4±0.6[6.4]
EB, %	∥	271±13	391±40	143±10	319±19[270]
	⊥	438±27	587±73 [520]	254±50[330]	651±49[650]

Sarlink® 3160 B TPV has a higher strength than NR75/PP25 TPV and Santoprene™ 101-55 TPV. As can be seen in Table 4.3, higher values of modulus are shown for parallel flow direction samples for all TPV materials. The opposite trend is observed for tensile strength and extension a break. A moderate anisotropy was displayed in tensile strength of Santoprene™ 101-55 TPV.

The anisotropy observed in injection moulded samples is believed to be due to orientation of the material arising as the material enters and fills the mould cavity. In the direction of flow, the polymer chains tend to stretch and become aligned parallel to each other, due to the action of shear forces. The orientation results in greater stiffness in the direction of flow (parallel samples) than perpendicular to the direction of flow (perpendicular samples).

Table 4.4 Hardness and tensile properties of extrudate of TPV materials.

Reference	NR75/PP25 TPV	Santoprene ™ 101-55 TPV	Sarlink® 3160B TPV
Properties			
Hardness,5sec, Shore A	50	48	59
M50, MPa	1.2±0.1	1.1±0.1	2.0±0.1
M100, MPa	1.7±0.1	1.6±0.1	2.6±0.1
TS, MPa	6.3±0.1	3.0±0.4	7.0±0.4
EB,%	473±7	259±36	619±37

The effect of orientation was further studied using samples cut from extruded strip. Greater orientation was expected for the extruded strip. However, as can been seen in Tables 4.3 and 4.4, the modulus, tensile strength and extension at break of the extrudate are more similar to the values for the perpendicular than parallel orientation in the injection moulded sheet. Unfortunately, since the strip was too narrow it was not possible to measure properties in the direction perpendicular to flow. Therefore it is not clear whether the lower than expected stiffness for the extrudate is due to lesser orientation or an overall lower stiffness caused by the extrusion process. There is a possibility that the flow behaviour of the 2 mm sheet is changing with changing the behaviour of the materials. Anisotropy of properties will be discussed in more detail in sections 4.3.3.6.

4.3.3 Tensile stress-strain behaviour

All materials, except for PP, show good reproducibility in their stress-strain curves. Therefore, for each material, one sample plot was selected to represent all the tested samples. A median curve was selected to represent PP behaviour. Samples were tested parallel and perpendicular to the direction of flow. However, all results reported in this section were tested parallel the direction of flow, in order simplify the understanding and explanation of the effect of blend composition.

4.3.3.1 Stress-strain behaviour of polypropylene

Figure 4.24 shows stress-strain data plotted for PP. The stress-strain curve of the perpendicular sample strained at 50 mm/min exhibits the phenomenon of cold drawing, as explained in Section 2.4.2. In the samples cut parallel to the direction of flow, the 'neck' region grows only a little and exhibits only limited cold draw before failure. This is because the molecules were already aligned in the flow direction and so maximum alignment is reached after introduction of only a small extension.

A reduction in cold draw is also observed with an increase in strain rate. On increasing the strain rate to 100mm/min and 500 mm/min, the shape of the yield point becomes broader and the amount of cold draw before failure drastically decreases. It has suggested that at lower test speeds, the transformation from spherullitic to fibrillar structure in the 'neck' zone occurs smoothly and the neck extends gradually to the point where eventually the fibrils break. As test speed increases, significant destruction of the crystalline phases occur, generating highly oriented amorphous regions that slowly convert to a crystalline state[27-31]. This increases the stiffness and as a result, corresponding fracture occurs at a lower extension. The stress-strain curve exhibits brittle tensile behaviour. The PP sample tested at 500 mm/min. also shows a largely brittle fracture surface as seen in Figure 4.25a and 4.25b.

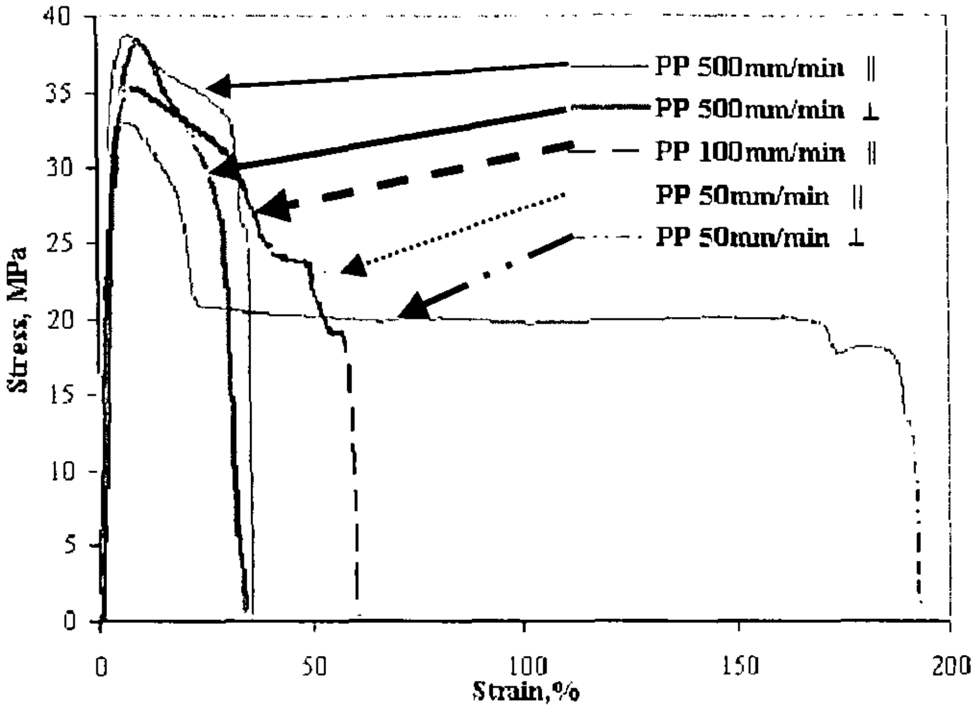
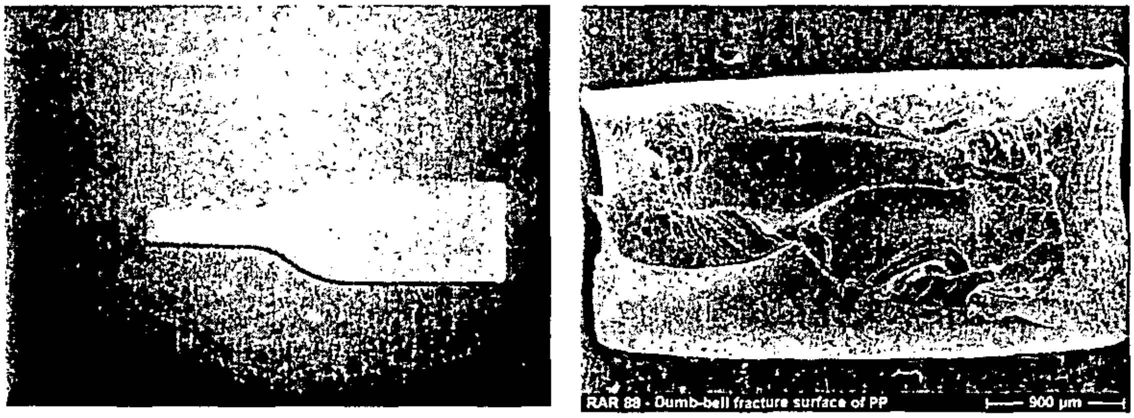


Figure 4.24 Effect of strain rate on stress-strain behaviour of polypropylene.



(a) (b)

Figure 4.25 (a) Dumb-bell fracture sample and (b) SEM micrographs of PP fracture surface.

4.3.3.2 Stress-strain behaviour of extracted, unvulcanised and TPV of NR60/PP40 blends and natural rubber compound

As can be seen in Figure 4.26, the stress-strain behaviour of the THF extracted unvulcanised NR60/PP40 blend shows a similar curve shape to the stress-strain behaviour of NR60/PP40 TPV, but at a lower stress value. The extracted unvulcanised NR60/PP40 blend has a lower tensile stiffness and strength than the unvulcanised NR60/PP40 and NR60/PP40 TPV. But, the tensile stiffness and strength is higher than the NR compound. The unvulcanised NR60/PP40 blend showed extensive cold draw behaviour while the extracted unvulcanised NR60/PP40 blend showed a more brittle failure (Figures 4.27a and b).

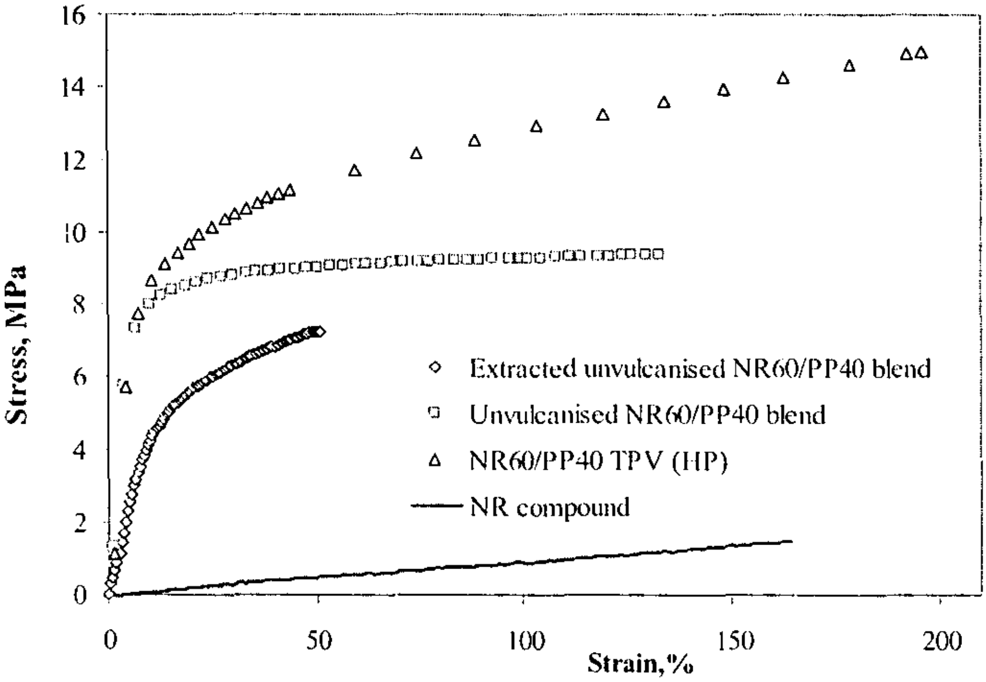
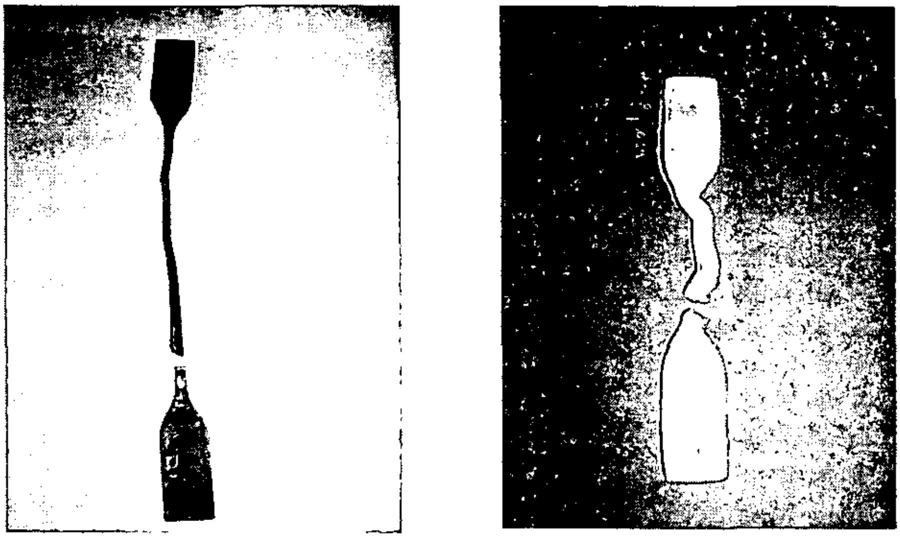


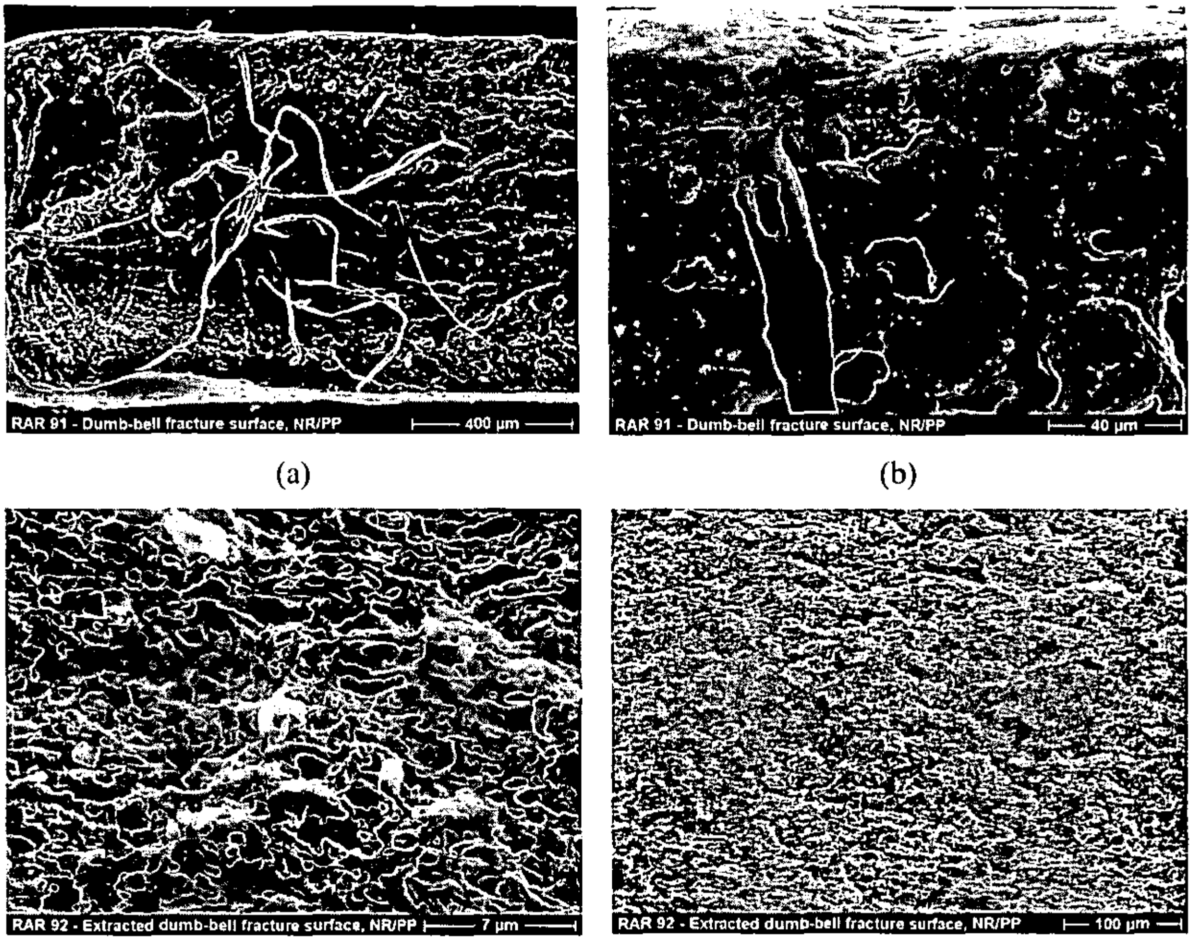
Figure 4.26 Stress-strain behaviour of THF extracted unvulcanised NR60/PP40 blend, unvulcanised NR60/PP40 blend, NR60/40 TPV and NR compound (stretched parallel to main direction of flow).



(a) (b)

Figures 4.27 (a) Dumb-bell fracture surface of unextracted unvulcanised NR60/PP40 blend and (b) extracted unvulcanised NR60/PP40 blend.

In Figure 4.28a, the fracture surface of the unvulcanised NR60/PP40 blend shows long fibrils of PP which have become drawn during the tensile test. While, micrographs in Figures 4.28b show a rough fracture surface, probably where the NR phase has been pulled out of the PP phase. The extracted unvulcanised NR60/PP40 blend broke at a lower extension (50%) than the unextracted blend, suggesting that the rubber, even though unvulcanised, is important in holding the sample together. However, the extension of 50% and lack of recovery after failure indicated that drawing of some of the PP has occurred. The fracture surfaces of the extracted blend shown in Figures 4.28b and 4.28c do not show any of the fibrils that were seen in the unextracted blend, and appear to show a more brittle fracture. It may be that the presence of the unvulcanised rubber in the blend was important in reducing brittle fracture, by absorbing energy and so allowed more extensive drawing of the PP.



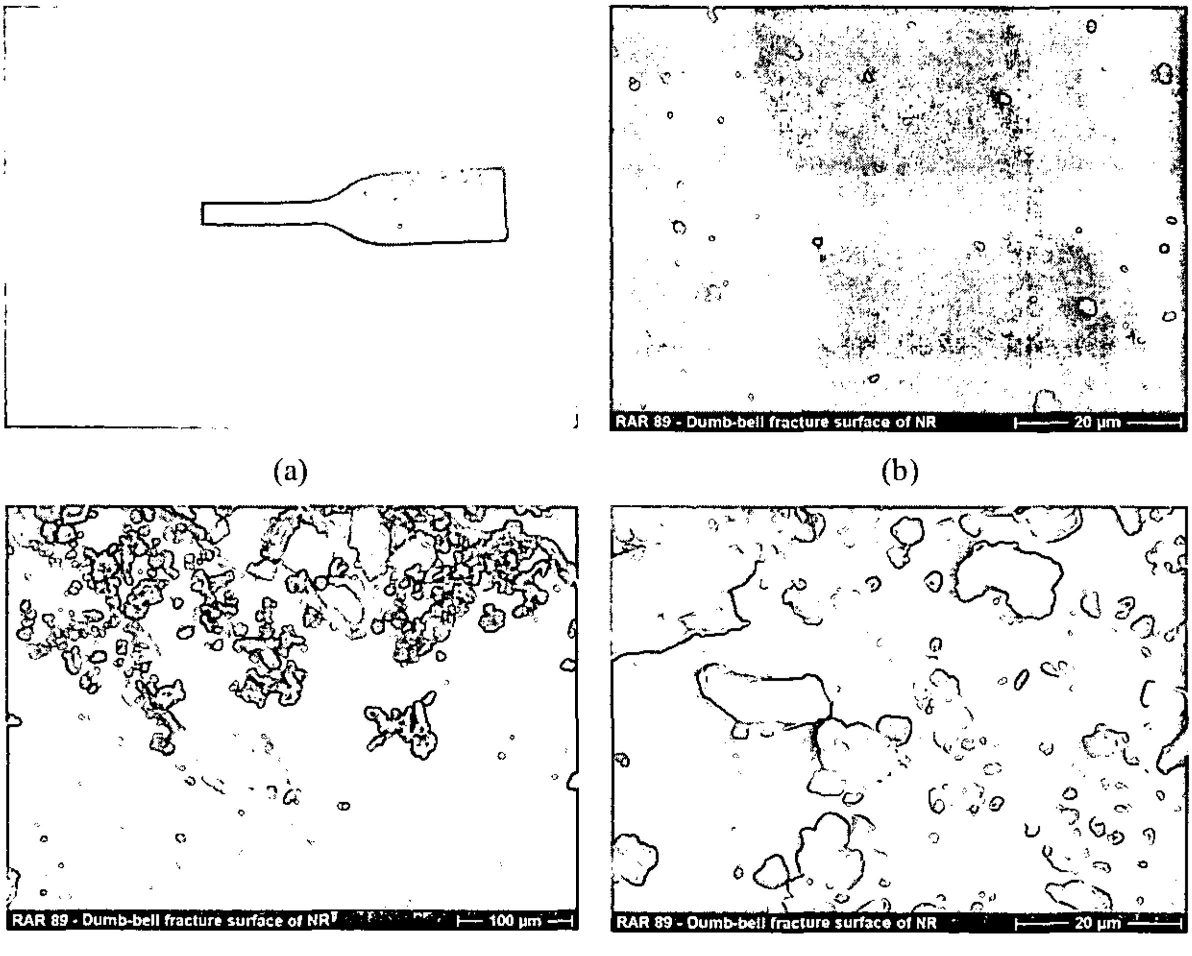
(a) (b)

(c) (d)

Figures 4.28 SEM micrographs of (a and b) unvulcanised NR60/PP40 blend (c and d) extracted unvulcanised NR60/PP40 blend fracture surface.

The extracted unvulcanised NR60/PP40 blend shows a continuous phase morphology that has a fibrous morphology in regions (Figure 4.20). Due to localised bending of the "fibres" allowed in the porous structure of the extracted blend, it would be expected to show more flexible stress-strain behaviour than that of the bulk PP (Figure 4.26) and NR/PP TPV.

The NR compound shows totally different stress-strain behaviour from PP. The NR compound exhibits a low increase in stress with strain, with no yield point and a tensile strength .The dumb-bell test pieces of natural rubber compound show a brittle fracture failure behaviour (Figure 4.29a). The micrographs of the fracture surface were fairly smooth and featureless but some areas were much rougher (Figure 4.29b to 4.29d). In the rougher areas a materials appears to be embedded in surface. However, since the compound does not contain filler or even zinc oxide it is more likely to be rubber than other material. The apparent particles may be more heavily crosslinked regions or perhaps regions that underwent strain crystallisation.



(a) (b) (c) (d)

Figures 4.29 (a) Dumb-bell fracture sample (b to d) SEM micrographs of NR fracture surface.

4.3.3.3 Stress-strain behaviour of thermoplastic vulcanisates

As can be seen from Figure 4.30, stress-strain curves of the TPV do not exhibit a maximum yield point and cold draw behaviour in the same way as does PP (Figure 4.24). Dumb-bell test pieces of NR75/PP25 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160B TPV samples also slightly show cold draw phenomenon in the fracture surface (Figure 4.31a).

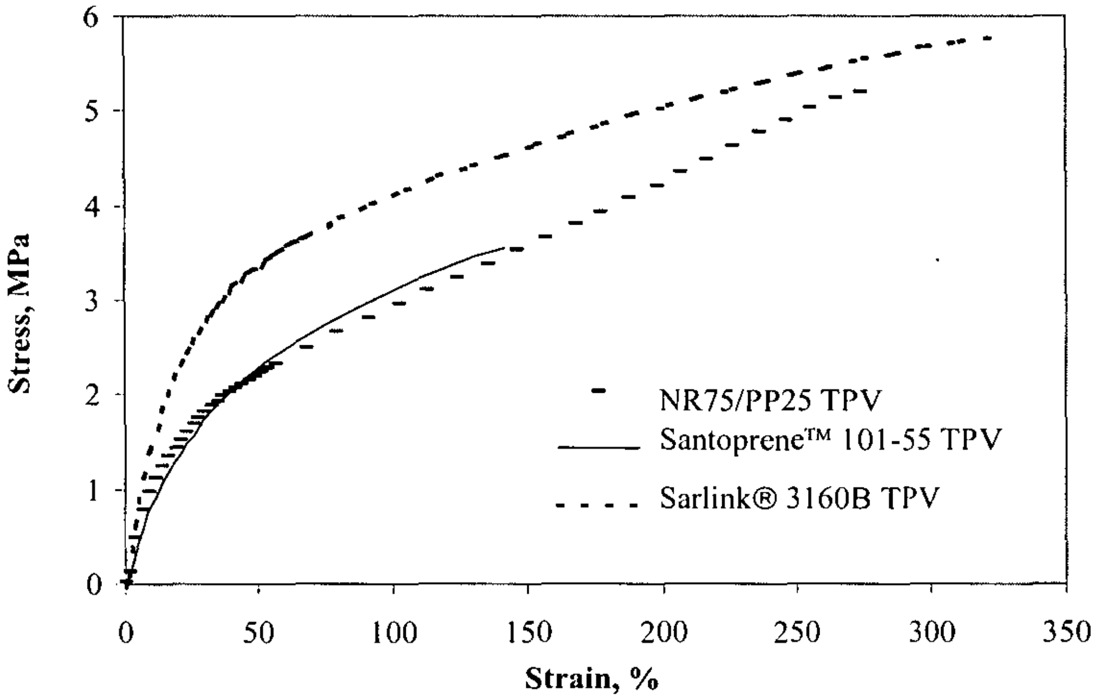
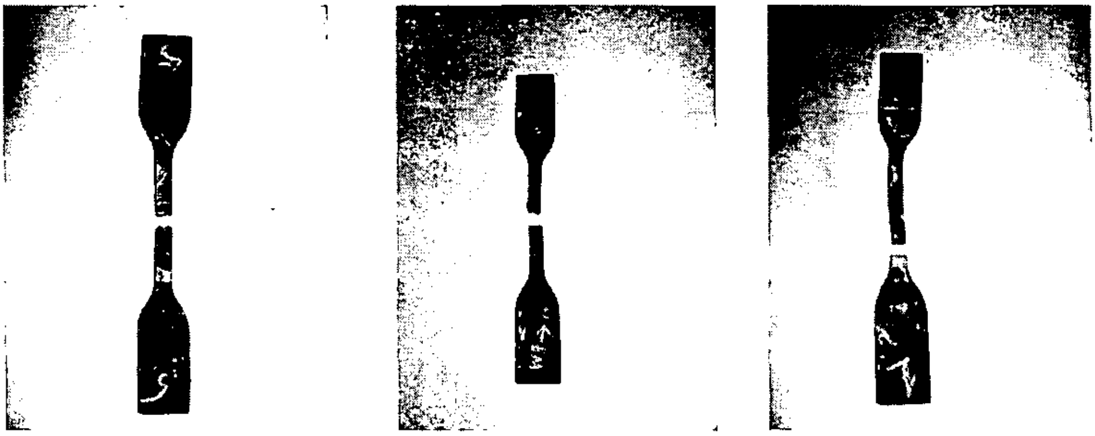


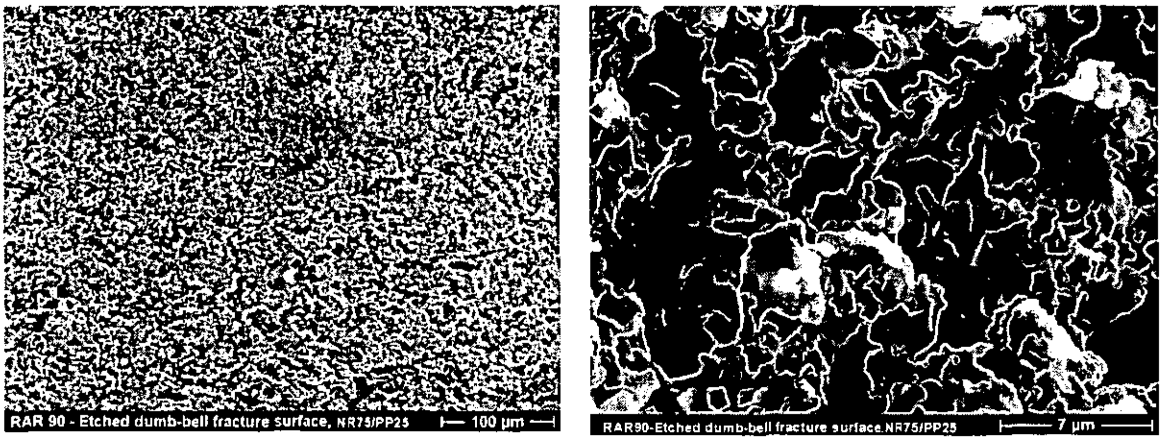
Figure 4.30 Stress-strain behaviour of NR75/PP25 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160B TPV (stretched parallel to main direction of flow).

It would appear that the PP behaves differently when it is in the TPV, possibly either because of its morphology or because of differences in internal structure of the PP as explained in section 4.3.3.2. In the elastic region, Sarlink® 3160B TPV exhibits stiffer behaviour than NR75/PP25 TPV even though has a similar hardness (62 Shore A). However, the stress-strain curve shows that Sarlink® 3160B TPV broke at a higher extension than NR/PP TPV and Santoprene™ 101-

55 TPV could be due to high level of process oil or the amount of ethylene content in the EPDM or the different types of PP has been used.


NR75/PP25 TPV   Santoprene™ 101-55 TPV   Sarlink® 3160B TPV

(a)



(b) (c)

Figures 4.31 (a) Dumb-bell fracture sample of NR75/PP25 TPV, Santoprene™ 101-55 TPV, Sarlink® 3160B TPV and (b) and (c) SEM micrographs of etched NR75/PP25 TPV fracture surface.

The micrographs of the surface fracture of etched NR75/PP25 TPV are similar to those of the extracted NR60/PP40 blend (Figures 4.28c, 4.28d and 4.31c and 4.31c). It can be assumed therefore, that the phase morphology of the PP in the blend and in the TPV was similar.

4.3.3.4 Effect of polymer ratio on stress-strain behaviour

Table 4.2 shows that the hardness, modulus and tensile strength values decrease with increased proportion of rubber in the unvulcanised NR/PP blends and TPVs. The unvulcanised NR60/PP40 blend shows stiffer behaviour and reaches the yield zone at higher stress than unvulcanised NR70/PP30 TPV(HP), as a result of higher proportion of PP in the NR60/PP40 TPV(HP). Similar behaviour shows by the TPVs (Figure 4.32). This shows that NR/PP ratio has an important role in contributing to stress-strain behaviour of polymer.

4.3.3.5 Effect of vulcanisation on stress-strain behaviour

As can be seen from Figure 4.32, the unvulcanised NR60/PP40 blend shows linear elastic deformation, a rapid increment in stress with strain at low strain, followed by rapid change in slope which is assumed to be related to yielding of the PP phase. At greater extensions there is very little increase in stress with increases in strain, as the PP phase experiences cold drawing and fracturing while the NR phase flows.

For the dynamically vulcanised blends, beyond the initial linear part of the curve, the stress continues to increase with increase in strain. This increase in stress with extension as compared with the unvulcanised blends is caused by crosslinking of the elastomer phase, which increases its stiffness. For the same reason the vulcanised NR60/PP40 TPV(HP) has a higher modulus and strength than the unvulcanised NR60/PP40 blend (refer to Table 4.2). The NR70/PP30 TPV(HP) shows similar behaviour, but has a lower stiffness and strength as a result of the smaller proportion of PP. In addition to the direct effect of rubber fraction on properties, as the rubber fraction increases, the concentration of peroxide in the rubber also decreases, resulting in further reduction in hardness, modulus and tensile strength.

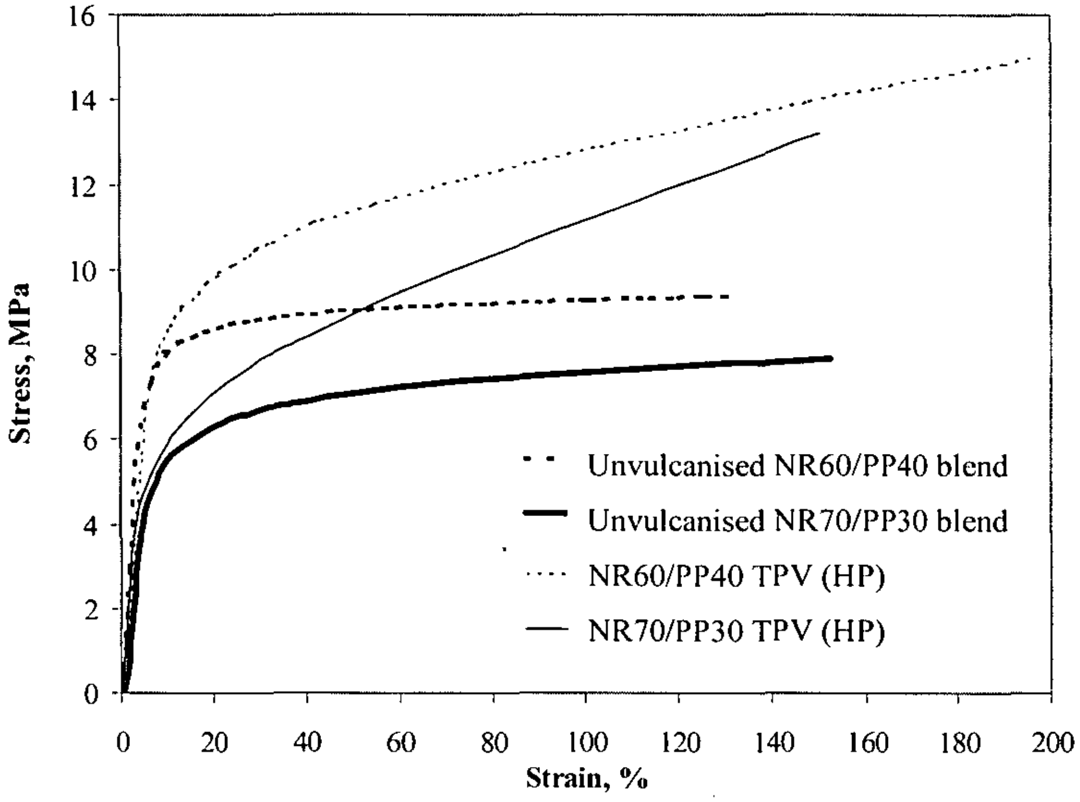


Figure 4.32 Effect of vulcanisation on unvulcanised NR/PP blends and NR/PP TPVs (stretched parallel to main direction of flow).

Different concentrations of peroxide were employed in these studies; 0.036php (LP) and 0.36php(HP). A relatively large difference in peroxide level was chosen in order to see how significant the effect on physical properties would be at very low and high concentrations of crosslinks in the rubber. Table 4.2 shows that the addition of 0.36php of peroxide increases the hardness from 90 to 93 Shore A, while the parallel and perpendicular extension at break decreases from 166% to 158% and 478% to 399%, respectively. It has been reported that for blends containing more than 60 percent of rubber, partial crosslinking of the rubber phase with peroxide increased the hardness[3]

Figure 4.33 shows the effect of peroxide level on stiffness and strength of injection moulded of NR70/PP30 TPV(HP), tensile tested parallel to the direction of flow. The curves are drawn between median values, while the error bars correspond to minimum and maximum values. The addition of peroxide shows a sharp increment in tensile strength and M100 between 0 and 0.036php. This is expected due to the increase in crosslinking. With further increasing peroxide level the tensile strength and M100 increases only slightly. On the other hand, the M50 does not show such a sharp increase with increase in peroxide level form 0 to 0.036. This suggested that at low extension, the tensile behaviour is dominated by PP.

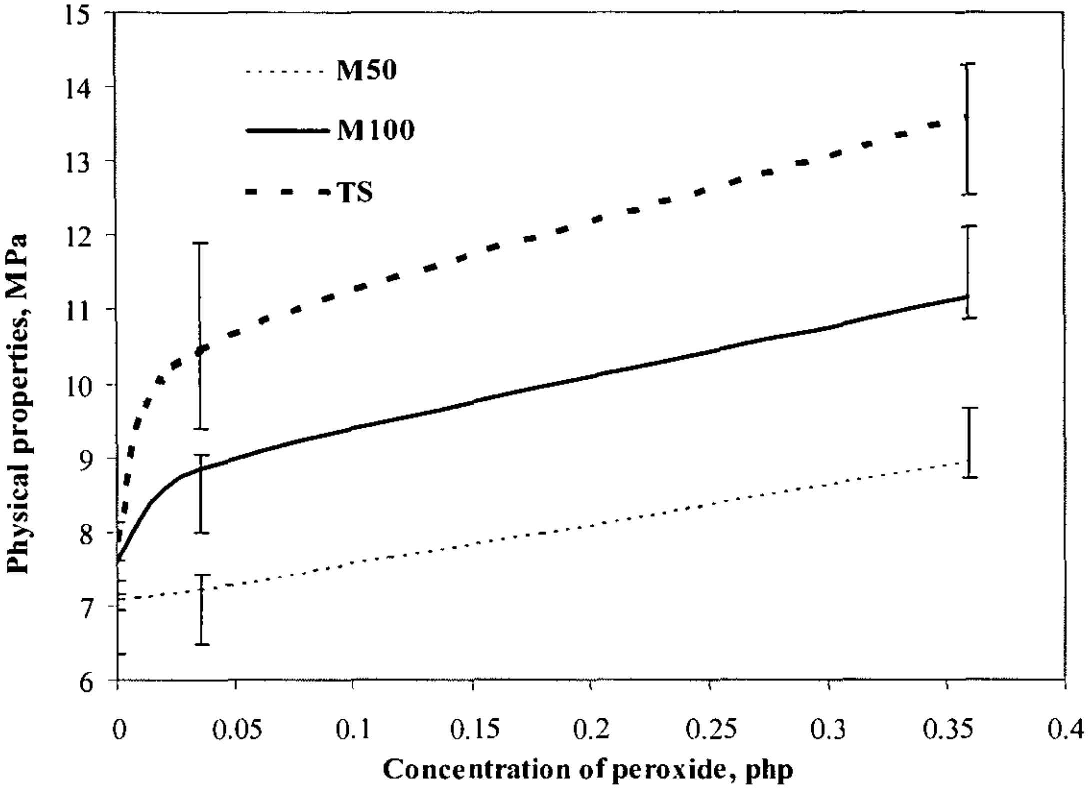


Figure 4.33 The effect of peroxide concentration on physical properties of NR70/PP30 TPV(HP)(stretched parallel to main direction of flow).

4.3.3.6 Effect of orientation on stress-strain behaviour

Injection moulded TPVs show anisotropic behaviour where parallel and perpendicular main direction of flow samples give different property values. It is believed that the differences in orientation of the material arise as the material enters and fills the mould cavity. The polymer chains tend to stretch and become aligned parallel to each other, due to the action of shear forces. The alignment causes the material to have 'soft' and 'stiff' direction, stiff in the orientation direction (parallel sample) and soft at 90° to the orientation direction (parallel sample). As is shown in Table 4.2, higher values of modulus are shown for parallel flow direction samples for unvulcanised NR/PP blends and NR/PP TPVs. The opposite trend is observed for extension at break. Similar results have been reported for an NR/PP TPV with a 70 Shore A hardness[13].

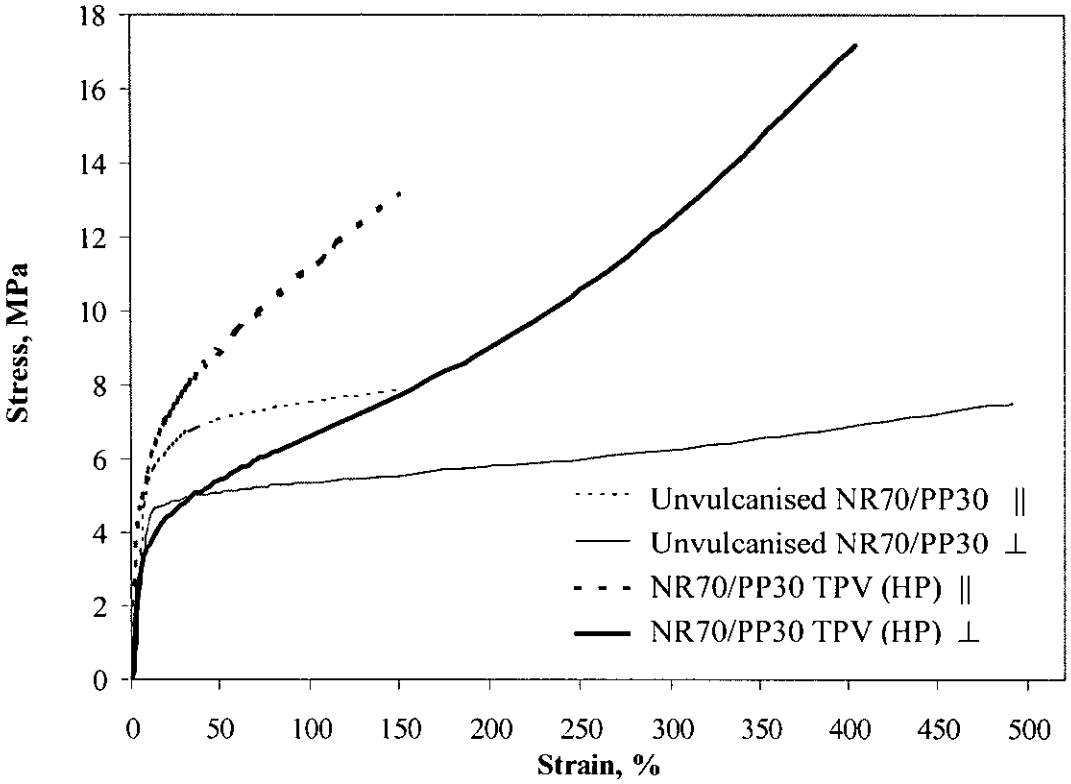


Figure 4.34 Effect of orientation on stress-strain behaviour of unvulcanised NR/PP blends and NR/PP TPVs.

Anisotropic tensile behaviour is also illustrated in Figure 4.34. In the parallel sample, stretching results in high stresses because the PP and NR chains are already aligned in the direction of stretching. In the perpendicular sample, stretching causes the PP and NR chains to first slip and rotate, and because this requires a lower stress than stretching chains, a lower stiffness is observed. A similar trend is shown by unvulcanised NR/PP blends, but the degree of anisotropy is less.

The parallel of NR/PP TPV shows a higher modulus than the unvulcanised NR/PP blend. This is expected because of the crosslinking in the TPV. However, as yet unexplained behaviour is shown by the perpendicular NRTPV samples at low strain. The stiffness at extensions between 5 to 40% is unexpectedly lower for the NRTPV sample than the unvulcanised NR/PP blend. It was speculated that this behaviour might be due to the more laminar phase morphology of the unvulcanised NR/PP blend and more linear phase morphology of TPV blends (as discussed in Section

4.3.3.7 Effect of annealing on stress-strain behaviour

The percentage changes in physical properties on annealing are shown in Table 4.5 based on median values of three samples. It can be seen from the table that annealing causes an increase in hardness and a decrease in M50, M100, tensile strength and extension at break. The decrease in tensile stiffness and strength may suggest that thermal degradation occurred. Alternatively, the increased hardness could be due to increased crystallinity, while the reduction in tensile stiffness and strength could be due to the formation of intercrystalline voids.

Table 4.5 Effect of annealing on physical properties.

	NR60/PP40 TPV (HP)	NR70/PP30 TPV (HP)	NR70/PP30 TPV (LP)	NR75/PP25 TPV (LP)	NR80/PP20 TPV (LP)	Santoprene™ 101-80 TPV
Property						
Hardness, 5s,Shore A	+1	+ 4	-	+9	+12	+1
Percent retention,%						
M50, MPa	-11.	-10	-13	-17	-32	-8
M100,	-24	-23	-13	-18	-31	-15
MPa TS,	-31	-32	-34	-41	-49	-14
MPa EB,%	-51	-28	-24	-31	-20	-35

It was reported that annealing of polypropylene (similar type to the one in this study) caused intercrystalline voids to form in the annealing period, weakening

It was reported that annealing of polypropylene (similar type to the one in this study) caused intercrystalline voids to form in the annealing period, weakening the propagating neck during tensile loading[33]. This causes the samples to break earlier than the unannealed ones (Figure 4.35). It has also been shown that annealing of the same PP greatly increases crystallinity and produced more brittle materials[34]. Annealing of PP fibre was also shown to decrease the tensile strength[35].

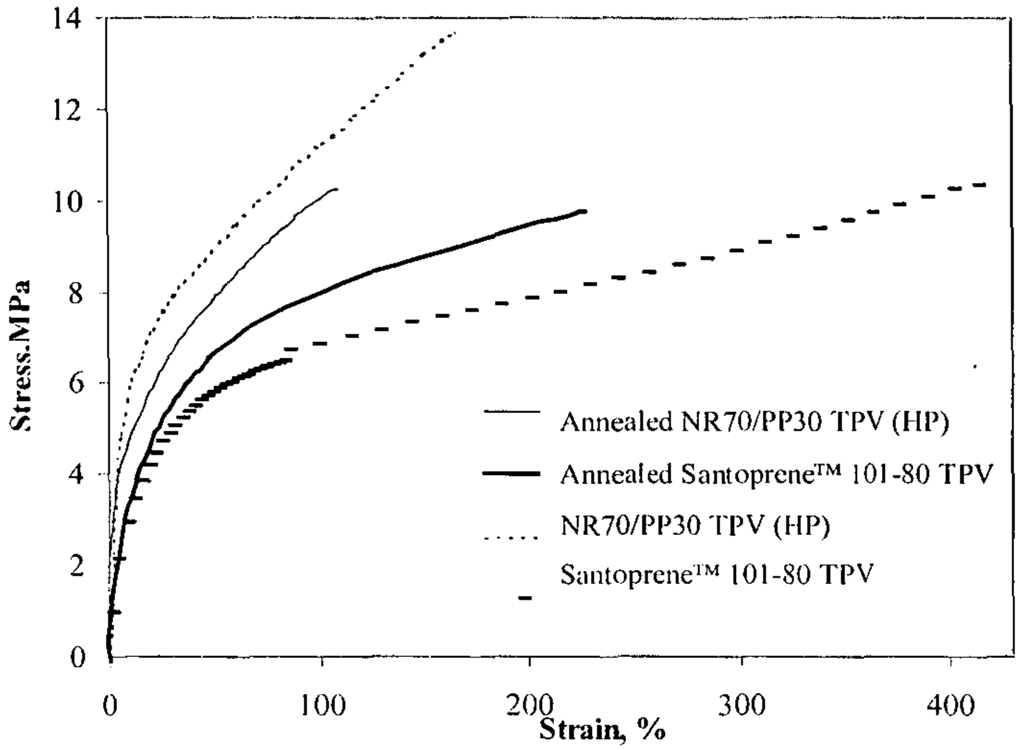


Figure 4.35 Effect of annealing on stress-strain behaviour of TPVs.

4.4 Deformation and recovery behaviour

The ability of a material to return to its original shape after load is removed is called recovery. The recovery behaviour of a material can be measured at low or high strain , and short time scales, such as by tension set measurement, or longer time scales such as by compression set measurement. Recovery behaviour can be also be measured after cyclic deformation.

4.4.1 Compression set

Compression set test pieces were cut from a 6mm thick, injection moulded plaque and were measured at different conditions as shown in Table 3.7 (Chapter 3). There was no significant difference in compression set value measured for samples taken from the eight different areas measured. Figure 4.36 shows 24 hours compression set values for NR75/PP25 TPV and commercial TPVs. It can be seen that the NR/PP TPV shows a considerable increasing in compression set, consequently worse recovery behaviour over the two EPDM based TPVs by increasing a test temperature. TPV ™ 101-55 has better recovery behaviour compared to the other TPVs at all conditions measured. Table 4.6 shows that, for longer periods of compression, the recovery behaviour of

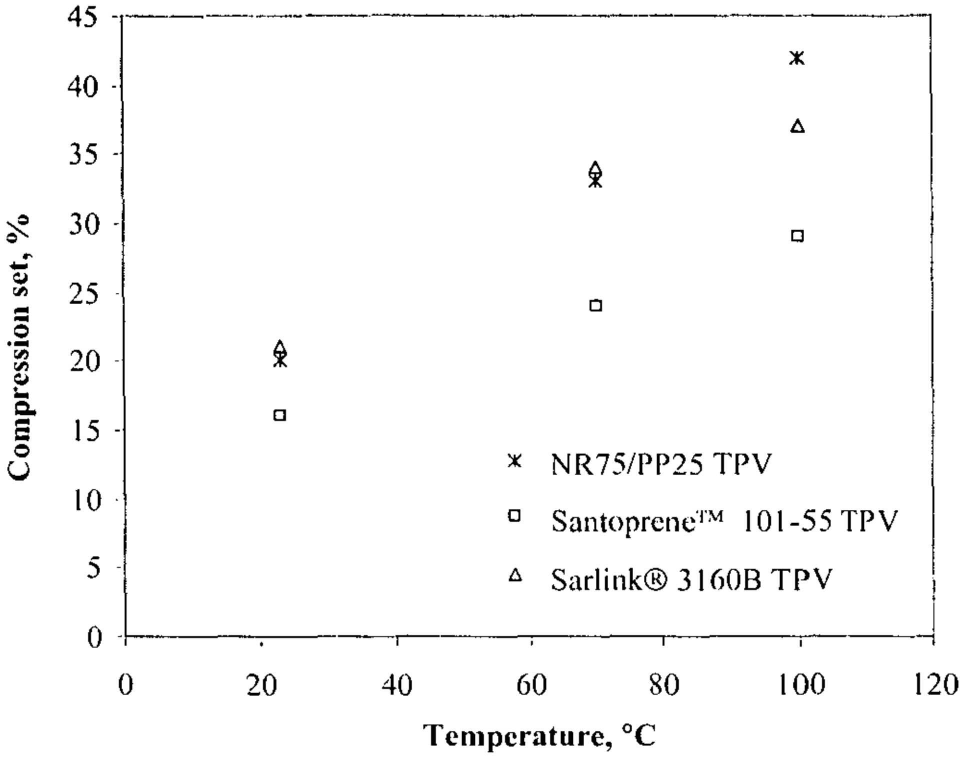


Figure 4.36 Effect of temperature on compression set of TPVs after compression for 24 hours.

Table 4.6 Compression set of TPVs after compressed for 170 hours.

	NR75/PP25 TPV	Santoprene™ 101-55 TPV	Sarlink® 3160B TPV
Property			
Compression set, %			
23°C	26	21	27
100°C	47	42	45

4.4.2 Tensile recovery behaviour

4.4.2.1 Change in 'set' with recovery time

The recovery behaviour of bulk PP and TPVs was investigated by following the change in set values with recovery time (Figure 4.37). 'Bongo' test pieces, cut from 2mm injection moulded sheet were extended up to 30% extension at strain rate of 500mm/min to enable a comparison between the behaviour of bulk PP and TPVs. Set values were measured at medium to long time scales of between 1 minute and 15 days. After just one minute of recovery, the set value for PP had decreased to about 6% and the set value for TPVs had decreased to between about 3% and 4.5%. Over the medium to long time scale shown in the graph, the recovery of the NR TPV seems faster than the commercial EPDM based TPVs.

It was found that there were no significant differences in recovery behaviour between pre-strain rates of 20 mm/min and 500 mm/min.

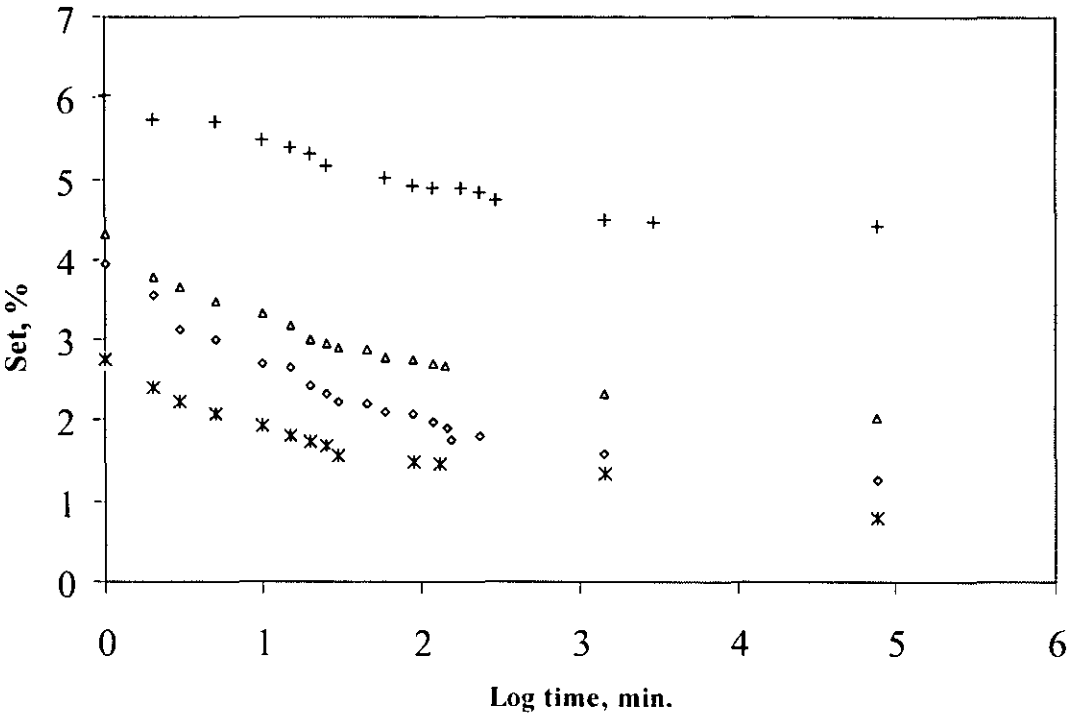


Figure 4.37 Recovery behaviour of bulk polypropylene and TPVs. (+) Polypropylene (◊)NR75/PP25 TPV, (Δ) Sarlink® 3160B TPV, (*) Santoprene™ 101-55 TPV.

4.4.2.2 Tension set

Tension set is a quick and simple method of detecting differences in recovery properties over medium time scales. The median value of tension set for samples cut parallel and perpendicular to the main direction of flow of an injection moulded sheet is shown in Table 4.7. A complete set of results is shown in Appendix A.

The tension set of unvulcanised NR/PP blends is extremely high. The poor recovery is a result of the NR phase not being crosslinked and therefore it experiences a significant amount of viscous flow during deformation. Table 4.7 shows that there is a marked reduction in tension set resulting from dynamic vulcanisation. Introducing a small amount of peroxide in the blend, reduces the average tension set from 52% to 35%. Increasing the peroxide level further, results in a further reduction in tension set due to increased crosslinking in the NR phase. Similar results are also shown in other researcher's findings[35-37] where the elastic recovery properties of soft TPV grades were reported to be significantly improved if the rubber was crosslinked during blending (dynamic vulcanisation).

Table 4.7 Tension set of NR/PP blends and TPVs.

Samples	Tension set, 100%, 10min, 23°C(%)		
	Parallel	Perpendicular	Average
Unvulcanised NR60/PP40 blend	50	54	52
Unvulcanised NR70/PP30 blend	50	53	52
NR70/PP30 TPV(LP)	35	34	35
NR80/PP20 TPV(LP)	26	22	24
NR60/PP40 TPV(HP)	39	39	39
NR70/PP30 TPV(HP)	30	26	28
NR75/PP25 TPV	11	13	11
Santoprene™ 101-80 TPV	25	23	24
Santoprene™ 101-55 TPV	8	9	9
Sarlink® 3160B TPV	13	15	14

Rubber content does not have a significant effect on tension set of the unvulcanised NR/PP blends, but the tension set of NR/PP TPVs decreases with increasing rubber content. The tension set decreases from 35% to 24% by increasing rubber content by 14.3%, as shown by results for NR70/PP30 TPV(LP) and NR80/PP20 TPV(LP). Crosslinked rubber shows better recovery than PP so it is not surprising that better significantly recovery behaviour is observed when there is a greater proportion of rubber in the TPV. A similar trend is shown by NR/PP TPV(HP). It has also been previously reported that set decreases with increases in rubber concentration[21,38].

is shown by NR/PP TPV(HP). It has also been previously reported that set decreases with increases in rubber concentration[21,38].

4.4.3 Cyclic tensile stress-strain behaviour

Short term recovery behaviour of bulk PP, extracted unvulcanised NR/PP blend, NR compound and TPVs was studied by measuring cyclic tensile stress-strain using tensile stress-strain equipment. Three samples for each materials were tested and all test results of the same materials showed good reproducibility, with the exception of unvulcanised NR60/PP40 blend samples. For comparison purposes, for each material, a median value was selected in each case to represent all the tested samples. All results reported in this section were tested stretching parallel to the main direction of flow, unless stated otherwise.

4.4.3.1 Cyclic tensile stress-strain behaviour of bulk polypropylene and NR compound

Figure 4.38 shows cyclic tensile stress-strain behaviour of 'bongo' test pieces of injection moulded PP sheet up to 60% extension at strain rates of 5 mm/min, 50 mm/min and 500 mm/min. At a lower strain rate, increases in extension will arrange the amorphous region aligned with the main direction of strain [12]. A similar behaviour is shows by increasing the strain rate where the cyclic behaviour is also shows a high yield stress (refer to Figure 4.4). The PP sample shows a high 'set' value (27%), indicating poor recovery behaviour. It is believed that the recovery behaviour is due largely to true elastic recovery and rubbery elastic recovery of the amorphous PP region and PP ligaments (Figure 4.41). The 'set' of PP sample tested at low strain rate (5mm/min) is greater than the sample tested at high strain rate (50mm/min) due to more plastic deformation able to take place at a lower strain rate, 27% and 35% respectively. The energy loss during deformation (the region enclosed by the stress-strain curve) is significantly higher in cycle one than the subsequent cycles[3] for all strain rates measured.

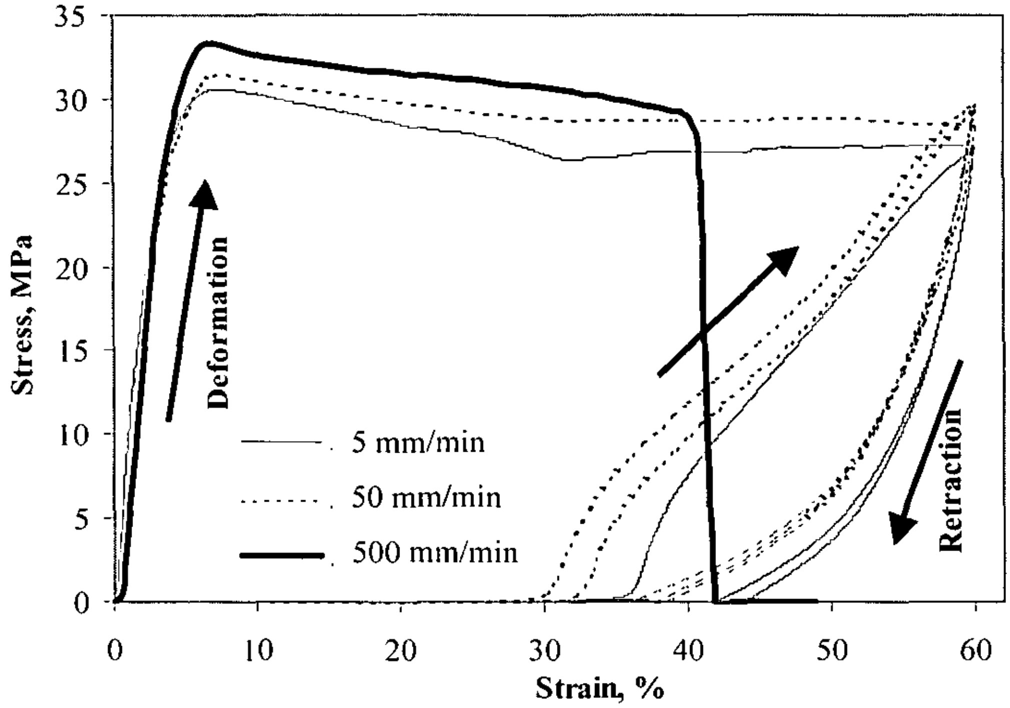


Figure 4.38 Cyclic tensile stress-strain behaviour of bulk PP (3 cycles).

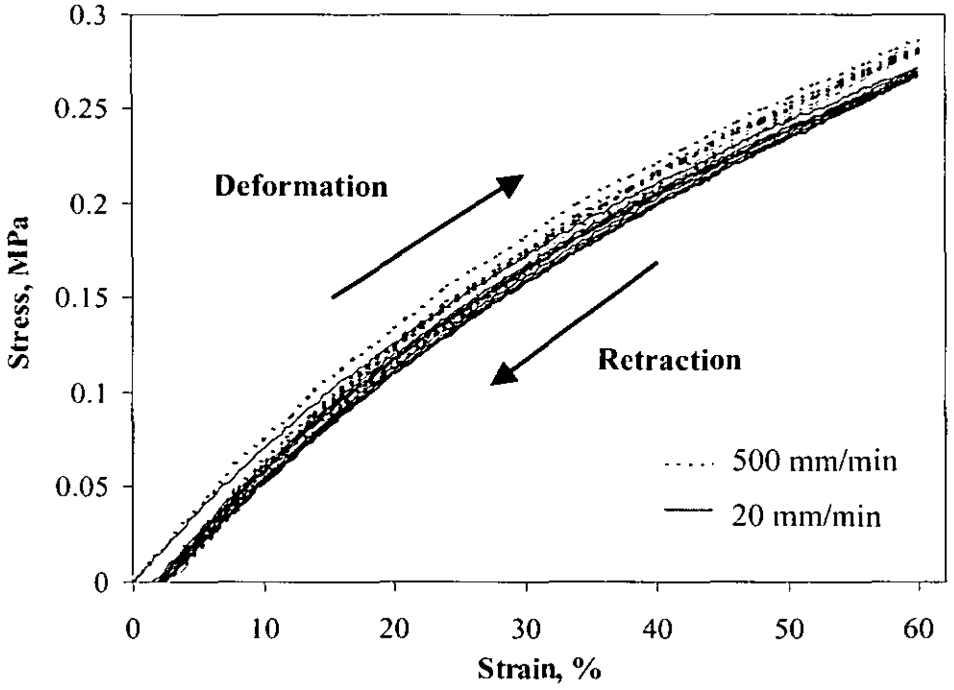


Figure 4.39 Cyclic tensile stress-strain behaviour of NR compound (5 cycles).

Figure 4.39 shows cyclic tensile stress-strain behaviour of 'bongo' test pieces of 2 mm compression moulded NR compounds up to 60% at strain rate at 20 mm/min and 500 mm/min. The NR compound shows good recovery behaviour due to the high elasticity of crosslinked NR. A similar recovery behaviour is observed for both strain rates but test pieces tested at 500 mm/min show a slightly higher maximum stress at the same percent extension. The increase in modulus with increase in strain rate is normal for polymeric materials above their Tg because, at higher strain rates there is less time available for concurrent stress relaxation.

4.4.3.2 Cyclic behaviour of thermoplastic vulcanisates

Cyclic deformation behaviour of NR60/PP40 TPV(HP) is shown in Figure 4.40. 'Bongo' specimens were cut from a 2 mm injection moulded sheet and were strained for 5 cycles between 0% and 60% extension at a strain rate of 20 mm/min. No sharp yield point or necking was shown by NR/PP TPV as compared with the PP cyclic behaviour in Figure 4.39. Similar behaviour has also been reported for EPDM/isotactic PP blends tested at strain rate of 50 mm/min[42].

The deformation cycles of NR/PP TPV are represented by numbers 1 to 5. It is noticeable that there is a large difference in curve shape between extension cycles one and two, but, more similar behaviour shown between cycles 2,3,4 and 5. The deformation and recovery cycles 2 to 5 display a loop called a "hysteresis loop". The area enclosed by the loop is proportional to the energy dissipated when the system goes through a cycle; this represents a considerable energy loss. A large amount of energy is lost in cycle one, but there is a much smaller energy loss in the subsequent cycles. The first extension cycle shows a steep, almost linear initial slope, which becomes flatter beyond about 5% extension. The change in slope occurs over a range of extension values and so is called a 'yield zone', rather than a 'yield point'. The subsequent cycles show a steep initial slope which then reduces in slope with increasing extension although to a lesser extent than in cycle 1. The retraction curves for each cycle are however, very similar.

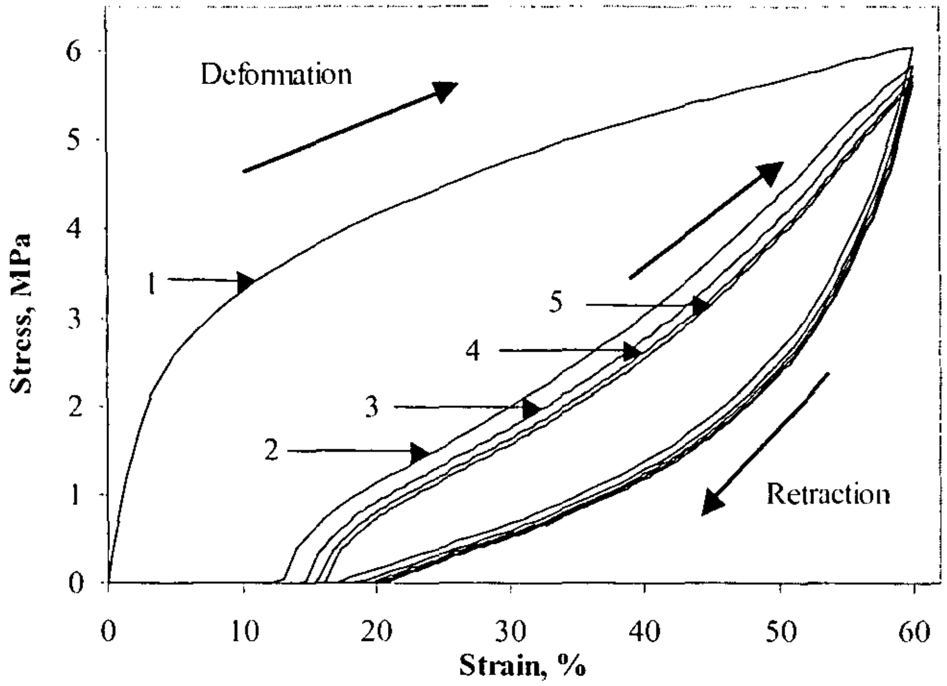


Figure 4.40 Cyclic tensile stress-strain behaviour NR70/PP30 TPV (HP) (stretched parallel to main direction of flow).

The shift of the subsequent cycle loops away from the original can be explained by local destruction[43] of the virgin structure of the NR/PP TPV system during the first cycle, which results in 'set'. Micrographs of etched NR/PP TPV show that the PP phase in TPV comprises both comparatively large and very small PP domains (Figure 4.41).

Micrographs of chromic acid etched NR75/PP25 TPV samples, unstretched, stretched to 200% extension and after recovery for 24 hours are shown in Figure 4.41. The etched surface shows that PP phase consists of domains of various shapes and sizes, including tiny ligaments (Figure 4.41a). There is a possibility that the deformation will occur by "uncoiling of the thin ligaments" and stretching beyond yield point that form the small PP regions, resulting in little actual deformation in the remainder of the PP phase. Such localised deformation in the PP phase may result in breakage as also shown in AFM studies of EPDM/nylon 6 TPV[44]. These confirm the early suggestion that PP and NR phases deform and retract back during recovery after force was released (refer to figures 4.38 and 4.39).

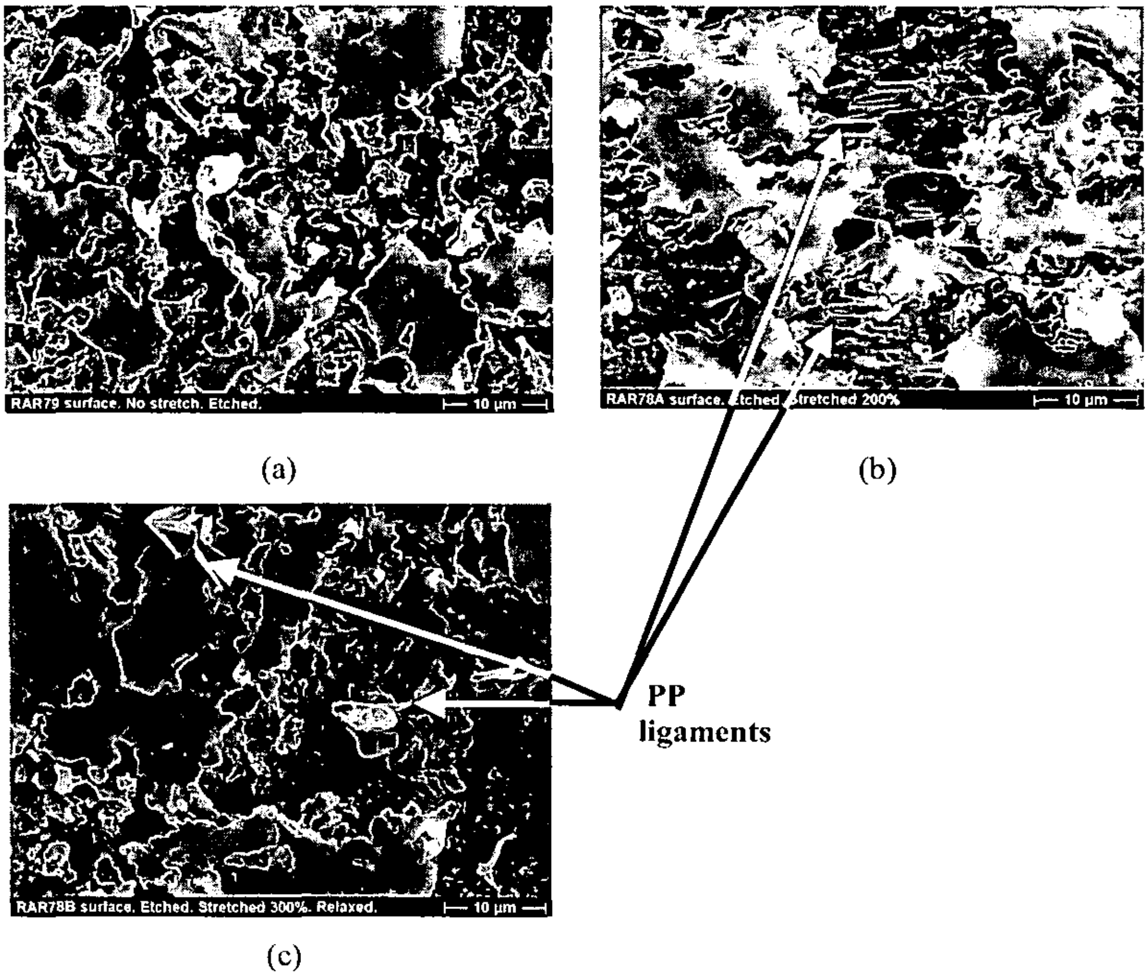


Figure 4.41 Micrograph of surface etched injection moulded NR75/PP25 TPV (a) unstretched, (b) 200% extension (c) after 24hours recovery time.

4.4.3.3 Effect of polymer ratio on cyclic behaviour

Figure 4.42 shows cyclic loading curves of the NR60/PP40 TPV(HP) and NR70/PP30 TPV(HP). The first cycles of the TPVs exhibit a yield zonebetween 2 to 5% extension. The NR60/PP40 TPV(HP) generally shows stiffer behaviour and reaches the yield zone at higher stress than NR70/PP30 TPV(HP), as a result of the higher proportion of PP in the NR60/PP40 TPV(HP) material.

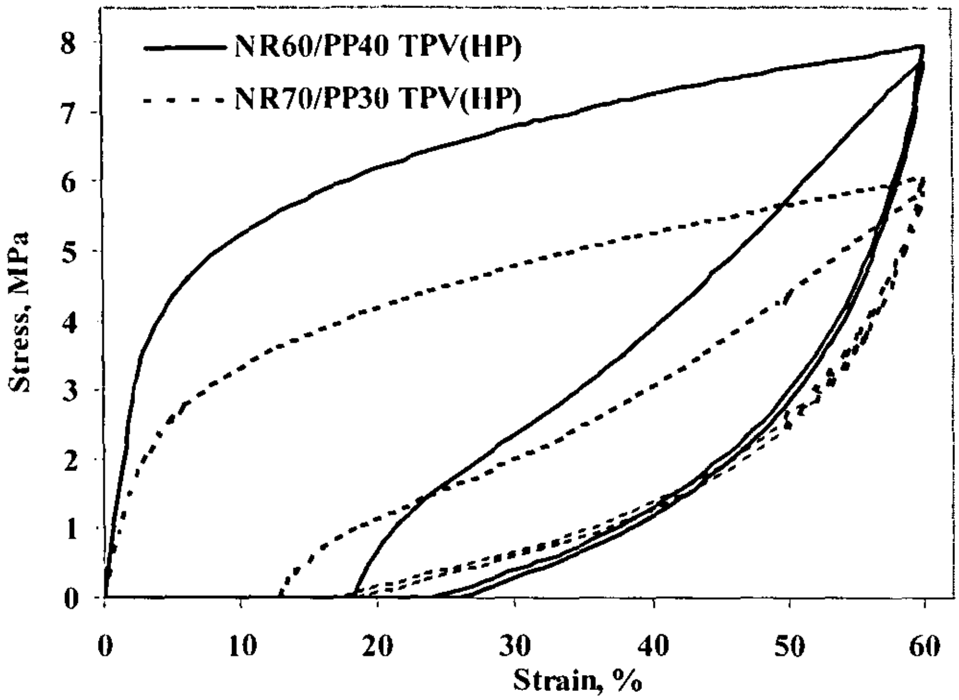


Figure 4.42 Effect of polymer ratio on NR/PP TPV(HP) (stretched parallel to main direction of flow).

Table 4.8 'First cycle set' of unvulcanised NR/PP and TPVs materials.

	'First cycle set',%		
Materials	Parallel	Perpendicular	Average
Unvulcanised NR60/PP40 blend	32	25	29
Unvulcanised NR70/PP30 blend	23	24	24
NR60/PP40 TPV(HP)	18	18	18
NR70/PP30 TPV(HP)	13	12	13
NR75/PP25 TPV	9	7.9	8
Santoprene™101-55 TPV	5.7	5.7	5.7
Sarlink® 3160B TPV	7.6	7.9	7.7

The 'first cycle set' of unvulcanised NR/PP and NR/PP TPV materials are shown in Table 4.8. The 'first cycle set' describes the unrecovered deformation caused by the first cycle. It is defined as the strain range over which the stress value in the second extension cycle is zero. The lower the 'set' value, the better the recovery behaviour. As can be seen in Table 4.8, the average 'first cycle set' for parallel and perpendicular samples of NR60/PP40 is also higher than for the NR70/PP30 materials, 18% and 13%, respectively. As suggested above, not all of the PP phase is exposed to full extension[45]. Increasing the PP content is likely to increase the disruption within in the PP phase affecting the ability of the TPV to retract after deformation.

Santoprene™101-55 TPV shows a slightly better recovery behaviour than the other TPVs. It is believed that Santoprene™101-55 TPV has a high amount of rubber phase (higher crosslinked, good elasticity) contributes to a lower 'set' value, consequently better recovery behaviour. A similar recovery behaviour is shown from the tension set value (Table 4.7).

4.4.3.4 Effect of vulcanisation on cyclic behaviour

Figure 4.43 presents the stress-strain recovery behaviour of the NR70/PP30 blend [unvulcanised NR/PP blend] and NR70/PP30 TPV (HP)[vulcanised TPV]. Both first cycles show a yield zone at about 2% to 5% extension. Beyond 10% extension, the NR70/PP30 blend exhibits a high degree of plastic deformation with a large increase in strain giving comparatively little increase in stress. Conversely, the vulcanised material exhibits rubbery elastic behaviour where the stress increases with increased strain. Recovery, as measured by tension set is significantly greater as a result of vulcanisation of the rubber phase (Table 4.7). Vulcanisation crosslinks the rubber phase, so as to increase the elastic contribution to the deformation of the blend. The results are similar to those for EPDM/PP(60/40) TPV as studied by Chung and Coran[37].

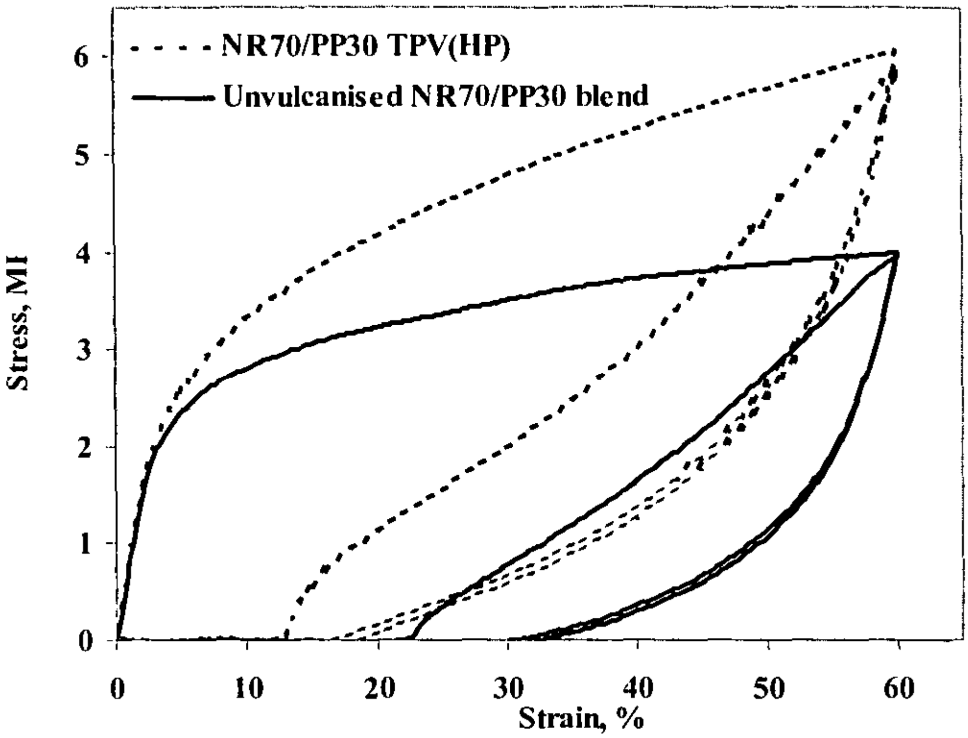


Figure 4.43 Effect of vulcanisation on NR60/PP40 TPV (HP) (stretched parallel to main direction of flow).

4.4.3.5 Effect of orientation on cyclic behaviour

The effect of flow orientation in moulded sheets from which test pieces of unvulcanised NR/PP and NR/PP TPV is shown in Figures 4.44 and 4.45. Different cyclic stress-strain behaviour is shown when samples are stretched parallel and perpendicular to the main flow direction.

Both the 'parallel' and 'perpendicular' materials in Figures 4.44 and 4.45 exhibit a yield zone ranging from about 3% to 8% extension. However, the parallel samples exhibit the yield zone at a higher stress than perpendicular samples. In addition, the 'parallel' NR70/PP30 TPV(HP) samples also exhibit the yield zone at a higher stress than the 'perpendicular' NR70/PP30 sample. The lack of effect of vulcanisation on the yield zone shows that at low extension, the deformation behaviour was largely dominated by the PP phase. The crystalline and amorphous regions of PP phase become aligned in the direction of strain. For the parallel sample there is already orientation in the stretching direction, giving higher stresses.

Both the unvulcanised NR/PP blend and NR/PP TPV materials produced a higher maximum stress in 'parallel' samples. At 60% strain the 'parallel' and 'perpendicular' NR70/PP30 samples have a maximum stress at about 4 MPa and 2.5 MPa, respectively. While the 'parallel' and 'perpendicular' NR70/PP30 TPV(HP) samples have a maximum stress at 6 MPa and 4 MPa, respectively. There is not a significant difference in the average 'first cycle set' between 'parallel' and 'perpendicular' samples for both unvulcanised NR/PP blends and NR/PP TPVs.

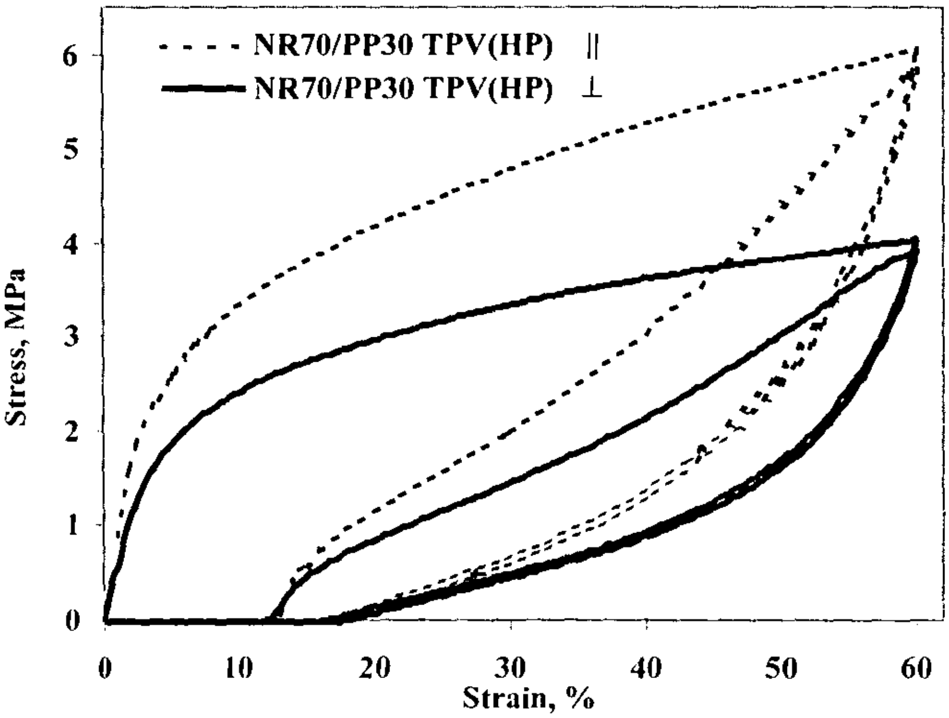


Figure 4.44 Effect of orientation on NR70/PP30 TPV (HP).

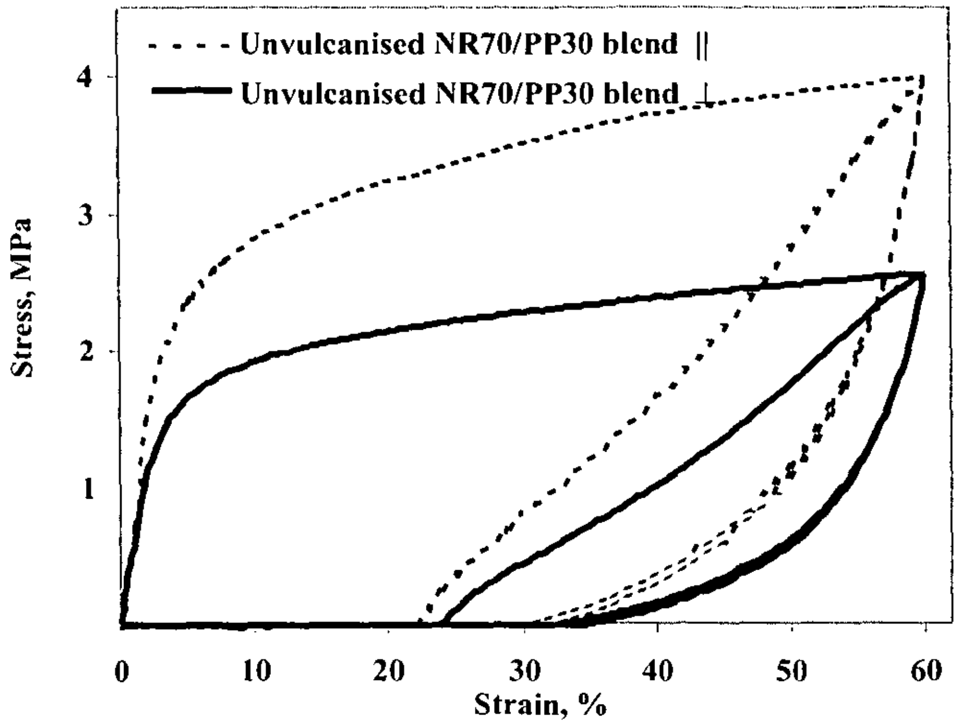


Figure 4.45 Effect of orientation on unvulcanised NR70/PP30 blends.

4.4.3.6 Plasticised TPVs based on NR/PP and EPDM/PP blends

Plasticised TPVs referring to NR75/PP25 TPV and other commercial TPVs that have a process oil as plasticiser in the formulations. In general, the addition of plasticiser in the TPV will reduce a modulus at 50% or 100% extension compared with the non plasticised TPVs. The cyclic stress-strain curves of TPVs based on NR/PP blend (NR75/PP25 TPV) are similar to TPV based on EPDM/PP blend (Figures 4.46 and 4.47). The Sarlink® 3160B TPV materials exhibit a steeper initial slope in the elastic deformation region than NR75/PP25 TPV and Santoprene™ 101-55 TPV. The 'parallel' samples exhibit increased stiffness where the yield zone is reached and achieve higher maximum stress at 60% extension than 'perpendicular' samples. Similar trends are shown for 'parallel' and 'perpendicular' NR75/PP25 TPV and Santoprene™ 101-55 TPV samples.

The Santoprene™101-55 TPV exhibits slightly better 'first cycle set' than the other TPVs. A similar trend is seen in the recovery behaviour of NR75/PP25 TPV and Sarlink® 3160B TPV indicated by tension set and 'set' of tensile recovery tests (section 4.4.2).

All TPVs describe in this section exhibit an anisotropic behaviour where the 'parallel' maximum stress is higher than the 'perpendicular' one. The maximum stress of 'parallel' and 'perpendicular' NR75/PP25 TPV, Santoprene™ 101-55 TPV and Sarlink® 3160B TPV is 1.6 MPa, 1.7 MPa, 2.4 MPa and 1.1 MPa, 1.15 MPa and 1.6 MPa, respectively.

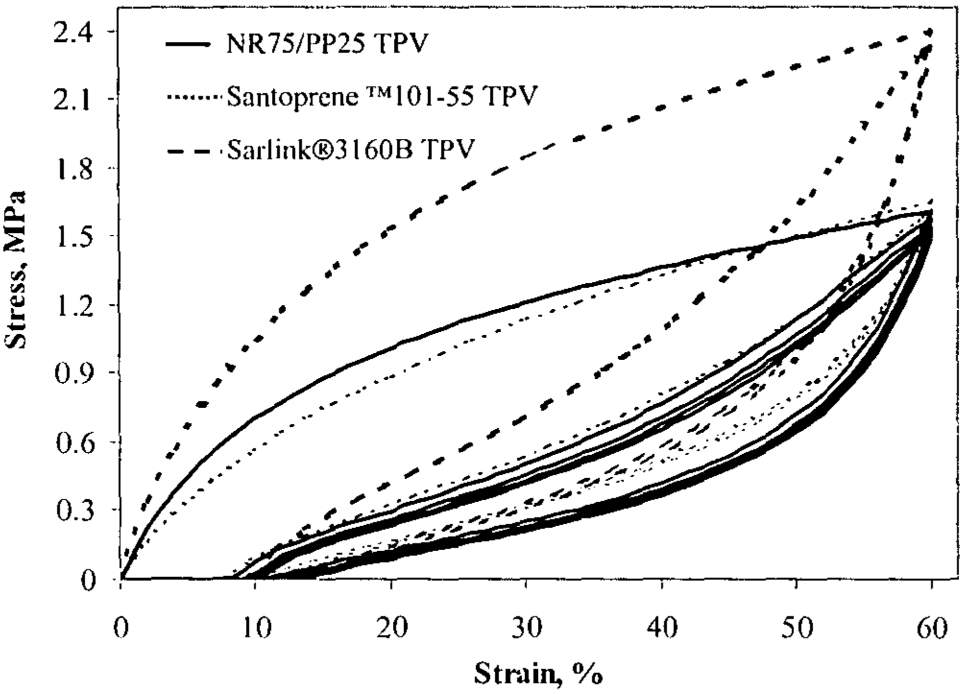


Figure 4.46 Deformation behaviour of TPVs (stretched parallel to main direction of flow).

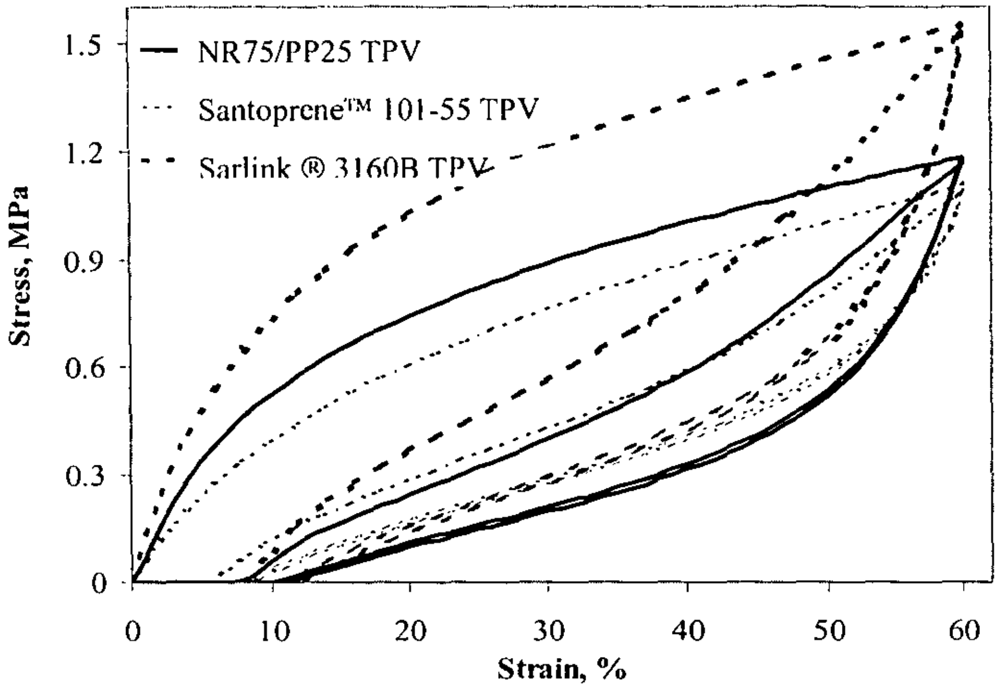


Figure 4.47 Deformation behaviour of TPVs (stretched perpendicular to main direction of flow).

4.4.3.7 Effect of pre-strain on cyclic behaviour

Pre-strain, followed by cyclic test is one technique to represent a product that operates over many cycles in their actual conditions such as door seals. In this section, the cyclic test was done after 30 minutes recovery time the pre-strain end. 'Bongo' test pieces cut from 2 mm extrudate strip that has been pre-strained up to 100% at a strain rate of 500 mm/min, show stress-strain behaviour similar trends to the the second cycle of cyclically tested samples that have not been pre-strained. (Figures 4.48 and 4.49). At 5% extension the second cycle stress-strain curve is the same as the first, indicating that there is no disruption to the structure. At 100% extension the second cycle is different from the first, indicating that further disruption to the structure has occurred. However, the change in slope of the first cycle deformation curve indicates that the disruption occurs at greater than about 90% extension. This is because,

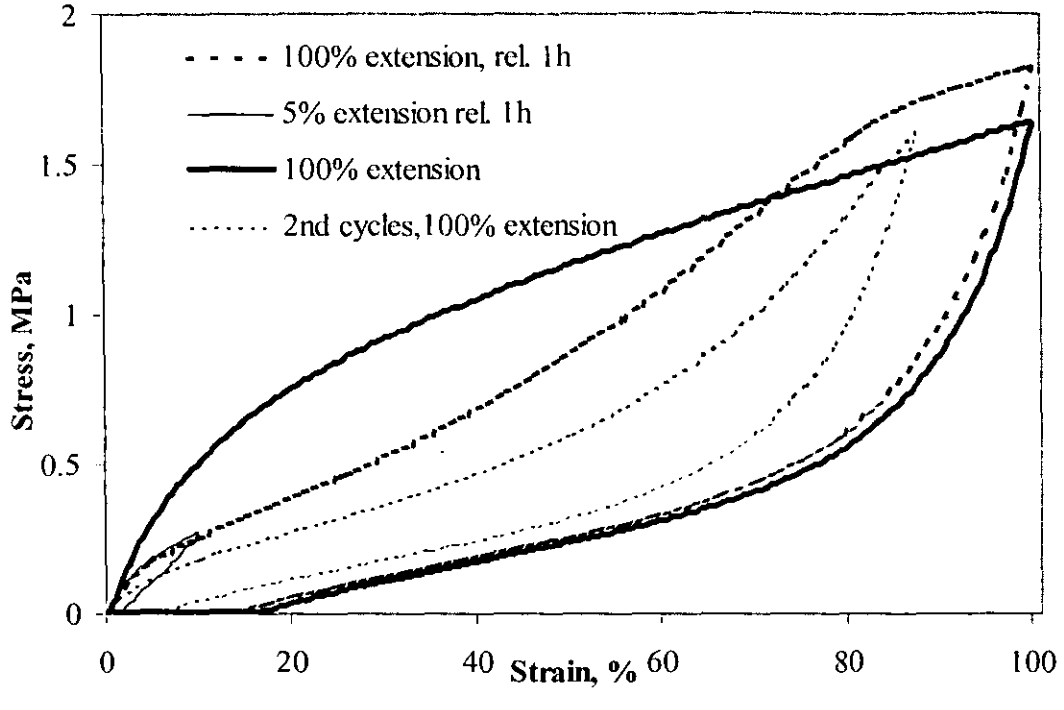


Figure 4.48 Effect of cyclic behaviour of 'bongo' test pieces NR75/P25P TPV (5% and 100% extension, no pre-strain and 1h relaxation time).

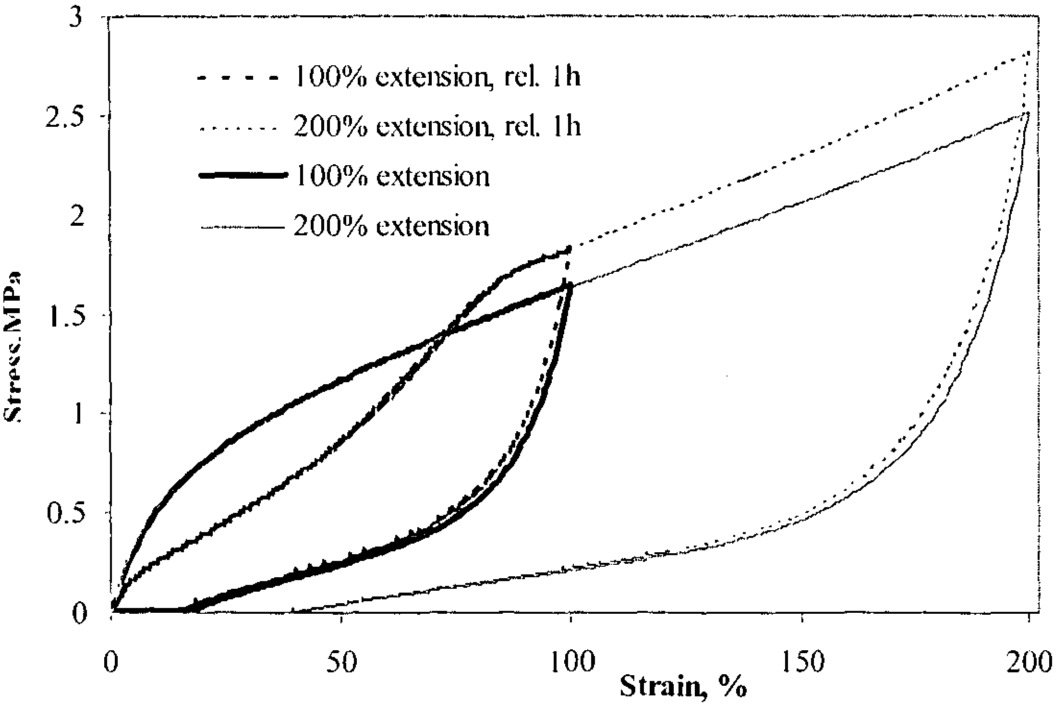


Figure 4.49 Effect of cyclic behaviour of 'bongo' test pieces of NR75/P25P TPV (100% and 200% extension after 1h relaxation time).

although the pre-strain was 100%, the sample did not return to its original length but exhibited some "permanent set". Therefore, when the sample after pre-strain was extended to 100% it was effectively being stretched to more than 100% of its original length (before pre-strain). At 200% extension there is further damage caused to the structure.

4.4.3.8 Cyclic behaviour with increasing amplitude

The effect of continuous cyclic stress-strain cycling whilst immediately increasing the strain achieved immediately after each cycle can be seen in Figure 4.50. Similar behaviour to that seen following pre-strain is observed, that is the extension move for a particular cycle follows a lower stress path until the strain reached exceeds that previously experienced by the sample. At this point the extension move reverts to following the anticipated stress path of a previously unstrained sample. The stress-strain behaviour shown by the sample is similar to that shown by conventional black filled rubber sample undergoing cyclic stress softening. A similar trends as the effect of pre-strain in section 4.4.3.7 (Figures 4.48 and 4.49). The NR75/PP25 TPV has about 85% recovery after 100% extension.

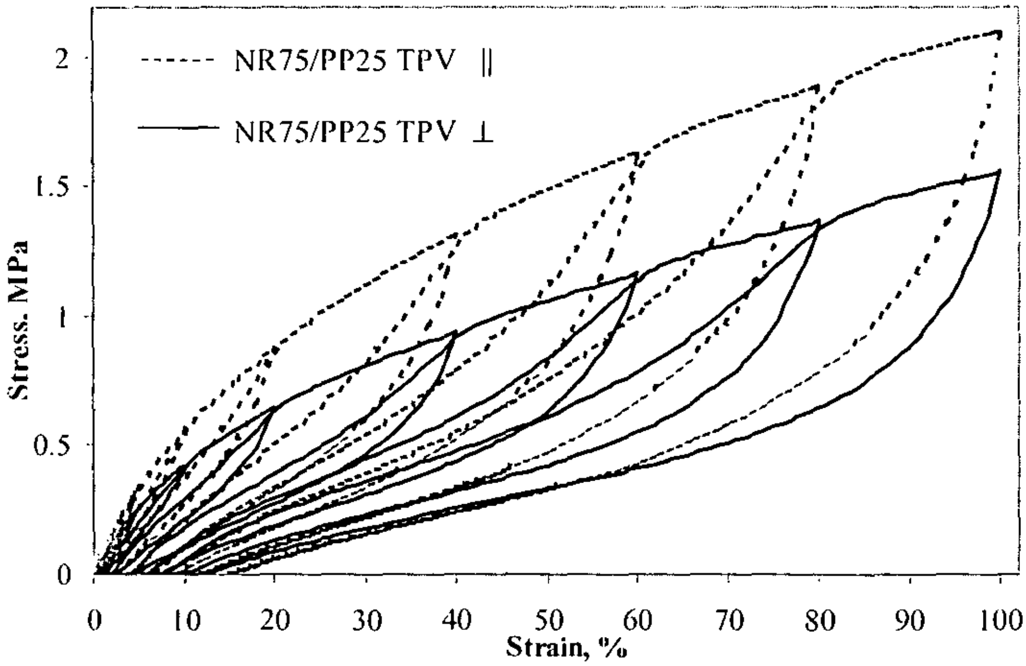


Figure 4.50 Continuous cyclic stress-strain cycling of 2 mm 'bongo' injection moulded NR75/PP25 TPVs at strain rate of 20 mm/min.

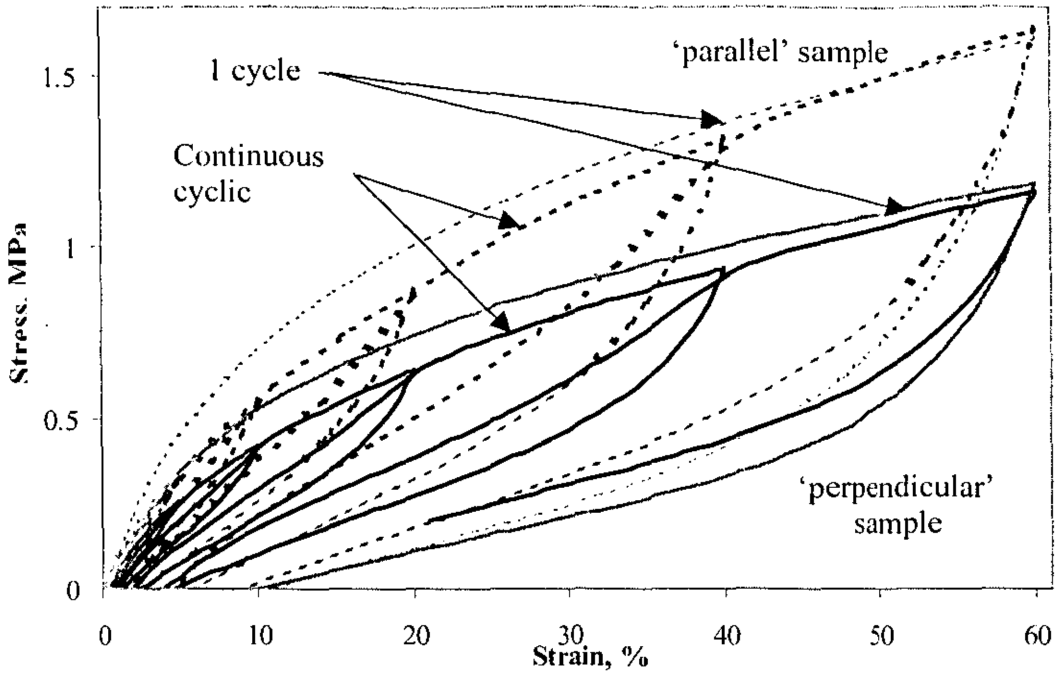


Figure 4.51 Cyclic tensile stress-strain of 2 mm'bongo' injection moulded of NR75/PP25 TPVs, one cycle and continuous cyclic stress-strain cyclic up to 60% extension at strain rate of 20 mm/min.

Figure 4.51 compares the 1 cycle continuous cyclic stress-strain cycling whilst immediately increasing the strain achieved immediately after each cycle up to 60% extension. The 1 cycle charts shows a higher maximum stress than the continuous cycle for both 'parallel' and 'perpendicular' samples. This is due to the ability of the continuous cyclic sample to relax before the next cycle and stress softening of the previous cycles. Similar behaviour also shows by Sarlink© 3160B TPV sample.

4.4.3.9 Effect of relaxation time on cyclic behaviour

The effect of relaxation time on cyclic tensile stress-strain behaviour of extrudate NR75/PP25 TPV is shown in Figures 4.52 and 4.53. Figure 4.52 shows that after 7 days from initial pre-strain of 100%, the first cycle has a relatively high energy loss approximately 66% of the original pre-strain cycle. This indicates that the stress-strain behaviour of the NR75/PP25 TPV has recovered at high proportion of its original characteristics after 7 days. A similar trends show by increasing relaxation time up to 4 months (Figure 4.53). Cycle two and subsequent cycles however show a significant reduction in energy loss aith comparatively little difference in energy loss between subsequent cycles. It is proposed that the energy loss is largely due to distruption of the PP structure within the TPV.

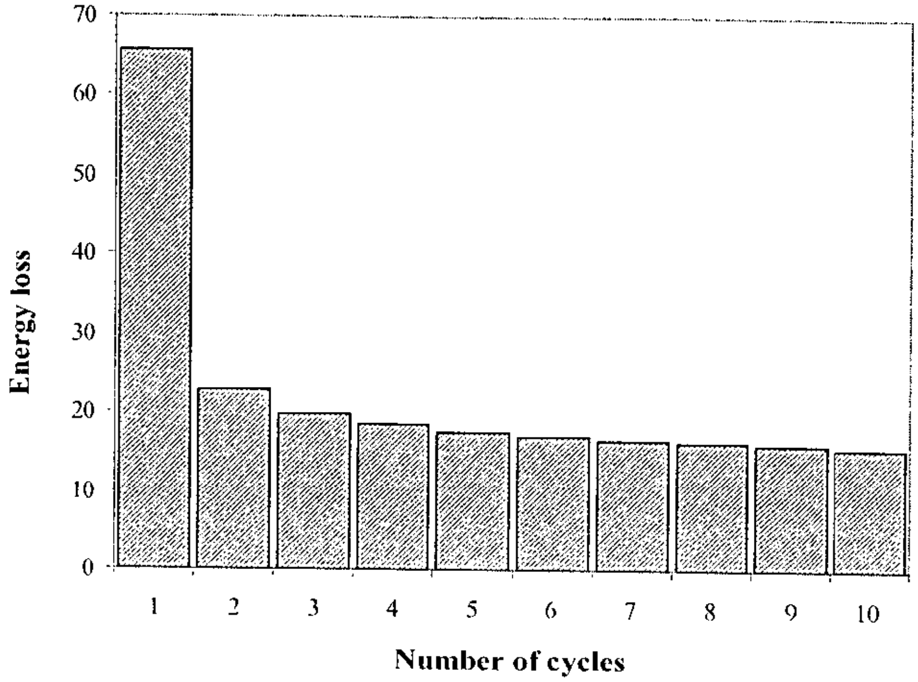


Figure 4.52 Energy loss during deformation of extrudate NR75/P25 TPV (after 7 days relaxation time).

The effect extended reduction period on the shape of the cyclic stress-strain curve is seen in Figure 4.54. The curves compare the first and second cycle behaviour of the TPV (with no pre-strain) with the behaviour of a period of relaxation time of up to 4 months (following an initial pre-straining of 100%). The material becomes stiffer as it recovers and the extension curve become increasingly linear with increased the relaxation time but still falls short of the original behaviour of the TPV upon extension. The retraction curve however is almost identical in each case, irreaoective of relaxation time.

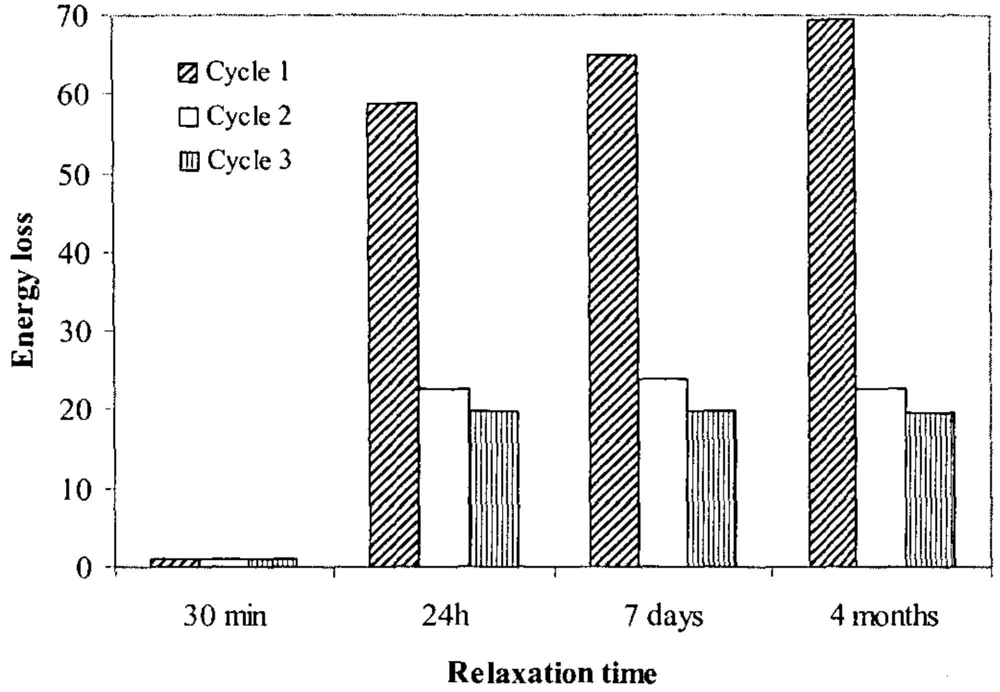


Figure 4.53 Energy loss after long relaxation time of extrudate NR75/P25P TPV (after 100% pre-strain at strain rate of 500 mm/min).

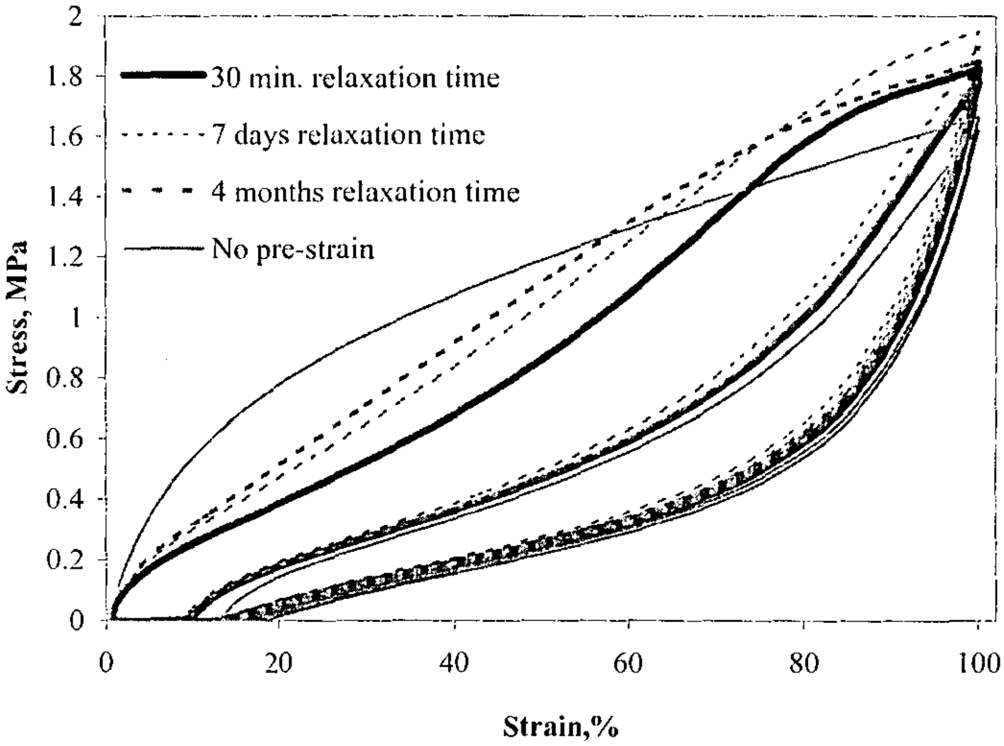


Figure 4.54 Effect of relaxation time of extrudate NR75/P25P TPV (after 100% pre-strain at strain rate of 500 mm/min).

References

1. D.J. Elliot and A.J. Tinker (1988) "Chapter 9. Blends of natural rubber with thermoplastic" in "Natural Rubber Science and Technology (Ed. A.D. Robert)". Oxford University Press, Oxford, New York, pp.327-57.

2. P. L.C. Sawyer and D.T. Grubb (1987) "Chapter 4. Specimen preparation methods" in "Polymer Microscopy". Chapman and Hall. London New York, p. 95.

3. S.Y. Hobbs and V.H. Watkins (1981) The use of chemical contrast in the SEM analysis of polymer blends, *J. Polym.: Polym.Phys.* Ed. **20**, pp. 651-658.

4. C.L. Riddiford and A.J. Tinker (1990) TPENR, A new oil-resistant thermoplastic elastomer. Presented at a meeting of the Rubb. Div., ACS, Washington DC, Paper 33.

5. S. Cook, N.A. Jones, J. Patel and A.J. Tinker (2001) Fatigue properties of thermoplastic elastomers, *Int. Rubb. Conf. 2001*, Birmingham.

6. S. Cook, R.T. Davies, J. Patel, K.M.E. Lawrence and G. Sica (2003) Morphological studies of thermoplastic vulcanisates, *Int. Rubb. Conf. 2003*, Nurnberg.

7. J. Orderkerk and G. Groeninckx (2002) Morphology development by reactive compatibilisation and dynamic vulcanisation of Nylon6/EPDM with a high rubber fraction, *Polymer* **43**, pp. 2219-2228.

8. D.J. Elliot (1986) Some properties and prospects of thermoplastic natural rubber blends, *Kaut. Gumm. Kunst.* **39**, pp. 621-624.

9. D.S. Campbell, D.J. Elliott and M.A. Wheelans (1978) Thermoplastic natural rubber blends, *NR Technol.* **9**, pp. 21-31.

10. Santoprene® Rubber 101-55 – Advanced Elastomer System –thermoplastic elastomer data provided by IDES or http://www.matweb.com/search/SpecificMaterial.asp?bassnum=PADV10 (accessed on 12 Feb. 2006)

11. Santoprene® Rubber 101-80 – Advanced Elastomer System –thermoplastic elastomer data provided by IDES or http://www.matleb.com/search/SpecificMaterialPrint.asp?bassnum.PADV14 (accessed on 8 August, 2005)

12. DSM Elastomer Sarlink series 3000 http://www.dsm.com/en_US/downloads/sarlink/Sarlink_3160_iso.pdf (accessed on 1 Oct 2006)

13. I.R.Gelling and AJ.Tinker (1988) Thermoplastic natural rubber, performance and applications, Proceedings Int. Rubb. Technol. Conf., p. 216.

14. A.J. Tinker (2005) MPG lecture, Manchester (Power point presentation).

15. M.D. Wang and M. Cakmak (2001) Basic studies on development of structure hierarchy in tubular film blown dynamically vulcanised PP/EPDM blend, *Rubb. Chem. Techol.* **74**, pp. 761 -777.

16. M. Cakmak and S.W. Cronin (2000) The effect of composition and processing conditions on the structure development in injection molded dynamically vulcanised PP/EPDM blends, *Rubb. Chem. Techol.* **73**, pp. 753-778.

17. M. Fujiyama, T. Wakino and Y. Kawasaki (1988) Structure of skin layer in injection –moulded polypropylene, *J. Appl. Polym. Sci.* **35**, pp. 29-49.

18. M. Kamal and F. May (1983) Microstructural characterization of injection – molded articles, *J. Appl. Polym. Sci.* **28**, pp. 1787-1804.

19. M.R. Kantz, H.D. Newman and F.H. Stigale (1972) The skin-core morphology and pstructure–property relationships in injection-moulded polyropylene, *J. Appl. Polym. Sci.* **16**, pp. 1249-1260.

20. M. Fujiyama and K. Azuma (1979) Skin/core morphology and tensile impact strength of Iinjection-moulded polypropylene, *J. Appl. Polym. Sci.* **23**, pp. 2807-2811.

21. A.Y. Coran and R.P. Patel (1980) Rubber-thermoplastic compositions. Part 1. EPDM-Polypropylene thermoplastic vulcanisates, *Rubber Chem. Techol.* **53**, pp.141-150.

22. A.J. Tinker (1984) Preparation of polypropylene natural rubber blends having high impact strength at low temperature, *Polymer Commun.* **25**, p. 325.

23. D.J. Elliot (1986) Influence of crosslinking agents and interfacial aAdhesion promoters on the properties of natural rubber – polypropylene blends. Int. conf. on rubber and rubber-like materials, Jamshedpur, India, (Ed., S.K. De) Kharagpur : India Institute of Technology.

24. D.J. Elliot (1990) "Chapter 4. Natural rubber-polypropylene blends" in "Thermoplastic Elastomers from Rubber-plastic Blends (Eds. S.K. De and A.K. Bhowmick)". Ellias Horwood Ltd., Chichester, pp. 103-129.

25. A.J. Tinker (1984) Preparation of polypropylene natural rubber blends having high impact strength at low temperature, *Polymer Commun.* **25**, p. 325.

26. D.J. Elliot (1986) Influence of crosslinking agents and interfacial adhesion promoters on the properties of natural rubber – polypropylene blends. *Int. Conf. on Rubber and Rubber-like Materials*, Jamshedpur, India, (Ed. S.K. De) Kharagpur : India Institute of Technology.

27. G. Meinel and A. Peterlin (1971) Plastic deformation of polyethylene II. Change of mechanical properties during drawing, *J. Polym. Sci. Part A-2: Polym Phys.* **9**, pp. 67-83.

28. A. Peterlin (1971) Molecular model of drawing polyethylene and propylene *J. Mat. Sci.* **6** , pp.490-508.

29. C.A. Daniels (1989) "Chapter 4 .Tensile properties" in "Polymer: Structure and Properties". Technomic Publishing Co. Ltd., Lancaster, pp. 43-55.

30. R.J.Samuels (1974) "Chapter 4. Application : Quantative correlation of polymer structure with end-use properties" in "Structured Polymers Properties The Identification, Interpretation, and Application of Crystalline Polymer Structure". John Wiley & Sons, New York London Sydney Toronto, Pp. 160-164.

31. J. Kotek, J. Kratochvil, J. Baldrian and M. Raab The effect of annealing on structure and mechanical behaviour of isotactic polypropylene. Ins. of Macromolecular Chemistry, Academy of Science of the Czech Republic (accessed on 25.01.04).

32. R.L. Miller (1960) On the existence of near-range order in isotactic polypropylenes, *Polymer* **1**, pp. 135-143.

33. W.K. Fischer (1973) Thermoplastic blend of partially cured monoolefin copolymer rubber and polyolefin plastic, US 3758643 (to Uniroyal, Inc.).

34. A. M. Gessler and W.H. Haslett (1962) Process for preparing a vulcanised blend of crystalline polypropylene and chlorinated butyl rubber, US 3037954 (to Esso Research and Engineering).

35. O. Chung and A.Y. Coran (2002) The effect of dynamic vulcanisation on the morphology and mechanical property of rubber/plastic blends, ANTEC 2002 Plastics: Annual Technical Conference, Vol III, San Francisco. *Vol. 3*, pp. 3192 – 3196.

36. A.Y. Coran and R. Patel (1980) Rubber-thermoplastic compositions. Part II. NBR-nylon thermoplastic elastomeric composition, *Rubb. Chem. Technol.* **53**, pp. 781-794.

37. http://www.cmse.ed.ac.uk/AdvMat45/Lecture3_Polymer%20Structure.pdf (accessed on 8 August. 2004) (Reproduced with permission from J. Schultz, *Polymer Material Science*, Prentice-Hall,New Jersey, 1974, pp.500-501.

38. C.B. Bucknall (1977) Toughened plastics, Applied science, London, pp. 359.

39. A. Dasari, R.D.K. Misra (2003) On the strain rate sensitivity of high density polyethylene and polypropylene, *Material Sci. Eng.* A **358**, pp.357-371.

40. D.B. Cavanaugh and C.H. Wang (1981) Effect of the chain alignment on the brillouin scattering spectra of hydrostatically extruded polypropylene, *Macromol.* **14**, pp. 1061.

41. S. Kawabata, S. Kitawaki, H. Arisawa, Y. Yamashita and X. Guo (1992) Deformation mechanism and microstructure of thermoplastic elastomer estimated on the basis of its mechanical behaviour under finite deformation, *J. Appl. Sci. :Appl. Polym. Symp.* **50**, pp.245-259.

42. S. Toki, I. Sics, C. Burger, D. Fang, L. Liu, B.S. Hsiao, S. Data and A.H. Tsou (2006) Structure evolution during cyclic deformation of an elastic propylene-based ethylene-propylene copolymer, *Macromol.* **39**, pp. 3588-3597.

43. A. Datta, J. J. Zhou, J. J. Yuan and A. Monisera (1997) The Effects of annealing conditions on the structure and properties of polypropylene fibers. Technical paper series of Medical Plastics and Biomaterials Magazine, http://www.devicelink.com/mpb/archive/97/11/005.html (accessed on 23 May 2005).

CHAPTER 5
CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The following conclusions can be drawn from the work that has been done in this project.

1. Feasibility of producing and processing NR/PP TPVs

It is possible to make soft thermoplastic vulcanisates (TPVs) from natural rubber (NR) and polypropylene (PP) across a broad range of compositions (from 60/40 to 80/20, NR/PP). The TPVs have properties comparable to commercial TPVs based on EPDM/PP, and can be easily processed by injection moulding and extrusion.

2. Phase morphology of TPVs

TPVs containing between 60% and 80% NR have a co-continuous NR and PP phase morphology, as determined by solvent extraction, etching and microscopic examination. Microscopy of etched materials showed that the TPVs consist of relatively large domains (1.0 to 7.0 μm) of PP phase joined by thinner PP ligaments. It is believed that the PP ligaments are important in the deformation and recovery behaviour of the TPVs. They can absorb stress during extension by bending, rotating and stretching and can buckle after the stress is released. In this way, PP ligaments can contribute to the overall recovery behaviour of the TPV.

3. Recovery behaviour of TPVs

The ability of a material to return to its original shape after an applied load is removed is called recovery. The recovery behaviour of the NR/PP TPVs, as measured by tension and compression set measurement and cyclic tensile behaviour, was similar to commercial TPVs, e.g. Sarlink® 3160B. The relatively good recovery behaviour of the TPV materials is believed to be largely due to elastic recovery in the rubber domain. However, a contribution is also due to some elastic recovery of the PP ligaments in the PP phase.

4. Effect of dynamic vulcanisation on properties of NR/PP blends

Dynamic vulcanisation crosslinks the rubber phase increasing its stiffness, strength and elasticity and hence, increases the modulus, strength and recovery properties of the NR/PP blends. The peroxide co-agent system possibly also increases the interfacial adhesion between two phases as a result of grafting reactions between the rubber and polypropylene and consequently contributes to the improvement of the mechanical and recovery properties.

5. Effect of polymer ratios on deformation and recovery behaviour of NR/PP TPVs

The NR to PP ratio in unvulcanised NR/PP blends and TPVs has a large effect on the physical and deformation behaviour of the materials. An increase in the amount of PP in the blends increases the hardness, the stress at 50% and 100% elongation, and increases the tensile strength and decreases the elongation at break. An increase in rubber content of TPVs improves recovery behaviour as there is more crosslinked rubber present to provide a retractive force. The deformation behaviour of the first cycle at low extension (up to 5%), below the yield point of the PP, is dominated by the PP phase. At higher extension, beyond the yield point of the PP, the stress-strain behaviour is dominated by the NR phase.

6. Anisotropy in NR/PP TPV properties

Unvulcanised NR/PP blends and TPVs exhibit anisotropy in tensile stiffness, being stiffer when stretched parallel to the main direction of flow. The anisotropy in properties is largely attributed to flow-induced molecular orientation within the individual phases, because phase morphology showed only a weak linear orientation.

7. Effect of annealing on properties of NR/PP TPVs

Annealing of NR/PP TPVs results in an increase in hardness and decrease in tensile strength which is thought to be due to greater crystallinity in the PP phase, resulting in a more brittle material which is more prone to fracture.

8. Effect of plasticiser addition on NR/PP TPV properties

The inclusion of process oil as a plasticiser in NR/PP TPVs results in a finer phase morphology and a softer, more extensible material with better recovery behaviour than the material obtained when plasticiser is not used. The volume fraction of the rubber phase increases from 72% to 82% by addition of the plasticiser to the TPVs formulation. The plasticised material is also softer somewhat weaker, but is still comparable in strength to those of a range of commercial TPVs of similar hardness.

The plasticised NR75/PP25 TPV shows recovery behaviour in between that of the commercial TPVs, Santoprene™ 101-55 and Sarlink® 3160B which have similar compression set, tension set, stress-strain behaviour and cyclic behaviour to the NRPP TPV.

9. Stress-softening behaviour of NR/PP TPVs

Stress-softening behaviour, reminiscent of that shown by conventional black filled rubber vulcanizates, is observed for the NR/PP TPVs at room temperature, either during cyclic deformation or after application of pre-strain. After experiencing deformation to an initial strain level, the stress exhibited during subsequent deformation follows a lower stress path, up to that initial strain level. When deformed beyond the initial pre-strain level, or beyond the first cycle strain level, the stress-strain behaviour then observed is similar to that of the previously undeformed material.

Increasing the relaxation time between pre-strain, or the first deformation cycle and following cycles, results in greater recovery and the deformation behaviour starts to approach that of the original, undeformed material. Although the recovery behaviour of bulk PP (1%) and TPVs (1.2% to 1.6%) within 30 minutes of the deformation being removed, a significant proportion, about 98%, of the material does not fully recover, even after 54 days. The origin of the stress-softening behaviour is believed to be mostly due to a permanent alteration of the thermoplastic phase of the blend, probably by either breaking or stretching the PP ligaments beyond their yield point.

5.2 Recommendations for future work

Several aspects of the work described need further exploration. The project outline in this report provides the basis for possible future research in the field of deformation and recovery of TPVs.

- Polarised FTIR and Raman spectroscopy

Spectroscopy studies by using polarised FTIR or Raman can be applied to examine the effect of orientation on the deformation and recovery behaviour of bulk PP and the TPVs. A better technique of film preparation must be developed before proceeding with the spectroscopy research.

- Crystallinity

The effect of spherullite size and percentage of crystallinity in the PP phase can be explored further using a range of annealed and quenched samples. The crystallinity difference between bulk PP and that in the TPV also needs to be studied. The changes in crystallinity can be revealed by differential scanning calorimetry (DSC), x-ray diffraction and Raman spectroscopy.

- Long term recovery behaviour

Long term recovery behaviour of the TPVs can be studied by carrying out compression or tension stress relaxation (CSR or TSR) tests. The ability of a material to maintain stress is not constant but decreases with time (stress relaxation). So, CSR can be run in order to determine how the TPV behaves after extended time intervals, after cyclic deformation or exposure to elevated temperatures. Further long-term deformation and recovery behaviour of TPVs can be studied by example exposing the samples to 5 cycles in a tensile extensometer, followed by fatigue tests for several thousand cycles. After completion, the cycle stress-strain behaviour of the sample can be examined to see the effect of fatigue on deformation and recovery properties. It is also of interest to observe the changes in microstructure, including phase morphology, the nature of the interface, orientation and crystallinity. Fatigue behaviour is of interest because the TPV based on NR/PP blend has been shown to be very good in recovery behaviour.

Appendix A

Tension Set

$$\text{Tension set,\%} = \left(\frac{L_l - L_0}{L_s - L_0} \right) \text{x } 100$$

Where, L_0 is the original unstrained reference length = 37.3 mm

L_s is the strained reference length = 74.6 mm

L_l is the reference length after recovery, mm

L_s-L_0 = 37.3mm

Sample Reference	**L_l**	**L_l -L_0**	**Set,% = $\frac{L_l - L_0 \text{ x } 100}{L_s - L_l}$**	**Median set,%**
Unvulcanised NR60/PP40, parallel	57	19.7	52.8	50.1
	56	18.7	50.1	
	56	18.7	50.1	
	57	19.7	52.8	
	56	18.7	50.1	
Unvulcanised NR60/PP40, perpendicullar	57.5	20.2	54.2	54.2
	57	19.7	52.8	
	58	20.7	55.5	
	57.5	20.2	54.2	
	57	19.7	52.8	
Unvulcanised NR70/PP30, parallel	56	18.7	50.1	50.1
	56	18.7	50.1	
	56	18.7	50.1	
	56.5	19.2	51.5	
	55.5	18.2	48.8	
Unvulcanised NR70/PP30, perpendicullar	57	19.7	52.8	52.8
	57	19.7	52.8	
	57.5	20.2	54.2	
	57	19.7	52.8	
	57	19.7	52.8	
NR60/PP40 TPV(HP), parallel	52	14.7	39.4	39.4
	52	14.7	39.4	
	52	14.7	39.4	
	52	14.7	39.4	
	52	14.7	39.4	
NR60/PP40 TPV(HP), perpendicullar	52	14.7	39.4	39.4
	52.5	15.2	40.8	
	52	14.7	39.4	
	52.5	15.2	40.8	
	52	14.7	39.4	

Sample Reference	**L_1**	**$L_1 - L_0$**	**Set,% = $\frac{L_1 - L_0}{L_s - L_1} \times 100$**	**Median set,%**
NR70/PP30 TPV(HP), parallel	48.5	11.2	30.0	30.0
	53	15.7	42.1	
	48	10.7	28.7	
	50	12.7	34.0	
	48	10.7	28.7	
NR70/PP30 TPV(HP), perpendicullar	47	9.7	26.0	26.0
	53	15.7	42.1	
	47	9.7	26.0	
	53	15.7	42.1	
	46	8.7	23.3	
NR70/PP30 TPV(LP), parallel	50.5	13.2	35.4	35.4
	50.5	13.2	35.4	
	50.5	13.2	35.4	
	50.5	13.2	35.4	
	50.5	13.2	35.4	
NR70/PP30 TPV(LP), perpendicullar	50	12.7	34.0	34.0
	50	12.7	34.0	
	50	12.7	34.0	
	50	12.7	34.0	
	50	12.7	34.0	
NR75/PP25 TPV(LP), parallel	47.5	10.2	27.3	27.3
	47.5	10.2	27.3	
	47.5	10.2	27.3	
	47.5	10.2	27.3	
	47.5	10.2	27.3	
NR75/PP25 TPV(LP), perpendicullar	47	9.7	26.0	26.0
	47	9.7	26.0	
	47	9.7	26.0	
	47	9.7	26.0	
	47	9.7	26.0	
NR80/PP20 TPV(LP), parallel	47	9.7	26.0	26.0
	47	9.7	26.0	
	47	9.7	26.0	
	47.5	10.2	27.3	
	47	9.7	26.0	
NR80/PP20 TPV(LP), perpendicullar	45.5	8.2	22.0	22.0
	45.5	8.2	22.0	
	45.5	8.2	22.0	
	45.5	8.2	22.0	
	45.5	8.2	22.0	

Sample Reference	**L_1**	**$L_1 - L_0$**	**Set,% = $\frac{L_1 - L_0}{L_s - L_1}$ x 100**	**Median set,%**
NR75/PP25 TPV, parallel	41.5	4.2	11.3	11.3
	41.7	4.4	11.8	
	41.5	4.2	11.3	
	41.5	4.2	11.3	
	41.7	4.4	11.8	
NR75/PP25 TPV, perpendicullar	42	4.7	12.6	12.6
	42	4.7	12.6	
	42	4.7	12.6	
	42	4.7	12.6	
	42.5	5.2	13.9	
Santoprene™ 101-80, parallel	46.5	9.2	24.7	24.7
	46.5	9.2	24.7	
	46.5	9.2	24.7	
	46	8.7	23.3	
	46.5	9.2	24.7	
Santoprene™ 101-80, perpendicullar	46	8.7	23.3	23.3
	46	8.7	23.3	
	46	8.7	23.3	
	46	8.7	23.3	
	46	8.7	23.3	
Santoprene™ 101-55, parallel	40.5	3.2	8.6	8.0
	40.3	3	8.0	
	40	2.7	7.2	
	40.3	3	8.0	
	40.5	3.2	8.6	
Santoprene™ 101-55, perpendicullar	40.5	3.2	8.6	8.6
	40.5	3.2	8.6	
	40.5	3.2	8.6	
	41	3.7	9.9	
	*			
Sarlink® 3160B, parallel	42	4.7	12.6	12.6
	42	4.7	12.6	
	42.2	4.9	13.1	
	42	4.7	12.6	
	42.5	5.2	13.9	
Sarlink® 3160B, perpendicullar	43	5.7	15.3	15.3
	43.5	6.2	16.6	
	43	5.7	15.3	
	43	5.7	15.3	
	43.5	6.2	16.6	

* Sample broke on extension