IPTME The Institute of Polymer Technology and Materials Engineering

Loughborough University

Interpenetrating polymer networks based on natural rubber and poly(methylmethacrylate)

by

Madhupani Mekhala Jayasuriya

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University

September 2006

Supervisor: Professor Douglas J. Hourston

Institute of Polymer Technology and Materials Engineering

This Thesis is

Dedicated to

My Loving Son and Husband

Acknowledgement

I would like to extend my gratitude to my Supervisor, Prof. D. J. Hourston, for his great support rendered throughout my studies, including guidance, commitment and helping me to obtain financial support from SSL International in the UK and also from the university of Loughbourough.

My special thanks also goes to my Research Director, Prof M. Gilbert for her kind co-operation

I also thank the academic staff and technical staff and friends, especially, Mrs. Roha Majid for their numerous support.

I would like to extend my sincere thanks to the Director, Rubber Research Institute of Sri Lanka and the Rubber Research Boards for granting study leave and for the financial support given for me to carry out my studies leading to this PhD thesis. I am also very thankful to the former Chairman of the Rubber Research Board, Mr. R. I. Obeysekera for his great support and encouragement for carrying out my studies.

The support extended by the Akzo Nobel by freely providing Triganox 21S initiator for this study should also be acknowledged.

Among the various others who supported me in numerous ways, and who should not be forgotten, include Dr. David Grandy for the DMTA work for the latter part of the study, Dr. Nnada Fernando, one of the experts in this field for helping to get Mooney viscosity and stress-relaxation data, Mr. Sampath Weragoda for the enormous support given with software applications. Mr Silva, Chemanex Ltd , for providing some important chemicals, Mr. Manju perera of Ansell Lanka Ltd., for providing natural rubber latex throughout this study. I thank Prof. Ravi Wejesundara, Prof Kshanika Hiriburegama, Mr. Premadasa and Mrs Nilakshi of University of Colombo, Mr. Sagara Prasad of University of Sri Jayawardenepura for FTIR studies and Dr. Razzak and Mr. Keerthe of Medical Research Institute for their support.

It is also my duty to thank all the staff of the Department of Rubber Technology of the rubber Research Institute, especially, Mr. Piyatissa, Mrs. Sriyani Yapa, , Mr. Rnajith and Mrs Poson for their support during my work conducted in Sri

Lanka. Support from persons of other departments, namely Dr. A. Nugawela, C. K. Jayasinghe and Mr. Ananda is also acknowledged herewith

Last, but not least, to my husband and my dear son for their patience and sacrifice, and for the enormous support given to met to complete this study. Finally, I would like to take this opportunity to thank my loving parents and sisters and brothers for their moral support as well as guidance and help.

ABSTRACT

Several series of sequential interpenetrating polymer networks using natural rubber and poly(methylmethacrylate) were prepared. Three types of IPNs known as semi-1 IPNs, semi-2 IPNs and full IPNs have been prepared at various compositions In addition, blends of natural rubber and poly(methylmethacrylate) were prepared for comparison. These materials have been characterized by dynamic mechanical thermal analysis, modulated-temperature thermal differential scanning calorimetry, stress-strain analysis and some soxhlet extraction studies. The effects of composition and cross-linking of NR component and/or PMMA component on the physical and dynamic mechanical properties have been evaluated.

All types of IPN and the blends produced in this study were phase separated. However, the blends exhibited considerable amounts of mixing of components resulting most probably from grafting PMMA chains on to natural rubber. In addition, incorporation of PMMA in to the natural rubber matrix rendered high tensile strength and modulus which tended to increase with increasing PMMA content.

Cross-linking of the natural rubber in the semi-1 IPNs reduced the extent of mixing of the NR component as was evident from DMTA data. In general, cross-linking of the first polymer natural rubber, increased the extent of mixing of the PMMA component resulting in a extensive interphasial regions in the semi-1 IPNs. Tensile properties significantly improved with cross-linking of the NR component

Some mixing of the NR component was evident for the semi-2 IPNs. Cross-linking of the PMMA component increased the extent of component mixing resulting in a substantial interphase content in the semi-2 IPNs The tensile strength of these semi-2 IPNs increased with cross-linking and the optimum tensile strength was found to be dependent on the EGDM level.

Cross-linking of both components in the full IPNs improved the extent of mixing of the components over the corresponding semi-2 IPNs The tensile properties and the interphase content of full IPNs were comparable to the semi-1 IPNs.

Attempts were been made to improve the compatibility between the natural rubber and poly(methylmethacrylate) components by incorporating epoxidised natural rubber (ENR) in to this system. Incorporation of ENR-45 and ENR-60 improved the extent of mixing of natural rubber component as was evident from the prominent shift of the NR glass transition to the higher temperature. With increase of the epoxidation level to a 60 mole %, the miscibility between the ENR component and PMMA component was increased when compared to the ENR with 45 or 50 mole % Apart from this, the physical properties such as tensile strength and tear strength increased with incorporation of ENR

Because of the phase separation between the ENR and PMMA components, further attempts were made to improve the compatibility. This target was achieved using 10 wt.% of acrylic acid which resulted in significant shifts in the NR and PMMA transitions. Moreover, compatibilization/miscibility between the ENR and PMMA components has been improved to achieve a virtually miscible system by incorporating acrylic acid at a level of 20-30 wt.%.

Interpenetrating polymer networks
based on
natural rubber and poly(methylmethacrylate)

Table of Contents

1.0 Introduction, literature review and objectives

2.0 Experimental methods and characterisation

4.0 A critical overview of the effects of cross-linking of the natural rubber and/or the poly(methylmethacrylate) components on the dynamic and physical properties of the blends, semi-1, semi-2 and full IPNs

List of Figures

List of Tables

CHAPTER 1

1.1 General description

This chapter describes the composition, preservation and biosynthesis of natural rubber (NR) latex. In addition, the methods which have been used for the modification of NR are also included Among the modified forms of NR, interpenetrating polymer networks (IPNs) based on NR has been considered as one of the novel modified forms of NR, as this modification method had not been previously investigated thoroughly. Hence, the present investigation is fundamentally concerned with IPNs based on NR and polymethylmethacrylate (PMMA) A literature survey on the chemical modification of NR and on IPNs based on NR and PMMA has been carried out and will be presented in the latter part of this chapter.

1.2 Natural rubber latex

NR latex can be described as the cytoplasm of anastomosed cells stored in parenchyma cells or laticifers (d'Auzac, 1989). Laticifers are primarily divided into articulated and non-articulated types. Articulated-type laticifers have a single or branched series of cells in which the end walls are perforated and form a anastomosed system. In *Hevea* and *Manihot glaziovii* of Euphorbiaceae, a branched articulated laticiferous system is present and forms lateral anastomoses (Figure 1 1) (d'Auzac, 1989).

Even though *ca.* 7000 plants possess latex, exploitation of latex in the majority of plants is impossible due to the presence of resin in the latex. Therefore, the *Hevea brasiliensis* tree, the best plant for obtaining latex, has been cultivated on a commercial scale in most of the South Asian countries The NR industry plays a vital role in the economics of these countries.

1.2.1 Composition of rubber latex

NR latex is obtained from the tree bark by a process called tapping, which helps to exploit the secondary laticifer vessels of the trunk. As these laticifers are located in the phloem tissues, tapping process will not cause any damage to the tree (Figure 1.1) (d'Auzac, 1989).

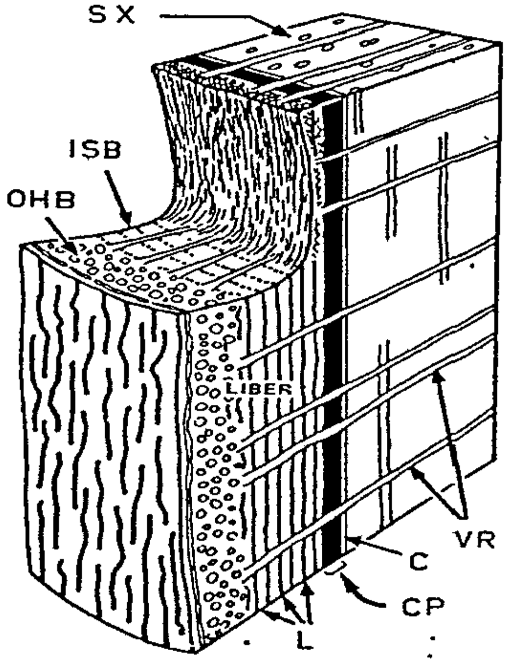


FIGURE 1 1 Sketch of the general organization of *Hevea brasiliensis* bark at tapping cut level. (C) cambium; (CP) conducting phloem, (ISB) inner soft bark, (L) laticiferous vessels, (OHB) outer hard bark, (SX) secondary xylem, and (VR) vascular ray. (Adapted from Hébant, C , Devic, C., and de Faÿ, E , *Rev Gen. Caoutch Plast* . 614, 97, 1981.)

Fig.1.1 Diagram of *Hevea brasiliensis* bark

Field latex, thus obtained, consists of 25-40 % (w/w) of rubber. Details of the rubber particles have been thoroughly investigated and it was found that most of the rubber particles (*ca* 3 - 5 μm sizes) are spherical, but some are pear-shaped, surrounded by a thin skin, which is phospho-lipoproteinic in nature (d'Auzac, 1989) Further, it is covered with a protein layer, whose isoelectric point is recorded as 3 0 to 5 0 (d'Auzac, 1989). Further, *H brasiliensis* latex particles are found to be possessed of a negative charge (d'Auzac, 1989). In addition, the most important protein in fresh latex is identified as α- globulin with a low content of sulphur [0.06 % (w/v)] (d'Auzac, 1989). NR latex also consists of non-rubber substances such as proteins, lipids, sugars, minerals etc Fresh latex contains *ca.* 0 9 % (w/v) of lipids. Lipids are present in various types such as phospholipids, sterols, sterol esters etc. Phospholipids are long chain fatty acid esters of glycerophosphoric acid. However, most of the lipids are found in the rubber phase and a lesser amount could be found in Frey-Wyssling particles (resinous globules bearing the yellow-orange colouring matter of latex which are bounded by a double membrane) Latex can be differentiated into various fractions and a systematic diagram of the various fractions obtained from latex via the ultra-centrifuging method is shown in Figure 1.2.

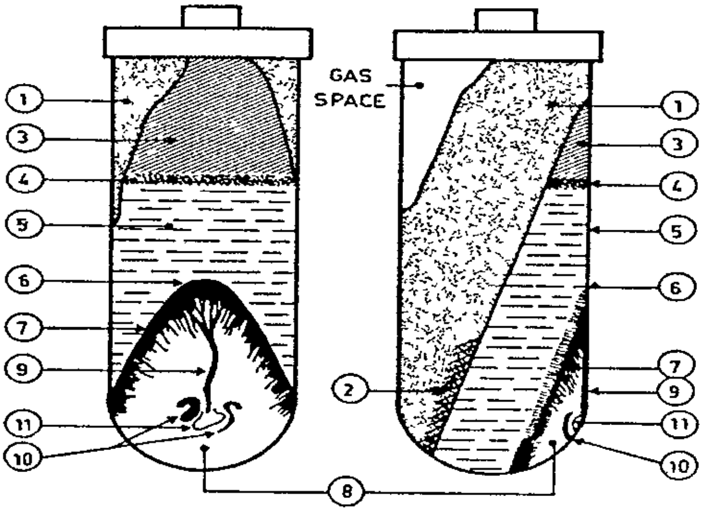


FIGURE 1 2 Ultracentrifugation of *Hevea* latex Fresh latex collected in ice-chilled flask, 30 min after tapping, was centrifugated (53,620 g max × 40 min) at a temperature between 0 and 5°C Fractions 1–3 correspond to the white rubber phase Fraction 4 is a yellow-orange layer constituted by Frey-Wyssling particles Fraction 5 is an almost clear serum (C-serum) corresponding to the latex cytosol Fractions 6 to 11 constitute the bottom fraction" in which fraction 8, quantitatively the more important is the lutoid fraction

Fig. 1.2 Fractions of NR latex (Adapted from Moir G. F J , *Nature* (London), 184, 1626, 1959).

Accordingly, the white fraction, obtained by ultra-centrifuging of NR latex, mainly consists of rubber particles The underlying layer, which appears yellow-orange in colour, mainly consists of Frey-Wyssling particles. They are 4-6 μm in diameter and covered by a double membrane (d'Auzac, 1989). These particles contain carotenoids and enzymes, which are involved in the yellow colouration of rubber and isoprenic synthesis pathway, respectively, (d'Auzac, 1989).

The bottom fraction contains lutoids (B serum) and it occupies 10-20 % (v/v) of fresh latex These are spherical in shape (1-3 μm), covered with osmosensitive single membranes As a result, they swell and then burst in a hypotonic medium (d'Auzac, 1989) Acid hydrolases present in lutoids (d'Auzac, 1989) can serve as coagulating agents of the latex. In addition, due to the presence of Ca $^{2+}$, Mg^{2+} ions and positively charged proteins, they have a destabilizing effect on the latex. Hence, bursting of lutoid particles releases acid hydrolases and the above-mentioned into the medium, which ultimately cause the coagulation of the latex. Lutoids also contain anionic proteins. Gel filtration studies indicated that B serum contains three basic proteins: hevamine A and B, hevein, and ergothioneine (d'Auzac *et al.*, 1989). Among these proteins, hevein is considered as the major protein (molecular weight *ca* 5 kDa) (d'Auzac, 1989) Apart from that, lutoids also contain microhelices, microfibrils, intralutoid enzymes such as polyphenoloxidase.

Various elements and organic solutes such as 1% (w/v) quebrachitol, glucose and fructose are found to be present in cytosol serum (C- serum). Furthermore, organic acids such as citric, succinic, fumaric, aconitic, and lactic acid (d' Auzac, 1989) are also available in C- serum In addition to these non-volatile materials, volatile fatty acids (VFA) such as formic, acetic, propionic, butyric acids are also present in latex. Furthermore, it is evident that nucleic acids such as soluble RNA, DNA and messenger RNA are present in C-serum (d'Auzac, 1989)

1.2.2 Preservation of latex

NR latex is a dispersion of rubber particles in water having *ca.* 30 % (w/w) of dry rubber content (DRC) However, field latex could not be directly used for product manufacturing due to the low level of DRC and therefore, centrifuging and creaming processes are commonly employed to increase the DRC in latex.

It is a well-known fact that NR latex undergoes pre-coagulation, due to the formation of formic and acetic acids, resulting from the microbial action on the sugars, such as quebrachitol, present in NR latex These acids are capable of coagulating the latex and this process is referred to as pre-coagulation of latex. In addition to this process, bacteria can act on proteins and produce fatty acids, which thereafter partially replace the protein layer. These fatty acids can react with Mg^{+2} ions available in the medium and form insoluble magnesium soaps, which facilitate coagulation of latex (Peiris and Fernando, 1983).

Therefore, prevention of pre-coagulation is vital in the NR latex industry and preservatives are used for this purpose. Basically, latex can be preserved either for short or long periods.

Short-term preservatives can also be referred to as anti-coagulants. Ammonia is the most widely used anti-coagulant as it destroys the bacteria present in the medium and helps to neutralise any acid already formed in the latex. In addition, the stability of latex is improved by the formation of ammonium salts of the fatty acids and by removing the magnesium ions, present in NR latex, by precipitating magnesium ammonium phosphate as a sludge.

Instead of ammonia, sodium sulphite, washing soda, and formaldehyde can also be used as anti-coagulants. Among these chemicals, sodium sulphite is preferred as the anti-coagulant in the crepe rubber manufacturing process as it helps to prevent the enzymatic discolouration. NRL can be preserved for longer periods by using the preservative systems given in Table 1.1.

1.3 Natural rubber

Previous studies based on NR indicated that the structure of NR is essentially a 1,4-polyisoprenoid in which monomer units are joined in head-to-tail fashion (Harries, 1919, Pummerer *et al*, 1931). IR studies revealed that NR contains a minimum of 97 % (w/v) 1,4-polyisoprene. The presence of 1,2-structures was hardly evident. 3,4-Structures apparently exist as indicated by the presence of weak infra-red absorption at 390 cm^{-1} (Salomon *et al.*, 1954; Dinsmore, 1955) In addition, X-ray studies indicated that repeat distance of the chain molecule is 0 81 nm which is shorter than that of fully extended plain chain (Katz, 1925) This suggests that the rubber molecule is non-planar and shortening has occurred due to the rotation around single bonds.

NR exhibits excellent properties such as high tensile strength, good green strength, which is attributed to the strain crystallization, low hysteresis, high resilience, resistance to fatigue and excellent tack. Therefore, it is an extremely important material in manufacturing articles, which require these properties

Table. 1.1 Preservative systems for centrifuged NR latex (Rubber handbook, 1983)

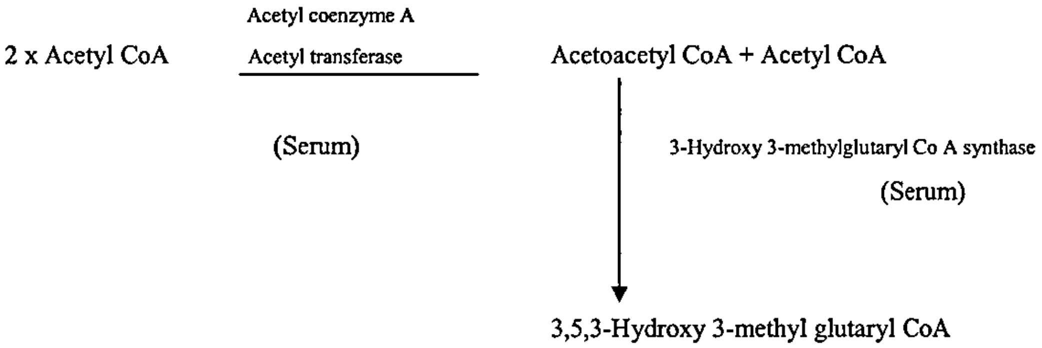
Type of latex		Amount of chemicals use for preservation
High ammonia latex (HA)		0.7 % ammonia
Low ammonia latex (LA)	LA-SPP	0 2 % ammonia + 0 2 % sodium pentachlorophenate
	LA-BA	0 2 % ammonia + 0 2 % boric acid + 0 05 % lauric acid
	LA - ZDC	0.2 % ammonia + 0.1 % zinc diethyldithiocarbamate + 0 5 % lauric acid
	LA-TMTD-ZnO	0.2 % ammonia + 0 013 % tetramethyl thiuram disulphide + 0.013 % ZnO + 0.05 % lauric acid

About 70 % of NR is used in the tyre sector, especially for manufacturing radial and heavy-duty tyres.

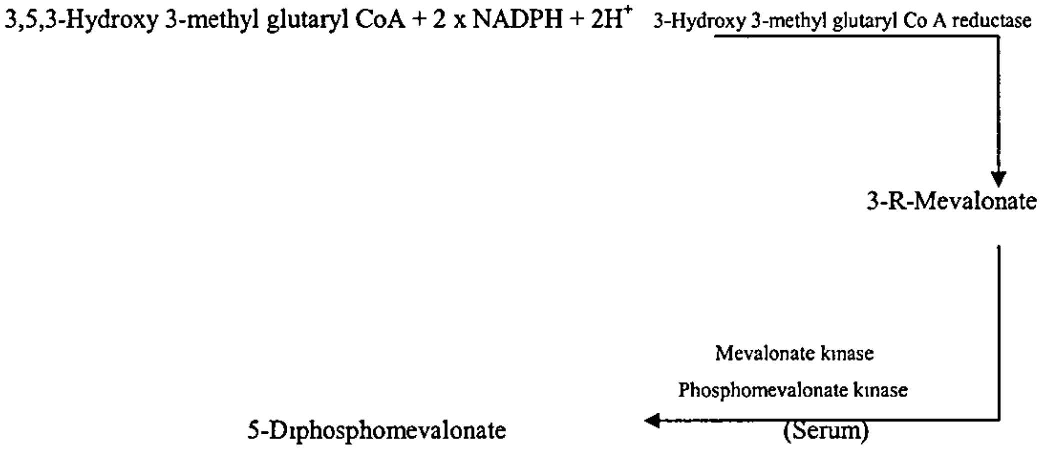
NR is marketed in various forms such as ribbed smoked sheets (RSS), crepe grades, technically specified rubber (TSR). Sri Lanka produces 40 % of its rubber in crepe form for which attractive prices are offered. RSS, traditional grades of rubber are produced in most of the rubber producing countries. For the RSS manufacturing process, latex from various *H brasiliensis* clones is mixed together in bulking tanks and diluted to 10-12 5 % (v/v). Addition of formic acid at a particular concentration as the coagulant facilitates the coagulation of this diluted latex. Dilution is essential as it facilitates the uniform distribution of chemicals in the latex and it helps to form a soft coagulum In addition, acetic acid and oleic acid can also be used as the coagulant. During crepe manufacturing, most of the carotenoid pigments present in the latex are removed by fractionation or a bleaching process. In addition, sodium bisulphite and metabisulphite are used in the crepe manufacturing process in order to prevent enzymatic discoloration. However, the coagulum thus obtained in both processes is subjected to the milling and drying processes.

1.3.1 Biosynthesis of natural rubber

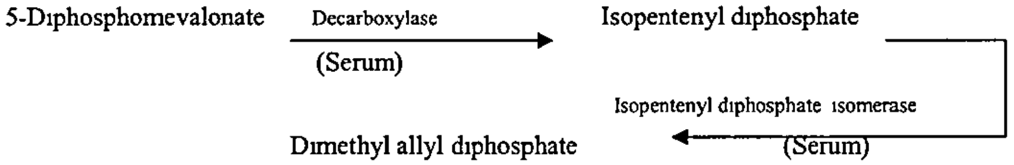
A vast amount of research had been carried out on the biosynthesis of polyisoprene in laticiferous plants. Studies carried out using (^{14}C) acetate, derived from acetic acid, indicated that most of the carbon atoms of rubber were derived from this carbon source (Arreguin and Bonner, 1950; Arreguin *et al.*, 1951). Furthermore, the isoprene unit could be obtained by isolation of mevalonic acid (2, 4-dihydroxy-2-methylvaleric acid) (Wolf *et al.*, 1957). Further, isoprene monomer was identified as 3-isopentenyldiphosphate (IPP) (Bloch *et al.*, 1959; Lynen *et al.*, 1958) and it has been proven that this material can be incorporated into *H. brasiliensis* latex (Lynen and Henning, 1960; Henning *et al*, 1961, Archer, *et al*, 1963; 1961). It is necessary to undergo isomerisation of one molecule of this monomer prior to polymerisation to provide the primer, di-methylallyldiphosphate (DMADP), which acts as a starter for polyisoprene synthesis (Agranoff *et al.*, 1960). Latex contains enzymes and co- factors, which are required to convert acetic acid, mevalonic acid and IPP to NR. Nevertheless, non-rubber particles are not involved in the conversion of IPP into NR and the locus of reaction is found to be on the surface of rubber particles as the rate of incorporation is increased with decreasing particle size (Archer *et al.*, 1960) Barnard *et al.* (1965) also investigated the importance of DMADP in the formation of polyisoprenoids by *H. brasiliensis* latex and showed that incorporation of (1-^{14}C) IPP into farnesol by serum from fresh latex occurred in the presence of DMADP (Barnard, 1965).



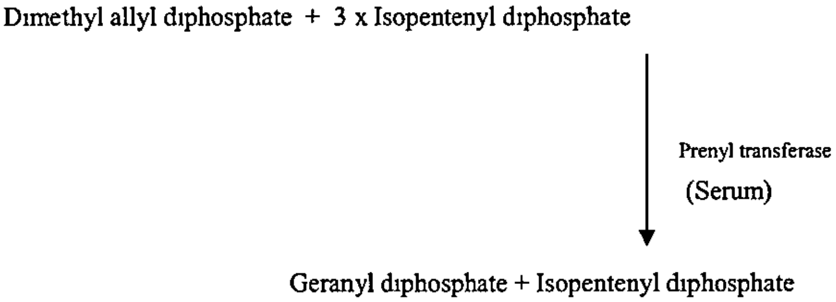
Stage 1 Formation of 3,5,3-hydroxy 3-methyl glutaryl CoA



Stage 2 The reduction of 3,5,3-hydroxy 3-methyl glutaryl CoA and formation of 5-diphosphomevalonate



Stage 3. The formation of isoprenoid monomer-isopentenyl diphosphate and primer, dimethyl allyl dophosphate



Stage 4 Formation of the all-trans prenol diphosphate primer

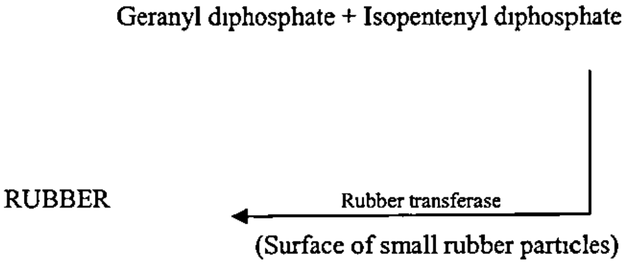


Fig. 1.3 Biosynthesis of natural rubber

On the other hand, IPP was incorporated into farnesol isomers, nerol, and geraniol, in the absence of DMADP (Archer and Audley, 1987). Further, 3-hydroxy –3-methylglutarate is involved in the biosynthesis of rubber (Johnston *et al.*, 1954) and mevalonate formed from 3-hydroxy 3-methylglutaryl CoA (HMGCoA) is also incorporated into NR (Hepper and Audley, 1969) It has been shown that 5-HMGCoA could be incorporated into the white fraction of NR in the presence of the latex bottom fraction and in the presence of NADPH (Figure 1 3)

1.4 Modification of natural rubber

The NR industry is one of the prime industries, and has a major impact on the economies of most of the Asian countries. The present situation of NR production seems to be declining This may be due to several reasons such as moving away from agricultural development and due to lower prices currently prevailing in Sri Lanka.

Therefore, much attention has to be paid to the production of value-added products and to investigate ways of widening applications of NR in other areas including engineering and damping applications.

It is a widely accepted fact that NR properties have to be improved and similarly it is important to render new properties to NR by means of chemical and/or physical modification methods Various research work had been carried out on chemical modifications of NR.

However, very few products such as epoxidised natural rubber (ENR), methylmethacrylate grafted NR (MG rubber) and depolymerised NR have been commercialised to any extent. However, it is an indispensable task to investigate various chemical modification methods in order to increase the usage of NR and widen its applications.

Modification of NR can be performed by means of chemical methods and by physical methods. Physical methods include either blending of NR with other polymers or by blending with other forms of NR during the milling process or in a solution stage Examples for the latter process are superior processing (SP) rubber containing 50 or less parts of vulcanised rubber. SP rubbers are used to improve processing qualities

1.4.1 Blends of NR with other polymers

NR can be modified by melt-mixing with various other polymers Blending of two or more polymers can yield materials, having a combination of the physical properties of the homopolymers In the past, usage of polymer blends has increased remarkably to meet industrial requirements. Reasons *viz* cost reduction, improved processing characteristics and enhanced final product performance have been pointed out for using polymer blends rather than individual polymers. Elastomer blends such as natural rubber/butadiene rubber (NR/BR), natural rubber/styrene-butadiene rubber (NR/SBR), natural rubber/styrene-butadiene rubber/ ethylene-propylene-diene rubber/synthetic isoprene rubber (NR–SBR-EPDM-IIR) are used in tyre applications such as treads, black side walls and white side walls, respectively.

A recent study based on natural rubber and BR blends indicated that the modulus of these blends increased with time depending on the storage temperature (Warley and Halladay, 2005). Oligomer-bound paraphenylene diamines as antioxidants had been tested for the NR/BR blends as well as for other vulcanizates of SBR or IIR and it was found that this type of bound antioxidants imparted flex resistance, ozone resistance and better mechanical properties to these blends (Sulekha *et al*, 2002). Attempts had been also made to incorporate poly (vinyl chloride) (PVC) into NR and the results of this study revealed that the tensile strength and elongation at break lowered with the addition of PVC, but oil resistance has increased due to its polarity (Abdel-Bary *et al.*, 1974)

Findik *et al*, 2004 has studied NR/SBR blends and reported that the tensile properties and wear properties were enhanced with increasing NR content. A study conducted using pyrolysis-mass spectrometry revealed that the interactions of the components in the NR/BR/SBR blends are small (Lattimer *et al.*, 1985) With the incorporation of carboxylated SBR in to NR/BR blends indicated that the thermal stability of these blends improved (Stephen *et al.*, 2006). Comparison of blends based on NR and diclorocarbene modified SBR or chloroprene were made and the mechanical properties and oil, thermal, ozone resistance were found to be higher in the NR/dichlorocarbene-modified SBR blend (Ramesan, 2004 and Ramesan *et al.*, 2005) than the corresponding blend of NR/chloroprene (Ramesan *et al*, 2005) As the NR content was increased the flame resistance and oil and ozone resistance decreased and it could be accepted that as NR is a non-polar substance.

Nano-or micro-composite based on natural rubber and carboxylated SBR were prepared by using layered silicates such as sodium bentonite and sodium fluorohectorite as the nano fillers (Stephen *et al* , 2006)

In addition to these blends, natural rubber is blended with reclaimed rubber or buffing dust with the aim of reducing the cost and often used to produce rubber based articles like mats, retreading, etc. The studies conducted on this subject clearly indicated that the hardness and modulus increase with increasing tyre crumb or buffing dust while adversely affecting the other properties at high concentrations such as 50 wt. % (Rattanasom *et al* , 2005) Dynamic mechanical analysis of blends of natural rubber and reclaimed rubber was performed and found that the Tg increased with increasing content of reclaimed rubber and this was attributed to the increase of cross-link density (Kumnuantip and Sombatsompop, 2003)

Apart from elastomer blends, attention had been paid to thermoplastic natural rubber (TPNR), which is prepared by mixing NR and polyolefines such as polypropylene. Depending on the blending ratio, various properties can be obtained from rubber-toughened polypropylene to thermoplastic elastomers. Rubber-modified polypropylene exhibits high impact resistance and stiffness (Kadir, 1990). Compared to other (TPEs), TPNR also exhibits higher tensile properties due to the strain crystallization of NR. Further, it has better resistance to ageing; especially to ozone (Kadir, 1990). Potential applications of TPNR include the hose, footwear, and automotive industries. Ground tyre crumbs (GTR) has also been incorporated into low density polyethylene (LDPE) in combination of natural rubber, EPDM and SBR with the aim of producing TPE. The best performance was found in the EPDM containing TPE and it is associated with the compatibility of the ethylene units in EPDM with the similar counterpart in LDPE (Kumar *et al.*, 2002). Unlike their counterparts of natural rubber blends, for TPE prepared with LDPE, and NR and reclaimed rubber (1:1) did not exhibit inferior physical properties indicating that NR can be replaced with reclaimed rubber without any adverse effect on mechanical properties (Al-Malaika and Amir, 1989). Nevertheless, this study indicated that the TPE prepared from NR or EPDM possess better resistance for photo-degradation than

TPE's containing reclaimed rubber in which deterioration of properties had occurred when exposed to UV light.

1.4.2 Chemical modification of natural rubber

In recent times, research interests have changed from synthesising new polymers towards modification of existing polymers. Basically, modification of polymers can be achieved by physical or chemical methods. Chemical modification of polymers has greater potential to impart new combinations of properties to the resultant materials Attempts had been paid in the recent past to produce chemically modified NR with the aim of rendering new properties to NR and thereby widening the applications of NR. Nevertheless, most of the products developed by chemical modification of NR can not be implemented on the commercial scale. Only a few products such as methyl methacrylate (MMA) grafted NR (MG rubber) and ENR have been produced on a commercial scale.

The following methods had been employed to produce chemically modified NR (Kadir, 1990).

1. Rearrangements of the bonds without introduction of new chemical groups. E.g. isomerized NR, cyclised rubber.
2. Attachment of pendent groups by olefinic addition or by substitution E.g. halogenated NR and ENR.
3. Grafting of another polymer to NR. E g. methyl methacrylate grafted NR.
4 Reduction of molecular weight by scission. E.g. liquid natural rubber (LNR)

1 Rearrangement of bonds

(i) Isomerised natural rubber

Because of the presence of the methyl group in the isoprene unit, it facilitates different possible configurations such as *cis*, *trans,* syndiotactic and isotactic structures. *Cis/ trans* ratio of diene polymers can be changed by chemical treatments and it is referred to as *cis/ trans* isomerisation. Golub (1957), Cunneen and Higgins (1963) conducted research on *cis/ trans* isomerisation of polybutadiene and natural rubber, respectively, (Brydson, 1978) Chemicals such as selenium, sulphur dioxide (Figure 1 4) and butadiene sulphone have proven to be effective isomerisation agents for polyisoprene (Brydson, 1978). Among these chemicals, butadiene sulphone can be applied during solid state mixing and further heating leads to *in situ* formation of sulphur dioxide which reacts with polyisoprene to produce isomerised rubber (Brydson, 1978). *Cis/trans* isomerisation had been quantitatively determined by using NMR spectra (Golub *et al*, 1962). Partially isomerised NR exhibits non-crystallizing and rubbery properties.

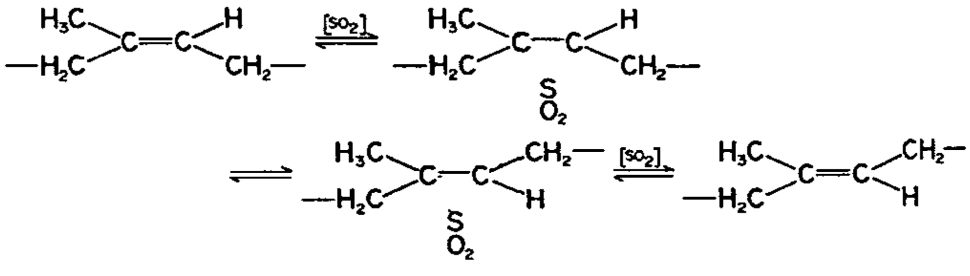


Fig 1.4 Part A Isomerisation of polyisoprene (Brydson, 1978)

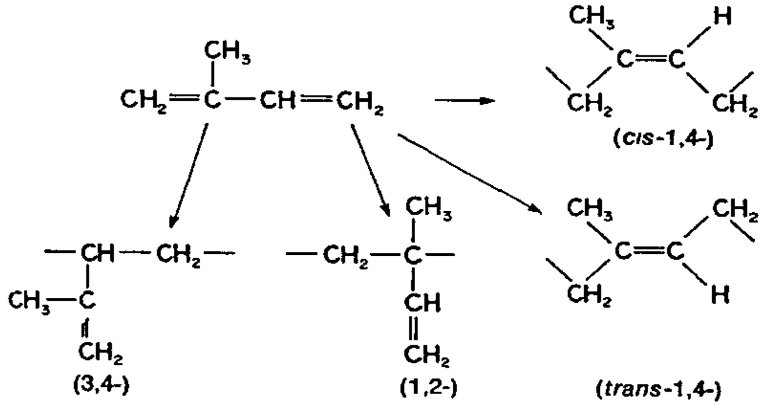


Fig. 1.4 Part B. Possible structures of isomerization of the repeating unit (Brydson, 1978)

(ii) Cyclized NR

Concentrated sulphuric acid (Harris, C. 1910), *p*-toluene sulphonic acid (Fisher, 1926) and a Lewis acid such as stannic chloride (Bruson *et al.*, 1927) have been used to produce soluble, less elastic products referred to as cyclised rubber. During cyclisation, unsaturation is reported as declining (Brydson, 1978) Initial reaction steps for polyisoprene are presented in Figure 1.5. Accordingly, H^+ ions add to the double bond according to Markownikoff's rule (Patterson and Koeing, 1987) to create carbonium ions (Patterson and Koeing, 1987). This ion reacts with the adjacent double bond followed by deprotonation resulting in a cyclic structure. NR seems to possess tri-and bicyclic structures as shown in Figure 1 6. Cyclised NR is used in various applications such as adhesives, paints and inks (Patterson and Koeing, 1987)

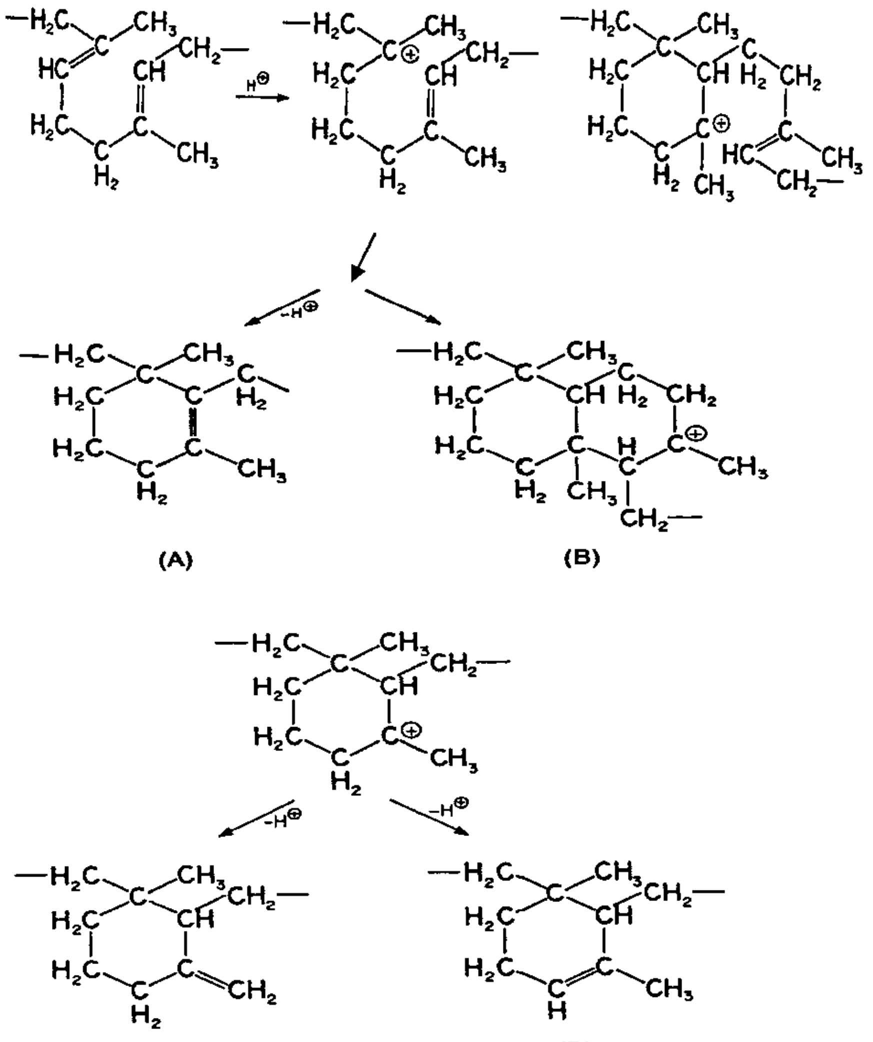


Fig. 1.5 Cyclization of polysioprene

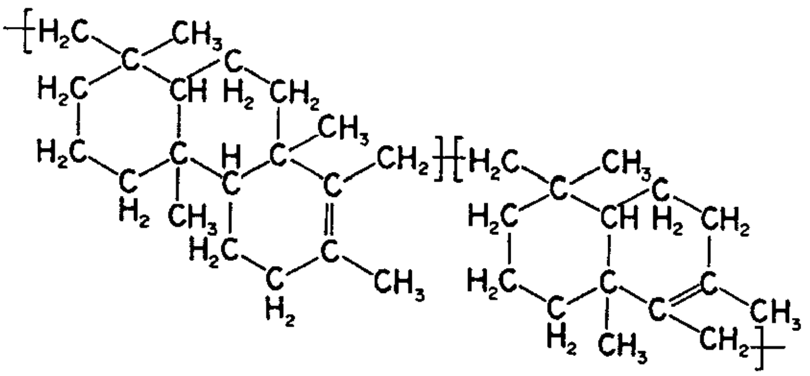


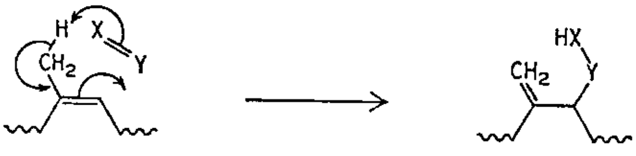
Fig 1 6 Structure of cyclized NR

2. <u>Modification of NR by the introduction of pendent groups</u>

NR contains secondary carbon atoms at the double bonds, and, therefore, it is more reactive towards free radicals and carbonium ions (Brydson, 1978). Therefore, the reactivity of the double bond of NR can be made use of to incorporate various functional groups Basically, pendent groups can be introduced to the NR backbone via the following reactions

(i) Ene reactions

During the recent past, extensive research have been carried out to modify NR using “ene” reagents (Figure 1.7) (Baker *et al.*, 1970; Barnard, 1975). These reactions occur via a direct reaction between the “ene” reagent (C = C, C = O, C = S, N = N, N = O) and the isoprene double bonds of NR without any intermediates In order to functionalise NR, X or Y should bear the substitute groups, which should not interfere with the addition reaction. One such addition is the reaction of nitroso-arenes ($O = N\text{-}C_6H_5\text{-}X$, X= NHAr or X=OH) with NR (Barnard, 1975) and it is illustrated in Figure 1 8.



X = Y can be $-N=O$, $-N=N-$, $>C=S$, $>C=O$, $>C=C<$

Fig. 1.7 Addition of an “ene reagent” to isoprenic double bond

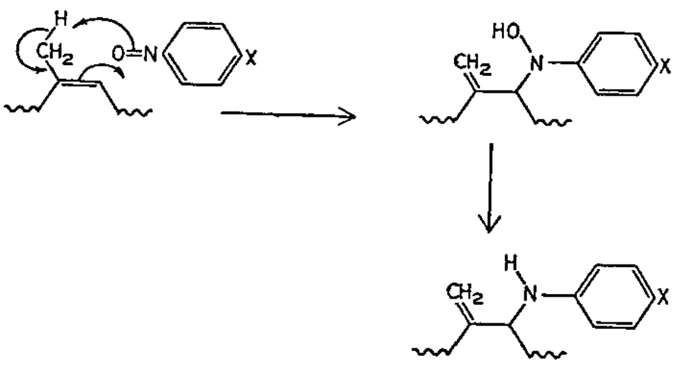


Fig 1 8 Addition of nitroso-arenes with NR [*After* Bernard *et al.* (1975)]

It is reported that if the substitute is an electron-releasing group then higher amounts of hydroxylamine primary product is formed (Knight and Pepper, 1971). On the other hand, the presence of electron withdrawing groups enhances the formation of secondary-amine products (Knight and Pepper, 1971) This kind of reaction has been used to develop rubber bound antioxidants by attaching pendent *p*-phenyldiamine (Cain *et al.*, 1968) produced by the reaction of *p*-nitroso phenylaniline. Nitroso-arenes with hydroxy groups as the substitute resulted in aminophenol which had been used in a polyurethane vulcanisation system (Baker *et al*, 1970).

Azo ene reactions had also been used to modify NR (Rabjohn, 1948; Flory *et al.*, 1949). Azo-tipped polymers are useful in preparing graft copolymers since this process has certain advantages such as the molecular weight of the polymer chain and the number of grafted polymer chains per rubber molecule can be controlled. In addition, azo tipped functional groups facilitate the efficient grafting process (Barnard, 1982).

Various types of azodicarboxylates had been synthesized and the reaction with NR had also been studied (Rabjohn, 1948). These reactions are insensitive to radical initiators, scavengers and to solvent type (Hoffmann, 1969) and a report indicated that primary hydrogen is more easily transferred to nitrogen than secondary and tertiary hydrogens (Thaler and Franzus, 1964). Further, the reaction of ENPCAF (ethyl-N-phenylcarbamoylazoformate) with NR was carried out in solid NR, as well as in de-ammoniated latex with high efficiency and it increased T_g, resistance to hydrocarbon solvents and the permeability of gases (Barnard, 1975).

(ii) Epoxidation

a. General description of Epoxidised Natural rubber

Recently, emphasis has been placed on ENR due to its interesting characteristics. Most of chemically-modified NR grades are apparently resinous substances. Nevertheless, ENR retains an elastic property even at quite high epoxidation levels. ENR is commercially available in two forms. i e ENR 25 and ENR 50. The epoxidation reaction led to an increase in T_g by 1°C per mole percentage of epoxidation (Baker, 1987). In addition, it increases resistance to non-polar solvents, decreases air permeability and resilience (Baker, 1987). The most interesting features of ENR are its low rolling resistance and high wet skid resistance (Baker, 1987). Further research based on GPC measurements indicated as the epoxidation level increases, molecular weight decreases (Bac and Mihailov, 1991) and this is may be due to the occurrence of chain scission through a free radical mechanism as hydrogen peroxide is present in the system (Hashim and Kohjiya, 1993). Furthermore, X ray studies revealed that ENR can undergo strain induced crystallisation (Davies *et al*, 1983) and due to the former reason it exhibits higher tensile strength, but epoxidation levels greater than 50 % produce non-strain crystallizing rubbers (Baker, 1985).

Ageing properties of ENR seem to be inferior (Gelling and Morrison, 1985). During ageing, carbonyls, alcohols, tetrahydrofuran (Chaki, 1992) and ether cross-links (Gelling and Morrison, 1985; Chaki, 1992) are formed which is due to the acid catalysed reaction of ring opening of epoxide groups. Acid can be either residual acid (Chaki, 1992) or acid formed by thermal decomposition of oxidized sulphides (Gelling and Morrison, 1985)

b Epoxidising agents

Perbenzoic acid (Kolthoff, 1973; Saffer and Johnson, 1948), perphthalic acid (Roux *et al*, 1964) and peracetic acid (Mairs and Todd, 1932) have been used to synthesize ENR. When H_2O_2/acetic acid is used for epoxidation, catalysts such as *p*-toluene sulfonic acid (Colclough, 1962, Badran and Abdel, 1977) have been used to promote peroxy acid formation

Epoxidation can be carried out successfully with either preformed peracid or *in situ* formed peracid. The latter process is preferred due to the instability of preformed peracids. This reaction can be performed either in solution or in latex form and the latter process is more convenient and feasible due to the compatibility of the peracid with the aqueous phase. Much attention had been paid to the synthesis of epoxidised natural rubber by *in situ* preparation of per-acid. The reaction (Figure 1.9) is known to proceed via a transition state involving bond formation and breaking between the oxygen and the double bond (Gelling and Porter, 1988).

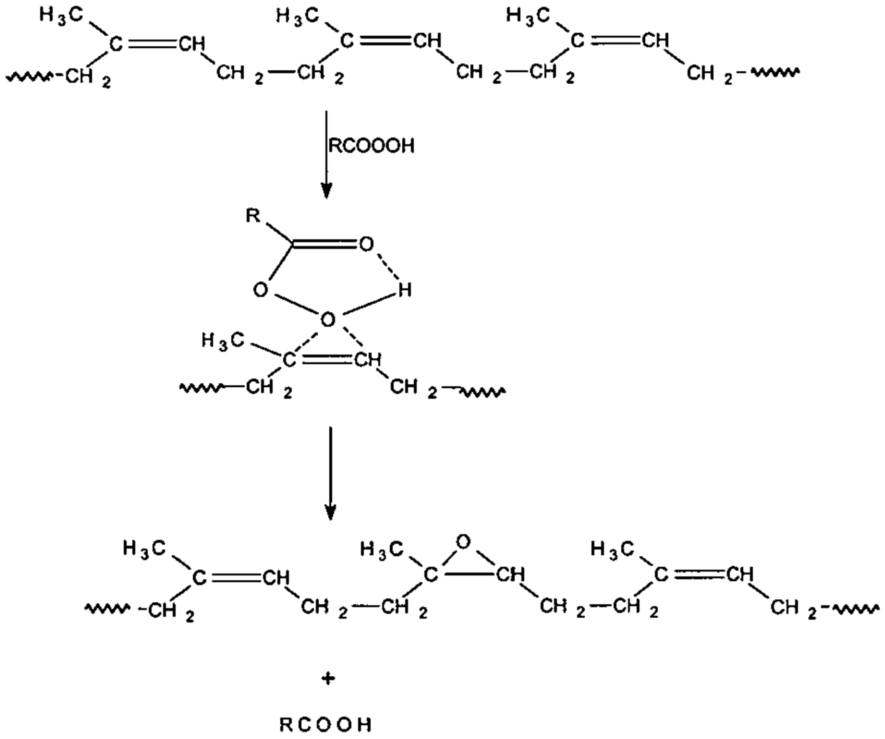


Fig. 1 9 *In situ* epoxidation of NR with performic acid and hydrogen peroxide (*After* Kohjiya and Hashim, 1996)

Kinetic parameters of epoxidation of NR latex by in situ performic acid had been investigated and it was reported that formation of performic acid is the rate determining step and the activation energy is 55±6 kJ mol^{-1} (Gan and Ng, 1986). Epoxidation is considered as a stereospecific reaction (Gelling, 1988) and it leads to randomly distributed epoxy groups along the rubber chains (Bradbury and Perera, 1985). Nevertheless, it is important to prevent side reactions such as ring opening reactions. Ring opening of simple isolated epoxy groups produces (Figure 1.10) glycols, hydroxy esters, and derived products (Rosowsky, 1964). Further, it was found that ring opening of adjacent epoxide groups of polyunsaturated compounds results in cyclic ethers (Sefton and Merrill, 1976).

Epoxy groups present in ENR can be used as reactive sites for further modification of ENR (Lye and Toh, 1984; Gan and Burfield, 1989, Jayawardena *et al*, 1984, Perera, 1990). Feasibility of reactions of amino functional groups with epoxy groups of ENR has been evaluated in several reports (Lye and Toh, 1984; Gan and Burfield, 1989) In addition, reactions of aromatic amines with ENR have been performed in order to synthesize polymer-bound or macromolecular antioxidants (Jayawardena *et al*, 1984; Perera, 1990) It is reported that phenol (Jayawardena *et al.*, 1984), bisphenol A (Hashim and Kohjiya, 1992), hydroxy methyl groups (Hashim and Kohjiya, 1995) in epoxy resins, and mica (Okwuand and Okieimen, 1999), are capable of accelerating the rate of cure with amines It was found that reinforced ENR vulcanisates prepared with *p*-phenylene diamine exhibit relatively higher Tgs which may be due to the bulkiness of the amine cross-links and hydrogen bonds (Kohjiya and Hashim, 1996). ENR can be modified through grafting reactions (Okwuand and Okieimen, 1999, Burfield *et al.*, 1984).

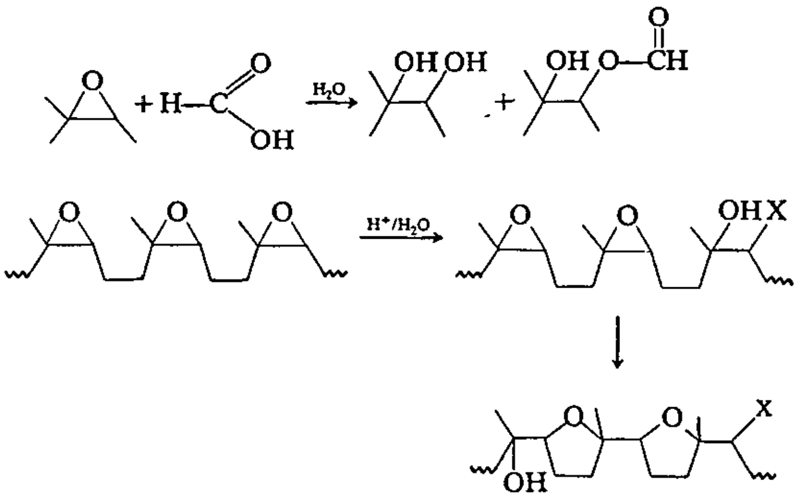


Fig. 1.10 Ring opening reaction of ENR in an acidic medium

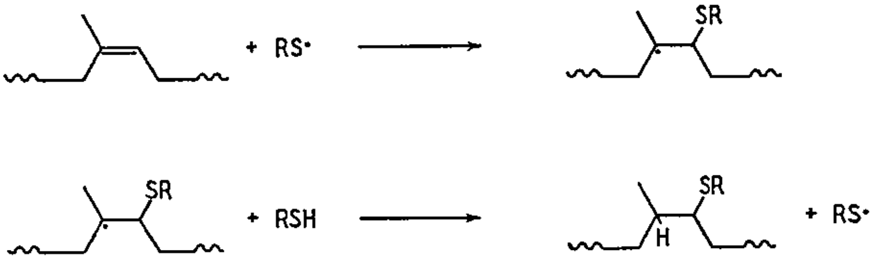
Research work also available on grafting formate and acetate groups to ENR found that the reaction rate and properties depend on the acidity of the medium (Burfield *et al.*, 1984; Ng and Gan, 1981). In addition, acrylate groups have been grafted to ENR and epoxidised liquid natural rubber (ELNR) using acrylic acid through a ring opening reaction and kinetic studies performed using IR spectroscopy (Xuan and Decker, 1993). Results indicated that acrylation follows first-order kinetics. During the acrylation process, it was reported that formation of small amounts of tetrahydrofuran structures occurred and this was due to the low acidity of formic acid. UV curing of acrylated NR and acrylated LNR occurs through polymerization of acrylic groups and polymerization of isoprene double bonds (Xuan and Decker, 1993). The rate of polymerization depends on the degree of acrylation. Products thus obtained exhibited excellent solvent resistance, impact resistance and flexibility (Xuan and Decker, 1993).

Modification of ENR has been achieved by reacting it with thioglycollic acid and 17 % conversion could be achieved. The resistance to solvent and oil of the resultant product has been increased while the reverse trend has been observed for the tensile strength (Okwu and Okieimen, 2001). The epoxy group of ENR can further act as a reactive site, and, therefore, ENR had been reacted with benzoic acid. This led to an increase in the Tg in the resultant product depending on the amount of benzoic acid (Gan and Burfield, 1989). In addition, research had been done to convert epoxy groups to diols To achieve this target, two methods had been employed. Boiling of ENR latex and heating of ENR in toluene with a mixture of water, acetic acid and THF at 60°C. The extent of conversion was found to be extremely low for the former method and the latter method yielded 23 mol% diol content on rubber (Gan and Hamid, 1997).

Epoxidised liquid natural rubber is also commercially available and it is usually prepared by epoxidation reaction of liquid natural rubber or depolymerisation of ENR. This product is commonly used as a plasticizer (Akinlabi *et al*, 2005 and as polymer in blends (Akinlabi *et al*, 2006) The latter study indicated that the physical properties of the blend depend on the mixing procedure of rubber (Akinlabi *et al.*, 2006).

(iii) Addition of thiols and related compounds

Addition reactions of thiols having a functional group to NR have been studied by Cunneen *et al*, 1960 and Marvel *et al.*, 1953 and were found to proceed via a free radical reaction (Figure 1.11) (Cunneen and Shipley, 1959).



HS- $(CH_2)_n$-X   X = CO_2H, CO_2 Et, CH_2OH, CN

Fig. 1.11 Addition reaction of thiol to natural rubber

(iv) Addition of maleic anhydride

Maleic anhydride is frequently used for modification of polymers with the aim of improving miscibility between components in a composite or blend (Coran, 1988; Suma *et al*, 1990). Maleic anhydride is also used to modify NR (Pinnazi *et al*, 1960). The reaction between NR and maleic anhydride takes place via a free radical pathway. This reaction was accelerated using benzoyl peroxide, AIBN and chlorobromodimethyl hydantoin (Bacon and Farmer, 1939; Pinnazi *et al.*, 1951). Though it was originally assumed that the reaction takes place across the double bonds IR spectroscopy studies indicated that the reaction takes place at the allylic-α-methylene carbons (Figure 1.12) (Farmer, 1942; 1943).

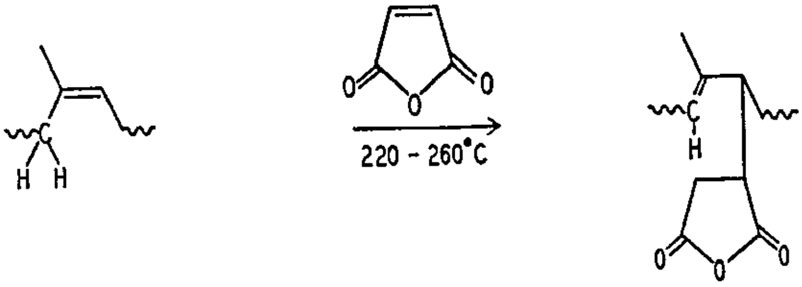


Fig 1.12 Structure of maleated natural rubber

Maleated NR vulcanizates possess superior solvent resistance, flex cracking resistance and ageing resistance (Brydson, 1978). Photosensitive copolymers based on NR had been produced by introducing photoreactive cinnamoyl group through a reaction of NR with maleic anhydride followed by ring opening and condensation with oxyalkylcinnamate esters (Leila *et al.*, 1990)

(iv) Addition of carbenes and nitrenes

Carbenes or nitrenes have been introduced to NR (Figure 1.13) through either addition or insertion reaction (Barnard, 1982). Nitrenes and carbenes can be generated by thermolysis of azido compounds (Spurlin, 1971; Sayigh *et al.*, 1970) and by diazoxide compounds (Sayigh *et al* , 1970), respectively.

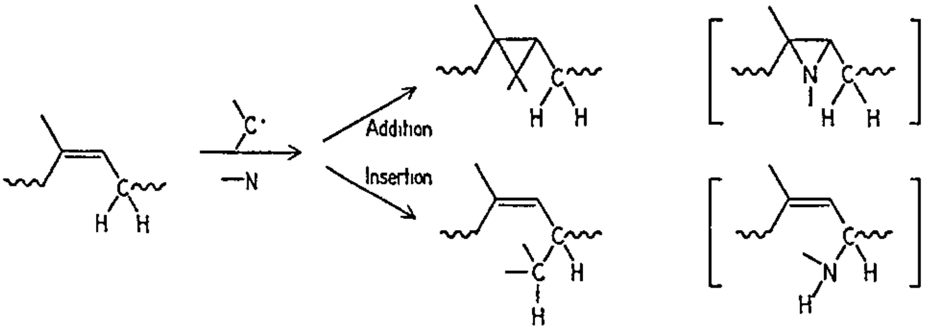


Fig. 1 13 Additions of carbenes and nitrenes (Adopted from Barnard, 1982)

Reaction of NR with aryl sulphonyl azide ($X-C_6H_5-SO_2N_3$) has been studied and it is mentioned that 1,3-cycloaddition of azide occurred before releasing the nitrene. Break down of bonds results in bound aryl sulphonyl groups, which are fixed through an imine bond to the NR. Phenyl azides are also capable of releasing nitrenes by photolysis or thermolysis process and it can insert in to CH or NH bonds resulting covalently bonded products (Scriven, 1984). This technique has been applied to modify natural rubber in latex stage by using bio-material functionalized perflurophenyl azides (PFPA). Polyethylene glycol and hyaluronic acid were used as the bio materials In addition, the presence of fluorine atoms on phenyl group facilitates the insertion of nitrene intermediates in to CH or NH bonds. Therefore, use of bio-material modified perfluorophenyl azides resulted in biocompatible coatings which will reduces the leaching of proteins which are present in natural rubber. This can be used to produce natural rubber latex with low proteins contents with the aim of minimizing the latex allergy problem (Yan, 2000). Addition of carbenes had been used in the production of a bounds- hindered-phenol antioxidant to NR (Kadir, 1975) and to other polymers (Kaplan *et al.*, 1973).

In addition, dichlorocarbene modified NR was synthesized by hydrolysis of NR in chloroform solution and it exhibited flame retardancy when the chlorine content was higher than 27.5 % (Sang, 1978). Nevertheless, tensile properties were not satisfactory, but damping properties improved (Sang, 1978)

(v) Hydrohalogenation

Hydrochlorinated NR, one of the modified grades of NR, is produced by passing HCl into a chloroform solution of NR This product is used in applications such as transparent wrapping films and rubber-to-metal adhesives (Brydson, 1978). The hydrochlorinated product is polycrystalline and less elastic. However, it has a relatively low stability towards light and heat due to the possibility of liberation of HCl. Adding heat stabilizers and UV absorbers are advisable to minimize this effect (Brydson, 1978).

(vi) Halogenation

Halogenated NR is obtained by reacting natural rubber with a halogen Cyclisation, addition, and substitution reactions are involved in the cyclisation process and it is found that the empirical formula of halogenated NR is $C_5H_8Cl_{3-5}$ (Brydson, 1978). A study conducted on the elucidation of the composition of chlorinated rubber indicated that if the composition is Cl/C_5 is ≤ 1, then, structures due to addition of chlorine to the double bond was hardly evident (Eskina *et al*, 1990) This study indicated that the cyclization is possible during the fast stage of reaction (up to $Cl/C_5 = 1$) resulting in formation of 5-6 member cycles. Chlorination of synthetic polymers such as a styrene-butadiene-styrene block co-polymer or styrene-butadiene rubber had been performed by trichloro-isocyanuric acid (Jaén *et al.*, 1999; Sánchez *et al.*, 2001). Chlorinated rubber is also commonly used in chemical and heat resistant coatings applications (Brydson, 1978)

Bromination of NR proceeds via a free radical mechanism and substitution takes place at the allylic positions (Bloomfield, 1943). In this reaction, side reactions such as cyclisation (Bloomfield, 1943) or cross-linking (Bloomfield, 1943) can occur. Bromine water (Nakagawa *et al*, 1990), bromine in dichloromethane solution (McNeill and Ćoskun, 1989) and N-bromosuccinimide (Kim *et al.*, 2005) had been used for bromination of NBR, polystyrene and EPDM, respectively.

3. Grafting polymer chains to NR

Attention had been paid mostly to the modification of NR by grafting synthetic polymers on to NR. However, only methylmethacrylate-grafted rubber has been commercialised and is available in various types such as MG_{15}, MG_{30}, MG_{40}, and MG_{49} where the classification is based on the PMMA content. In general, MG rubbers are stiff and non-tacky, but processable due to the softening at higher temperatures. It is widely used in the adhesives industry and in impact resistant articles as it can be vulcanised to give self-reinforced vulcanisates (Bacon *et al.*, 1938; Perera, 1999)

In general, grafting of vinyl monomers on to NR is achieved through *in situ* polymerisation of the monomer in the presence of rubber either in solid or latex form. It is well known that the following types of materials are produced (Bateman, 1963).

Type1:Mixture of NR and homopolymer

Type 2.Rubber with grafted individual monomer molecules

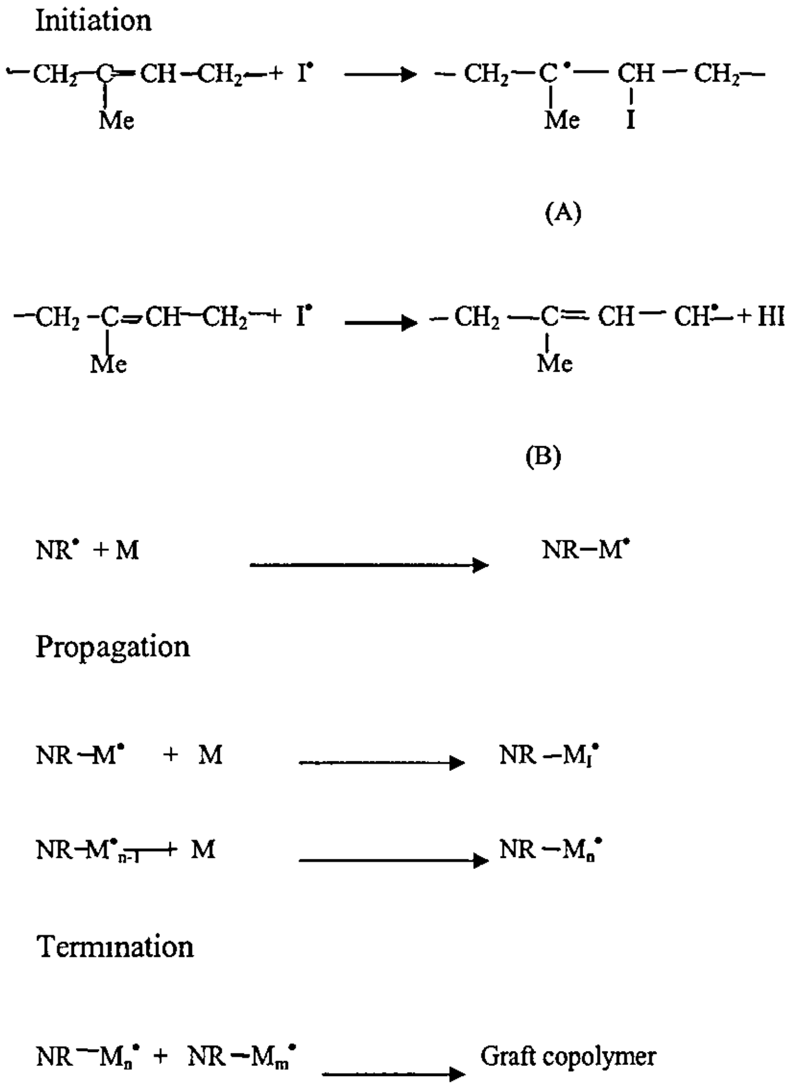
Type3:Rubber with a series of grafted short polymer chains

Polymerisation of either methylmethacrylate (MMA) or styrene in the presence of NR has been investigated (RABRM, 1951; Misra and Kaul, 1983; Campbell and Tinker, 1984, Dafader *et al*, 2006).

Polymerisations of vinyl monomers in the presence of natural rubber occur via a free radical pathway and three main types of radical intermediates are involved in this reaction (Bateman, 1963).

1. Radicals derived from an initiator
2. Radicals produced from the polymerization of monomers
3. Radicals derived from rubber molecules (RH).

Radicals on NR are formed either by addition reaction or by removing H atoms from rubber molecules as shown below (Figure 1.14). However, most of the studies (Angier and Watson, 1956; Misra and Kaul, 1983; Roberts and Skinner, 1949) indicated that initiation takes place by the abstraction of allylic hydrogens present in NR molecules, thus creating a radical centre on the rubber The resulting radicals are stabilised by resonance. Further evidence (Angier and Watson, 1956) also indicated that the polyisoprenic radical is structurally related to B in Figure 1.14 which is capable of vinyl polymerisation. IR studies further revealed that the B radical is involved in grafting due to the presence of a peak at 830-900 cm^{-1} due to C=C (cis) absorption (Misra and Kaul, 1983)



Initiation

$$-CH_2-\underset{Me}{C}=CH-CH_2- + I^{\bullet} \longrightarrow -CH_2-\underset{Me}{C^{\bullet}}-\underset{I}{CH}-CH_2-$$

(A)

$$-CH_2-\underset{Me}{C}=CH-CH_2- + I^{\bullet} \longrightarrow -CH_2-\underset{Me}{C}=CH-CH^{\bullet}- + HI$$

(B)

$$NR^{\bullet} + M \longrightarrow NR-M^{\bullet}$$

Propagation

$$NR-M^{\bullet} + M \longrightarrow NR-M_1^{\bullet}$$

$$NR-M^{\bullet}_{n-1} + M \longrightarrow NR-M_n^{\bullet}$$

Termination

$$NR-M_n^{\bullet} + NR-M_m^{\bullet} \longrightarrow \text{Graft copolymer}$$

Fig.1.14 Steps in the grafting reaction

It was proposed that graft polymer is formed by the following reactions (Figure 1.14) (Cooper and Vaughen, 1959).

1. Reaction of rubber radicals and monomer.
2. Reactions of rubber radicals and polymeric radicals.
3. Reactions of monomer radicals with rubber molecules.

Among these reactions, Kobryner and Banderet, (1959) proposed reaction No 2 considering that the polyisopernyl radical cannot initiate polymerisation due to its resonance stabilization.

Nevertheless, this idea could not be confirmed by further studies (Allen *et al.*, 1959) and, therefore, it was assumed that the polyisoprenyl radicals react with the monomer to yield graft polymer (Bateman, 1963).

(i) Types of Initiators

Earlier research work based on polymerisation of monomers in NR latex was not successful because of the inhibitory action of ammonia and non-rubber substances (Bacon *et al.*, 1938) Nevertheless, by using water soluble initiators such as persulphates and organic hydroperoxide graft polymerisations have been successfully performed Furthermore, the *t*-butyl hydroperoxide and tetraethylene pentamine system was found to be an effective initiator system for polymerization of MMA in the presence of NR (Bloomfield and McSwift, 1955). However, the *t*-butyl hydroperoxide/tetraethylene pentamine redox initiator system helps to promote a core-shell structure, as the locus of polymerisation is at the monomer swollen particle/water interface. As a result, film-forming properties of the resultant product may not be satisfactory due to the inferior adhesion between particles (Bateman, 1963). However, when a lipophilic redox system such as t-butyl hydroperoxide/dimethylaniline is used more or less similar grafting efficiencies to that of polyamine can be obtained (Bateman, 1963) In addition, it leads to the formation of sub-inclusions inside the NR seed latex since polymerisation takes place within the monomer swollen NR latex particles (Schneider *et al.*, 1994). Maleic anhydride has been grafted to natural rubber using BPO as the initiator, and the grafting efficiency increased with increasing temperature, initiator and monomer concentration. The final product exhibited higher Tg than the NR (Nakason *et al*, 2004) Cumene hydroperoxide and tetraethylene pentamine system had been used to graft MMA or dimethylaminoethyl methacrylate (DMAEMA) on to NR in latex stage (Oliveira *et al*, 2005; Rouilly *et al*, 2004, Lamb *et al.*, 2001) and the former study indicated that the radical on natural rubber, the site needed for grafting was formed by the abstraction of H atom from the allylic carbon MMA grafted rubber particles exhibited core-shell morphology with inclusions of PMMA in the NR particles and the DMAEMA grafted latex exhibited a core-shell morphology (Oliveira *et al.*, 2005).

The dimethylaniline (DMA)-cupric ion redox initiator system has been used for grafting MMA onto NR. In this work, attempts have been made to evaluate the effect of monomer concentration, DMA concentration, temperature and acid concentration on the grafting reaction. It is found that grafting efficiency increased with increasing DMA concentration, MMA concentration, acid concentration and reaches an optimum value, and, thereafter, tends to decrease (Lenka *et al.*, 1986). In addition, the hydrazine/cupric ion initiating system (Menon and Kapur, 1959), where hydrazil radicals initiate the polymerisation reaction, can also be used for grafting vinyl monomers to rubber in latex stage.

Effects of initiator, monomer, ascorbic acid concentrations on graft copolymerization of MMA onto NR using the potassium permanganate–ascorbic acid redox system has been investigated (Nayak and Basak, 1986). Results indicated that as the temperature increases the rate of grafting increases to an optimum level and then follows a downward trend, which may be due to the formation of homopolymer at high temperatures. A similar trend has been observed for monomer and initiator concentrations. Lower grafting percentages at higher concentration of initiator are described due to the formation of homopolymer at higher initiator concentration. However, the presence of small amounts of solvent facilitates the grafting process and it was due to an increase of swelling capability, which ultimately led to an increase the miscibility of monomer (Nayak and Basak, 1986).

Metallic compounds have also been used for graft copolymerisation of MMA onto chlorinated NR (Nogues and Dawans, 1981). Among these metallic compounds low valent Ni compounds such as tetrakis(triphenylphosphate) nickel are most efficient initiators and their activity is further enhanced in the presence of dimethylformamide It is reported that compared to free radical initiators these initiators exhibit higher grafting efficiencies (Nogues and Dawans, 1981).

In addition to MMA, methacrylic acid, styrene, ethylacrylate, isobutyl methacrylate and acrylonitrile (Claramma *et al*, 1989) had been grafted to NR latex using aminehydroperoxide, TEP and ferrous ions as the initiator (Menon and Kapur, 1959). Misra and Kaul (1982; 1983) also studied the reactivity of graft copolymerisation of ethylacrylate, butylacrylate and methylacrylate onto natural rubber using benzoylperoxide as the initiator. This study showed that the order of reactivity of monomers to grafting onto NR was as follows, EA >BA > MA (Misra and Kaul, 1982). Further, these studies indicated that grafting percentage increases as BPO concentration increases up to a optimum level and then decreases with further increase of BPO concentration. It is thought that at higher BPO concentration termination of growing radicals lead to decrease the grafting yield. Effect of temperature has also been studied and results indicated that grafting efficiency decreased with increasing temperature. This is due to the occurrence of chain transfer reactions having higher activation energies at high temperatures. Thermograms revealed that the graft product has lower thermal stability, which is due to depolymerisation of polyacrylates upon pyrolysis (Misra and Kaul, 1983). Misra and Kaul (1982) have proposed a mechanism of grafting of methylacrylate onto NR by direct attack that occurs in two modes (Misra and Kaul, 1983) and it is in accordance with previous research findings (Roberts and Skinner., 1949, Angier and Watson, 1956).

Methylvinylketone grafted NR (*cis* 1,4-polyisoprene) had been prepared using benzoyl peroxide (BPO) as initiator and the effects of reaction conditions on graft yield have been investigated. Results indicated that as the BPO amount was increased, grafting efficiency was increased and it was ascribed to the increase of production of radicals, which help to form reactive sites Further, it is reported that graft yield increases remarkably with increasing monomer concentration. Kinetic studies (Egbon and Fagbuli, 1988) revealed that the rate of polymerisation has first order dependency on monomer concentration and the rate of grafting has half order dependency on BPO concentration (Egbon and Fagbuli, 1988).

In addition to the above-mentioned initiators, initiation can be done by means of ultra-violet light with ferric ions as a photosensitizer (Menon and Kapur, 1959). Recently research studies (Lenka *et al.*, 1985, Nayak and Basak, 1986) indicated that grafting of monomers could be performed by gamma irradiation and the grafting efficiency is comparatively higher than chemical initiation

Grafting of monomers on to the polymers can be performed using radiation. Razzak *et al.* (1988; 1989) have investigated the grafting process of hydrophilic monomers such as N,N-dimethylamine ethylacrylamide or N,N-dimethylaminoethylacrylate onto NR and it produced a blood-compatible product. Earlier studies (Razzak *et al*, 1993) conducted on this subject showed that the simultaneous grafting technique provides comparatively lower grafting efficiency. Therefore, peroxidation and/or pre-irradiation method has been used for grafting of DMAA onto NR and the results obtained clearly indicated that the peroxidation method provides high grafting efficiency. In this peroxidation method, the sample is irradiated by γ-rays in the presence of air prior to the grafting by a heating process. Therefore, it creates peroxide groups, which dissociate into peroxide radicals on heating and it facilitate the initiation of grafting process. The optimum degree of grafting was recorded as 42 wt. %. In this study, the simultaneous irradiation technique were capable of imparting 22 wt % degree of grafting even at very low dose and it indicated that grafting takes place by direct attack of radicals formed on natural rubber during irradiation. It can induce formation of monomer radicals indirectly and it reacts with radicals on NR to initiate grafting (Razzak *et al*, 1993) Studies conducted on radiation grafting of MMA onto NR indicated that higher grafting efficiencies could be obtained at a lower dose rate (Perera, 1999). In radiation grafting, free radicals are created by the abstraction of hydrogen atoms from the monomer and natural rubber. It is evident that the main radical formed is the allylic radical (Hill *et al*, 2000) and it can undergo cross-linking or initiation of polymerisation of MMA, which results in the graft product It is reported that at higher dose rates formation of allylic radicals are higher and this leads to cross-linking reactions and as a result number of allylic radicals available for initiation of grafting becomes less. Further, higher dose rates cause formation of radicals on the monomer molecules which enable the polymerisation of MMA and thereby decrease the grafting efficiency. However, it is noted that phase separation in the chemically-grafted product is less compared to the radiation-grafted product (Perera, 1999). Radiation had been used for grafting of different acrylates and methacrylate on to natural rubber latex (Dafader *et al*, 2006). It has been found that the stability of the latex grafted with acrylates are inferior than the corresponding methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA) grafted products. Maximum amount of grafting was obtained at a radiation dose of 4 kGY (Dafader *et al.*, 2006) .

(b) Effects of initiator system on the morphology and film forming properties

Depending on the nature of the initiator system, the morphology and film-forming properties are varied. When the hydroperoxide and amine initiator system was used, film-forming properties were inferior due to the non-uniform distribution of PMMA within the natural rubber particles As the locus of polymerisation is at the interface of monomer-swollen rubber particles and water, higher concentration of PMMA seems to be located near the rubber particle surface and this prevents the adhesion between particles. However, MG prepared with AIBN exhibited better film-forming properties, but it does not contain a considerable amount of grafted products (Bateman, 1963).

4. Polymer modification by cleavage of bonds

(i) Liquid natural rubber

Liquid rubber was first synthesized by heating crude natural rubber under carefully controlled pressure, temperature and time and the resultant product was called depolymerised NR (DPNR). DPNR exhibits low creep and stress relaxation properties and is used in metal-rubber bonded components (Kadir, 1990). A new, convenient method has been used to produce liquid NR (LNR) by using phenyl hydrazine (Brosse *et al.*, 1981) and the resultant product contains phenyl hydrazine-type chain extremities. This process is commonly used for the manufacturing of liquid rubber. The extent of depolymerisation occurring during the depolymerisation process primarily depends on the amount of phenyl hydrazine and the reaction time.

LNR is used as adhesives, in paints and as a reactive plasticiser and compatibiser in rubber processing. LNR is used as a compatibiliser in improving homogeneity and the physical properties of rubber/ polyolefin blends (Dahlan, 1988; Dahlan *et al.*, 2002) It is reported that LNR is capable of reducing the interfacial tension and thereby improve the mechanical properties (Dahlan, 1988). In addition, liquid natural rubber was proven to be an effective viscosity modifier and can be used as a processing aid (Lloyd, 1991)

(d) Surface modification

Surface modification is a widely used technique for modifications of polymers and it can be performed by chemical, photochemical and by high-energy techniques (Waddell *et al.*, 1992). Chemical methods such as oxidation, addition reactions, halogenation (Sánchez *et al.*, 2001) are used to reduce the surface friction and tack. Surgical gloves are also subjected to halogenation on the inner and outer surface of the gloves to balance the ease of release with gripping requirements (Momose, 1986). Photo-halogenation is used to improve surface properties of polymer products without affecting the bulk properties. It is found that by spray deposition of an alkyl halide on the surface of NR, and NR/SBR blends, followed by UV irradiation helps to reduce air permeability, enhances ozone resistance and improves release properties for applications in tyres (inner liners) (Gillick *et al.*, 1989). In addition, surface modification of NR/SBR blend had been carried out in the presence of allylamine (Shanmugharaj *et al.*, 2006) using benzophenone as the photo-initiator. The modified rubber revealed a low thermal degradation rate due to the presence of the allylamine coating on the rubber surface (Shanmugharaj *et al.*, 2006).

Physical methods, including electron beam treatments have been used to reduce surface stickiness of moulded rubber articles consisting of fluorinated NR. Research had also been conducted on plasma modification of NR using C_2F_4, acrylic acid, oxygen and argon (Mattson and Stenberg, 1993). The surface modification provided surfaces which were less permeable to oxygen and with improved resistance to ageing. In addition, argon plasma treatment followed by grafting of monomers such as acrylamide and 2,2,3,3,4,4,4-heptafluorobutylacrylate on to natural rubber by UV radiation had been carried out (Wang *et al.*, 2000) and the results indicated that the hydrophilicity of the modified products is high in acrylamide grafted product. These modifications lead to reduced surface roughness. In addition, chemical doping of natural rubber using a halogen such as iodine would result in conjugate bonds which is the prime requirement for conductivity (Thakur, 1998)

Surface modification of polymers could be achieved by an ion implantation technique. This result in changes in polymer structure and properties such as degradation of polymer molecule referred to as carbonisation, splitting of bonds and changes in polarity, improved wettability, conductivity and sticking properties, respectively (Svorcik *et al*, 1992, Birdwell, 1992 and Predeep *et al.*, 2005).

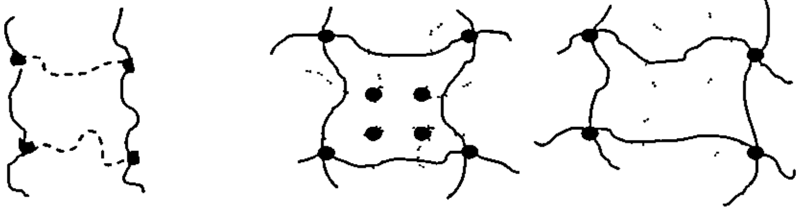
1.5 Interpenetrating networks

1.5.1 Definition and history

1.5.1.1 Definition

IPNs may be considered as both one of the newest in the sense that modern research did not begin until the classical types of blends, grafts and blocks had already become well established, but also as one of the oldest because there is excellent evidence that they were commercial materials in 1914 (Aylsworth, 1914; Sperling, 1987) An IPN is defined as a combination of two or more polymers in network form in which at least one is polymerized and/or cross-linked in the presence of the other (Sperling, 1981). The term "interpenetrating" was given prior to the understanding of their phase separated morphology. At present, it is reported that most of IPNs do not interpenetrate on a molecular scale, but it leads to the formation of fine phases (Sperling, 1994) Compared to blends, IPN phase domains are comparatively small, often in the order of 20-80 nm and exhibit better dispersibility. Therefore, due to the presence of fine phases and interpenetration between phases, IPNs, can improve miscibility, physical properties and broaden the transition region.

a. Polymer blend b. graft copolymer c. block copolymer



d AB graft copolymer e. IPN f. Semi-IPN

Fig. 1.15 Schematic representation of different types of combinations of polymers (*After* Sperling, 1994)

IPNs can be classified under polymer blends, which are combinations of two or more polymers. Polymer blends can be divided into six sub-classes and the schematic representations are given in Figure 1 15. According to the synthesis process, IPNs can be placed under the sub-class of graft polymers (Sperling, 1971). However, they differ from graft polymers due to the absence of covalent bonds between the homopolymers (Sperling, 1994). On the other hand, IPNs are related to block copolymers in which the length of the blocks determines the size of the domains.

1.5.1.2 History of IPNs

The person to invent rubber-toughened plastics similar to IPNs was Aylsworth (Aylsworth, 1914). He had made attempts to mix rubber and sulphur with monomers of phenol-formaldehyde compositions followed by polymerization and simultaneous cross-linking of rubber. However, during his period, the term IPN was not established

In 1941, Staudinger and Hutchinson prepared homo-IPNs based on polystyrene or polymethylmethacrylate with the aim of smoothing the surfaces of transparent sheet (Staudinger *et al.*, 1951). Solt (1955) developed cationic and anionic ion exchange resins in which the networks were oppositely charged, to improve the exchange efficiency. Millar (1960) is considered as the person who introduced the term "interpenetrating networks". Shibayama and Suzuki (1967); Lipatov and Sergeeva (1967); Frisch *et al.*, (1969) and Sperling and Friedman (1969) were also pioneers in this field.

1.5.2 Types of IPNs

According to the synthesis method, IPNs are divided into two major categories i.e. sequential IPNs and simultaneous IPNs (Figure 1 16). Further, the mode of preparation has a pronounced effect on domain size, shape, connectivity, interface mixing and bonding (Sperling, 1989). Furthermore, these IPNs can be divided into sub-classes.

1. **Semi-1 IPNs,** where the first polymer is present in network form and the second network is present in the uncrosslinked state.
2. **Semi-2 IPNs** where second polymer is crosslinked and first polymer is present in linear form.
3. **Full IPNs** in which both polymers are crosslinked to form networks.

1.5.2.1 Sequential IPNs

This project explores the possibilities of synthesizing IPNs based on NR and PMMA by the sequential mode of preparation. In this method, the second polymer is prepared by incorporating monomer with other ingredients to the first polymer, which is in sheet form, by a swelling procedure. This is followed by *in situ* polymerization of the monomer in the presence of the first-formed polymer. However, wide ranges of composition are unable to be produced by this method, due to the fact that the maximum amount of second monomer that can be incorporated depends on the equilibrium swelling of polymer1.

Sequential IPNs based on NR and PMMA could be prepared in the latex state and in the solid state However, polymerization of the monomer in swollen NR in sheet form possesses advantages such as the lack of film cracking at higher glassy polymer contents. In general, the description of sequential polymerizations is given below.

A. Sequential polymerization step

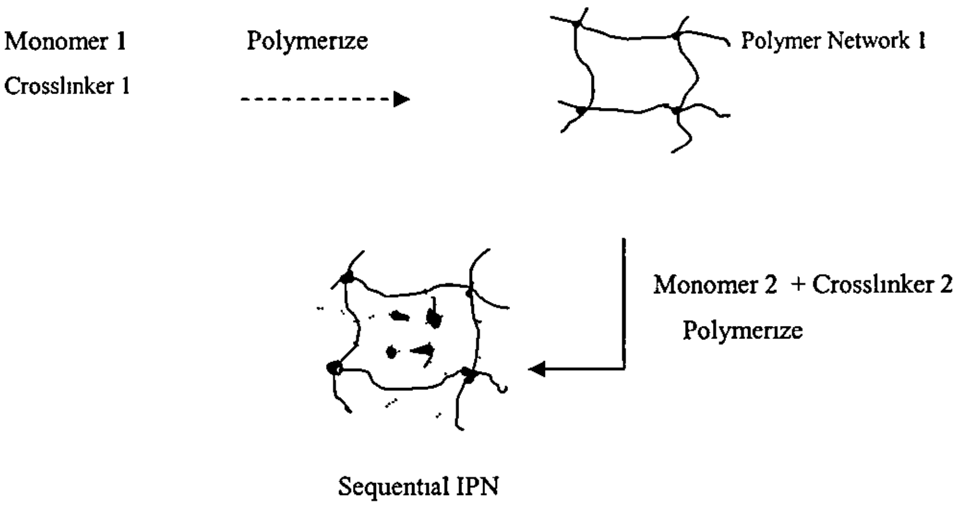


Fig 1.16 Synthetic routes to IPN formation (Part A)

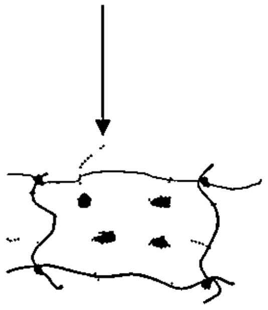
Results of many investigations (Sperling, 1994) conducted on sequential IPNs indicated that in sequential IPNs, polymer1 tends to be the continuous phase for most of these IPNs In addition, they might exhibit dual phase continuity for the mid-range and high concentrations of the second polymer Furthermore, phase separation occurs via a short period of nucleation and growth followed by spinodal decomposition. Depending on the miscibility of the components, different domain sizes such as 100 nm, 10 nm could be obtained for highly immiscible systems and for micro-heterogeneous systems, respectively (Sperling, 1994) In addition, in sequential IPNs, gelation appears to occur prior to the polymerization of the second polymer, and, thereby leads to curtailed spinodal coarsening and ageing This will result in smaller domain sizes and improved miscibility (Sperling, 1994). In sequential IPNs, due to the swelling effect, the first-formed polymer chains are in extended and less probable conformations. As a result, the second polymer chains exist in relaxed conformations (Mishra *et al*, 1995). Thermodynamic studies (Cuadrado *et al.*, 1988) conducted using a model IPN indicated that sequential polymerization results in more incompatible systems as it enters the metastable region at lower concentration. However, certain research work revealed that compatibility of sequential IPNs is better than the simultaneous IPNs (Erbil *et al.*, 2004)

1.5.2.2 Simultaneous IPNs (SIN)

Simultaneous polymerization step

Monomer 1 + Monomer 2

Crosslinker 1 Crosslinker 2



Simultaneous IPN

Fig 1.16 Synthesis route to SIN IPN formation (Part B)

SINs are prepared by simultaneous polymerization of monomers and/or pre-polymers via non-interfering reaction routes: e g. chain and step polymerizations. Though all reactants are fed simultaneously for the preparation of SIN IPNs, they can be formed according to three methods (Sperling, 1986).

1. Network of first polymer is formed before the onset of the reaction of second monomer (*In situ* sequential IPNs (Jin *et al.*, 1988).
2. Network of second polymer is formed prior to the formation of first polymer
3. Both networks are formed simultaneously.

However, these three systems render different morphologies, densities and properties. Jin *et al.* (1988; 1993) conducted extensive research on *in situ* sequential IPNs. *In situ* sequential semi-1 IPNs based on PU/PS (Nevissas *et al.*, 1988; Jin *et al*, 1993) have been synthesized. In this method, the modes of polymerization of the two monomers are reported as chain polymerization and step polymerization. Further, they are pioneers in developing *in situ* sequential IPNs where both polymers are prepared by a free radical pathway. This could be achieved by different reactivities of the monomers (e g. reactivity of allylic double bonds is less than acrylic and methacrylic bonds) towards free radicals or by using different initiators, where each one is specific for one system One such example of preparation of *in situ* sequential IPNs based on PMMA/poly(diallyl carbonate of bishenol A) by using two different experimental conditions At first, PMMA was synthesized at a moderate temperature using AIBN and then the temperature was increased to facilitate formation of network using t-butyl peroxy isononate (TBPIN) (Rouf *et al.*, 1994). Suzuki and coworkers studied an acrylate/epoxy system, where they found that when the acrylic monomer was first subjected to polymerization it would result in a heterogeneous structure, but other methods resulted in more homogeneous products (Suzuki *et al.*, 1980). NMR studies conducted on PUR/PAC IPN indicated that sequentially synthesized PUR/cross-linked PMMA (PAC) SIN exhibited a finer morphology than the corresponding true IPNs (Parizel *et al*, 1993;1995). It was stated that the first formed network impede the gross-phase separation and the sequentially prepared IPNs exhibited more interactions between PUR and PMMA components than the SIN IPNs (Parizel *et al.*, 1995). Research conducted on PUR/PMMA SINs indicated that when PUR is polymerized using dibutyltin dilaurate as a catalyst before the onset of PMMA polymerization leads to improved phase mixing compared to SIN IPNs (Tung *et al*, 1992).

IPNs can be further divided as follows into various categories depending on the nature of the product.

a. Latex IPNs

Latex IPNs are produced by two methods Cross-linked latex particles are swollen with a second monomer, initiator and cross-linker and polymerized *in situ* in latex form. The resultant IPNs can exhibit core-shell structures (Sperling *et al.*, 1974). Latex IPNs can be prepared by mixing of two types of cross-linked latexes followed by coagulation (Klempner *et al*, 1971)

b. Gradient IPNs

Gradient IPNs can be described as IPNs in which the composition or cross-link density is varied from one location to another on the macroscopic level. These can be produced by rapid polymerization of polymer, which is partially swollen with monomer before reaching the diffusional equilibrium

c. Thermoplastic IPNs

These are hybrids between thermoplastics and IPNs. Because of the presence of physical cross-links such as block copolymer morphologies, semi-crystallinity or ionic groups, these materials behave as thermoplastic materials at elevated temperatures and act as thermoset materials at lower temperatures (Sperling, 1994). Thermoplastic IPNs based on polypropylene-EPDM combinations are used in automotive bumpers because of its high energy absorption (Sperling and Mishara, 1996). If EPDM with long ethylene sequences is used, it tends to crystallize slightly and hence cross-linking is not required.

1.5.3 Factors affect morphology of IPNs

Morphology and physical properties of sequential IPNs primarily depend on the kinetics and extent of swelling, rate of polymerization, cross-linking and phase separation (Utracki, 1994).

In general, during interpenetrating polymerization four types of morphology can be seen (Lipatov *et al*, 1985; Sperling *et al.*, 1989). In the first stage, due to solubilization of polymer II in monomer, an optically clear product results in which no phase separation would be found. This was followed by phase separation indicated by cloudiness due to nucleation and growth, one of the major mechanisms of phase separation. As a result, controlled spheres are formed (Fernandez *et al.*, 1984). Thereafter, appearance of cylinders occurs and the number of cylinders increased due to spinodal decomposition Finally, the morphology become less distinct due to reduction in diffusion as the viscosity of the medium increased. When phase separation is considered, initiation of nucleation arises from nuclei and an activation energy is required for that purpose. As a result, spherical domains are formed and increase in number with time. In this case, diffusion of monomers into nucleus occur result in positive diffusion.

Spinodal decomposition leads to the formation of inter-connected cylinders as mentioned above, but the size of the phases remains constant and composition is subject to change with time. Here, negative diffusion from low concentration region into domain takes place resulting in inter-connectivity (Sperling, 1994) Immiscibility of IPNs is ascribed to positive thermodynamic binary interaction parameters and unfavorable contributions to free energy from the elastic stretching of the first-formed polymer (Sperling, 1994).

Factors affecting morphology can be summarized as follows.

1. Compatibility (Manson and Sperling, 1976; Frisch *et al.*, 1980)
2. Polymerization sequence
3. Cross-link density (Donatelli *et al*, 1977; Coleman *et al.*, 1987)
4 Chemical interactions (Xiao *et al*, 1983; 1984; Patsis *et al.*, 1986; Lu *et al.*, 1995; Anzlovar and Malavasic 1990; Chen and Chen, 1993)
5. Experimental conditions, which affect the reaction rates and network formation rates (Lee and Kim, 1984 a,b,c; 1992)

1.5.3.1. Compatibility

Compatibility plays an important role in determining the degree of mixing in polymer blends. Compatibility can be defined in different ways and commonly used definitions are as follows.

1. Frequently defined as the miscibility of components at the molecular level. This definition is confined only to blends, which show true thermodynamic miscibility.
2. When gross-phase separation of individual constituents is absent, then such materials are considered as compatible blends. Nevertheless, this still excludes some blends, which do not possess necessarily fine morphology and hence desired physical properties.
3. Compatible blends are blends which possess a set of (commercially important) desirable properties. Technological compatibilization is widely employed in the rubber industry in order to obtain less incompatible blends with improved ultimate properties. The term technological compatibilization does not imply obtaining a true thermodynamic miscibility in molecular terms (Coran and Patel, 1993).

Extensive research work had been carried out to improve compatibility between various polymer pairs. As a result, the following were identified as the potential methods, which could lead to the compatibility in polymer blends.

1. **Introduction of interactions**

   The introduction of strong interactions such as acid-base, ion-dipole, hydrogen bonding (Santos and Guthrie, 2005) is known to impart thermodynamic miscibility.

2. **Introduction of cross-linking**

   Introduction of cross-linking results in fine morphologies and prevents coalescence (Machado and Duin, 2005). Furthermore, dynamic vulcanisation is used as an efficient technique for achieving compatibilization in rubber blends. In the field of IPNs, forced compatibilization was used to achieve compatibilization between components (Sánchez *et al*, 2001). Sequential IPNs based on poly(methyl acrylate) and poly(methyl methacrylate) were found to be immiscible at low cross-link densities Nevertheless, a homogeneous single phase structure could be obtained when it was cross-linked using 10 wt % ethyleneglycol dimethacrylate (Sánchez *et al*, 2001)

3. **Introduction of interfacial agents**

   Introduction of an interfacial agent, which can concentrate at the interface causing an emulsifying effect, is commonly used as compatibilizer as it reduces the interfacial tension. Moreover these compatibilizers improve the interfacial adhesion at phase boundaries providing improved stress transfer. In addition, it would stabilise the dispersed phase against growth and coalescence. In these aspects, block or graft co-polymers, which are synthesised in-situ or separately, are commonly used to improve compatibility (Bonner and Hope, 1993) Inoue *et al* (1970) indicated that when the molecular weight of a homo-polymer is less than that of the corresponding domain then only the solubilization of homo-polymer in the corresponding domain of the block copolymer occurs. The effect of molecular architecture of copolymers on compatibility was investigated by several researchers. Studies by Riess *et al* (1967) indicated that di-block copolymers are more effective than tri-block copolymers in dispersing two homopolymers. Similar conclusions were drawn by Koklas and Kalfoglou (1992) from their study based on epoxidised styrene-butadiene (ESB) block copolymers of varying architecture with chlorinated polyethylene and poly(vinyl chloride). They indicated that the di-block ESB is more miscible with chlorinated polymers than the tri-block ESBS In addition, research carried out by Jiang *et al.*, (1986) also showed that the miscibility of polyisoprene in polyisoprene and polystyrene co-polymers decreases in the order of diblock > tri block > four-arm star compatibilizers. This was due to the greater complex of the conformation which results restriction in conformation in micro-domain formation. As a result, solubility of homo-polymer in the corresponding domain become reduced. However, one of the drawbacks of using a preformed block copolymer is the tendency for formation of micelles and therefore only a fraction of the block copolymer is actually situated in the interface region.

Graft co-polymers are employed as compatibilizers for blends containing corresponding homopolymers. A graft copolymer of natural rubber and polystyrene had been used to compatibilize NR and polystyrene blends. It is reported (Oommen *et al.*, 1997) that the addition of a small amount of compatibilizer reduces the domain size and the effect levelled off at higher concentration due to the formation of a critical micelle concentration (Oommen *et al*, 1997; Aravinda *et al.*, 2004) leading to interfacial saturation. In addition, mechanical properties were found to be improved due to compatibilization. Further, the actual conformation of co-polymer at the interface was found to be neither fully extended nor completely flat indicating that the conformation is between these two extremes, so that only a part a of co-polymer exists at the interface and the rest penetrates the corresponding homo polymer phase (Aravinda *et al*, 2004).

4. Addition of functional/reactive polymers

Reactive processing is a comparatively novel technique, in which reactive functional groups are used to enhance the compatibility through fast and irreversible reaction Most commonly used functional groups are anhydrides (Shi *et al*, (2001); Heinen *et al.*, (1996); Pagnoulle and Jérôme (2001)) hydroxyalkyl, carboxylic acids, methyl esters, amines (Aert *et al.*, 2001) oxazolines (Vainio *et al*, 1996) and glycidyl methacrylates (Al-Malaika and Kong, 2005b). In addition, graft or block co-polymers formed via blends containing cross-linkable units are usually utilized in reactive processing to impart compatibility between the individual constituents (Xantos and Dagli, 1991). In addition, it is found that the micro-structure of functionalised rubber has a prominent effect on morphology as well as dynamic properties (Al-Malaika and Kong, 2005a).

Having studied the literature on the compatibility of blends containing PMMA, reports on miscible blends of PMMA are available. Kalkar and Parkhi studied PMMA/poly(*t*-butyl phenol formaldehyde) (PTBF) blends by using differential thermal and dynamic mechanical analyses. Results of their study indicated that this blend system exhibited a composition dependent single glass transition temperature indicating miscibility between the individual components and further revealed that PTBF acts as a compatible plasticizer in PMMA/PTBF blends (Kalkar and Parkhi, 1995) Miscibility of this polymer pair was attributed to the specific inter-molecular interaction between the carboxyl groups of PMMA and the hydroxyl groups of PTBF. Research conducted on various poly(n-alkyl methacrylates), mainly PMMA, indicated that PMMA is miscible with poly(vinyl chloride), and is independent of tacticity and the composition of the blend (Vorenkamp *et al*, 1985; Lemieux, *et al*, 1988). This system exhibits a lower critical solution temperature (LCST), which shows a declining trend with increase of the content of the isotactic component of PMMA (Vorenkamp *et al.*, 1985; Lemieux, *et al.*, 1988). Nevertheless, miscibility of poly(alkyl methacrylates) was found to be dependent on the size of the alkyl chain, and, therefore, decreases with increasing the size of side group of the alkyl chain

Research conducted on binary blends containing PMMA, indicated that PMMA is completely miscible with poly(epichlorohydrin) (PECH) (Min *et al*, 1987; Fernandes *et al*, 1986) and poly(vinyl acetate) (PVAc) (Song and Long, 1991; Crispim *et al*, 2000; Zidan *et al*, 2003). and the latter combination is miscible at low temperature (Qipeng, 1990a). However, these two binary systems do exhibit lower critical solution temperatures (LCST).

The first report on a ternary system based on poly(epichlorohydrin), PMMA and poly(ethylene oxide) was reported by Min *et al.*, 1987 and this system was identified as completely miscible over the entire composition. Qipeng (1990b) investigated ternary systems where poly(vinyl acetate) was used as the third component to replace poly(ethylene oxide). For this ternary system, a single Tg could be found from the DSC measurements, but still the interactions between the components appeared to be weak. This system was found to be miscible over the entire composition range at low temperatures, but it does undergo phase separation showing LCST behaviour.

In addition, PMMA is found to be miscible with copolymers such as poly(styrene-co-acrylonitrile) and poly(α-methylstyrene-co-acrylonitrile) and with poly(p-methylstyrene-co-acrylonitrile) (Goh *et al*, 1991) The miscibility of such systems was described by recent theories having considered inter-molecular and intra-molecular attractions between different segments (Kambour *et al*, 1983; ten Brinke *et al*, 1983, Paul and Barlow, 1984). Furthermore, the interaction between methacrylates and styrene is weakly repulsive as shown by the small positive χ (interaction parameter) value and dependent upon the pendent groups of methacrylates. Therefore, with increasing the size of pendent group, the interaction decreases Dependence of interaction between methacrylates and acrylonitrile shows a reverse trend and the repulsive interaction appear to be strong (Goh *et al.*, 1991).

In an incompatible systems, thermodynamic forces leading to phase separation are higher, and, hence, phase separation occurs prior to the kinetic ramifications preventing it. It is reported that as compatibility increases phase separation of the second polymers occur at a later stage and thereby allows a greater amount of mixing of the two networks. In this case, more interpenetration on molecular scale can occur (Manson and Sperling, 1976).

Studies carried out to date on the miscibility of IPNs were conducted by using grafting reactions and by introducing specific interactions such as hydrogen bonds and ion-ion interactions. Grafting between two networks is expected to enhance the compatibility and thereby change the IPN morphology (Chou and Lee, 1993). Hsieh *et al.*, (1995, 2001) studied the graft-interpenetrating polymer networks based on a polyurethane and bismaleimide system. Grafting was achieved via an incorporation of one end maleimide group in the polyurethane prepolymer with bismaleimide (BMI) The results obtained from their study indicated that the grafted IPNs exhibited superior tensile properties and a large improvement in flexural strength, especially when short polyurethane segments were introduced However, a heterogeneous morphology was proved by the DMA and SEM studies, even for these grafted IPNs.

Studies conducted by Chou and Lee (1995) stated that the reaction sequence is one of the prime factors in determining the extent of component mixing and the morphology. They have studied polyurethane-unsaturated polyester IPNs, where the reaction rate and the level of grafting were compared. It was found that when PU reaction was faster, extensive mixing occurred and it was attributed to strong grafting or chain interpenetration.

5. Chemical interactions

Miscibility of large molecules can be achieved through a negative ΔH of mixing which can be obtained by chemical interaction between functional groups. Introduction of functional groups and the grafting process lead to increased miscibility and various research publications are available on this topic Xiao *et al.* (1983, 1984), Patsis *et al.* (1986) introduced tertiary amine groups into a PU backbone and carboxylic acid groups to the polymethacrylic backbone. Xiao *et al.* (1984) reported that by introducing these functional groups greater interpenetration of the components can be obtained due to the formation of hydrogen bonds. In addition, studies revealed that as the NCO/OH ratio increased, compatibility also increased due to lowering of enthalpy of mixing and it was further confirmed by improved physical properties. Lu *et al.* (1995) also introduced silanol groups and amide groups as hydrogen bond donors and hydrogen bond acceptors, respectively. Anzlovar and Malavasic (1990) also conducted research on grafted PU/methacrylic copolymers by introducing carboxylic acid groups to the PU and tertiary amine groups to the methacrylic component. Results indicated that as the functional groups increased, miscibility increased. Similar study was conducted by Čulin *et al.*, (2005) by using the electron spin resonance (ESR) spin label method. This study revealed that the miscibility increased and the disorganization of the ordered domains occurred at higher functional groups. Furthermore, their study clearly indicated that better interpenetration and more interactions occurred between the components in semi IPN than the corresponding equivalent blend (Čulin *et al*, 2005). SIN IPNs of PU/PS, prepared by a microgel process lead to an increase in compatibility due to the occurrence of a grafting reaction in between the phases and it is revealed that the urethane component readily interpenetrates to the microgel to promote entanglements (Chen and Chen, 1993) This study leads to only one transition for the IPN prepared by this microgel process

In addition, research work based on IPNs had been conducted by introducing ion-ion interactions. Ion-ion interactions were introduced to components of IPNs containing polyurethane and PMMA via introducing tertiary amine groups to the polyurethane and by copolymerizing MMA with acrylic acid A single phase morphology with a single glass transition was obtained at a level of 9 –20 mol % acrylic acid units. Nevertheless, SEM studies showed a phase-separated structure Hernandez *et al.*, (2005) studied the interactions and motions of IPNs of poly(vinyl alcohol) and poly(acrylic acid) (PAAc) using ^{13}C spin–lattice relaxation times. This study indicated that the complex will form between the OH group of poly(vinyl alcohol) and between the carbonyl group of acrylic acid. Compatibility of PVA and PAAc was confined to low concentration of PVA content (25 - 30 wt. %). Xiao *et al* (1994) studied sequentially prepared poly(butyl acrylate) and modified polystyrene with hydroxy groups as the basic components and by varying the hydroxyl content. It is found that the apparent miscibility improved with increasing hydroxyl content However, unlike their blend counterparts for which only 2 % was sufficient to obtain complete miscibility, IPNs still exhibited a two-phase system even at high hydroxyl contents (30 mole %) (Xiao *et al*, 1994). The effect of cross-linking for the same IPN system was studied by the same researchers and they found that the cross-linking of poly(butyl acrylate) has two effect on the miscibility. They concluded that the miscibility tends to increase with cross-linking in IPNs prepared with the immiscible polymer pair with low hydrogen bonding On the other hand, as the cross-link density increases, micro-heterogeneity could be obtained for the IPNs prepared with miscible polymer pairs due to hydrogen bonding.

6. Introduction of chemically similar components such as isomeric components:

Studies conducted (Manson and Sperling, 1976) on an incompatible poly(ethyl acrylate) and polystyrene system indicated that by replacing PS with MMA compatibility increased and it this is due to the isomeric nature of PEA and PMMA. SEM studies indicated that the cellular structure becomes smaller in size. When it is completely replaced by PMMA, the cell structure disintegrates to a structure with greater interpenetration (Manson and Sperling, 1976).

However, one phase can be formed with a completely compatible pair, but still topological differences can be found between the networks. Frisch *et al.* (1980) obtained a single glass transition for SIN PU-polyester and SIN PU-polyacrylate materials indicating no phase separation. These materials consisted of fine domains so that the instrument could not distinguish the phase separation (Sperling, 1971).

1.5.3.2 Polymerization sequence

The polymerization sequence has a pronounced effect on morphology. The first formed polymer in sequential IPNs primarily governs phase continuity In the case of simultaneous IPNs, phase continuity depends on the relative rate formation of networks Research conducted on IPNs based on polyisobutene (PIB) and PS, by Vancaeyzeele *et al.*, (2006) indicated that when the polyisobutene network was allowed to form first, the highest interpenetration was obtained. The same conclusion was drawn for the IPN system consisted of PIB and PMMA (Vancaeyzeele *et al.*, 2005)

1.5.3.3. Cross-link density

As described earlier (Sperling, 1994), phase separation occurs through nucleation and growth or spinodal decomposition, which ultimately results in inter-connected cylinders. Later growth of these cylinders leads to coarsening and coalescence. Presence of cross-links can suppress these changes and in other words they can restrict phase separation due to physical interlocking. Therefore, it helps to improve the compatibility and results in small domains. However, this process is facilitated when gelation occurs prior to phase separation and it helps to restrict phase separation and improved miscibility. Donatelli *et al.* (1977) indicated that as cross-link density increased domain size decreased. Studies on the effect of gamma rays on phase diagram of polyvinylmethylether/deuterated polystyrene IPNs (Briber and Bauer, 1988) indicated that the spinodial temperature increased remarkably with radiation dose from zero to 125 Mrad. Contradictory results could be found in work by Bauer *et al.* (1989), who studied semi IPNs. They indicated that when cross-link density was increased in the PS phase beyond the level of equilibrium support, the sample phase separated during polymerization This behavior was ascribed to the lowering of mutual solubility.

1.5.3.4. Experimental conditions

By controlling the rate of phase separation, the extent of inter-mixing of an IPN can be controlled Research publications indicated that homogeneity and interpenetration of SIN PU/PMMA IPNs could be achieved by applying high pressure (Lee and Kim, 1984 a,b,c; 1985; 1992). Such systems consist of small domains and exhibited near molecular level mixing. Polymerization at low temperature also leads to a reduction in phase separation and improved homogeneity by increasing the viscosity of the medium (Lee *et al*, 1992).

1.5.4 IPNs based on PMMA

PMMA has been widely used for synthesizing IPNs with various other polymers. These include simultaneous as well as sequential IPNs Recently reported IPNs based on PMMA are documented as follows.

Xiao *et al*, (1994) studied the rate of formation of networks based on castor oil PU/PMMA and it was found that the rate of PU formation was higher than for the acrylic. These materials exhibited a broad glass transition temperature. Similar materials have been used in applications such as coatings for iron in order to increase the rust resistance (Honquan, 1993).

Xiao *et al.* (1994) and Zhou and Frisch (1993) developed meta-stable phase diagram for PU/PMMA SINs (Zhou and Frisch (1993), Frisch and Zhou. (1993). Mishara *et al.* (1994) studied the distribution of the remaining monomers during PU-PMMA SIN preparation and it was found that monomer was partitioned 50/50 between phases. This was further confirmed by the dominant entropy of mixing over a wide range of enthalpies of mixing (Mishara *et al*, 1994; Mishara and Sperling 1995). This finding can be applied to most of the SIN or IPN polymerization with few exceptions such as crystalline polymers, highly cross-linked polymers and polymer systems where monomer II is insoluble in polymer I. (Mishara and Sperling, 1995). Jin *et al.* (1988) have undertaken identical studies and showed that in the PU/PMMA SIN preparation, the reaction of the remaining MMA takes place both at the interface and within the PU phase at later stages of polymerization

Several researchers had also conducted research on *in situ* sequential full IPNs based on PU/PMMA (Hermant *et al.*, 1983; Morin *et al.*, 1983; Djomo *et al*, 1983; Jehl *et al.*, 1983). It was observed that the tan delta peaks shifted inwards and broadened. It was mentioned that these materials were incompletely phase separated (Hermant *et al.*, 1983; Morin *et al.*, 1983; Djomo *et al.*, 1983; Jehl *et al.*, 1983). The kinetics of reaction of these IPNs, using FTIR spectroscopy, was studied (Jin and Meyer, 1986; Jin *et al.*, 1988) In addition, Hourston and his coworkers made attempts to relate cross-link density and morphology of IPNs to the mechanical properties of PU/ PMMA semi-2 IPNs (Hourston and Zia, 1983; Hourston and McCluskey, 1985). These studies indicated that the reduction of molecular weight between two cross-links, improved the mixing and its effect was more pronounced in systems where the first network was cross-linked than the semi-2 IPNs (Hourston and McCluskey, 1986).

First report on the use of IPNs as energy damping materials was published by Huelck *et al.* (1972). Damping depends on several factors such as the material's loss factor, modulus, substrate modulus and constraining layer modulus. Keskkula *et al* (1971) quantified damping performance by using the area under the tan delta against temperature curves (Keskkula *et al.*, 1971). In addition, the area under the loss modulus curve has been expressed as a damping function (Fradkin *et al*, 1986), or the loss area (LA) (Fradkin *et al*, 1986, Chang *et al.*, 1987). Latex IPNs based on poly(ethyl methacrylate) and poly(methyl methacrylate) exhibited high tan delta values over a broad range of temperature (Sperling and Thomas, 1974). Therefore, it led to the formation of micro-heterogeneous structures as the heat of mixing is near zero since these materials are isomers. Bauer *et al.* (1994) has studied IPNs based on PMMA by varying the grafting reaction with the aim of developing miscible systems. Attempts have been made to graft alkylcrylate, methacrylate, acrylate and α-methylstyrene on to PMMA In this study, acrylate and methacrylate chain ends were attached via an ester linkage and alkylacrylate chain end was attached through the α-methylene group SANS have been utilized to evaluate the effect of IPN structure on the miscibility of two components. SANS data revealed that grafting significantly enhances miscibility. Further, thermal studies showed that one transition in a grafted sample for PMMA/PEG diacrylates and two transitions for non-grafted IPNs. Furthermore, this study showed that by controlling the chemistry of cross-linking and grafting during IPN polymerization, the morphology of the resultant IPNs could be varied. LIPNs based on polybutylacrylate/polystyrene/PMMA (Liucheng, 1989) have been synthesized using potassium persulphate as the catalyst and the latex particle distribution and the dynamic mechanical properties have been evaluated. It was found that when PMMA was added drop-wise during synthesis, this led to a narrower particle size distribution Increase of catalyst concentration led to a decrease in the average particle size, but had no effect on the distribution. Furthermore, these materials exhibited a phase-separated morphology Dynamic mechanical studies have been carried out for LIPNs based on PMMA/P (n-BA) and good damping properties were obtained for a 40 60 PMMA/P(n-BA) IPN and this is ascribed to a core-shell structure of the latex particles (Shucai *et al.*, 1991). LIPNs based on linear BA- ethylene glycol dimethacrylate copolymer, divinyl benzene-styrene copolymer and PMMA was synthezised using either AIBN, or potassuim pursulphate, as the initiator (Liucheng *et al*, 1992). Effect of composition on phase inversion had been evaluated for LIPNs based on poly(MMA)/poly (ethyl acrylate) At low levels of EA, the PEA cell structure is dispersed in PMMA as the continuous phase However, increasing EA content results in phase inversion. Dual-phase continuity has observed at the EA contents 48-86 % (volume) (Yucai *et al.*, 1992) Forced compatibilization of poly(methylacrylae) and poly(methylmethacrylate) sequential IPNs was achieved by using 10 % EGDM resulting single transition. However, a two phase structure was obtained for the materials having low cross-link density (Sánchez *et al.*, 2001). IPNs based on PMMA and polybutadiene (Wang *et al*,2000; Jia *et al*, 1988), polydimethyl siloxane (He *et al.*, 1992,1989, Frisch *et al*, 1994), polymethylphenyl siloxane (Brachais *et al*, 2002) and polyisobutene had been studied. The network formation of PMMA/PIB and the extent of interpenetration had been studied by FTIR spectroscopy and DMTA, respectively Results indicated that these materials though they exhibit transparency, still possess a two phase morphology. Nevertheless, when the PIB network was synthesized first in the in situ sequential preparation of IPNs, it results in higher interpenetration (Vancaeyzeele *et al*, 2005)

Sequential IPNs based on PMMA have been used for developing solid electrolytes For an example, sequential semi-1 IPNs based on methoxyoligo(oxy ethylene)methacrylate and PMMA had been synthesized and this material resembles a solid polymer electrolyte and exhibited ionic conductivity in the order of 10^{-3} S cm^{-1} at 25 °C (Hou and Siow, 2001). In addition, membranes prepared from semi IPNs based on poly(ethylene glycol) grafted poly(methacrylates) and PMMA exhibited conductivity as 10^{-5} S cm^{-1} at 30 °C. DMTA analysis clearly demonstrated that these materials are phase separated (Elmér and Janasch, 2006). IPNs based on poly(methylmethacrylate) and poly(ethylmethacrylate) or poly(butylmethacrylate) were synthesized by suspension polymerization of MMA in the presence of other polymers (MacCallum and Smith, 2000) and it is found that that these materials also exhibit phase separation as evident by the presence of two glass transitions corresponds to their homopolymers.

Ribelles *et al.* (2002) had studied the sequential IPNs based on poly(ethylacrylate) and poly(methylmethacrylate) and the fraction of material which has a conformational mobility characteristics of liquids had been calculated, This study also indicated that the miscibility of these materials are governed by the cross-link density of the first formed polymer (poly(ethylacrylate)) Homogeneous IPNs have been obtained for the highly cross-linked material and phase separated IPNs have been obtained for the lightly cross-linked system. This trend is observed by various researchers. Nevertheless, an opposite trend which reveals that the phase separation increases with increasing cross-link density is found for the IPNs prepared from natural rubber and will be explained in the following section.

1.5.5 Use of natural rubber for development of IPNs

Interpenetrating polymerization can be considered as one of the novel methods of modifying existing natural rubbers. According to the synthesis method, IPNs are closely related to graft copolymers, where polymerization of monomers is performed in the presence of natural rubber either in the latex stage, solution form or in dry form However, compared to graft copolymers, IPNs do not consist of covalent bonds between each constituent and possess different morphologies because of the presence of cross-links. Available literature on IPNs based on NR is relatively few and recent research work done on this subject will now be summarised

Hourston and Romaine (1990) have focused on NR and PMMA composite latex In their study, the emphasis was on synthesizing NR/PMMA composites which can be referred to as IPNs by varying the initiator system, the plastomer type and the elastomer/ plastomer ratio. Full and semi latex IPNs (LIPN) based on NR and PMMA have been synthesized by using, t-butylhydroperoxide – tetraethylenepentamine systems as the initiator and it was found that the resultant latex IPNs exhibited long-term stability. Nevertheless, film-forming properties were not satisfactory when the PMMA content is greater than 10% and this was ascribed to the formation of PMMA at the aqueous phase/rubber interface, which will prevent the adhesion between particles. Further, the cast films, prepared from the resultant latex were transparent, stiffer and less tacky than NR film. The extent of miscibility of these IPNs was studied using DMTA and it was indicated that the introduction of PMMA up to 20 %, did not cause any significant shift of the Tg of NR. DMTA data further showed that these materials were phase separated and exhibited two Tgs with little or no evidence of mixing. Further, stress-strain data indicated that the introduction of PMMA causes an increased initial modulus and tensile strength. Cross-linking of

PMMA led to further improved properties The morphology of these IPNs was studied by TEM and it was evident that the IPNs exhibited very heterogeneous morphologies.

Semi-IPNs based on NR/PS were synthesized by varying the nature of the initiator system, the vulcanizing method, the cross-link level and by varying the composition (Hourston and Romaine, 1989, 1991). Physical properties, tensile, tear and hysteresis, of these IPNs were investigated. Furthermore, the morphology of these materials was evaluated by TEM studies and DMTA was utilized to determine the extent of miscibility. It was found that when amine-activated hydroperoxide was used as the initiator, a complex morphlogy exists in these IPNs materials in which pure PS domains and core-shell structured particles of PS-NR are present Nevertheless, the AIBN system provided a much finer morphology. It was concluded that in this system, polymerization occurred within the NR particles. From this study, it was further confirmed that AIBN caused degradation of the NR molecules and it also causes significant grafting. Stress-strain data indicated that the introduction of PS to the NR matrix and/or cross-linking improved the initial modulus and tensile strength. DMTA data showed that there was no significant change in the T_g of the NR, but the PMMA transition tends to shift towards lower temperature for the semi-2 and full IPNs for compositions of NR80:PMMA20 indicating that pre-cross-linking of NR latex improved mixing.

This is an indication of the effect of the tightness of the first formed polymer on the morphology of the IPN. Similar trend were not observed for the corresponding compositions prepared using amine-activated hydroperoxide as the initiator and it indicated that these IPNs were highly immiscible and phase separated (Hourston and Romaine, 1989). Significant shift of T_g transitions and satisfactory mechanical properties could be obtained by using an oil-soluble initiator t-butyl peroxy 2-ethyl hexanoate (Triganox 21S) as the initiator for the production of LIPNs based on NR/PS.

Attempts had been made to synthesize IPNs based on NR and either PMMA (Das and Gangopadhyay, 1992) or PS (Das *et al.*, 1993) by a sequential mode of preparation. This research work was mainly focused on semi-1 IPNs and full IPNs, which were prepared by varying the composition and cross-linker level. The effect of cross-linking and the blending ratio (composition) on physical properties and morphology of these IPNs were investigated. Results obtained from the study based on NR/PMMA revealed that with increase of PMMA content, or cross-linker dose, the initial modulus and tensile strength has increased. A different trend was obtained for the composition of NR25:PS75 where tensile strength increases up to an optimum point and thereafter showed a downward trend. In general, it was concluded that the tensile strength and the thermal stability (Mathew *et al.*, 2001) of full IPNs were comparatively higher than semi-1 IPNs. The high thermal stability of full IPNs was attributed to the high entanglement density in the full IPN (Mathew *et al*, 2001) Scanning electron microscopy studies showed that in NR-rich samples, PMMA exists as loosely bound diffused fibrils. The increase in the plastomer content imparts a more tight structure with lower fibril width and lower average distance between fibrils (Das and Gangopadhyay, 1992). A similar observation was made for the IPNs based on NR/PS. These studies showed that cross-linking of the plastomer phase improved the miscibility and resulted a much finer morphology (Das *et al.*, 1993). The study by Mathew and Thomas (2001) indicated that the toughening mechanism of NR/PS full IPNs will be the crazing followed by the shear yielding. Further, they have indicated that the impact performance depended on cross-linking level of PS phase, blend ratio and morphology. Nano-scaled full IPNs based on NR and PS had been synthesized using different initiators, dicumyl peroxide, benzoyl peroxide and AIBN and by varying the level of cross-linker. Among these initiators, DCP has resulted in better properties than the other initators. It is reported that the component mixing increased with increase of the PS content and cross-linking level However, high PS content and high cross-link density resulted lowering of the extent of phase mixing (Mathew *et al*, 2001a).

NR, obtained from *Manihot glaziovii*, has been used in the preparation of full and pseudo IPNs using poly(2,6-dimethyl-1,4-phenylene oxide) as the second polymer by the simultaneous method (Barros *et al*, 1992). It was noted that similar $\overline{M}n$ (1 5 × 10^3) values were obtained for each polymer by the cross-linking process using divinyl benzene and ethylene diamine for natural rubber and for brominated phenylene oxide (Br-PPO), respectively. Despite the solubility differences of the pure components, fully miscible compositions for full IPNs with higher percentage of NR (70% - 90%) and for higher percentages of Br-PPO (90 %) could be obtained. In these cases, only one Tg was obtained and SEM studies showed that a single-phase morphology for full IPNs with 90 % of Br-PPO. In pseudo IPNs, micro phase separation was observed as indicated by the presence of two separate Tgs in-between those of the homo-polymers. Diffuse particulate morphologies are observed for pseudo and full IPNs with 50 wt% of Br-PPO. However, IPNs prepared based on PPO with other polymers such as PS, PMMA, polybutadiene, and polyurethane were homogeneous indicating no micro phase domains (Frisch *et al*, 1980; 1989; Singh *et al.*, 1990; Frisch and Hus, 1989; Mengnjoh *et al*, 1989). Sequential pseudo IPNs based on natural rubber (from *Manihot glaziovii)* and PMMA was studied by varying the cross-link density. This study indicated that the miscibility decreased with increasing cross-link density. In other words, a single transition was obtained as the cross-link density was decreased. The extent of cross-linking of natural rubber and the composition are the decisive factors in determining the morphology (Alcântara *et al*, 1999)

Studies conducted on SIN IPNs based on NR-poly(carbonate-urethane) (PCU) indicated that morphology varies from totally homogeneous to microphase domains could be obtained depending on the molecular weight between cross-links. (Barros *et al.*, 1990). Research work has been carried out to utilize core-shell latexes based on NR/PS-X linked LIPNs as a part of a study to investigate the use of core-shell latexes based on NR, PMMA or PS as impact modifiers in a at brittle polymer matrix (Schneider *et al.*, 1994). It is found that NR-cross-linked PMMA core-shell particles improved the impact energy of PMMA and NR-PS LIPNs could effectively toughen PS.

Attempts have been made to prepare IPNs based on epoxidised liquid NR (ELNR) in the presence of hexanediol diacrylate (Decker *et al*, 1995). In this study, ELNR was cross-linked by means of a photoinitiator and the *in situ* polymerization of diacrylate led to the formation of two networks. It was found that by using a two-step curing process i e. at first attempt, acrylate monomer was polymerized by irradiation to form a semi-IPN and the rubber epoxy was exposed to full emission as the second step which enables quasi-instant transformation of the semi-1IPN to a true IPN (Decker *et al*, 1995). Harun and Kassim (1993) studied the thermal properties and morphology of latex IPNs based on semi-2 NR/ polyacrylamide with ethylene glycol dimethacrylate as the cross-linker (Harun and Kassim, 1993). Results indicated that IPNs possess greater thermal stability than NR. In addition, SEM studies indicated that these IPNs exhibited phase separation Pillai *et al.* (1995) has studied the physical, mechanical thermal properties of semi-IPNs (Pillai and Francis, 1994) based on liquid natural rubber, PU and linear PS and full IPNs (Pillai, 1995). The results obtained from this study showed that physical properties such as tensile strength, hardness and density of the resultant IPNs increased with increasing the PS content. A similar trend had been observed with increasing NCO/OH ratio. Furthermore, the results indicated that IPNs produced using PU/PS components exhibited improved thermal stability and mechanical properties than that of the corresponding semi IPNs.

1.6 Objectives of present investigation

At present, synthetic polymers are widely used in many industries. Therefore, NR has to compete with these synthetic counterparts. In the past, various modifications have been carried out with the aim of widening the applications of NR. In fact, only a very few chemical modifications were successful in commercial terms and one such modification of NR is MMA grafted NR which is referred to as MG rubber. MG rubber is used in impact resistant articles and as reinforcing agent (Barnard, 1956).

Recently, attention had been paid to the preparation of NR/PMMA combinations, but the physical properties of the resultant blends were found to be inferior due to the incompatibility of components (Oommen and Thomas, 1993, 1996) However, the physical properties had been improved by the addition of PMMA-grafted NR (Oommen, 1997) Therefore, the IPN polymerization method can be identified as a potential method for preparation of materials based on NR and PMMA with improved miscibility and physical properties due to its unique structure, which will prevent phase separation to a greater extent. Such materials may be employed in applications such as impact resistant articles and reinforced materials In addition, these materials can be used in manufacturing automobile components and moulded parts (Oommen, 1997).

Having looked at the research work undertaken on IPNs based on NR (section 1 5.5), it has been noted that comprehensive studies based on IPNs contains NR are relatively few when compared to the IPNs based on other polymers such as polyurethanes.

This present study basically explores the physical and dynamic mechanical properties of IPNs based on natural rubber and PMMA. In the initial part of the study (Chapters 3 and 4) is confined to an evaluation of the physical properties and dynamic mechanical properties of four different types of materials, namely, the blends, semi-2 IPNs, semi-1 IPNs and full IPNs based on natural rubber and PMMA In this part, semi-2 IPNs and full IPNs were prepared by varying the cross-linker level in the PMMA phase using EGDM at 0.5, 1.0 and 1.5 mole percent. In addition, the elastomer/plastomer ratio was also varied to evaluate the effect of the plastomer content on physical properties, miscibility and dymnamic mechanical properties. The objectives of this part are described under 1.6.1.

The first part of this study (Chapters 3 and 4) clearly indicated that the materials discussed in Chapter 3 were phase separated Therefore, it is essential to investigate any potential materials which could enhance the compatibility between these two components namely, NR and the PMMA. In this exercise, epoxidised natural rubber had been identified as a potential material which could impart compatibility between NR and the PMMA components. In addition, the effect of epoxidation level and the effect of experimental conditions used to synthesis of ENR on the compatibility were explored.

In the latter part of this study (Chapter 5), attempts had also been made to exploit the possibilities of synthesizing grafted IPNs in order to enhance the compatibility between the ENR component and the PMMA component. This was to be achieved via grafting of acrylic acid on to ENR. The main objectives of this latter part of this study (Chapter 5) will be presented under 1.6.2 section

1.6.1 Objectives of the synthesis of blends and different types of IPNs based on the NR and the PMMA components.

1.0 Evaluation of the physical and dynamic mechanical properties of NR/PMMA blends prepared at various compositions.

2.0 Synthesis and evaluation of the dynamic and mechanical properties of semi-2 IPNs based on NR and PMMA by varying the composition and cross-link density of the second component (PMMA).

3.0 Synthesis and evaluation of the dynamic and mechanical properties of semi-1 IPNs based on NR and PMMA, where the NR component was cross-linked using a conventional sulphur vulcanizing system.

4.0 Synthesis and evaluation of the dynamic and mechanical properties of full IPNs with a range of compositions and cross-link densities in the second polymer component.

5.0 Determination of the extent of miscibility of the constituents in the above IPNs by dynamic mechanical thermal analysis and the modulated temperature differential scanning calorimetric techniques.

1.6.2 Objectives of the investigation of the effect of the addition of epoxidised natural rubber on the miscibility and /or compatibility of semi-1 IPNs based on NR and PMMA

1.0 Investigate the effect of the level of epoxidation on the compatibility of the NR and PMMA components in semi-1 IPNs and their effect on the physical properties of these semi-1 IPNs.

2 0 Investigate the effect of the epoxidised natural rubber content on the compatibility of the individual components in IPNs based on NR and PMMA and their effect on the physical properties of these semi-1 IPNs

3.0 Investigate the effect of method of synthesis of epoxidised natural rubber on the compatibility and the effect on the physical properties of the IPNs.

4.0 Investigate the effect of the incorporation of acrylic acid on the compatibility of IPNs based on NR and PMMA.

Chapter 2

EXPERIMENTAL METHODS AND CHARACTERISATION

2.1 Preparation of blends, semi-1IPNs, semi-2 IPNs and IPNs based on natural rubber and Poly(methylmethacrylate)

2.1.1 Materials

Materials used for the IPN syntheses are given in Table 2.1. In this study, most of the chemicals were used as received, except for the monomers and the cross-linker, EGDM, which needed purification Therefore, purification of the monomer and the cross-linker was carried out by passing them through a disposable column of quaternary ammonium anion exchange resin, to remove inhibitors such as hydroquinone and hydroquinone monomethyl ether.

2.1.2 Determination of extent of monomer absorption by pre-vulcanised NR / uncross-linked NR

Preliminary experiments were conducted to determine the extent of absorption of various monomers either by pre-vulcanised NR or uncross-linked NR. A sample of known weight of pre-vulcanised NR with a thickness of *ca* 0 8 mm was placed in a closed bottle containing a 25 ml of the particular monomer. Samples were allowed to swell for different time intervals. Then, each sample was removed and immediately blotted in order to remove the excess surface monomer and the weight of the swollen sample was recorded. The extent of monomer absorption by pre-vulcanised natural rubber / uncross-linked NR was calculated as follows

Monomer absorption percentage = [(weight of the swollen sample – initial weight of rubber sample)/ (initial weight of rubber)] x 100.

2.1.3 Determination of solubility parameters for methacrylate type polymers

Solubility parameters of methacrylate-type polymers were calculated using the Small and Hoy equations (Polymer Handbook, 1975, 1999) according

Table 2.1 Materials used in the syntheses of IPNs based on NR and PMMA

Material	Purpose	Abbreviation	Supplier
60 % NR latex	To prepare cast NR films	NRL	Ansell Lanka Pvt. Ltd.
Pre vulcanised NR latex	To prepare cast NR films	-	-
Methyl methacrylate (MMA)	Monomer	MMA	Aldrich
Tertiary-butyl peroxy-2-ethylhexanote	Initiator	Triganox 21S	Akzo Nobel Co
Disposable Columns (Quaternary ammonium anion exchange resin)	To remove inhibitors	-	Aldrich
Ethylene glycol dimethacrylate	Cross-linker	EGDM	Aldrich
Ammonia	To prepare ammonium oleate	NH_3	BDH
Oleic acid	To prepare ammonium oleate	-	BDH
Sulphur	Vulcanising agent	S	Monsanto Co.
Zinc dithiocarbamate	Accelerator	ZDC	Monsanto Co.
Dibenzothiazole disulphide		MBTS	Industrial grade
Tetramethyl thiuram disulphide (TMTD)	Accelerator	TMTD	Industrial grade
Zinc oxide	Activator	ZnO	Industrial grade
Dispersible agent	To prepare dispersions		Monsanto Co.
Acetone	For extractions	-	Analar grade
Formic acid	For epoxidation		Analar grade
Hydrogen peroxide	For epoxidation		Industrial grade

to the group contribution method where it was assumed that the contribution of different functional groups to the thermodynamic property is addititive

Small's method

Small values were derived from heat of vaporization and it can be described by following equation.

$$\Delta E^{v}_{i} = \sum_j n_j \Delta e_j \tag{1}$$

ΔE^{v}_{i} and Δe_j are energy of vaporization of species and contribution of group j, respectively. In addition, n_j is considered as number of groups of type j in the molecule.

Therefore, solubility parameter is described as follows.

$$\delta_i = (\Delta E^{v}_{i}/V_i)^{1/2} \tag{2}$$

V_i is the molar volume of species i. Therefore, by combining these two equations δ_i can be further expressed as follows.

$$\delta_i = [\{\textstyle\sum_j nj\ \Delta e_{j)}/V_i\}]^{1/2} \tag{3}$$

According to the Small method, the molar attraction constant, $F_{,j}$ is defined below

$$F_j = (\Delta E^{v}_{i,j}, V_{i,j})^{1/2} \tag{4}$$

Therefore, the solubility parameter can be calculated using the following equation

$$\delta_i = [\Delta E^{v}_{i}\ V_i/V_i^{2}]^{1/2} = \textstyle\sum_j F_j/V_i = \rho_i \sum_j F_j/M_i, \tag{5}$$

ρ_i is the density of polymer and M_i is the molecular weight.

Hoy's method

Solubility parameters for these polymers were also calculated using Hoy's method (Polymer Handbook, 1999) using the following equations.

$$\Delta\delta = (\delta^{2}_{t} - \delta^{2}_{p} - \delta^{2}_{h})^{1/2} \tag{6}$$

δ_t, δ_p, δ_h can be calculated from following equations

$$\delta_t = [F_t + B/n]/V, \tag{7}$$

where B = 277, F_t is $\sum n_i F_t$ and $\tilde{n} = 0\ 5/\Delta^{(p)}{}_{T}$,

n is considered as number of repeating units per polymer chain segment where $F_p = \sum n_i F_{p,i}$

$$\delta_h = \delta_t[\{\alpha^p - 1\}/\alpha^p]^{1/2}, \qquad (9)$$

where $\alpha^P = 777\ \Delta_T^{(p)}/V$ and where α is the molecular aggregation number, using below mentioned equations.

$$V = \sum n_i V_i \qquad (10)$$

$$\Delta^{(p)}{}_T = \sum n_i\ \Delta T^{(p)} \qquad (11)$$

2.1.4 Synthesis/preparation of materials

2 1 4 1 Pre-vulcanisation of NR latex

Table 2.2 Pre-vulcanisation formulations

Materials	Formulation (phr)
60 % Centrifuged high ammonia latex	167
10 wt % Ammonium oleate	2.6
10 wt % KOH	2.5
50 wt % Sulphur dispersion	1
50 wt % Zinc dithiocarbamate dispersion	0 5
50 wt % Zinc oxide dispersion	0 2

NR latex compound was prepared according to the combinations given in Table 2.2. This formula was designed to obtain a comparatively low cross-link density, and, hence, the amount of vulcanising agents including sulphur, ZDC, ZnO had been adjusted to meet this requirement. Furthermore, in this attempt, instead of using 60 % dry rubber content (DRC) of centrifuged latex, the DRC of centrifuged latex was adjusted to 50% by adding deionised water Heating of latex compound at 60°C was carried out for nearly 4 hours. However, the extent of curing was determined by the visual appearance of the coagulum, obtained by coagulating latex sample in $CHCl_3$ until it can be easily broken and the broken pieces are non-tacky This is commonly used to determine the state of cure i e whether the sample is cured or under-cured If it is cured then the coagulum can be easily broken and the broken pieces are appeared to be non-tacky

Pre-vulcanised latex was cooled to the room temperature as quickly as possible in order to prevent further reaction. The chemicals, which precipitated were removed to prevent any further reaction and this pre-vulcanised latex was used to synthesise semi-1 IPNs and full IPNs where the first polymer was in cross-linked state.

Preparation of NR films

NR latex with 60% DRC was obtained and diluted to 45 wt.% by adding deionised water and used for preparing the NR films. A known amount of diluted NR latex was sieved using a mesh and poured on to open glass trays to obtain the final NR film with a thickness of *ca.* 1 mm Thereafter, these cast films were dried at room temperature until the films were transparent. These films were further dried by heating the sheet at 70°C for 1 hour in an oven Films thus obtained were then placed in sealed polythene bags and used in the preparation of NR/PMMA blends and semi-2 IPNs

Pre-vulcanised NR films were similarly prepared, as mentioned earlier, by using pre-vulcanised NR latex. These cast films were mainly used in the synthesis of semi-1 and full IPNs

2.1.4.2 Synthesis of blends and IPNs based on NR and PMMA

(i) Synthesis of NR/PMMA blends

Preliminary studies indicated that the materials produced using the initiator (Triganox 21S) do not undergo 100% polymerisation in the presence of oxygen in the medium. Therefore, a predetermined excess amount of monomer had to be added in order to gain the required amount of PMMA in the final product.

NR film was cut into the required shape and the initial weight of the NR sample was recorded. Then this sample was placed in a closed container, containing a mixture of monomer and initiators. The initiator was added at 1 mole percent on monomer content. The immersed sample was allowed to swell in the monomer/initiator mixture and the sample was removed after it reached a predetermined weight (10 minutes to 30 minutes) Different compositions of elastomer and plastomer ratios were obtained by allowing swelling for different periods of time The swollen NR sheets were then placed in sealed polythene bags and stored at *ca* 5°C- 8°C for about 24 hours allowing uniform distribution of MMA within the NR matrix. Thereafter, the swollen samples were placed in a mould, as shown in Fig. 2.1, and polymerisation of the MMA was allowed to take place by heating the mould at 80°C for 22 h Samples were removed from the mould, weighed and further dried in a vacuum oven at room temperature for one week in order to remove any residual monomer. Details of the compositions of the NR/PMMA blends are given in Table 2 3 Sample codes indicate the approximate composition by weight.

Table 2.3 Composition range of the NR/PMMA blends

NR/PMMA blend	**Target composition**		**Experimental composition**	
	NR (wt %)	PMMA (wt.%)	NR (wt.%)	PMMA (wt %)
NR90 PMMA10	90	10	91	9
NR80 PMMA20	80	20	83	17
NR70 PMMA30	70	30	73	27
NR60.PMMA40	60	40	61	39
NR50.PMMA50	50	50	52	48

ii) Preparation of semi-2 IPNs

Semi-2 IPNs were synthesized in an identical manner to the above-mentioned procedure except that the first polymer, NR was allowed to swell in a mixture containing monomer, initiator and cross-linker, EGDM.

Table 2.4 Details of semi-2 IPNs synthesis including composition and cross-linker level

Target composition		EGDM (mole percent on monomer) (Experimental composition)					
NR (wt %)	PMMA (wt.%)	0 5		1.0		1.5	
		NR (wt %)	PMMA (wt.%)	NR (wt.%)	PMMA (wt %)	NR (wt.%)	PMMA (wt.%)
90	10	91	9	92	8	91	9
80	20	83	17	81	19	81	19
70	30	71	29	71	29	72	28
60	40	63	37	58	42	63	37
50	50	52	48	51	49	53	47

As described earlier, IPNs with various elastomer and plastomer contents were synthesised by varying the swelling time. Furthermore, semi-2 IPNs were synthesised by varying the EGDM concentration as shown in Table 2 4. In addition to the sample codes given in the Table 2 4, the value given in the parenthesis indicates the mole percentage of the EGDM.

(iii) Preparation of semi-1 IPNs

Semi-1 IPNs were synthesised by following the same procedure mentioned earlier for NR/PMMA blends Nevertheless, instead of using un-vulcanised cast NR films, cast films prepared using pre-vulcanised latex were used for the preparation of the semi-1 IPNs to meet the main requirement of semi-1 IPN, where the first-formed polymer should be in the cross-linked state

Semi-1 IPNs with different NR/PMMA ratios were synthesised by varying the swelling time. Details of semi-1 IPNs are given in Table 2 5.

Table 2 5 Compositions of the semi-1 IPN

Target composition	**Experimental composition**	
NR PMMA (wt %)	NR, (wt %)	PMMA (wt %)
90 10	97	3
80 20	92	8
70 30	68	32
60 40	63	37
50 50	49	51

(iv) Preparation of IPNs

The IPNs were also synthesized according to the procedure given for the semi-1 IPNs except that the pre-vulcanised NR sheets were allowed to swell in a mixture which contained monomer, initiator and cross-linker. The IPNs with various compositions were prepared by swelling the material up to different levels by varying the swelling time. In the IPNs, both the NR and PMMA phases are in the cross-linked state. The IPNs with various cross-link levels were prepared by varying the EGDM content as shown in Table 2 6

2.2 Preparation of the semi-1 IPNs based on NR, PMMA and the ENR as the third component

2.2.1 Synthesis of Epoxidised Natural Rubber

Materials

Formic acid (98%) and 50% hydrogen peroxide, non-ionic surfactant (Wettem), potassium hydroxide and methanol were used without further purification.

Method:

High ammonia centrifuged natural rubber latex having 60% dry rubber content (kindly donated by Ansel Lanka Ltd., Sri Lanka) was used through out this study Natural rubber latex was stabilized with a non-ionic surfactant, Wettem at a level of 10 phr. Stabilized latex was diluted up to the required dry rubber content by adding distilled water followed by stirring for 5-10 minutes The latex mixture thus prepared was allowed to stand for 24 hours for maturation Matured latex was poured into the reaction vessel, in a water bath, which was set at 60°C Stirring was continued for 1 hour to facilitate the removal of ammonia and to achieve the required temperature. The required amount of formic acid (0.2 moles/isoprene unit) was added quickly so that it would pass the iso-electric point of latex at which coagulation takes place Thereafter, hydrogen peroxide (concentration - 50 wt.%) was added drop-wisely over 20 minutes.

ENR latex with different epoxy contents such as 50 mole %, 45 mole %, 15 mole%, was obtained by performing the reaction in latex (20% dry rubber content (DRC)) at 60°C using a higher level of hydrogen peroxide (rubber. formic acid: hydrogen peroxide, 1.0.2 1 5 (mole ratio) at 20%, for 10 hours, 8 hours and 3 hours, respectively. For these ENR materials, the level of hydrogen peroxide is given in the parenthesis and denoted by – **H** symbolising higher level

Table. 2.6 Details of the composition of the full IPNs.

Target composition		EGDM level (mole percent)					
		0.5		1.0		1.5	
NR (wt.%)	PMMA (wt.%)	NR (wt.%)	PMMA (wt.%)	NR (wt.%)	PMMA (wt.%)	NR (wt.%)	PMMA (wt.%)
80	20	93	7	97	3	95	5
70	30	73	27	74	26	73	27
60	40	66	34	63	37	64	36
50	50	52	48	51	49	52	48

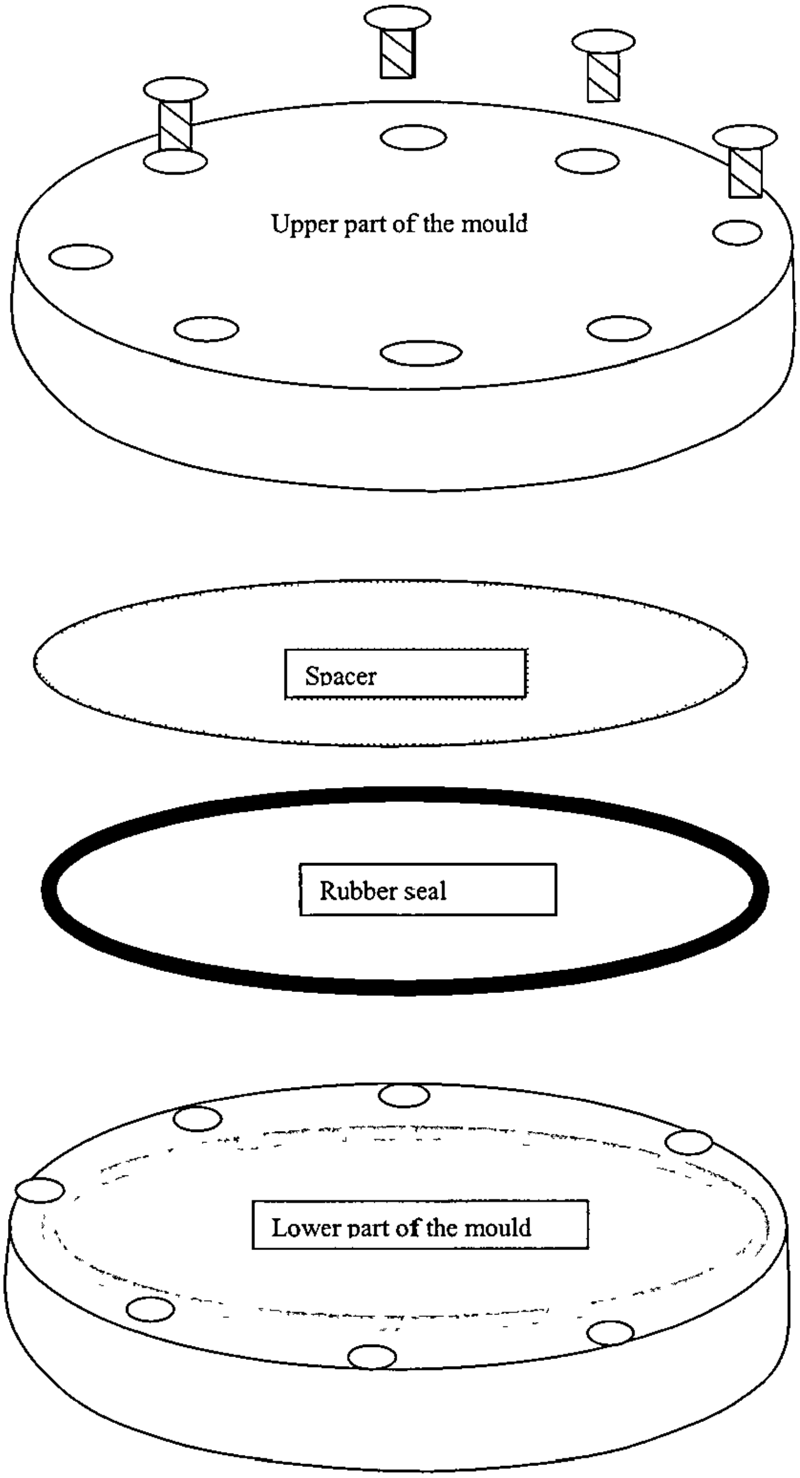


Fig 2.1 Diagram of mould used for the preparation of IPNs

In addition, ENR with 45 mole% epoxy content (error - ±3) (ENR-45 (M)) was synthesized using a low level of hydrogen peroxide (rubber formic acid hydrogen peroxide; 1 0.2·1 0 (mole ratio)) at a level of 20% DRC (reaction time 11 hours) Nonetheless, it was difficult to produce 60% ENR using a low level of hydrogen peroxide at a level of 20% DRC as it requires a rather long reaction time, and due to the destabilisation of the latex due to the presence of acid. As such, 60 % epoxidation level was achieved using latex with 30% DRC content and using an equivalent lower level of hydrogen peroxide (rubber: formic acid hydrogen peroxide; 1 0.2 1 0 (mole ratio)), which was used for preparing ENR-45 (M) (reaction time 8 hours). It is stated that the level of DRC, up to 40%, will not cause ring opening reactions and side reaction (Vernekar *et al*, 1992) Hence, variation of DRC level up to 40% would not have a significant effect on the final properties of ENR After completion of the reaction, the resultant ENR latex was neutralized using 10% KOH, followed by the coagulation of latex using methanol The coagulum, thus obtained was passed several times through a smooth mill to obtain a thin lace that was thoroughly washed prior to drying in a drying tower at 32°C – 35°C Drying of ENR was continued for one week.

The epoxy content can be measured using different techniques, such as NMR, FTIR spectroscopy, DMTA, determination of oxygen content (elemental analysis) and by titrimetric methods. In this study, the epoxy content was measured by FTIR spectroscopy technique. For this purpose, the ratio of the intensity of the epoxy peak to the total intensities of the epoxy peak (870cm^{-1}) and the olefin peak (830 cm^{-1}) was measured (Nakason *et al.*, 2004, Rahaman, 1990). Nevertheless, DMTA data also provide an indication of the Tg of ENR based on the fact that 1 mole percent of epoxidation increases the Tg by 1°C (Gelling, 1991). Both of these techniques would help to evaluate the epoxy content of the ENR

2.2.2 Preparation of the blends of natural rubber and ENR

Rubber was compounded according to the formulae given in Table 2.7 and the compositions of rubber blends prepared in this series are given in Tables 5.11 - 5 16.

For these experiments, natural rubber, in lace form, was obtained by coagulating the high ammonia centrifuged latex (the same material used for reactions) by using 1 % (w/v) formic acid followed by washing the coagulum with water. Then the coagulum was passed through a series of smooth mills while washing the rubber during milling in order to obtain the rubber in lace form The final lace was also washed thoroughly in order to remove any residual acid The NR laces thus prepared were dried in the drying chamber (32°C – 35°C) for one week

300g of NR laces were milled for 3-4 minutes using a two-roll mill (Kansai, Japan). Then the required amount of synthetic polymer/ modified rubber was added and milled properly before the one at a time addition of compounding ingredients The curatives were added last and milled for 1-2 minutes. A low level of sulphur was intentionally used in these blends because free sulphur has an inhibition effect on the polymerization of MMA as evident from literature (Bartlett and Trifan, 1956, Ghosh, 1971) as well as discussed in the section 3. 4.1.

Table 2.7 Formula for preparation of rubber compound

Material	Amount (g)
Rubber blend/ Rubber	100
ZnO	5
Stearic acid	2
Dibenzothiazole disulphide (MBTS)	1.5
Tetramethyl thiuram disulfide (TMTD)	0.75
Sulphur	0.6

Determination of cure time:

Rheographs were obtained at 150°C for these rubber compounds using MDR 2000 instrument in order to determine the time required for 90% curing Cured rubber sheets were prepared by heating the samples in a mould, for the required period of curing time at 150°C, using a hydraulic press.

2.2.3 Synthesis of IPNs using blend of NR and ENR and MMA as raw materials

Purification of methyl methacrylate was done by adding 10 % (w/v) aqueous sodium hydroxide solution followed by washing it with distilled water several times. The purified MMA was dried over anhydrous calcium sulphate The initiator and the acrylic acid were used as received

The mixture of methyl methacrylate and the initiator, dibenzoyl peroxide (5 % w/v), was prepared by stirring the individual components for 5-10 minutes. A circular sample having diameter of 4 inches was cut out from the cured sheet of rubber blend and the weight of the sample was recorded. The sample was immersed in the monomer/initiator mixture for a certain time until it reached the required weight. Then the swollen sample was kept for 24 hours at 8°C until it reached an equilibrium state. The sample was placed in a pre-heated (80°C) mould, after covering it with a polyester film, and then heated for 24 hours at 80°C in an oven. The detailed compositions of the blends and the IPNs are given in Tables 5.11 - 5 16.

2.2.4 Synthesis of semi-1 IPNs based on NR, ENR, acrylic acid and PMMA

Mixture of initiator dibenzoyl peroxide and monomers; methyl methacrylate and acrylic acid were prepared by stirring all ingredients for 5-10 minutes Acrylic acid content was varied at 10, 20 and 30 w/v% on the PMMA content. Circular shaped samples from the cured sheets of the blend of 50/50 of NR/ENR-70 (M) was taken and immersed in the mixture containing methyl methacrylate and acrylic acid and allowed to swell until the predetermined weight was reached. The swollen samples were kept in the refrigerator (0 to -5°C) for 24 hours until they reached the equilibrium condition Thereafter, the samples were covered with a polyester film and placed in a pre-heated mould (80°C) and heating was continued for 24 hours at 80°C. Details of the compositions of these semi-1 IPNs are given in Table 5 15

2.3 Characterisation of IPNs and IPNs based on ENR

2.3.1 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA has the advantage of higher sensitivity in resolving transition positions than the conventional DSC technique, and it basically measures the molecular motions in polymers. Various instruments are used in DMTA experiments and modern techniques utilize direct phase measurements between stress and strain sine waves. Various deformation modes such as bending, shear, tensile, compression, torsion etc are used depending on the nature of materials.

Two basic models (Figure 2 2) are used to express the response to load of a perfect elastic material or an ideal viscous material. The former can be explained by a massless spring and the latter is described by a Newtonian dashpot

Response of perfectly elastic material can be given by following equation.

$$\sigma/\epsilon = E \tag{12}$$

σ is the tensile stress, E is Young's modulus and ϵ is the tensile strain.

Similarly, the response of an ideal viscous liquid is described by a Newtonian dashpot and can be expressed by the following equation (Birley *et al*, 1991)

$$\sigma = \eta \, d\epsilon/dt \tag{13}$$

η is the coefficient of viscosity and t is time.

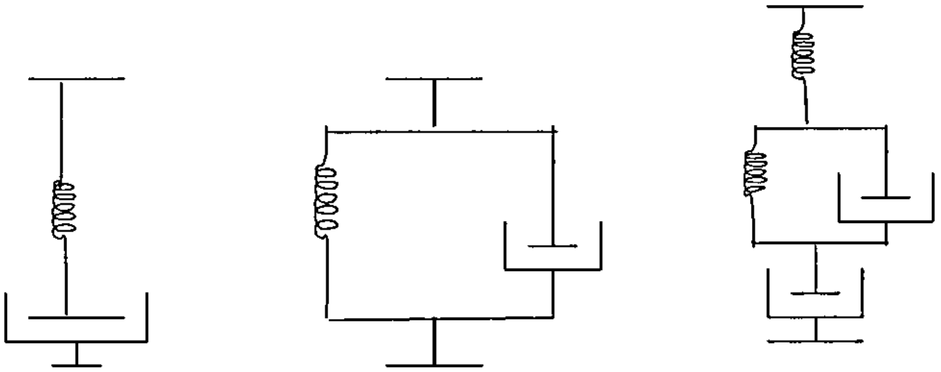
$$\sigma = \epsilon_0 \, E' \sin \omega t + \epsilon_0 \, E'' \cos \omega t \tag{14}$$

The above equation indicates that σ (induced stress) can be divided into two parts (Figure 2.3) i.e. stress in-phase with the applied strain (δ- phase lag, δ = 0), and stress out-of-phase (δ =90) with the applied strain.

The in-phase stress is due to the elastic nature and is governed by the storage modulus The out-of-phase stress is due to the viscous nature and is governed by the loss modulus.

(a) Spring

(b) Dashpot



(c) Maxwell Element

(d) Kelvin – Voigt Element

(e) 4 – Element Model

Fig. 2 2 Different types of spring and dashpot models

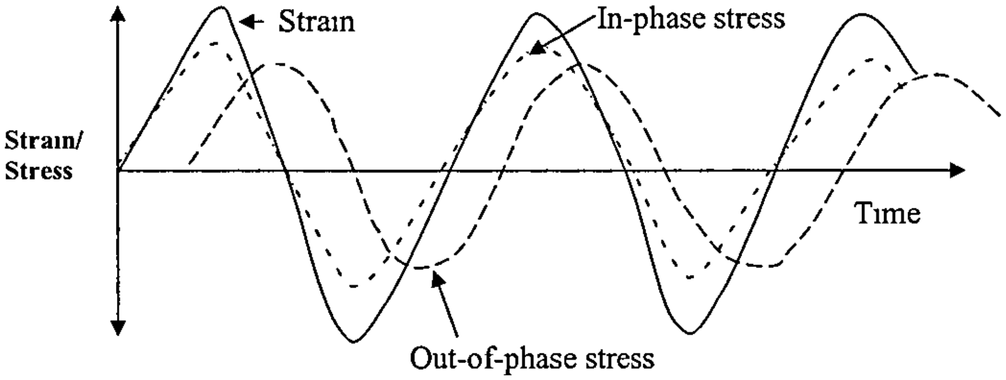


Fig. 2 3 Variation of response of stress to the applied strain

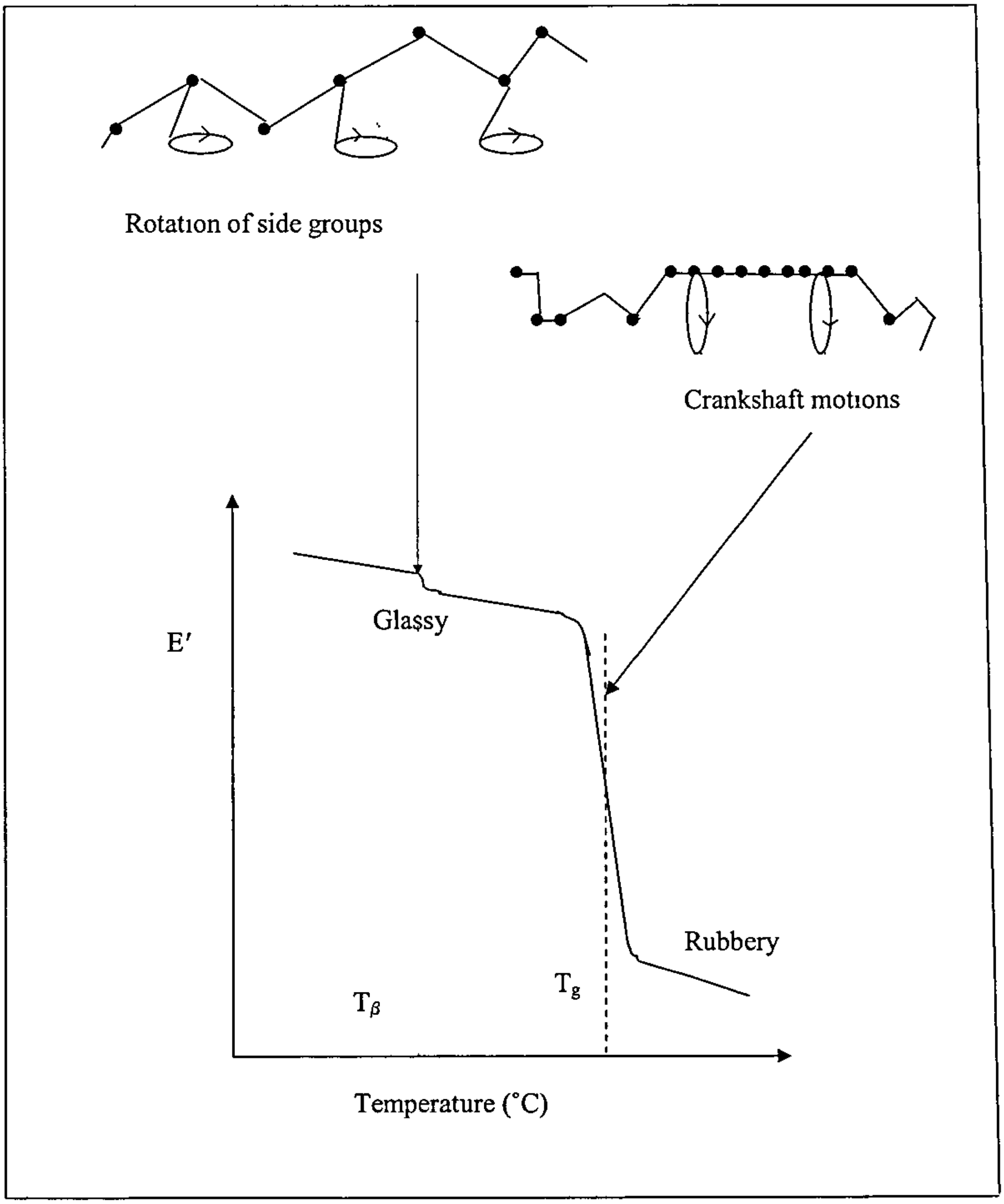


Fig. 2.4 Variation of storage modulus with temperature for amorphous polymers (*After* Powell, 1983)

In addition, the storage modulus, loss modulus, tan δ and complex modulus (E^*) can be further described as shown below (Birley *et al*, 1991, Clegg and Collyer, 1993).

$$E' = \text{in-phase amplitude} / \text{strain amplitude} \qquad (15)$$

$$E'' = \text{Out-of-phase amplitude} / \text{strain amplitude} \qquad (16)$$

$$\text{Tan delta} = E'' / E' \qquad (17)$$

$$E^* = E' + iE'', \text{ where } i = (-1)^{1/2} \qquad (18)$$

DMTA applications

DMTA is extensively used to determine glass transitions temperatures and damping properties of polymeric substances The glass transition temperature can be described as the temperature at which the transition from the glassy to the rubbery state of amorphous polymers takes place If a polymer is below Tg, the polymer chains are frozen and unable to move During slow heating, a β transition may be reached due to the rotation of side groups and the storage modulus is reduced to a certain extent. (Powell, 1983) (Figure 2 4). On further heating, polymer segments start to move by crankshaft motions leading to drastic reduction in storage modulus (Powell, 1983) The actual mode of chain motion is considered as reptation in which 10-50 atoms of the backbone are involved (de Gennes, 1971; Sperling, 1992) Because of these movements, at the glass transition temperature, mechanical energy of vibrations can be converted to thermal energy and this technique is used in commercial damping devices and materials

When a visco-elastic material is heated from a temperature which is below the glass transition temperature (Tg), it undergoes a transition from the glassy to the rubbery state and thereafter it attains liquid-like characteristics (Sperling, 1992, Cowie, 1991). However, depending on the material, the regions may be varied (Sperling, 1992). Moreover, Tg depends on a number of factors which include free volume, steric effects, pendent groups, flexibility, interactions, polarity, crystallinity and the extent of cross-linking (Murayama, 1978). In addition, DMTA data can be used to determine the extent of miscibility as depicted in Fig. 2.5, which indicates that for an immiscible system two transitions that are similar to the homopolymers are present However, in a completely miscible system, a single transition is observed This shift of the transition is also be observed in partially miscible polymer blends In addition, a broad transition is normally obtained for micro-heterogeneous systems. The broadening of the transition also provides information about the extent of heterogeneity (Perera *et al*, 2000) In addition, DMTA also provides information about ageing of glassy polymers (Perera *et al*, 2000), and molecular relaxation of polymeric materials

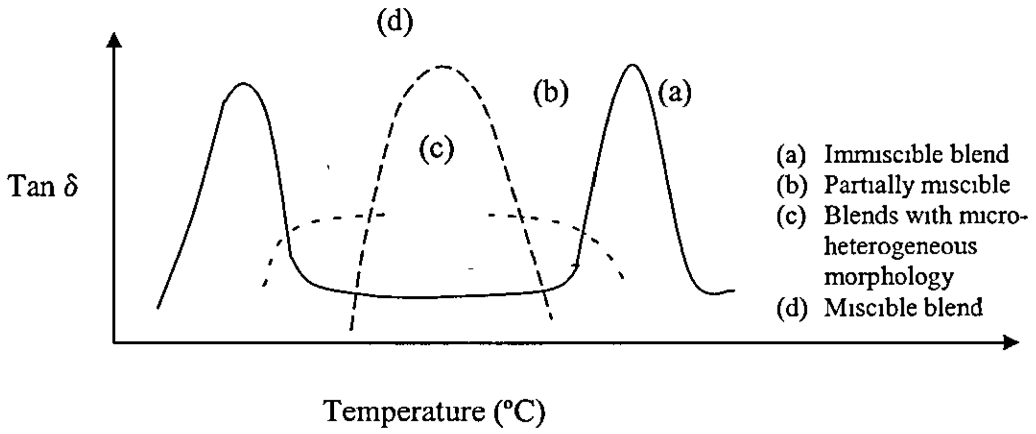


Fig 2.5 DMTA spectra for blends with various degrees of miscibility

Types of instrument

Dynamic testing is performed by subjecting the material to a deformation pattern and cyclic stress/strain behaviour is calculated ((Murayama, 1978) Dynamic mechanical instruments can be basically be divided into two types depending on the nature of the dynamic motions.

1 Free vibration in which the test piece is subjected to oscillations and the amplitude is allowed to decay due to damping in the system This type of vibration is commonly measured by using a torsional pendulum method and it covers the frequency range 0.01 –10 Hz (Murayama, 1978)

2 Forced vibration in which oscillations are maintained by external means. This type of instrument is further sub-divided into forced vibration machines operative at resonance, or away from resonance, transient loading (as opposed to continuous) loading, and wave propagation (Murayama, 1978)

These instruments can be further classified according to the method of oscillation such as mechanical or electromagnetic

Electromagnetic vibrations are commonly used in small instruments at low strains and cover a wide range of frequencies up to 100 Hz. Electromagnetic, or hydraulic, vibrations are used basically in the Rheovibron, and it can cover free vibration apparatus as well as forced vibration apparatus The Polymer Laboratories instrument is operated electro-magnetically where automatic scanning is allowed through frequency or temperature range.

Hydraulic activation can be considered as the most versatile technique and this facilitates the control of stress/strain and is able to use waveforms other than sinusoidal.

Experimental conditions for DMTA

Dynamic mechanical properties of the IPNs based on NR and PMMA were determined using a dynamic mechanical thermal analyser (DMA 2980, *TA* Instruments) Rectangular strips with uniform width (3 mm) and known thickness (*ca.* 1 mm) were clamped on to the mechanical head and the length between clamps measured. The DMA multi-frequency mode was selected and the sample was clamped in slight tension mode. The sample oscillates sinusoidally up to a preset strain maximum (amplitude 20 μm) at a frequency of 1 Hz The temperature ramp was set at 3°C min^{-1} and a static force 0 01 N was used. Scans were recorded from -100°C to 200°C.

The dynamic mechanical thermal analysis of the samples for Chapter 5 was carried out using different experimental conditions because samples were thick and apparently looked like rubber toughened plastics Therefore, dual cantilever bending mode was chosen because of the convenience instead of using shear mode, and the measurements were made at 10 Hz Amplitude was selected as 20 μm and the heating rate was 3°C min^{-1}.

2.3.2 Scanning calorimetry techniques

Differential scanning calorimetry (DSC)

Thermal analysis techniques are widely used for polymer characterization Phase changes, such as crystallization, are usually accompanied with energetic effects (Richardson, 1989). During a phase change in a sample, which has a heat of transition, the sample temperature is increased. This can be recorded as either ΔT in a heat flux DSC or as ΔP in a power compensation DSC.

However, the signal on heating is related to the difference between the thermal capacity of the sample and the reference This thermal capacity is generally based on the mass and heat capacity of the material and the heat exchange between the two cells (Richardson, 1989) It can be used successfully to determine the glass transition temperatures of polymers.

Modulated differential scanning calorimetry (MDSC)

Modulated differential scanning calorimetry (MDSC) is a recent technique possessing certain advantages over the conventional DSC technique. In this technique, the conventional heating programme is modulated by a perturbation and the resultant heat flow is deconvoluted into the response of the perturbation and the response of the underlying heating program (Jones *et al.*, 1997) Therefore, the heat flow signal is split into an underlying and a periodic part In this technique, the underlying response is obtained by employing an averaging procedure and then a Fourier transform to the response of temperature modulation and phase lag (Jones *et al.*, 1997, Reading and Hourston, 2006).

Theoretically, different types of contributions to the heat flow could be expressed by below mentioned equation.

$$dQ/dt = C_{pt}\, dT/dt + f(t,T) \qquad (19)$$

dQ/dt -heat flow into the sample

C_{pt}, - reversing heat capacity of the sample owing to its molecular motions such as vibrational, rotational and translational motions).

$f(t,T)$ is the heat flow which is irreversible and is the result of kinetically hindered events.

However, at the glass transition the heat capacity as a function of temperature depends on the frequency.

In MDSC, the sample is subjected to a sinusoidal modulated heating programme

$T = To + Bt + \beta \sin \omega t$ (20)

To - initial temperature,

B - heating rate

β - amplitude of modulation

ω - angular frequency

$dQ/dt = \beta Cpt + f(t,T) + \omega\beta C_{pt} \cos \omega t + C \sin \omega t$ (21)

(underlying signal) (cyclic sgnal)

f (t,T) - average f (t,T)

C- amplitude of the kinetically hindered response

C_{pt} and C vary with time and temperature, but it is assumed to be a constant over the duration of a single modulation and the heat flow depends on temperature modulation Further, heat flow and temperature are given by the superimposition of the underlying and the cyclic parts. Therefore, C_{pt} is independent of B (heating rate), but C is proportional to it

The cyclic component will have an amplitude and a phase shift, which is determined, by $\omega\beta C_{pt}$ and by C.

$C = A_{HF}/A_{HR}$, Cyclic heat capacity (22)

A_{HF} – amplitude of heat flow modulation

A_{HR} - amplitude of heating rate modulation

$C_{pt} = C \cos \delta$

$C = \omega\beta C \sin \delta$

δ - Phase shift

Three basic signals, the average or underlying signal, the in-phase cyclic component and the out-of-phase signal, C, from which C_{pt} is calculated, are used in MTDSC. Reading *et al* suggested (Reading *et al*, 1992; 1993) that it is useful to calculate the non-reversing signal, which is governed by the difference between the underlying, and the cyclic signals.

Therefore, the non-reversing heat flow is governed by the subtracting reversing heat flow from the underlying heat flow and can be expressed as follows.

Non-reversing heat flow = underlying heat flow - $\beta C_c \cos \delta$

If $\cos \delta = 1$, then the phase angle shift during transition is small.

The non-reversing process involves the loss of a volatile material, cold crystallization or a chemical reaction etc.

Experimental conditions for MDSC

In this present study, the MDSC technique was used basically to determine the glass transition temperatures (T_g), the weight fraction of NR component in interface region, the total interface fraction and the miscibility of the components. For this purpose, all measurements were obtained using a TA Instruments (2920 Modulated DSC). IPN samples (*ca.*5 mg) were weighed and placed in aluminium pans and carefully sealed. The sealed pan, containing the sample, and the reference pan were placed in the sample holders. The sample was heated from -130°C to 180°C at a heating rate of 3°C $\min^{-1}$. Experiments were performed using nitrogen as the purge gas at a flow rate of 60 ml $\min^{-1}$. Scans were obtained over the temperature range -130°C to 180°C. Plots of dCp/dt, or dCp/dT, versus temperature were plotted, and the ΔCp at a particular transition was obtained using a computer programme.The data was then used to determine the weight fraction of the individual components (δ_{NR} and δ_{PMMA}) in the interphase as follows.

For this calculation, it is assumed that ΔCp is proportional to the weight fraction (Hourston *et al*, 1997). Hourston *et al* (1997) further indicated that the weight fraction of the interfacial layer can be obtained from the missing amounts of each component. In other words, it is assumed that the reduced amount of homopolymers participated in the formation of the interfacial layer with a finite thickness, which is formed by the inter-diffusion of the two components driven by the chemical potential gradient (Song *et al.*, 1999). Therefore, in this case, ΔCp_{NR} and ΔCp_{PMMA} are considered as the increments of heat capacities at their corresponding T_gs before mixing.

$\Delta Cp_{NR\text{-}IPN}$ and $\Delta Cp_{PMMA\text{-}IPN}$ are referred to as increments in heat capacity at their corresponding T_gs in the IPN. The morphology of an IPN system based on NR/ PMMA can be assumed to contain mostly a three-phase structure, which includes pure NR, pure PMMA (homo PMMA) and the interphase. Hence, the total interphase content and ΔCp can be stated as follows.

$$\Delta Cp = \Delta Cp_{NR\text{-}IPN} + \Delta Cp_{PMMA\text{-}IPN} + \Delta cpi \qquad (23)$$

ΔCpi refers to the increment of heat capacity of the interface.

However, it was noted that graft polymer can also be formed during the polymerization of MMA in the presence of NR. Therefore, it is assumed that graft polymer may also be present in the interface layer.

Therefore, the weight fraction of NR and PMMA (δ_{NR} or δ_{PMMA}) in interphasial layer for each IPN was calculated using following equations (Hourston *et al.*, 1997).

$$\delta_{NR} = w_{NR} - \Delta Cp_{NR\,IPN} / \Delta Cp_{NR}, \qquad (24)$$

where w_{NR} is the weight fraction of NR in the sample.

Similarly, $\delta_{PMMA} = w_{PMMA} - \Delta Cp_{PMMA\,IPN} / \Delta Cp_{PMMA}$, (25)

w_{PMMA} is the weight fraction of PMMA in the sample.

2.3.3 Stress-strain measurements

Stress-strain measurements can be determined in various modes such as the tension mode, the compression mode etc However, among these modes, the tension mode is commonly used to determine stress-strain data and it provides information about stress at any given strain, tensile strength, yield strength and elongation at break. These properties are used as measures of performance of the material.

In this method, stress is applied to the material and it is defined as the force exerted on a unit cross-sectional area and is expressed as follows.

$$\sigma = F/ A_0 \qquad (26)$$

σ, F and A_0 are the tensile stress, tensile force and original cross-sectional area respectively.

The induced tensile strain, caused by the applied stress can be expressed as a ratio of increased length to that of original length.

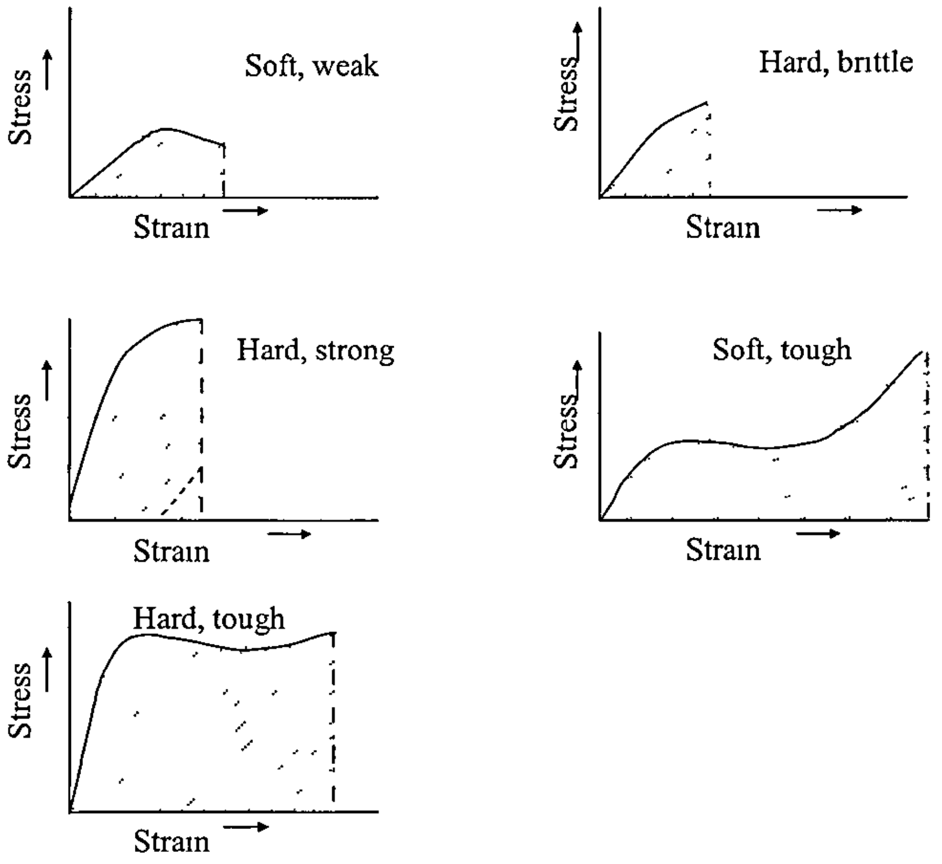
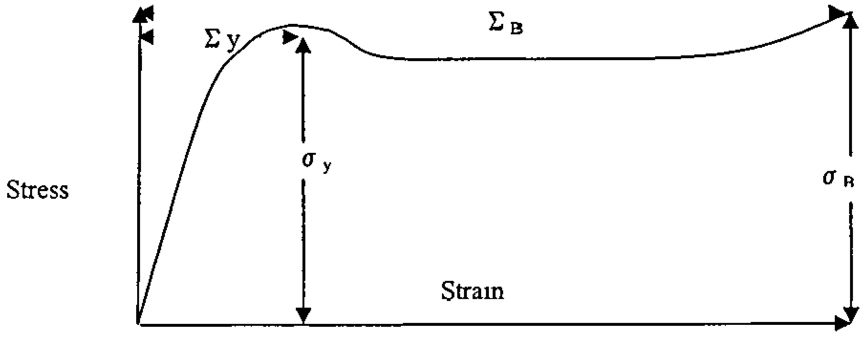


Fig 2 6 Stress-strain behaviour for different of polymer types



σ_y - yield stress

Σ_y - elongation yield

σ_B – ultimate tensile strength

Σ_B – ultimate tensile strain

Fig 2.7 General representation of a stress-strain curve

$$\varepsilon = l_1 - l_0 / l_0 \qquad (27)$$

Tensile strength is calculated as the stress at break. However, in this calculation, though the dimensions of the cross sectional area varies as it stretches, for experimental convenience the original cross sectional area is used to calculate the tensile strength.

According to Hooke's law, the stress is proportional to the strain for ideal elastic solids. Despite this, most polymers deviate from Hooke's law and stress may be proportional to strain only at extremely low levels of strain. Carswell and Nason (1944) indicated five possible stress-strain diagram types. See Figure 2 6 In addition, a more general representation of a stress-strain curve is presented in Figure. 2.7.

2.3.3.1 Determination of stress-strain properties

A tensometer is used to perform tensile, flexural, compression, tear and adhesion tests. Though there are two types of machine available, the constant rate of loading and the constant rate of traverse types, the latter is a perfect machine for rubber testing. In this machine, the test piece is stretched at a constant rate and the force measurements are measured. These instruments possess electric transducers for determining the force measurements (Brown, 1996).

In addition, a very wide range of forces can be measured by varying the amplification of the electrical signal which allows recording and further automatic handling of data. Further, certain facilities such as off-set zero and automatic test piece cross-sectional area compensation are also available with these instruments. In addition, modern machines use data capture systems and computers to store data and digital display facilities. An extensometer is commonly used to determine the extension. Various types of extensometers are available including contact types and non-contact types. The traditional types of extensometers have grips which have to be fixed on to the test piece. This has several disadvantages such as slippage and may cause failures at the attachment points Hence, the grips are designed to be light and pressure compatible in order to minimize those effects.

A non-contact optical extensometer, which uses visible and infrared light, has advantages such as eliminating slippage and damage to the test piece. On the other hand, this system also exhibits some disadvantages such as difficulties of marking the surfaces or where coloured surfaces are present.

In addition to optical extensometers, laser extensometers and video extensometers are currently available. However, accuracy at low strains is limited in laser extensometers. Video extensometers have the unique advantage of recording the mode of fracture as the image of test piece is produced by a video camera, which is fed to a computer. However, the choice of extensometer depends on the strain range, accuracy and cost. Non-contact types can be used with lack of interference by the test piece (Brown, 1996) Nevertheless, in this study a extensometer with grips (traditional type) fitted to the sample has been used to determine tensile properties of the NR/PMMA IPNs.

Experimental conditions

Tensile testing was performed according to ISO 37 by using a Hounfield tensometer (Model No. H 5000M). Dumb-bell shaped test pieces, in which stress and strain are assumed to be uniform throughout the central parallel portion, were used in these experiments.

The dumb bell test pieces were fixed to eccentric roller grips and strained at a constant speed of 500 mm $\min^{-1}$ using a 500 N load cell. Test was performed at room temperature (25°C) using 5 test pieces for each sample and the average values are recorded.

Cycling test

The Hounsfield test machine, controlled by a computer programme, was used for the cycling tests. For this purpose, dumb bell test pieces were fitted between the eccentric rollers and subjected to three consecutive cycles up to 300 % strain at an extension ratio of 20 mm $\min^{-1}$ (temperature (25°C)). As shown in the Lloyd instrument program, force against extension was plotted for each cycle and the area in between extension and retraction curves was calculated as an energy value (J). In addition, hysteresis was determined by plotting stress versus strain curves for extension and retraction of the first cycle For each sample, 4 or 5 test pieces were tested and the average values are reported.

2.3.4 Determination of Tear strength

Tear strength of the semi-1 IPNs containing ENR was performed according to the ISO 34 (BS903) Standards using crescent type samples. Tear testing had been carried out at a constant traverse rate (500 mm/min) at 25°C temperature. The tear strength was calculated as the ratio of maximum force to the thickness of the sample.

2.3.5 Determination of cross-link density

In this study, the cross-link density was determined by using the Flory-Rehner equation (Flory and Rehner, 1943) based on swelling measurement data (Brydson, 1978).

Experimental Method

A sample of vulcanised NR (*ca.* 0 25 g) was weighed and placed in a bottle containing 25 ml of toluene and allowed to swell for three days in order to attain its equilibrium level. The swollen sample was blotted immediately after its removal from the toluene and reweighed and then oven dried at 100°C for 30 minutes. Thereafter, the final weight of the sample was recorded and the volume of rubber in the swollen sample was calculated by considering the de-swelled, the swollen, the initial weight of the sample and the densities for rubber and toluene Furthermore, the cross-link density and M_c (the molecular weight between two cross-links) were calculated using the Flory-Rehner equation given below (χ =-.42 (Polymer Handbook, 1999)).

$$V_e = (-1/V_s)\ \frac{\ln(1-V_r) + V_r + \chi V_r^{2}}{V_r^{1/3} - 2\,V_r/f} \tag{28}$$

$$M_c = 1/V_e \tag{29}$$

V_e is the moles of effective network chains per cm^3 of rubber, V_s is the molar volume of the swelling agent, V_r is the volume fraction of rubber in the swollen gel and f is the functionality of cross-linking (f = 4).

2.3.6 Determination of sol-gel content

Sol-gel contents of the IPNs and MG rubber have been determined by various researchers with the aim of determining the content of homopolymer and the amounts of grafted polymer present in such materials (Romaine, 1988; Perera, 1999). However, recently published reports indicated that this method is not an accurate method for the estimation of homopolymers and the extent of grafting, as it depends on the extraction procedure (Lehrle and Willis, 1997). Therefore, in this study this method has been used only for approximate quantitative analysis of the sol contents of the IPNs.

Method

A sample (0 1 g) was weighed and placed in a glass bottle containing 75 ml of acetone and the soluble material extracted at room temperature for about one month. During this period, the solvent was stirred for 2 hours per day and once a week, the acetone was replaced by a fresh quantity in order to the facilitate the extraction process. This experiment was performed at room temperature in order to prevent degradation. After extraction, the sample was removed and allowed to dry at 100°C for 30 minutes. After that the final weight of the sample was recorded and used in the determination of the soluble material present in the IPN sample. Thereafter, the same extraction and drying procedures were followed for the extraction of dried sample by using petroleum ether (40/60) which is a moderate solvent for NR and it is reported that this solvent will not remove PMMA (Lehrle and Willis, 1997). The amount of soluble material extracted by petroleum ether was calculated by considering the weight difference before and after extraction

An IPN sample (*ca.* 0.2 g), which is weighed accurately, cut into small square pieces and the weight of the sample was recorded. Thereafter, it was placed in thimble. This paper thimble, containing the sample was placed in a extraction apparatus, which was attached to the round bottom flask, contained ca.150 ml of acetone (Figure 2.8). Acetone was used to extract the homo PMMA content present in the IPN samples. Hot extraction of the sample was carried out for 16 h. The extracted samples and the residual acetone was kept separately for further studies. The extracted samples were further dried in an air-circulating oven for 30 minutes at 100°C. Thereafter, the weight of the dried material was determined. The amount of soluble material was determined by the ratio of difference of weights before and after extraction to the initial weight of the dried sample.

2.3.7 Determination of Mooney viscosity and Mooney stress-relaxation data

Mooney viscosity of the compounded rubber as well as the raw rubber was determined according to the ISO 289 method. The NR sample was pre-heated for 1 minute at 100°C. Then the sample was subjected to a shearing force at a rate of 2 rpm (1 6 s^{-1}) for 4 minutes. The torque finally achieved was recorded and expressed as ML(1+4). Thereafter, the rotor was stopped and the decaying Mooney torque, which is a characteristic of the rubber relaxation, was measured.

Chapter 3

RESULTS AND DISCUSSION OF THE BLENDS, SEMI-1 IPNS, SEMI-2 IPNS AND FULL IPNS

3. 1 General Description

This chapter discusses four types of materials *viz.* blends, semi-1 IPNs, semi-2 IPNs and full IPNs. The effect of composition on the physical and dynamic properties of these materials has been evaluated using the results of stress-strain tests and dynamic testing. In addition, the dependence of miscibility of the components of the IPNs/blends on the PMMA content has also been determined using the data obtained from MDSC.

In this study, the natural rubber and the PMMA has been chosen since such a combination of elastomer and thermoplastic polymers would anticipate to provide synergistic properties. The evaluation of compatibility of these two components is vital as it affects the morphology, physical and dynamic mechanical properties of the IPNs, based on these two polymers. The most extensively used parameter to predict compatibility is the solubility parameter, but this has been limited to non-polar materials. Nevertheless, attempts had been made to evaluate solubility parameters for acrylic polymers whose dielectric constants are rather low (Polymer Handbook, 1975; Hourston and Satgurunathan, 1984) Similarly, the solubility parameters for natural rubber and PMMA were determined according to the Small's and Hoy's methods as explained in chapter 2, section 2.1.3. The values of solubility parameter for each polymer are listed in Table 3.1.

According to the empirical criterion established by Pazonyi and Dimitrov (1967), compatibility is feasible when the difference of the cohesive energy densities, δ^2, is less than 6.69×10^4 J/m^3 (Hourston and Satgurunathan, 1984). Based on that, the difference between the cohesive energy densities ($\delta_{PMMA}^2 - \delta_{NR}^2$) of the natural rubber and the PMMA is 66.1×10^6 Jm-^{3} (calculated using Small's values). It is clear that natural rubber is predicted to be incompatible with PMMA

Table 3.1 Solubility parameter (δ) values for natural rubber and poly(methylmethacrylate) determined according to Small's and Hoy's methods.

Method		Solubility parameter ($MPa^{1/2}$) Polymer Natural rubber	 PMMA
Small		16.73	18.6
Hoy	δ	18.02	19.4
	δ_p	4.58	9.25
	δ_h		10.3
	δ_d		13.4

δ_p – accounts for the permanent dipole-dipole interactions
δ_h – accounts for the hydrogen bonding forces
δ_d – accounts for the dispersive forces (Brandrup *et al*, 1999)

An alternative method for determining the compatibility of polymers, proposed by Krause (1972;1978), utilizes the interaction parameter between two polymers as well as the interaction parameter at the critical point on the phase diagram for a binary system. In this method, the two parameters were calculated as follows.

$$\chi_{12} = \left[V_r/RT\right](\delta_1 - \delta_2)^2 \qquad (3.1)$$

Where V_r is the molar volume of the smaller repeating unit, R is the gas constant and T is the temperature, which is 298 K.

$$(\chi_{12})_{cr} = ½\,(1/n_1^{1/2} + 1/\,n_2^{1/2})^2 \qquad (3.2)$$

n_1 and n_2 represent the degree of polymerisation of each polymer.

The molecular weight for the poly(isoprene) was considered as 100,000 g mol^{-1} for this calculation. The molecular weight of the PMMA was varied from 5,000-80,000 g mol^{-1}. The calculated values for the $(\chi_{12})_{cr}$ coefficients are given in the Table 3.2.

According to the Krause method, if χ_{12} is greater than the $(\chi_{12})_{cr}$ (Hourston and Satgurunathan, 1984), then it implies the existence of incompatibility between the components of a particular polymer pair at some compositions. For this system, χ_{12} was found to be 0.11. Hence, it can be assumed that poly(isoprene) and PMMA are incompatible in the given range of molecular weight

Table 3 2 The calculated values for $(\chi_{12})_{cr}$ for the binary system consisting of poly(isoprene) and PMMA

Polymer system	Molecular weight of PMMA (g/mol)	$(\chi_{12})_{cr}$
Poly(isoprene)/PMMA	80,000	0.0019
	60,000	0.0022
	40,000	0.0029
	20,000	0 0046
	10,000	0 0079
	5,000	0.014

3.2 NR/PMMA blends

Blends with different compositions of NR and PMMA were successfully synthesized using Triganox 21S as the initiator (Table 2.3) These blends were prepared by a process which is similar to the preparation of IPNs, with the exception of the absence of cross-links in both components These samples are transparent and less tacky than the NR heated under the same conditions, and these observations are in agreement with Romaine (1988). Moreover, compared to NR treated under the same conditions, the hardness of the blends containing PMMA was found to be high.

3.2.1 Effect of blend composition on miscibility

3.2.1.1 Analysis of dynamic mechanical properties

Dynamic mechanical thermal analysis is the most widely used technique to determine the miscibility between components in blends. It is accepted that a single glass transition would result due to mixing of components at the molecular level for a fully miscible system On the other hand, two glass transitions, corresponding to the homopolymers, could be identified for the individual components in an immiscible blend (George *et al*, 1997). However, with increasing miscibility, the two glass transitions shift to intermediate positions (Arenas *et al.*, 2002) Therefore, the extent of miscibility of components in a blend can be determined depending on the position of glass transition and its characteristics.

The effect of composition on the loss tangent of the NR component for the NR/PMMA blends is shown in Figures 3.1 and 3.2. Throughout this study, the Tg was determined as the temperature at which highest loss tangent value was obtained.

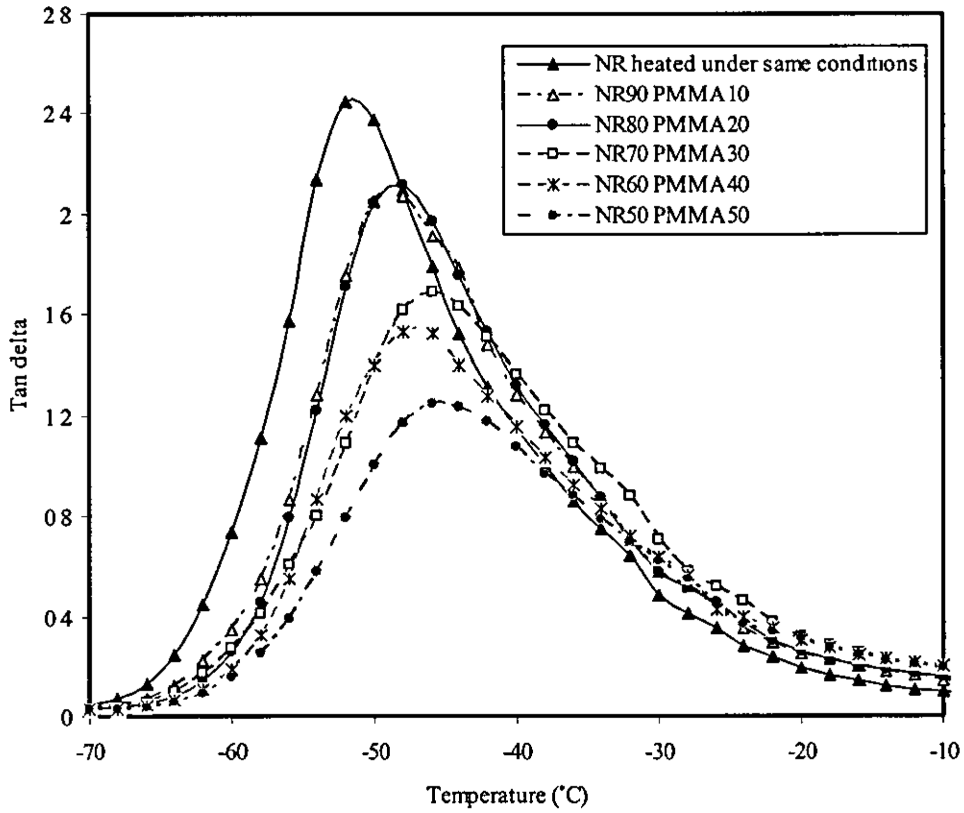


Fig. 3.1 Effect of composition on the loss tangent of the NR component of the NR/PMMA blends

Compared to the NR, heated under the same conditions, the T_g of the NR component has shifted to higher temperatures by 2°C to 6°C in all the NR/PMMA blends (Figure 3 2 and Table 3.3). This can be considered as evidence for some mixing of the components in these samples (Hourston and Romaine, 1990). Interpenetration and/or grafting of PMMA onto NR are believed to be the reasons for this behaviour. Grafting of a polymer on to another polymer chain improves the extent of mixing and simultaneously restricts the segmental motions resulting in an increase in the glass transition temperature of the rubbery component. A similar trend had been observed in the study carried out on graft IPNs based on caster oil-based polyurethane and nitrolignin. T_g of the PU component increased due to the grafting of the latter component to the former component (Huang and Zhang (2002). Work done by Hourston and Zia (1984) also indicated that the segmental restrictions of polyurethane occurred due to the grafting process, which was revealed by a shift of T_g of the polyurethane component to higher temperature. A shift of 4°C has been observed in the NR T_g transition in PMMA (18 wt.%) grafted natural rubber by radiation (Perera, 1999). It also suggest that the grafting of PMMA to natural rubber will result in an increase of the NR T_g

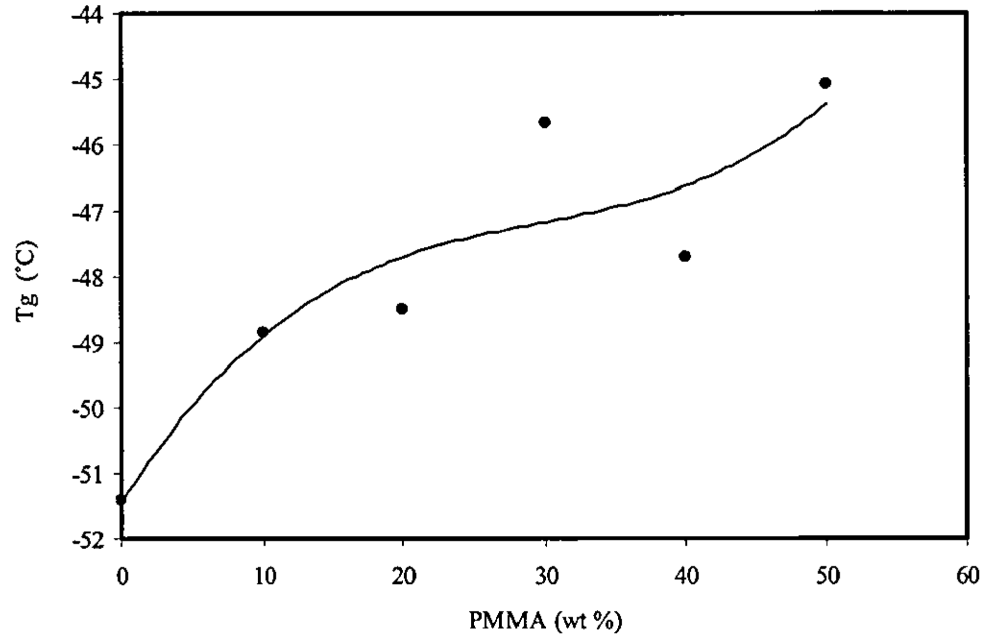


Fig. 3.2 Effect of composition on the NR T_g of the NR/PMMA blends
(Experimental error 5 %)

Among these blends, the T_gs of NR70 PMMA30 and NR50:PMMA50 samples were 3°C and 4°C (Figure 3.2 and Table 3.3), higher than the NR90:PMMA10 and NR80 PMMA20 samples Furthermore, the results indicated that the half-peak-widths of the loss tangent of the NR70:PMMA30 and

NR50 PMMA50 compositions were 5°C – 6°C higher than the NR90:PMMA10 and NR80 PMMA20 samples (Table 3.3). This evidence further verified some component mixing in these samples. MDSC data listed in Table 3.5 (section 3.2.1.2) also indicated that the extents of mixing of components in the aforementioned samples were relatively higher than the sample having 20 wt.% of PMMA.

Table 3.3 Half peak widths of the NR transition and the T_gs of the NR and PMMA transitions (from DMTA data)

Sample	NR T_g (°C)	Half peak width (°C)	PMMA T_g (°C)
Natural rubber*	-51	16	
NR90 PMMA10	-49	17	-
NR80 PMMA20	-49	17	-
NR70.PMMA30	-46	22	156
NR60 PMMA40	-48	21	158
NR50.PMMA50	-45	23	154

* Natural rubber treated under same conditions

As Figure 3.1 indicates, increasing the percentage of PMMA caused a reduction in tan δ_{max} of the NR component Similar trends have been observed in other studies of MMA-grafted NR (Perera, 1999) and NR/PS IPNs (Hourston and Romaine, 1989). As the height of the tan δ peak reflects the relative quantities of each component present in such composites, this reduction can be primarily attributed to the reduction in rubber content, (McCrum, 1958, 1959a, 1959b).

As revealed by the dynamic data, the transition due to the PMMA component is not fully resolved in the dynamic spectra of NR/PMMA of 90/10 and 80/20 samples (Figure 3.3). However, the absence of a prominent PMMA transition in the DMTA spectra is not an indication of complete mixing of PMMA component because of the resolution limitations of this technique Moreover, the PMMA transition of the NR70:PMMA30 blend is present as a broad minor peak, indicative of improved mixing of the components. Results for the blends indicated that as the percentage of PMMA increased, the magnitude of the PMMA loss tangent also increased.

However, as shown in Table 3.3 and Figure 3.3, as the PMMA content is increased from 40 wt.% to 50 wt.%, the PMMA T_g has shifted to lower temperature by 4°C (Table 3.3). This is in accordance with the MDSC data presented in Table 3.5. This could be the result of enhanced mixing with increasing PMMA content (Table 3 5)

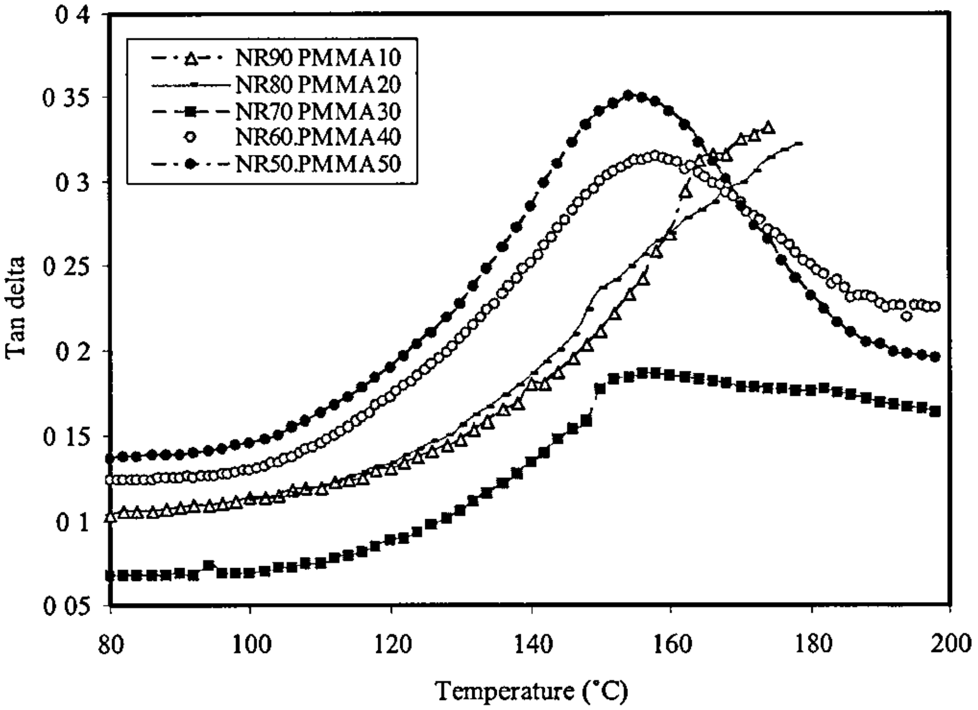


Fig. 3.3 Effect of composition on the loss tangent of the PMMA Component of the NR/PMMA blends

Unlike the blends investigated in this study, PMMA grafted natural rubber containing 18 wt.% and 33 wt.% PMMA content (MG rubber), prepared by the radiation method, exhibited a broad peak around 80°C (Perera, 1999). In fact, a broad peak extending from 0°C to 175°C was observed for the MG rubber containing 47 wt.% of PMMA, prepared by a chemical method. These observations suggest that there is some considerable amount of component mixing in the PMMA-grafted natural rubber. Comparison of the DMTA results of the blends (present investigation) and the PMMA-grafted natural rubber (Perera,

1999) indicated that the extent of mixing of the NR and the PMMA components in the blends was lower than in the grafted product. It is obvious that the extent of mixing is higher in the grafted material because grafting takes place on a molecular level. In addition, performing the grafting reaction in a latex of rubber particles, undoubtedly leads to more mixing than performing a reaction in dry rubber. Moreover, the technique, applied to prepare the blends, involved swelling of the NR by the monomer, methyl methacrylate Thus, the natural rubber has undergone a deformation due to stretching, which might lead to an unfavourable entropic condition In addition, under the experimental conditions used in this study, the homo-polymerisation of MMA will be favoured (Perera, 1999). Because of these reasons, it may be assumed that the extent of component mixing in the blends is relatively lower than in their graft counterparts.

From the DMTA studies, it can be concluded that the NR and the PMMA components are phase separated due to the presence of two glass transitions corresponding, approximately, to the homopolymers. This is in agreement with the prediction of compatibility using solubility parameters, as stated in section 3.1 The same conclusion was drawn by other researchers (Perera, 1999), indicating natural rubber and PMMA are phase separated even in the graft product as well as in IPNs.

Figure 3.4 depicts the effect of PMMA content on the storage modulus for the NR/PMMA blends. Below the glass transition, molecules are in glassy state. No co-operative motions occur in the back bone chains. Therefore, in this region, the molecules are present in a frozen state with only limited motions of side groups. Moreover, the material behaves as a nearly perfect elastic material and, therefore, it could store energy without dissipation. As a result, the storage modulus is significantly higher below the T_g. When the transition from glassy to rubbery states takes place, there will be a distribution of glassy phases and rubbery phases. Therefore, during transition, softening takes place and, therefore, the storage modulus decreases. This trend can be clearly seen in the storage modulus values for the NR transition as well as for the PMMA transition.

It is noted in Figure 3 4 that with increase of the PMMA content from 30 wt.% to 50 wt.%, the storage modulus value at 20°C had increased from 1.53 MPa to 6.71 MPa An identical trend had been observed for polyisobutene (PIB) -

PMMA semi-1 IPNs when the PMMA content was increased from 0 to 50 wt.% (Vancaeyzeele *et al.*, 2005). This behaviour is the result of the reinforcement effect imparted by the hard, glassy PMMA phases.

In addition, phase continuity can be determined using DMTA data. As the NR transition is prominent (Figures 3.1, 3.2, 3.3 and 3.4) and the height between glassy region and the rubbery region of NR transition is greater than that of the PMMA component (Figure 3 4), it can be concluded that the NR phase is the continuous phase in all these samples (Figure 3.4). Therefore, the materials behave as reinforced elastomers as the modulus increased in a similar way to the addition of a hard filler (Vancaeyzeele *et al*, 2005)

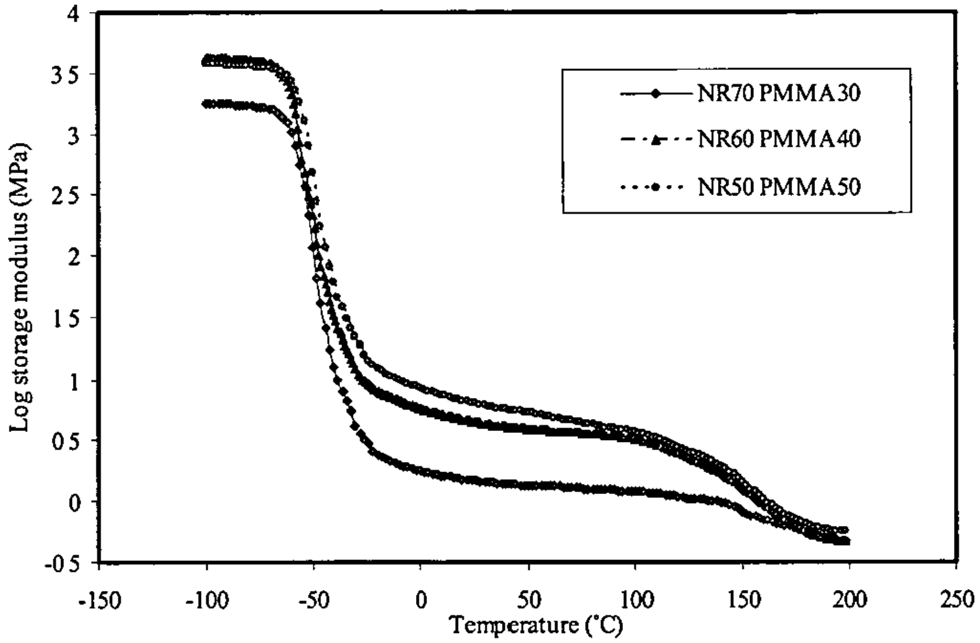


Fig. 3.4 Effect of composition on the storage modulus of the NR transition of the blend

It has been reported (Chang *et al*, 1987) that the activation energy of the backbone motion is related to the area under the tan delta curve. Therefore, the activation energy for a particular transition can be calculated by using the following equation (Lin and Lee, 1997).

$$T_A = (\ln E_G - \ln E_R)(R/E_A)(\pi/2)(Tg)^2 \qquad (3.3)$$

T_A is the area under the tan delta curve, E_G and E_R are the storage modulus values in the glassy and rubbery regions, respectively. E_A is considered as the activation energy. R and T_g refer to the gas constant and the glass transition, respectively.

In this study, compared to the data for NR treated under the same conditions, this equation had been used for the calculation of the normalized activation energy. The area under the loss tangent peak was calculated using following equation.

$$T_A = \int \tan \delta \, dT \tag{3.4}$$

The results obtained for the normalized activation energies of the blends of NR and PMMA are listed in Table 3 4.

Table 3 4 Calculated normalized activation energies of the NR transition for the NR/PMMA blends

Sample	Normalized Activation Energy
Natural rubber*	1.0
NR90:PMMA10	1.04
NR80 PMMA20	1.06
NR70 PMMA30	1 05
NR60 PMMA40	1.11
NR50 PMMA50	1 21

* Natural rubber, treated under the same conditions

Increasing the percentage of PMMA caused an increase in the normalized activation energy. A similar trend had been found for the normalized activation energy of the PMMA grafted natural rubber samples in which grafting was performed by radiation (Perera, 1999) This behaviour had been attributed to the reduction of backbone motion with increasing PMMA content resulting in an increase of the activation energy (Perera, 1999) It could be anticipated that the presence of hard, glassy PMMA phases would hinder the backbone motions of the rubber chains leading to increase in the activation energy.

This deviation of the NR70 PMMA30 blend may possibly be attributed to changes in the interfacial region (Perera and Rowen, 2000) probably caused by improved component mixing as evident not only from the shifts of NR transition of DMTA spectra (Table 3.3), but also from the MDSC data indicated in Table 3 5.

3.2.1.2 Analysis of MDSC data

Effect of composition on the complex Cp for the blends is shown in Figure 3.5. Two distinct glass transitions were observed for the blends containing 10 wt. % and more PMMA. From these data, attempts were made to calculate the weight fraction of NR (δ_{NR}) or PMMA component (δ_{PMMA}) in the interface region.

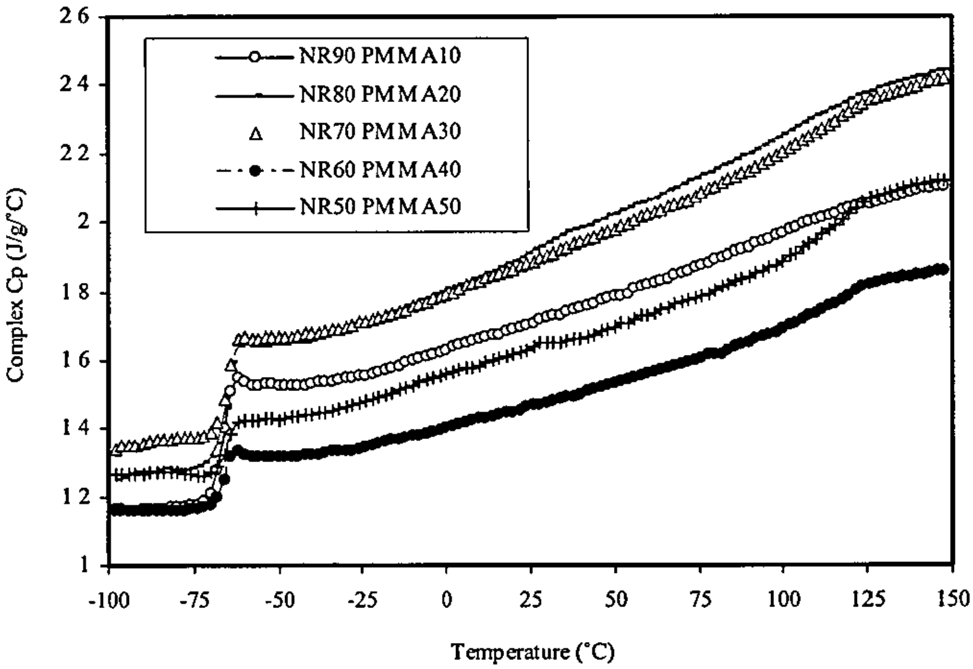


Fig. 3 5 Effect of composition on the complex Cp for the NR/PMMA blends (*Complex Cp refers to the ratio of amplitude of the heat flow to the heating rate)

According to the results (Table 3.5), a definite trend for the values of δ_{NR} and δ_{PMMA} was not observed. However, when the whole set of results are considered, a substantial amount of the NR, or PMMA, component was found in the interface region Nonetheless, the total interface contents and the δ_{NR} values of samples containing 30 wt.% to 50 wt.% of PMMA were significantly higher than the samples with 10 wt.% and 20 wt.% of PMMA and were in agreement with the DMTA data. This is an expected trend since the higher the PMMA content, the greater are the chances for mixing of the NR with the PMMA component. In addition, grafting of PMMA onto natural rubber can be considered as one of the probable causes for improved mixing.

Table 3.5 Calculated interphase fractions (δ) and multiple peak analysis data for the NR/ PMMA blends

NR/PMMA ratio (wt.%)	NR T_g (°C)	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
				Interphase (%)	NR-rich phase	PMMA-rich phase
100/0*	-68	-	-			
90/10	-67	0.02	**			
80/20	-66	0.09	**	25***		
70/30	-65	0.16	0.0	16	12	11
60/40	-66	0.11	0.0	19	15	18
50/50	-66	0.16	0.04	23	16	14

*NR treated under the same conditions

** The δ_{PMMA} content has not been calculated because of the difficulties in resolving the PMMA transition

*** Mixed phases (NR-rich phase, PMMA-rich phase and interphase)

δ_{NR}, calculated with respect to the un-vulcanized NR

δ_{PMMA}, calculated with respect to the uncross-linked PMMA

Data were obtained from the plot of dCp/dt Vs Temperature plot for the calculations of δ_{NR} and δ_{PMMA}

MTDSC data have been used for the analysis of multiphase systems by Hourston *et al.* (1997). Furthermore, according to their study, the area under the peak corresponding to glass transition region can be obtained by integrating the signal over a glass transition region and is related to the heat capacity of the phase represented by the peak. As such, multi peak analysis for the dCp/dT curves is done using a computer program. For this purpose, a baseline correction was made. In this attempt, the curve has been resolved into five Gaussian curves (Song *et al.*, 1997) corresponding to NR phase, NR-rich phase, interphase, PMMA-rich phase and PMMA phase. The percentage interphase was calculated as the ratio of the area of the middle peak corresponding to interphase to the total area of peaks and by multiplying it by 100. Similarly, percentage of NR-rich phase and PMMA-rich phase were also calculated as the ratio of the peak area of relevant peak to the total peak area and the resultant value multiplied by 100. Nevertheless, these values only provide approximate values According to the data shown in Table 3.5, there are discrepancies between the values calculated from the equation (weight fraction of PMMA incorporated into the interphase; $\delta_{PMMA} = w_{PMMA} - (\Delta Cp_{\text{PMMA-IPN}} / \Delta Cp_{\text{PMMA (homopolymer)}})$) and from the multi peak analysis method Reasons for this variation may be connected to the peak area determined by two methods. When the weight fraction was calculated using the above mentioned equation, in order to determine the $\Delta Cp_{\text{PMMA-IPN}}$, the baseline positions of the PMMA transition were taken as the onset point of glass transition peak and the end point of the glass transition If the PMMA transition was broader then the resultant $\Delta Cp_{\text{PMMA-IPN}}$ was higher than the $\Delta Cp_{\text{PMMA(homopolymer)}}$. As such, the calculated δ_{PMMA} values were significantly low. However, the multiple peak analysis clearly indicated that this peak consists of two peaks corresponding to PMMA rich phase and pure PMMA phase. This is possible because sometimes a shoulder appeared on the PMMA transition (Figure 3.6).

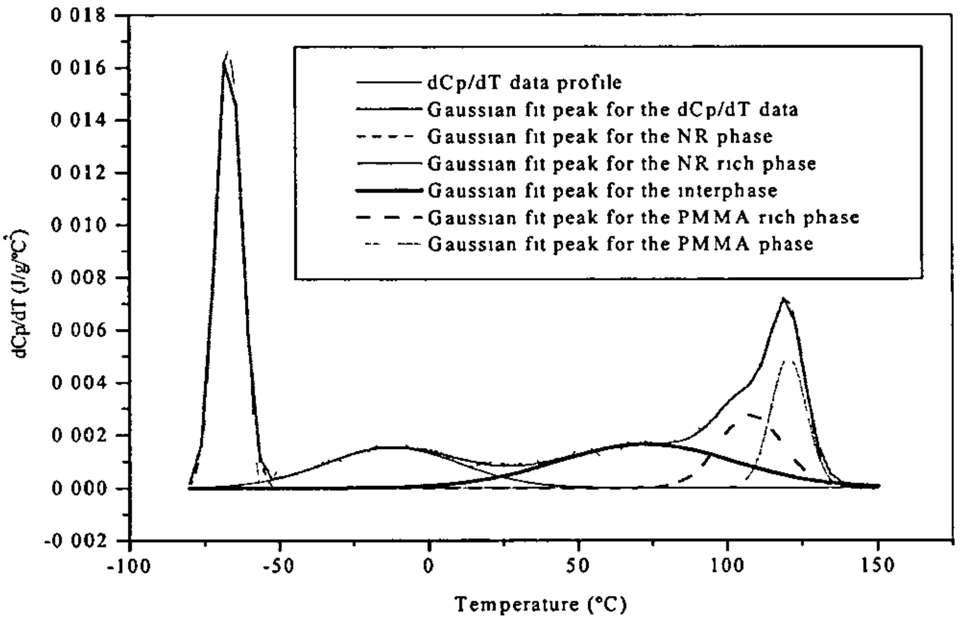


Fig 3 6 Temperature dependence of dCp/dT for the NR50:PMMA50 blend

When comparison of the T_gs of the PMMA transitions in the NR/PMMA blends with the T_g of the homopolymer (91°C, determined by MDSC) was made, it was found that the T_gs of the PMMA transitions in the blends were comparatively higher. Therefore, this shift of T_g of the PMMA component to higher temperature is primarily attributed to a reduction of mobility of PMMA chain segments in the final material and it may also be due to changes in the conformation of PMMA molecules (Pandit *et al.*, 1994) caused by packing constraints. Vancaeyzeele *et al* (2005) also reported a higher T_g of the PMMA component in a PIB/PMMA semi-1 IPN than the T_g of the single PMMA network. The confined environment experienced by the PMMA chains present inside the PIB network was considered as the prime reason for their observed trend.

3.2.2. Effect of composition on stress-strain behaviour

3.2.2.1 Tensile properties

Figures 3.7 - 3.9 show the effects of composition on the tensile properties of the NR/PMMA blends The graphs showing physical properties such as tensile strength, modulus and elongation at break were plotted with the error bars by taking the standard error in to consideration

Incorporation of PMMA leads to a significant increase in tensile strength of the NR90:PMMA10 blend compared to NR treated under the same conditions. Furthermore, the results clearly show that the tensile strength had increased significantly with increased PMMA content This was accompanied by a decrease in the elongation at break with increase in the PMMA content. These results are in agreement with other studies (Das and Gangopadhyay, 1992) Therefore, the improved tensile properties of these blends are probably a result of a synergistic effect of the reinforcement and improved miscibility resulting from some interpenetration and/or grafting of PMMA onto NR chains. Nevertheless, comparison of the tensile strength for the blends used for this study and the blends prepared by solution state mixing (Oomman and Thomas, 1996) indicated that the tensile strength of these blends are significantly higher than the tensile strength values reported for the solution state mixing of NR and PMMA (Oomman and Thomas, 1996). It is expected that when polymer molecules with high molecular weight are mixed together, the entropy of mixing is very little (Bauer *et al*, 1994) resulting in immiscibility between the components. Whereas, in this case, natural rubber mixed with the monomer, in which the latter particles are present as small molecules with an appreciable amount of entropy of mixing. Hence, one would expect that the extent of mixing of components is at high when one component is at the small molecular level. Therefore, a high level of mixing would render better physical properties than the blends prepared by mixing two polymers.

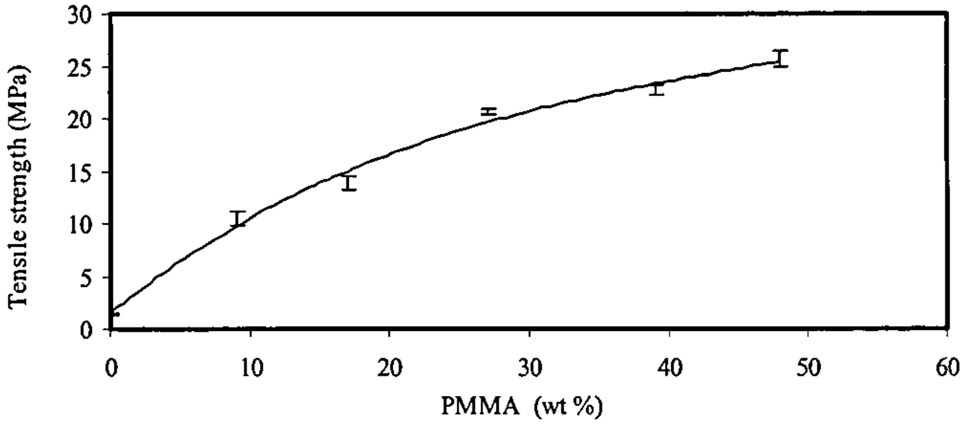


Fig. 3 7 Effect of composition on the tensile strength of the NR/PMMA blends

Higher value of tensile strength (5 MPa) was reported for the latex composites based on natural rubber and 10 wt.% of PMMA prepared using hydroperoxide and an amine-activated redox initiator system. However, higher compositions could not be reached due to the inferior film formation properties. The locus of polymerization was considered as the rubber/aqueous phase since amine activator is water soluble. Therefore, it can be assumed that the polymerization of MMA would take place mostly on the outer surface of rubber particles which may affects the film formation properties as well as tensile properties due to lack of adhesion between rubber particles. However, the higher values obtained for the tensile strength of these blends could be primarily associated with the better film formation properties due to lack of considerable amount of polymerisation of MMA on the outer surface of NR particles, improved extent of mixing between components which may resulted by the use of oil soluble initiator; Triganox 21S, which was proven to be an effective initiator for enhanced mixing (Romaine, 1988)

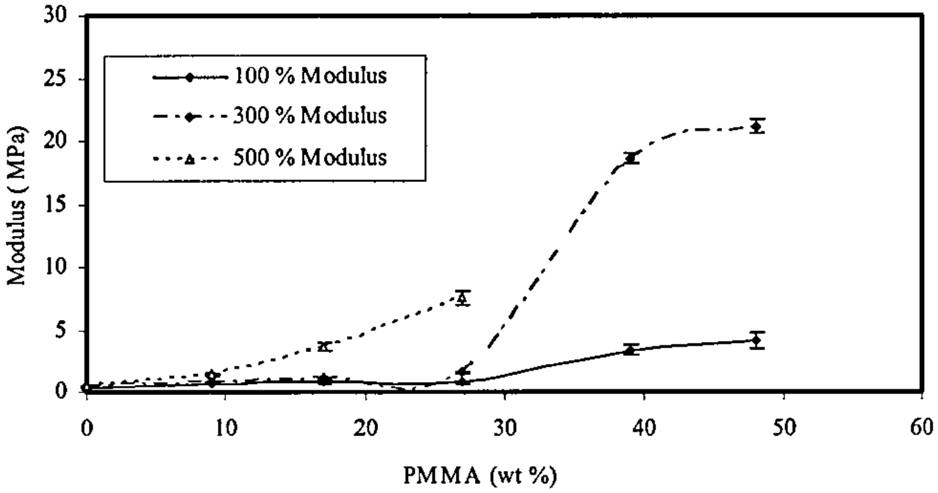


Fig 3 8 Effect of composition on the 100, 300 and 500 % moduli of the NR/PMMA blends

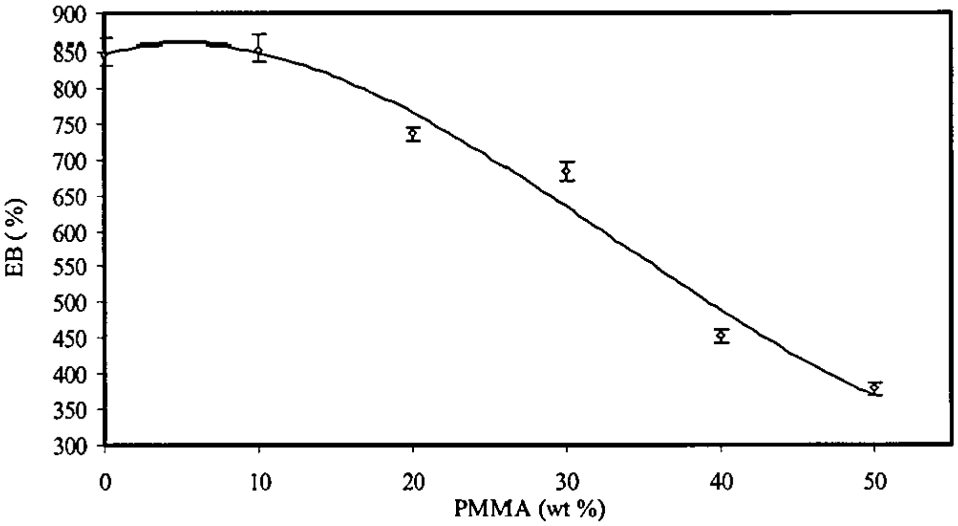


Fig. 3 9 Effect of composition on the elongation at break for the NR/PMMA blends

Analysis of hysteresis data

Softening behaviour associated with a hysteresis test whether it is performed by cyclic tensile testing or by compression, is mostly studied for vulcanizates with fillers

Various basic concepts (phenomenological approach) which had been presented for this softening behaviour will be discussed in detail prior to the discussion of the hysteresis results.

The concept forwarded by Mullins and Tobin (1957) deals with two types of region in a rubber matrix referred to as soft and hard It was believed that the most of the straining takes place in the soft regions. According to their theory, hard regions (domains) break down to form soft regions and as a result, the fraction of soft regions increases resulting in amplification of strain (Qi and Boyce, 2005)

Nevertheless, some researchers (Medalia and Kraus, 1994, Bergstrom and Boyce, 1999) have forwarded an idea about the entrapped vulcanizates particles within the hard domains. Therefore, in the case of a thermoplastic, plastic deformation leads to release of entrapped vulcanizate particles so that a pseudo-continuous elasotomer phase will be formed, thus resulting in softening in subsequent cycles (Qi and Boyce, 2005).

The theory of Bueche (1960) deals with the breaking of bonds between the chains and filler particles. As the load (stress) is applied, the chains attached to filler particles will stretch and it is presumed that the shorter chains rupture initially. Subsequently, intermediate and longer chains rupture at moderate stretch values and very large extension, respectively. Consequently, the chains separated, or torn off have undergone deformation and will not be elastically effective. Due to the fact that those chains are unable to contribute to entropy changes, softening on reloading after retraction takes place.

Green and Tobolsky (1946) forwarded a theory which is known as the transient network theory based on breaking and reforming of cross-links (junction points). The rate dependent viscous behaviour of the polymer network could be explained using this theory. Generalization of the breakage mechanism of Buche has been considered by Dannenberg (1974) and Rigbi (1980) and it would help to explain viscoelastic and stress softening effect In this theory, under the applied load, the polymer chains move relative to the filler particles without rupture allowing stress distribution. Thus, a random distribution of chains with longer contour lengths will result during unloading.

Cycling tests have been carried out to determine the effect of PMMA content on the hysteresis behaviour (HL) and hystereis (energy loss) of the blend In most of the research work, hysteresis was considered as the area between the loading and unloading curves which is a measure of energy loss In this study, energy loss had been determined and tabulated in Table 3.6. Moreover, the hysteresis behaviour which is referred to as the ratio of the energy lost to the energy recovered (stored) were also determined (Kohjiya *et al*, 2005) and presented in Table 3 6.

Natural rubber possesses thixotropic characteristics and, therefore, undergoes structure break down during stretching. In the case of un-vulcanised natural rubber, entanglements play a predominant role in the stress softening and probably this is associated with a disentangling process. In addition, hysteresis is associated with the strain-induced crystallites (Indukuri and Lesser, 2005; Toki *et al*, 2000) and their transformation to the secondary strain induced crystallites Toki *et al.* (2000). However, it is doubtful whether strain-induced crystalliszation is probable at 300% strain, which is the limit applied for the cyclic stress-strain test. Toki *et al.* (2000) indicated that two strain levels at which strain induced crystallization takes place depend on the method of stress-strain measurements with wide-angle X-ray scattering In sequentially performed stress-strain measurements, strain-induced crystallization occurred at 200% strain. On the other hand, 400% strain was required for crystallization when stress-strain measurements were performed simultaneously. Variation in dynamic deformation and equilibrium state would have been the probable causes for the discrepancy in results governed by these two techniques Toki *et al* (2000). They have indicated that during stretching molecular orientation takes place and strain-induced crystallization takes place at 400% strain However, during retraction, most of the crystallites convert into secondary strain-induced crystallites which are in the form of folded-chain lamellae and do not contribute to the stress. As a result, stress softening takes place. X-ray diffraction analyses on natural rubber (Mitchell,1984, Shimomura *et al.*, 1982) indicated that strain-induced crystallization occurs even at 200% strain. Andrew (1962;1964) indicated that the sperulites will be formed at 0 – 50% strain, and, thereafter, row-nucleated kebab like structures appear at 100–200% strain. He further showed that extended-chain crystals are formed when the strain exceeds 400%. Therefore, due to the differences in theories, it is difficult to confirm whether the strain-induced crystallization takes place in the range of strain applied. Nevertheless, it can be assumed that strain-induced crystallites can form to a certain extent and if any are formed, they might undergo transformation to secondary, strain-induced crystallites during reloading which involves reduction of stress. The latter type of crystallites do not contribute to the stress, and, therefore, drastic reduction of stress takes place during retraction leading to hysteresis (energy loss).

Results of cyclic stress-strain are given in Table 3 6. Furthermore, as shown by the hysteresis loop of the first cycle (Figures 3.10 and 3.11). Accordingly, the amount of energy dissipated as heat also increased with increasing PMMA content. The increase in the amount of energy dissipated during cycling testing with increase of PMMA could be attributed to the reduction in the amount of the elastic component, which leads to a diminution in the recoverable stored energy. This leads to an increase in the heat build up in the material. In addition, it is stated that the reduction of segmental mobility by the presence of filler would enhance the hysteresis (Agarwal *et al.*, 2005). The same effect might imparted by the presence of hard, glassy PMMA phases resulting in increase of hysteresis with increase of the PMMA content. This general trend is in agreement with the findings of earlier studies conducted on IPNs based on NR and PMMA (Romaine, 1988). Study based on poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) thermoplastic elastomers (TPEs) and natural rubber also exhibited higher permanent set with increasing glassy PS content (Indukuri and Lesser, 2005). This also indirectly indicates that the hysteresis is higher in the samples containing higher amount of glassy components. However, it may be assumed that in these blends, the PMMA phases have undergone a plastic deformation and they may have undergone breakdown of structure resulting in a softening of the material. It could be anticipated that the most of the phase structures break down in the first cycle resulting in maximum strain softening in the first cycle. Thus, the strain softening and hysteresis is low in the subsequent cycles as revealed from Table 3.6. After several cycles, the stress-strain behaviour would be stabilized (Qi and Boyce, 2005)

Table 3.6 Energy loss and hysteresis behaviour for the NR/ PMMA blend

Composition	Cycle 1		Cycle 2		Cycle 3	
NR/PMMA Ratio	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
NR**	0.57	0.45				
90/10	0.11	0.28	0.04	0 11	0 03	0 07
80/20	0 15	0.47	0.07	0.23	0 07	0 21
70/30	0 64	1.26	0.38	0 84	0 33	0 75
50/50	4 01	2 5	x	X	x	x

* HL-Hysteresis behaviour calculated as the ratio of the amount of energy lost to the amount of recovered in each cycle

** NR, treated under the same conditions

x Permanent set exhibited by the stretched sample

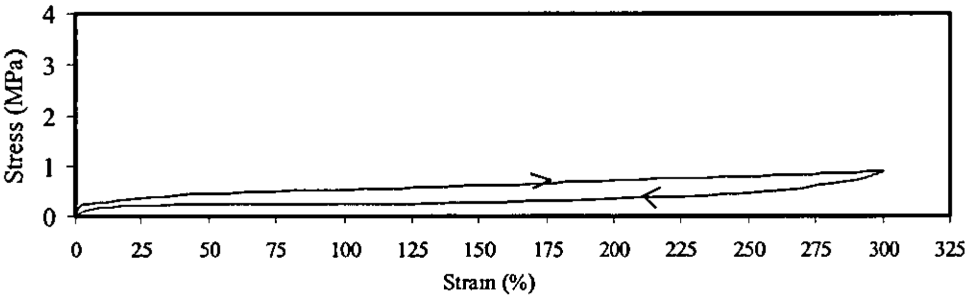


Fig. 3.10 The first hysteresis cycle for the NR80.PMMA20 blend

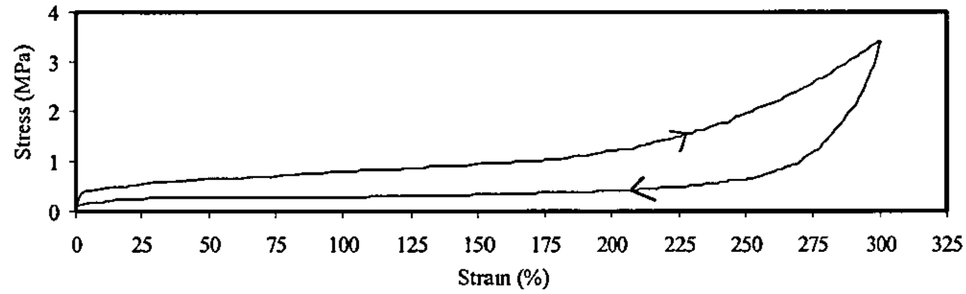


Fig. 3 11 The first hysteresis cycle for the NR70.PMMA30 blend

Furthermore, comparison of hysteresis data (Table 3.6) of the blends and NR, treated under same conditions indicated that the hysteresis data for the NR/PMMA blends with 90/10 and 80/20 compositions are significantly lower than that of NR, probably due to the effect of entanglements resulting from the interpenetration of PMMA It is assumed that the entanglements help to regain the original position of polymer chains and their coil conformations during unloading, thus reducing the hysteresis. It could also be due to the presence of smaller phases of PMMA, which reduces the hysteresis unlike big domains or aggregates (Hourston and Romaine, 1991).

3.2.3 Effect of composition on the sol-gel ratio of the NR/PMMA blends

Results of gravimetric analysis of the extracted samples are given in Table 3.7. The data were obtained by performing the hot extraction for the blend sample using acetone as the solvent with the aim of extracting homo PMMA (Perera, 1999; Lehrle and Willis, 1997). This solvent was chosen as it is a good solvent for PMMA, but a non-solvent for natural rubber (Perera, 1999) Nevertheless, it has to be mentioned that acetone can extract PMMA with natural rubber, when it is present in the form of a graft material. In this study, a minor peak due to NR could be observed in the IR spectra of the extract. The other researchers (Perera, 1999; Lehrle and Willis, 1997) also confirmed the presence of NR in acetone extract by NMR studies They have considered that it would be a result of the presence of PMMA grafted NR. Normally, it is expected that only one graft is present per rubber molecule, but more than one graft per molecule could result under circumstances where higher grafting efficiencies prevailed. These molecules could be extracted with acetone (Perera, 1999).

The amount of extractable material increased at higher PMMA content, (Table 3.7). It is well established that as the monomer concentration increases the efficiency of grafting decreases and the tendency for homopolymerisation of MMA increases (Perera, 1999). Therefore, it can be assumed that homopolymerisation is favoured in the blends containing 40wt.% to 50wt.% PMMA. Homopolymerisation of methyl methacrylate monomer resulting in higher homopolymer content and, therefore, the soluble materials in those two samples were relatively higher than the blends containing 10 wt.% to 30 wt.% PMMA content. However, the observed lesser amount of soluble fraction in the NR50 PMMA50 blend than the NR60 PMMA40 blend may be attributed to the presence of a comparatively lower amount of the PMMA homopolymer as indicated by the MDSC data (Table 3.5).

Table 3 7 Sol content of the NR/PMMA blends calculated from the hot acetone extraction process

NR/PMMA ratio	Sol fraction (wt.%)
100 0	2 5
90:10	3 0
80.20	5 3
70 30	6 5
60.40	12.1
50 50	8 8

3.3 Semi-2 IPNs

Semi-2 IPNs were prepared with varying percentages of PMMA and with varying levels of PMMA cross-linker. Details of the semi-2 IPN series are described in Table 2 4

The resultant semi-2 IPN samples were non-tacky and stiffer than the NR/PMMA blends Even though, the IPNs were expected to be opaque due to phase separation, this series of IPNs were less transparent This may be because of the improved miscibility because of the grafting of the PMMA on to the NR during the MMA polymerisation.

3.3.1 Effect of composition on the physical properties of the semi-2 IPNs (EGDM crosslinker 0.5 mole %)

3.3.1.1 Effect of composition on miscibility

Analysis of the dynamic mechanical data

NR transition

Loss tangent data for the NR component in the semi-2 IPNs (0.5) are illustrated in Figure 3.12. The T_g of the NR component in all the semi-2 IPNs are approximately 3°C to 5°C higher than the NR treated under the same conditions, indicating some mixing of the NR component (Table 3 8)

Table 3 8 Half peak widths of the NR transition and the T_gs of the NR and PMMA transitions of semi-2 (0 5) IPNs

Sample	NR T_g (°C)	Half peak width (°C)	PMMA T_g (°C)
Natural rubber*	-51	16	-
NR90:PMMA10	-48	21	-
NR80:PMMA20	-46	22	-
NR70:PMMA30	-46	24	160
NR60:PMMA40	-46	23	159
NR50:PMMA50	-48	27	154

*Natural rubber heated under the same conditions

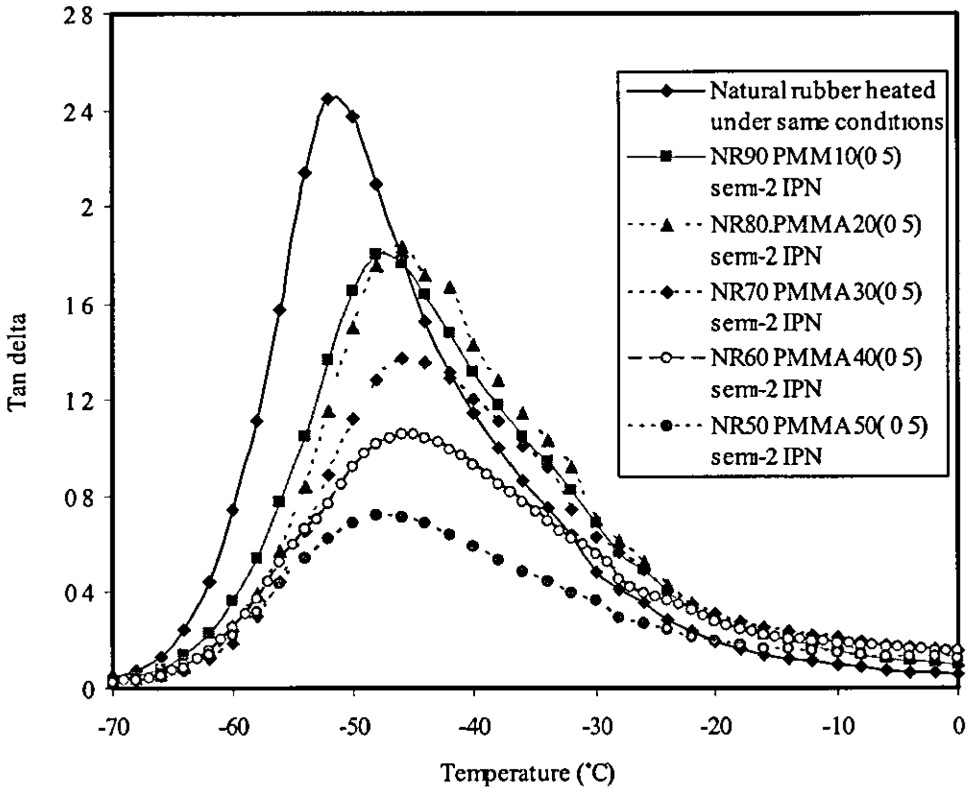


Fig. 3.12 Effect of composition on the loss tangent of the NR component of the semi-2 IPNs prepared using 0.5 mole % EGDM crosslinker

Interpenetration of PMMA phases into the NR matrix and /or grafting of PMMA onto NR can be considered as the prime causes of this limited extent of mixing. It may be assumed that the enhanced component mixing has primarily resulted from the grafting process and the interpenetration process The unique feature imparted by interpenetration is the formation of entanglements between components and this will impart forced component mixing, probably in a similar way to the enforced mixing resulting from a cross-linking process. The NR T_g of the NR50.PMMA50(0.5) semi-2 IPN was relatively lower than the NR60:PMMA40(0.5) semi-2 IPN. A similar trend observed for the T_g of the polyurethane component in the semi-IPNs based on polyurethane and nitro-chitosan was attributed to the phase separation (Zeng *et al* (2005). Nevertheless, in this case, the lowering of NR $T_g$of the NR50:PMMA50 blend can not be considered as a significant shift because it is with in the experimental error.

It should be noted that the extent of mixing of the NR component in the NR50 PMMA50 (Table 3.10) is higher than the NR60.PMMA40. Therefore, the key factor for the improved NR component mixing in the NR50:PMMA50 blend can be considered as the interpenetration of polymer chains. Moreover, as the PMMA content is higher, the likelihood of component mixing will be higher.

Table 3.9 Calculated relative activation energies for the semi-2 (0.5)IPN for the NR transition

Sample	Normalized Activation Energies
NR90 PMMA10	1.08
NR80 PMMA20	1.08
NR70 PMMA30	1.17
NR60.PMMA40	1.13
NR50:PMMA50	1.38

Similar to the NR/PMMA blends, the results of the calculated normalized activation energies (Table 3 9) do exhibit an increasing trend with increase of PMMA content, with the exception of the NR60:PMMA40(0.5) semi-2 IPN. In fact, the activation energy should be increased with incorporation of PMMA due to the restrictions in mobility of the NR polymer chain segments. However, deviation of the NR60 PMMA40(0.5) semi-2 IPN from this general trend is perhaps related to a lower extent of mixing of the NR component as was also evident from the MDSC data shown in Table 3 10.

PMMA transition

When the loss tangent of PMMA component is considered (Figure 3.13), the transition due to PMMA component appeared as a minor peak in the NR70:PMMA30 sample. In this series, compared to the NR60 PMMA40(0.5) semi-2 IPN, the T_g of the PMMA transition shifted towards lower temperature by 5°C (Table 3.8) with increase of PMMA content indicating improved mixing of the PMMA and NR components. A similar trend had been observed for a poly(isobutene) - PMMA IPN, where the PMMA T_g decreased with increasing the PMMA content (Vancaeyzeele *et al.*, 2005).

This trend is probably attributed to the increase of contact area between phases with increase of PMMA content, thus enhancing the possible extent of mixing between components. In this case, the PMMA is mixed with a more mobile component (NR) with a lower T_g thereby increasing the segmental motions of PMMA polymer chains resulting in a lowering of the PMMA T_g (Jha and Bhowmick, 1997).

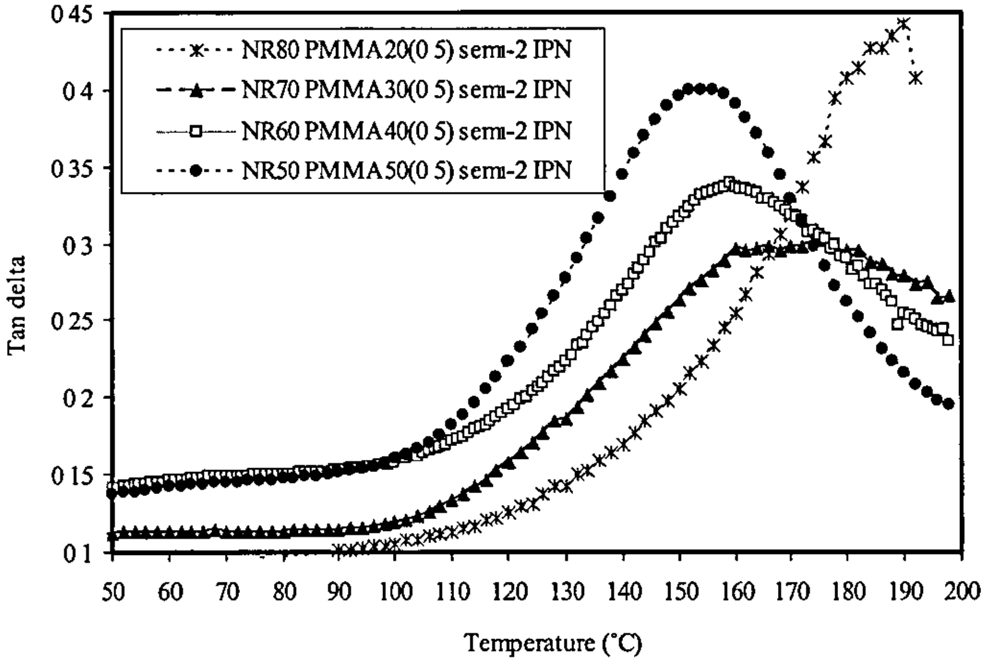


Fig. 3.13 Effect of composition on the loss tangent of the PMMA component for the semi-2 IPNs prepared using 0.5 mole % EGDM crosslinker

Storage modulus data

The storage modulus data provide information on degree of interpenetration, and the extent of interactions between the components depending on the slope in the modulus plateau between the two transitions (Vancaeyzeele *et al.*, 2006). The height and position of the plateau are governed by the relative amount of each polymer. The extent of flatness depends on the extent of phase separation suggesting that the higher the insensitivity of the modulus to temperature the greater the phase separation (Vancaeyzeele *et al*, 2006). Apart from this information, phase continuity can also be determined using storage modulus data. The storage modulus data for some of the semi-2 (0.5) IPNs are shown in the Figure 3.14.

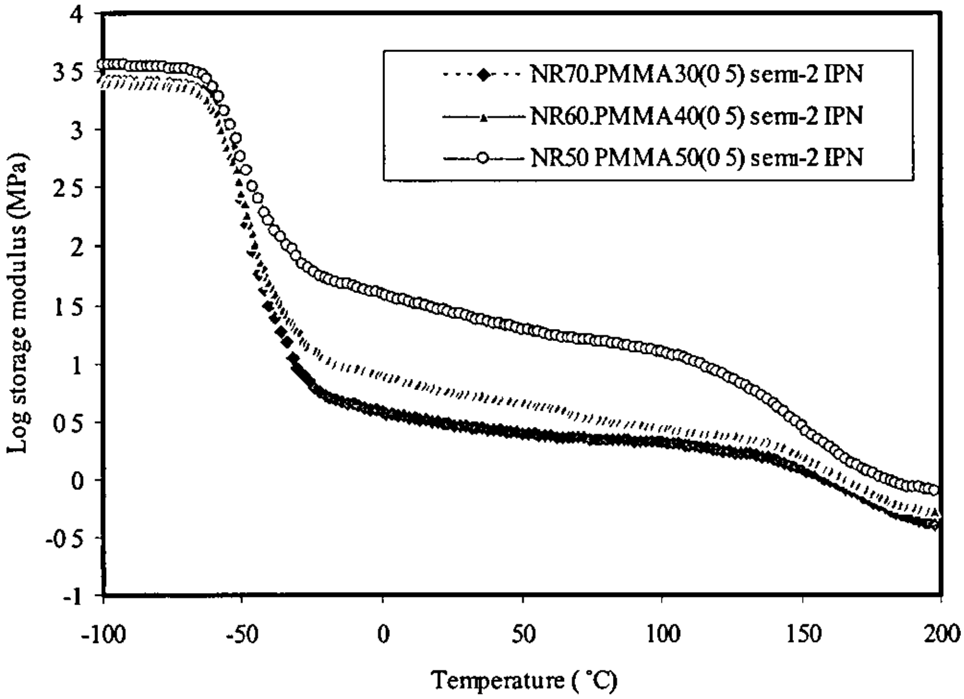


Fig. 3.14 Effect of composition on the storage modulus the semi-2 IPNs prepared using 0.5 mole % EGDM crosslinker

As can be seen from Figure 3.14, the plateau between the two transition in the NR70:PMMA30(0.5) semi-2 IPN do not vary considerably with the temperature. Nevertheless, slope of the plateau region tended to increase with increasing the PMMA content suggesting interactions between two components in the NR50:PMMA50(0.5) semi-2 IPN. In addition, it is noted that the E' of the rubbery region of the NR transition increased from 3.1 MPa to 29 MPa at 20 °C with increasing the PMMA content from 30 wt.% to 50 wt % Vancaeyzeele *et al*, (2005) also reported such a trend in their study of poly(isobutene) - PMMA semi-1 IPNs. This behaviour is probably associated with the reduction of mobility of polymer chains due to the presence of PMMA

It was noted that the both transitions are prominent in the NR50:PMMA50(0.5) semi-2 IPN (Figure 3 14 and Table 3 8). Therefore, it may be deduced that the PMMA phase is present as a co-continuous phase in this particular sample.

Analysis of MDSC data

The weight fractions of the NR component in the interphasial regions of the semi-2 IPNs are given in Table 3.10.

Table 3.10 Calculated interphase fractions (δ) and multiple peak analysis data for the semi-2 (0 5) IPNs

Sample	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR90.PMMA10	0.46	0.05			
NR80:PMMA20	0.12	0.0	27*		
NR70:PMMA30	0.14	0.05	25	8	12
NR60 PMMA40	0.15	0 0	27	13	8
NR50 PMMA50	0.20	0 0	30	20	16

*Mixed phases

δ_{NR},and δ_{PMMA} were calculated with respect to the un-vulcanized NR and cross-liked PMMA, respectively

Data were obtained from the plot of dCp/dt vs temperature plot for the calculations of δ_{NR} and δ_{PMMA}

The multiple peak analysis data are also included in Table 3.10. Semi-2 IPNs with 10 wt.% to 20wt.% of PMMA content, the intermediate region between two glass transitions could not be resolved into three peaks corresponding to NR rich phase, interphase and PMMA rich phase. Therefore, this area was considered as one region and the whole spectra differentiated into three peaks corresponding to NR phase, mixed phases and PMMA phase. Therefore, the term mixed phases has been used to express the regions including NR-rich phase, PMMA-rich phase and interphase. In this series, the highest δ_{NR} content was observed for the NR90 PMMA10(0.5) composition. Despite this, a considerable amount of interface region was found for the other samples containing 20 wt.% to 50 wt.% of PMMA (Figure 3.15). An increasing trend of the total amount of mixed phases with the PMMA content was found with increase of PMMA content from 40 wt.% to 50 wt.%. The enhanced mixing found in the NR90:PMMA10(0 5) semi-2 IPN is probably associated with enhanced grafting of the MMA on to natural rubber. Reasons for having extremely low values for the δ_{PMMA} values were given in section 3.2.1.2.

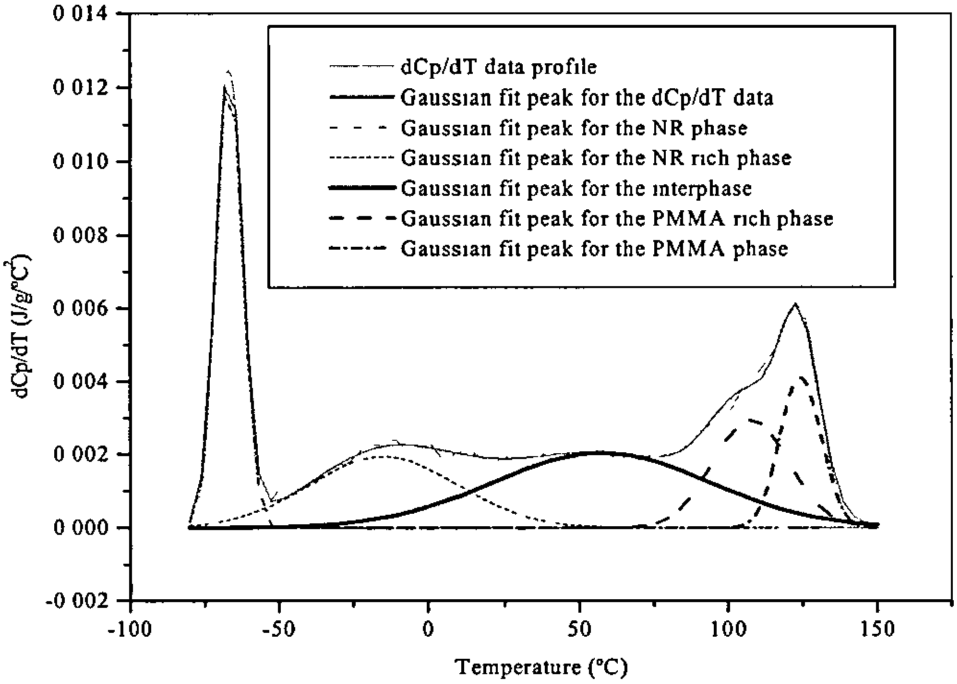


Fig. 3.15 Temperature dependence of dCp/dT for the NR50:PMMA50 (0 5) semi-2 IPN

3.3.1.2 Effect of composition on the stress-strain behaviour

Tensile data

Dependencies of tensile properties on the composition of the semi-2 (0.5) IPNs are illustrated in Figures 3.16 - 3.18. It is evident that the tensile strength of these compositions has increased with increasing the PMMA content. A dramatic increase in the 300% and 500% moduli was observed in these semi-2 IPNs, when the PMMA content was between 30 and 50 wt.% (Figure 3.17). Therefore, the improved tensile properties thus obtained could be ascribed to the interpenetration and reinforcement effects, imparted by the glassy cross-linked PMMA phases.

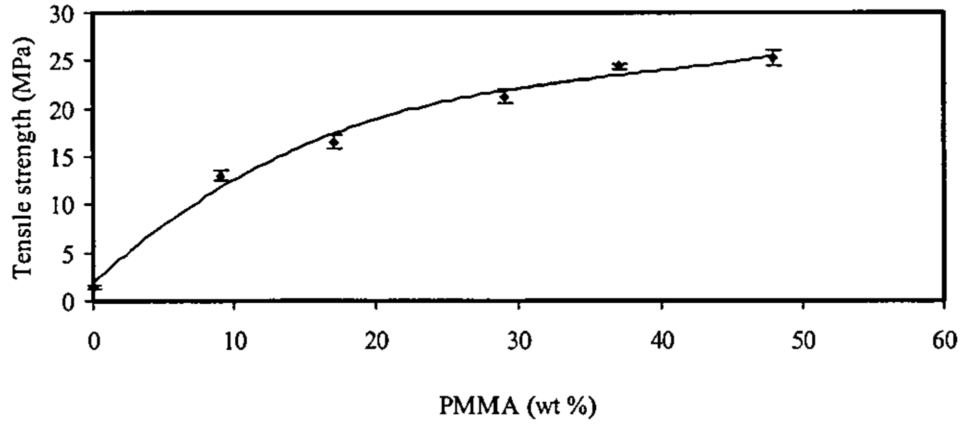


Fig 3.16 Effect of composition on the tensile strength for the semi-2 (0.5) IPN series

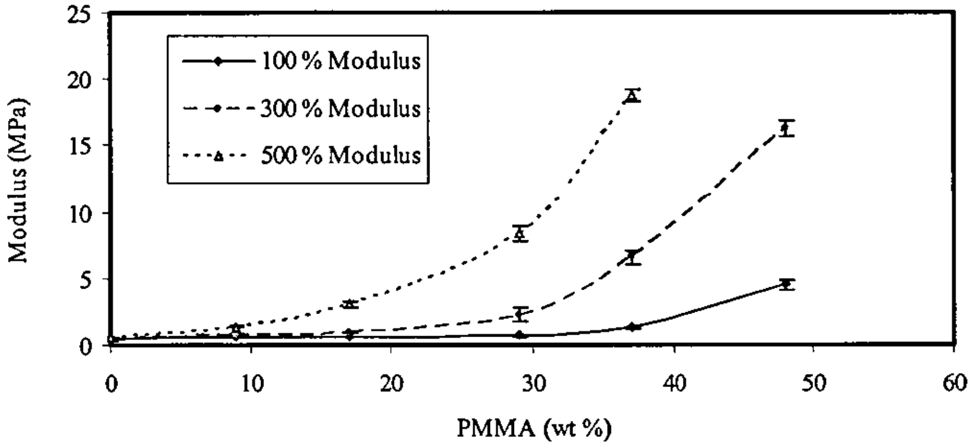


Fig. 3.17 Effect of composition on the 100, 300 and 500 % moduli of the semi-2 (0.5) IPN series

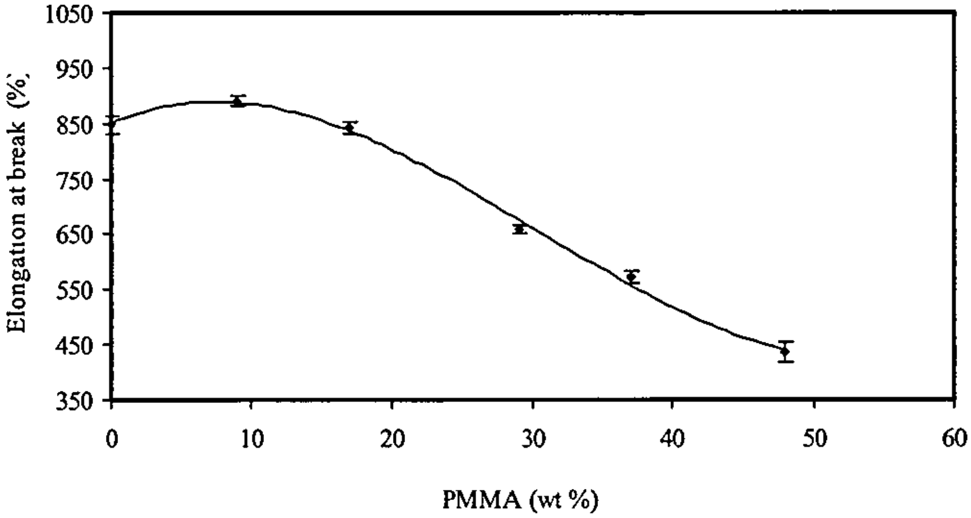


Fig 3.18 Effect of composition on elongation at break for the semi-2 (0.5) IPN series

As shown in Figure 3.18, the elongation at break decreased with increasing PMMA content, which may be simply due to the lowering of the amount of the elastic component, the prime component that determines the EB value (Pillai, 1995). A similar observation was made for the NR/PMMA blends in previous studies (Das and Gangopadhyay, 1992).

Hysteresis data

Energy losses during the cycling tests of semi-2 (0.5) IPNs are listed in the Table 3 11. In addition, the hysteresis of these IPNs is illustrated in Figures 3.19 – 3.21. The amount of energy dissipated as heat markedly increased with increasing PMMA content This may be associated with the plastic deformation of PMMA phases and/or due to the break down of structure in the PMMA phases. A similar trend was observed in the NR/PMMA blends. However, the amount of heat dissipated in the NR90.PMMA10(0.5) semi-2 IPN does not vary strongly from the corresponding control sample This behaviour could be ascribed to the higher degree of mixing of the NR with the PMMA component in that particular sample as shown by MDSC data (Table 3.10).

Table 3.11 Energy loss and hysteresis behaviour results for the semi-2 (0.5) IPN series

Sample composition	Cycle 1		Cycle 2		Cycle 3	
NR/PMMA (wt %)	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
100/0*	0.57	0.45			-	-
90/10	0.12	0.31	0.03	0.11	0.02	0.07
80/20	0.22	0.51	0.13	0.33	0.09	0.24
70/30	0.44	0.96	0.28	0.72	0.25	0.73
60/40	1.34	2.8				
50/50	7.03	5.3				

*Natural rubber treated under the same condition

HL-Hysteresis behaviour was calculated as the ratio of the energy lost to the energy recovered in each cycle

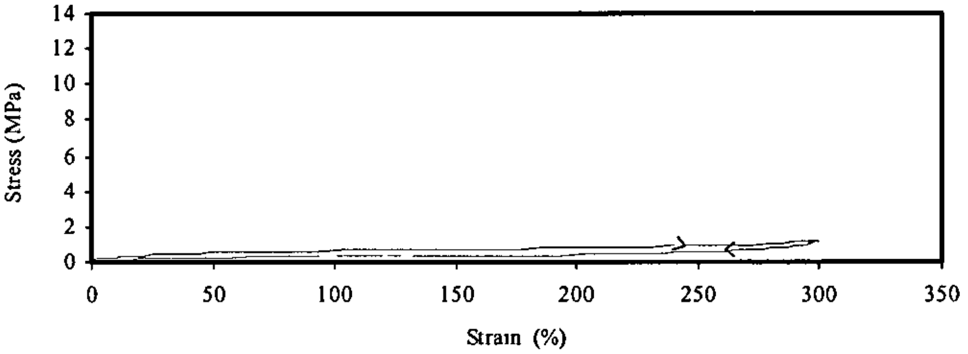


Fig 3.19 The first hysteresis cycle of the NR70 PMMA30(0.5) semi-2 IPN

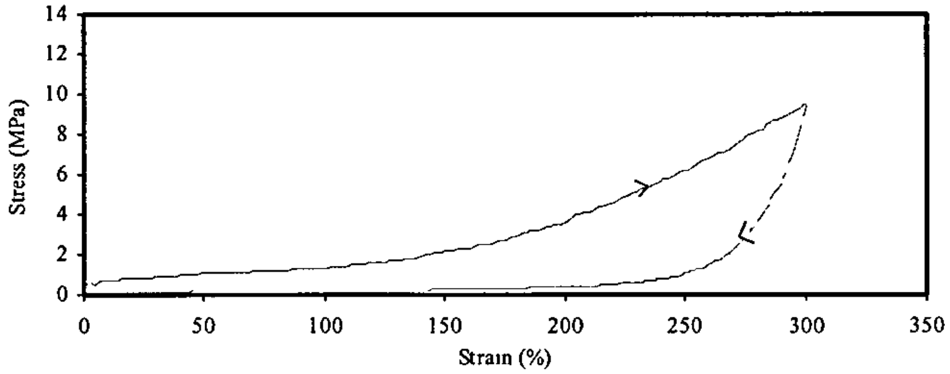


Fig 3.20 The first hysteresis cycle of the NR60.PMMA40(0.5) semi-2 IPN

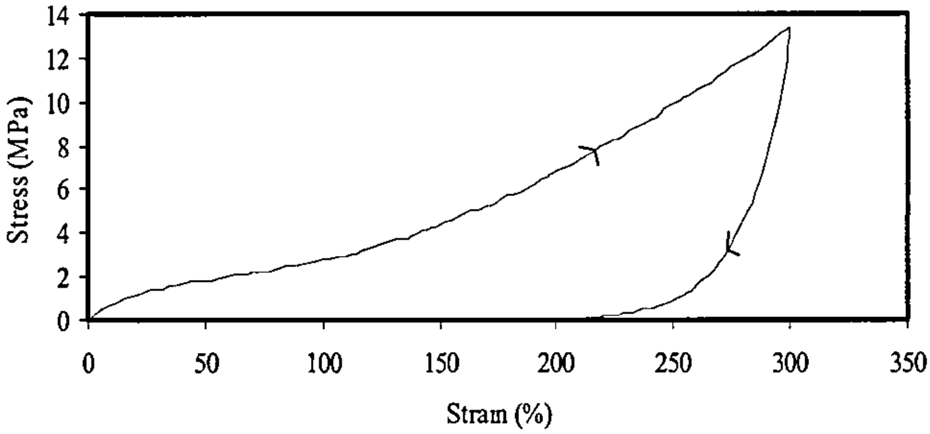


Fig 3 21 The first hysteresis cycle of the NR50:PMMA50(0.5) semi-2 IPN

In addition, a large increase in hysteresis (energy loss) was observed when PMMA content was increased from 40 wt.% to 50 wt.%.

3.3.2 Semi-2 IPNs prepared using EGDM crosslinker at a level of 1.0 mole percent

3.3.2.1 Effect of composition on miscibility

Analysis of dynamic mechanical data

NR transition

The effect of composition on the loss tangent of the NR component is presented in Figure 3.22. Accordingly, comparison of NR T_g data for the semi-2 (1 0) IPNs and the control sample indicated that the NR T_g has increased by 4°C with increasing PMMA content from 0 to 40 wt % indicating enhanced mixing in these materials (Table 3.14). Reasons for such behaviour were given for the preceding series. MDSC data also provide supportive evidence for the improved mixing of the NR component at these compositions (see Table 3.14).

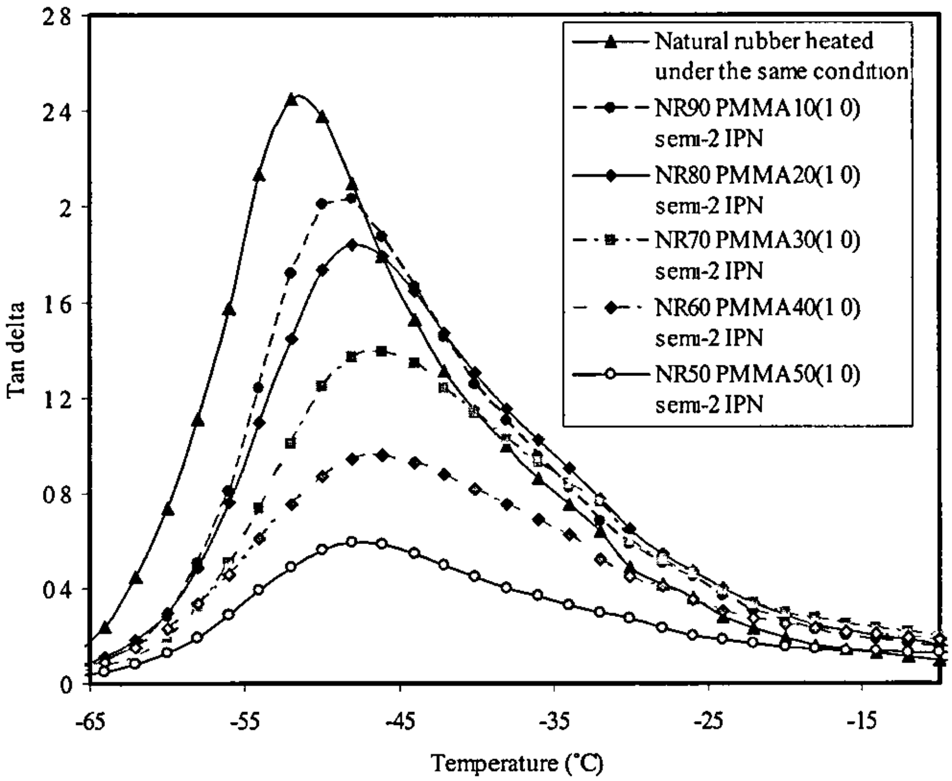


Fig.3.22 The effect of composition on the loss tangent of the NR component for the semi-2 (1 0) IPN series

In these semi-2 (1.0) IPNs, the PMMA phase had been cross-linked using 1 mole % of EGDM on MMA. Cross-linking of the PMMA component probably increases the rigidity of the material, and also reduces the segmental mobility of NR polymer segments if there are connections between those two components. This effect could be more pronounced in the samples having higher PMMA content resulting in an increase in NR T_g. This probably explains the reason for absence of significant lowering of NR T_g in the NR50.PMMA50(1.0) semi-2 IPN. However, this trend probably suggests interlinking of components. It is accepted that the conformational mobility of polymer chain segments of each component in the immiscible blend will not be affected by the presence of other component (Arenas *et al.*, 2002). As such, the observed T_g shift has been resulted from the inter-linking (mixing) of components due to interpenetration and/or due to grafting.

Table 3.12 Half peak widths of the NR transition and the NR and PMMA T_g transitions for the semi-2 (1.0) IPNs

Sample	NR T_g (°C)	Half peak width (°C)	PMMA T_g (°C)
Natural rubber*	-51	16	-
NR90 PMMA10	-49	18	
NR80:PMMA20	-48	21	
NR70 PMMA30	-47	25	162
NR60 PMMA40	-47	25	154
NR50·PMMA50	-49	24	150

*Natural rubber heated under the same conditions

Further, it is evident that tan $\delta_{max\text{-}NR}$ decreased with increasing PMMA percentage A similar trend has been observed not only for the previously mentioned NR/PMMA blend series, but also in other reported work (Vancaeyzeele, 2005, Perera, 1999). As the transition from the glassy to the rubbery state takes place via co-operative motions, the segmental mobility is the decisive factor in determining the tan delta values (Vancaeyzeele *et al.*, 2005). Hence, the tan delta values will be affected by the composition (Vancaeyzeele. *et al.*, 2005). Therefore, as the amount of glassy polymer content increases, the tan $\delta_{max\text{-}NR}$ should decrease due to the reduction of mobility of NR polymer chains.

The normalized activation energies for the semi-2 (1.0) IPNs are presented in Table 3.13.

Table 3.13 Calculated relative activation energies for the NR transition of semi-2 (1.0) IPN

Sample	Normalized activation energy
NR90 PMMA10	1.07
NR80.PMMA20	1 07
NR70 PMMA30	1.17
NR60:PMMA40	1.29
NR50 PMMA50	1.54

As was seen for the semi-2 (0.5) IPNs, the normalized activation energy increased with increasing PMMA content As stated earlier for the blends and the semi-2 (0.5) IPNs, it is primarily associated with increase of the activation energy of the back bone motions of the NR polymer chains caused by a reduction of mobility with incorporation of higher amounts of PMMA.

PMMA transition

Variation of the loss tangent of the PMMA component with composition is illustrated in Figure 3.23.

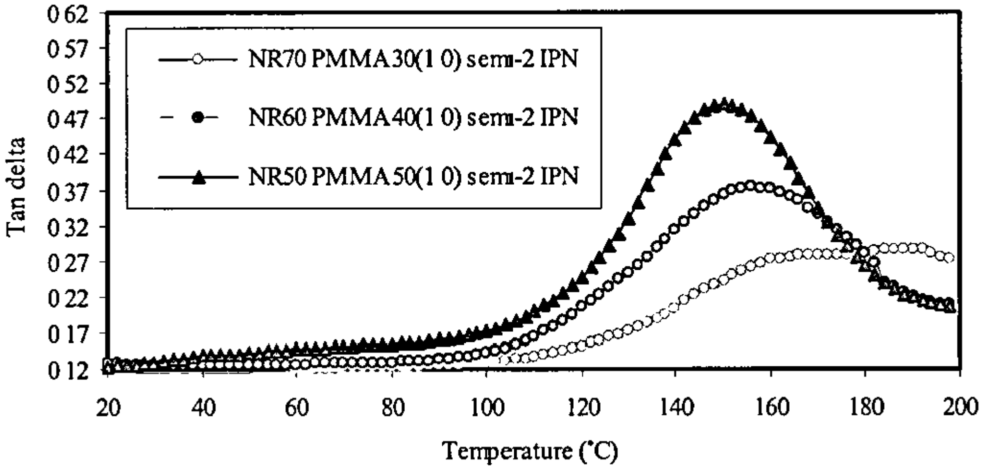


Fig.3 23 Effect of composition on the loss tangent of the PMMA component of the semi-2 (1 0) IPN series

It was found that the PMMA transitions is broad in the relaxation spectra of the NR70.PMMA30(1.0) semi-2 IPN indicating increased microheterogenity. Nevertheless, compared to the NR70.PMMA30, the T_gs of the PMMA transition in the NR60:PMMA40(1 0) and NR50 PMMA50(1 0) samples tend to shift towards lower temperatures. A probable reason for this behaviour has been proposed in section 3.3.1.1.

Furthermore, tan $\delta_{max\text{-}PMMA}$ tends, as expected, to increase with increasing PMMA content As mentioned earlier, the loss tangent is sensitive to the relative weight fraction of the components in multi-component materials (McCrum, 1958, 1959a, 1959b) Therefore, the increase in the magnitude of the PMMA loss tangent is the result of the increase of PMMA in these samples.

Analysis of MDSC data

The temperature dependence of dCp/dT for the NR70.PMMA30(1 0) semi-2 IPN compositions are presented in Figures 3 24

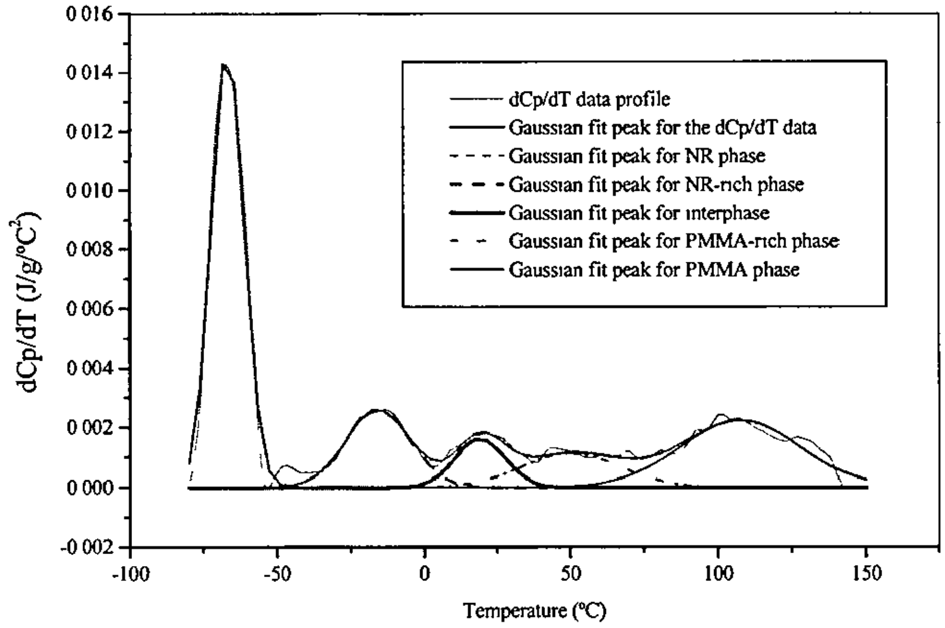


Fig 3.24 Temperature dependence of dCp/dT for the NR70 PMMA30(1.0) semi-2 IPN

Considerable amount of NR-rich and PMMA-rich regions can be seen in Figure 3.24, indicative of some enforced component mixing in the NR70 PMMA30(1 0) semi-2 IPN. In addition, a considerable amount of mixed phases could also be found for the semi-2 IPN having 20 wt.% PMMA content For these composition, it is difficult to differentiate regions into NR rich phases, PMMA rich phase and interphase. Therefore, the phases will be referred to as mixed phases which includes the interphase region too for convenience From these data, it is noted that the extent of mixing of the components in the NR60:PMMA40(1.0) semi-2 IPN was significantly higher than the other samples

Table 3.14 Calculated interphase fractions (δ) and multiple peak analysis data for the semi-2 (1 0) IPN

			Multiple peak analysis data		
Sample	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Interphase content (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR 90:PMMA 10	0.10	**			
NR 80:PMMA 20	0.18	**	31*		
NR 70:PMMA 30	0.18	0 0	7	15	12
NR 60 PMMA 40	0.18	0.04	27	25	15
NR 50:PMMA 50	0 21	0.13	19	35	3

* Mixed phases

** The δ_{PMMA} content has not been calculated because of the difficulties in resolving the minor PMMA transition

δ_{NR},and δ_{PMMA} were calculated with respect to the un-vulcanized NR and cross-liked PMMA (EGDM 1 0 mole %), respectively

3.3.2.2 Effect of composition on stress-strain behaviour

Tensile data

Effects of composition on the tensile properties of the semi-2 (1.0) IPN series are presented in Figures 3.25 - 3.27. Unlike in the semi-2 (0 5) IPNs series, the tensile strengths of these IPNs increased with increasing PMMA content up to 40 wt.%, and thereafter showed a downward trend (Figure 3.25). Improved tensile properties of the NR60 PMMA40(1 0) sample is perhaps related to the enhanced mixing of components in this particular sample as seen from the MDSC data (Table 3.14). These results may suggest that the cross-linking of the PMMA component using EGDM at 1.0 mole%, leads to a reduction in the tensile strength of the NR50.PMMA50(1.0) composition. A feasible explanation for this trend can be proposed as follows.

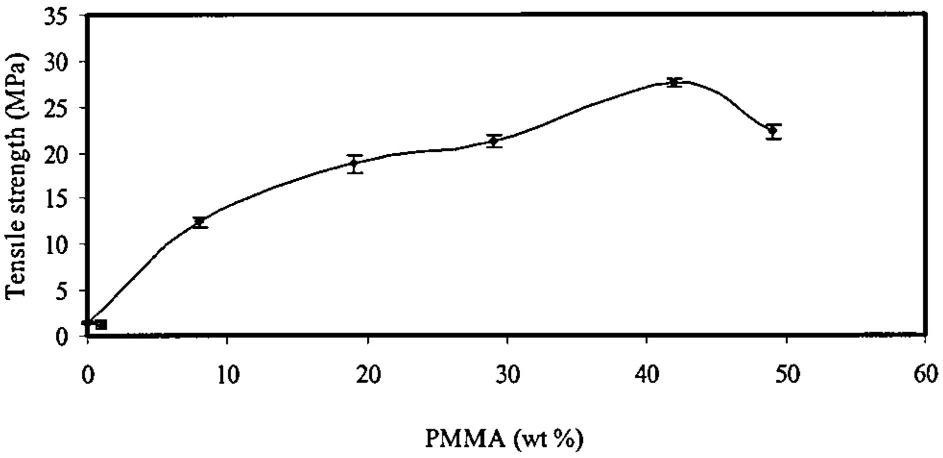


Fig. 3.25 Effect of composition on the tensile strength of the semi-2 (1 0) IPN series

Cross-linking of the PMMA component of these IPN, especially those with higher PMMA contents, will result in harder materials. When a stress is applied to the harder material, stress will be carried by the effective PMMA polymer chains and the NR polymer chains. However, the mobility of both the NR and PMMA polymer chains will be reduced as a consequence of cross-linking, resulting in a reduction of the efficient distribution of stress among the neighbouring polymer chains. A study based on nano-structured full IPNs based on natural rubber and polystyrene (Mathew *et al*, 2001) indicated that as the PS content and the cross-link density of PS phase are high, there is a tendency to form agglomerates which results in brittleness and poor mechanical performance.

This phenomenon may have occurred here. Accordingly, such materials may break at a lower force causing a reduction in tensile strength.

Results obtained from this series (Figure 3.26) indicated that the 100%, 300% and 500% moduli increased with increasing PMMA content and was similar to the trend observed in the other semi-2 IPNs series. This is mainly attributed to the filler reinforcement effect caused by the glassy PMMA particles in the NR matrix and/or due to the cross-linking effect of PMMA phase. In addition, the elongation at break decreased with increasing amount of PMMA (Figure 3 27), which could be attributed to the lowering of the mobility of polymer chains due to interpenetration of PMMA phases into the NR matrix (Pillai, 1995)

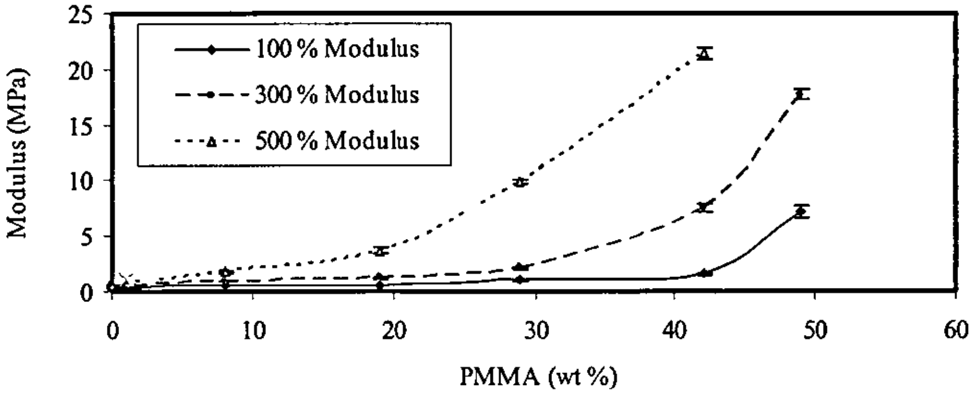


Fig. 3.26 Effect of composition on the 100, 300 and 500% moduli of the semi-2 (1.0) IPN series

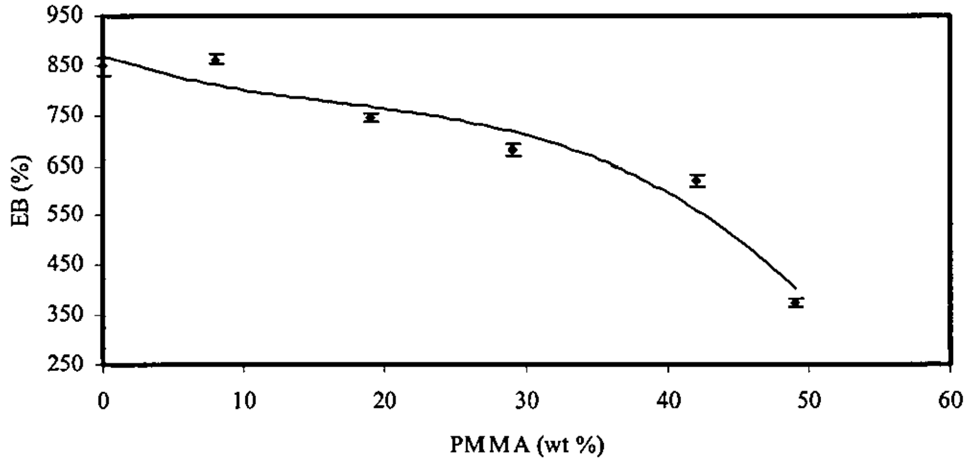


Fig. 3 27 Effect of composition on the elongation at break of the semi 2 (1.0) IPN series

Hysteresis data

Energy losses (hysteresis) and hysteresis behaviour found for the cyclic tests on the semi-2 (1.0) IPNs series are reported in Table 3 15. The hysteresis loops for these IPNs are presented in Figures 3.28 to 3 30. As the PMMA content increased, the hysteresis shown by the IPNs also increased strongly. Comparatively high hysteresis values were obtained for the IPNs with the

NR60.PMMA40(1.0) and the NR50.PMMA50(1.0) compositions Most probably this behaviour results from the increased presence of PMMA which has high hysteresis properties. As the PMMA content increased, resultant friction between PMMA domains and NR polymer chains also increased as a result of orientation of PMMA domains by overcoming interactions between PMMA hard segments and NR polymer chains. The same trend was found in NR/PMMA blend and the semi-2 (0.5) IPNs series.

Table 3.15 Energy losses and hysteresis for the semi-2 (1.0) IPN series

NR/PMMA Ratio	Cycle 1		Cycle 2		Cycle 3	
	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
90/10	0.13	0.39	0.03	0.07	0.01	0 07
80/20	0 31	0.72	0 16	0.40	0 13	0.28
70/30	0 72	1 59	0 35	0.86	0.35	0.84
60/40	3.00	3.78				
50/50	7.9	6.17				

HL-Hysteresis behaviour calculated as the ratio of the energy lost to the energy recovered in each cycle

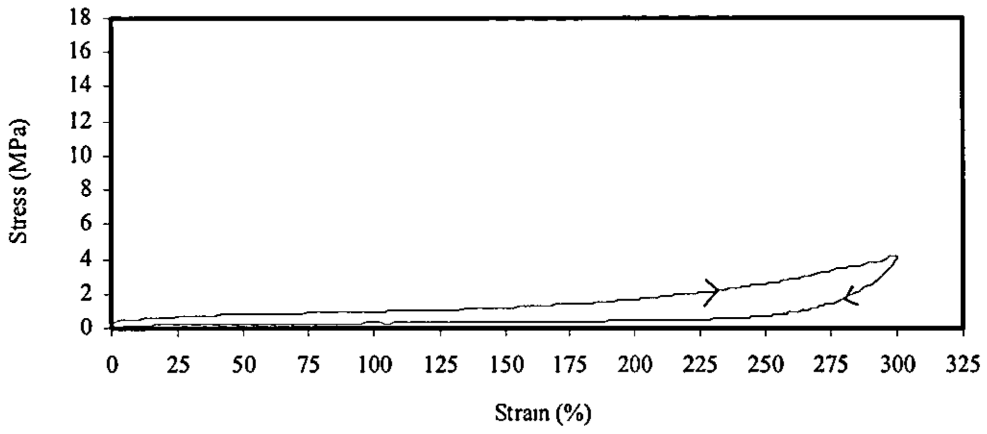


Fig 3.28 The first hysteresis cycle of the NR70:PMMA30(1 0) semi-2 IPN

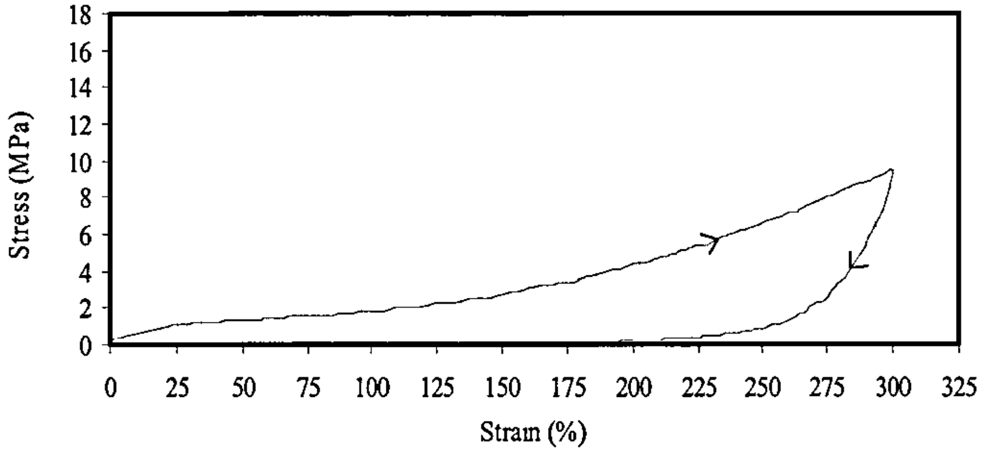


Fig 3.29 The first hysteresis cycle of the NR60.PMMA40(1.0) semi-2 IPN

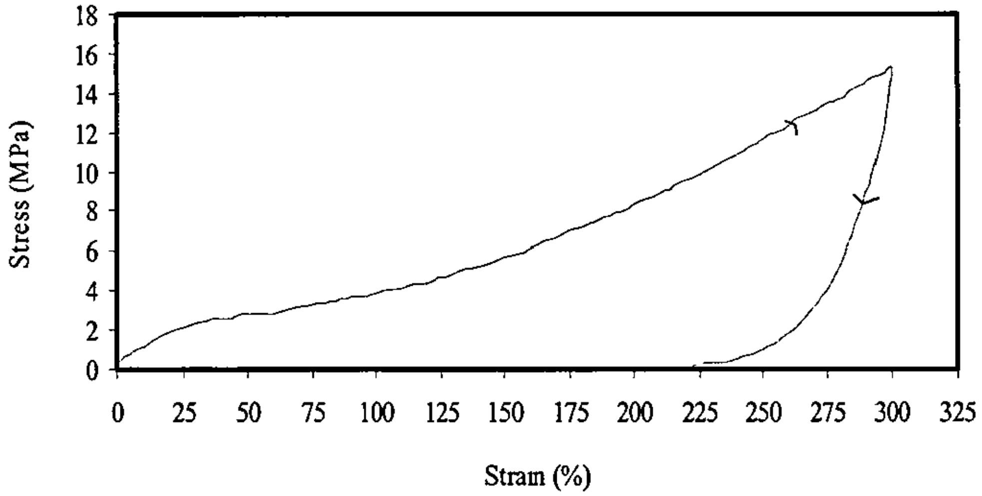


Fig. 3.30 The first hysteresis cycle of the NR50 PMMA50(1 0) semi-2 IPN

3.3.3 Semi-2 IPNs prepared using EGDM cross-linker at a level of 1.5 mole percent

3.3.3.1 Effect of composition on miscibility

Analysis of dynamic mechanical data

NR transition

The effect of composition on the NR loss tangent of the semi-2 (1.5) IPNs is shown in Figure 3.31 Comparison of tan delta values of the NR components of these semi-2 IPNs with the corresponding control sample showed that the glass transition temperatures of former samples were relatively higher by 3°C to 6°C than the control sample (see Table 3.16), indicating some mixing of the NR and PMMA components in these semi-2 IPNs. This observation is akin to the observations made for the other semi-2 IPN series. This trend is primarily attributed to some interpenetration of the PMMA network phases into the NR matrix (Donatelli *et al.*, 1976). As a result, adhesion between phases would be expected to increase (Xanthos and Dagli, 1991). On the other hand, cross-linking of the PMMA component leads to the formation of smaller domains, which may also lead to improved miscibility. Nevertheless, the chances of grafting of the PMMA network onto NR are probable and such a process most probably improves the miscibility of the two components.

Table 3.16 Half peak widths of the NR transition and the T_gs of the NR and PMMA transitions of semi-2 (1.5) IPNs

Sample	NR T_g (°C)	Half peak width (NR) (°C)	Tan δ_{max} (NR)	PMMA T_g (°C)	Tan δ_{max} (PMMA)
Natural rubber*	-51	16	2 4	-	
NR90.PMMA10	-48	19	2.0		
NR80:PMMA20	-47	20	1.9	173	0.33
NR70:PMMA30	-46	22	1.6	178	0.20
NR60:PMMA40	-45	26	0 8	156	0.40
NR50:PMMA50	-49	23	0 5	150	0.54

*Natural rubber heated under the same conditions

Moreover, as previously reported (Perera, 1999, Romaine, 1988), tan $\delta_{NR\text{-}max}$ gradually decreased with increasing PMMA content. The reasons for this trend have been explained earlier. As seen in section 3 3 2.1, the tan $\delta_{NR\text{-}max}$ values for the semi-2 (1.5) IPNs containing more than 30 wt.% PMMA are significantly lower than the values calculated on a pro rata basis (see Table 3.16). As such, it may be anticipated that the fraction of natural rubber remaining as homopolymer was lower in these two semi-2 (1.5) IPNs Study of IPNs based on poly(isobutene) (PIB) and polystyrene (PS) clearly indicated that as the cross-linking density of PS phase was increased from 0 to 20 wt.%, the height of the loss tangent of PIB relaxation decreased (Vancaeyzeele *et al* , 2006). Therefore, the influence made by the cross-linking of PMMA phase on mobility of the NR polymer chains should also be considered for the interpretation of lowering of heights of loss tangents of semi-2 IPNs with 40 wt.% and 50 wt.% of PMMA content, than the pro rata values Therefore, it is reasonable to assume that the lowering of the heights of the NR loss tangent in semi-2 (1.5) IPNs are due to the combined effect of improved mixing of the components (Table 3.17) and also due to the reduction of mobility of NR polymer chains due to cross-linking of the PMMA phase. The calculated weight fractions of natural rubber in the interphase are shown in Table 3.17. It also indicated that these two samples possess substantial interface regions.

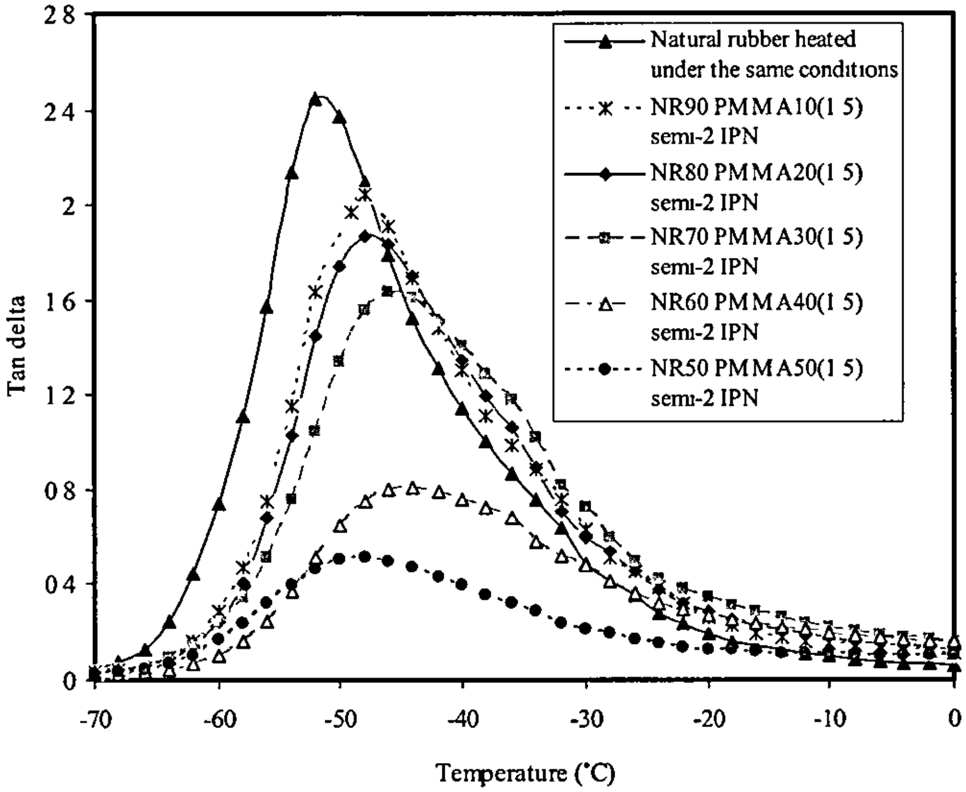


Fig 3 31 Effect of composition on tan delta of the NR component of the semi-2 (1 5) IPN series

PMMA transition

The loss tangent due to the PMMA component tends to shift to lower temperatures by 27°C with increasing PMMA content from 30 wt.% to 50 wt.% (Figure 3.32). This is, again, an indication of improved mixing of the components as was evident from the MDSC data shown in Table 3.17.

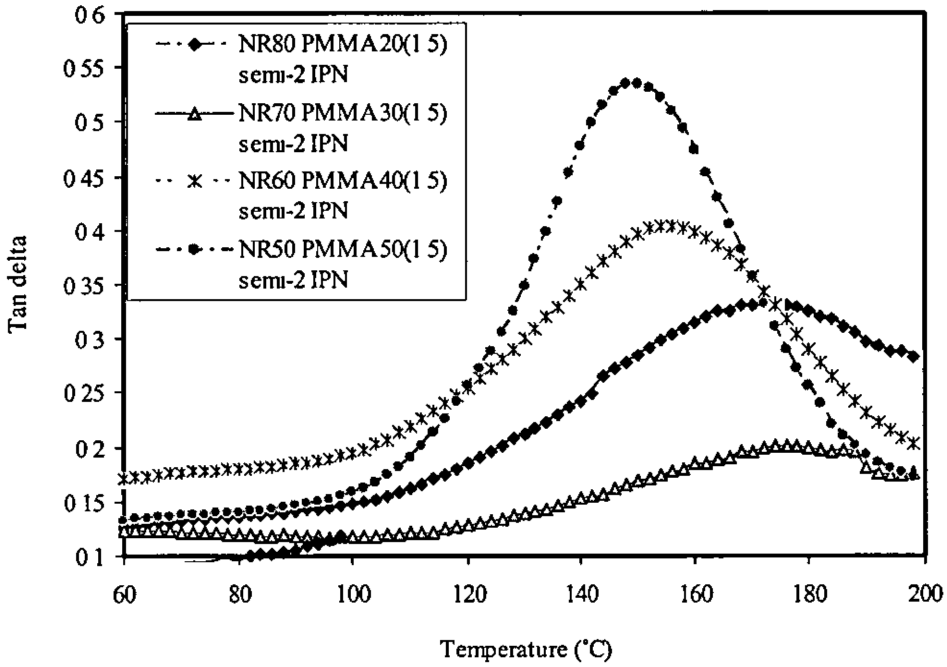


Fig. 3.32 Effect of composition on the loss tangent of the PMMA component in semi-2 IPN (1.5) series

Increase in the contact area with increasing PMMA content is believed to be the primary reason for this trend. In addition, the PMMA component in the NR70.PMMA30(1.5) semi-2 IPN appeared as a broad minor peak (Figure 3.32). The same situation has been encountered for the NR80:PMMA20(1.5) semi-2 IPN. Nevertheless, it is noted that the height of the PMMA transition in the NR70:PMMA30(1.5) semi-2 IPN was lower than the NR80.PMMA20(1.5) semi-2 IPN Since the height of the loss tangent is a measure of the quantity of polymer which is present as homopolymer, it may be postulated that the reduction of the PMMA transition in the NR70 PMMA30(1.5) semi-2 IPN is primarily due to the reduction of homo PMMA. This indicated that the considerable amount of the PMMA component is present in a mixed state rather than a pure PMMA phase in the NR70 PMMA30(1.5) semi-2 IPN, indicating improved component mixing in this sample. With the exception of the NR70:PMMA30(1.5) semi-2 IPN composition, the loss tangent data revealed that the tan δ_{max} of the PMMA peak gradually increased with increasing PMMA content. Weight fraction of a particular component in the composites can be considered as one of the factors which determine the height and the magnitude of the loss tangent of a particular component. Therefore, it is expected that the height of the PMMA transition should increase with increase in the PMMA content. A similar trend was found in the previously discussed semi-2 IPN (0.5 and 1.0) series.

When the heights of the loss tangent of the NR transition and the PMMA transition are compared, it is noted the PMMA phase is the continuous phase in the NR50.PMMA50(1.5) semi-2 IPN and as a result the tensile strength and the elongation at break was relatively low (Figures 3 34 and 3 35)

Storage modulus data

The dependence of storage modulus on composition of the semi-2 (1.5) IPNs is presented in Figure 3.33. E' values of the plateau between the two transitions increased gradually with increasing PMMA content, with the exception of NR70 PMMA30(1 5) semi-2 IPN. The increase of E' in the plateau region of these IPNs is primarily attributed to a reduction in mobility of the both polymer chains with increase of PMMA content. The PMMA transition of the NR50 PMMA50(1.5) semi-2 IPN appeared to be the prominent transition. Therefore, it can be concluded that the PMMA phase is either present as a continuous phase or a co-continuous phase in this particular sample. Nevertheless, exceptionally, the lower E' of the NR70:PMMA30(1.5) sample can be attributed to the slightly higher phase continuity arising from improved component mixing, as was evident from the DMTA data as well as the MDSC data.

When the plateau region between the two glass transitions were taken into consideration, it was noted that there was a gradual increase in the slope with increase of temperature, probably indicating some interactions between components, except for the NR80 PMMA20(1.5) semi-2 IPN. In the latter sample, E' values between the transitions do not change with increase of the temperature perhaps indicating a relative lack of interaction between the NR and PMMA components in this sample

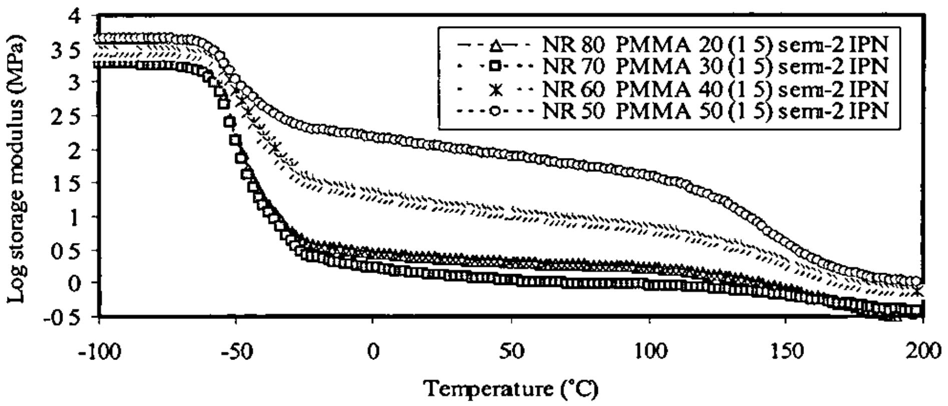


Fig. 3.33 Effect of composition on E′ of the NR component for the semi-2 IPN (1.5) series

Analysis of MDSC data

The calculated interface fractions for the semi-2 (1.5) IPNs are given in Table 3.17.

Table 3.17 Calculated interphase fractions (δ) and multiple peak analysis data for the semi-2 (1 5) IPNs

Sample	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase content (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR90·PMMA10	0.02	**	28*		
NR80.PMMA20	0 11	0.14	26*		
NR70 PMMA30	0.41	**	31	18	3
NR60 PMMA40	0.08	0.39	25	11	0.8
NR50 PMMA50	0.20	0.38	28	27	0.5

*Mixed phases

** The δ_{PMMA} content has not been calculated because of the difficulties in resolving the PMMA transitionδ_{NR} and δ_{PMMA} calculated with respect to the un-vulcanized NR and the cross-linked PMMA (EGDM 1 5 mole %)

It was noted that the weight fraction of the NR component in the interphase, NR-rich phase and the interphase content of the NR70.PMMA30(1.5) semi-2 IPN were considerably high indicating some mixing of the components. With the exception of the NR70.PMMA30(1.5) semi-2 IPN, the NR-rich phase increased with increase in the PMMA content (Table 3.17). This result is in agreement with the DMTA results which indicated that the PMMA transition of the loss tangent of the NR50 PMMA50(1 5) semi-2 IPN had shifted by 5°C towards lower temperature with increasing the PMMA content from 40 wt.% to 50 wt.%.

3.3.3.2 Effect of composition on the stress-strain behaviour

Tensile data

Variations of tensile strength of the semi-2 (1 5) IPNs with composition are illustrated in Figure 3.34. The tensile strengths of the semi-2 IPNs have significantly increased up to 30 wt.% PMMA and thereafter they showed a clear downward trend. The comparatively higher tensile strength of the NR70:PMMA30(1.5) semi-2 IPN could be attributed to improved mixing of the components, as indicated by DMTA and MDSC data

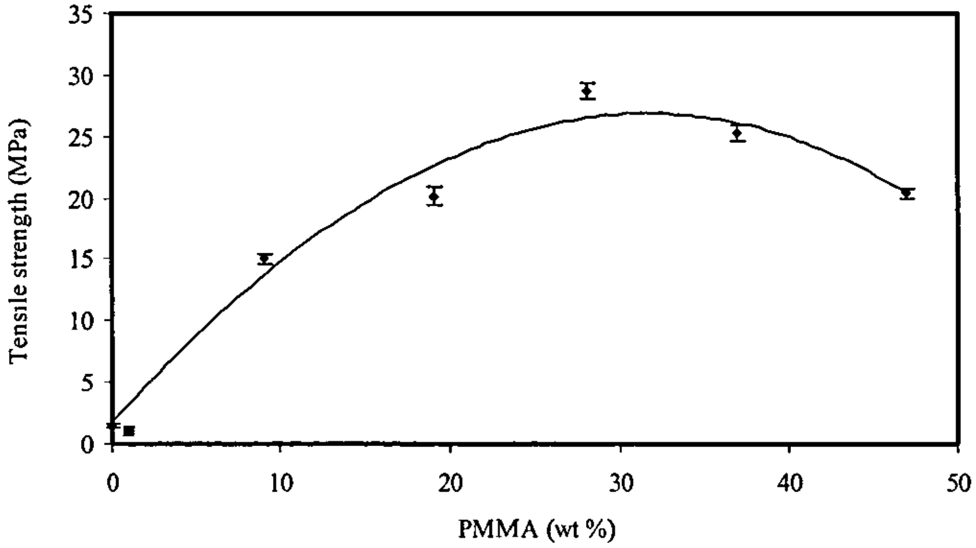


Fig.3.34 Effect of composition on the tensile strength of the semi-2 (1.5) IPN Series

It is apparent from the results that cross-linking of the PMMA component using 1.5 mole % of EGDM tends to cause a reduction of the tensile strength of the semi-2 (1.5) IPNs, especially those with higher plastomer content. The probable reason for such behaviour is considered to be the presence of hard, cross-linked PMMA domains, which hinder the segmental mobility of the NR polymer chains resulting in an inefficient stress distribution in the continuous phase. As a result, the samples may break at relatively low loads. Nair *et al* (1990) found a similar trend for a polyurethane-polyacrylamide IPN, which they ascribed to phase separation Figure 3 35 shows the effect of composition on the elongation at break and the results clearly indicate that EB decreases with an increase in the PMMA content.

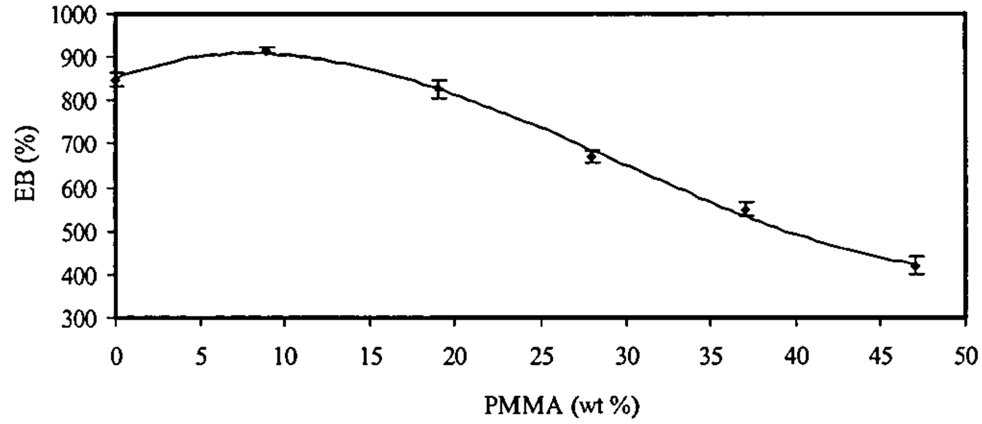


Fig 3 35 Effect of composition on the elongation at break of the semi-2 (1.5) IPN series

Hysteresis data

The effect of composition on the energy losses during cyclic tests of the semi-2 (1.5) IPN is presented in Table 3 18.

The results clearly indicated that hysteresis (Figures 3 36 to 3.38) in this series of IPNs increased with increase of the PMMA content and the probable reason for this behaviour has been explained in section 3.3.2.2.

Table 3.18 Energy losses during stress-strain testing of the semi- 2 (1.5) IPN series.

Composition NR/PMMA Ratio	Cycle 1		Cycle 2		Cycle 3	
	Energy Loss (J)	HL	Energy Loss (J)	HL	Energy Loss (J)	HL
90/10	0.20	0.46	0.070	0.17	0.06	0.15
80/20	0.39	0.93	0.23	0.59	0.21	0.60
70/30	0.93	2.1	0.53	1.14	0.44	0.96
60/40	3.50	4.0	**	**	**	**
50/50	8.42	4.84	**	**	**	**

* HL-Hysteresis behaviour calculated as the ratio of the energy lost to the energy recovered in each cycle

** - Sample had undergone permanent set

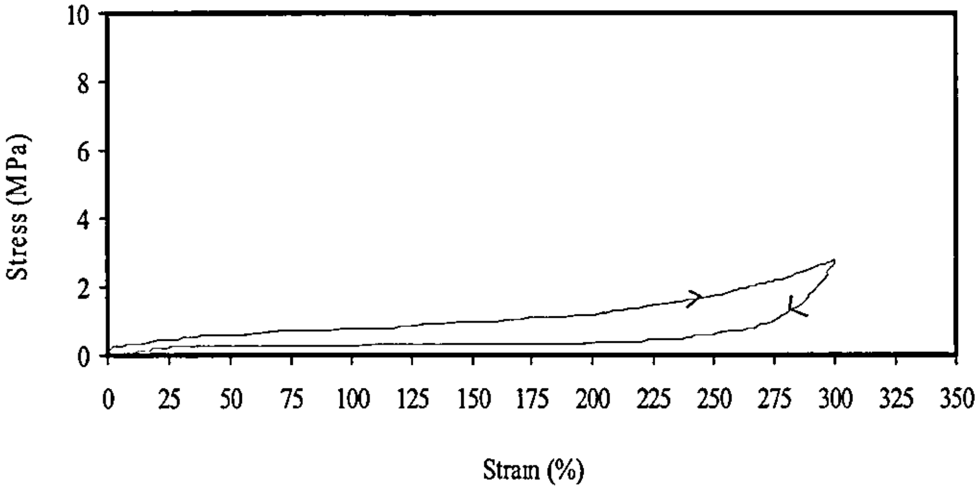


Fig.3.36 The first hysteresis cycle of the NR70 PMMA30(1.5) semi-2 IPN

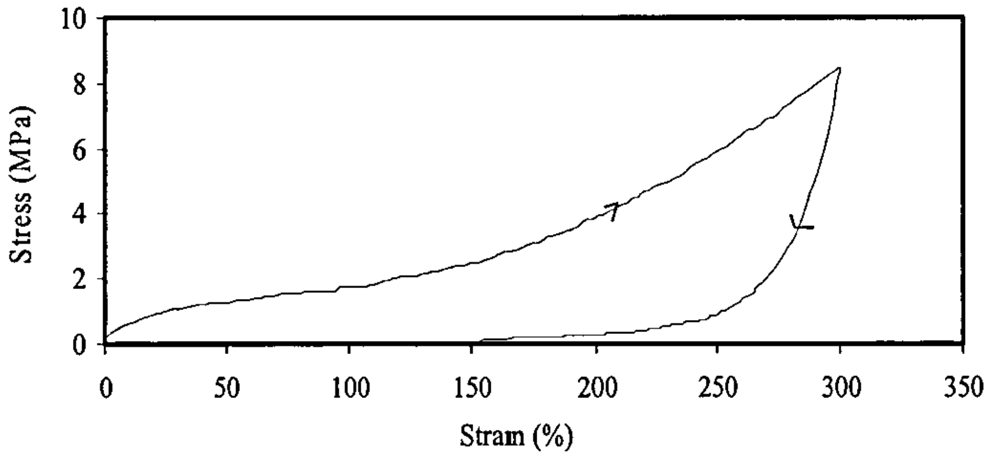


Fig. 3.37 The first hysteresis cycle of the NR60 PMMA40(1.5) semi-2 IPN

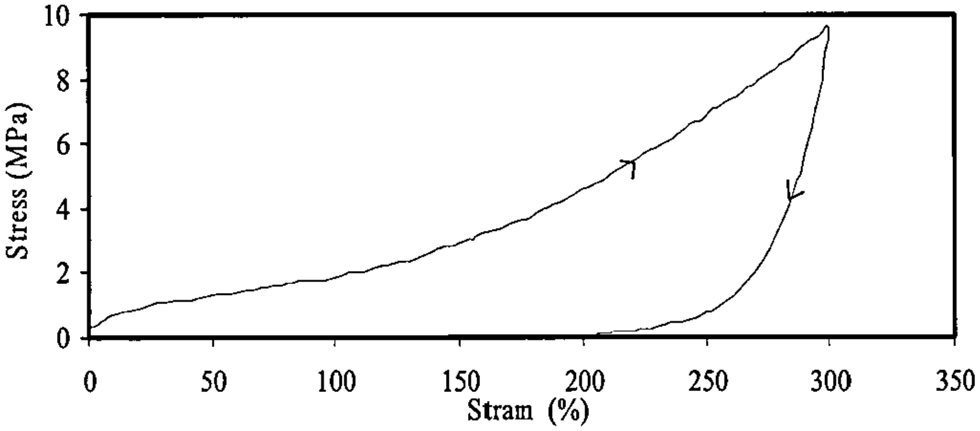


Fig. 3.38 The first hysteresis cycle of the NR50:PMMA50(1.5) semi-2 IPN

3.3.3.3 Effect of composition on the sol-gel ratio

According to the gravimetric results, there is no significant difference in the sol content of these semi-2 IPNs with increase in PMMA content (Table 3.19) In comparison with the NR90·PMMA10(1.5) semi-2 IPN, a marginally higher level of extractable materials is present in the NR70.PMMA30(1 5) semi-2 IPN sample which was subjected to the hot extraction process using acetone as the solvent.

Table 3. 19 Amounts of extractable materials present in different types of IPN.

Type	Amount of extractable material (%)											
	NR/PMMA blend			Semi-1 IPN			Semi-2 IPN (1. 5)			IPN (1. 5)		
Extraction Type	SE	RTE		SE	RTE		SE	RTE		SE	RTE	
Solvent	Ace.	Ace.	PET	Ace	Ace.	PET	Ace.	Ace.	PET	Ace	Ace.	PET
Composition NR/PMMA												
90.10	3	2.9	24.3	3.0	3.6	31.2	2.2	2.2	28.4	3.1	4.2	20.5
70:30	6.5	7.1	7.8	14.4	17.0	16.4	3.3	2.6	11.2	3.1	5.3	17.0

SE: Soxhlet extraction using acetone, RTE – Extraction was carried out at room temperature (27 ± 3°C)

Solvent used: Acetone (Ace.) and Petroleum ether 40/60 (PET)

It is expected that the homo PMMA content present in these semi-2 IPNs should increase with increase of the PMMA content, The solubility of the PMMA component in acetone will be reduced resulting in lowering of extracted materials because of the cross-linked nature in the PMMA component As such, a big variation in acetone-extractable materials was not be observed with increasing the PMMA content from 10 wt.% to 30 wt.%. A similar trend was obtained for the full (1.5) IPN, in which PMMA phase is also cross-linked using 1 5 mole% of EGDM crosslinker The amount of soluble material extracted using petroleum ether at room temperature clearly indicated that the amount of extractable material decreases with increasing the PMMA content. Petroleum ether was expected to remove natural rubber (Romaine, 1988) and, therefore, the amount of extractable material by petroleum ether will be reduced with a decrease of the natural rubber content in the sample. This is the reason for obtaining lowers amount of extractable material in the NR70 PMMA30(1.5) semi-2 IPN when petroleum ether was used as the solvent

3. 4 Semi-1 IPNs

3.4.1 General information on the semi-1 IPNs

Semi-1 IPNs were prepared as described in chapter 2 and the details of the compositions are given in Table 2 5. Unlike in the NR/PMMA blends and the semi-2 IPNs, these samples were less transparent, probably due to the gross phase separation of the components.

In general, the semi-1 IPNs with higher PMMA contents are hard and non-tacky when compared to the vulcanized NR. However, the IPNs with low amounts of PMMA are more or less similar in appearance to the vulcanised NR control, indicating an absence of stiffness usually resulting from the incorporation of the PMMA in to a NR matrix. This indicated that the polymerization of MMA had not fully taken place as was evident from the gravimetric data. Furthermore, these samples were slightly tackier than the vulcanised NR control sample. Therefore, this is considered as evidence that degradation of the NR has occurred in the absence of a considerable amount of MMA polymerisation by the initiator, Triganox 21S A similar observation was made for Triganox 21S in earlier studies of latex IPNs based on NR and polystyrene (Romaine, 1988). It is evident from the gravimetric data (Table 2 5) that the actual (experimentally determined) amounts of PMMA in the NR/PMMA (90:10) and (80.20) IPNs are extremely low (3 and 8 wt %, respectively). Therefore, hereafter these two semi-1 IPNs are referred to as NR97:PMMA3 semi-1 IPN and NR92:PMMA8 semi-1 IPN. Drastic reduction in PMMA content in these samples may be attributed to an inhibition of the polymerisation of MMA, most probably caused by one of the NR vulcanising agents. Therefore, hereafter, the samples which had significantly varied from the target composition will be represented by their experimental composition.

However, this effect is apparently minimised in IPNs, containing 30 - 50 wt.% PMMA. This could be attributed to the comparatively higher amounts of initiator and /or monomer present in these systems. Elemental sulphur is known to exist as cyclic S_8 molecules (Bartlett and Trifan, 1956; Ghosh, 1971) and it is capable of undergoing homolytic cleavage at elevated temperatures resulting in di-radicals that take part in polymerisation by radical coupling reactions On the other hand, the S_8 molecules can be involved in chain transfer reactions with vinyl monomers resulting in a polysulphur radical ($HS_8^{\bullet}$) (Bartlett and Trifan, 1956, Ghosh, 1971). These radicals react subsequently with another vinyl monomer to yield $RSx^{\bullet}$ which can undergo a vigorous termination reaction with growing polymer chain radicals causing a inhibitory action on the polymerisation of vinyl monomers (Bartlett and Trifan, 1956; Ghosh, 1971).

As shown above, although MMA radicals may link with sulphur, due to the large number of MMA radicals, the MMA homopolymerisation reaction would also take place. This may overcome the inhibition process in samples containing higher percentages of MMA

Therefore, preliminary studies were carried out to investigate the effect of each vulcanising chemical on the final properties of the resultant NR/PMMA (50·50) blends. In this attempt, each chemical has been incorporated alone in to the NR phase in the same amounts as used in the pre-vulcanization formula Blends based on NR and PMMA were prepared according to the procedure given in Chapter 2.1.

The results of these preliminary studies (Table 3.20) indicated that among the chemicals used, the presence of zinc dithiocarbamate (ZDC) in the NR matrix had no detrimental effect on the tensile strength of the blends. When compared to the equivalent blend with no added chemicals and the blends which contain added chemical, the results clearly indicated that the tensile strength had declined when sulphur was incorporated into the matrix This is perhaps due to the PMMA with low molecular weight resulting from inhibition of the MMA polymerization by sulphur.

Although sulfur compounds are involved in the vinyl polymerization, the mechanism is unclear (Ghosh, 1971). However, sulphur is known to be an initiator, modifier, and chain terminating agent or inhibitor (Ghosh, 1971) Clear evidence of the inhibitory effects of elemental sulphur on free radical vinyl polymerizations is available (Bartlett and Kwart, 1950). Studies based on the inhibition of the thermal polymerization of styrene in the presence of sulphur indicated that sulphur combines with styrene radicals to form a low molecular weight product containing 8 sulphur atoms per styrene unit (Barlett and Trifan, 1956)

In the present investigation, such an inhibitory effect on the polymerization of MMA in the presence of sulphur has been observed in the semi-1 IPNs and in the full IPNs, especially those having lower PMMA contents, where the NR component is cross-linked using conventional sulfur vulcanizing systems.

3.4.2. Effect of composition on miscibility

Dynamic mechanical data

Figures 3 39 and 3.40 depict the effect of the composition on the loss tangent data for the semi-1 IPN series. The T_g of vulcanized NR was slightly higher (3°C) than that of un-vulcanized NR because of the cross-linking of the NR component.

As far as T_g of the NR component is concerned, the Tg_{-NR} of the semi-1 IPNs did not vary much from the T_g of vulcanized NR (Table 3.21). These results suggested that under the experimental conditions used in this study, cross-linking of the NR component does not lead to improvement in the extent of mixing of the NR component and the PMMA.

Table. 3.20 Tensile properties and sol content of blends, prepared by adding vulcanizing chemicals to NR phase.

Description of the sample	Tensile properties				
	100% Modulus (MPa)	300% Modulus (MPa)	500% Modulus (MPa)	Tensile strength (MPa)	EB (%)
NR50:PMMA50 without vulcanizing chemicals	3.9	21.1	-	26.1	378
ZDC incorporated sample (0.25 phr)	4 7	17 5	-	26 0	403
Sulphur incorporated sample (0.5phr)	7.0	-	-	18.0	283
ZnO incorporated sample (0 1 phr)	5.4	13 6	-	22 0	413

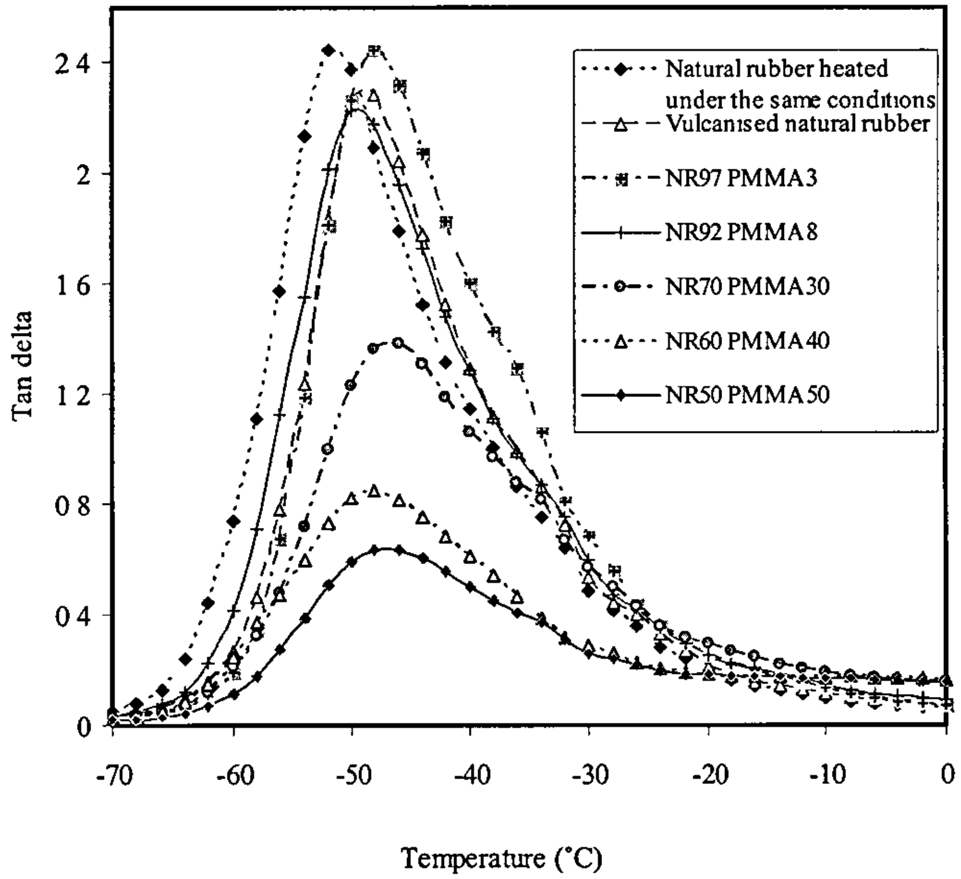


Fig. 3.39 Effect of composition on the loss tangent of the NR component of the semi-1 IPNs

As seen earlier, tan δ_{max} decreased with an increase in the PMMA content, except for the NR97·PMMA3 sample (experimentally determined), in which tan δ_{max} was just slightly higher than that of vulcanised NR Reduction of magnitude of the NR loss tangent with increasing PMMA content is as expected because the loss tangent reflects the volume fraction of each component. Nevertheless, deviation of the NR97 PMMA3 sample from the expected trend probably may be attributed to some degradation of the NR component results in lowering of the cross-link density.

Table 3.21 Half peak widths of the NR transition and the T_gs of the NR and PMMA transitions of semi-1 IPNs

Sample	NR T_g (°C)	Half peak width (NR) (°C)	Tan δ_{max} (NR)	PMMA T_g (°C)	Tan δ_{max} (PMMA)
Vulcanised natural rubber*	-49	15	2.3		
NR97 PMMA3	-48	19	2.4		
NR92:PMMA8	-49	18	2.2		
NR70:PMMA30	-47	22	1.4	150	0.19
NR60.PMMA40	-48	21	0.9	145	0.39
NR50:PMMA50	-47	23	0.6	146	0.44

*Vulcanised natural rubber heated under the same conditions

When the PMMA transition is taken into consideration, it is present as a broad minor peak in the NR70·PMMA30 semi-1 IPN (Figure 3.40)

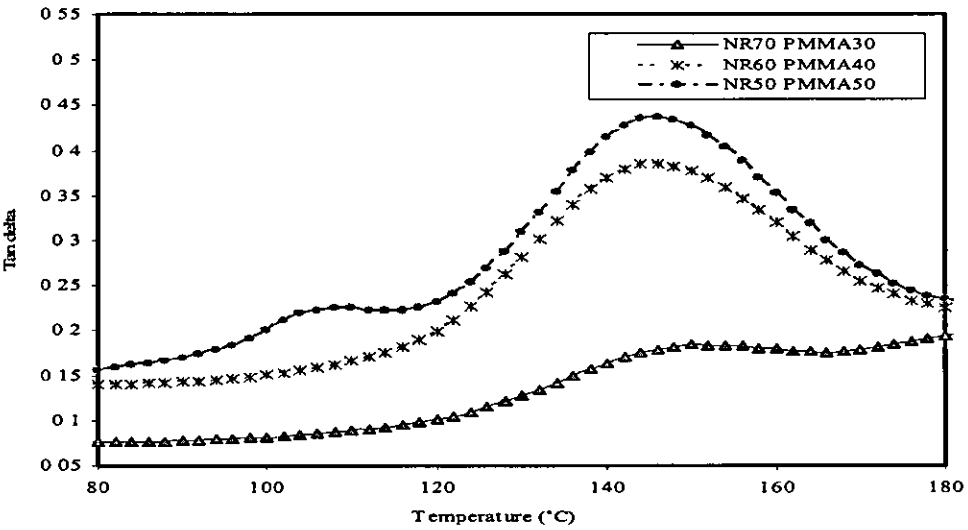


Fig 3.40 Effect of composition on the loss tangent of the PMMA component of the semi-1 IPNs

As expected, the height of the PMMA loss tangent had increased by a factor of 2.3, with increasing the PMMA content from 30 wt % to 50 wt.%. Compared to the PMMA T_g of the NR70 PMMA30 semi-1 IPN, the T_gs of the PMMA transitions of the NR60 PMMA40 semi-1 IPN and NR50·PMMA50 semi-1 IPN had relatively shifted towards lower temperature by 4°C to 5°C. This shift probably arise from the plasticization of PMMA by the NR component due to enhanced interpenetration of components (Vancaeyzeele *et al*, 2005). Furthermore, it is noted that there is a minor transition at 108°C prior to the α transition As there is a possibility to appear β-transition (usually 0.75 times of the Tgα-transition ((Murayama, 1978)) as a shoulder in the α transition for the amorphous polymers (Murayama, 1978), this minor peak can be referred to as a β-transition probably raised due to rotations of the side groups methyl (Sanchez *et al.*, 2001) or ester group (Murayama, 1978) of PMMA.

Analysis of MDSC data

According to the data listed in Table 3.22, there is no prominent effect of the PMMA content on the extent of mixing with the cross-linked NR component The effect of PMMA content on the NR-rich phase and interphase content in these semi-1 IPNs was not significant. However, the weight fraction of PMMA component which had been incorporated in to the interfacial layer and and the PMMA-rich phase content tends to increase with an increase of the PMMA content from 30 wt.% to 40 wt.%.

Table 3 22 Calculated weight fractions of components and the multiple peak analysis data for the semi- 1 IPNs

Composition NR/PMMA (wt.%)	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
97. 3	-	-			
92 8	-	-			
70 30	0.15	0.07	30	14	9
60· 40	0.20	0.13	26	14	15
50 50	0.21	0.23	30	13	26

(δ_{NR} was calculated with respect to the derivative of the complex Cp of un-vulcanised NR However, δ_{NR} calculated with respect to the vulcanised rubber for the semi-1 IPNs are not given due to the high variation in values obtained using the equation)

3.4.3 Effect of composition on stress-strain behaviour

Tensile data

Compared to the vulcanised natural rubber, the tensile strength of the NR97: PMMA3 semi-1 IPN (Figure 3.41 and Table 3.23) was significantly lower and which is perhaps related to degradation of the rubber caused by the initiator in the absence of significant polymerisation of MMA. However, the NR92 PMMA8 sample exhibited improved tensile strength When compared to the vulcaonised natural rubber, the improved tensile strength obtained for the NR92 PMMA8 sample may due to some reinforcement effect caused by rigid PMMA domains. A further increase of the PMMA content up to 30 wt.% caused a marginal increase in the tensile strength. On the other hand, increasing the PMMA content from 30 wt.% to 50 wt.% led to a marginal decrease of the tensile strength (Figure 3.41). The optimum tensile strength has resulted probably because of better interpenetration of NR and PMMA components at this particular composition (Kumar *et al*, 2006, Wang *et al*, 1992).

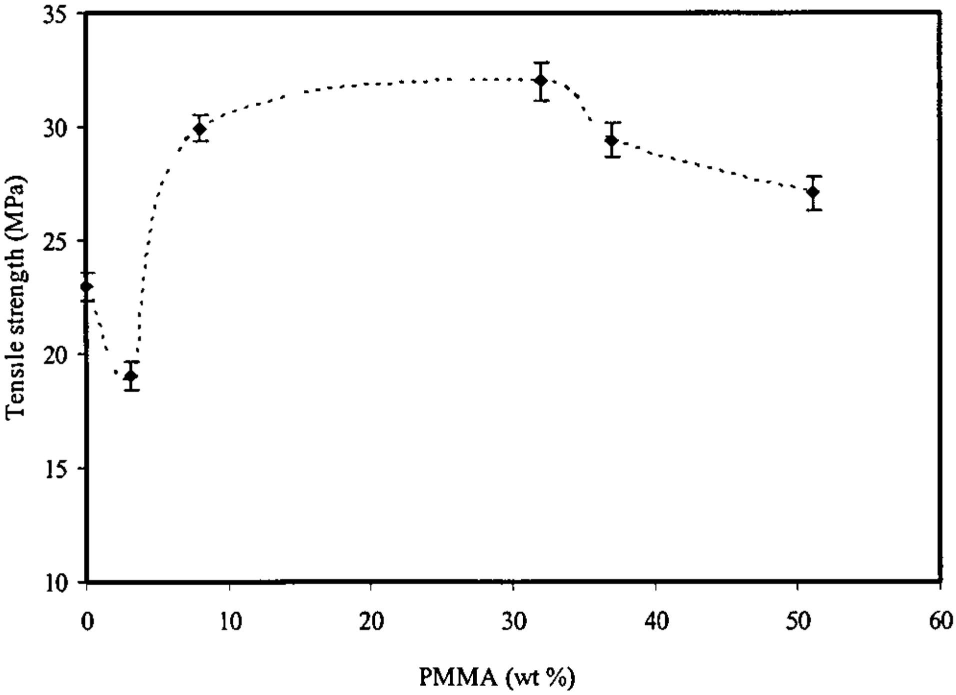


Fig 3 41 The effect of composition on the tensile strength of the semi-1 IPNs

Table 3.23 The tensile data for the semi-1 IPNs

Composition NR/PMMA (wt.%)	Tensile strength (MPa)
100:0	23 (1.3*)
97: 3	19 (1.2*)
92: 8	30 (1.1*)
68: 32	32 (1.6*)
63: 37	29 (1.5*)
49: 51	27 (0.7*)

* Standard deviation

Besides this observation, with the exception of the NR97:PMMA3 sample, the improved tensile strength of these semi-1 IPNs, can be ascribed to the reinforcement imparted by the PMMA phases in the cross-linked NR matrix

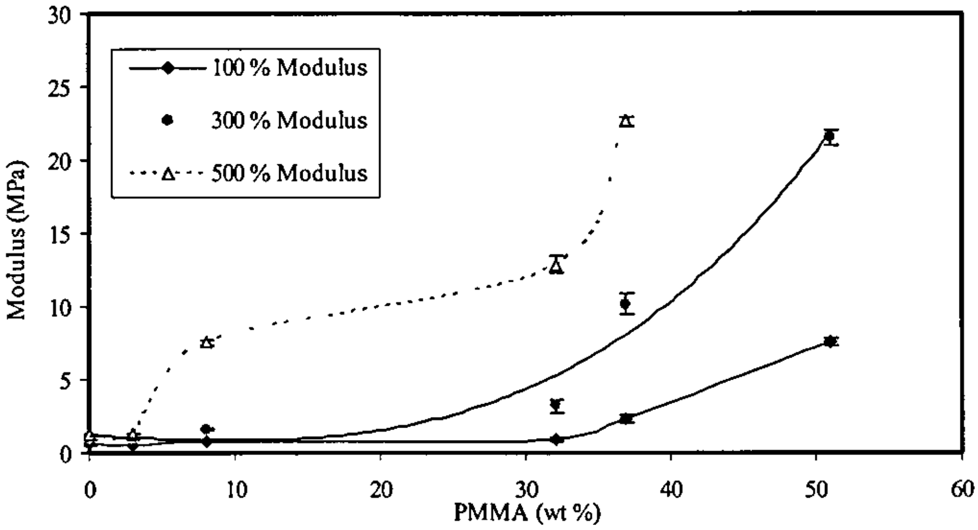


Fig. 3.42 Effect of composition on 100, 300 and 500 % moduli of the semi-1 IPNs

In general, as the PMMA content increases, the modulus of the material should increases due to the reinforcement by the hard, glassy PMMA particles. It could be anticipated that the PMMA may exert a similar effect to a filler dispersed in a cross-linked NR phase. As shown in the Figure 3 42, a marked increase of the 100% moduli were found at 40 wt.% of the PMMA content. If the 300% moduli values are considered, the modulus increased significantly at 30 wt.% PMMA (Figure 3.42). As expected, the elongation at break tended to decrease with increasing PMMA content (Figure 3.43). A feasible explanation has been given in section 3.3.1.2.

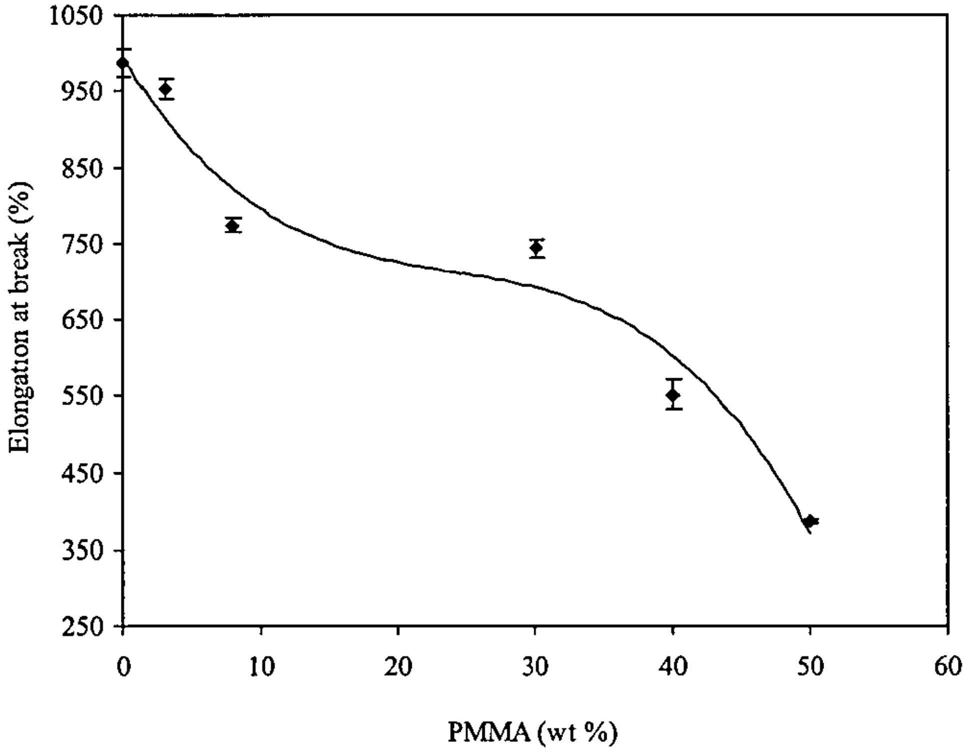


Fig. 3.43 Effect of composition on the elongation at break of the semi-1 IPN series

Hysteresis data

The amounts of the energy lost during the cyclic tests of these semi-1 IPNs are listed in Table 3.24. A comparison of hysteresis behaviour of uncross-linked NR and cross-linked NR, heated under the same conditions, can be made using the data presented in Table 3.24. This indicates that even thought the energy loss in vulcanised NR is apparently higher; the hysteresis behaviour, the ratio of energy lost to the energy recovered during the retraction is also significantly lower than the corresponding un-vulcanised sample This is basically due to the higher amount of energy recovered during retraction, due to the presence of cross-links. These results also agree with the DMTA data.

In addition, the data presented in Table 3.24 clearly indicate that the energy loss also increases when the percentage of PMMA is increased, except for the NR97:PMMA3 semi-1 IPN sample. This is an expected trend which results from the plastic deformation and breakdown of the PMMA phases.

Table 3.24 Energy loss and hysteresis behaviour data for the semi-1 IPN series

Composition NR/PMMA (wt.%)	Cycle 1		Cycle 2		Cycle 3	
	Energy Loss (J)	HL	Energy Loss (J)	HL	Energy Loss (J)	HL
100/0	0.06	0.45				
100/0*	0.08	0.15	0.04	0.09	0.03	0.04
97/3	0.10	0.14	0.05	0.07	0.04	0.06
92/8	0.34	0.49	0.27	0.42	0.26	0.43
70/30	0.97	1.3	0.61	0.83	0.71	0.86
60/40	2.59	3.43				
50/50	11.8	7.67				

*Prevulcanised natural rubber heated under the same conditions

HL-Hysteresis behaviour calculated as the ratio of the energy lost to the amount of energy recovered in each cycle

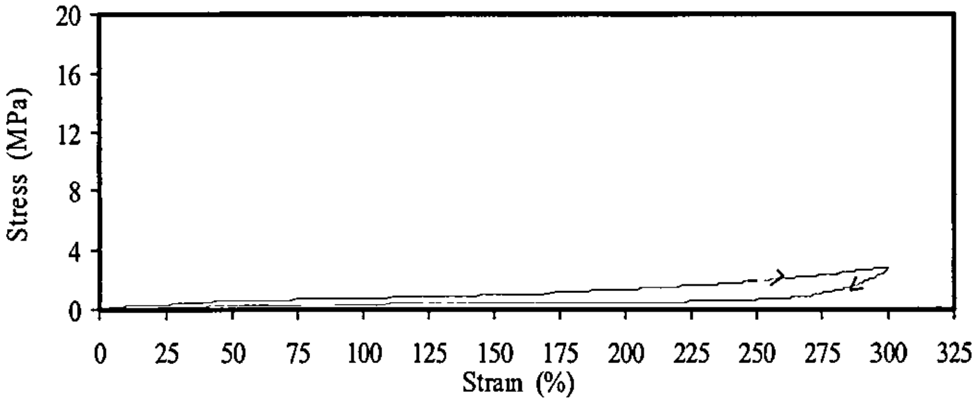


Fig. 3.44 The first hysteresis cycle for the NR70 PMMA30 semi-1 IPN

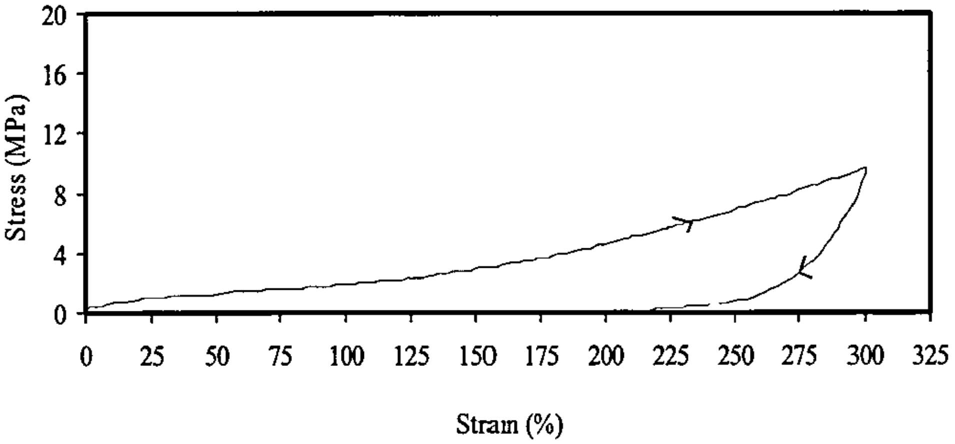


Fig. 3.45 The first hysteresis cycle for the NR60:PMMA40 semi-I IPN

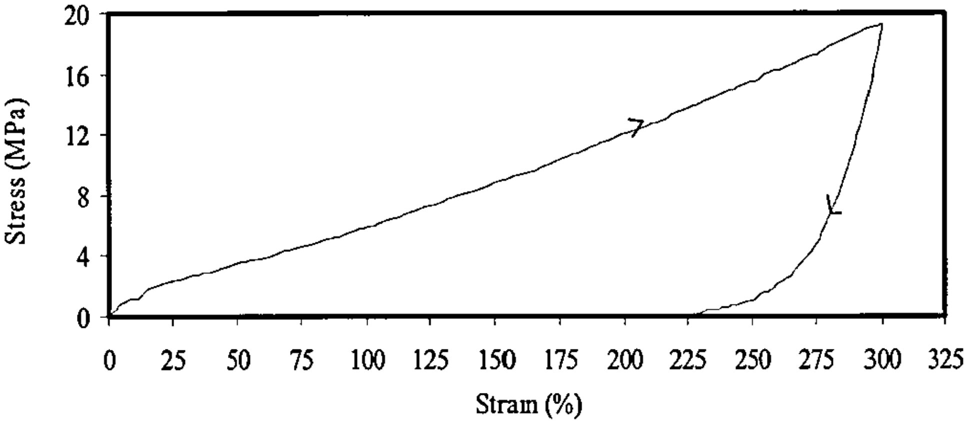


Fig.3 46 The first hysteresis cycle for the NR50 PMMA50 semi-I IPN

However, when compared to the corresponding control sample, the absence of significant differences in hysteresis values in the NR97: PMMA3 semi-I IPN sample can be attributed to the presence of an extremely low amount of PMMA (3 wt.%) and/or to degradation of the NR component (Table 3.24) Further, it has been noted that the difference in energy loss between cycles 1 and 2 was higher than those between cycles 2 and 3. A similar observation was made for the NR/PMMA blends.

3.4.4 Effect of composition on sol-gel ratio

IPNs having NR97:PMMA3 and NR70 PMMA30 compositions were subjected to the extraction process using hot acetone as the solvent in order to determine their sol and gel contents. The results (Table 3.19) clearly indicated that as the PMMA content increases, the sol content also increased which was attributed to the presence of a higher amount of PMMA homopolymer in the latter samples. This observation is consistent with the trends found in the blend series.

3.5 Full IPNs

3.5.1 General information

The appearance of the IPNs are somewhat similar to the equivalent semi-1 IPN samples. IPNs having less than 30 wt % PMMA content were prone to the inhibition of the MMA polymerization reaction. The full IPNs with 30 - 50 wt % PMMA were hard and non-tacky. Furthermore, these samples containing more than 20 wt.% PMMA were less transparent As observed in the semi-1 IPNs, the full (0.5) IPNs which were expected to contain 10 wt.% and 20 wt.% PMMA were unable to reach the expected target composition due to the inhibition effect exerted by the vulcanizing agent, as discussed in section 3.4.1. Therefore, in this section, the samples which varied significantly in their compositions between the target composition and the experimental values were denoted using the experimental values.

3.5.2 Effect of composition on the dynamic and mechanical properties of the IPNs series (EGDM level - 0.5 mole %)

3.5.2.1 Effect of composition on miscibility

Dynamic mechanical data

Selected DMTA traces are presented in Figures 3.47 and 3.48 As shown in Figure 3.47, the Tg of the NR component of the 70/30 of NR/PMMA composition had shifted by 4°C towards higher temperature (Table 3.25).

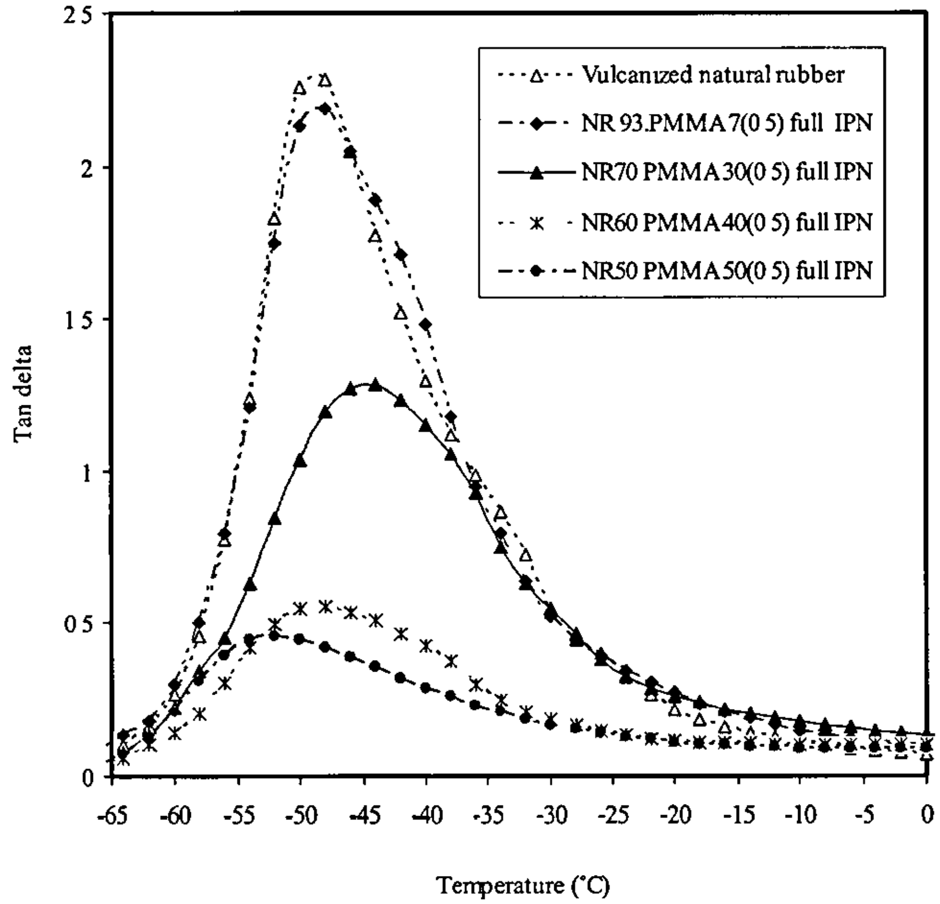


Fig. 3.47 Effect of composition on the loss tangent of the NR component of the full (0.5) IPN series

If the NR component had been mixed with the PMMA component, the Tg_{NR} value should be increased due to the reduction in mobility. Therefore, the observed trend has probably resulted from the improved mixing of the NR network with the PMMA network. Further evidence for some mixing is also available from the MDSC data (Table 3 26). In addition, the maximum tensile strength was obtained for this particular composition suggesting improved miscibility of the components in this sample.

Tan δ_{max} has decreased (Table 3.25) with increase in the PMMA content, in the same manner as seen in other studies (Romaine, 1988; Perera, 1999) and also in the previously studied semi-1 IPNs in this present investigation (section 3.3.2.1).

Furthermore, Akhtar and Bhagawan, (1987) also reported that the area under the loss tangent curve increased with increase in the NR content in NR/high density polyethylene (HDPE) blends. The same trend has been observed in the IPN series of the present study (Figure 3.47).

Table 3 25 The loss tangent data for the full (0.5) IPNs

NR/PMMA (wt. %)	NR T_g (°C)	Tan $\delta_{NR\text{-}max}$ (°C)	PMMA T_g (°C)	Tan $\delta_{PMMA\text{-}max}$ (°C)
100/0*	-49	2.3		
93/7	-49	2 2		
70/30	-45	1 3	152	0.17
60/40	-49	0.55	145	0.56
50/50	-52	0.45	146	0.51

* Vulcanised natural rubber heated under the same condition

The ddependence of the PMMA component loss tangent on the composition of the full (0.5) IPNs is shown in Figure 3 48 As also seen for the blends, semi-2 (1.0) IPNs and semi-1 IPNs studied in this investigation, the PMMA transition exists as a broad minor peak in the NR70 PMMA30(0.5) full IPN sample.

Moreover, the results clearly showed that the T_g of the PMMA transition has shifted towards lower temperature by 6°C with increasing the PMMA content from 30 wt.% to 50 wt.%. The tan $\delta_{max\text{-}PMMA}$ of the NR/PMMA of the 50/50 sample was lower than that of the 60/40 NR/PMMA sample suggesting enhanced mixing of components in the NR50:PMMA50 sample (Table 3.25) This suggestion is further confirmed by the MDSC data listed in Table 3 26. In addition, the results in Table 3 25 indicated that the PMMA phase is the continuous phase in the full (0.5) IPN having 50 wt.% PMMA (Figure 3.49).

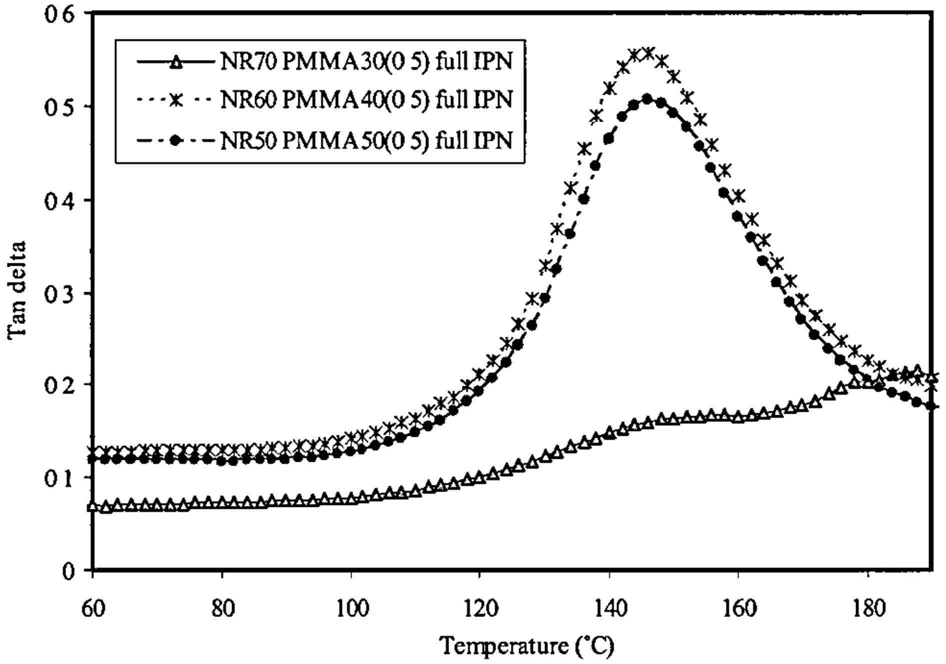


Fig. 3.48 Effect of composition on the loss tangent of the PMMA component of the full (0 5) IPN series

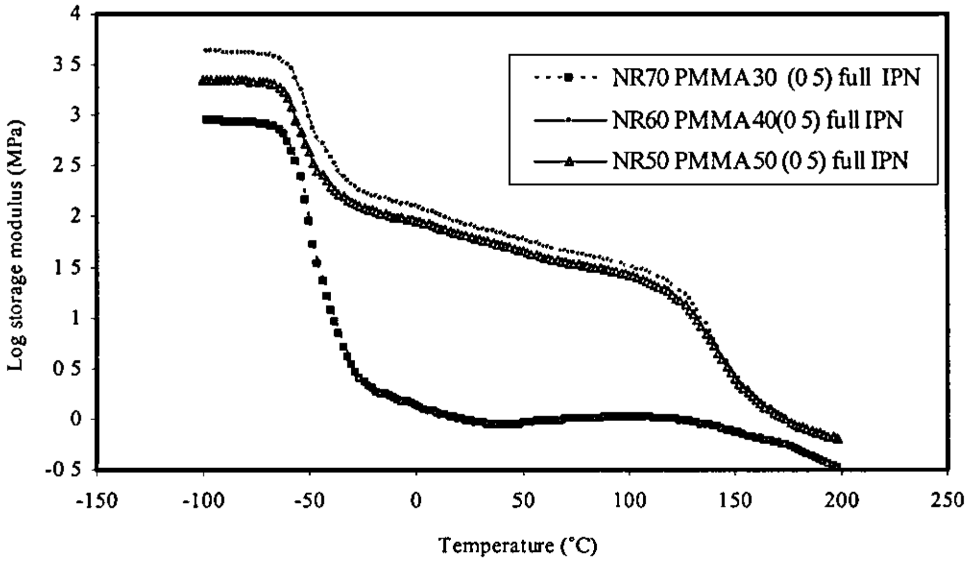


Fig. 3 49 Effect of composition on the storage modulus of the full (0.5) IPN series

Analysis of MDSC Data

The weight fraction (δ) of each component in the interface region for the IPNs (0.5) was determined in two different ways.

δ_{NR} values were calculated with respect to the differential heat capacity values of vulcanised NR as follows.

$\delta_{NR} = w_{NR} - (\Delta Cp_{NR\ IPN} / \Delta Cp_{vulcanised\ NR})$

The calculated δ_{NR} data are listed in Table 3 26.

Table 3.26 Weight fraction of components in the interphase and the multiple peak analysis data for the full IPNs (0.5)

NR/PMMA (%)	δ_{NR}* (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
70 30	0.25	0.17	29	10	13
60. 40	-	0.15	29	13	17
50: 50	0 15	0.23	20	20	23

δ_{NR}* was calculated with respect to the derivative of the complex Cp of vulcanised NR

A considerable amount of the NR component and the PMMA component had been incorporated in to the interphase of all full (0.5) IPNs. Furthermore, calculated weight fraction of the PMMA component in the interphase indicated that the extent of mixing of the cross-linked PMMA component increased with increasing the PMMA content from 30 wt.% to 50 wt.% (Table 3.26) Moreover, multiple peak analysis data also provide supportive evidence for enhanced mixing of PMMA component with increase of PMMA content.

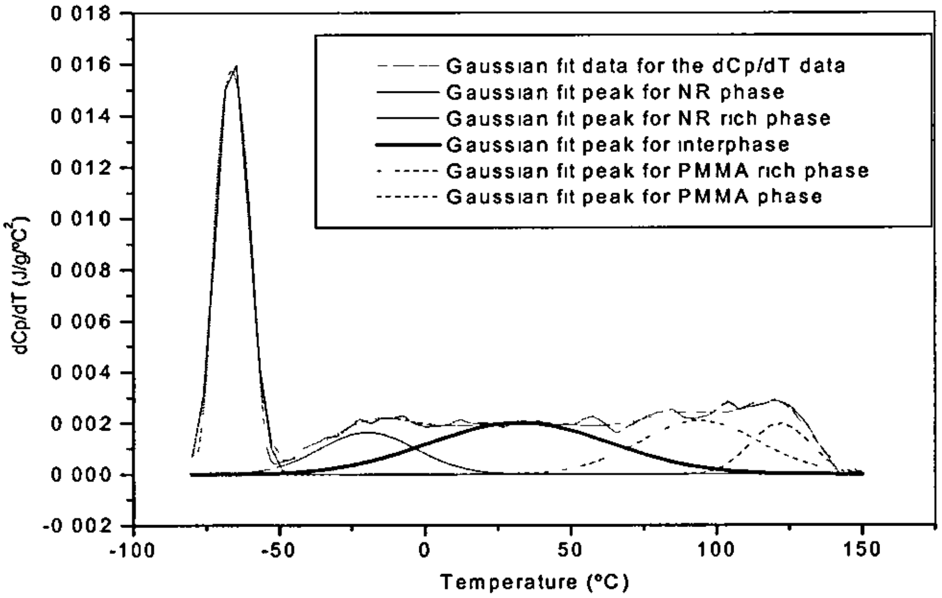


Fig 3.50 Temperature dependence of dCp/dT of the NR60.PMMA40(0 5) full IPN

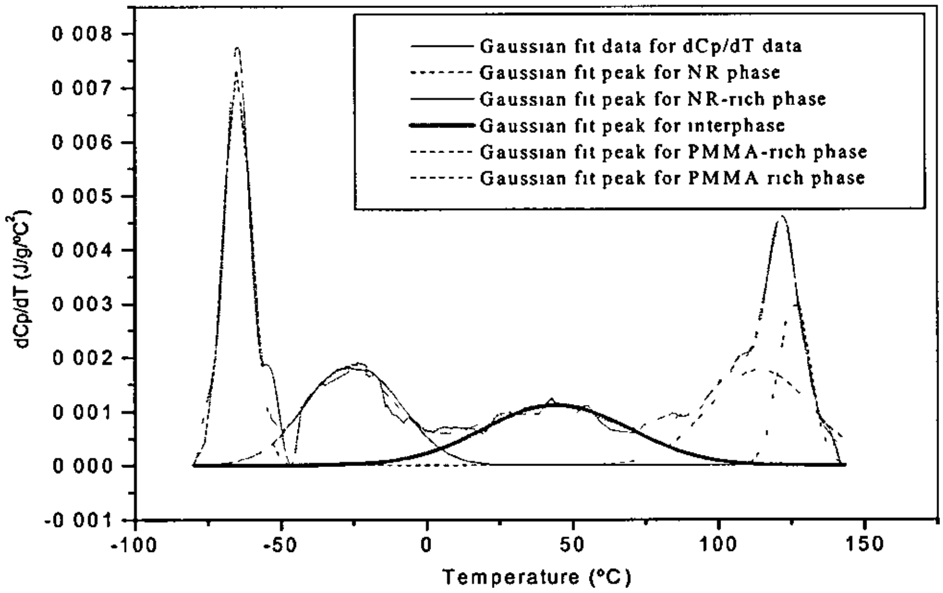


Fig. 3.51 Temperature dependence of dCp/dT of the NR50 PMMA50(0.5) full IPN

3.5.2.2 Effect of composition on the stress- strain behaviour

Tensile data

The effect of composition on the tensile strength of the full (0 5) IPN series is presented in Figure 3.52. Relatively low tensile strength of the NR93:PMMA7(0.5) full IPNs can probably be attributed to the some degradation of rubber matrix due to the presence of initiator and the absence of complete MMA polymerization. However, incorporation of 30 wt.% PMMA led to a clear increase in tensile strength. Further, an increase of the PMMA content up to 50 wt.% caused a significant reduction in tensile strength. This observation is akin to the trend found for the semi-1 IPNs. A similar trend has been obtained for IPNs based on a polyurethane–urea and a polyacrylate co-polymer, which were cross-linked by a conventional sulphur system (Frisch *et al.,* 1972).

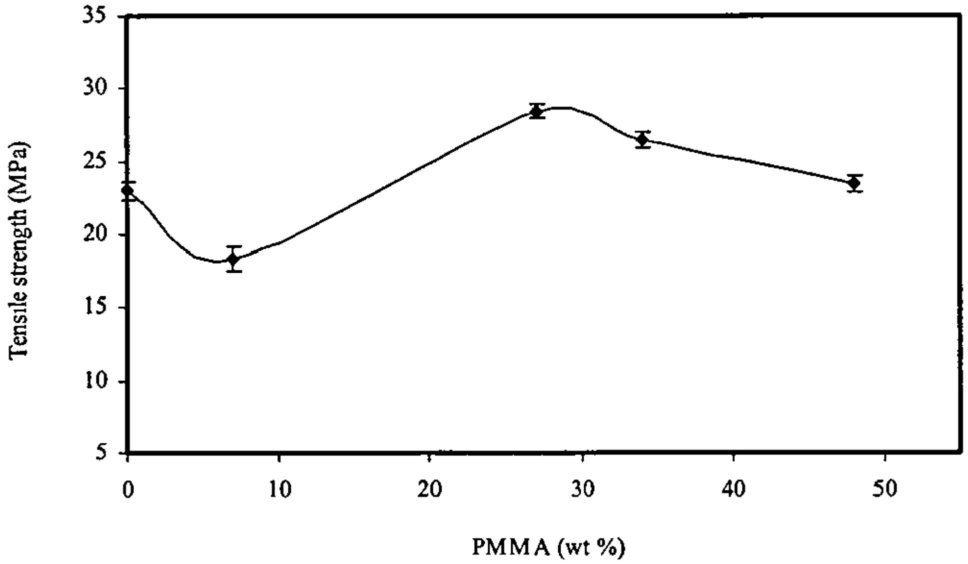


Fig. 3.52 Effect of composition on the tensile strength of the full (0.5)IPNs

Furthermore, interpenetration at the phase boundaries leads to a reduction in the domain size and thereby improves the adhesion between particles (Morton *et al.*, 1969; Morton and Healy, 1967). It was assumed that the reinforcement was not directly dependent on the physical entanglements caused by interpenetration, but depends on the reduced domain size and improved adhesion between phases because of interpenetration (Kim *et al.,* 1977). The results of this study also support this view as the maximum tensile strength was observed for the sample for which the highest miscibility of components was obtained.

Variation of modulus data of the full (0.5) IPN series with PMMA content is illustrated in Figure 3.53 As was seen in semi-1 IPNs, the 100% and 300% moduli values are significantly increased with increasing PMMA content from 30 wt.% to 50 wt % The improved modulus properties could be attributed to the reinforcement effect caused not only by the incorporation of glassy, hard, cross-linked PMMA phases in the NR matrix, but also to the entanglements caused by interpenetration of the PMMA network. It is reported that the contribution from a second network to the modulus is comparatively high and may be attributed to molecular entanglements (Gent *et al.*, 1974).

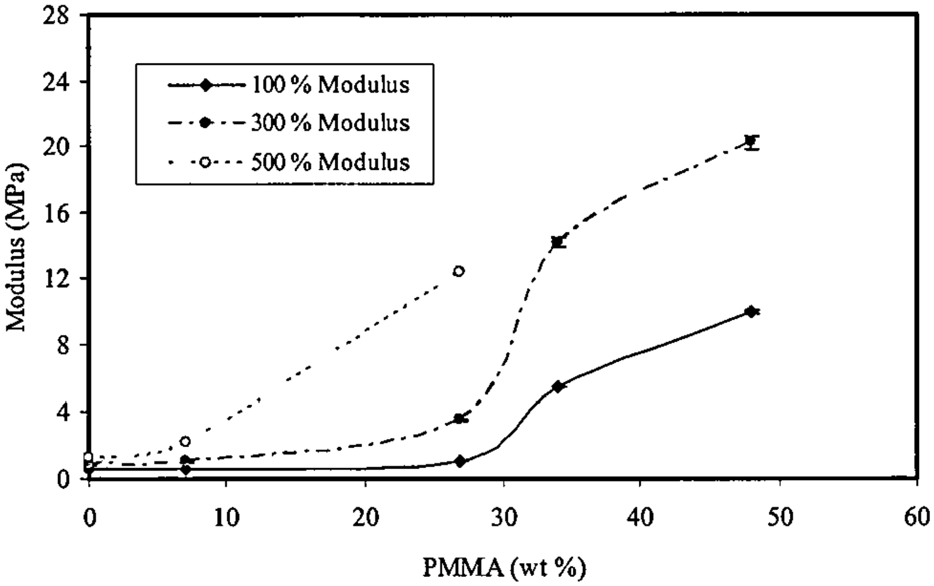


Fig. 3.53 Effect of composition on the 100, 300 and 500% moduli of the full (0.5) IPN series

Nevertheless, the absence of a pronounced increase in modulus values in the IPNs, containing less than 30 wt % PMMA is mainly attributed to the existence of low amounts of PMMA in these IPNs Furthermore, the elongation at break has decreased with increasing PMMA content (Figure 3.54). This is due a the reduction in mobility of the polymer chains as a result of interpenetration of the glassy PMMA phases. This result is consistent with the findings of earlier work (Pillai, 1995; Lee and Kim, 1985).

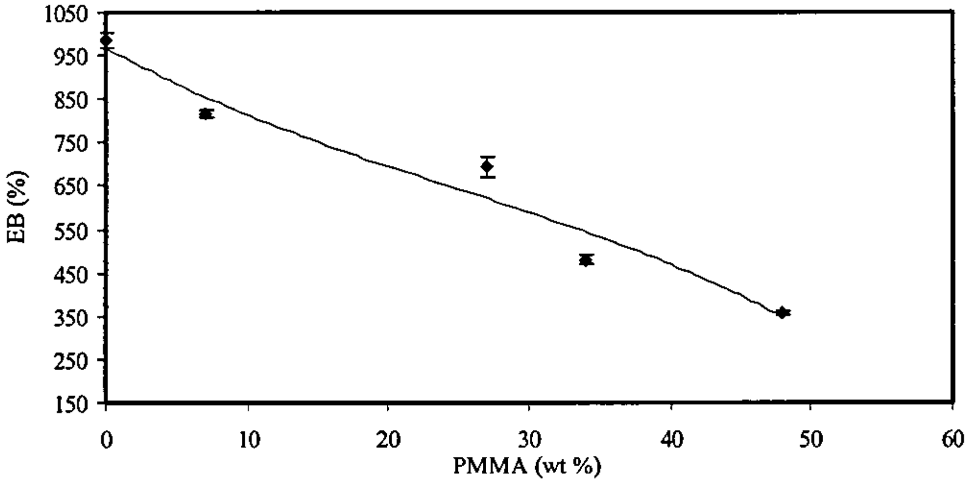


Fig 3 54 Effect of composition on the elongation at break for the full (0.5) IPN series

Hysteresis data

The energy loss during cycling tests and hysteresis behaviour data are summarised in Table 3.27 and Figures 3 55 to 3 56 The amount of energy dissipated during stress-strain testing increased sharply with increase in the PMMA content. This trend is the same as the trends observed in the previously studied series of semi-1 IPNs in the present investigation. As the PMMA content increases, there is a reduction in the elastic component in the material, which ultimately reduces the elastic response. As a result, hysteresis increases with increasing PMMA content

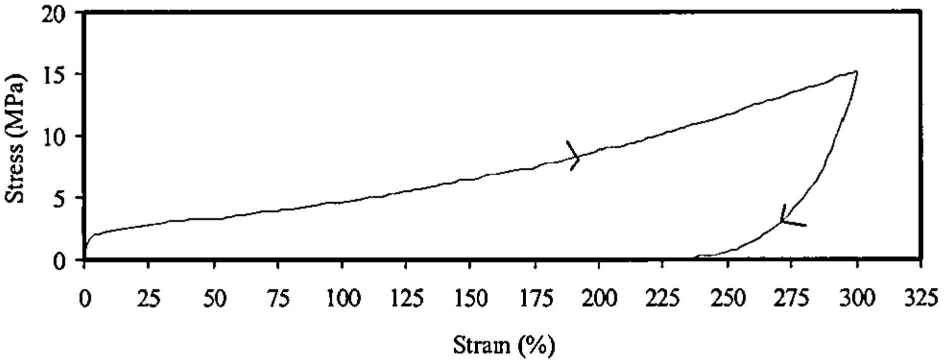


Fig. 3 55 The first hysteresis cycle of the NR60.PMMA40(0.5) full IPN

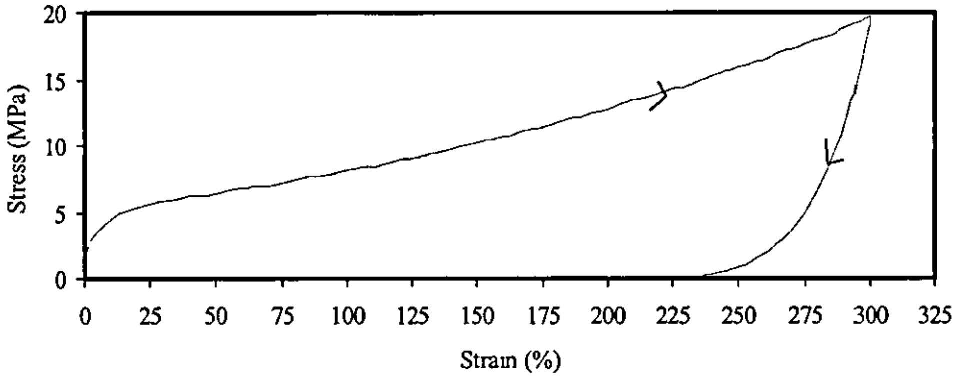


Fig. 3.56 The first hysteresis cycle of the NR50.PMMA50(0.5) full IPN

Table 3.27 Energy loss and hysteresis data for the full (0.5) IPNs

Sample	Cycle 1		Cycle 2		Cycle 3	
NR/PMMA (wt %)	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
Control sample*	0.76	0.15	0.35	0.09	0.28	0.04
100/0**	0.04	0.08	0.02	0.03	0.02	0.04
93/7	0.14	0.26	0.10	0.19	0.09	0.17
70/30	0.94	1.39	0.49	0.86	0.43	0.79
60/40	7.2	9.44	-	-	-	-
50/50	10.4	10.7		-	-	-

HL- Hysteresis behaviour is the ratio of energy lost to the energy recovered during the cycling test

* Similarly treated vulcanised NR

** Full (0.5)IPN which had been expected to contain 10 wt. % PMMA content, but actual value was 0 % due to inhibition of MMA polymerisation by the presence of vulcanising ingredients.

3.5.3 full IPNs prepared using EGDM at a level of 1. 0 mole percent

3.5.3.1 Effect of composition on miscibility

Please note that the DMTA spectra were unable to be obtained for this series of full (1.0) IPNs due to lack of time in the first part of this study programme which was planned to be on a split basis.

Analysis of MDSC data

According to the MDSC data shown in Table 3.28, the weight fraction of NR component incorporated into the interphase was found to be low. This probably suggests that the extent of mixing of cross-linked NR was low. However, multiple peak analysis data is considered, a considerable amount of interphase could be found for these full (1 0) IPNs (Figure 3.57 and Table 3.28). Moreover, the amount of mixed phases apparently increased with increase of PMMA content from 40 wt.% to 50 wt.%.

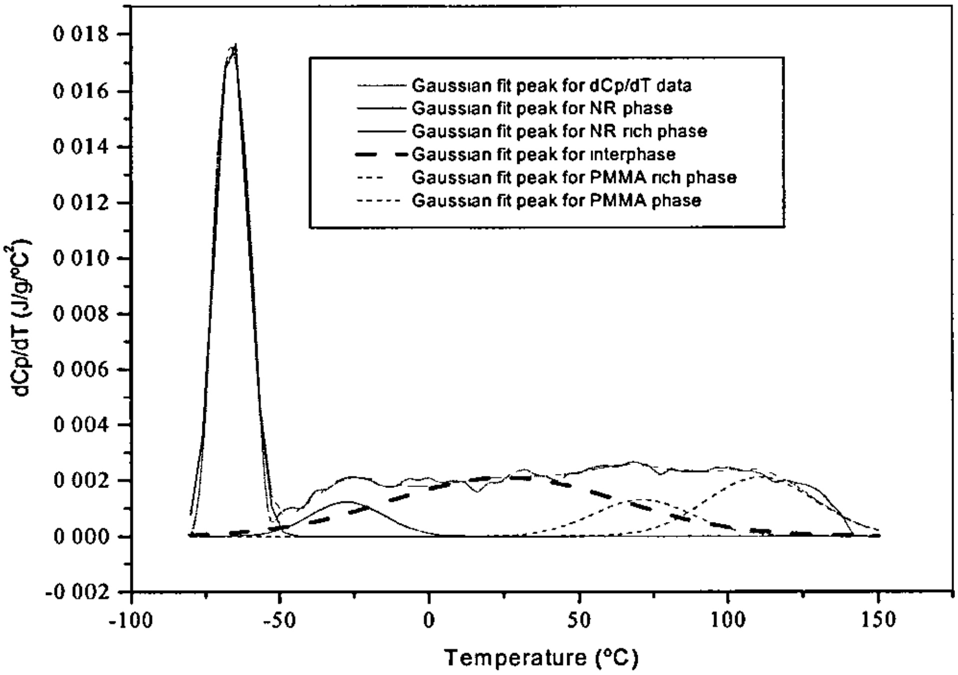


Fig. 3.57 Temperature dependence of dCp/dT of the NR70·PMMA30(1.0) full IPN

Table 3.28 Weight fraction of components in the interphasial layer and multi-peak analysis data for the full (1 0) IPNs

Composition NR/PMMA (wt %)	δ_{NR}* (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase (%)	NR-rich phase	PMMA-rich phase
97.3	0.07	-			
70:30	-	0.12	31	6	8
60:40	-	-	35	8	6
50:50	-	-	33	6	29

δ_{NR}* were calculated with respect to the derivative complex of the Cp of vulcanised NR and cross-linked PMMA (EGDM 1 0 mole%), respectively

3.5.3.2 Effect of composition on stress-strain behaviour

Tensile data

The effects of composition on the tensile properties of this IPN series are presented in Figures 3.58 to 3.60 The tensile strength (20 MPa) of the full (1.0) IPN which should have contained 10 wt % of PMMA content (experimentally determined PMMA content was negligible) was marginally lower than that of the corresponding control sample (23 MPa) This may be attributed not only to the presence of a low amount of PMMA in this sample due to inhibition of polymerisation, but may also be due to the degradation of NR, which could occur during the polymerisation of MMA. Preliminary studies conducted on samples, prepared using Triganox 21S indicated that the tensile properties of these samples are lower than that of the NR control Such a reduction in tensile strength could be attributed to some degradation of the NR A similar observation has been made in earlier studies based on NR/PS blends prepared using the same initiator (Romaine, 1988). The tensile strength of the NR97 PMMA3(1.0) full IPN does not vary significantly from the corresponding control sample indicating that this amount of PMMA is not sufficient to impart significant reinforcement. However, a further increase of PMMA content up to 40 wt.% led to a small increase in the tensile properties of these IPNs.

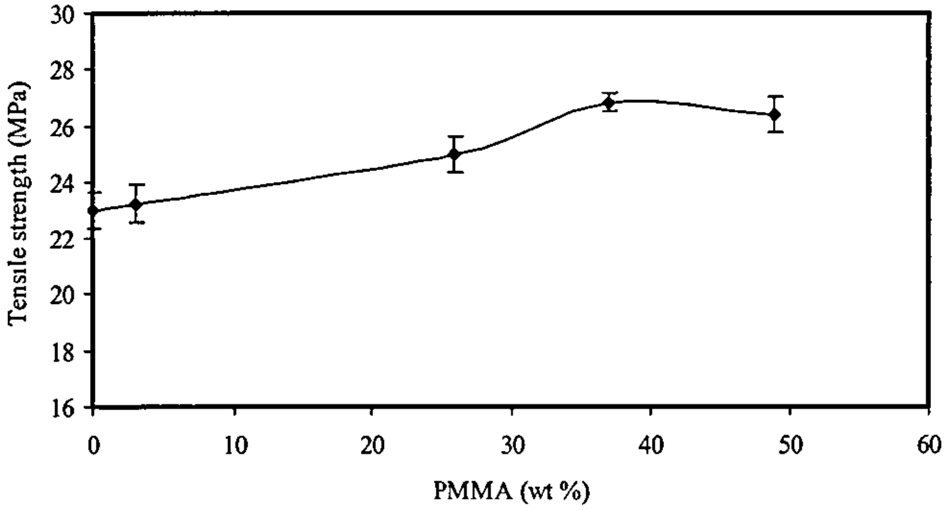


Fig 3 58 Effect of composition on the tensile strength of the full (1.0) IPN series

The 100%, 300% and 500% moduli have significantly increased at a level of 30 wt.% of PMMA content and further increased with increasing PMMA up to 50 wt.%. The combined effects of reinforcement and entanglements caused by the cross-linked PMMA phases and interpenetration contribute to the improved tensile properties (modulus) of these full (1 0) IPNs (Figure 3.59).

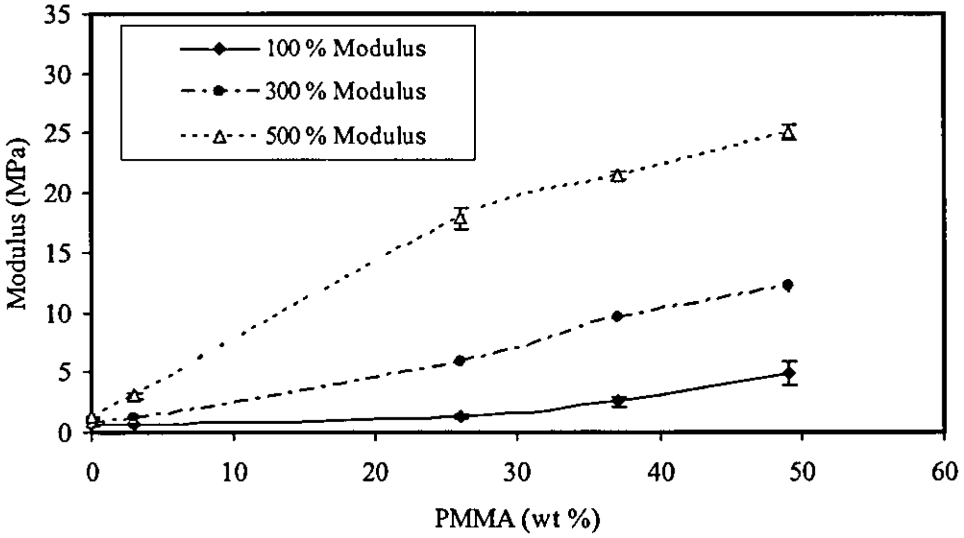


Fig. 3.59 Effect of composition on the 100, 300 and 500% moduli of the full (1.0) IPN series

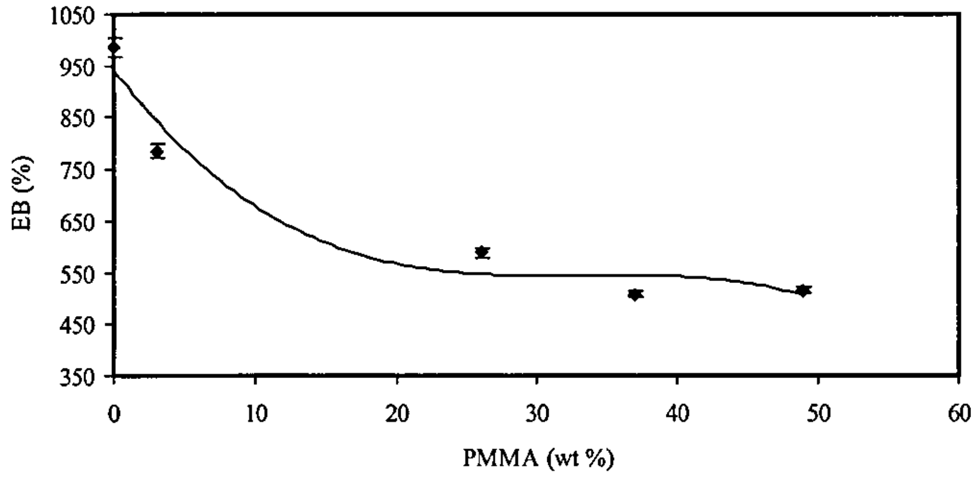


Fig 3 60 Effect of composition on the elongation at break for the full (1.0) IPNs

As expected, the elongation at break decreased with increasing PMMA content (Figure 3.60), due to a reduction in the elastomer content and due to the presence of the interpeneted cross-linked PMMA phases.

Hysteresis data

Energy losses during the cyclic tests are listed in Table 3 29. Hysteresis data of these full IPNs are also shown in Figures 3 61 to 3 63

Table 3 29 Energy loss and hysteresis behaviour data for the full (1.0) IPNs

Sample	Cycle 1		Cycle 2		Cycle 3	
NR/PMMA (wt. %)	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
Control sample*	0.76	0.15	0 35	0 09	0 28	0.04
97/3	0 12	0 27	0 09	0.2	0.06	0.12
70/30	1 21	2 19	0.5	1 16	0.47	0.98
60/40	3 55	4 87	-	-	-	-
50/50	10 0	12.8	-	-	-	-

HL-Hysteresis behaviour is the ratio of energy lost to the energy recovered during the cycling test

*Similarly treated vulcanised NR

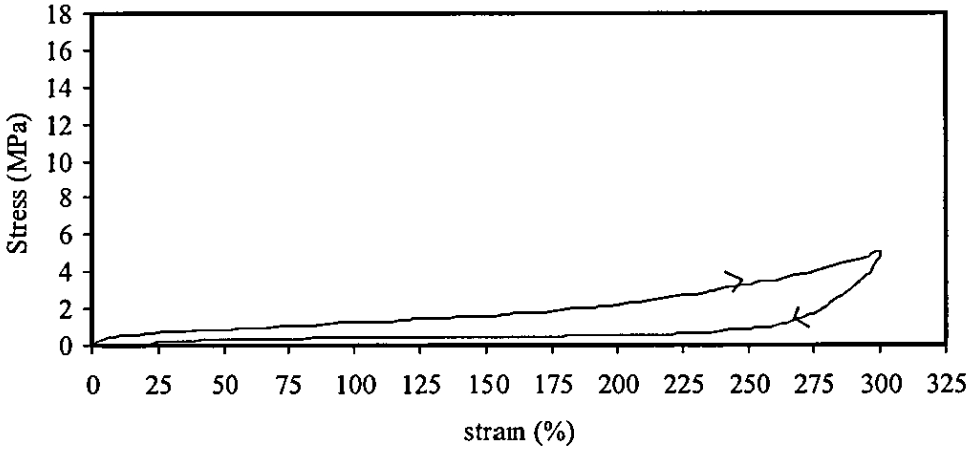


Fig. 3.61 The first hysteresis cycle for the NR70 PMMA30(1 0) full IPN

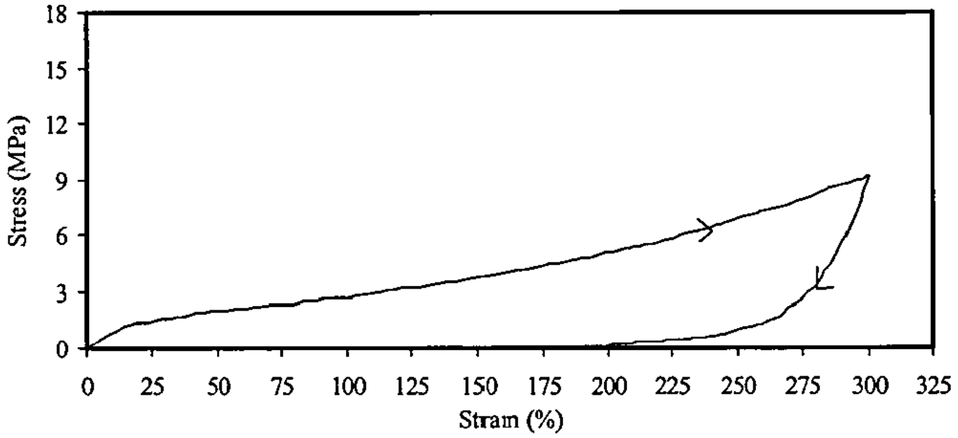


Fig. 3 62 The first hysteresis cycle for the NR60 PMMA40(1 0) full IPN

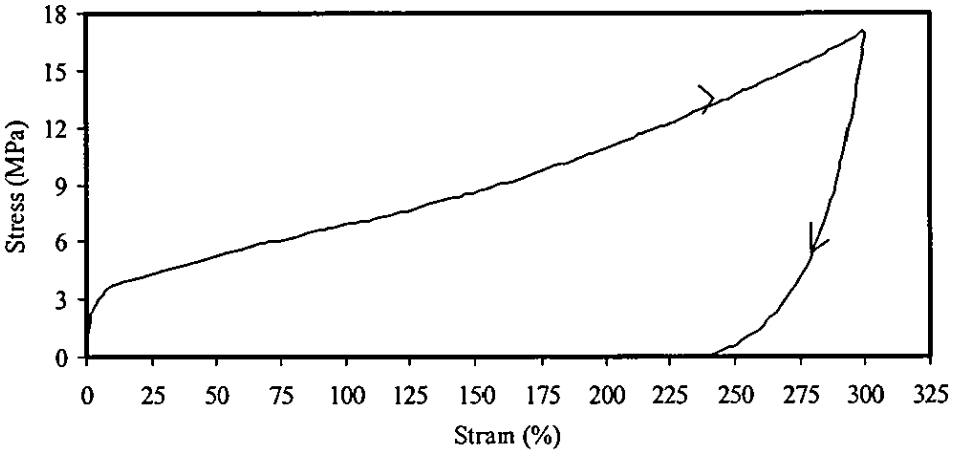


Fig. 3.63 The first hysteresis cycle for the NR50:PMMA50(1 0) full IPN

In general, hysteresis has increased with increasing PMMA content. The same trend has been observed for other IPN series studied in the present investigation. As reported earlier (Roland and Lee, 1990), higher hysteresis values can be obtained by increasing carbon black flocculation The relevance of this in this discussion is that the PMMA phases may act as filler particles and may undergo structural breakdown resulting in a softening of particles This process ultimately leads to a decrease in the fraction of hard component (Mullins and Tobin, 1957). In addition, if there are any trapped NR phases in the PMMA phase, breakdown of the PMMA phase would release such trapped NR phases resulting in increase of fraction of effective soft component in the material. Both these effects may also lead to an increase in the hysteresis of the IPN samples. It is stated that the structure of domains/phases to evolve in deformation is the prime cause of hysteresis and stress-softening (Qi and Boyce, 2005). Stress softening takes place mostly in the first cycle, and thereafter in subsequent cycles stress softening will be reduced and ultimately reach an equilibrium (Qi and Boyce, 2005). Therefore, reduction of energy loss during cycles 2 and 3 may be associated with the reduction of stress softening and breakdown of the PMMA phases present in IPNs.

3.5.4 Full IPNs prepared using EGDM at a level of 1.5 mole%

3.5.4.1 Effect of composition on miscibility

Dynamic mechanical analysis data

The data derived from loss tangent spectra for the full (1.5) IPNs with composition is shown in Table 3.30. The results indicate that there is no clear compositional trend of NR T_g with increase in the amount of PMMA. Nevertheless, the NR loss tangent seems to be broadened by increasing the amount of PMMA up to 50 wt.%, indicating the occurrence of some degree of component mixing (Figure 3.64). As shown from Figure 3.65, the height of the intermittent area between the two glass transitions had increased and a broad peak appeared in the region of 4°C to 110°C. Therefore, it may be assumed that some amount of mixing of the components has occurred in the NR50 PMMA50(1.5) full IPN and further verified from the MDSC data illustrated in Table 3 31. Furthermore, PMMA apparently exists as the continuous phase in the NR50:PMMA50(1.5) full IPN composition as indicated by the presence of a prominent PMMA transition (Table 3.30 and Figure 3.66).

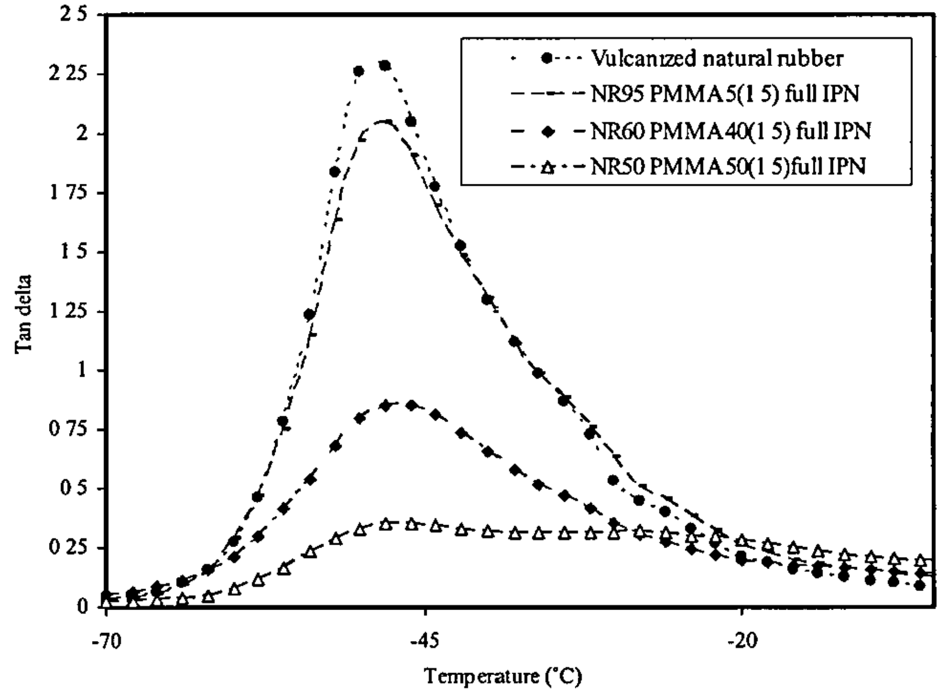


Fig. 3.64 Effect of composition on the NR loss tangent of the full (1.5) IPN series

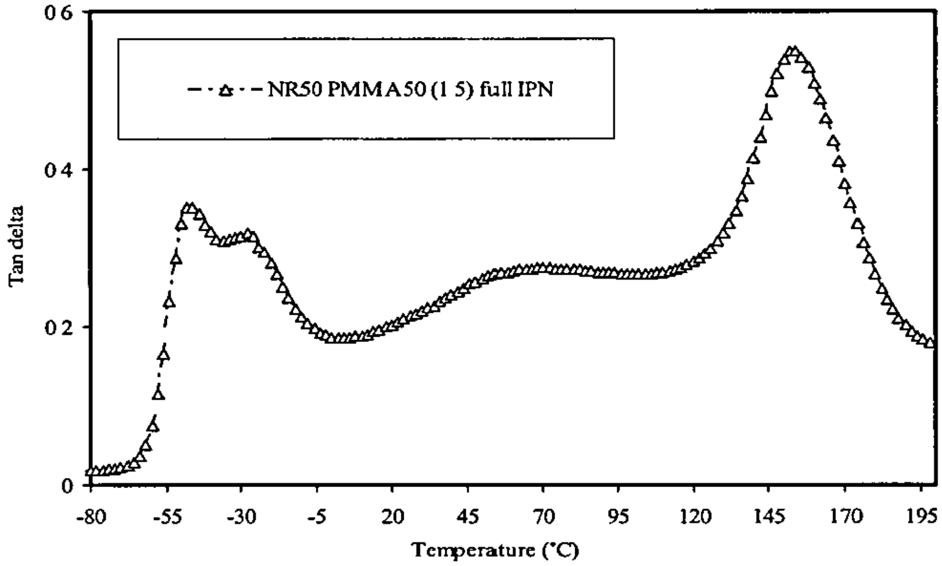


Fig. 3 65 Temperature dependence of the loss tangents of the NR50:PMMA50(1.5) full IPN

Table 3.30 The loss tangent data for the full (1.5) IPNs

NR/PMMA (wt. %)	NR T_g (°C)	Tan $\delta_{NR\text{-}max}$ (°C)	PMMA T_g (°C)	Tan $\delta_{PMMA\text{-}max}$ (°C)
100/0	-49	2.3		
95/5	-48	2 0		
60/40	-47	0.85	154	0.25
50/50	-48	0.35	154	0.55

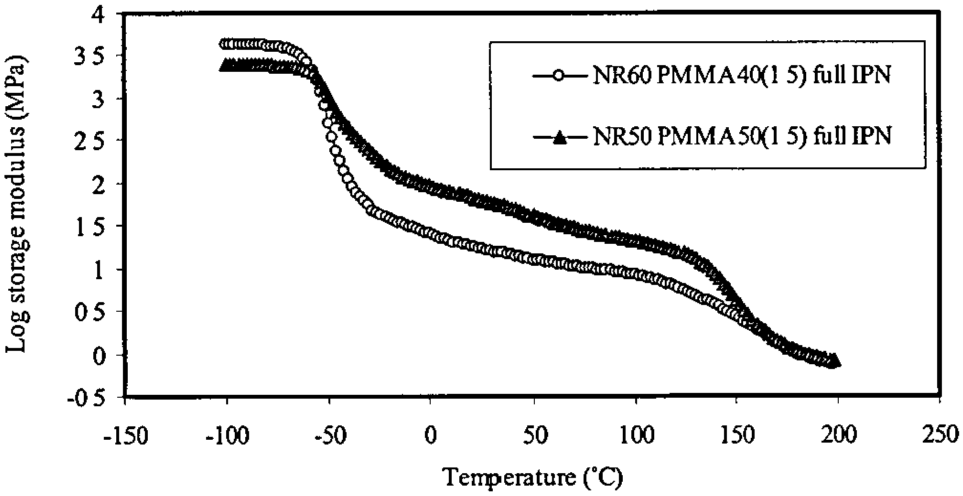


Fig. 3 66 Temperature dependence of the storage modulus for the full (1.5)IPNs with 40 wt.% and 50 wt.%. PMMA content

The behaviour of tan δ_{max} of the NR transition with increase in the PMMA content is similar to the other IPN series (Table 3.30). Diminution of tan δ_{max} with increasing PMMA content is possibly due to two reasons. Firstly, it is attributed primarily to the reduction of the NR content. Secondly, it could be related to the lowering of molecular mobility, caused by interpenetrated cross-linked PMMA network chains in the NR matrix.

The tan δ_{max} of PMMA transition has increased with an increase of the PMMA content (Table 3 30) This trend is obvious as the magnitude of loss tangent reflects the relative amounts of the polymers in the system. Nevertheless, the PMMA transition of the NR60:PMMA40(1.5) full IPN is significantly broad, which is indicative of some mixing of the PMMA component. This is further confirmed by the MDSC data.

Despite some evidence for mixing, these IPNs can be considered as phase separated as indicated by the presence of two distinct transitions due to the NR and PMMA components.

Analysis of MDSC data

The data derived using derivative complex Cp full (1 5) IPNs are illustrated in Table 3.31. According to the data in Table 3.31, the NR50:PMMA50(1.5) full IPN composition does exhibit significant amount of interphasel content and are in agreement with the DMTA data. .

Table 3.31 Calculated interphase fractions (δ) and multiple peak analysis data for the full (1.5)IPNs

Sample composition	MDSC data				
NR/PMMA (%)	δ_{NR}^{*} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
			Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
70: 30	0.16	0.22	25	26	16
60: 40	0 15	0.28	28	20	19
50: 50	-	**	38	2	16

** The δ_{PMMA} content has not been calculated because of the difficulties in resolving the broad PMMA transition

δ_{NR}^{*}, calculated with respect to the vulcanized NR

δ_{PMMA}, calculated with respect to the cross-linked PMMA (EGDM 1.5 mole %)

Table 3.32 Effect of composition on the tensile strength for the IPNs prepared using EGDM at a level of 1.5 mole percent

Sample composition	Tensile properties				
NR/PMMA ratio	100 % Modulus (MPa)	300 % Modulus (MPa)	500 % Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
95/5	0.6	0.96	1.9	21.3	873
	(0.03*)	(0.08*)	(0.44*)	(1.7*)	(39.7*)
73/27	1.2	3.9	14.6	31.2	692
	(0.09*)	(0.76*)	(1.5*)	(0.77*)	(32.5*)
64/36	3.8	11.6	26.8	30.2	575
	(0.37*)	(0.46*)	(0.92*)	(1.2*)	(17.9*)
52/48	9.5	19.4	-	25.9	407
	(0.39*)	(0.92*)		(1.6*)	(28.4*)

* Standard deviation

3.5.4.2 Effect of composition on stress-strain behaviour

Tensile data

Deviations of the tensile strength with composition of the full (1.5) IPNs are given in Table 3.32 Unlike for the full (0.5) IPNs, the optimum tensile strength was obtained at a level of 30 wt.% to 40 wt.% PMMA.

The effect of composition of these IPNs on the modulus is also shown in Table 3.32. Accordingly, the 100%, 300%, 500% moduli values showed an increasing trend with an increasing PMMA content, except for the samples containing 5 wt % of PMMA The improved modulus values of the full (1.5) IPNs having 30 – 40 wt.% PMMA are primarily the result of the filler reinforcement caused by the hard, glassy cross-linked PMMA phases. In addition, the elongation at break decreased with increasing PMMA content (Table 3.32). Similar findings were obtained in most of the IPNs investigated in this study. The reduction of elongation at break may be mainly the result of lowering of mobility of polymer chains due to interpenetration of PMMA particles into the NR network.

Hystereis data

The energy losses during cyclic tests are listed in Table 3.33. In addition, the hysteresis data for the full (1.5) IPNs are presented in Figures 3.67 to 3.68. A general trend of increasing hysteresis with increasing PMMA content was observed.

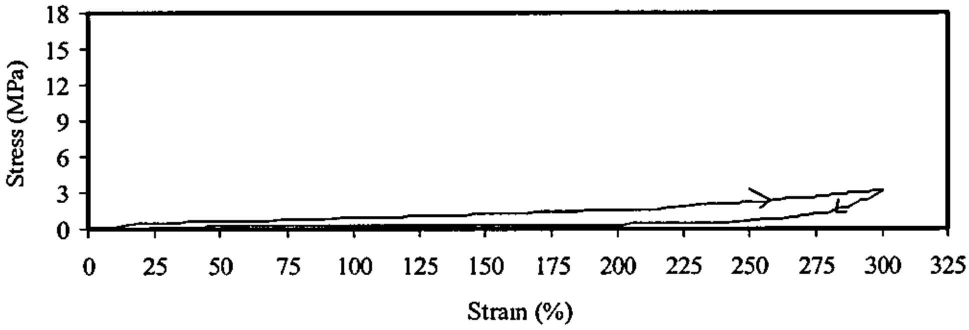


Fig 3 67 The first hysteresis cycle of the NR 70. PMMA 30 (1.5) full IPN

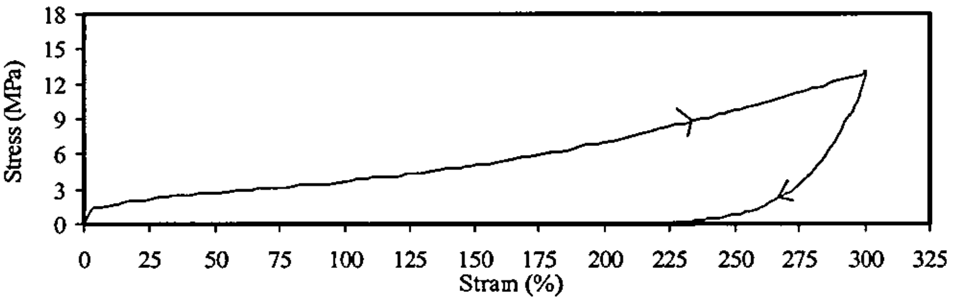


Fig. 3.68 The first hysteresis cycle of the NR60 PMMA 40(1.5) full IPN

Table 3.33 Energy loss and hysteresis behaviour for the (1.5) IPNs

Sample	Cycle 1		Cycle 2		Cycle 3	
NR/PMMA Ratio	Energy loss (J)	HL	Energy loss (J)	HL	Energy loss (J)	HL
Control sample*	0.76	0.15	0.35	0.09	0.28	0.04
95/5	0.10	0.16	0.05	0.09	0.04	0.07
70/30	1.83	2.17	0.70	1.07	0.53	0.91
60/40	7.10	10.20				
50/50	13.5	17.70				

HL- Hysteresis behaviour is the ratio of energy lost to the energy recovered during the cycling test

* Similarly treated vulcanised NR

3.5.4.3 Effect of composition on the sol gel ratio

Results of extraction experiments (Table 3.19) clearly indicate that as the IPN PMMA content increased the amount of soluble, extractable material obtained by hot acetone extraction process had not markedly increased as expected. A similar trend was obtained in the semi-2 IPN series. This trend had been attributed to the cross-linking of the PMMA phase which reduces dramatically the solubility of the PMMA in the acetone solvent.

CHAPTER 4

A critical overview of the effects of cross-linking of the NR and/or the PMMA components on the dynamic and physical properties of the blends, semi-1, semi-2 and full IPNs

4.1 Introduction

In this study, different types of IPNs based on NR and PMMA were prepared at various EGDM levels by the sequential polymerisation method. The resultant blends and IPNs possessed distinctive morphologies and physical properties. A detailed comparison of the dynamic and other mechanical properties of these materials will now be presented In addition, the effects of cross-linker level on the dynamic and mechanical properties of these IPNs and the blends are discussed.

4.2 Effect of cross-linking of the NR component on the dynamic and other mechanical properties

4.2.1 Effect of cross-linking of the NR component on miscibility

Cross-linked polymers are being increasingly used as engineering materials. Substantial attention has been drawn to the effect of cross-linking of the components on the morphology and mechanical properties of multi-component materials. The effect of cross-linking of the first-formed polymer on the IPNs morphology is well documented (Sperling, 1994; Donatelli *et al*, 1976; Hourston and McCluskey, 1985; Hourston and Romaine, 1991). In this study, attempts were made to investigate the effect of cross-linking of the first formed polymer (NR) on the extent of mixing of the components

Cross-linking of the first-formed polymer results in smaller domains often with a large inter-phase component (Sperling, 1994). Theoretically, this leads to an improvement in the extent of mixing of the components resulting in shifts of the glass transition relaxations corresponding to the individual components present in the material In the case of cross-linked systems, the morphology of the IPNs vary depending on the sequence of the processes of gelation and phase separation. As this study is limited to the sequential IPNs, it is known that the gelation of the first polymer has occurred prior to the phase separation of the second polymer. Therefore, it would be expected that the cross-linking of the-first-formed polymer leads to increase the extent of mixing of the components.

Semi-1 IPNs and full IPNs which were expected to contain 10 wt.% and 20 wt.% PMMA, varied significantly in their actual and target compositions due to the inhibition of MMA polymerisation. Hence, these IPNs are represented by their actual values of the composition instead of the target composition

The effect of cross-linking of the NR component on the NR loss tangent for the semi-1 IPN with a NR92:PMMA8 composition is presented in Figure 4.1 The DMTA spectrum for the cross-linked NR is also shown in Figure 4.1. Accordingly, compared to the NR, the height of the loss tangent has been marginally reduced by cross-linking.

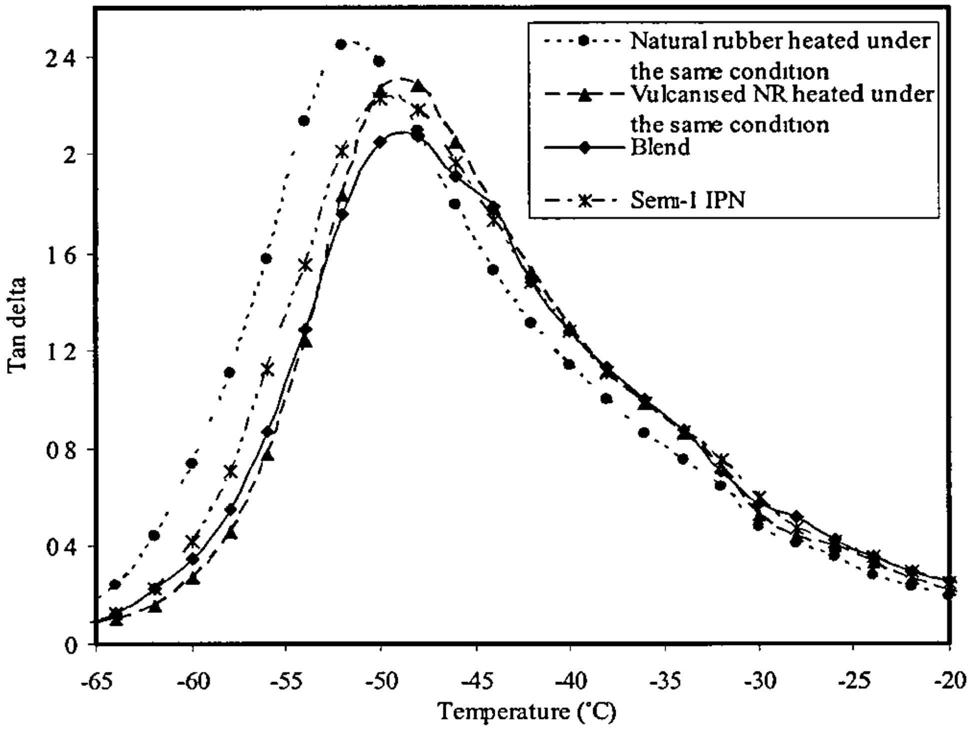


Fig. 4.1 Effect of cross-linking of the NR component on the NR loss tangent for the blend and semi-1 IPN with a NR90:PMMA10 composition

In general, cross-linking of the NR component results in a network with an increased number of effective network chains. As a result, the elastic response to a sinusoidal stress, or strain, has increased, simultaneously decreasing the heat-build up during the recovery. As a consequence, tan δ decreased with the cross-linking of the NR component (Akhtar and Bhagawan, 1987) This is in agreement with the results of Hur *et al.* (1989), which also indicated that when the number of effective network chains has increased, tan δ_{max} decreased.

In addition, compared to the uncross-linked natural rubber, the T_g of the vulcanised NR component has increased by 3°C. In this case, it should be noted that the extent of cross-linking of the NR component had been kept intentionally low, as such; the effect of cross-linking of NR component on the tan δ_{max} of the NR transition is not prominent. Similar observations were made by Reichenboch *et al.* (1990) and Liau (1999). Lian and Chen (1998) indicated that the cross-links would not result in significant change in molecular motions when the cross-linker level is low for example less than 1phr of sulphur on natural rubber.

As it can be seen from the Figure 4.1, the height of the NR loss tangent of the blend is lower than that of the semi-1 IPN. It is expected that the height or the magnitude of the loss tangent of the NR component should decrease with the cross-linking of the NR phase, Nevertheless, the semi-1 IPNs having NR92 PMMA8 (Figure 4.1) composition deviate from this general trend. As explained earlier, the polymerisation of MMA has not occurred to the desired level due to the inhibition of the polymerisation reaction of MMA by sulphur, leaving higher level of NR in this sample. Therefore, degradation of NR may have occurred to a certain extent in this semi-1 IPN where complete polymerisation of the MMA monomer had not been occurred. As the loss tangent reflects the mobility of the NR polymer chains, one would expect an increase of the height or magnitude of loss tangent due to the degradation of polymer.

Unlike for the NR92:PMMA8 semi-1 IPN, tanδ_{max} of the NR70 PMMA30 semi-1 IPN (Figure 4.2 and Table 4.1) was lower than for the NR/PMMA blend. It has been established that the intensity of the loss tangent at the glass transition temperature represents the extent of mobility/movement of polymer chains (Roberts and White, 1973). The both effects; cross-linking of the NR component and the enhanced mixing of the PMMA component as was evident from the MDSC data (Table 4 2), would restricts the mobility of the NR polymer chains, and, therefore, can be identified as the potential factors which affected the intensity of the NR loss tangent in the semi-1 IPNs

Table 4.1 Dynamic mechanical data for the blends and semi-1 IPNs

Sample	NR T_g (°C)	Tan $\delta_{\mathrm{NR\,max}}$	PMMA T_g (°C)	Tan $\delta_{\mathrm{PMMA\,max}}$
NR90:PMMA10 blend	-49	2.1	-	-
NR90:PMMA10 semi-1 IPN	-49	2.2	-	-
NR70.PMMA30 blend	-46	1.7	156	0 2
NR70.PMMA30 semi-1 IPN	-47	1.4	150	0.2
NR50:PMMA50 blend	-45	1.3	154	0 4
NR50:PMMA50 semi-1 IPN	-47	0.6	146	0.4

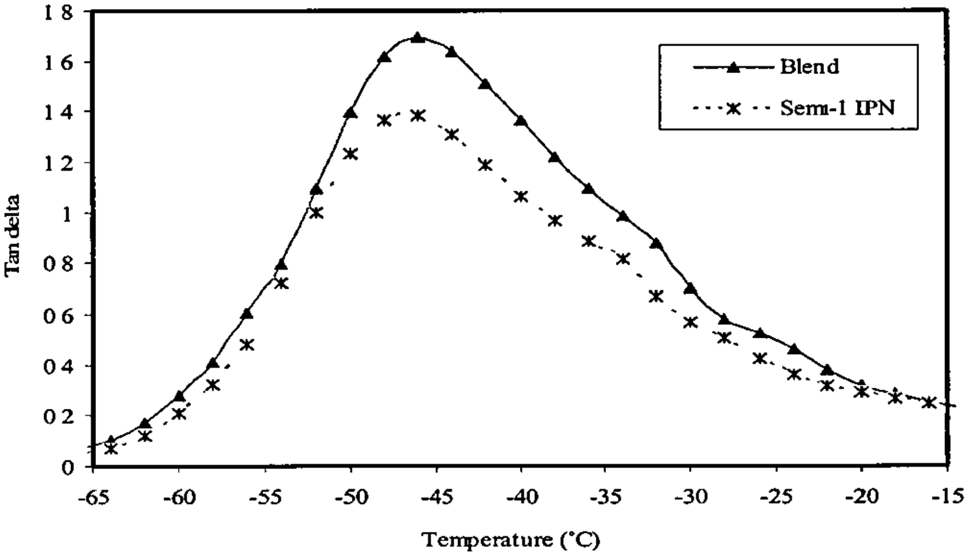


Fig. 4 2 Effect of cross-linking of the NR component on the NR loss tangent for the blend and the semi-1 IPN with a NR70.PMMA30 composition

Moreover, the DMTA data clearly indicated that the height of the NR loss tangent of the semi-1 IPNs containing 40-50 wt % PMMA (Table 4 1) is significantly lower than the corresponding blend, indicating some molecular mixing of the components and/or hindering of segmental mobility of the NR polymer chain segments. The values of dCp/dT vs temperature signals for the NR transition of the semi-1 IPNs exhibited the same trend (Figure 4 4) As dCp/dT is proportional to the weight fraction, it may be anticipated that the reduction of the magnitude of the derivative of the complex Cp for the NR transition could result from the reduction of pure rubber content or be due to cross-linking of the NR. The multiple peak analysis data support the former view

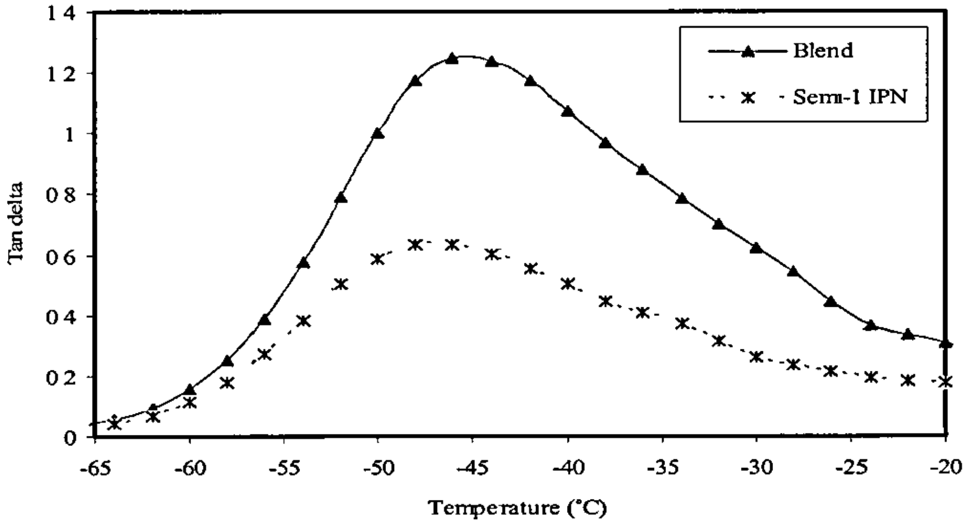


Fig. 4.3 Effect of cross-linking of the NR component on the NR loss tangent for the blend and the semi-1 IPN with a NR50:PMMA50 composition

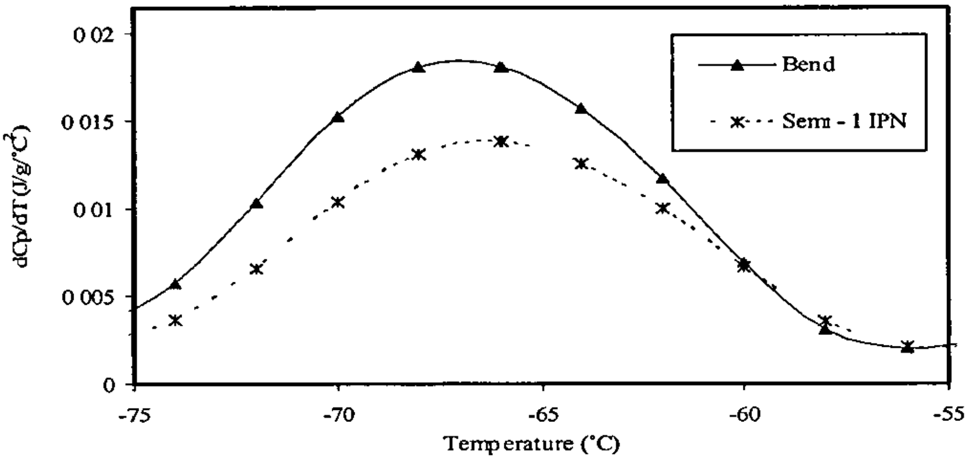


Fig. 4 4 Effect of cross-linking of the NR component on dCp/dT as a function of temperature for the NR component of the blend and semi-1 IPN with a NR50·PMMA50 composition

Table 4.2 Calculated weight fractions of the natural rubber and poly(methylmethacrylate) components in the interphase and multiple peak analysis data for the blends and semi-1 IPNs

Sample	MDSC data				
			Multiple peak analysis data		
Type of the material	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR70:PMMA30 Blend	0.16	0.0	16	12	11
NR70:PMMA30 semi-1 IPN	0.15	0.07	30	14	9
NR50:PMMA50 Blend	0.16	0.04	23	16	14
NR50 PMMA50 semi-1 IPN	0.21	0.23	30	13	26

δ_{NR}, calculated with respect to the un-vulcanized NR

By taking the degree of shift of NR T_g in to an account, it is noted that the shift of TgNR was higher in blends (5°C to 6°C) than the semi-1 IPN (2°C) compared to its control sample without having any PMMA. This may reveal that the extent of mixing of natural rubber in the semi-1 IPNs was relatively lower than their equivalent blend counterparts implying cross-linking of the NR component reduces the extent of mixing of the NR component. With respect to the dynamic mechanical properties, the effect of cross-linking of the NR component does not have a prominent effect on the T_g of the NR loss tangent in comparison with the equivalent blend (Figures 4.2 and 4.3 and Table 4.1). Reduction of the mobility of NR polymer chains due to interpenetration of PMMA and/or due to the grafting of PMMA onto the NR polymer chains are considered as the prime reasons for having higher NR T_g for the compositionally identical blend. The presence of graft copolymer and entrapped molecules resulting due to the interpenetration (Sperling, 1971) would enhance the degree of mixing of the NR component resulting in a prominent inward shift of the NR transition in the blend. As such, a significant divergence in the corresponding T_gs of the semi-1 IPN and the equivalent blend could not be distinguished.

When the PMMA transition is taken into consideration, the DMTA data (Table 4 1) indicated that the T_g of the PMMA transition of the semi-1 IPNs containing 30 - 50 wt.% PMMA has shifted to lower temperature by 6°C to 8°C indicating some molecular mixing of the components (Table 4.1 and Figure 4.5). A similar trend has been obtained for the complex Cp data shown in Figure 4.6 The multi-peak analysis data calculated using MDSC data clearly indicated that the interphase content increased significantly with cross-linking of the NR component. These results suggest that the cross-linking of the NR component improves the extent of mixing of the PMMA component. Similar observations were reported by Donatelli *et al.* (1976); Hourston and McCluskey, (1985); Hourston and Romaine, (1991). As a result of the cross-linking of the NR component, smaller domains are formed, and, subsequently, the specific surface interactions were increased (Donatelli *et al*, 1976). This process leads to enhanced miscibility. However, it has been reported that many of the interactions occur at the phase boundaries and the actual amount of molecular mixing is in fact very small (Donatelli *et al*, 1976).

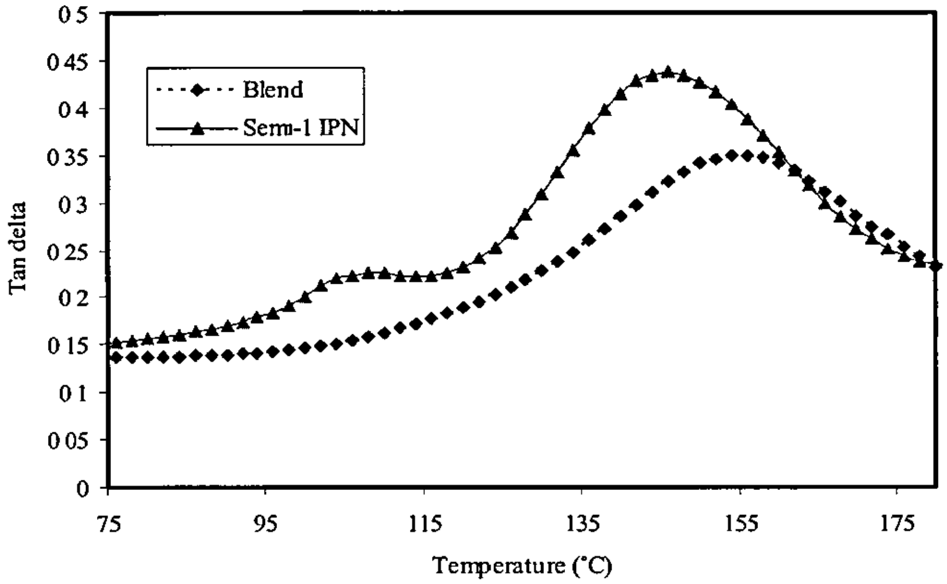


Fig 4.5 Effect of cross-linking of the NR component on the PMMA loss tangent for the blend and the semi-1 IPN with a NR50 PMMA50 composition

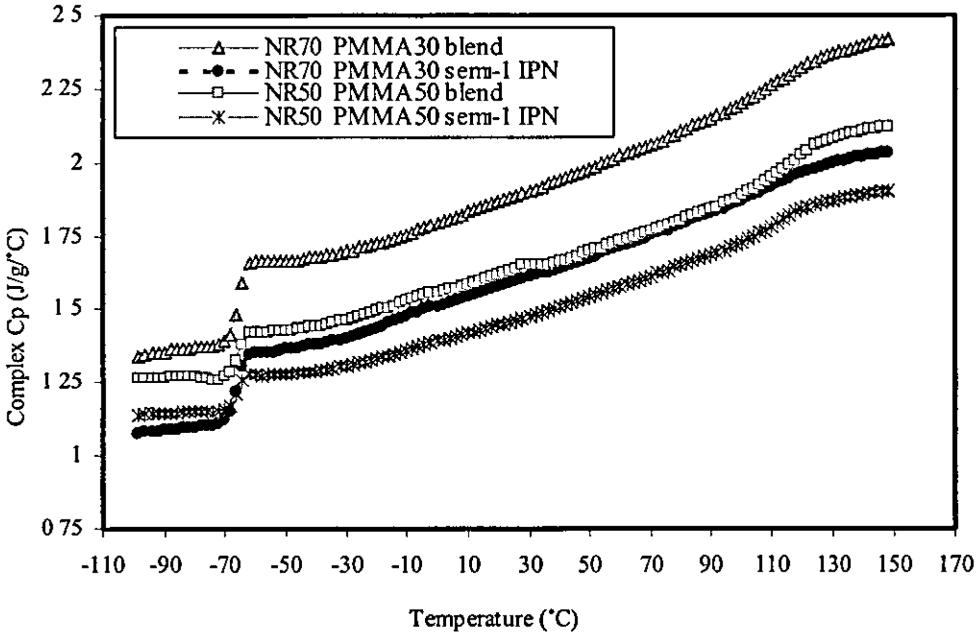


Fig. 4.6 Dependence of the complex heat capacity with temperature for the blends and semi-1 IPNs with a NR70 PMMA30 and NR50:PMMA50 composition

4.2.2 Effect of cross-linking of the NR component on the stress-strain behaviour

Tensile data

Compared to the corresponding NR/PMMA blend, cross-linking of the NR component of these materials imparted a significant increase of tensile strength of the semi-1 IPNs containing 10 to 40 wt.% PMMA (Figures 4.7 and 4.8)

NR is an amorphous polymer at ambient temperature and it was assumed that amorphous chain segments are oriented with strain and this is then followed by crystallization (Toki *et al.*, 2002). However, they have used the *in situ* synchrotron wide-angle X-ray diffraction (WAXD) technique to show that crystallization starts at a strain of *ca* 2.5, at which point the fraction of oriented chain segments decreases and the fraction of induced crystals begin to increase. At a strain of 3, the fractions of oriented chains and the induced crystals become equal At strains larger than 3, the crystalline phase becomes the dominant one. The oriented amorphous chain segments are the precursors of the induced crystals Their study further suggests that the strain-induced crystallites form a physical cross-linked network which bears most of the applied load (Toki *et al*, 2002). Nevertheless, it is concluded that the majority of polymer chains (75 %) (Toki *et al*, 2002) of NR remain in the coiled state (Gehman and Field, 1939, Luch and Yeh, 1973; Shimomura *et al.*, 1982) even at a larger strain indicating that only 20% strain-induced crystallites and about 5% oriented amorphous chains are present. When cross-links are considered, they may have a dual effect on strain-induced crystallisation. Sulphur cross-links can also facilitate the orientation of polymer chains and thereby induce strain crystallisation (Toki *et al*, 2002). On the other hand, these cross-links may hinder the growth of crystalline structures especially in the regions containing polymer chains with lower molecular weight between cross-links (lower M_c)

When a force is applied to a cross-linked material, the load applied may be borne by chemical cross-links as well as the physical network of strain-induced crystals. This process imparts a higher tensile strength. On the other hand, improved tensile properties could be ascribed to the cross-linking of the NR component by the conventional vulcanising system containing sulphur as the curing agent. The tensile rupture depends on the degree of crystallisation (Bateman, 1963), cross-link density, type of cross-link, filler type and on the size of filler particles (Bateman, 1963) etc Accordingly, the type of cross-link plays a vital role in tensile rupture. In this study, a conventional sulphur system has been used for vulcanisation of the NR. In fact, a system of this nature usually provides a higher number of polysulphidic linkages, which possess the lowest bond energy. It has been reported that the lower the bond energy, the higher the tensile strength of such vulcanizates (Brydson, 1978) This is mainly due to the occurrence of a yield mechanism for the dissipation of stress at the critical point of failure with the break down of labile bonds under stress (Brydson, 1978).

However, the variation of the tensile strength of the NR50 PMMA50 semi-1 IPN (Figure 4 9) from the corresponding NR/PMMA blend was less significant.

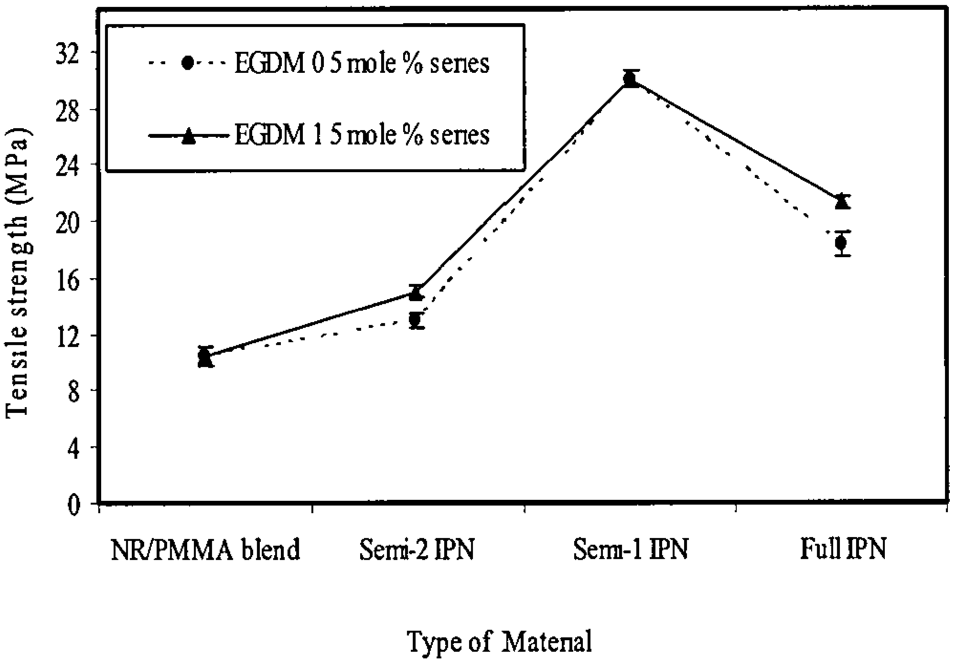


Fig. 4 7 Effect of cross-linking of the components on the tensile strength of the blend and the IPNs with a NR90.PMMA10 composition

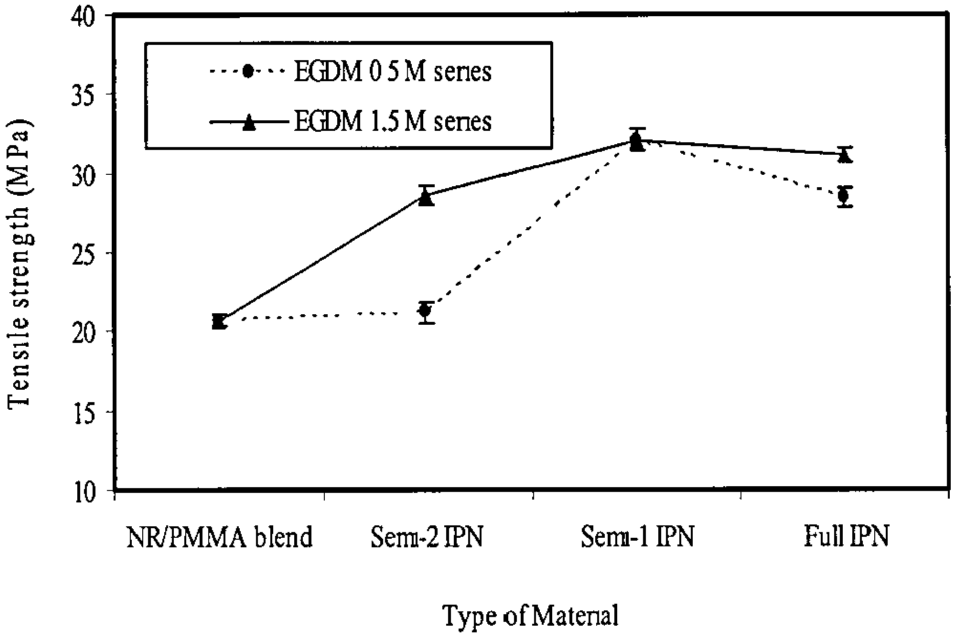


Fig 4.8 Effect of cross-linking of the components on the tensile strength of the blend and the IPNs with a NR70:PMMA30 composition

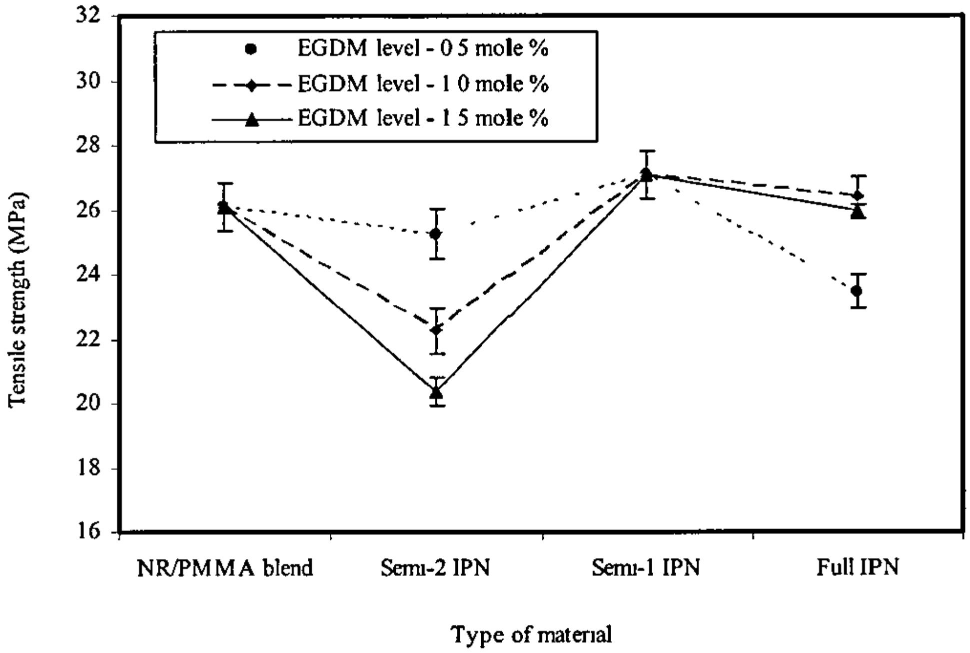


Fig. 4.9 Effect of cross-linking of the components on the tensile strength of the bend and the IPNs with the NR50:PMMA50 composition

4.3 Effect of cross-linking of the PMMA component on the dynamic and mechanical properties of the semi-2 IPNs

4.3.1 Effect of cross-linking on miscibility

Dynamic mechanical data analysis for the NR transition

The effects of cross-linking of the PMMA component on the NR loss tangent are presented in Figures 4.10 to 4 12. A comparison of the data for the corresponding NR/PMMA blend and the semi-2 IPNs (Figures 4 10 and 4.11 and Table 4 3) show that the T_g derived from the loss tangent does not vary much, with the exception of the NR80.PMMA20(0 5) semi-2 IPN (Figure 4.10) and the NR60 PMMA40(1.5) semi-2 IPN (Figure 4.12).

In Figure 4 12, the T_g of the NR component of the semi-2 IPN (1.5) has been shifted towards higher temperature by 3°C, which is indicative of enhanced component mixing A similar observation had been seen for the T_g of the PU component in semi IPNs based on PU/polyvinyl acetate, which has been ascribed to some molecular mixing of the components (Hourston and Zia, 1984)

Table 4.3 Dynamic mechanical data for the blends and the semi-2 IPNs

Sample	NR T_g (°C)	Tan δ_{NR} max	PMMA T_g (°C)	Tan δ_{PMMA} max
NR90:PMMA10 blend	-49	2.1	-	-
NR90:PMMA10 semi-2 (0.5)IPN	-48	1.8	-	-
NR90:PMMA10 semi-2 (1.5)IPN	-48	1.9	-	-
NR80:PMMA20 blend	-49	2.1	-	-
NR80:PMMA20 semi-2 (0.5)IPN	-46	1.8	-	-
NR80:PMMA20 semi-2 (1.5)IPN	-47	1.9	173	0.3
NR70:PMMA30 blend	-46	1.7	156	0.2
NR70:PMMA30 semi-2 (0.5)IPN	-46	1.4	160	0.3
NR70:PMMA30 semi-2 (1.5)IPN	-46	1.6	178	0.2
NR60:PMMA40 blend	-48	1.5	158	0.3
NR60:PMMA40 semi-2 (1.5)IPN	-45	0.8	156	0.4
NR50:PMMA50 blend	-45	1.3	154	0.4
NR50:PMMA50 semi-2 (0.5)IPN	-48	0.7	154	0.4
NR50:PMMA50 semi-2 (1.5)IPN	-49	0.5	150	0.5

* PMMA transition present as a broad asymmetric peak

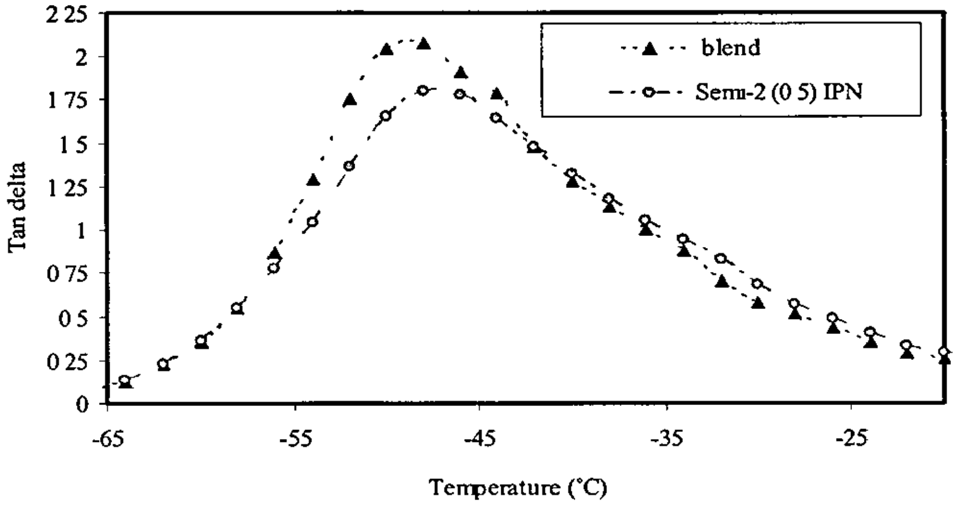


Fig 4.10 Effect of cross-linking of the PMMA component on the NR loss tangent for the blend and the semi-2 (0.5) IPN with a NR90:PMMA10 composition

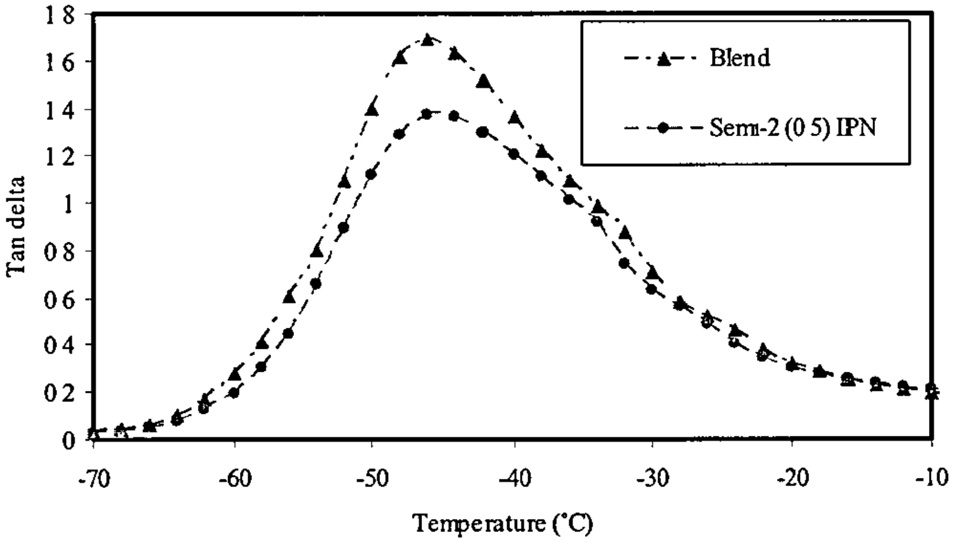


Fig. 4.11 Effect of cross-linking of the PMMA component on the NR loss tangent for the blend and the semi-2 (0.5) IPN with a NR70 PMMA30 composition

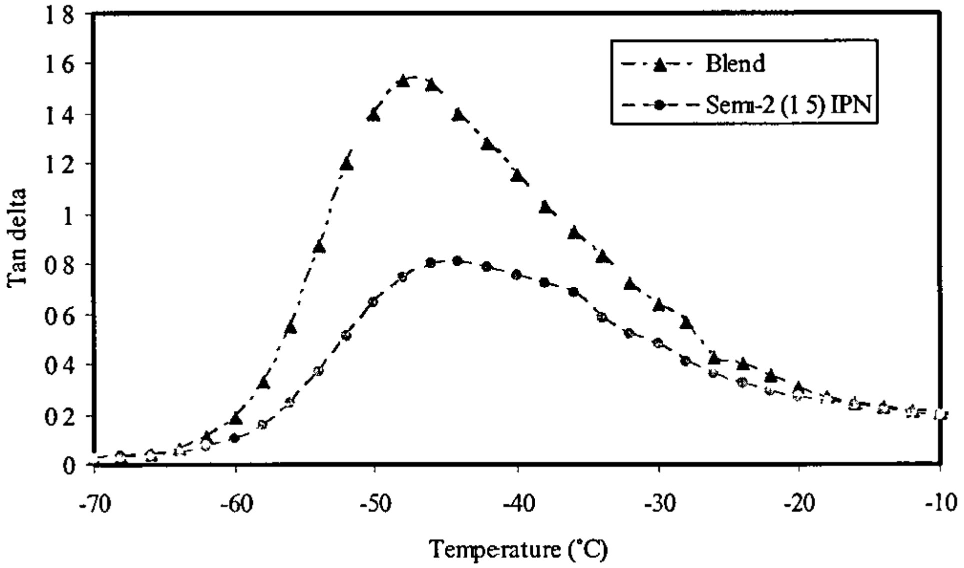


Fig. 4 12 Effect of cross-linking of the PMMA component on the NR loss tangent for the blend and the semi- 2 (1.5) IPN with a NR60 PMMA40 composition

Despite the evidence obtained for the NR T_g shift of the NR60.PMMA40(1.5) semi-2 IPN sample to higher temperatures, in general, the results clearly indicate that the cross-linking of the PMMA component does not have a strong effect on the T_g of the NR component.

However, the values obtained for the tan $\delta_{NR\text{-}max}$ of most of the semi-2 IPNs are substantially lower than those of the corresponding NR/PMMA blend (Table 4.3). The same trend was found from the MDSC data shown in the Figure 4.13. In addition, as the cross-link density increased from 0 5 mole% to 1 5 mole%, the magnitude of the NR transition obtained by the MDSC data had also declined significantly

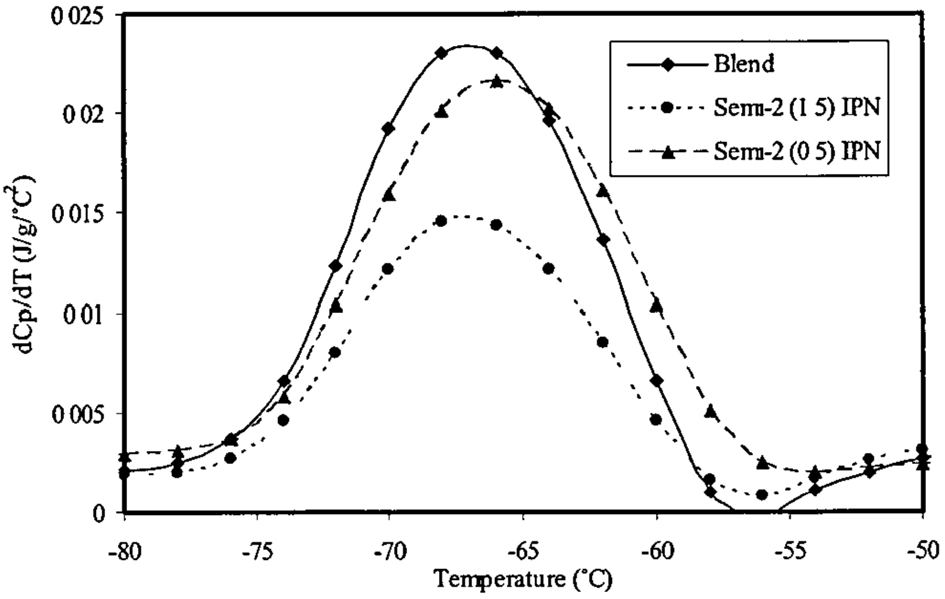


Fig. 4 13 dCp/dT vs temperature for the NR transition of the blend and the semi-2 IPNs with a the NR70 PMMA30 composition

Therefore, the reduction in the magnitude or in the height of the NR transition of the semi-2 IPNs than the identical blend, may be due to two reasons the reduction in the pure NR component (homopolymer); and/or to the lowering of mobility of the NR polymer chains It may be assumed that the reduction of homopolymer content of NR could be resulted from the formation of interfacial layers by inter-diffusion of components driven by chemical potential gradient If such processes have occurred, then the weight fraction of the NR component in the interfacial region would be expected to be high in the semi-2 IPN sample. Data shown in Table 4.4 provide strong evidence for the presence of higher interphase content in the semi-2 IPNs than the equivalent blends indicating cross-linking of the PMMA component facilitates mixing of components. The restriction of the phase separation of components by the cross-links (Lee *et al*, 1992) in the PMMA phase is considered as the reason for this behaviour.

Table 4 4 Calculated weight fractions of the NR and PMMA components present in the interphase and multiple peak analysis data for the blends and semi-2 IPNs

Sample	MDSC data				
			Multiple peak analysis data		
Type of the material	δ_{NR} (weight fraction)	δ_{PMMA} (weight fraction)	Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR70 PMMA30 Blend	0.16	0 0	16	12	11
NR70 PMMA30 semi-2 (0.5)IPN	0.14	0.05	25	8	12
NR70:PMMA30 semi-2 (1 5)IPN	0.41	0 00	31	18	3
NR50:PMMA50 Blend	0.16	0.04	23	16	14
NR50.PMMA50 semi-2 (0 5) IPN	0.20	0 0	30	20	16
NR50 PMMA50 semi-2 (1.5) IPN	0.20	0.38	28	27	0.5

δ_{NR}, calculated with respect to the un-vulcanized NR

Several studies indicate that the addition of a bi-functional monomer such as divinyl benzene, triethylene glycol dimethacrylate (Shukla and Athalye, 1993) in small quantities leads to an increase in the amount of grafted products

Therefore, it may be assumed that EGDM perhaps enhances the grafting of PMMA onto the NR, thus improving the miscibility with the NR component.

Therefore, it can be assumed that the major contribution to the lowering of the height of the NR loss tangent in the semi-2 IPNs comes from the improved mixing of the NR components because of the cross-linking of the PMMA component This view is further confirmed by the MDSC data shown in Table 4 4, where significantly higher weight fractions of the NR components were found for the semi-2 IPNs, prepared using 1 5 mole% of EGDM. Moreover, considerably high level of mixed phases including interphase were obtained for the NR70 PMMA30 and NR50:PMMA50 semi-2 IPNs, prepared using EGDM at a level of 1 5 mole% (Table 4 4). This is further evident from the complex heat capacity data at the NR transition of NR70:PMMA30 semi-2 IPN (1.5) (ΔCp = 0.12) (Figure 4.14), which indicated that the increment of complex Cp at the NR transition is relatively low compared to the compositionally analogous blend (ΔCp = 0.22).

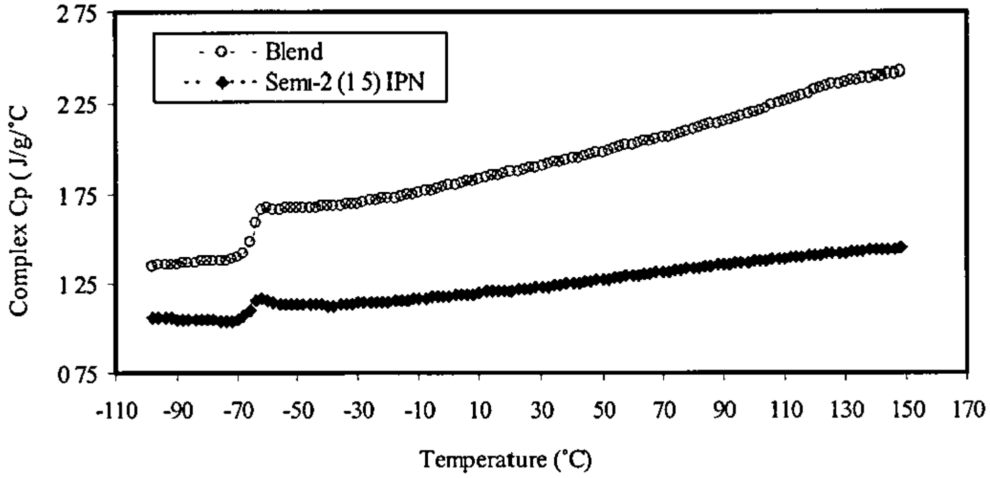


Fig. 4.14 The effect of cross-linking of the PMMA component on the complex heat capacity of the blend and semi-2 (1 5) IPN with a NR70:PMMA30 Composition

As the heat capacity of a particular component depends on its weight fraction, reduction of the heat capacity at the NR transition may indicate the presence of a smaller amount of NR in the semi-2 IPN (1 5) sample.

This evidence possibly indicates that the extent of mixing of the NR component increases substantially with cross-linking of the PMMA component. The effect of level of EGDM on the extent of mixing of the NR component is shown in Table 4.4. Accordingly, the extent of mixing of the NR component of semi-2 IPNs containing 30 – 40 wt.% PMMA apparently increases with increase in the level of EGDM from 0.5 to 1 5 mole%. This could be a result of the improved component mixing (Table 4 4) due to a reduction in the size of domains an/or the chain length between cross-links of the PMMA polymer chain, as a result of increased cross-link density in the PMMA phase Mathew and Thomas (2001) stated that uniform distribution of phases and appreciable reduction in domain size resulted due to interpenetration and cross-linking of the second component in a full IPN when compared to the semi-1 IPN based on NR/PS IPN (Mathew and Thomas, 2001). This implies that the cross-linking of the second phase also leads to a reduction in domain size.

Dynamic mechanical data analysis of the PMMA transition

The consequence of cross-linking of the PMMA component on its miscibility apparently depends on the composition of the material Comparison of the T_g of the PMMA loss tangent for the materials having 10 wt.% PMMA content could not be made because of the difficulty encountered in the resolving the minor PMMA transition

The effect of cross-linking of the PMMA component on its PMMA loss tangent for the semi-2 IPNs with a NR70 PMMA30 composition is shown in Table 4 3 and Figure 4.15 (DMTA data) and Figure 4 16 (MDSC data). Compared to the compositionally identical blend, shifting of the PMMA T_g of NR70 PMMA30(0 5) semi-2 IPNs towards a higher temperature region signifies a reduction in the mobility of the PMMA polymer chains due to cross-linking (Figure 4 15) Further increase of the EGDM cross-linker level up to 1.5 mole% led to a further increase of the PMMA T_g in the semi-2 (1.5) IPN (Table 4 3 and Figures 4 15) This would be an expected trend as cross-linking of the PMMA polymer chains results in a diminution of the mobility of PMMA polymer chains segments and thereby affects the cooperative motions. Vancaeyzeele *et al.* (2006) also observed such a trend for the Tg of the PS transition in poyisobutene/polystyrene (PS) IPNs and they ascribed this effect to the cross-linking effect of the PS phase.

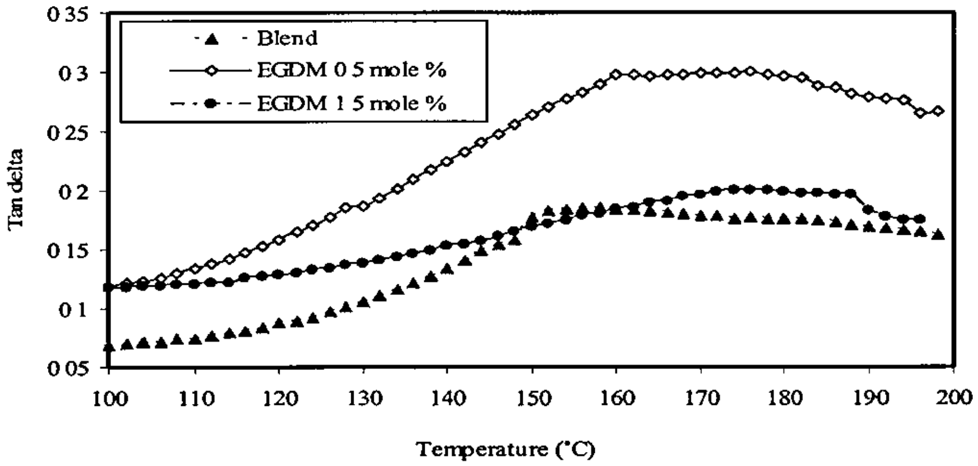


Fig. 4.15 The effect of cross-linking of the PMMA component on the PMMA loss tangent for the semi-2 IPNs with a NR70:PMMA30 composition

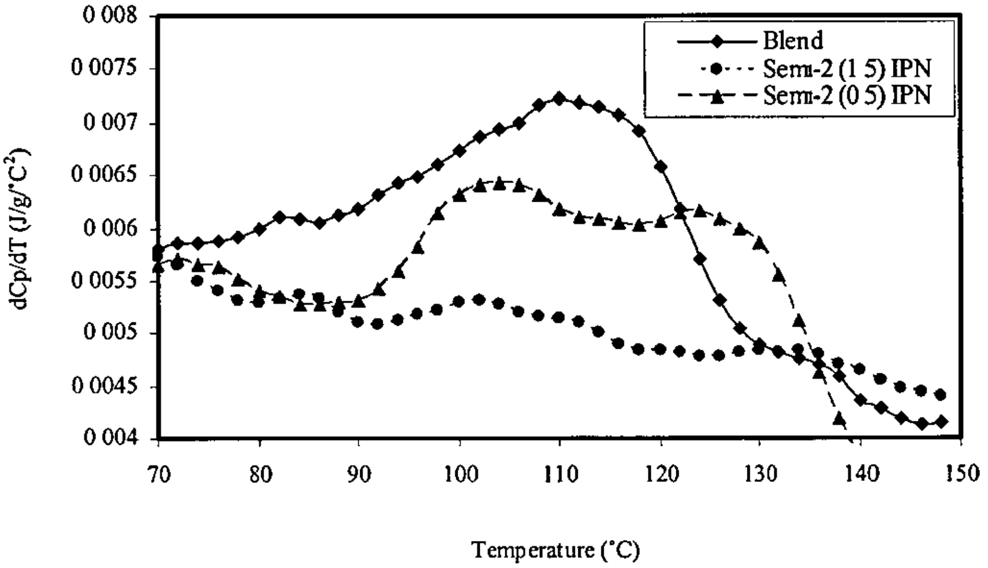


Fig. 4.16 dCp/dT vs temperature for the PMMA transition of the blend and semi-2 IPNs With a NR70:PMMA30 composition

The MDSC data shown in the Figure 4.16 follow the same trend indicating that the PMMA T_g increases with increasing the cross-link level in the PMMA phase However, it has been noted that the cross-linking of the PMMA phase using 0 5 mole percent of EGDM led to a broadening of the PMMA transition, probably indicating an increase of micro-heterogeneity in the PMMA phase resulting from some mixing. On the other hand, PMMA transition had been markedly reduced with increase of the cross-linker level up to a 1 5 mole%. This reduction is not primarily due to the increase of cross-linking of the PMMA phase, but due to improved component mixing as indicated in Table 4.4 in which weight fraction of PMMA phase was calculated by taking the cross-linking of the PMMA phase in to an account

However, the shift of the PMMA transition could also be considered as phase separation of the PMMA phase. Min *et al.*, 1983 and Okubo *et al.*, 1982, indicated that the cross-linking in immiscible polymer pairs resulted in phase separation. In addition, a study based on phase separation in PS latex IPNs indicated that as the degree of cross-linking increased in the PS particles, phase separation also increased (Sheu *et al.*, 1990). Therefore, it is difficult to decide which factor; phase separation or cross-linking contributed to the shift of PMMA T_g towards higher temperature As the MDSC data clearly indicated that the extent of mixing of components in semi-2 IPNs was relatively higher than the corresponding blend, it is reasonable to assume that the cross-linking of the PMMA component resulted in increase of T_g of the PMMA component This effect was evident because, the blend exhibited relatively lower T_g for its PMMA component most probably due to the grafting of PMMA onto natural rubber.
Such effect was not prominent in the semi-2 IPNs having higher PMMA content where homopolymerisation is preffered than the grafting process

Tg-PMMA of the semi-2 IPN with 40 wt.% and 50 wt.% PMMA content(Figure 4.17), shifted towards lower temperature by 4°C and probably associated with the improved mixing of the PMMA component due to cross-linking of the PMMA phase.. The mixing of the PMMA with the NR polymer chains which might have a plasticising effect resulting in an increase of mobility of the PMMA polymer chains leading to decrease in the PMMA T_g. The same trend has been observed for polyisobutene - PMMA IPNs when the EGDM level was higher than 10 wt.% on MMA (Vancaeyzeele *et al.*, 2005) These authors considered the lowering of T_g-PMMA as a character caused by the improved interpenetration. The same phenomenon could have arisen in the semi-2 IPNs with increase of the EGDM content from 0 to 1 5 mole%.

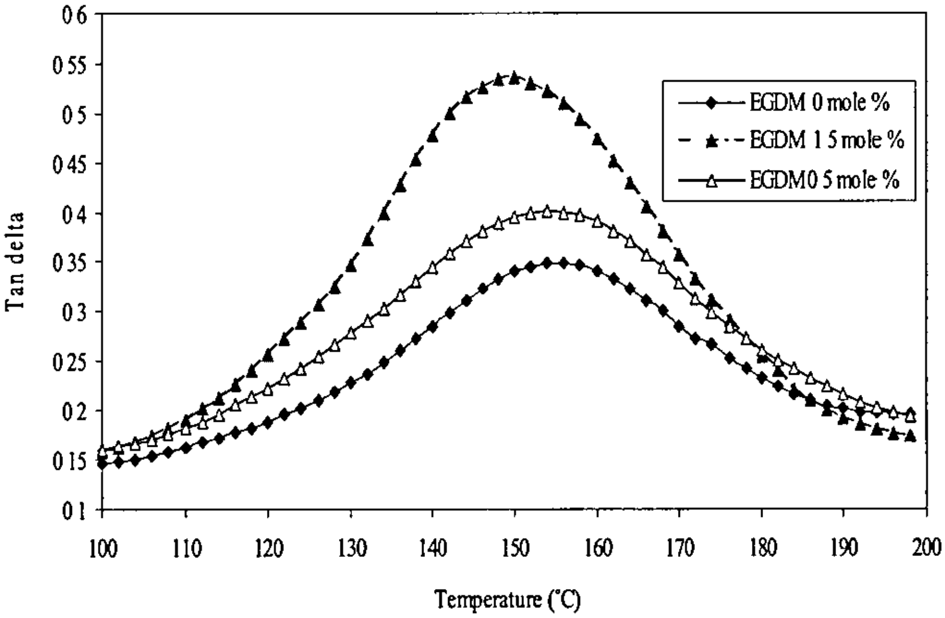


Fig 4.17 The effect of cross-linking of the PMMA component on the PMMA transition of the blend and the semi-2 IPNs with a NR50.PMMA50 composition

Therefore, in general, it can be stated that the cross-linking of the PMMA component enhances the extent of mixing of the components in the semi-2 IPNs. An identical trend was found for the PIB – PMMA IPNs when the EGDM level increased from 10 wt.% to 30 wt %. (Vancaeyzeele *et al.*, 2005).

Figures 4.18 and 4.19 clearly indicate the effects of cross-linking of the PMMA component as well as the EGDM content on the storage modulus at the NR transition Accordingly, with cross-linking of the PMMA phase, the storage modulus values in the rubbery region of the NR transition increased noticeably. For a example, E' at 20°C increased from 6 MPa to 15 MPa with increase of the EGDM level from 0.5 to 1 5 mole% in the semi-2 IPN with a 40 wt % PMMA. An increase from 29 MPa to 113 MPa was noted for the semi-2 IPNs with 50 wt.% PMMA content when the EGDM level was raised from 0 5 mole to 1.5 mole percent.

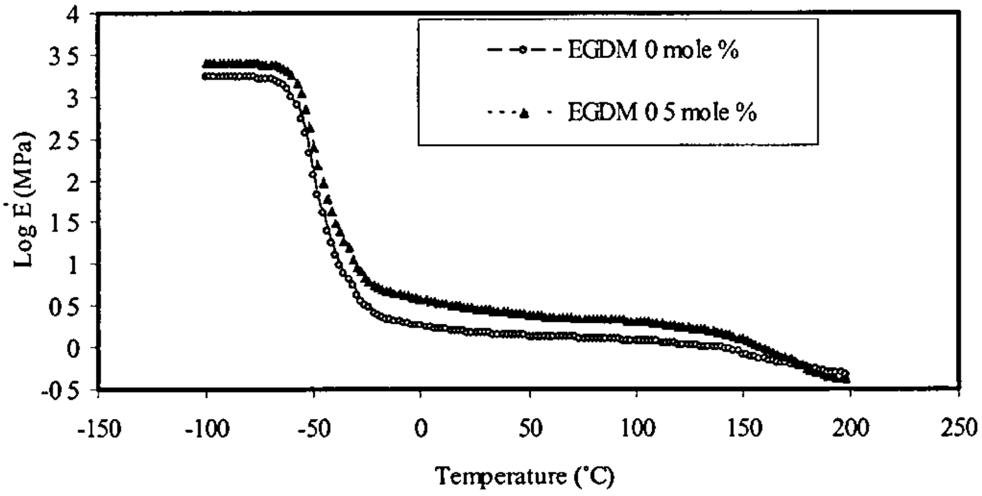


Fig. 4.18 The effect of cross-linking of the PMMA component on the storage modulus data for the semi-2 IPNs with a 30 wt. % PMMA content

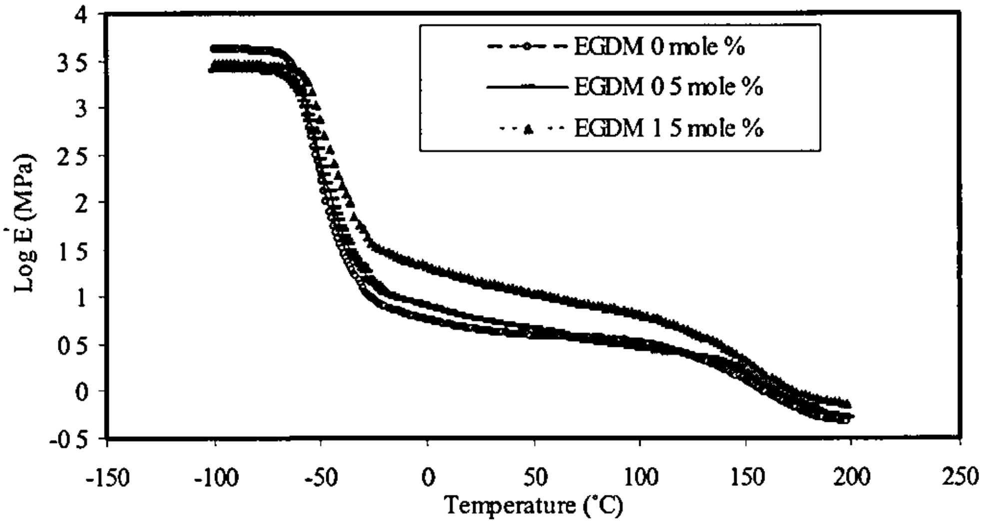


Fig. 4.19 The effect of cross-linking of the PMMA component on the storage modulus data for the semi-2 IPNs with a 40 wt. % PMMA content

In general, the storage modulus increased with the level of EGDM with the exception of semi-2 IPN with 30 wt.% PMMA content. These trends are associated with the lowering of the mobility of polymer chains (Sombatsompop, 1998), as a consequence of cross-linking of the PMMA phase to a higher degree. An analogous trend had been observed in the study by Li *et al.* (2002), based on nanometre-dispersed polypropylene/polystyrene IPNs, which they also attributed to the higher cross-link density.

4.3.2 Effect of cross-linking on the stress-strain behaviour

The tensile properties of various types of IPNs having 10 wt.% - 50 wt.% PMMA are presented in Figures 4 7 to 4 9. The effect of cross-linking of the PMMA component on the tensile strength is less significant when the PMMA component was cross-linked using 0 5 mole% EGDM. This is in accord with Donetelli *et al.* (1976), who showed that the effect of cross-linking of the second polymer on the mechanical properties of the resultant IPN is not strong. Nevertheless, a further increase of EGDM level up to 1.5 mole% caused a significant increase in the tensile strength in the semi-2 IPNs with 10 - 30 wt.% PMMA contents (Figure 4.8). Therefore, these data demonstrate that the effect of cross-linking of the PMMA component on the tensile properties is significant only at a relatively high cross-link density. As the cross-link density of PMMA phase increases, the number of effective network chains has also been increased. As a result, in addition to the strain-induced crystals present in the NR phase, applied load will also be borne by the cross-linked PMMA polymer chains, thus requiring a higher force for tensile rupture In addition, the improved tensile properties could be ascribed to the reinforcement caused by hard, cross-linked PMMA domains dispersed in a continuous NR matrix.

The effect of cross-linking of the PMMA component of the semi-2 IPNs having higher plastomer contents (50 wt.%) (Figure 4 9) differs from that of the semi-2 IPNs having lower plastomer content. The tensile strength of the NR50:PMMA50 semi-2 IPNs follow a decreasing trend with increasing EGDM level. These results suggest that when the PMMA phase is highly cross-linked, the tensile strength of these IPNs decreases and such an effect is prominent in the IPNs with a higher PMMA content. This is in accord with previous studies conducted on IPNs based on NR and PS (Das *et al*, 1993) This behaviour may be attributed to the presence of highly cross-linked PMMA domains, which restrict not only the formation of strain-induced crystals, but also retard the efficiency of the stress distribution in the matrix

Hysteresis data

Comparison of data for the blend and the semi-2 IPN indicated that the hysteresis values increased significantly with increasing cross-linking level in the

PMMA component using EGDM at a level of 1.5 mole percent. This is understandable as the cross-linking of the PMMA component may reduce the mobility of the neighbouring NR polymer chains. This might affect the reorientation of NR polymer and thereby increases the hysteresis.

Table 4.5 Energy loss and hysteresis behaviour for the blend and semi-2 IPNs

Sample composition NR/PMMA (wt. %)	Cycle 1		Cycle 2	
	Energy loss (J)	HL	Energy loss (J)	HL
NR90:PMMA10 blend	0.11	0.28	0.04	0.11
NR90:PMMA10 semi-2 (0.5) IPN	0.12	0.31	0.03	0.11
NR90:PMMA10 semi-2 (1.5) IPN	0.20	0.46	0.07	0.17
NR70:PMMA30 blend	0.64	1.26	0.38	0.84
NR70:PMMA30 semi-2 (0.5) IPN	0.44	0.96	0.28	0.72
NR70:PMMA30 semi-2 (1.5) IPN	0.93	2.1	0.53	1.14
NR50:PMMA50 blend	4.01	2.5	**	**
NR50:PMMA50 semi-2 (0.5) IPN	7.03	5.3	**	**
NR50:PMMA50 semi-2 (1.5) IPN	8.42	4.84	**	**

* HL-Hysteresis behaviour calculated as the ratio of the amount of energy lost to the amount of recovered in each cycle.

x Permanent set exhibited by the stretched sample

4.4 Effect of cross-linking of the NR and PMMA components

4.4.1 Effect of cross-linking on miscibility

Dynamic mechanical data

NR trasition

In this section, the term full IPN refers to the material in which the NR and PMMA components are both present in the cross-linked state.

Evaluation of the effect of cross-linking of the NR and PMMA components of the full IPNs having 20 wt.% PMMA content is difficult because of the presence of the low level of PMMA (3 wt.% to 7 wt.%) in these samples. The DMTA data for the semi-1 IPNs, semi-2 IPNs and for the full IPNs are shown in Table 4.6.

In general, the effect of cross-linking of both the NR and PMMA components on the T_g of the NR is not dramatic (Figures 4.20 and 4.21 and Table 4.6) when compared to the corresponding semi-1 IPNs. This may emphasise that the effect of cross-linking of both components will not result in a significant improvement in the extent of mixing of the NR component compared to the identical semi-1 IPN. Compared to the corresponding semi-1 IPN, the height of the NR transition tended to decrease when PMMA was cross-linked using 0.5 mole percent EGDM as indicated in Table 4.6. As the height of the NR transition is dependent on the fraction of homo polymer which is not in the form of a mixed state, and the mobility of back bone of the NR polymer chain, it is difficult to distinguished both these effect. As shown in earlier studies (Vancaeyzeele *et al.*, 2005), cross-linking of the PMMA phase in full IPNs should affect the mobility of the cross-linked NR polymer chains resulting in lowering of the height of the NR transition.

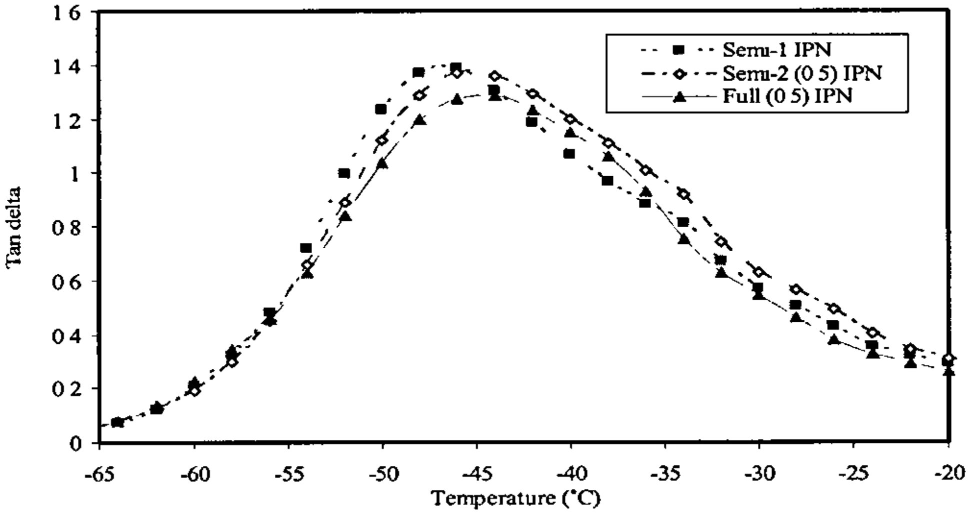


Fig. 4.20 The effects of cross-linking of the NR and the PMMA components on the NR loss tangent of the semi-1 IPN, semi-2 (0.5) IPN and full (0.5) IPN with a 30 wt.% PMMA content

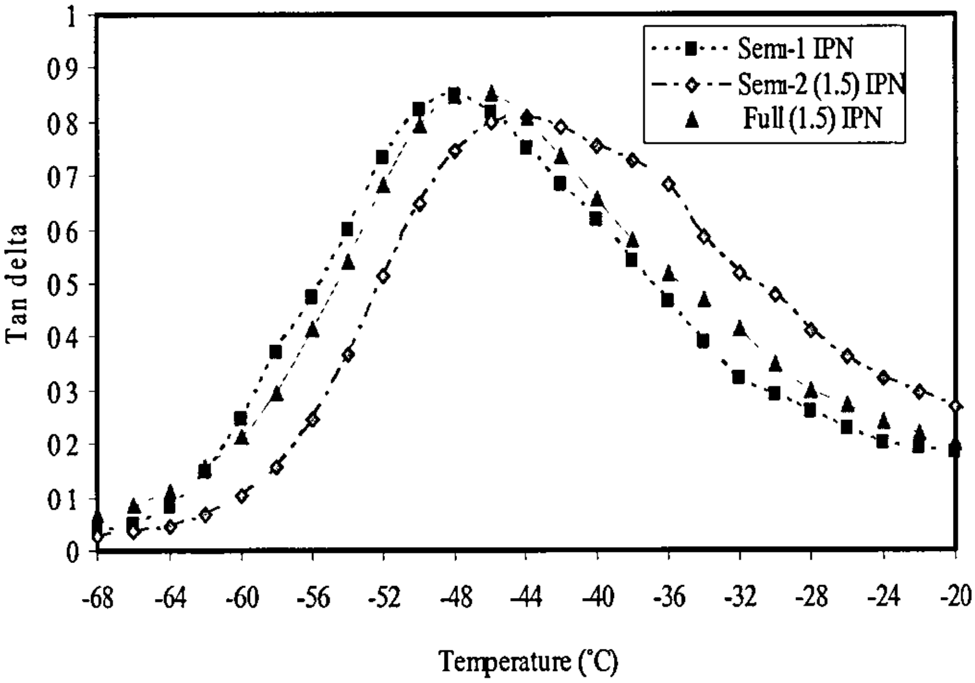


Fig. 4.21 The effect of cross-linking of the NR and the PMMA components on the NR loss tangent of the semi-1 IPN, semi-2 (0.5) IPN and full (0 5) IPN with a 40 wt % PMMA content

Having considered the data presented in Table 4.7, it can be stated, in general, that the extent of mixing of the NR component in the full IPNs was slightly higher than in the equivalent semi-1 IPNs (Table 4.7) and mostly ascribable to the cross-linking of the PMMA component in the IPN.

When the DMTA data of full IPNs are compared with the semi-2 IPNs, it is worth mentioning that the T_g of the NR transition of the full IPN has shifted slightly towards lower temperature by 3°C to 4°C, than the corresponding semi-2 IPNs containing 40 wt.% and 50 wt.% of PMMA, except the NR50 PMMA50 (1.5) full IPN (Table 4 6). These results also indicated that the extent of mixing of the NR component in the IPNs are relatively low In other words, the extent of mixing of the NR component in the semi-2 IPNs is relatively higher than the equivalent full IPNs and it can probably be attributed to interpenetrated PMMA and /or to grafting of PMMA on to NR chains.

Table 4 6 DMTA data for the semi-1 IPNs, semi-2 IPNs and for the full IPNs

Sample	NR T_g (°C)	Tan δ_{NRmax}	PMMA T_g (°C)	Tan δ_{MMAmax}
NR70 PMMA30 semi-1 IPN	-47	1.4	150	0.19
NR70 PMMA30 (0.5) semi-2 IPN	-46	1.4	160	0.29
NR70 PMMA30 (0.5) full IPN	-45	1.3	152	0.16
NR70.PMMA30 (1.5) semi-2 IPN	-46	1.6	178	0.20
NR60:PMMA40 semi-1 IPN	-48	0.85	145	0.39
NR60 PMMA40 (0.5) semi-2 IPN	-46	1.4	159	0.32
NR60·PMMA40 (0.5) full IPN	-49	0 55	145	0 56
NR60 PMMA40 (1.5) semi-2 IPN	-45	0 8	156	0 40
NR60:PMMA40 (1.5) full IPN	-47	0.35	154	0.25
NR50.PMMA50 semi-1 IPN	-47	0 64	146	0.44
NR50:PMMA50 (0.5) semi-2 IPN	-48	0 71	154	0.4
NR50.PMMA50 (0 5) full IPN	-52	0.45	146	0.51
NR50·PMMA50 (1.5) semi-2 IPN	-49	0.5	150	0.54
NR50 PMMA50 (1.5) full IPN	-48	0.35	154	0.55

PMMA transition

Comparison of the DMTA data for the semi-2 IPNs and the full IPNs can be done using the data presented in Table 4.6 and in Figures 4 22 and 4.23 The plot of tan delta versus temperature data for the PMMA transition for the different types of IPNs having 30 wt.% PMMA are shown in Figure 4.22. Comparison of the T_gs of the PMMA transitions of the semi-2 IPN and the IPN prepared using 0.5 mole percent of EGDM, indicated that the T_g of the IPN has significantly shifted towards lower temperature by 8°C. The same trend has been observed for the IPNs with 40 wt.% (Figure 4 23) and 50 wt.% of PMMA (Table 4.6). This behaviour could be ascribed to improved mixing of the PMMA component due to cross-linking of both components Further evidence for the improved mixing of the NR components can be seen from the MDSC data shown in Table 4 7 Nevertheless, comparison of the PMMA T_g values of the semi-2 IPN and the full IPNs with a 40 wt.% PMMA, prepared using EGDM at a level of 1.5

mole percent indicate that there is no significant shift in the T_g of the PMMA transition towards lower temperature in the full IPNs.

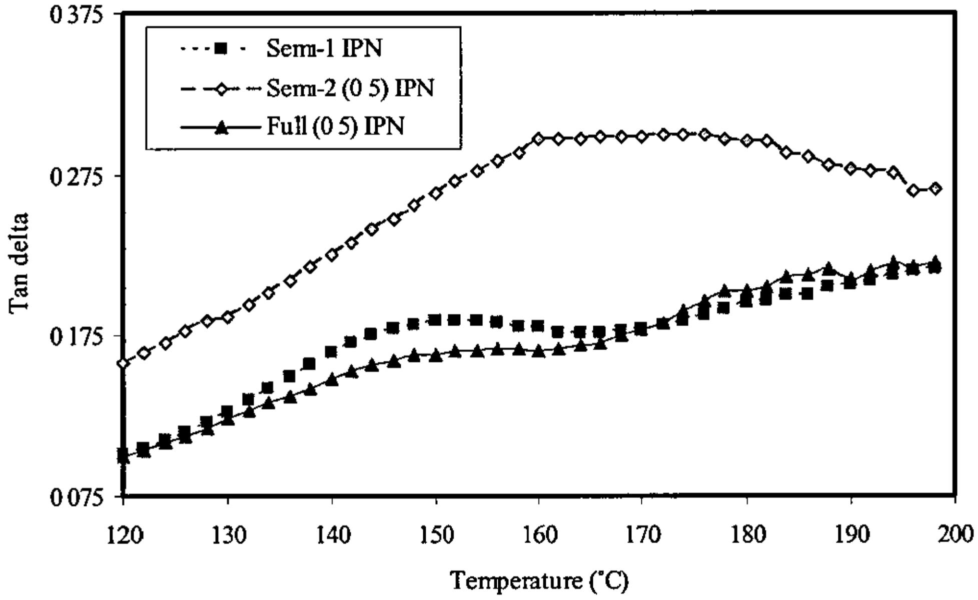


Fig. 4 22 The effect of cross-linking of the NR and the PMMA components on the PMMA transition of the semi-1 IPN, semi-2 IPN and full IPN with a 30 wt.% PMMA

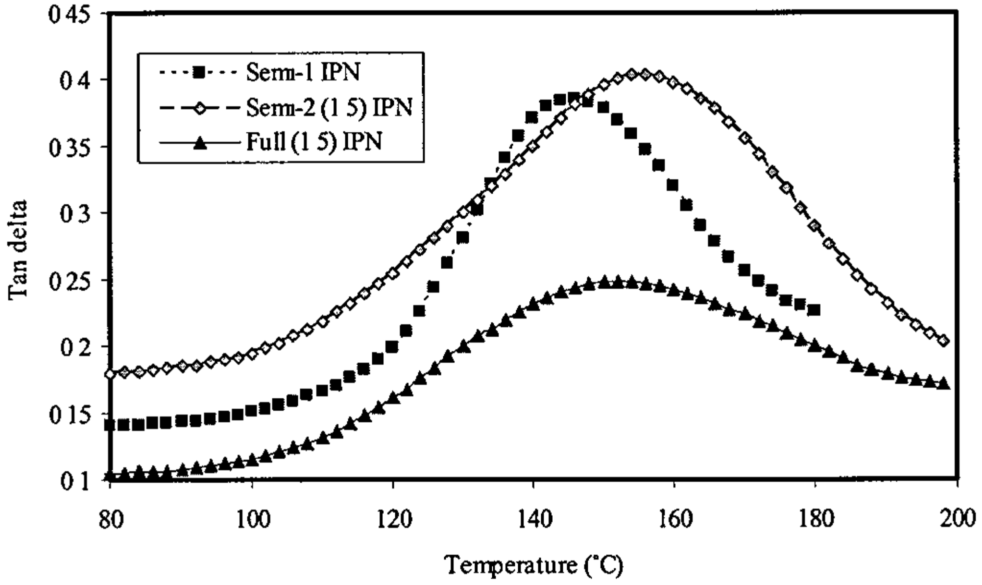


Fig 4.23 The effect of cross-linking of the NR and the PMMA components on the PMMA transition of the semi-1 IPN, semi-2 IPN and full IPN with a 40 wt.% PMMA

Table 4.7 Calculated weight fractions of the NR and PMMA components and multiple peak analysis data for the semi-1IPN, semi-2 IPN and full IPNs

Sample	MDSC data					
Type of the material	δ_{NR} (weight fraction)	δ_{NR}^{*} (weight fraction)	δ_{PMMA} (weight fraction)	Multiple peak analysis data		
				Interphase (%)	NR-rich phase (%)	PMMA-rich phase (%)
NR70.PMMA30 semi-1 IPN		-	0.07	30	14	9
NR70 PMMA30 semi-2 (0.5) IPN	0.14		0.05	25	8	12
NR70 PMMA30 full (0.5) IPN		0.25	0.17	29	16	13
NR50:PMMA50 semi-1 IPN		-0	0 23	30	13	26
NR50·PMMA50 semi-2 (0.5) IPN	0.20		0.0	30	20	16
NR50.PMMA50 full (0.5) IPN		0.15	0.23	20	20	23

δ_{NR}, calculated with respect to the un-vulcanized NR

δ_{NR}^{*}, calculated with respect to the vulcanized NR

Moreover, T_g of the PMMA transition of the NR50:PMMA50(1 5) IPN has shifted to higher temperatures by 4°C (Table 4.6) compared to the equivalent semi-2 IPN This behaviour is probably attributed to high level of cross-linking.

Hence, based on this evidence, it can be concluded that in the full IPNs prepared using 0 5 mole percent EGDM, the cross-linking of both components improved the extent of the mixing of the PMMA component compared to the corresponding effect caused by the cross-linking of the PMMA component alone. This was primarily attributed to two reasons: the reduction of phase separation due to cross-linking of the PMMA component; and formation of smaller domains as a consequence of the cross-linking of the NR and PMMA components. As a result, the interphase region would be increased and thereby adhesion of the PMMA phases with NR would be improved due to the combined effect of an increase of the surface area and an increase of interpenetration at these surfaces. However, when the T_gs of the semi-1 IPN and the full IPN, prepared using 0 5 mole percent EGDM are considered, no significant variation was observed either in the NR T_g or PMMA T_g See Table 4 6

A different trend was found for the full IPNs prepared using 1 5 mole percent of EGDM. In this case, the PMMA T_g of the full IPN is considerably higher than the semi-1 IPN (Figure 4.23) This trend was purely due to the reduction of mobility of PMMA molecular segments caused by the cross-linking of the PMMA chains. Broadening of the PMMA transition of the full IPN compared with the corresponding transition of the semi-1 IPN was also attributed to the cross-linking effect of the PMMA component.

4.4.2 Effect of cross-linking on stress-strain behaviour

Tensile data

Comparison of the full IPNs, prepared using different EGDM levels, indicated that as the EGDM level increased from 0.5 to 1 5 mole%, the tensile strength of the full IPNs with an approximate composition of NR90·PMMA10 (Figure 4.7) has also been increased marginally. As the PMMA content is low in these full IPN samples, it could be assumed that the EGDM may cross-link natural rubber resulting in greater cross-linking As the cross-link density in NR increases, the mobility of the NR polymer chains decrease which causes inefficient stress distribution among the neighbouring polymer chains resulting in a lowering of tensile strength. In addition, compared to the NR/PMMA blend and the semi-2 IPN, the tensile strengths of the IPNs (Table 4.8) were significantly higher, probably due to the cross-linking of the NR component using the conventional vulcanising system, as discussed in section 4.2.2.

Comparisons of the stress-strain data for the IPNs with the NR70.PMMA30 (Figure 4 8) and NR60:PMMA40 compositions (Figure 4.24) indicate that the tensile strength of the full (0.5) IPN is lower than that of the equivalent semi-1 IPN.

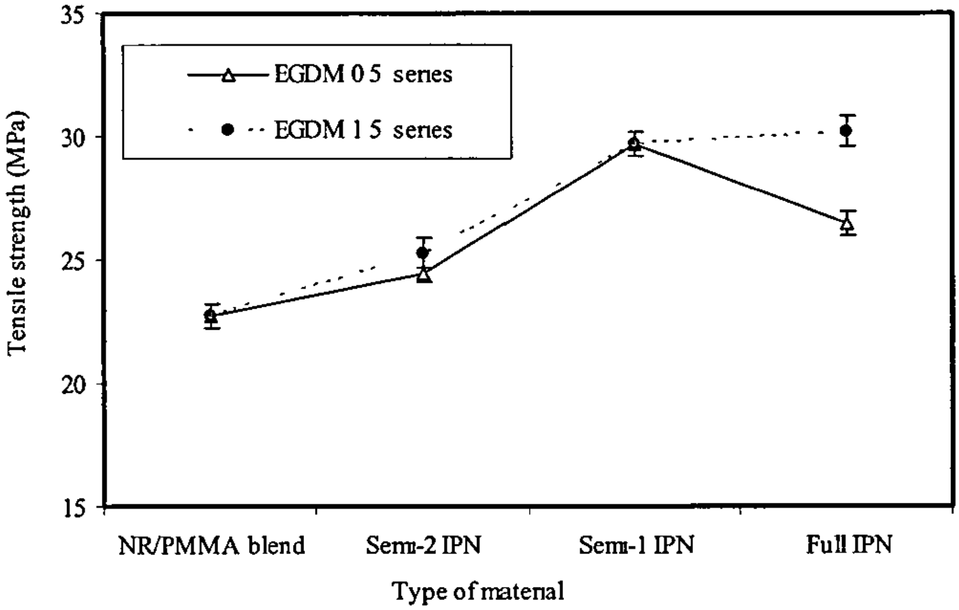


Fig. 4.24 The effect of cross-linking of components on the tensile strength of the blend, semi-1 IPN, semi-2 IPN and full IPN with a NR60 PMMA40 composition

In the full IPN, the NR polymer chains are tied by polysulphidic cross-links with low mechanical strength (Bateman, 1963). However, the introduction of C-C cross-links in the PMMA component, using EGDM, may lead to a system which not only consists of different types of cross-links which have greater bond strength. As such, unlike polysulphidic linkages which are capable of easy bond breaking, and, therefore, capable of distributing stress efficiently, the C-C cross-links present in the PMMA phase may break instead of distributing stress when they experience high loads (Bateman, 1963). Therefore, tensile rupture may initiate in these areas leading to lower tensile strength. However, the tensile strength of the full IPNs increased marginally (11%, 15%, 17%, respectively, for 70/30, 60/40 and 90/10 NR/PMMA compositions with increasing cross-link density of the PMMA phase.

Table 4.8 The tensile strength of the semi-1 IPN, semi-2 IPN and the full IPN

Sample	Tensile strength (MPa)
NR92.PMMA8 semi-1 IPN	19 (1.1*)
NR90:PMMA10 (0.5) semi-2 IPN	13 (1.1*)
NR93:PMMA7 (0.5) full IPN	18 (0.9*)
NR90:PMMA10 (1.5) semi-2 IPN	15 (0.8*)
NR95 PMMA5 (1.5) full IPN	21(1.7*)
NR70 PMMA30 semi-1 IPN	32 (1.6*)
NR70 PMMA30 (0.5) semi-2 IPN	21 (1.4*)
NR70.PMMA30 (0.5) full IPN	28 (1.1*)
NR70:PMMA30 (1.5) semi-2 IPN	27 (1.3*)
NR70:PMMA30 (1.5) full IPN	31(0.8*)
NR60·PMMA40 semi-1 IPN	30 (1.5*)
NR60 PMMA40 (0.5) semi-2 IPN	24 (0.7*)
NR60 PMMA40 (0.5) full IPN	26 (1.0*)
NR60 PMMA40 (1.5) semi-2 IPN	25(1.2*)
NR60 PMMA40 (1.5) full IPN	30 (1.2*)

* Standard deviation

According to Flory (1949), the tensile strength of materials is governed by the fraction of material capable of orientation and by the fraction of active network chains. Therefore, as the cross-link density increased, the number of active network chains in the PMMA phases also increased resulting in a higher tensile strength. These results also suggest that the cross-linking of the second component does not have a marked effect on the tensile properties of the materials in which the first polymer is moderately cross-linked. The same trend had been obtained for the NR/PS full IPNs in which, the first polymer has been highly cross-linked (Das *et al*, 1993).

4.4.3 Effect of cross-linking on hysteresis data

The hysteresis data indicate that there was no marked variation in hysterersis between the semi-1 IPN and the full (0.5) IPN with the 30 wt.% PMMA content (Table 4.9). On the other hand, the hysteresis shown by the full IPNs is apparently higher than that of the corresponding semi-2 IPNs. Similar observations were made for the NR50 PMMA50 compositions.

Table 4.9 Energy loss and hysteresis behaviour for the blend and semi-2 IPNs

Sample composition NR/PMMA (wt. %)	Cycle 1		Cycle 2	
	Energy loss (J)	HL	Energy loss (J)	HL
NR70.PMMA30 semi-1 IPN	0.97	1.3	0.61	0.83
NR70 PMMA30 semi-2 (0.5) IPN	0.44	0.96	0.28	0.72
NR70 PMMA30 full (0.5) IPN	0.94	1.39	0.49	0.86
NR70:PMMA30 full (1.5) IPN	1.83	2.17	0.70	1.07
NR50.PMMA50 semi-1 IPN	11.8	7.67	x	x
NR50 PMMA50 semi-2 (0.5) IPN	7.03	5.3	x	x
NR50:PMMA50 full (0.5) IPN	10.4	10.7	x	x
NR50:PMMA50 full (1.5) IPN	13.5	17.7	x	x

* HL-Hysteresis behaviour calculated as the ratio of the amount of energy lost to the amount of recovered in each cycle.

x Permanent set exhibited by the stretched sample

As stated earlier, during stretching some polymer chain segments orient parallel to the stretching direction and act as precursors for strain-induced crystals. On the other hand, when the stress is relieved during the retraction process, these polymer segments regain their non-oriented conformations. However, the presence of cross-links in the NR phase and the presence of PMMA domains within the NR network may impede reorientation and break down of crystals delaying the return to original conformations. This process leads to higher hysteresis. A similar trend has been obtained for the hysteresis of semi-2 IPNs and LIPNs of NR/PS with 80/20 compositions, in which the NR phase has been cross-linked by gamma irradiation (Romaine, 1988).

CHAPTER 5

Semi-1 IPNs based on epoxidised natural rubber and/or acrylic acid

5.1 Introduction

Micro-phase separation is known to occur during the formation of IPNs resulting in heterogeneous two phase systems (Alekseeva *et al.*, 2005). The same observation was made for the IPNs reported in chapter 3 and 4, as these IPNs exhibited two glass transitions corresponding essentially to their constituent homopolymers. This is an expected observation as natural rubber and poly(methylmethacrylate) are known to be a pair of incompatible polymers (Oommen *et al.*, 1997:1996; Oommen and Thomas, 1993). Different solubility parameters and unfavourable thermodynamic factors can be considered as the prime reasons for the incompatibility between NR and PMMA. In an incompatible blend, strong interfacial adhesions are absent and presumed to contain only few entanglements and such a system would impart inferior physical properties. Physical properties of NR/PMMA blends are inferior resulting from the incompatibility of the two components Nevertheless, IPNs based on NR and PMMA possess better physical properties and enhanced component mixing due to the unique characteristics of IPN formation.

Extensive work had not been carried out on the compatibilization of these immiscible polymer components in such IPNs. Several studies have been carried out using fillers (Lipatov *et al*, 1988) and compatibilizing agents (Lipatov *et al*, 1999). In one of these studies (Lipatov *et al*, 1988), compatibility was achieved by introducing fillers into polyurethane - polyester acrylate IPNs. It was reported that with the introduction of fillers, compatibility improved with the reduction of phase segregation indicated by the appearance of a broad transition instead of two of mechanical loss maxima. This behaviour was attributed to the effect of interactions such as Coulombic interactions between the filler and the IPN components on microphase separation (Lipatov *et al.*, 1988). Compatibilizers such as the monomethacrylester of ethylene glycol (MEG), oligourethane dimethacrylate (OUDM) and a triblockurethane have been used in semi-1 IPNs based on cross-linked polyurethane (PU) and poly(*n*-butyl methacrylate) (PBMA) (Lipatov *et al*, 1999; Alekseeva *et al.*, 2001). This study indicated that incorporation of MEG, OUDM and a triblock polyurethane with two $-CH_3CH_2-O-CH_2CH_2-$ units markedly improved the compatibility resulting in a single broad transition Formation of graft polymer, cross-linking with butyl methacrylate via double bonds and segregation of a triblock PU at the interface were considered, respectively, as the reasons for improved compatibility in these IPNs They have extended their study using OUDM for a system which consists of a cross-linked polyurethane and linear polystyrene. It was found that a single transition could be obtained at 20 wt.% OUDM and the T_g depended on the composition and the reaction conditions (Alekseeva *et al*, 2005) In addition, forced compatibilization (Li *et al.*, 1994, Fradkin *et al.*, 1996) resulting from a cross-linking process was found to be a potential method to obtain a compatible system For example, poly(methylacrylate) and poly(methylmethacrylate) sequential IPNs were found to be compatible with just a single relaxation, when they were cross-linked using 10 wt.% EGDM (Sánchez *et al*, 2001) In addition, the cross-link density of the first formed network had a profound effect on the compatibility of the IPNs (Li *et al.*, 1994; Sánchez *et al*, 2001)

In this present investigation, attempts were made to explore the possibilities of improving the compatibility/miscibility of NR and PMMA by introducing substances which interact with, or are capable of forming interactions between, the individual components at the interface If the chemical nature of natural rubber and PMMA is taken into consideration, natural rubber is a non-polar substance, while PMMA is a polar component as it contains oxygen with unpaired electrons which exerts a dipole moment and/or polarity. Based on these facts, if a polar group/material is incorporated on to either the NR molecule or in to the NR matrix, compatibility of NR and PMMA could be improved The former path may be the more effective since the polarity will be introduced at the molecular level. In addition, introduction of potential materials with functional groups would be helpful in improving miscibility as they can undergo formation of chemical interactions which can impart true thermodynamic miscibility in some cases. When PMMA is concerned, it has a carbonyl group which can act as a hydrogen bond accepter. Therefore, introduction of material with functional groups which can act as a hydrogen bond donating groups would lead to formation of hydrogen bonds between the PMMA and the functional groups of the added material and thereby help to improve the miscibility of the components (Eastwood *et al*, 2005).

Based on these facts, chapter five is designed to investigate the effect of the addition of epoxidised natural rubber on the compatibility of the individual components, natural rubber and PMMA, in the semi-1 IPNs with 50 wt.% of PMMA.

Epoxidised natural rubber, one of the modified forms of natural rubber is weakly polar and partially compatible with PMMA (Yusof, 1999), was chosen for this investigation. It has been reported that the ENR-50 - PMMA polymer pair is a partially miscible system as the IPNs still exhibited two glass transitions (Yusof, 1999). Technological compatibilization does not refer to a system with complete miscibility at the molecular level.

The effect of the addition of epoxidised natural rubber (ENR) on the compatibility/miscibility of IPNs containing NR and PMMA has been investigated. For a comparison of results, 100% ENR materials have been used. In addition, epoxidised natural rubber with different epoxy contents (epoxidation levels), was used and their effect on the compatibility of NR and PMMA were evaluated. Moreover, the effect of the experimental conditions used for the synthesis of ENR on the physical properties of the IPNs were evaluated In this investigation, two different levels of hydrogen peroxide were used for the in-situ preparation of a peracid. For convenience, the letter given in the parenthesis represents the level of hydrogen peroxide which was denoted by either the symbol H or M referring to a higher level or a moderate level, respectively. The experimental details relevant to this chapter are located in the section 2.2.

NR sheets prepared from prevulcanised natural rubber latex were used as the basic material for the preparation of the IPNs discussed in chapters 3 and 4. Since chapter 5 investigates the potentiality of ENR which are capable of enhancing the compatibility/miscibility between the components, NR and PMMA, the most appropriate way is to incorporate the ENR by solid state mixing of the components in a two-roll mill Therefore, the NR sheets were prepared by mixing natural rubber with the ENR in a two-roll mill followed by preparing sheets using a hot press, in which the curing process took place. In a two-roll mill, rubber is usually subjected to a mastication process in which mechanical rupture of primary bonds is possible resulting in a lowering of the physical properties (Blow, 1971).

The Triganox 21S, the initiator used for the in-situ polymerization of MMA in the preparation of the IPNs discussed in chapters 3 and 4, was not available in Sri Lanka, where this part of the investigation was carried out. Under these circumstances, the IPNs were synthesized using dibenzoyl peroxide as the initiator for the polymerization of MMA. Apart from these differences, the synthesis route for the IPNs and the basic components of the IPNs were the same, and, therefore, the differences described above should not have any adverse influence on the determination of the effect of the addition of ENR as a third, polar component on the compatibility/miscibility of the NR and the PMMA components of these semi-1 IPNs.

There may be structural changes in the ENR depending on the rate of epoxidation reaction as well as on the level of hydrogen peroxide. As such, in order to highlight the ENR prepared using different hydrogen peroxide levels, the letter H and M are given in the parenthesis for 1.5 mole and 1.0 mole of hydrogen peroxide per repeating unit of rubber, respectively. The number in the code represents the approximate level of epoxidation

5.2 Raw rubber characteristics

5.2.1 Infra red spectroscopic analyses of the raw materials

FTIR spectra of the ENR with different epoxy contents are shown in Figures 5.1 to 5.6 Absorption frequencies of the relevant groups are shown in Table. 5.1.

It is noted that the epoxy peak at 870 cm^{-1} increased with increase in the epoxy content. Peaks at 1065 cm^{-1}, due to furan structures caused by secondary reactions, were not observed. The hydroxyl absorbance observed in these spectra could arise because of the moisture present in the material and/or due to ring opening of ENR during the reaction. The peak observed at the 1700 cm^{-1} in the FTIR spectra of natural rubber (Figure 5.1) is associated with the carbonyl groups probably resulted by the degradation process.

Table 5.1 Absorption frequencies of relevant functional groups or bonds (Williams and Fleming, 1989)

Group	Band	Remarks
$R_2C=CHR$	840-790 (m)	
$-CH_3$	1390-1370 (m)	$-CH_3$ symmetrical deformation
-CH	2890-2880 (w)	
Epoxy group	900-800	
Furan group*	1065	
Free OH	3650-3590 (v)	O-H stretching
H-bonded-OH	3600- 3200 (s)	
Acid -OH	2500-3300	Strong and broad
Intra-molecular H- bonded-OH	3200-2500(v)	
-O—H	1410-1260(s)	O—H bending
C—OH	1150-1040(s)	C—O stretching

(m) – medium; (w) – weak; (s) – strong; (v) – variable

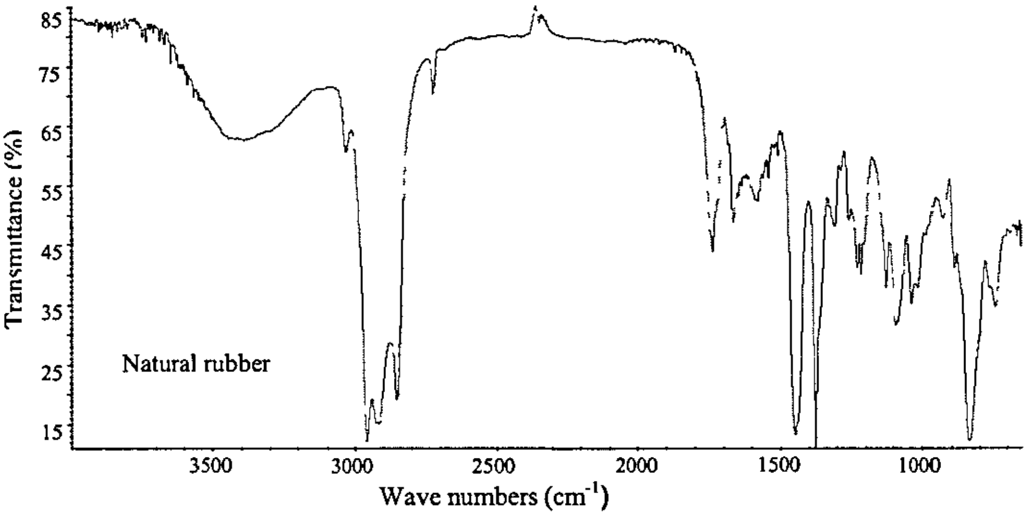


Fig. 5.1 ATR-FTIR spectrum of the natural rubber (spectrum obtained using a thin film which was produced from the NR latex)

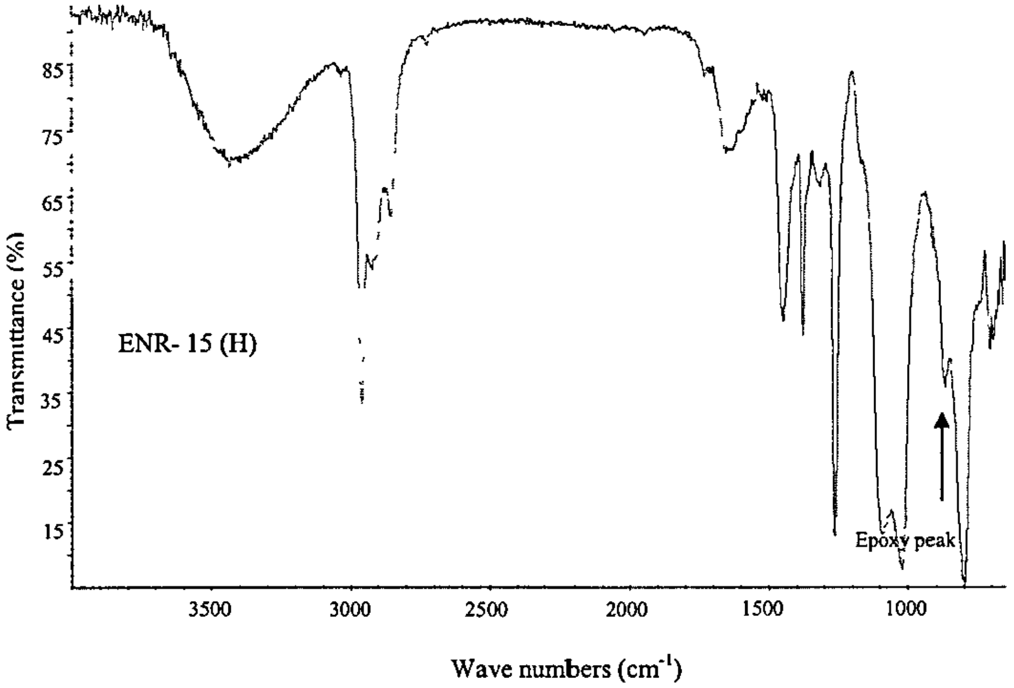


Fig. 5.2 ATR-FTIR spectrum of the ENR-15 (H) (spectrum obtained using a thin film which was produced from the ENR latex)

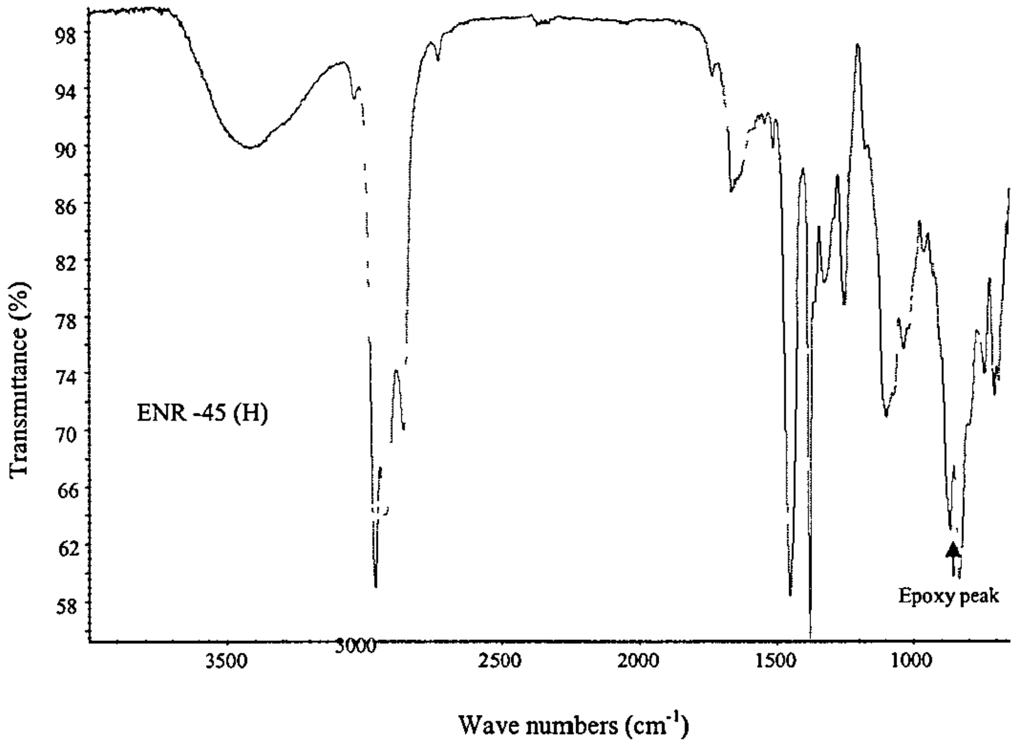


Fig 5.3 ATR-FTIR spectrum of the ENR-45 (H) (spectrum obtained using a thin film which was produced from the ENR latex)

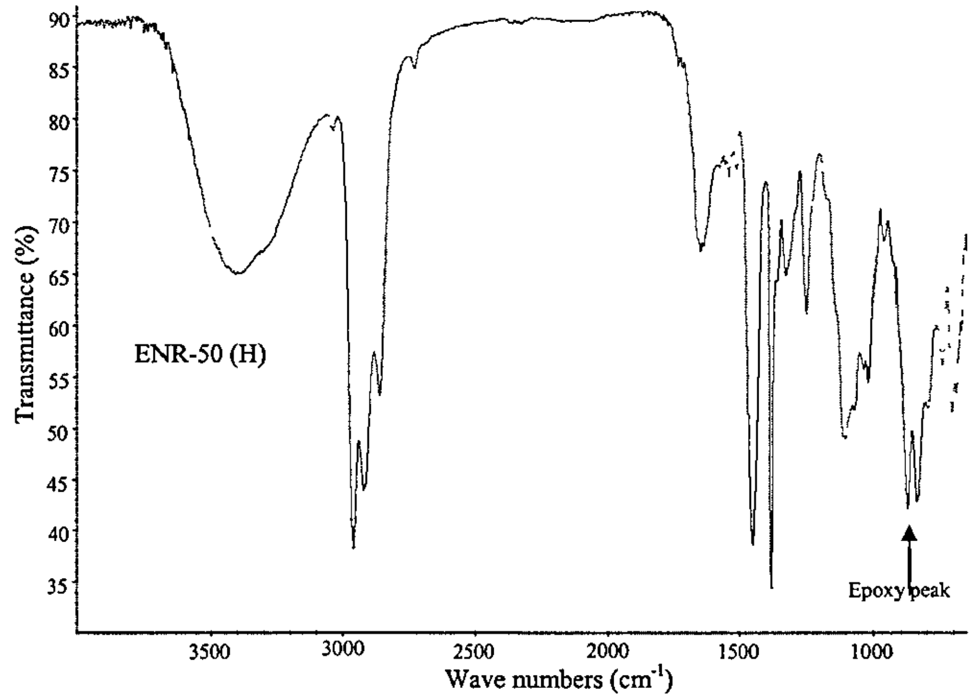


Fig 5.4 ATR-FTIR spectrum of the ENR-50 (H) (spectrum obtained for thin film which was produced from ENR latex)

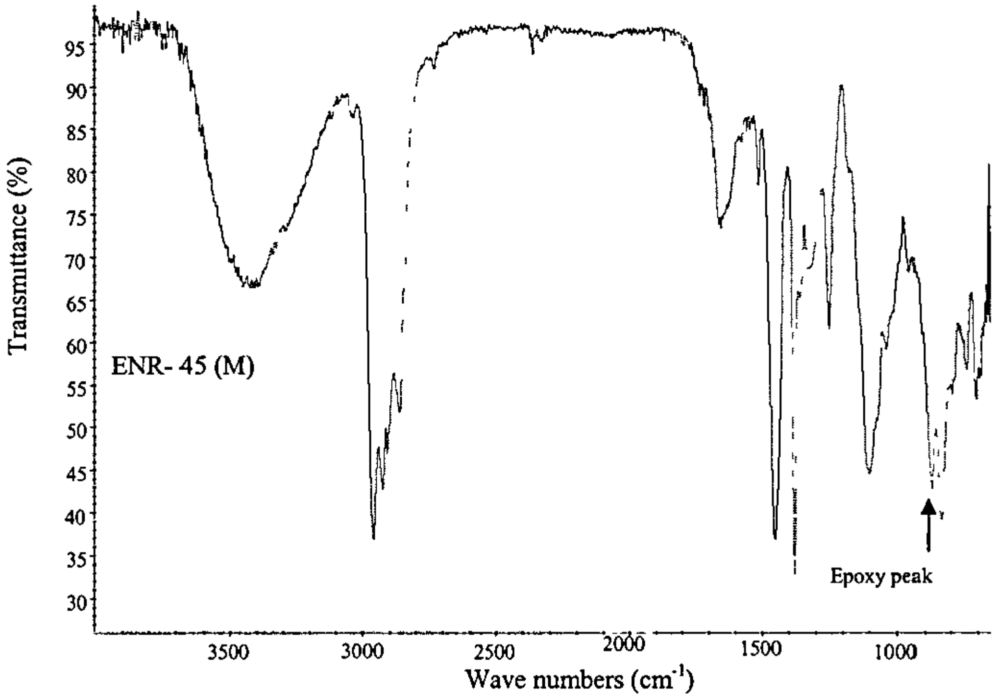


Fig. 5.5 ATR-FTIR spectrum of the ENR-45 (M) (spectrum obtained using a thin film which was produced from the ENR latex)

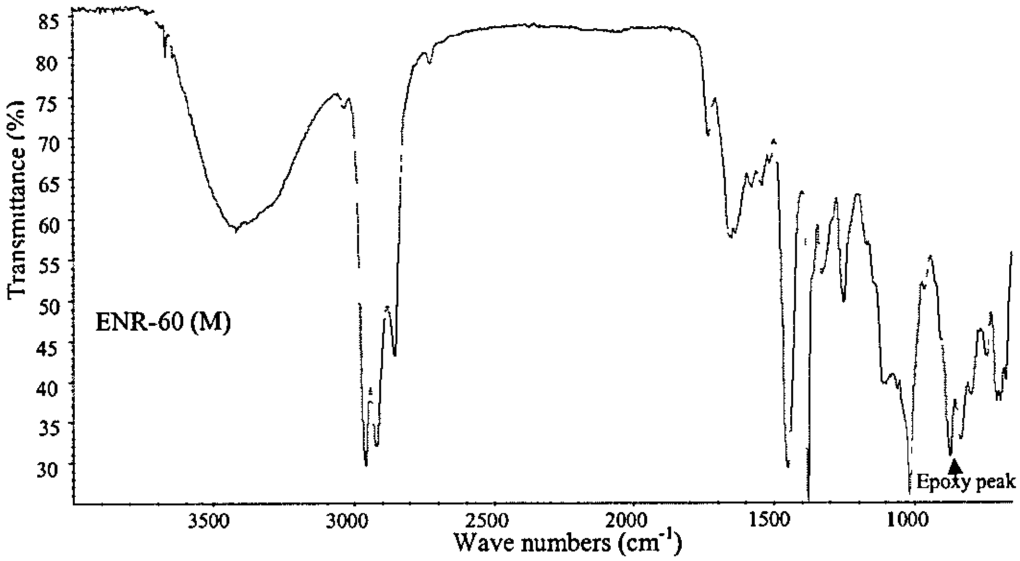


Fig. 5.6 ATR-FTIR spectrum of the ENR-60 (M) (spectrum obtained using a thin film which was produced from the ENR latex)

5.2.2 Mooney viscosity data and Mooney stress-relaxation data for the raw materials

Raw Mooney viscosity data and the Mooney stress-relaxation data for the natural rubber and for the ENR samples which were prepared using a fairly high level of hydrogen peroxide (denoted by – H) are illustrated in Table 5.2

The theory behind the stress relaxation determined by measuring the decaying torque after performing a normal Mooney test is described in the following text.

In this study, an MV2000E instrument was used to obtain the Mooney viscosity data as well as the Mooney stress relaxation data. The relaxation response was used for characterization of the raw polymers and the compound stock behaviour. It is stated that the stress relaxation data obeys the power law (Dimauro, Monsanto Company (Private communication)) and can be expressed by an equation as follows.

$$ML = kt^{-a}$$

Where ML is the decaying Mooney stress, t is the relaxation time after the rotor stops, k is the stress value at 1 second and "a" is a measure of speed of relaxation (Dimauro, private communication).

$$\text{Log } ML = - a \log t + \log k$$

The value of the gradient, "a", was obtained by plotting the log ML values against the log t values. Therefore, negative gradient can be obtained and, therefore, the negative sign will not be taken into account for the interpretation of "a" values. k is a measure of stiffness and is proportional to the ML1+4 value. "a" is a measure of visco-elastic properties of the material without resolving the "a" into their individual components; viscous and elastic, respectively. The higher the "a" value, the higher the rate of relaxation, indicating a more viscous and less elastic nature. As such, "a" can conveniently be used to characterize the polymer and it facilitates prediction of the processing behaviour (Dimauro, private communication).

Table 5.2 Mooney viscosity data for the natural rubber and the ENR rubber prepared using higher amount of hydrogen peroxide

Property (Mooney units (MU))	Material		
	Natural rubber	ENR -15 (H)	ENR-50 (H)
Initial viscosity	92.6	120.3	174.4
Viscosity @ 10s	28.4	42.0	47.1
Viscosity @ 20s	22.7	35.8	40.8
Viscosity @ 100s	12.6	23.4	27.7
Viscosity @ 10 % decay	72.5	86.8	94.1
Viscosity @ 20 % decay	65.7	72.4	78.8
Final viscosity	83.3	98.5	107.0
ML 1+ 4	83.3	98.5	107.0
Intercept (K)	57.2	70.0	75.4
Slope (a) (MU/s)	-0.32	-0.23	-0.21

The concept of entanglement coupling is used to interpret visco-elastic behaviour. It is thought that these entanglements act as topological constrains. However, it had been indicated that, factors such as the molecular weight, branching, length of branches, molecular weight distributions and gel content affect the Mooney viscosity (Roberts, 1988). It was reported that the total gel content (macrogel plus microgel content) is related to the relaxation time. Accordingly, as the total gel content increases, the stress relaxation time increases (Ehabé *et al.*, 2005) Therefore, if the total gel content has increased under such circumstances, the relaxation time should be increased indicating a slow rate of relaxation with a low "a" value. This may be the reason for having a lower "a" value with increasing ENR content as the ENR gel content may increase due to the cross-linking process via secondary reactions during storage (ageing). Therefore, the higher "a" value obtained for the natural rubber indicated that the processing of natural rubber is comparatively easier than that for the epoxidised natural rubber. In addition, it should be noted that the Mooney viscosity and the initial viscosity increased with an increase in the level of epoxidation This may be attributed to increased gel content and/or to cross-linking during storage

5.3 NR/ENR blends

5.3.1 Cure characteristics of the NR/ENR blends

The cure characteristics of the NR/ENR blends containing ENR-60 (M) are shown in Table. 5 3. Comparison of the cure characteristics of the blends indicated that the cure rate index increased to a maximum value with increase in the ENR content up to 50 wt.% - 75 wt.% and then decreased with further increase in the ENR content up to 100 wt.% A similar trend has been obtained for the ENR-50(H) series (results were not given). The observed increase trend could be the result of the cross-linking of the ENR by sulphur and by cross-linking of the epoxy groups *via* ring opening (Gelling, 1991). These two processes may cause a synergistic effect, and, therefore, the cure rate index has increased with increasing ENR content up to 50 wt.%. The decreasing trend may be attributed to the reduction of unsaturation in the blend with increasing the ENR content (Amu *et al*, 1985) In fact in ENR-60, it can be considered that the unsaturation has declined by 60 mole percent, and therefore, expected to exhibit a slower cure rate (Amu *et al.*, 1985) However, in practice, this effect had not been observed in other studies conducted on ENR-50 vulcanizates prepared by using 1-1.5 phr of sulphur Hence, the observed trend may be associated with the availability of less unsaturation caused by the higher epoxidation level and also by the availability of a lesser amount of sulphur. In general, it can be concluded that scorch time decreases with incorporation of ENR-60 (M) content. This is an accepted trend since residual acid in ENR can cause ring opening of epoxy group and thereby introducing few ether cross-links. This would result a reduction in processing safety. However, the observed reduction in cure time is advantageous in processing

Table 5 3 Cure characteristics for the blends containing ENR-60 (M)

Composition NR/ENR-60 (M)	Scorch time ts_1 (minutes)	Cure time t_{10} (minutes)	Curetime t_{50} (minutes)	Cure time t_{90} (minutes)	Cure rate index $(100/(t_{90}- ts_1)$
100.0	4	4	6	12	13
97 5:2.5	4	5	7	10	17
75:25	2	3	4	6	25
50:50	2	3	3	5	33
25: 75	2	3	4	5	33
0.100	3	4	5	7	25

5.3.2 Mooney viscosity and Mooney stress relaxation data for the NR/ENR blends

Mooney viscosity data for the compounded rubber blends (with vulcanizing ingredients) which were prepared using both ENR-45 (M) and ENR-60 (M) are presented in Tables 5.4 and 5 5. The results clearly indicate that the Mooney viscosities of the mill-mixed compounds based on either 100% NR or 100% ENR were significantly lower than the corresponding Mooney viscosities of the raw materials, namely natural rubber (ML1+4 = 83), ENR-45 (M) (ML1+4 = 107.5) and ENR-60 (M) (ML1+4 = 114). This is basically attributed to the relatively high degrees of mill breakdown occurring during the mastication process. Nevertheless, when compared to the initial Mooney viscosities of natural rubber and ENR, the extent of reduction in Mooney viscosity is higher for the ENR than for the natural rubber A similar trend was observed in the mill break down behaviour of ENR-50 in which Mooney viscosity was reduced up to 25 Mooney units from the original value (105) at 24 hours mastication time (Amu *et al.*, 1985) It was reported (Amu *et al.*, 1985) that the reduction of Mooney viscosity of ENR-50 to half of its original value occurred within 4 minutes and the rate of reduction was higher for ENR than that of the natural rubber. Such behaviour was attributed to the relatively high degree of mill breakdown of the ENR rubber (Amu *et al* , 1985)

Table 5.4 Data obtained using a Mooney viscometer (MV 2000) for the blends containing ENR-45 (M)

Property (Mooney units (MU))	Composition (NR: ENR-45 Ratio)						
	100:0	90:5	90:10	87 5 12.5	50·50	25·75	0·100
Initial viscosity	73.9	61.5	71.6	61.4	67.1	69.2	76.1
Viscosity @ 10s	7.5	5.2	6 43	5 0	7.2	8 4	10 0
Viscosity @ 20s	5.1	3.5	4.3	3 3	4.9	6.0	7.5
Viscosity @ 100s	2.0	1.4	1 6	1 2	2.1	2.7	3 5
Viscosity @ 10 % decay	39 3	31.0	35.5	31.2	35.4	36 6	40.3
Viscosity @ 20 % decay	34 2	26.5	30.6	26 6	30.5	31.6	34 9
Viscosity @ 90 % decay	4.7	3.8	4.3	3.8	4.3	4 4	4.9
Final viscosity	46.9	38.0	42.9	38 4	42.9	44.4	48 6
ML 1+ 4	46.9	38.0	42.9	38 4	42.9	44.4	48.6
Intercept (K)	26 6	19.4	23.7	19 8	23.2	24.5	26.6
Slope (a)	–0 56	–0 57	–0.58	–0 61	–0.52	–0.48	–0.43

There were no distinguishable differences among the Mooney viscosities of the mill mixed compounds prepared using ENR-45 (M) (Table 5.4). Nevertheless, two different trends for the variation of "a" were noted for the NR/ENR-45 (M) blends and NR/ENR-60 (M) blends (Tables 5.4 and 5 5) For the former materials (Table 5.3), the "a" value tends to increase with increasing the ENR content and thereafter it exhibited a decreasing trend. In the case of the

ENR 60 (M) materials, a gradual decrease in the "a" value was observed. Since the "a" value represents a measure of the visco-elasticity of the material, the initial increase in "a" value could be attributed to the increase of flow properties resulting possibly from a reduction of the molecular weight caused by the presence of residual hydrogen peroxide which may cause a degradation process. Despite this fact, the decreasing trend of the "a" values of the materials with increase in the ENR content, or at higher epoxidation level, could be primarily attributed to the lowering of the mobility of the polymer chains due to the presence of less flexible epoxy rings

Table 5.5 Mooney viscosity data and Mooney stress relaxation data for the blends containing ENR-60 (M)

Property (Mooney units) (MU)	Composition (NR:ENR-60 Ratio)							
	100:0	97.5:2.5	92.5:7.5	87.5:12.5	75:25	50:50	25:75	0:100
Initial viscosity	73.9	76.0	69.7	63.7	69.8	65.1	70.3	105.62
Viscosity @ 10s	7.5	8.5	8.4	7.8	9.0	10.3	15.4	18.6
Viscosity @ 20s	5.1	5.9	5.9	5.5	6.5	7.7	12.3	14.7
Viscosity @ 100s	2.0	2.4	2.5	2.3	2.9	3.8	6.9	7.9
Viscosity @ 10 % decay	39.3	39.5	37.9	35.6	38.0	37.3	44.3	54.5
Viscosity @ 20 % decay	34.2	34.3	32.9	30.8	32.9	32.5	39.1	48.2
Viscosity @ 90 % decay	4.7	4.8	4.6	4.3	4.6	4.5	-	-
Final viscosity	46.9	47.8	45.7	43.2	46.1	45.1	52.8	64.84
ML 1+4	46.9	47.8	45.7	43.2	46.1	45.1	52.8	64.8
Intercept (K)	26.6	27.0	25.9	24.3	25.5	25.7	31.8	39.8
Slope (a)	−0.56	-0.52	-0.50	-0.50	-0.46	-0.41	-0.32	-0.34

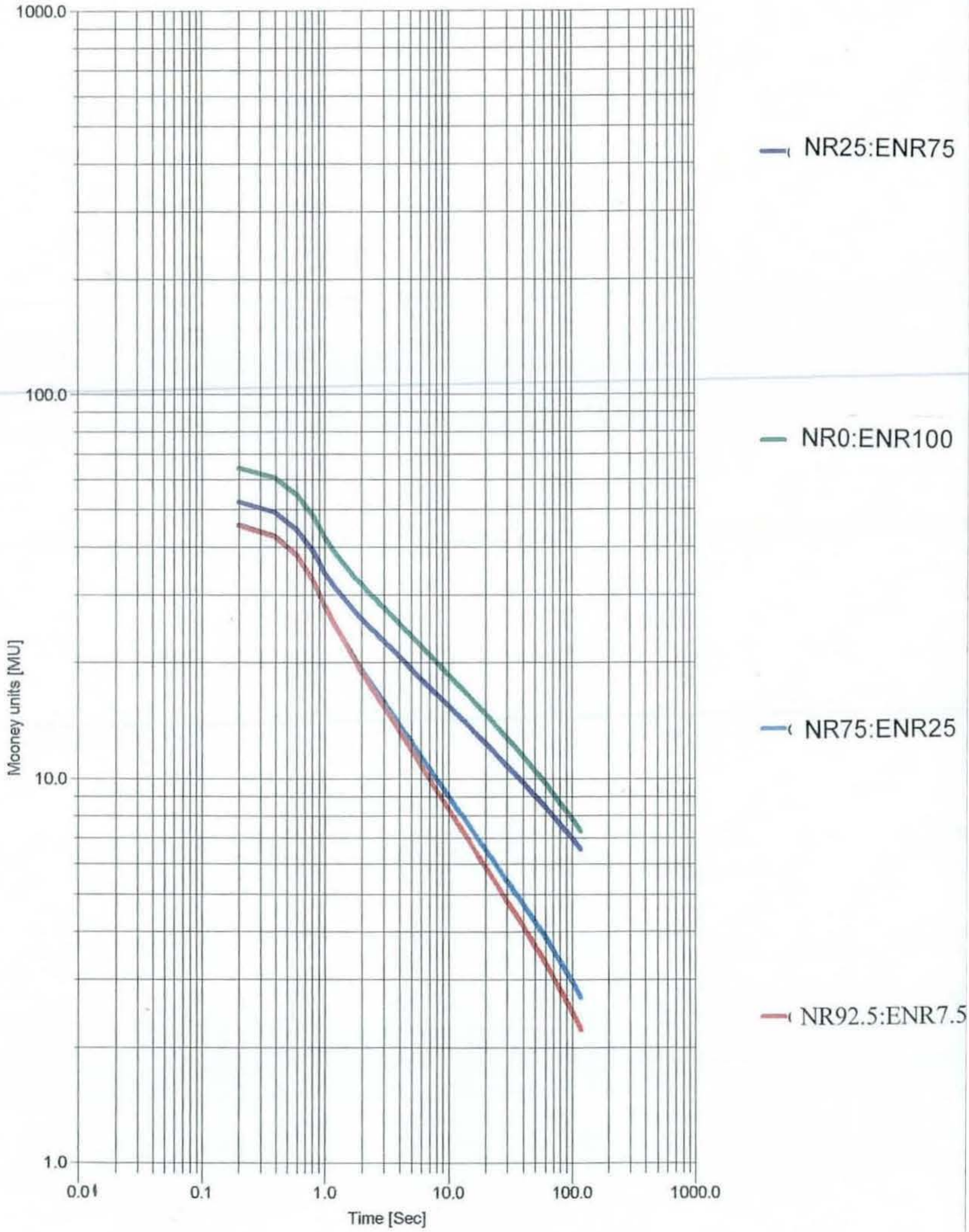


Fig.5.7 The effect of ENR-60 (M) content on Mooney stress-relaxation

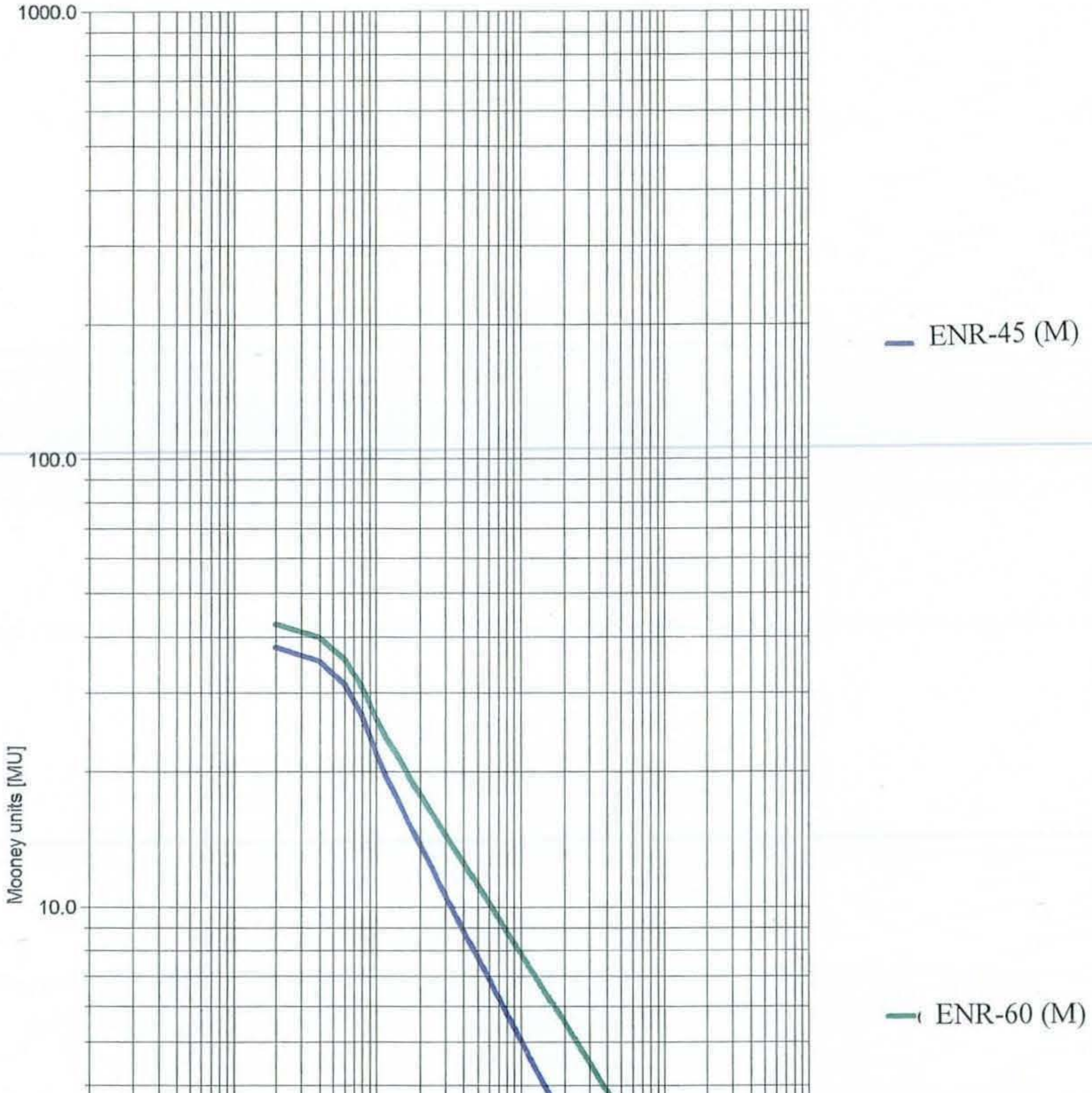


Fig. 5.8 Comparison of Mooney stress-relaxation for the NR/ENR-45 (M) and NR/ENR-60 (M) containing 12.5 wt.% ENR content

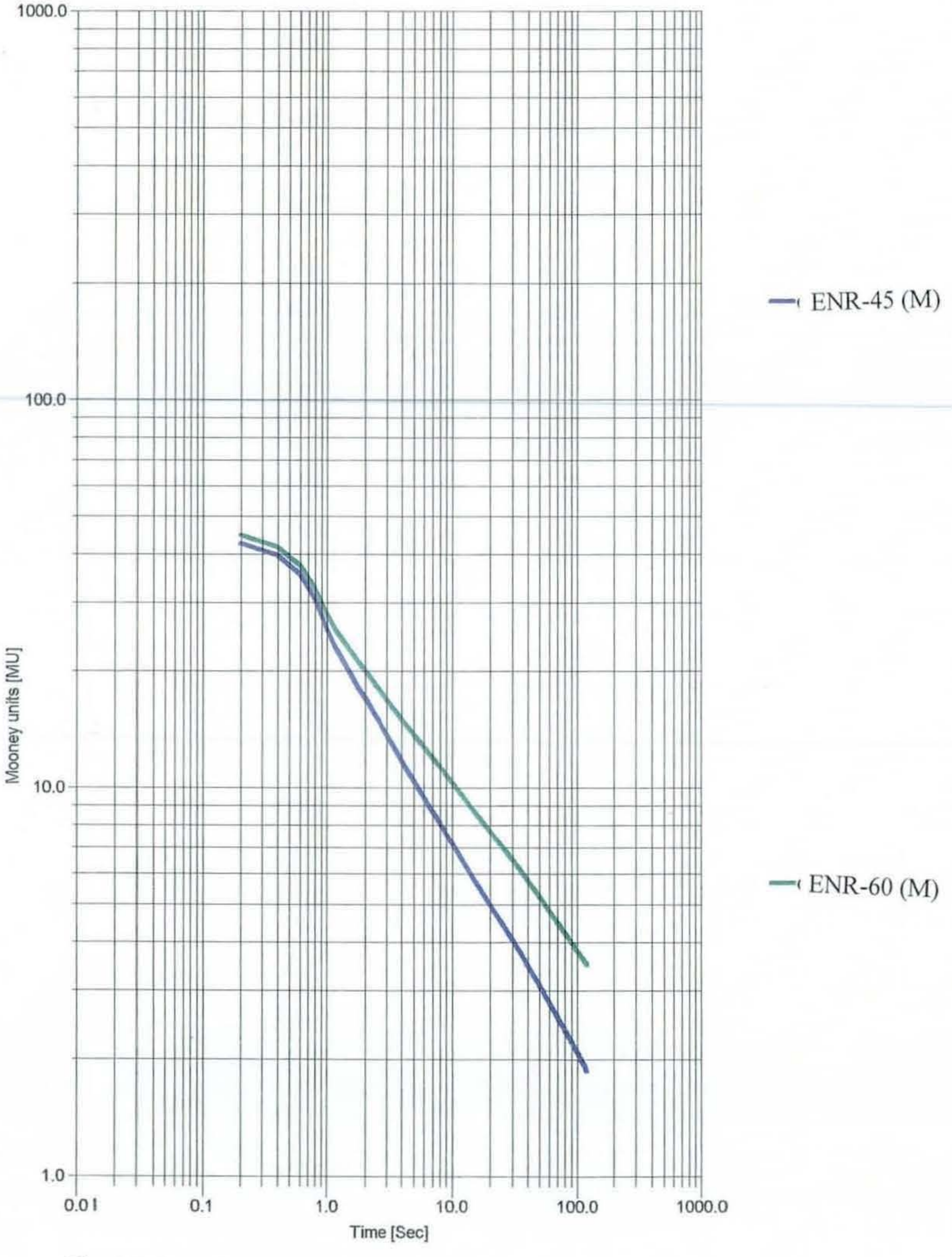


Fig. 5.9 The effect of epoxidation level on Mooney stress-relaxation data for the blends containing 50 wt.% ENR content

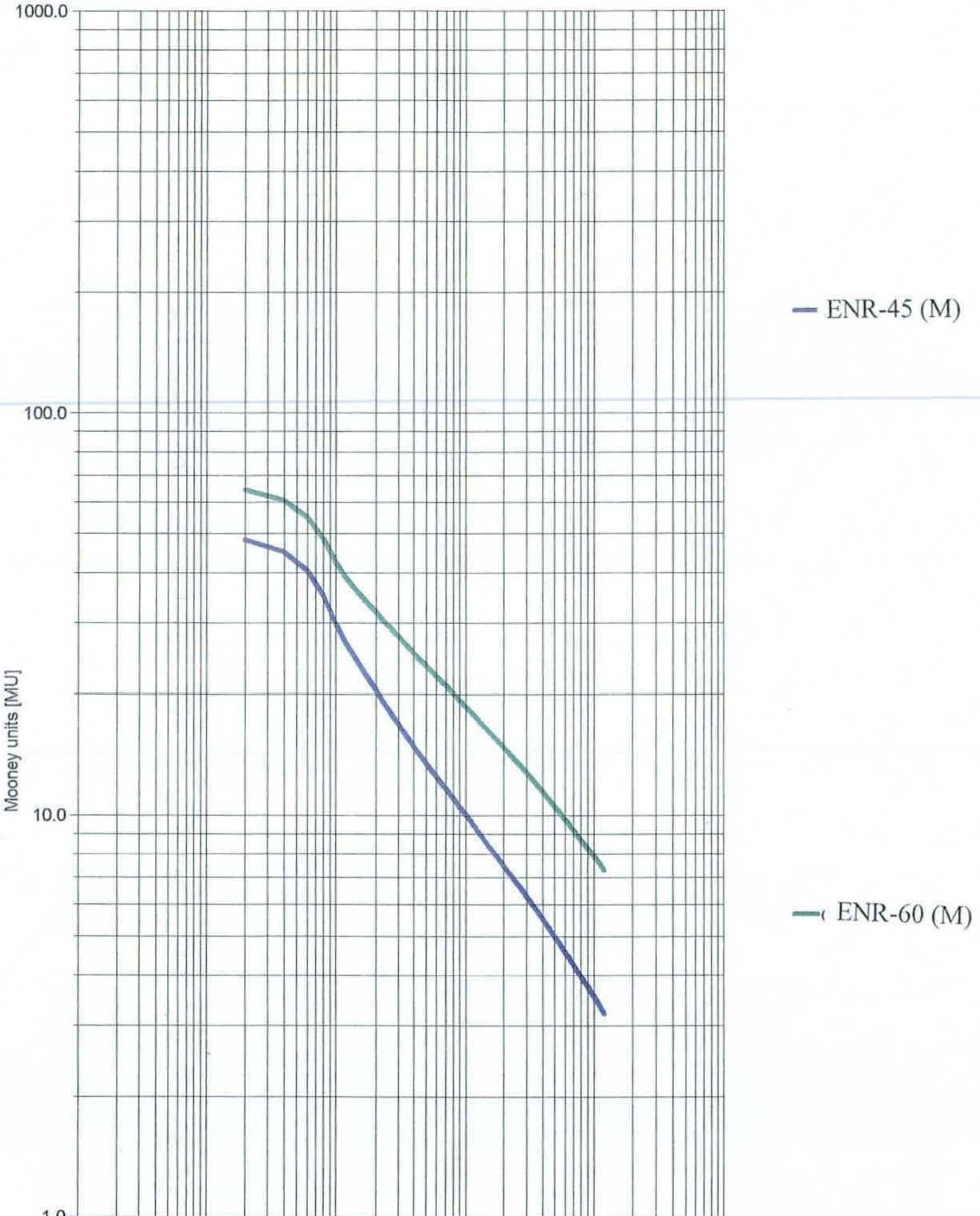


Fig. 5.10 The effect of epoxidation level on Mooney stress-relaxation for the blends containing 100 wt.% ENR content

The graphical representations presented in Figures 5.7 to 5.10 for the stress relaxation of ENR-45 (M) and ENR-60 (M) indicated that the "a" values (slope) decreased with an increase in the level of epoxidation. This is also due to the reduction in the mobility of the polymer chains with an increase in the number of epoxy groups. This result is in good agreement with the work by DiMauro, who confirmed that the reduction of mobility of polymer chains resulted in a slow relaxation with a decreasing "a" value (DiMauro (private communication) Hence, the processing characteristics such as die swell, nerve, rate of extrusion etc. will be affected at higher epoxy contents or with compounds containing only ENR.

5.3.3 Stress-strain data of the NR/ENR blends

Tables 5.6 and 5.7 summarise the results in terms of the tensile properties for the blends with ENR-15 (H) and ENR-50 (H).

Table 5.6 Tensile and tear properties of the NR/ENR-15 (H) blends

	Tensile properties							Tear strength (N/mm)
ENR-15-(H) (wt.%)	Modulus (%) (MPa)					Tensile strength (MPa)	Elongation at break (%)	
	50	100	300	500	700			
0	0.37 (0.04*)	0.55 (0.03*)	1.2 (0.06*)	2.2 (0.15*)	6.6 (1.1*)	16.0 (1.2*)	836 (32.1*)	51 (1.5*)
5	0.37 (0.04*)	0.53 (0.02*)	1.2 (0.02*)	2.1 (0.11*)	5.0 (0.3*)	16.4 (1.3*)	844 (28.2*)	53 (1.6*)
10	0.36 (0.02*)	0.57 (0.03*)	1.3 (0.12*)	2.5 (0.4*)	9.2 (1.1*)	18.9 (1.5*)	776 (18.4*)	49 (2.0*)
12.5	0.35 (0.01*)	0.57 (0.04*)	1.3 (0.08*)	2.3 (0.21*)	7.0 (1.8*)	17.0 (1.6*)	825 (13.3*)	52 (1.4*)
25	0.40 (0.02*)	0.65 (0.05*)	1.4 (0.13*)	2.9 (0.5*)	9.4 (1.4*)	16.1 (1.3*)	769 (23*)	48 (2.3*)
50	0.30 (0,04*)	0.50 (0.03)	1.2 (0.06*)	2.1 (0.27)	5.2 (1.1*)	10.8 (1.5*)	743 (28.5*)	40 (1.5*)

*Standard deviation

In relation to the moduli and the tensile strengths of the blends containing NR/ENR-15 (H) and ENR-50 (H), a significant improvement in the tensile strength was not observed. The tensile strength significantly decreased at higher ENR contents.

Unlike in the ENR series prepared using the higher level of hydrogen peroxide, a significant drop of tensile properties was observed at 75% ENR content for the NR/ENR blends prepared using a moderate amount of hydrogen peroxide (Refer to Tables 5.8 and 5.9). A similar observation was found for the elongation at break. Structural differences in these two ENR types may be responsible for of the observed differences in the ENR content at which a significant drop in tensile strength occurred. These structural differences may be related to some degradation caused by the use of excessive hydrogen peroxide which causes inferior strength properties. It is reported that the molecular weight of the natural rubber is reduced by oxidative degradation caused by peroxide (Tangpakdee *et al.*, 1988; Klinklai *et al.*, 2003) leading to the formation of aldehyde, ketone and α-β unsaturated carbonyl groups.

Table 5.7 Tensile properties of the NR/ENR-50 (H) blends

ENR-50 (H) (wt.%)	Tensile properties						
	Modulus (%) (MPa)					Tensile strength (MPa)	Elongation at break (%)
	50	100	300	500	700		
0	0.37 (0.04*)	0.55 (0.03*)	1.2 (0.06*)	2.2 (0.15*)	6.6 (1.1*)	16.0 (1.2*)	836 (32.1*)
5	0.35 (0.03*)	0.57 (0.04*)	1.2 (0.09*)	2.2 (0.24*)	6.1 (2.1*)	15.6 (1.9*)	702 (45.5*)
10	0.34 (0.06*)	0.57 (0.07*)	1.3 (0.05*)	2.4 (0.06*)	8.0 (1.1*)	15.2 (1.2*)	786 (17.2*)
12.5	0.35 (0.04*)	0.57 (0.04*)	1.2 (0.04*)	2.2 (0.05*)	6.3 (1.3*)	17.1 (0.63*)	820 (23.2*)
25	0.34 (0.04*)	0.53 (0.04*)	1.2 (0.06*)	2.1 (0.10*)	6.1 (1.1*)	16.6 (1.1*)	850 (24.6*)
50	0.35 (0.03*)	0.58 (0.02*)	1.5 (0.14*)	2.8 (0.33*)	-	5.9 (0.71*)	557 (29.0*)
75	0.39 (0.03*)	0.59 (0.02*)	1.3 (0.05*)	-	-	1.7 (0.31*)	396 (19.0*)

*Standard deviation

It was observed that the tensile strength decreased especially at higher ENR contents. Reduction in the tensile strength with increasing ENR content was reported in a study conducted on ENR/NR blends (Rahman,1990). The observed lower tensile strength values for the NR/ENR blends having more than 50% ENR content was primarily due to the low cross-link density arising because of the lower unsaturation level in the ENR, but is also due to the utilization of low levels of curative agents for vulcanization of these blends (Table 2.7).

Table 5.8 Tensile properties of the NR/ENR-45 (M) blends

ENR-45 (M) (wt %)	Tensile properties						
	Modulus (%) (MPa)					Tensile strength (MPa)	Elongation at break (%)
	50	100	300	500	700		
0	0.37 (0.04*)	0.55 (0.03*)	1.2 (0.06*)	2.2 (0.15*)	6.6 (1.1*)	16.0 (1.2*)	836 (32.1*)
7.5	0.36 (0.02*)	0.56 (0.04*)	1.2 (0.03*)	2.2 (0.03*)	5.6 (0.98*)	14.9 (1.8*)	714 (23.6*)
10	0.32 (0.02*)	0.54 (0.03*)	1.2 (0.04*)	2.1 (0.20*)	8.3 (1.5*)	15.6 (1.2*)	778 (22.1*)
12.5	0.33 (0.01*)	0.53 (0.01*)	1.2 (0.02*)	2.1 (0.19*)	6.4 (0.5*)	16.9 (0.6*)	729 (17.9*)
25	0.34 (0.01*)	0.59 (0.02*)	1.3 (0.03*)	2.6 (0.16*)	8.2 (1.2*)	14.9 (1.3*)	710 (11.2*)
50	0.32 (0.03*)	0.53 (0.03*)	1.2 (0.07*)	2.1 (0.18*)	6.5 (0.55*)	13.0 (1.2*)	730 (42.9*)
75	0.42 (0.02*)	0.51 (0.06*)	1.1 (0.08*)	1.8 (0.13*)	-	7.0 (1.2*)	596 (19.2*)
100	0.34 (0.02*)	0.55 (0.02*)	1.2 (0.01*)	2.2 (0.4*)		5.4 (0.80*)	585 (20.8*)

*Standard deviation

It is sensible to mention that, in this present investigation, an extremely low level of sulphur was used as the main curing agent because sulphur is capable of exerting an inhibition effect on the polymerization of MMA (Bartlett and Trifan, 1956; Ghosh, 1971). As the NR and the ENR materials are not a miscible pair, the distribution of vulcanizing agents in each phase depends on their solubility in each phase. This will cause changes in the distribution of cross-links in each phase depending on the reactivity of curing agents in each phase resulting in a heterogeneous morphology for these blends (Wang and Roland, 2005). Because of these factors, the tensile strength of the NR/ENR blends containing more than 50 wt.% of ENR was inferior probably owing to a low cross-link density in these materials. It was reported that the cross-link density decreased as the ENR content increased (Ismail and Suzaimah, 2000), Their results further indicated that the ENR phase would be the continuous phase when the ENR content is more than 50 wt.% .

Table 5.9 Tensile properties of the NR/ENR-60 (M) blends

ENR-60 (M) (wt %)	Tensile properties						
	Modulus (100%) (MPa)					Tensile strength (MPa)	Elongation at break (%)
	50	100	300	500	700		
0	0.37 (0.04*)	0.55 (0.03*)	1.2 (0.06*)	2.2 (0.15*)	6.6 (1.1*)	16.0 (1.2*)	836 (32.1*)
2.5	0.34 (0.03*)	0.56 (0.02*)	1.2 (0.04*)	2.2 (0.17*)	6.1 (1.0*)	12.9 (0.9*)	800 (13.9*)
5	0.45 (0.05*)	0.67 (0.06*)	1.5 (0.12*)	3.1 (0.34*)	10.7 (1.2*)	14.8 (1.3*)	757 (45.2*)
7.5	0.37 (0.02*)	0.58 (0.2*)	1.2 (0.09*)	2.4 (0.22*)	7.1 (0.71*)	13.2 (0.9*)	781 (24.0*)
10	0.36 (0.01*)	0.66 (0.05*)	1.5 (0.12*)	2.9 (0.44*)	9.2 (1.5*)	16.5 (1.3*)	849 (30.0*)
12.5	0.37 (0.02*)	0.58 (0.03*)	1.3 (0.09*)	2.4 (0.09*)	8.0 (0.7)	17.6 (1.1*)	802 (17.6*)
25	0.46 (0.08*)	0.70 (0.10*)	1.5 (0.12*)	2.8 (0.24*)	8.0 (1.6*)	21.1 (1.6*)	842 (37.1*)
50	0.40 (0.04*)	0.67 (0.07*)	1.7 (0.16*)	3.2 (0.23*)	9.2 (0.85*)	19.3 (1.1*)	833 (32.9*)
75	0.37 (0.06*)	0.59 (0.05*)	1.5 (0.11*)	3.1 (0.26*)	-	5.4 (1.1*)	442 (43.3*)
100	0.35 (0.01*)	0.59 (0.03*)	1.3 (0.08*)	-	-	2.0 (0.4*)	383 (30.7*)

*Standard deviation

The tear properties of the blends containing ENR-50 (H), ENR-45 (M) and ENR-60 (M) are presented in Figures 5.11 and 5.12. These materials exhibited very marginal initial increase in tear strength and thereafter showed a decreasing trend with increase in the ENR content.

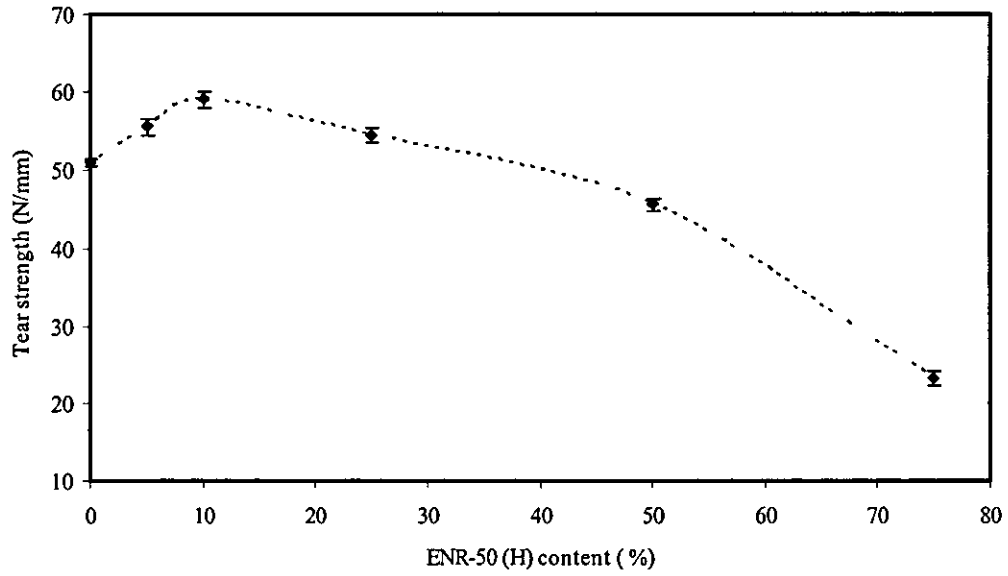


Fig.5 11 Variation of the tear strength for the NR/ENR-50 (H) blends

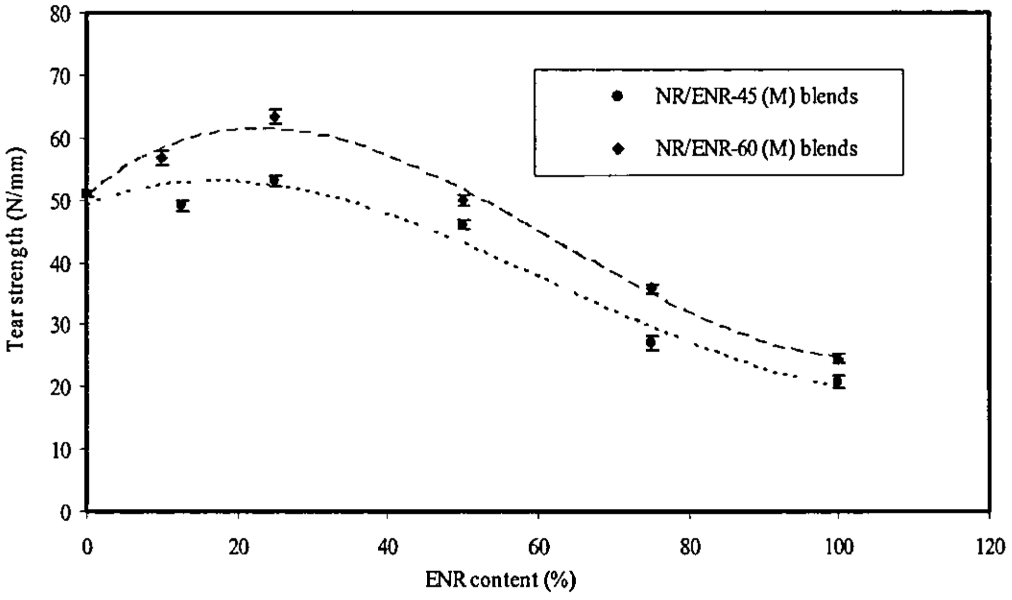


Fig. 5.12 Variation of the tear strength with the ENR content at two different epoxidation levels for the NR/ENR blends

5.4 Semi-1 IPNs based on ENR or ENR/acrylic acid

5.4.1 Semi-1 IPNs based on natural rubber, PMMA and the epoxidised natural rubber

In this chapter, the main objective is to investigate the effect of the addition of ENR as a third polar component on the miscibility, or compatibility, of the components of the IPNs based on natural rubber and PMMA. Epoxidised natural rubber is a form of modified rubber and it may be expected that it is partially compatible with natural rubber. On the other hand, as ENR contains oxirane group which render polarity it may be partially compatible with the PMMA component too Hence, epoxidised natural rubber is expected to act as a compatibilizer to improve the compatibility of the natural rubber and PMMA components in the IPNs. In this chapter, attention has been paid to the synthesis of semi-1 IPNs in which the composition was limited to 50/50 of elastomer (natural rubber, or a blend of natural rubber with ENR) and PMMA. For this purpose, blending of natural rubber and ENR was carried out prior to the synthesis of semi-1 IPNs Blending of polymers is a most extensively used technique to obtain desired physical and chemical properties. Blending can be achieved by various methods such as solution mixing, mixing of latexes or solid state mixing Solution state mixing is used to evaluate the miscibility of components since it will facilitate the reaching of equilibrium conditions. Compatibilizers is the term used for materials commonly used to enhance the compatibility between immiscible polymer pairs. This is generally achieved by means of adding a third component: homopolymer, graft co-polymer or a block co-polymer. In addition, the formation of covalent bonds between homo-polymers is employed using materials with reactive functional groups to impart compatibility and is referred to as reactive processing (Jeon *et al.*, 2005) It is being widely used by industry.

Mixing of the compatibilizer in the solid state can be performed in two ways.

1 Single-step mixing

2. Two-stage mixing.

Two-stage mixing can be performed according to two methods. In the first method, the compatibilizer (e g. ENR) can be mixed initially with the discrete phase (e g PMMA) Thereafter, this mixture will be mixed with the material (eg. natural rubber) which act as the matrix.

In the second method, the compatibilizer (e g. ENR) is mixed initially with the major component (eg. natural rubber) which acts as the matrix. Then this material will be mixed with the material (MMA, starting material for polymerization of PMMA) which serves as the dispersed phase.

However, in this present work, the first method, two-stage mixing of natural rubber and PMMA is difficult to apply as PMMA has to be synthesised within the cross-linked matrix. Hence, the second method was employed. In the first stage of mixing, ENR, which was used to improve the compatibility, was mixed with the natural rubber (matrix) and the resultant material is referred as the rubber blends. These rubber blends were vulcanised using a low level of sulphur. Unlike the normal second stage mixing where the second polymer is mixed in the solid state using a mill, here, the mixing of methyl methacrylate with the blend was carried out by swelling the NR in MMA. The MMA polymerization will then take place in the NR/rubber blend matrix This process will facilitate more mixing than the conventional mixing of polymers with high molecular weights as the mixing is carried out via the monomer. This facilitates interpenetration of PMMA in to the NR matrix and the simultaneous formation of catenane structures, which is the unique feature of interpenetrating networks.

In brief, five types of blends and semi-1 IPNs were prepared using following ENR types.

1. ENR- 15 (H) (0 - 50 wt.%)
2. ENR-45 (H) (0 - 50 wt.%)
3. ENR-50 (H) (0 - 75 wt.%)
4. ENR-45 (M) (0 - 100 wt.%)
5. ENR-60 (M) (0 - 100 wt.%)

In this investigation, the term "third component" is preferentially used instead of using the term compatibilizer for the ENR as most compatibilizer levels used for the blends are in general confined to below the 15 wt % level.

This study will investigate the effect of ENR on the compatibility of semi-1 IPNs based on natural rubber and PMMA over a wide range of composition

5.4.1.1 Detail description of the materials

Compositions of the blends and IPNs determined gravimetrically are given in Tables 5.10 to 5.14.

Table 5.10 Compositions of the semi-1 IPNs and the blends containing ENR-15(H)

Sample code	Composition		
		IPN	
	Blend (NR ENR-15) (wt %)	Target composition (Blend PMMA) (wt %)	Determined Composition* (Blend PMMA) (wt %)
NR 50 PMMA 50	100 0	50 50	53 47
NR/ENR-15 (H) (95/5) 50 PMMA 50	95 5	50 50	50 50
NR/ENR-15 (H) (90/10) 50 PMMA 50	90 10	50 50	52 48
NR/ENR-15 (H) (87 5/12 5) 50 PMMA 50	87 5 12 5	50 50	54 46
NR/ENR-15 (H) (75/25) 50 PMMA 50	75 25	50 50	50 50
NR/ENR-15 (H) (50/50) 50 PMMA 50	50 50	50 50	50 50

* Determined gravimetrically

Table 5.11 Compositions of the semi-1 IPNs and the blends containing ENR-45(H)

Sample code	Composition		
		IPN	
	Blend (NR ENR-45) (wt %)	Target composition (Blend PMMA) (wt %)	Determined Composition* (Blend PMMA) (wt %)
NR 50 PMMA 50	100 0	50 50	53 47
NR/ENR-45 (H) (95/5) 50 PMMA 50	95 5	50 50	52 48
NR/ENR-45 (H) (90/10) 50 PMMA 50	90 10	50 50	51 49
NR/ENR-45 (H) (87 5/12 5) 50· PMMA 50	87 5 12 5	50 50	50 50
NR/ENR-45 (H) (75/25) 50 PMMA 50	75 25	50 50	49 51
NR/ENR-45 (H) (50/50) 50 PMMA 50	50 50	50 50	53 47

* Determined gravimetrically

Table 5.12 Compositions of the semi-1 IPNs and the blends containing ENR-50 (H)

Sample code	Composition		
		IPN	
	Blend (NR: ENR-50) (wt %)	Target composition (Blend PMMA) (wt %)	Determined Composition* (Blend PMMA) (wt %)
NR 50 PMMA 50	100 0	50 50	51 49
NR/ENR-50 (H) (97 5/2 5) 50 PMMA 50	97 5 2 5	50 50	48 52
NR/ENR-50 (H) (95/5) 50 PMMA 50	95 5	50 50	50 50
NR/ENR-50 (H) (92 5/7 5) 50 PMMA 50	92 5 7 5	50 50	52 48
NR/ENR-50 (H) (90/10) 50 PMMA 50	90 10	50 50	50 50
NR/ENR-50 (H) (87 5/12 5) 50 PMMA 50	87 5 12 5	50 50	52 48
NR/ENR-50 (H) (75/25) 50 PMMA 50	75 25	50 50	51 49
NR/ENR-50 (H) (50/50) 50 PMMA 50	50 50	50 50	47 53
NR/ENR-50 (H) (25/75) 50 PMMA 50	25 75	50 50	50 50

* Determined gravimetrically

Table 5.13 Compositions of the semi-1 IPNs and the blends containing ENR-45 (M)

Sample code	Composition		
		IPN	
	Blend (NR ENR-45) (wt %)	Target composition (Blend PMMA) (wt %)	Determined Composition* (Blend PMMA) (wt %)
NR 50 PMMA 50	100 0	50 50	53 47
NR/ENR-45 (M) (97 5/2 5) 50 PMMA 50	97 5 2 5	50 50	51 49
NR/ENR-45 (M) (92 5/7 5) 50 PMMA 50	92 5 7 5	50 50	48 52
NR/ENR-45 (M) (87 5/12 5) 50 PMMA 50	87 5 12 5	50 50	52 48
NR/ENR-45 (M) (75/25) 50 PMMA 50	75 25	50 50	50 50
NR/ENR-45 (M) (50/50) 50 PMMA 50	50 50	50 50	46 54
NR/ENR-45 (M) (25/75) 50 PMMA 50	25 75	50 50	52 48
NR/ENR-45 (0/100) 50 PMMA 50	0 100	50 50	55 45

* Determined gravimetrically

Table 5.14 Compositions of the semi-1 IPNs and the blends containing ENR–60 (M)

Sample code	Composition		
		IPN	
	Blend (NR ENR-60) (wt %)	Target composition (Blend. PMMA) (wt %)	Determined Composition* (Blend PMMA) (wt %)
NR 50 PMMA 50	100 0	50 50	53 47
NR/ENR-60 (M) (90/10) 50 PMMA 50	90 10	50 50	51 49
NR/ENR-60 (M) (87 5/12 5) 50 PMMA 50	87 5 12 5	50 50	49 51
NR/ENR-60 (M) (75/25) 50 PMMA 50	75 25	50 50	50 50
NR/ENR-60 (M) (50/50) 50 PMMA 50	50 50	50 50	52 48
NR/ENR-60 (M) (25/75) 50 PMMA 50	25 75	50 50	47 53
NR/ENR-60 (0/100) 50 PMMA 50	0 100	50 50	50 50

* Determined gravimetrically

5.4.1.2 Physical properties of the NR-ENR-PMMA semi-1 IPNs

5.4.1.2.1 Solubility parameters and interaction parameters for ENR

Solubility parameters (δ) for different ENR grades, natural rubber and PMMA which are shown in Table 5.15.

Table 5.15 Solubility parameters and interaction parameters for ENR

Polymer	δ (MPa)$^{1/2}$
ENR-25*	17.4
ENR-50*	18.1
NR	16.7
PMMA	18.6

* Literature values

The difference between the solubility parameters of ENR and NR increases with an increase of the epoxidation level. On the other hand, the difference between the same parameter of ENR and PMMA components decreases with the epoxidation level. These data clearly indicate that the compatibility of ENR and NR decreases with increasing the epoxidation level The reverse trend is noted for the compatibility between ENR and PMMA components. Yusof (1999) and Nakason *et al* (2004) clearly indicated that the ENR and PMMA are phase separated, but could be described as a partially compatible polymer pair proven from the DMTA studies. Such a trend is attributed to the presence of interactions between the polar groups of the ENR and PMMA components (Nakason *et al.*, 2004)

5.4.1.2.2 Tensile properties of the NR-ENR-PMMA semi-1 IPNs

As is illustrated in Figure 5.13, a prominent enhancement in the tensile strength of the NR-ENR45 (M)-PMMA semi-1 IPNs was initially observed at 25 wt.% ENR content and it further improved with increasing the ENR content from 25 wt % up to 75 wt %. The optimum tensile strength was obtained at a level of 75 wt % ENR content on rubber. Nevertheless, if the additive rule is taken into consideration, a positive deviation was observed for the NR-ENR45 (M)-PMMA semi-1 IPNs with 50 wt % and 75 wt.% of content. This illustrates that the ENR-45 (M) compatibilizes the NR and the PMMA component at 50 wt.% and 75 wt.%. ENR -45 (M) content for these semi-1 IPNs

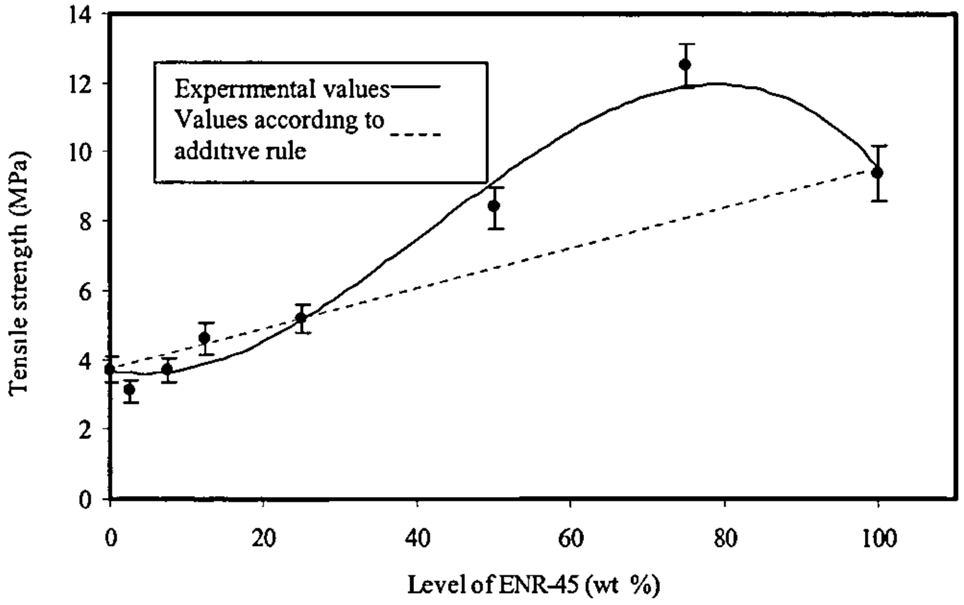


Fig. 5.13 Variation of the tensile strength with the level of ENR-45 for the NR-ENR45 (M)-PMMA semi-1 IPNs

A similar trend was obtained for the semi-1 IPNs with ENR-60 (M) (Figure 5.14). However, a positive deviation (synergism) from the additive rule was observed only for the NR-ENR60 (M)-PMMA semi-1 IPNs with 75 wt % ENR content

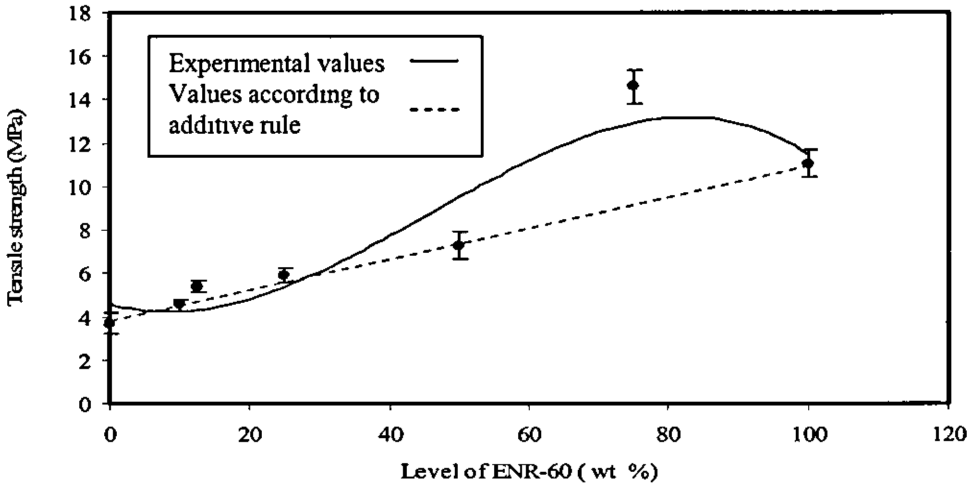


Fig. 5.14 Variation of the tensile strength with the level of ENR-60 for the NR-ENR60 (M)-PMMA semi-1 IPNs

This tensile property enhancement may be related to various reasons It could be primarily related to the interactions (Mohanty *et al.*, 1996) occurring between the oxygen of the carbonyl group of PMMA and the hydroxyl groups of ENR, formed via a ring opening reaction. Increase in the intensity of the peak due to hydroxyl groups was evident from the FTIR spectra of the semi-1 IPN compared to the corresponding blend (Figures 5.21 and 5.23). Therefore, the hydroxyl groups formed in the ENR (Figure 5.15) may possibly form hydrogen bonds with the oxygen of the carbonyl groups of the PMMA However, as there were no evidence for a prominent shift in the hydroxyl absorption peak towards lower frequencies, it may be assumed that the extent of formation of hydrogen bonds is not very significant. On the other hand, the likelihood of the occurrence of an ester interchange reaction between the ester groups of the PMMA and hyroxy groups as shown in Figure 5.16, cannot be under-estimated. Therefore, these factors will undoubtedly contribute for the enhancement of tensile properties. The factors affect the formation of hydrogen bonds can be identified as the amount of hydroxyl groups available and their proximity between the acceptor group (Eastwood *et al*, 2005). It is reported that as the amount of hydroxyl groups increases the probability to form intramolecular hydrogen bonds will be higher (Eastwood *et al*, 2005). It may be assumed that as the epoxidation level increased, the chances of hydrogen bonds between the hydroxyl groups in ENR chains are higher (self-association) and this may lead to a reduction in the formation of hydrogen bonds between ENR and PMMA. This may reduce the extent of compatibilization to a certain degree.

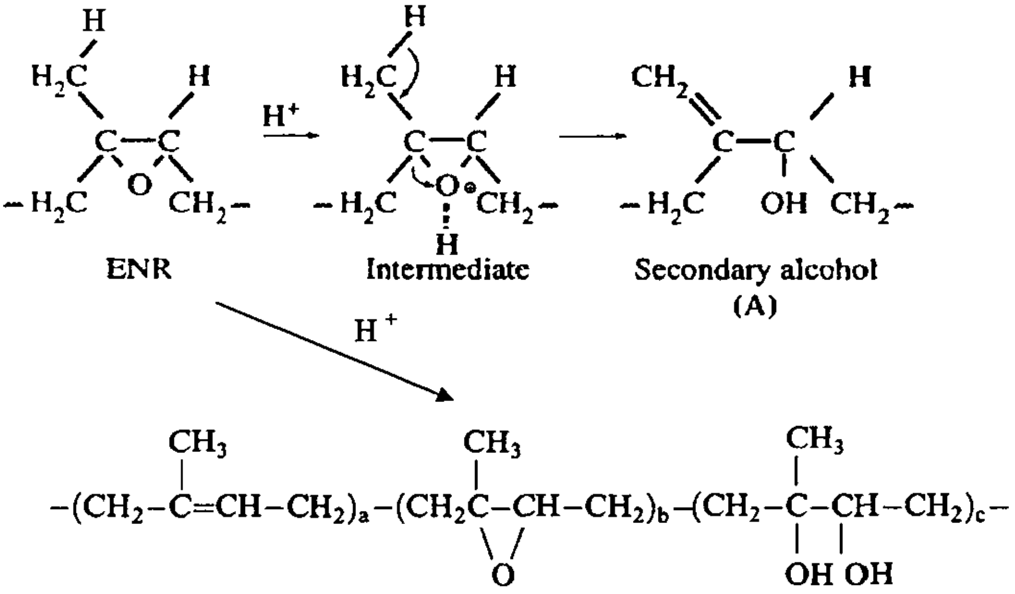


Figure 5.15 Ring opening of ENR groups and the some possible structures of ring-opened ENR (After Gan and Hamid, 1997; Mohanty and Nando, 1997)

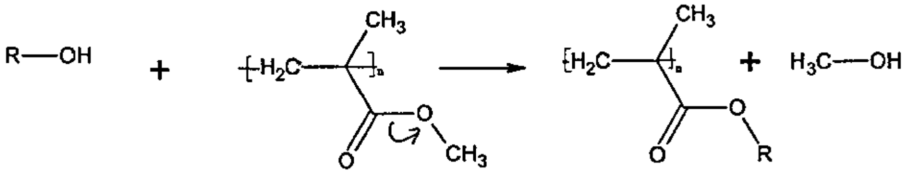


Figure 5.16 Ester interchange reaction

A lower tensile strength observed for the semi-1 IPNs having 100 % ENR is purely due to the lower cross-link density resulting from not only the low level of unsaturation, but because of the usage of a low level of sulphur as the prime curing agent. The cross-link density is considered as one of the decisive factors in determining the domain size (Yeo *et al.*, 1983). It is expected that if the cross-link density of the first-formed network is low, then the number of moles of the second monomer present between the tied polymer chain segments of the first polymer will be higher. With the polymerization of the second monomer, growing polymer chains of the second polymer repel the already existing polymer chains of the first polymer (Sánchez *et al*, 2001) resulting in large domains Therefore, it may be expected that the size of the domains, or PMMA phases, will increase with decreasing the cross-link density, resulting in a lower strength. However, it is noteworthy that the tensile properties of the semi-1 IPN based purely on 100 % ENR is still higher than those of the semi-1 IPN based on NR and PMMA.

Stress-strain plots for the ENR-45 (M), ENR-60 (M) and ENR50 (H) are shown in Figures 5.17 to 5 19. From these, it can be seen that the stress-strain behaviour varies from ductile behaviour to a more brittle behaviour.

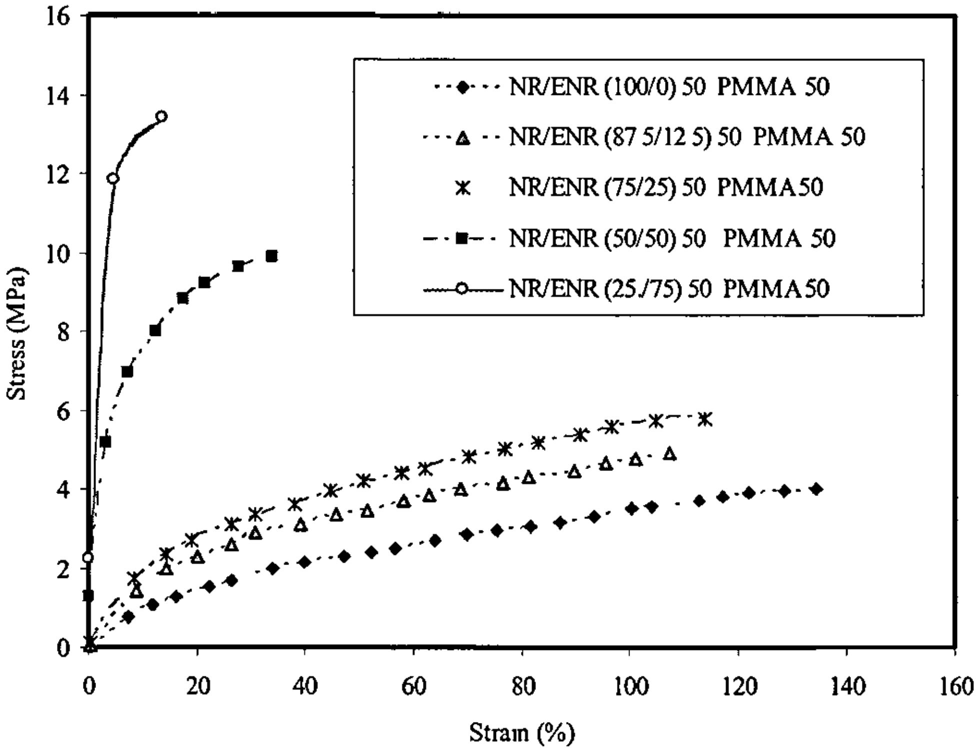


Fig. 5.17 The effect of addition of ENR-45(M) on the stress-strain properties for the NR-ENR-45 (M)-PMMA semi-1 IPNs

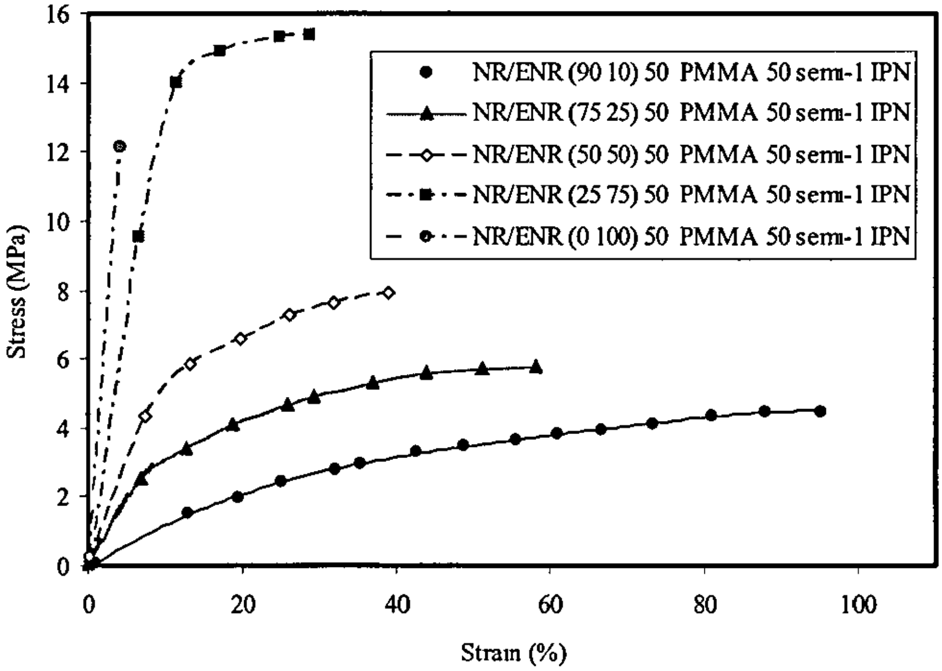


Fig. 5 18 The effect of addition of ENR-60(M) on the stress-strain properties for the NR-ENR-60(M)-PMMA semi-1 IPNs

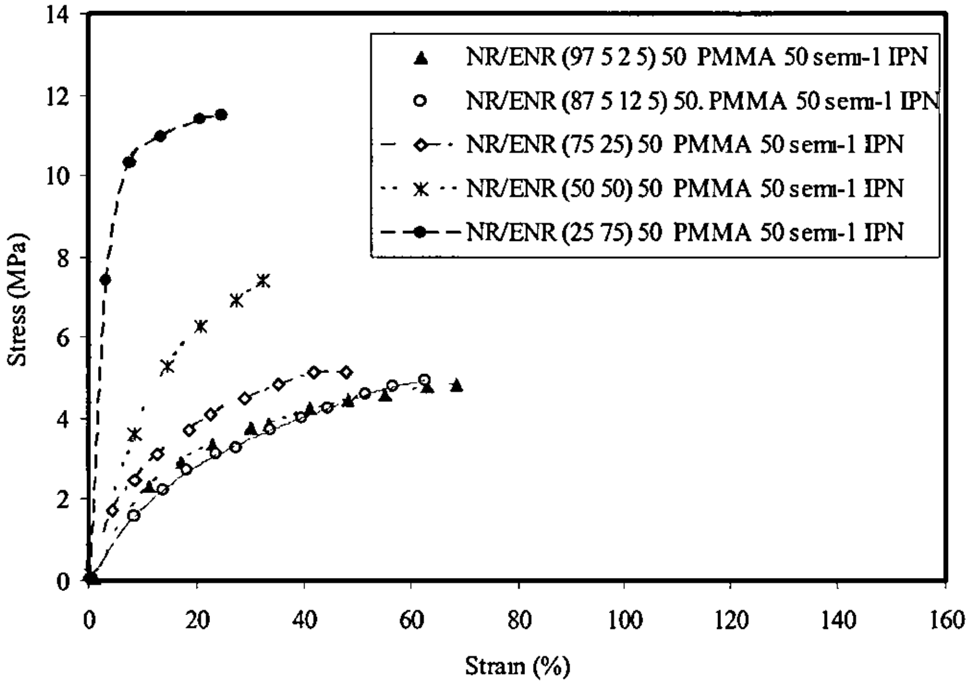


Fig. 5.19 The effect of addition of ENR-50(H) on the stress-strain properties for the NR-ENR50(H)-PMMA semi-1 IPNs

5.4.1.2.3 Tear properties of the semi-1 IPNs

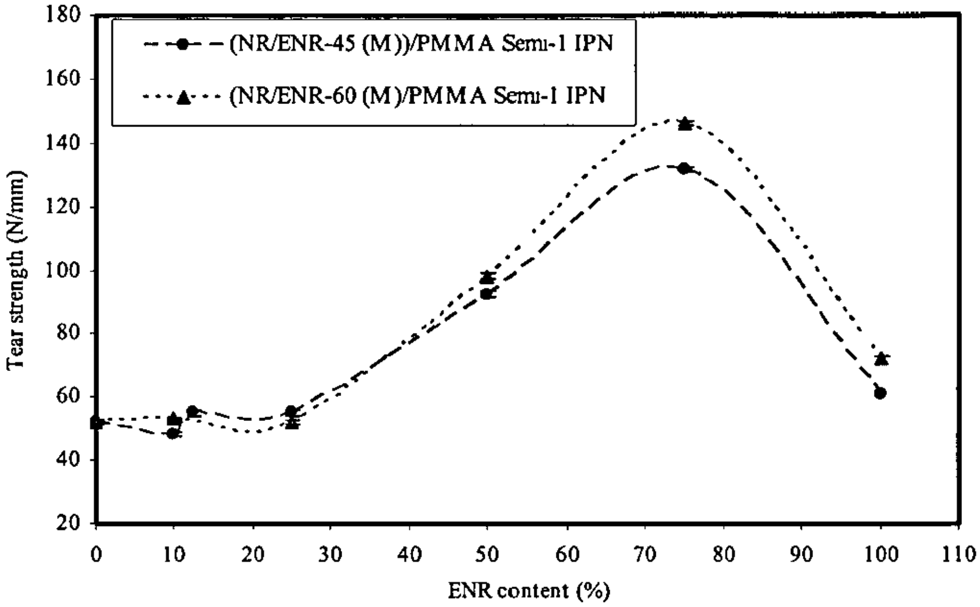


Fig 5.20 The tear strength with ENR content at two different epoxidation levels for the (NR/ENR)/PMMA semi-1 IPNs

Tear strength data for different ENR contents are shown in Figure 5.20. The results indicated that the tear strength increased significantly with increasing the ENR content up to 75 wt.%, regardless of the level of epoxidation. This improvement in tear strength could be a result of increased compatibility between NR and PMMA through the presence of the epoxidised natural rubber

The tear strength of the semi-1 IPNs containing 100 % ENR is significantly lower than the semi-1 IPNs containing 75 wt.% ENR and this might be expected as there is a possibility of a reduction in strain-induced crystallization with further cross-linking of the ENR.

5.4.1.2.4 FTIR spectroscopy analysis of the semi-1 IPNs

A comparison of FTIR spectra for the corresponding blend and the semi-1 IPN containing 100% ENR-60 (M) are given in Figures 5 21 and 5.23. The presence of a peak (medium) for the carbonyl absorption for the NR/ENR-60(M) (50/50) blend was noted in the Figure 5.21, which may be due to either carbonyl groups present in the natural rubber (proteinic layer on the rubber particles) or due to residual formic acid From these spectra, it can be seen that the hydroxyl peak height increased more in the semi-1 IPN than in the corresponding blend, indicating the formation of hydroxyl groups possibly by the ring opening of the epoxy group at 80°C during heat processing Therefore, some degree of hydrogen bonding can be present. The enhanced tensile and tear properties of the semi-1 IPNs with ENR could be the result of these interactions.

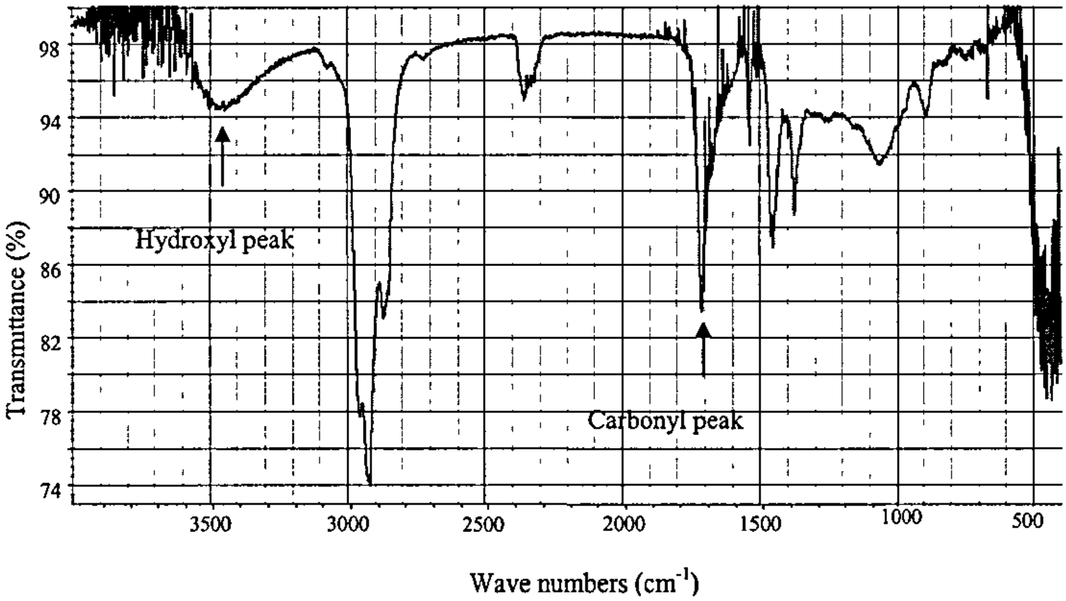


Fig. 5.21 The FTIR spectrum of the NR/ENR-60 (M) (50/50)blend

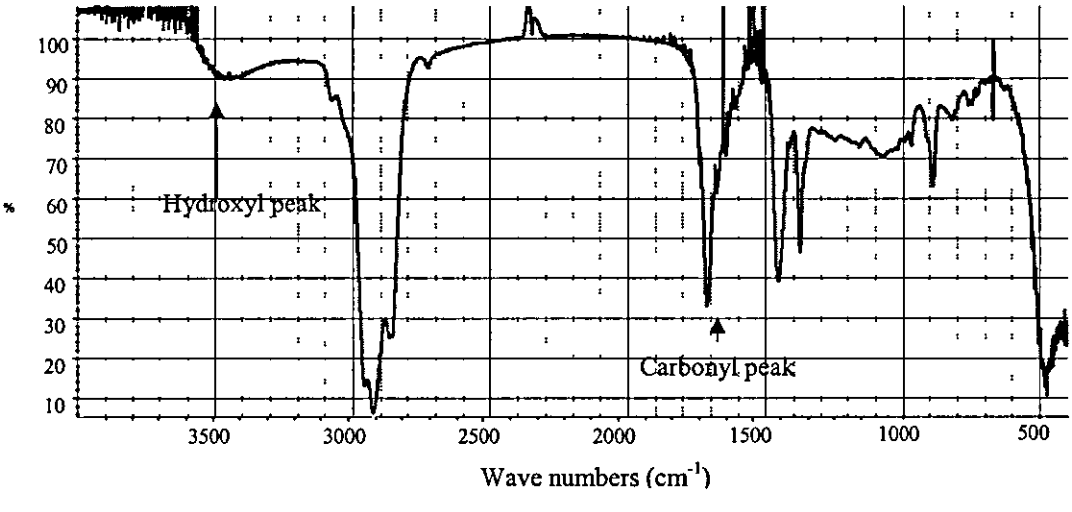


Fig 5.22 The FTIR spectrum of the NR/ENR-60 (M) (25/75) blend

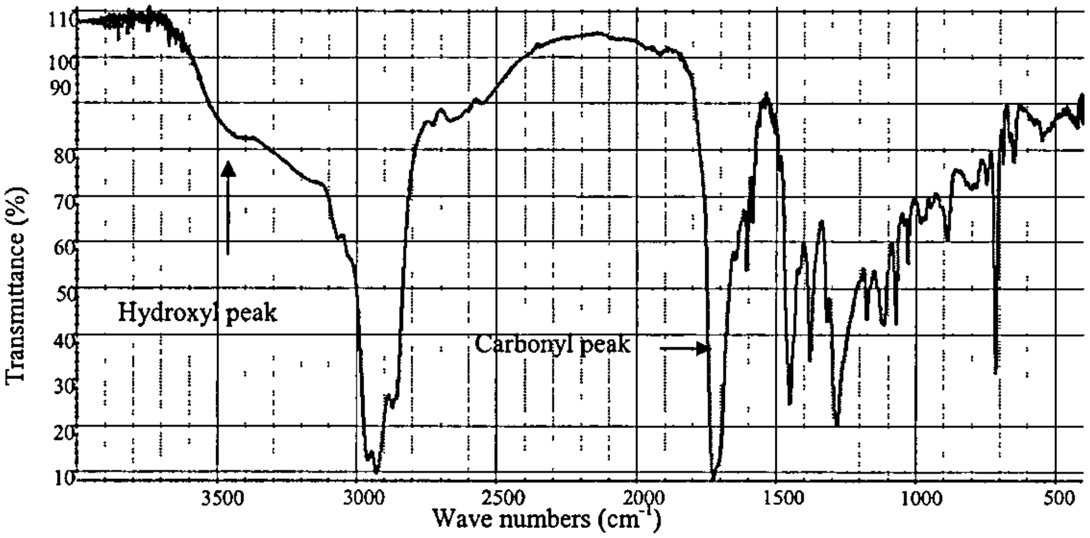


Fig. 5.23 The FTIR spectrum of the NR/ENR-60 (M) (50/50) 50 PMMA 50 semi-1 IPN

FTIR spectroscopic studies indicated that as the ENR content in the IPN is increased the hydroxyl peak height increased signifying increase of hydroxyl content perhaps due to ring opening of epoxy groups. Broadening of hydroxyl peak also evident and it may be an indication of the presence of hydrogen bonds. Broadening of hydroxyl peak in ENR-50 and PMMA blend had been attributed to the presence of hydrogen bonds (Latif *et al.*, (2006). Latif *et al.* (2006) concluded that ENR and PMMA are partially miscible via formation of hydrogen bonds between ENR-50 and PMMA.

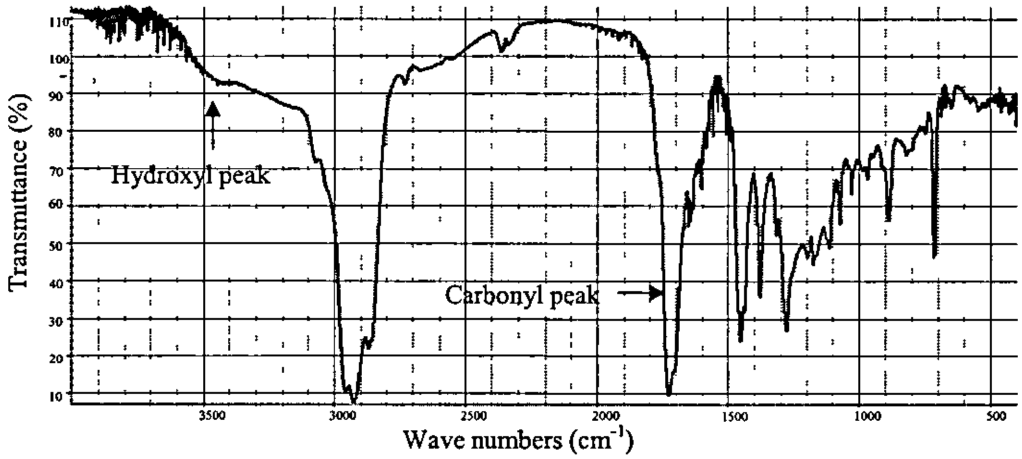


Fig. 5.24 The FTIR spectrum of the NR/ENR-60 (M) (90/10) 50:PMMA50 semi-1 IPN

Nevertheless, strong evidence for the presence of hydrogen bonds was not obtained as there was no significant shift in the carbonyl peak towards lower frequencies (Figures 5.24 to 5.26). A shift of the carbonyl peak is considered as strong evidence for the presence of hydrogen bonding (Huang *et al.*, 2006). Nevertheless, this does not mean that hydrogen bonds are not there, but just not in detectable amounts. Furthermore, peak broadening of the carbonyl absorption was observed with increase of the ENR content.

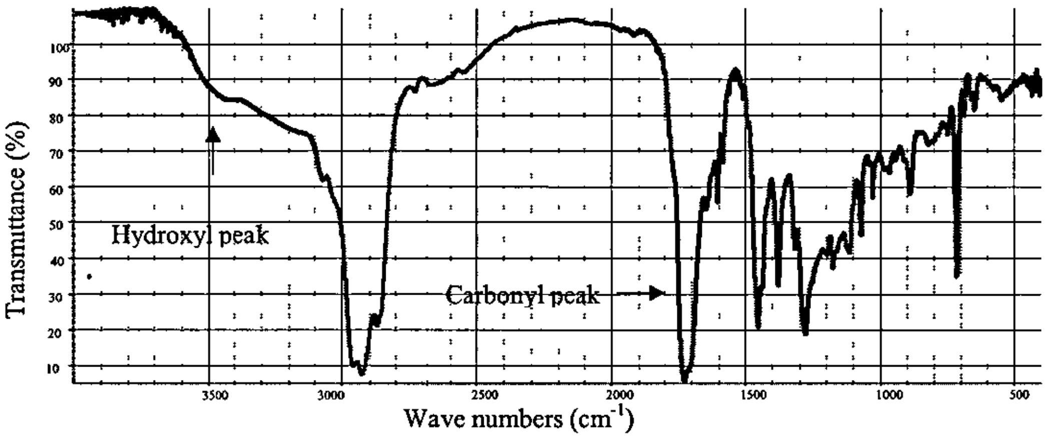


Fig. 5.25 The FTIR spectrum of the NR/ENR-60 (M) (75/25) 50:PMMA50 semi-1 IPN

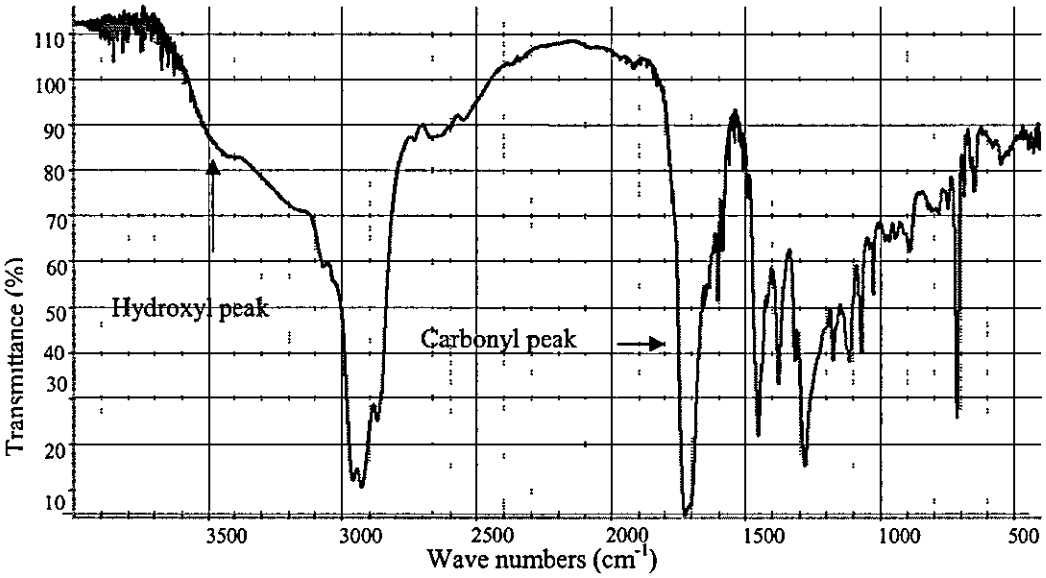


Fig. 5.26 The FTIR spectrum of the NR/ENR-60 (M) (25/75) 50:PMMA50 semi-1 IPN

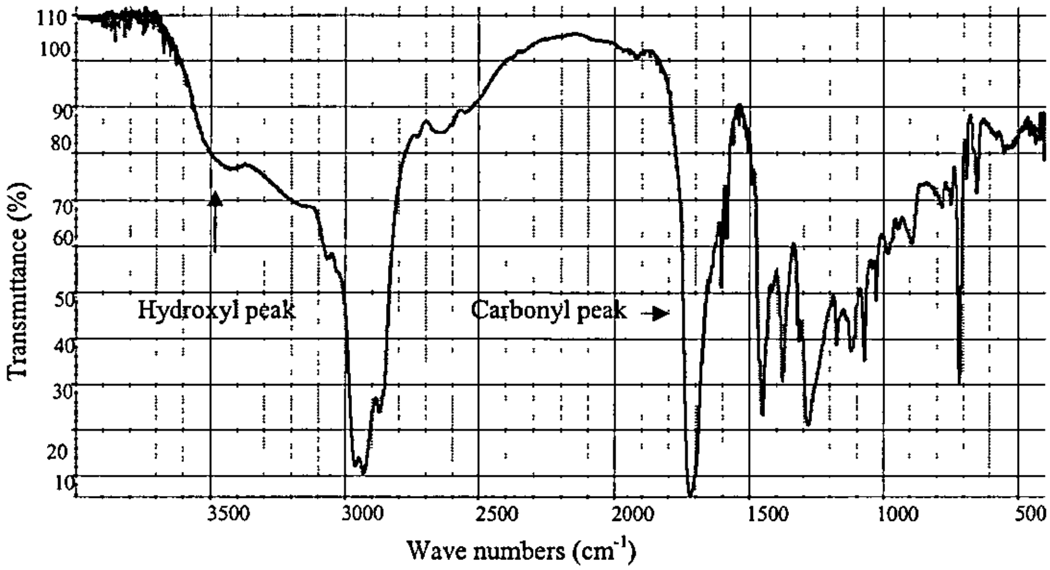


Fig. 5 27 The FTIR spectrum of the ENR-60 (M)50:PMMA50 semi-1 IPN

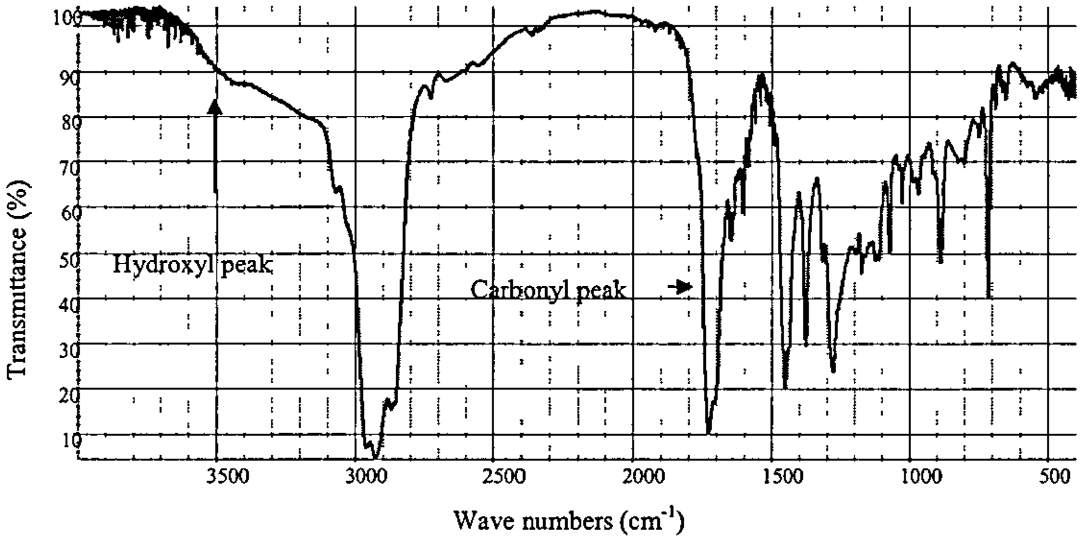


Fig 5 28 The FTIR spectrum of the ENR-45 (M)50:PMMA50 semi-1 IPN

Comparison of the FTIR spectra of the semi-1 IPN containing ENR-45 and ENR-60 (M) (Figures 5.27 and 5.28) indicated that with increasing epoxidation level, the peak height of the absorbance of the hydroxyl group increased.

Ritzenthaler *et al* (2000) have studied PMMA-modified epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA).They reported that there were no evidence for the presence of hydrogen bonding between PMMA and DGEBA from the FTIR studies due to lack of any shift of the carbonyl peak towards lower frequency and broadening of the lower frequency region which are considered as strong evidence for the presence of hydrogen bonded carbonyl groups. Further, the presence of a trans-esterification reaction between DGEBA and PMMA was also unable to be proved from FTIR studies due to lack of reduction in the peak due to the –O-CH$_3$ groups of PMMA (2850-2950 cm^{-1}) which is an indication of a trans-esterification reaction. In order to investigate further this, a small molecule, monoepoxy and a diamine were heated with PMMA and chromatograms (SEC) were obtained for the product. There was no prominent variation in PMMA peak indicating lack of grafting of epoxy-amine on to PMMA component (Ritzenthaler *et al*, 2000) Based on these facts, they have concluded that hydrogen bonds and trans-esterification reactions are absent between PMMA and DEGBA (Ritzenthaler *et al*, 2000). In this study too, a prominent variation in peaks between 2850 cm^{-1} - 2950 cm^{-1} were not obtained. However, even in the NR/ENR blends, three peaks were present in this region, but the peak at 2950 cm^{-1} is more prominent in the semi-1 IPN than the corresponding blend. However, there is not much variation in the peak height at 2950 cm^{-1}with the ENR content. If trans-esterification (ester-interchange) reaction occurs, it is expected that the peak height should decrease with ENR content. Nevertheless, such trend could not be found from the FTIR studies, and, therefore, it was concluded that the trans-esterifcation reactions are not present in the ENR/PMMA system to any significant level

In contrast, Janarathanan and Thyagarajan (1992) had found presence of hydrogen bonding between DGEBA and PMMA at room temperature mixing.

5.4.1.3 Dynamic mechanical thermal analysis data for the NR-ENR-PMMA semi-1 IPNs

5.4.1.3.1 NR-ENR-50 (H)-PMMA semi-1 IPNs

The data derived from the relaxation spectra of the semi-1 IPNs are shown in Table 5 16. The ENR-50 (H) content based on natural rubber is given in the first column. The α-transition corresponds to conformational molecular rearrangements which are considered as co-operative processes They were derived from the loss tangent data. As can be seen from the DMTA traces (Figure 5.29) of these semi-1 IPNs, three major transitions could be detected corresponding to natural rubber, ENR and PMMA depending on the ENR content, signifying these semi-1 IPNs are heterogeneous and phase separated in nature.

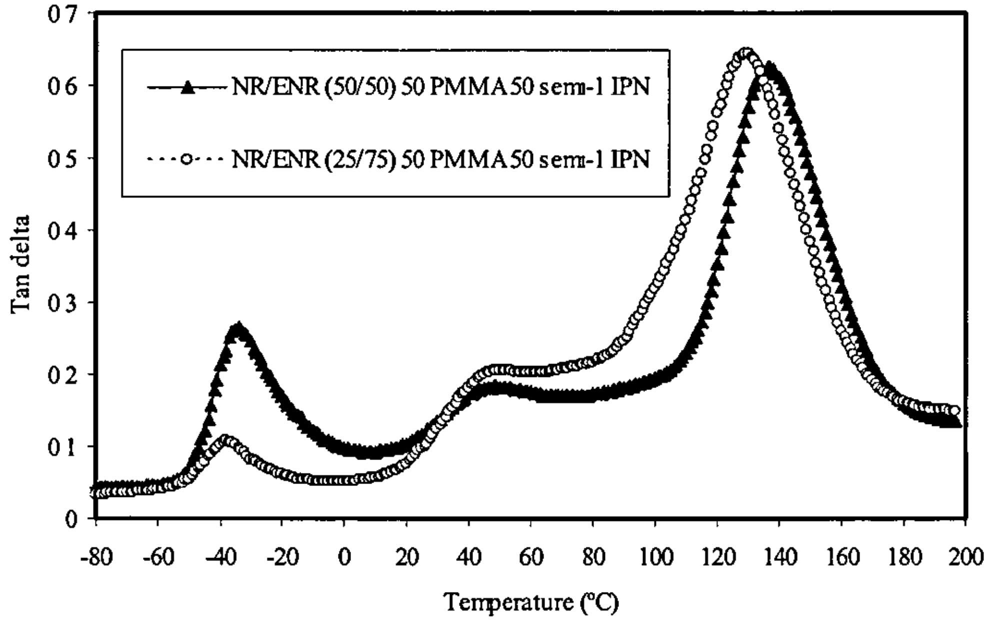


Fig. 5.29 The temperature dependence of loss tangent for the semi-1 IPNs with a levels of 50 wt.% and 75 wt% of ENR-50 (H)

Table 5.16 DMTA data for the semi-1 IPNs with ENR-50 (H)

ENR-50 (H) content (wt.%)	NR T_g (°C)	ENR T_g (°C)	PMMA T_g (°C)
0	-45		137
2.5	-44		134
7.5	-44		133
10	-39		130
12.5	-44		133
25	-43	58	133
50	-35	45	137
75	-38	48	131

In addition, it was noted that the transition corresponding to ENR-50 (H) component is prominent in the semi-1 IPNs with greater than 12.5 wt.% ENR. The absence of this transition in the semi-1 IPNs with 0 wt.% to 12.5 wt %

ENR50 (H) not considered as evidence for complete miscibility of the ENR component of these levels because of instrument limitations. As far as ENR transition is concerned, it is interesting to note that it has shifted approximately 34°C to 47°C compared to the ENR T_g (11°C) obtained for the vulcanizates of ENR-50 (H) A shift (8°C) of the ENR T_g was obtained for ENR-50/PMMA IPNs by Yusof (1999). Compared to the Yusof study, the higher shift of ENR T_g observed in this study is primarily attributed to the improved mixing obtained by the use of a low amount of curing agent (sulphur), the low PMMA molecular weight resulting from the use of a high amount of initiator and due to the presence of hydroxyl groups in the ENR caused by the experimental conditions employed. Moreover, improved mixing may be achieved via cross-linking and/or chemical interactions, especially hydrogen bonds. It has been stated that hydrogen bonds are one of the decisive factors which governs the miscibility of IPNs (Kim *et al.*, 1989). However, it could be anticipated that the interactions between ether group and carbonyl groups of epoxy and PMMA components is weak probably in the order of van der Waals forces as in the case of polyethylene oxide and PMMA (Rao *et al.*, 1985) Therefore, one could expect that the formation of hydrogen bonds most probably occur between the hydroxyl groups of ENR formed via the ring opening reaction, and the carbonyl groups of PMMA. This can be supported by the FTIR spectra of the semi-1 IPNs with ENR, in which the absorbance for the epoxy groups is no longer detectable perhaps due to ring opening and is further supported by the increased hydroxyl absorbance.

On the other hand, when the PMMA transition is concerned, generally, PMMA T_g shifted to lower temperature by 7°C when the ENR-50 (H) content increased up to 10 wt.%. This is clearly an indication of some mixing occurred through either interpenetration of the rubbery components into the PMMA phase via improved compatibility arising from specific interactions or to the similar polarities of the ENR and PMMA components However, a further increase of the ENR-50 (H) content up to 50 wt.% caused an increase (3°C to 7°C) of the PMMA T_g. This behaviour may be related to the high extent of interactions between, ENR and PMMA which may lead to a reduction in the mobility of PMMA polymer chain segments.

When the ENR-50 (H) content increased to 75 wt %, the PMMA T_g has shifted towards lower temperature by 6°C at a level of 75 wt.% ENR content.

This is basically attributed to the plasticizing effect resulting from improved inter-diffusion of components at the phase boundaries because of the similarities in polarities of ENR and PMMA components.

There is no noticeable definite trend in the NR T_g with ENR-50 (H) content. However, some improved mixing of the NR component was evident from the shift of NR T_g to higher temperature by 6°C to 10°C at level of 10 wt %, 50 wt % and 75 wt.%.

5.4.1.3.2 NR-ENR-45 (M)-PMMA semi-1 IPNs

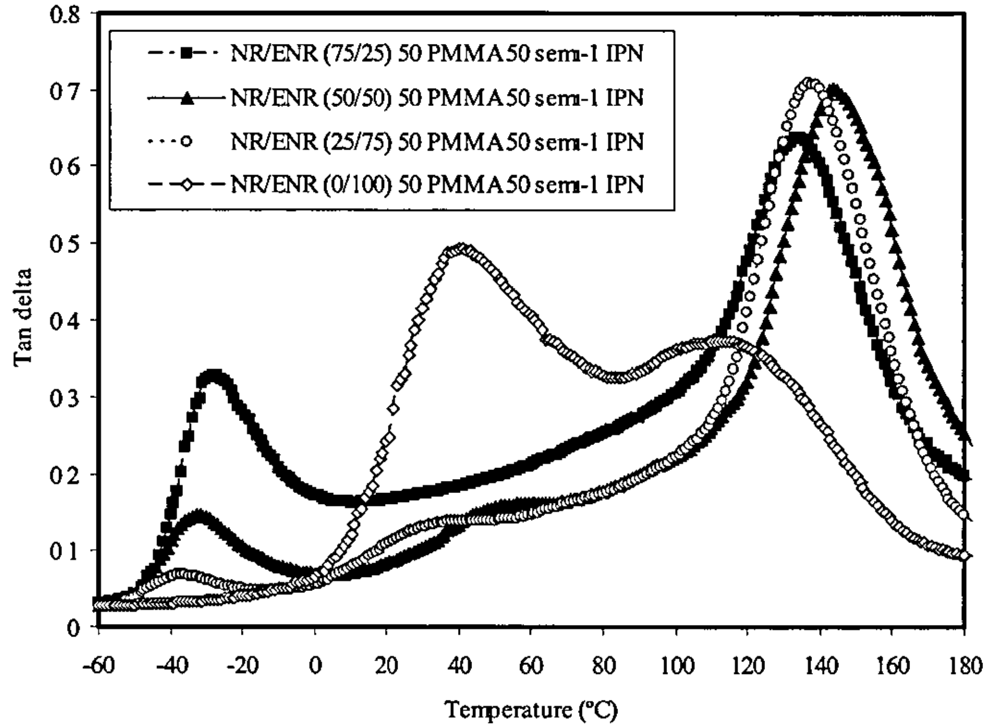


Fig. 5.30 The temperature dependence of loss tangent for the semi-1 IPNs with ENR-45 (M)

The loss tangent versus temperature plots for the NR-ENR-45 (M)-PMMA semi-1 IPNs are shown in Figure 5.30. Table 5.17 shows the glass transition temperatures derived from the loss tangent data for each component in these semi-1 IPNs. Unlike for the ENR-50 (H) series, the observed shift of the NR T_g by 7°C to 19°C towards higher temperature in all semi-1 IPNs is primarily associated with the reduction of mobility of NR polymer chains caused by the inter-mixing of PMMA component and/or ENR. This may be considered as strong evidence for improved mixing due to the incorporation of ENR-45 (M) with NR.

The ENR transition has shifted by more than 20°C to 39°C towards higher temperature signifying improved mixing of ENR with the PMMA component The reasons given for the observed identical shift in ENR T_g in the NR-ENR-50 (H)-PMMA semi-1 IPNs are also applicable to this situation.

The PMMA T_g initially decreased by 7°C at 2.5 wt.% ENR content, compared to the semi-1 IPNs without ENR. Thereafter, the PMMA T_g shifted to higher temperature by 13°C with increasing the ENR level up to 50 wt.%. An identical trend was observed for the ENR-50 (H) series and reason for this behaviour was given in section 5.4.1.3.1. Further increase of ENR up to 100 wt % caused an inward shift by 23°C, indicating enhanced mixing. This suggestion is further strengthened by the increase of the intermediate region between the ENR and PMMA transitions. It appears that these two transitions merged to form a broad transition perhaps indicating micro-heterogeneity (Figure 5 30) However, even at 100% ENR content, two transitions were resolvable, and therefore, considered as phase separated. The same conclusion was drawn by Yosof (1999) in his study based on ENR – PMMA IPNs Apart from that, a significant shift of the PMMA transition was found only at 2 5 wt % and 100 wt % ENR contents

Table 5 17 DMTA data for the semi-1 IPNs with ENR-45 (M)

ENR content (wt.%)	NR T_g (°C)	ENR T_g (°C)	PMMA T_g (°C)
0	-45		137
2.5	-26		130
7.5	-28		136
12.5	-29	49	136
25	-28	45	135
50	-34	50	143
75	-38	30	138
100		41	120

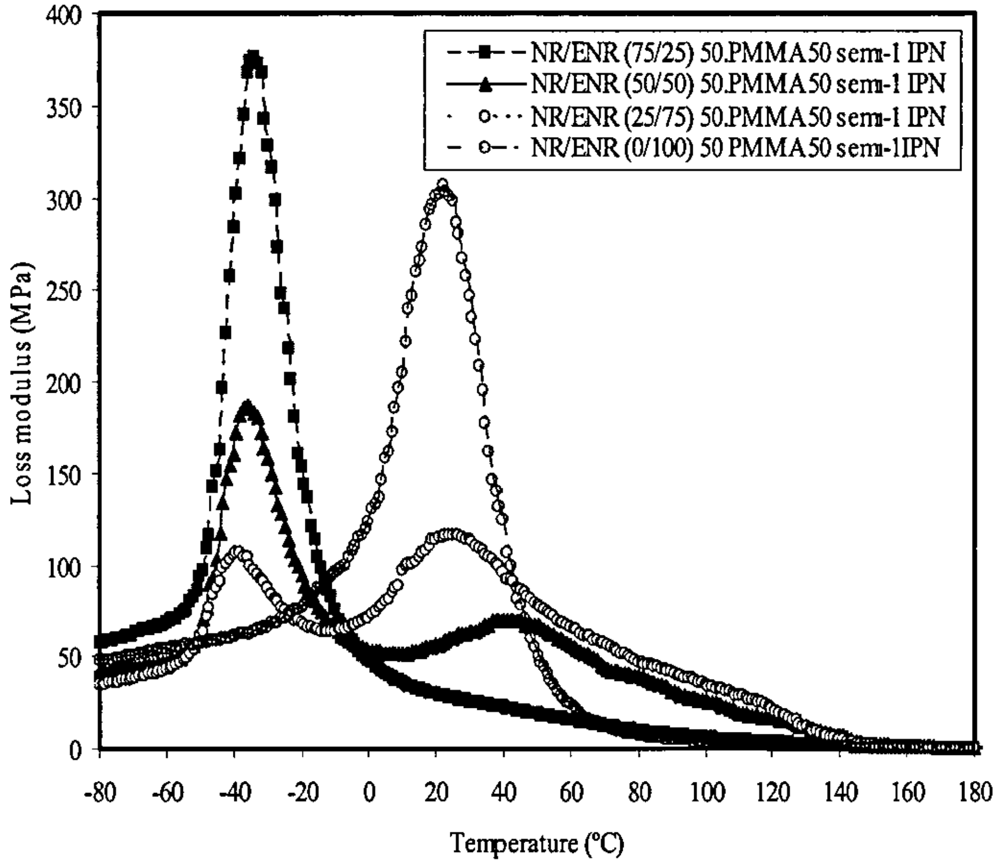


Fig. 5.31 The temperature dependence of loss modulus for the semi-I IPNs with ENR-45 (M)

The loss modulus data shown in Figure 5 31 illustrate that the magnitude of the ENR transition increased with increase in the ENR content indicating the damping characteristics of ENR However, the loss modulus peak of the PMMA component was not resolvable. This may implies that the extent of mixing of PMMA is also higher. The opposite trend was found for the loss tangent. The presence of a prominent PMMA loss tangent indicate that the PMMA phase would be the continuous phase and as a result tensile properties may be low due to the inherent brittleness of PMMA matrix. However, the absence of prominent loss modulus peak for the PMMA component is probably related to the improved mixing of the PMMA component.

5.4.1.3.3 NR-ENR-60 (M)-PMMA semi-1 IPNs

The NR T_g data presented in Table 5.18 indicated that incorporation of the ENR-60 (M) as a third component caused a shift of NR T_g towards higher temperature by 8°C to 18°C, indicating a significant extent of mixing of the NR component.

When ENR T_g is concerned, ENR T_g in these semi-1 IPNs shifted towards higher temperature by 44°C to 51°C compared to the ENR T_g (18°C) of the cross-linked ENR-60 (M) rubber without PMMA. Moreover, ENR transition has apparently merged with the PMMA transition resulting in a shoulder on the PMMA transition. This clearly indicates that ENR is present in a PMMA-rich phase resulting from the enhanced mixing of the ENR component with the PMMA component via interactions or by formation of chemical links between ENR and PMMA components.

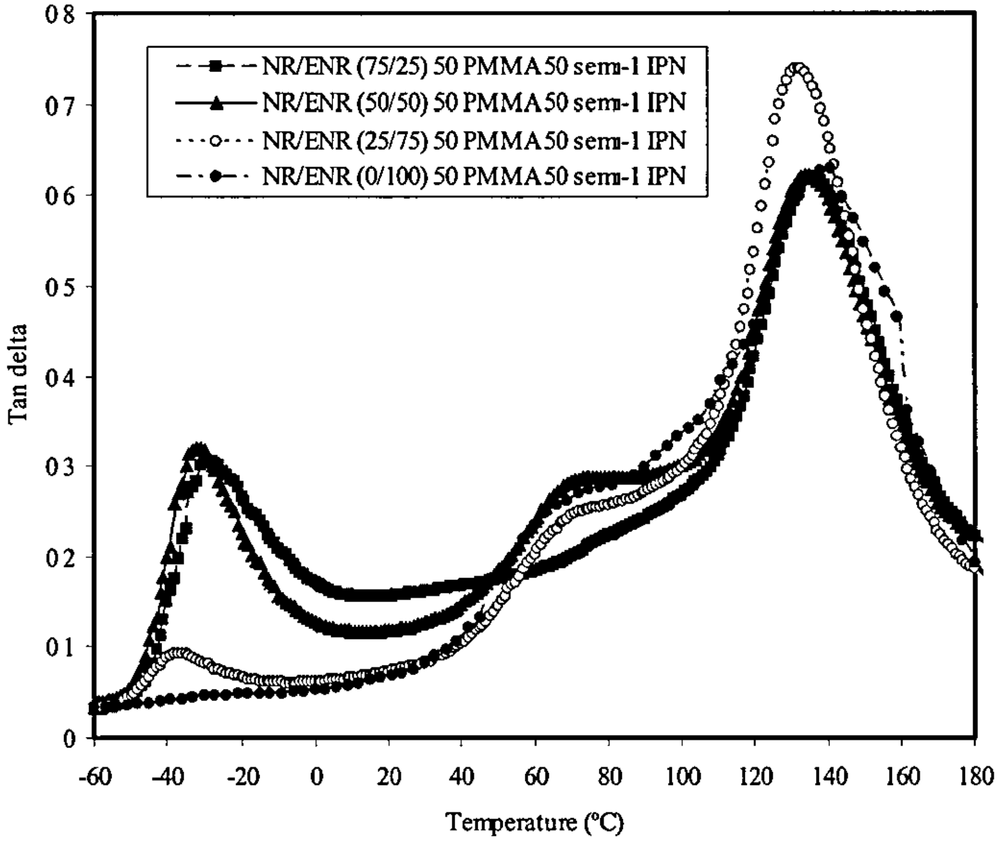


Fig. 5.32 The temperature dependence of loss tangent for the semi-1 IPNs with ENR-60 (M)

Table 5.18 DMTA data for the semi-1 IPNs with ENR-60 (M)

ENR-60(M) content (wt %)	NR T_g (°C)	ENR T_g (°C)	PMMA T_g (°C)
0	-45		137
12.5	-27		137
25	-30		137
50	-32	69	136
75	-37	68	133
100		62	141

Any prominent shift in the PMMA T_g towards lower temperature were not able to be detected from the DMTA traces of these ENR-60 (M) semi-1 IPNs. It is accepted that the conformational motions of individual component would not be affected by the presence of other components if there is prevailing macro-heterogeneity in the sample The observed prominent shift in not only NR T_g, but also in the ENR T_g would suggest that the extent of mixing of these two components with the PMMA component is higher in these samples. If the PMMA transition is considered, mixing of rubbery component with PMMA should impart a plasticization effect and therefore, one could expect that the PMMA T_g should be decreased upon mixing with the rubbery component In this case, it may be presumed that the interactions between ENR and PMMA may be higher resulting in a lowering of mobility of PMMA chain segments. In addition, if formation of covalent bonds occurs between ring opened ENR and PMMA, most probably via ester interchange reactions (Figure 5.16, section 5.4.1.2.1), this might lead to a reduction of mobility of each component resulting in increase in their glass transition temperatures. The likelihood of such a reaction may be higher at higher epoxidation levels and higher ENR contents. Therefore, the shift of T_g PMMA by 8°C towards higher temperature region in the semi-1 IPN based on 100% ENR-60(M) as the rubbery component, is primarily due to the formation of links (ester) and/or interactions between ENR and PMMA components. This could be the one of the reasons for significant shifting of ENR transition towards higher temperature region and the merging with the PMMA transition.

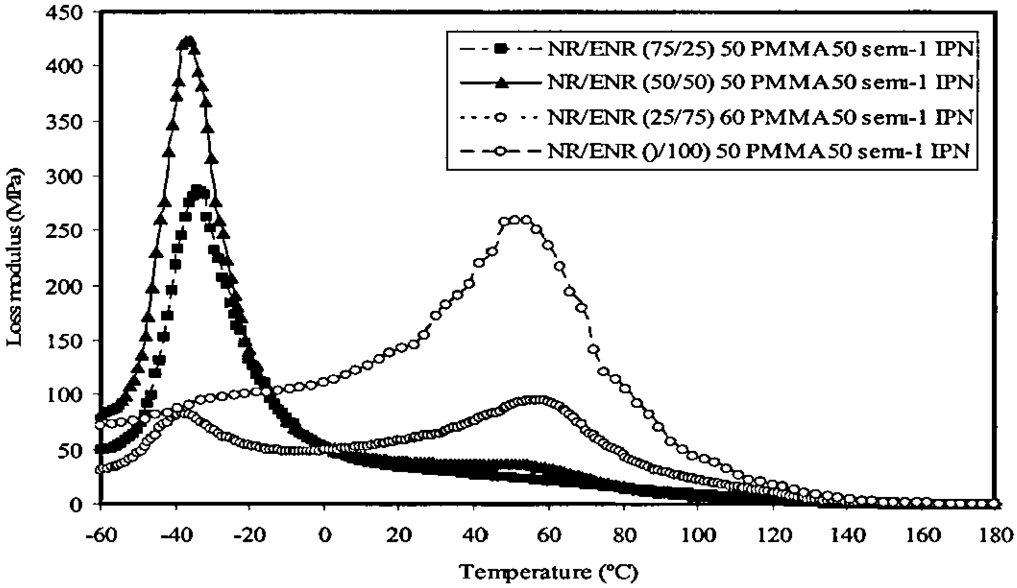


Fig. 5.33 The temperature dependence of loss modulus for the semi-1 IPNs with ENR-60 (M)

As can be seen from the loss modulus data for the semi-1 IPNs with ENR-45 (M) series (Figure 5.31), the magnitude of the loss modulus ENR peak increased with increasing the ENR content (Figure 5.33). It is well known that the ENR is a good damping (high hysteresis) material (Baker, 1985), and, therefore, it can be presumed that the magnitude of the loss tangent should increase with increase in the ENR content. The PMMA loss modulus peak is less prominent than the loss modulus peaks of the rubbery component. An identical trend was seen for the ENR-45 (M) series. The probable reason for this behaviour was given in section 5 4 1.3 2

5.4.2. Semi-1 IPNs based on natural rubber, ENR, PMMA and acrylic acid

5.4.2.1 General description

In this study, several semi-1 IPNs based on ENR and acrylic acid were prepared in order to investigate the effect of acrylic acid on the compatibility of NR, ENR and PMMA semi-1 IPNs. It is expected that when acrylic acid is used as a monomer together with MMA, three possible reactions can occur.

1. It can undergo formation of a copolymer poly(MMA-*co*-acrylic acid). Simultaneously, pendent carboxylic group of the acrylic component can react with hydroxyl groups of ENR which are formed through the ring opening reaction resulting in ester formation On the other hand, ester-interchange reaction between carboxylic group of acrylic component and the hydroxyl group of ENR is also possible. These two reactions lead to a formation of inter-grafts between the copolymer and ENR component. It is a well known fact that grafting reactions between components enhances the compatibility, micro-phase heterogeneity and mechanical properties (Hsieh *et al.*, 1995; 2001). Further, formation of hydrogen bonds between the hydroxyl group of acrylic acid and carbonyl group of PMMA or hydroxyl groups, if any formed through the ring opening of epoxy group, is possible All these factors would enhance the miscibility between ENR and PMMA component and thereby may exert an effect on the miscibility of NR and PMMA

2. Acrylic acid is capable of reacting with ENR directly to form acrylic acid grafted ENR (acrylic acid grafted ENR). If acrylic acid grafted ENR is formed, then the copolymerisation of acrylic component is still possible with either MMA or natural rubber due to the presence of olefin bond as a pendent group in the acrylic component. This will also lead to impart force miscibility between components. This process also leads to formation of inter-grafts.

3. Acrylic acid may graft on to natural rubber resulting grafted product (acrylic acid grafted natural rubber). This would facilitate the formation of hydrogen bonds with PMMA and ENR components and thereby enhancing miscibility between components.

The composition of the semi-1 IPNs based on acrylic acid are given in Table 5.19.

Table 5.19 Compositions of the semi-1 IPNs and containing acrylic acid

Sample code	Composition		
		IPN	
	Blend (NR:ENR-60) (wt.%)	Target composition (Blend:(PMMA/ Acrylic acid)) (wt.%)	Determined* composition (Blend PMMA/ Acrylic acid) (wt.%)
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (90/10) 50	50:50	50:50	53:47
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (80/20) 50	50 50	50:50	53:47
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (70/30) 50	50:50	50:50	51:49

* Determined gravimetrically

5.4.2.2 Solubility parameters and interaction parameters for the poly(MMA-*co*-acrylic acid)

Solubility parameters for the random poly(MMA-*co*-AA) was obtained by using following equation

$\delta = \Sigma \, \delta_i V_i$

δ_i is the solubility parameter of each component and V_i is the volume fraction of each component (Table 5 20).

Table 5.20 Solubility parameters and interaction parameters for poly(MMA-*co*-acrylic acid)

Acrylic acid content of poly(MMA-*co*-acrylic acid) (wt.%)	δ (MPa)$^{1/2}$
10	19.9
20	20.4
30	20.9
100*	24.39**

* Poly(acrylic acid)

** Data obtained from Mohanty *et al.* (1996)

From the data shown in Table 5.20, it can be clearly seen that the difference between the solubility parameters of co-polymer and ENR-50 (18.1) or PMMA (18.6) increased with an increase of the acrylic acid component in the co-polymer resulting in gradual increase in incompatibility between individual components.

5.4.2.3 Tensile and tear properties of the semi-1 IPNs based on natural rubber, ENR, PMMA and the acrylic acid

Table 5 21 Mechanical properties of the semi-1 IPNs based on acrylic acid

Composition	Tensile strength (MPa)	Tear strength (N/mm)
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (100/0) 50	8.4 (1.2*)	92.4 (3.3*)
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (90/10) 50	6.1 (0.99*)	76.7 (2.1*)
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (80/20) 50	4 6 (0 78*)	44.5 (1 9*)
NR/ENR-60 (M) (50/50) 50: PMMA /Acrylic acid (70/30) 50	5.2 (1.1*)	56.7 (1.5*)

* Standard deviation

From these results, it was noted that the introduction of up to 20 wt % acrylic acid resulted in a lowering of both tensile and tear strengths However, further increase of acrylic acid increased the tensile and tear strength. In comparison with the semi-1 IPN without acrylic acid, the observed lower mechanical properties of the semi-1 IPNs having acrylic acid is primarily ascribed to the reduction of the reinforcement caused by the lower PMMA content (less than 50 wt %) in these materials. However, the increase in tensile strength and tear strength with increase of the acrylic acid content from 20 wt.% to 30 wt.% possibly related to the simultaneous copolymerisation of acrylic acid with the MMA. As indicated from the DMTA results which will be discussed later, increased of miscibility between the ENR and PMMA, and increased chemical interactions may be the reasons for improved tensile and tear properties as the acrylic acid content increased from 20 wt % to 30 wt.% . However, a definite explanation could not be forwarded at this stage.

5.4.2.4 FTIR spectroscopy analysis of the semi-1 IPNs based on natural rubber, ENR, PMMA and acrylic acid

As far as FTIR spectra of the semi-1 IPNs containing acrylic acid are concerned, it was found that as the acrylic acid content increased from 10 to 30 wt.%, the hydroxyl absorbance increased (Figures 5.36 to 5.38) It is noteworthy that these spectra were obtained for the condensed material which was collected after heating the sample to red-hot condition (pyrolysed samples) As seen in the previous case, a significant shift of the carbonyl absorbance towards lower frequency was not detected, implying the absence of a large amount of inter-molecular hydrogen bonding between the oxygen in the carbonyl groups and the OH groups of the acrylic acid component. Nevertheless, self-association of OH groups present in ENR or in the acrylic acid groups is possible, but this type of interaction could not be clearly distinguished from these IR spectra. However, the carbonyl absorbance due to the ester groups (1735-1750 cm^{-1}) is prominent for the semi-1 IPNs containing 0 wt % (Figure 5.23) and 10 wt.% of acrylic acid (Figure 5.36). Then the carbonyl absorbance of acid groups (1700-1725 cm^{-1}) became prominent (Figure 5 37 and 5.38) with increasing acrylic acid from 10 wt.% (Figure 5.36) to 20 wt.% (Figure 5.37).

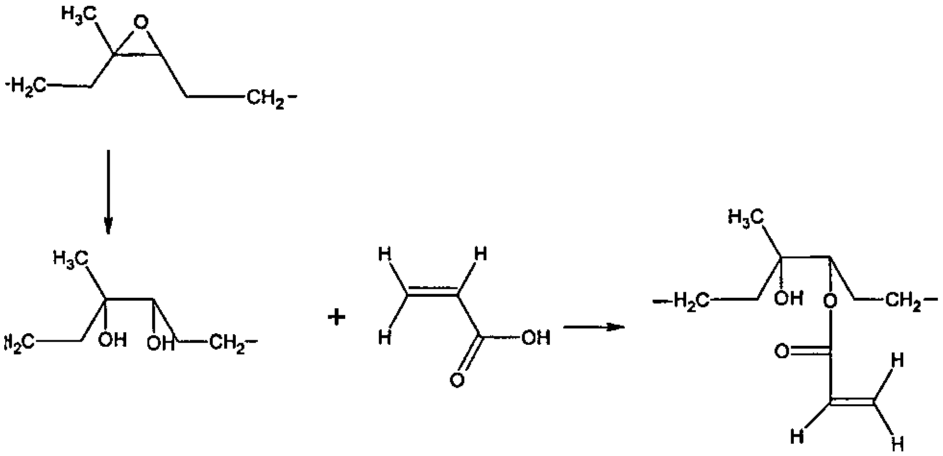


Fig. 5.34 Proposed reaction of acrylic acid and epoxidised natural rubber

As far as the probable reactions of the acrylic acid are concerned, acrylation of epoxy group (Figure 5.34) and/or co-polymerisation of acrylic acid with MMA can be identified as the two major competitive reactions. Phinyocheep and Duangthong (2000) reported that acrylic acid (acrylation) bound on to epoxide groups at 80°C and this reaction was accelerated by the presence of a photo-initiator Therefore, it may be assumed that at low levels of acrylic acid, the acid might undergo an acrylation reaction with epoxy groups resulting in graft IPNs having pendent acrylic groups on the ENR backbone. Thus, carbonyl absorbance due to acid was unable to be detected as it may have reacted with hydroxyl groups to from pendent groups on the ENR. On the other hand, at higher acrylic acid contents, co-polymerisation (Figure 5.35) would be more likely to be the dominant reaction, and, therefore, carbonyl absorbance due to acid would be observed at 20 to 30 wt.% of acrylic acid was incorporated in to the system.

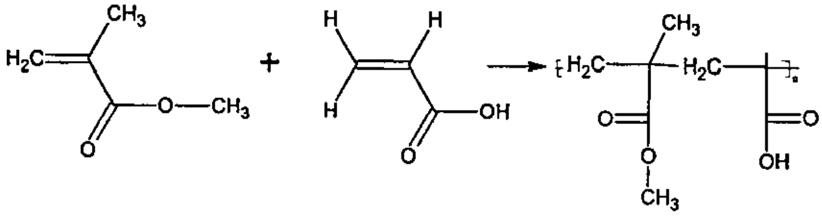


Fig. 5.35 Copolymerisation of acrylic acid and methyl methacrylate

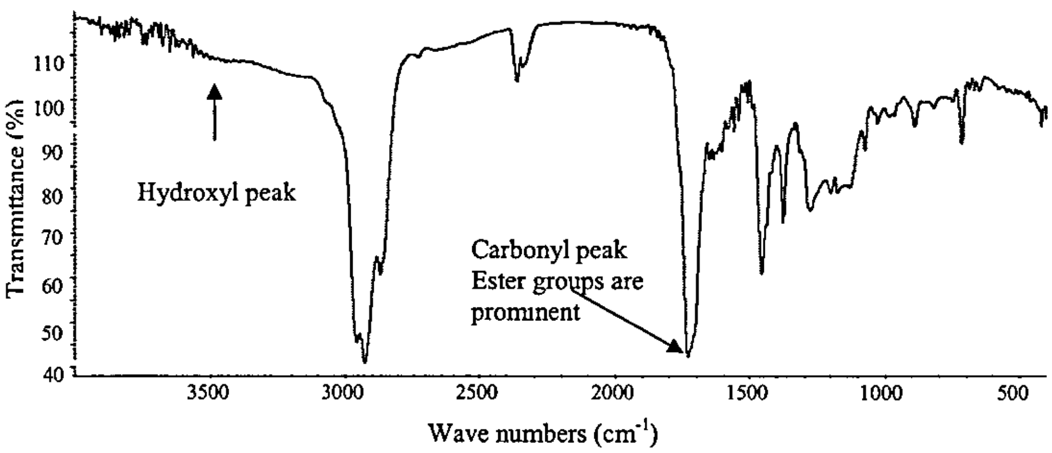


Fig. 5.36 The FTIR spectrum of the NR/ENR60(M)(50/50)50 PMMA/acrylicacid (90/10)50 semi-1 IPN

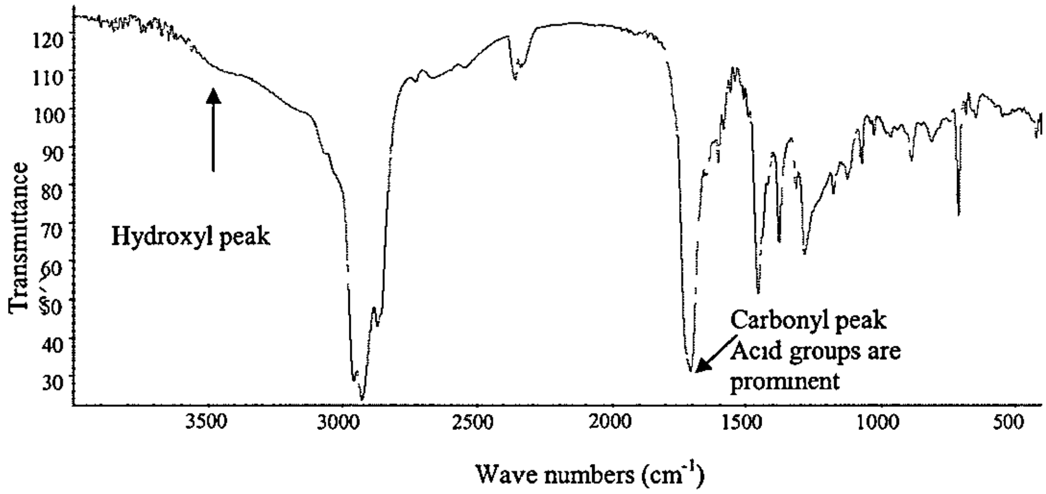


Fig. 5.37 The FTIR spectrum of the NR/ENR-60 (M) (50/50)50:PMMA/acrylic acid (80/20)50 semi-1 IPN

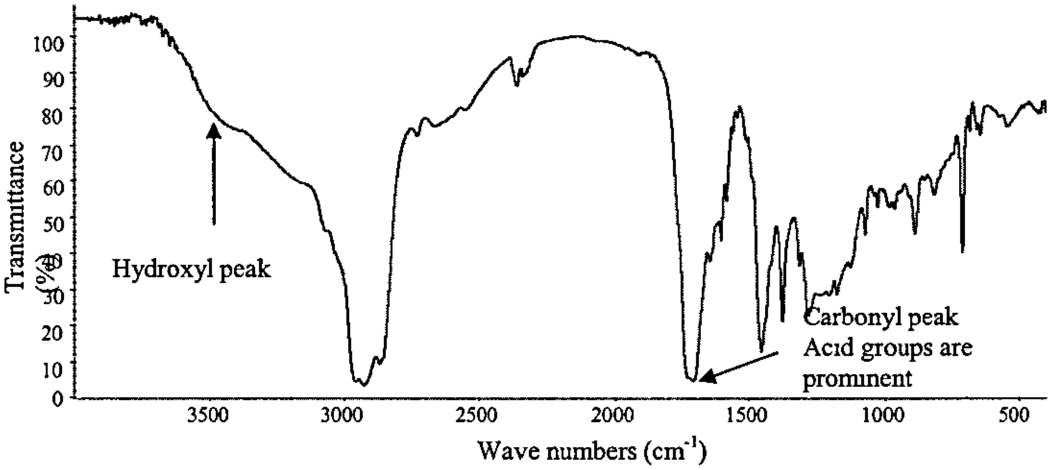


Fig. 5.38 The FTIR spectrum of the NR/ENR-60 (M) (50/50)50: PMMA/acrylic acid (70/30)50 semi-1 IPN

Miscibility increases with the introduction of interactions and some times it will lead to true thermodynamic miscibility. In addition, near similarities of the polarity of each component (van der Waals energies) result in improved miscibility (Wang and Roland, 2005). Hence, it may be expected that the incorporation of ENR and/or acrylic acid in to a NR and PMMA system would improve the compatibility. A study (Yusof, 1999) has been carried out on IPNs based on ENR and PMMA. It indicated that these materials are phase separated as indicated by the presence of two glass transitions. In this study (Yusof, 1999), attempts were made to incorporate methacrylic acid with MMA and revealed that the incorporation of methacrylic acid led to an increase in the T_g of the PMMA component, which was associated with co-polymerisation of methacrylic acid with MMA. Their study further indicated that the formation of a graft IPN depends on the rate of the acrylation reaction and the rate of phase separation. Compared to methacrylic acid, acrylic acid is more reactive, and, therefore, it may be expected that the incorporation of acrylic acid would impart higher compatibility by the formation of graft IPNs due to the acrylation of some of the epoxy groups.

The physical appearance of acrylic acid-based semi-1 IPNs was more transparent than their equivalent semi-1 IPNs, which does not contain any acrylic acid. This may indicate a lesser extent of phase separation and in agreement with the DMTA data which showed that the extents of mixing were higher in the semi-1 IPNs with acrylic acid. Moreover the product seems to be more flexible than the semi-1 IPN with no acrylic acid. This observation is further verified from the DMTA storage modulus data of which storage modulus decreased from 422 MPa to 240 MPa at 0°C by a factor of 0 6 times with increase in the acrylic acid content from 0 wt % to 30 wt % (Figure 5.40)

5.4.2.5 DMTA analysis of semi-1 IPNs containing acrylic acid

In comparison with the loss tangent data for the NR/ENR-60 (M) (50/50) 50.PMMA /acrylic acid (100/0) 50 semi-1 IPN, the NR T_g of the semi-1 IPN with 10 wt.% acrylic acid shifted by 9°C towards higher temperature (Figure 5 39 and Table 5.22) This is clearly evidence for a considerable amount of mixing due to incorporation of 10 wt.% of acrylic acid in to this system. Acrylic acid can form grafts on to natural rubber and if this occurs, it would enhance the compatibility between PMMA and ENR as well via formation of hydrogen bonds and by acrylation reaction with the ENR component resulting in grafts. As stated earlier, the most probable reaction is the acrylation of ENR Therefore, it could be expected that the pendent vinyl group (double bond) which will form as a result of acrylation of ENR can further undergo copolymerisation with MMA, or can react with natural rubber to form graft products. All these factors may lead to improved miscibility/compatibility between the components.

When the PMMA transition is taken into account, a shift of 23°C towards lower temperature resulted from the incorporation of 10 wt.% of acrylic acid. In addition, merging of ENR transition and PMMA transition is evident from the appearance of a broad peak perhaps indicating micro-heterogeneity with improved extent of mixing. Nevertheless, ENR transition is still resolvable indicating certain degree of phase separation. Copolymerisation of acrylic acid with MMA is also a plausible reaction which results pendent carboxylic groups capable of resulting in specific interactions with ENR and PMMA. The same time, the chances of formation of inter-grafts between the carboxylic groups of poly(MMA-*co*-acrylic acid) with ENR cannot be considered as negligible. Such inter-graft formation undoubtedly results better miscibility. Bauer *et al.* (1994) indicated that the grafting between the IPN components results in better miscibility than their blends or un-grafted products and tailor-made morphologies varying from phase separated to complete miscibility can be obtained by controlling the extent of grafting. Based on these facts, one would expect to enhance miscibility of components via introduction of acrylic acid in to this system This is achieved by incorporation of 10 wt.% acrylic acid as a co-monomer with MMA into the cross-linked NR/ENR matrix followed by polymerisation of monomers resulting in semi-1 IPN. Due to the unique feature of IPN preparation in which cross-linking of the first formed polymer retard the phase separation and more entanglements resulted by interpenetration would result ultimately a more miscible system. All these factors would contributed to the observed significant improvement in the miscibility of PMMA and NR components in the semi-1 IPNs having 10 wt % of acrylic acid (Figure 5 39 and Table 5 22).

Table 5.22 DMTA data for the semi-1 IPNs with acrylic acid

Acrylic acid content (wt %)	NR T_g (°C)	ENR T_g (°C)	PMMA T_g (°C)
0	-32	69	136
10	-23		113
20	-34		85
30	-33		84

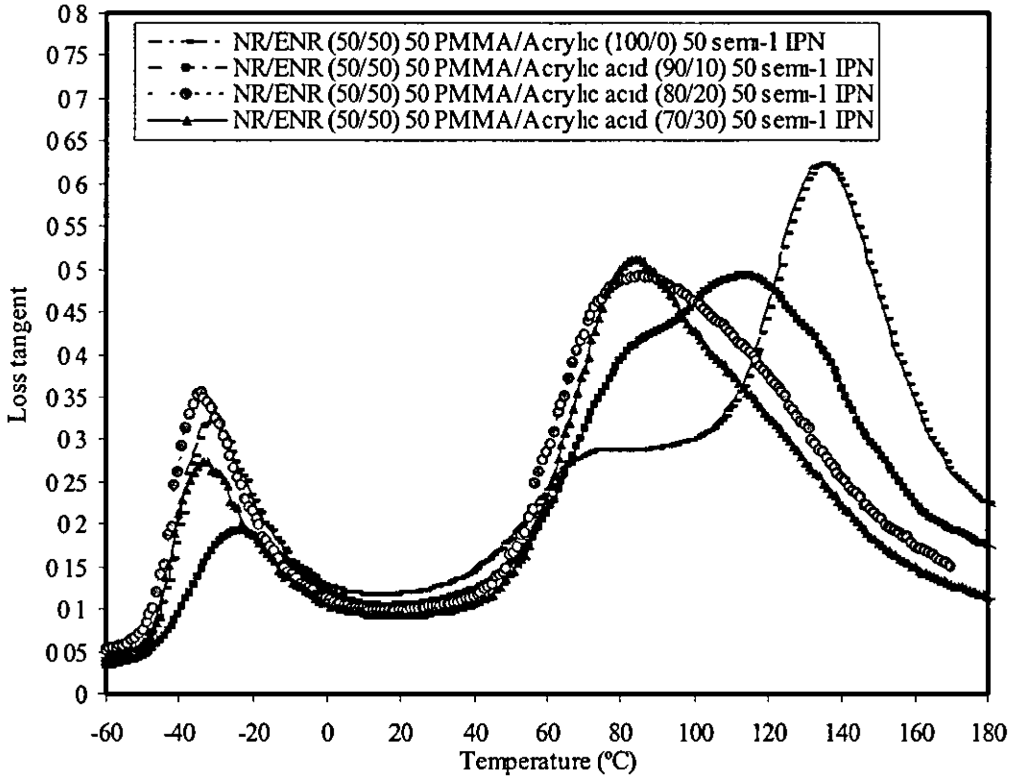


Fig. 5 39 The temperature dependence of loss tangent for the semi-1 IPNs with acrylic acid

If the loss tangent data of the semi-1 IPNs with 10 wt % of acrylic acid and without any acrylic acid are compared, the ENR transition appeared as a shoulder in the PMMA transition of the latter sample. However, in the former sample it has merged nearly completely to form a single broad peak, indicating a greater extent of mixing of the ENR-60 (M) and PMMA components in the semi-1 IPNs with 10 wt.% of acrylic acid. At this level of acrylic acid content (10 wt %), ENR and PMMA phases probably exhibit micro-heterogeneity and the miscibility of NR component has also increased to a significant extent

Attempts had been made to produce graft IPNs based on ENR-25 – PMMA by incorporating methacrylic acid (MAA) at level of 10 wt.% , 25wt.% and 50wt.% MMA (Yusof, 1999). From the DMTA studies, it was proven that these sequentially-prepared IPNs still exhibited two prominent transitions, corresponding to their individual components: ENR and PMMA were phase separated Incorporation of 25 wt.% and 50 wt % of MAA led to an increase of PMMATg by 49°C and 70°C, respectively (Yusof, 1999). Moreover, the shift of

ENR transition were not able to be obtained by incorporating MAA into the system. Use of dimethylbutylamine as a catalyst has also been tried (Yusof, 1999), but improvement in grafting reaction was not achieved. High level of cross-linking in each phase which would keep some of these reactive groups apart was the one of the reasons forwarded for the absence of grafting reaction and their ultimate effect on any shift of PMMA transition towards lower temperature. The other reason forwarded for the lack of formation of graft IPNs was the rate of phase separation was higher than the rate of oxirane reaction (Yusof, 1999). As far as the acrylation reaction is concerned, both acrylic acid and methacrylic acid should undergo an acrylation reaction. The polarization of the double bond by the adjacent carbonyl group would lead to enhanced neucleophilic additions. In addition, the presence of the methyl group in methacrylic acid would resist the reactions (Leonard, 1970). Therefore, in this study, improved miscibility was governed by the incorporation of acrylic acid into NR – ENR - PMMA semi-1 IPN is primarily attributed to the higher reactivity of acrylic acid than the MAA, structural variations in ENR (presence of hydroxyl groups as evidence from FTIR) In addition, low level of cross-linking in NR phase and/or ENR phase, the absence of any cross-links in the PMMA phase may also contributed to enhance the miscibility because high cross-link level leads to a reduction in miscibility (Bauer *et al.*, 1994; Coleman *et al.*, 1987; Felisberti, *et al.*, 1990; Briber and Bauer, 1991).

As can be seen clearly from the Figure 5 39, a single loss tangent peak for the ENR and PMMA transition was obtained when the acrylic acid content increased from the 10 wt.% to 20 wt % and 30 wt.% signifying more miscible ENR and PMMA systems. From this data, it was found that as the acrylic acid content increased from 10 wt.% to 20 wt.% and 30 wt.%, ENR transition became hardly evident and the PMMA transition shifted to lower temperatures by 28°C to 29°C, indicating a significant amount of mixing of the ENR and PMMA components. Comparison of the extent of the shift of PMMA transition for the semi-1 IPN with and without acrylic acid indicate that the PMMA transition has shifted to lower temperature by 51°C to 52°C indicating a greater extent of PMMA mixing in the system with 20 wt.% and 30 wt % of acrylic acid. However, if the NR transition is taken into an account, it can be clearly seen that the NR component is still phase separated from the rest of the components.

Moreover, it is interesting to note that this inward shift of the PMMA transition is levelled off at 20 wt.% of acrylic acid Any further increase of acrylic acid content did not result in any further reduction of the PMMA T_g. Therefore, it may be anticipated that the formation of inter-grafts may be levelled off due to the copolymerisation of acrylic acid at higher acrylic acid contents. However, if the PMMA transition of semi-1 IPN with 30 wt.% acrylic acid is compared with the same having 20 wt.% of acrylic acid, one would consider that the sharpness of the PMMA transition is higher in the former sample indicating more miscible system in the semi-1 IPN containing 30 wt.% of acrylic acid. However, the ENR, acrylic acid and PMMA components in the semi-1 IPNs will not referred to as fully miscible system as a single glass transition would appear for the systems with weak phase separation (Bauer *et al*, 1994). TEM studied would have been useful for the conformation of this, but unable to conduct due to difficulties encountered in the cryogenic sectioning of the sample due to unavoidable circumstances Since interaction parameter values indicate lack of molecular level mixing between ENR, acrylic acid, PMMA and poly(MMA-co-AA) components, the observed greater extent of mixing between ENR, acrylic acid and PMMA components, which one may interpret as a miscible system, is primarily governed from the formation of inter-grafts and specific interactions including hydrogen bonds, dipole forces between components. It is believed that chemical interactions alone may result true thermodynamic miscibility.

The plots of loss modulus versus temperature for the semi-1 IPNs based on acrylic acid are shown in Figure 5 40. When the difference between the T_g at the higher temperature region, derived from loss tangent data and loss modulus data (Figure 5.39) is concerned, it is noted that it decreases with increasing acrylic acid content. For example, the difference between the T_g derived from the loss tangent and from loss modulus data are found to be 34°C, for the semi-1 IPN containing 10 wt.% of acrylic acid. On the other, the difference between the T_g derived form the loss tangent data and the loss modulus data is 22°C, for the semi-1 IPN with 30 wt.% acrylic acid content. It was reported that the higher the difference between the T_g derived from loss modulus and loss tangent, the lower the mobility of the polymer chains (Perera, 1999; Hill *et al*, 1997). Therefore, it can be assumed that the increase in mobility of the PMMA polymer chain segments with increase in the acrylic acid content is attributed to the improved mixing of rubbery component with PMMA as well as due to co-polymerisation of MMA with acrylic acid which reduces the hardness or stiffness of PMMA phases.

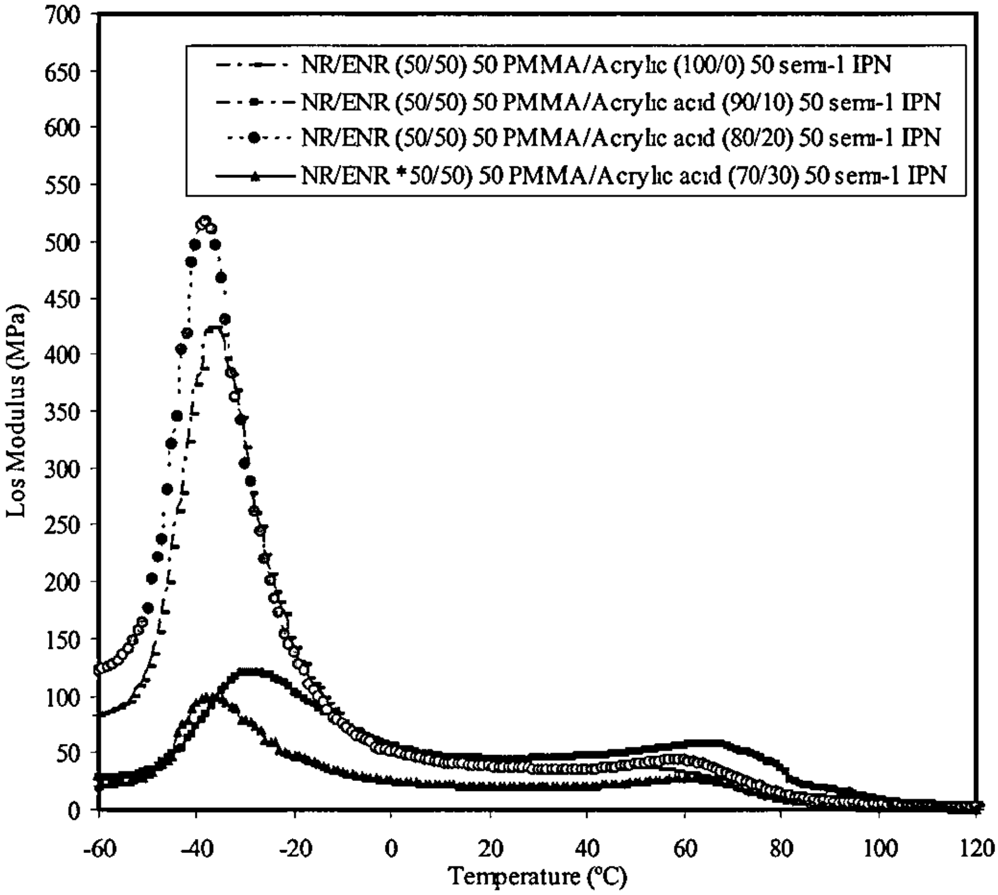


Fig 5 40 The temperature dependence of loss modulus data for the semi-1 IPNs with acrylic acid

It can be seen from the storage modulus data shown in Figure 5.41, that the semi-1 IPN with no acrylic acid content exhibited three transitions corresponding to the NR, ENR and PMMA components. However, with the incorporation of 10 wt.% to 30 wt.% acrylic acid content, only the NR and PMMA transitions are prominent, implying improved mixing of the ENR component.

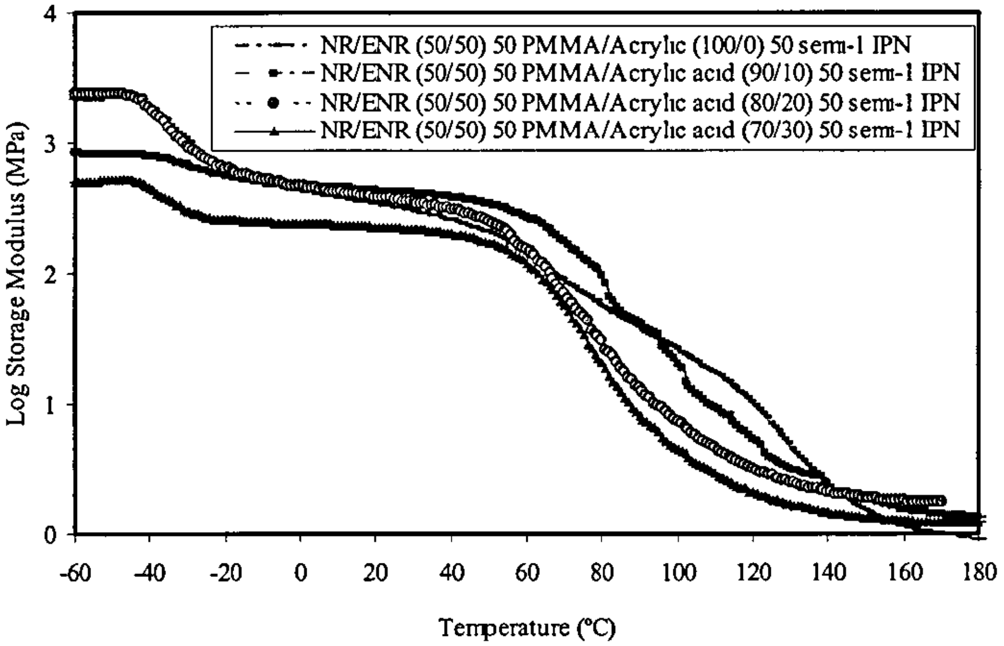


Fig. 5 41 The temperature dependence of storage modulus for the semi-1 IPNs with acrylic acid

In addition, the glass transition temperature of the PMMA component has shifted significantly towards lower temperature in the semi-1 IPNs with acrylic acid. The storage modulus values not only in the rubbery region of the NR transition, but also in the glassy region, decreased with an increase of acrylic acid content. This may be associated with the plasticising effect resulting from the introduction of acrylic acid and/or due to the reduction of extent of reinforcement resulting from lowering of hard glassy PMMA content in the semi-1 IPN.

CHAPTER 6

General conclusions and suggestions for future work

6.1 Introduction

This chapter briefly presents the conclusions drawn from the results presented in chapters 3, 4 and 5. In addition, suggestions for future work will be presented in the latter part of this chapter.

6.2 General conclusion

In this study, sequential IPNs were prepared using natural rubber and poly(methylmethacrylate) as the basic constituents because such a combination of elastomer and plastomer would result in a broad range of materials varying from thermoplastic elastomers to rubber toughened plastics depending on the composition. In fact, Hevea Plus: MG rubber is the term used for the commercial products based on natural rubber and poly(methylmethacrylate) in which PMMA is present as grafts on the NR polymer chains. This product is primarily used in adhesives and in shoe soles, where the MG rubber is used as a reinforcing filler. This product can be used to produce hard, the impact resistant mouldings by vulcanizing the rubber. Nevertheless, due to the drawbacks of film formation properties at higher PMMA contents limits it applications. Therefore, the route of IPN synthesis provides a novel path to produce useful products with improved physical properties without having any draw backs such as lack of film formation properties and lack of cracks on the surface of the products.

In the initial part of this investigation, blends, semi-1 IPNs, semi-2 IPNs and full IPNs based on NR and PMMA were prepared. The effect of composition, the effect of cross-linking of the NR component and/or the PMMA component and cross-linker level in the PMMA phase on the dynamic mechanical properties and physical properties of these materials were investigated. In addition, the extent of mixing of each component was determined by using MDSC data.

In the latter part of this study, the potentiality of ENR to improve the miscibility/compatibility between NR and PMMA in the semi-1 IPN with a 50/50 rubber/PMMA ratio was investigated using DMTA and physical properties. Moreover, the effects of the level of the epoxidation, epoxidised natural rubber content and the experimental conditions used for the preparation of ENR were also investigated. In addition, a study of the addition of acrylic acid to the semi-1 IPNs based on NR, ENR and PMMA was also undertaken

6.2.1 Blends

The blends of NR and PMMA were prepared by employing the same technique used to prepare sequential IPNs, with the exception of the cross-linking of NR component and/or PMMA component and the resultant material, perhaps in graft form, can be categorized as a thermoplastic material. Hence, unlike their graft product: MG rubber, the blends produce in this study do not exhibit any inferior film formation properties or film cracking at higher PMMA contents Therefore, this product can be processed as a thermoplastic and can be used to produce impact resistant articles. By taking dynamic DMTA data, MDSC data and physical properties as a whole, the following conclusions can be drawn.

- The blends, produced in this study using NR and PMMA, were phase-separated materials as they possessed two glass transitions corresponding to their homopolymers.
- Incompatibility of the NR and the PMMA components, as reflected by their solubility parameters, is considered one of the prime reasons for the phase separation.

- Some mixing of the NR component was found in all the blends. The extent of mixing of the components in the blends increased with increase of PMMA content from 30 wt.% to 50 wt.%.
- From the storage modulus data and tensile properties, it was concluded that the incorporation of PMMA into the NR matrix imparted a reinforcement effect.
- Comparison of the tensile properties for the blends produced in this study and the blends produced by melt mixing (Oommen and Thomas, 1993) or solution blending (Oommen and Thomas, 1996) of NR and PMMA by other researchers, concluded that the method employed in this study to produce the NR/PMMA blends resulted much better tensile properties.

6.2.2 Semi-1 IPNs

Semi-1 IPNs were produced by cross-linking the NR component by using sulphur as the vulcanizing agent A sulphur cross-linking system has not been commonly employed in the preparation of IPNs to date. Nevertheless, in this study, sulphur was chosen as the main curing agent for natural rubber, based on the fact that it is the most widely used curing agent for vulacanisation of the rubber on the commercial scale Conclusions drawn for the semi-1 IPNs by taking physical properties and dynamic mechanical properties into account are summarized as follows

- The semi-1 IPNs prepared in this study were phase separated.
- The extent of mixing of the NR component was significantly lower in the semi-1 IPNs
- These semi-1 IPNs exhibited high tensile strength, with the exception of the NR50:PMMA50 composition
- Hysteresis of the semi-1 IPNs increased with increasing PMMA content.

6.2.3 Semi-2 IPNs

The semi-2 IPNs were produced by cross-linking the PMMA component to different levels Following conclusions were drawn based on the physical properties and DMTA results of the semi-2 IPNs.

- The semi-2 IPNs also exhibited phase separation as indicated by the presence of two glass transitions corresponding to their homopolymers
- Some mixing in the NR component was evident from the DMTA and MDSC data in all the semi-2 IPNs.
- Composition of the material has a significant impact on the magnitude of the loss tangent at the glass transition region of the NR and the PMMA components.
- Tensile strength, moduli and hysteresis increased with increasing PMMA content in the semi-2 (0.5) IPNs. However, the PMMA content at which maximum tensile strength was observed varied with the EGDM content. For the semi-2 (1 0) IPNs and the semi-2 (1.5) IPNs, the maximum tensile strength was found to be at 40 wt. % and 30 wt % of PMMA, respectively

6.2.4 Full IPNs

Full IPNs were prepared by cross-linking of both the components, NR and PMMA. Conclusions drawn for these IPNs are as follows.

- Full IPNs are also phase separated and the extent of mixing of the natural rubber component was low
- Hysteresis increased with an increase in the PMMA content.

6.2.5 Conclusions drawn for the effect of cross-linking of each component

- According to the DMTA, it was concluded that the cross-linking of the NR component does not cause any significant improvement in the extent of mixing of the NR component in the semi-1 IPNs, when the NR component is moderately cross-linked using a conventional vulcanizing system.
- According to the MDSC data, the cross-linking of the NR component increases the extent of mixing of components resulting in high interphase content in semi-1 IPN over the equivalent blends.
- Compared to the equivalent blend, cross-linking of the PMMA component increased the interphase content resulted from improved component mixing in the semi-2 IPNs.
- With the semi-1 IPNs, it was concluded that cross-linking of both components has no marked effect on the extent of mixing of either the NR or the PMMA components perhaps indicating that cross-linking of the first formed network is more influential than the cross-linking of both components on physical properties and extent of mixing.
- In general, compared to the semi-2 IPNs, cross-linking of both components increased the mixing of the PMMA component in full IPNs with the exception of NR50:PMMA50 composition.
- The effect of cross-linking of the second component on the tensile strength is not significant, especially at low levels of cross-link density. Nevertheless, the tensile strength of the semi-2 IPNs with 10 wt.% to 30 wt.% PMMA content significantly increased at 1.5 mole percent of EGDM. Cross-linked PMMA domains also exert a reinforcement effect, as was evidence from the increase of storage modulus data.

6.2.6 Conclusions drawn for the effect of the addition of ENR and/or acrylic acid on the miscibility and physical properties of the semi-1 IPNs with 50/50 NR/PMMA ratio

- When the effect of the addition of ENR as a third component on the physical properties was considered, it was concluded that with incorporation of 25 wt.% ,or greater, of ENR-45 (M) or ENR-60 (M) the tensile strength increased by significant level

- However, compared to the NR50 PMMA50 semi-1 IPN, the tear strength of the semi-1 IPN only increased at a level of 50 wt.% to 75 wt.% of ENR-45 (M) or ENR-60 (M) content

- FTIR studies indicated that the presence of hydrogen bonds between ENR and the PMMA component were not as significant as expected.

- DMTA studies clearly indicated that the NR/ENR/PMMA semi-1 IPNs were also phase separated.

- When ENR-50 (H) was incorporated at a level of 10 wt.% and 75 wt.% on natural rubber, the extent of mixing of the NR components as well as the extent of mixing of the PMMA component has increased as was evident by the prominent shifts of their T_gs. In addition, some mixing of the PMMA component was evident from the PMMA T_g shift for the other levels of ENR-50 (H), with the exception of 50 wt.% case.

- Incorporation of ENR-45 (M) caused a marked increase of the NR T_g, which is a result of the improved mixing of the NR component with the PMMA component Addition of ENR-45 (M) at a level of 2 5 wt.% also improved PMMA mixing, as indicated by a prominent inward shift of PMMA T_g

- In all the semi-1 IPNs based on ENR-45 (M), the compatibility of ENR with PMMA was very much higher as shown by the shift of the ENR T_g towards higher temperatures.

- The ENR45(M)50.PMMA50 semi-1 IPNs exhibited a micro-heterogeneous morphology due to improved component mixing through chemical interactions.

- As shown from the DMTA data, the compatibility of NR was increased by adding ENR-60 (M) as the third component to the NR/PMMA system

- If the compatibility of ENR-60 (M) component is considered, it was concluded that the compatibility of ENR-60 (M) component with the PMMA component was significantly higher as it appeared as a shoulder in the PMMA transition in the loss tangent spectrum.

- ENR-60 (M) component was more compatible with the PMMA component in the ENR-60 (M)50:PMMA50 semi-1 IPN as revealed by the appearance of a single transition in which ENR transition is still resolvable as a shoulder.

- For the semi-1 IPNs with acrylic acid, the addition of 10 wt.% acrylic acid with MMA markedly increased the miscibility of the NR and PMMA components. Also, ENR - PMMA miscibility has significantly increased as was evident from the merging of ENR and PMMA transition with the addition of 10 wt.% acrylic acid on MMA.

- Higher acrylic acid contents of 20 wt % to 30 wt.% resulted in a more or less miscible system between the ENR and PMMA components. Nevertheless, the NR component was still phase separated.

- Therefore, in general, it can be concluded that addition of acrylic acid and/or ENR to IPNs based on NR and PMMA leads to improved compatibility of the NR and PMMA components to a considerable extent, as predicted

- The compatibility imparted by the addition of acrylic acid is purely governed by the specific interactions and the formation of inter-grafts between the components as explained in the section 5.4.2.4.

6.3 Suggestions for future work

As research on nano-composites is growing rapidly, it would be interesting to carry out an investigation based on nano IPNs based on natural rubber, ENR and PMMA components as there are no literature evidence in this field. Although fillers were not incorporated in the IPNs prepared in this study, the addition of fillers could enhance the physical properties as well as the damping properties. Therefore, an investigation of the effects of nano-scale fillers on the dynamic and physical properties of IPNs based on NR, ENR and PMMA is suggested.

Another possibility is to modify the filler chemically to improve the adhesion between filler and the matrix thereby expecting to improve the mechanical and physical properties.

As the study of the semi-1 IPNs based on NR-ENR-PMMA-acrylic acid is limited only to few compositions, it would be beneficial to extend this study by using higher acrylic acid contents and/or cross-linking the other components.

Chapter 7

REFERENCES

Abdel-Bary, E. M., Amin, M and Hassan, H. H , *Eur Polym. J* , **10** (8) (1974).

Aert, H. A. M , Steenpal, G. J. M., Nelissen, L , Lemstra, P. J., Liska, J. and C. Bailly, *Polymer,* **42**, (7), 2803 (2001)

Agarwal, K., Setua, D. K. and Sekhar., K., *Polymer Testing,* **24** (6), 781 (2005).

Agranoff, B. W , Eggerer, H., Henning, U. and Lynen, F , *J Biochem.* **253**, 320 (1960).

Akhtar, S and Bhagawan, S. S., *Rub. Chem. Tech.*, **60**, 591 (1987).

Akinlabi, A. K., Okieimen, F. C. and Aigbodian, A. I., *Polym. Adv Technol.* **16** 1 (2005)

Akinlabi, A. K., Okieimen, F. C., Egharevba, F. and Malomo, D., *Materials and Design*, 27(9), 783 (2006)

Alcântara, A. M., Rodrigues, A. P. P. and de. Barros, G. G , *Polymer*, **40,** 1651 (1999)

Alekseeva, T. T , Lipatov, Yu. S, Babkina, N. V., Grishchuk, S. I and Yarovaya, N. V., *Polymer,* **46** (2), 419 (2005).

Alekseeva, T. T , Lipatov, Y. S and Babkina, N. V.,. *Macromol Symp* , **164,** 91 (2001).

Allen, P. W , Ayrey, G. and Moore, C. G , *J. Polym Sci* , **36,** 35 (1959).

Al-Malaika, S. and Amir, E J., *Polymer Deg. and Stability,* **26** (1) 31 (1989)

Al-Malaika, S. and Kong, W., *Polymer Deg and Stability,* **90** (2), 197 (2005 b).

Al-Malaika, S. and Kong, W., *Polymer*, **46,** 209 (2005a).

Amu, A. B., Ismail, A. R. B. K. and Dulngali, S. B., *Proc. Inter Rubb Conf.*, (1985).

Andrews, E. H., *Proc. R Soc A.*, 270, 232 (1962).

Andrews, E. H., *Proc. R Soc A.*, 272, 562 (1964).

Angier, D. J. and Watson, W. F , *J Polym. Sci.*, **20,** 235 (1956).

Anzlovar, A. and Malavasic, T., *J. of Polym. Sci, Part A, Polymer Chemistry*, **34**, 2349 (1990).

Archer, B. L. and Audley, B. G , *Bot. J. Lin. Soc.*, **94**, 181 (1987).

Archer, B. L., Audley, B. G., Cockbain, E. L. and McSweeney, G P., *J. Biochem,* **89**, 565 (1963).

Archer, B L., Ayrey, G , Cockbain, E. L. and McSweeney, G. P., *Nature* (London) **189**, 663 (1961).

Archer, B. L , *Biochem J ,* **75**, 236 (1960).

Arenas, J. M.,. Mano, J. F. and Ribelles, J. L G , *J Non-Crystalline Solids*, **307-310**, 758 (2002).

Arreguin, B. and Bonner, J., *J. Arch. Biochem.*, **26**, 178 (1950)

Arreguin, B., Bonner, J. and Wood, B., *J. Arch Biochem Biophys ,* **31**, 234, (1951).

Aylsworth, J. W., U. S., Patent 1, 111, 284, (1914).

Bac, N V. and Mihailov, M., *J Appl Polym Sci ,* **42,** 2965, (1991)

Bacon, R. G. and Farmer, E. H., *Rubb Chem Technol ,* **12**, 200, (1939).

Bacon, R. G. R., Farmer, E. H. and Schidrowitz, P , *Proc. Rubb. Technol Conf.* (London), 525, (1938).

Badran, B. M. and Abdel- Bary, E. M , *Chem. Ind ,* 314, (1977).

Baker, C. S. L , Barnard, D and Porter, M. R., *Rub. Chem. Tech.*, **43**, 501 (1970).

Baker, C. S. L., *Dev Rubb Technol.* **4**, 87, (1987).

Baker, C. S. L., *Rubber India,* **37**, 9 (1985)

Barlett, P. D. and Trifan, D. S., *J. Poly. Sci ,* **20**, 457 (1956).

Barnard, D , *in Proc. Nat Rubb Prod. and Res. Asso Jubilee Conf.*, Ed., Mullins, L , McLaren &Sons, London, (1965).

Barnard, D., *Kautchuk und Gummi Kuntststoffe*, **35** (9), 747, (1982)

Barnard, D., *Proc Rubber Conf , Kuala Lumpur*, **4**, 215 (1975).

Barros, G. De, Huang, M. W. and Frisch, H. L., *J Appl. Polym. Sci.*, **44**, 255 (1992).

Barros, G. G. de; Frisch, H. L and Travis, J. C., *Elastomeric network*, (1990).

Bateman, L., The chemistry and physics of rubber-like substances, Mclaren (1963).

Bauer, B. J., *Adv Chem Ser*, **239**, 179 (1994)

Bauer, B. J., Briber, R. M. and Han, C. C., *Macromol.*, **22**, 940 (1989)

Bergstrom, J. and Boyce, M. C., *Rubber. Chem. Tech*, **72**, 633 (1999).

Birdwell, L. B., *Solid state Ionics*, 27, 163 (1992).

Birley, A. W., Haworth, B. and Batchelor, J., *Physics of Physics*, Hanser Publishers, Munich (1991).

Bloch, K , Chaykin, S , Phillips, A. H. and de. Waard, A., *J Biol. Chem.*, **234**, 2595, (1959).

Bloomfield, G. F. and McSwift, P., *J Appl. Chem.*, **5**, 609 (1955).

Bloomfield, G. F , *J Chem Soc*, 289 (1943)

Blow, C M., *Rubber Technology and Manufacturing*, Butterworth Scientific (1982).

Bonner, J. G., and Hope, P. S., *Polymer Blends and Alloys*, Eds Foikes, M. J. and Hope, P. S, Blackie Academic & Professionals, 46-74 (1993)

Brachais, L., Lauprêtre, F , Caille, J R., Teyssie, D. and Boileau, S., *Polymer*, **43** (6), 1829 (2002).

Bradbury, J. H. and Perera, M. C. S , *J. Appl. Polym. Sci*, **30**, 3347 (1985).

Brandrup, J. and Immergut, E. H., *Polymer Handbook*, 2nd Edn , Wiley-Interscience, New York (1975).

Brandrup, J. and Immergut, E. H and Grulke, E. A., *Polymer Handbook*, 4th Edn , Wiley-Interscience, New York (1999).

Briber, R. M. and Bauer, B. J., *Macromol*, **21**, 3296 (1988).

Brosse, J. C , Baccaccio, G. and Pautrat, R., *Proc. Symp. On Powdered, Liquid and Thermoplastic NR*, Phuket, Thailand, 195 (1981).

Brown, R. P , *Physical Testing of Rubber*, 3rd Edn, Chapman & Hall (1996)

Bruson, H. A., Sebrell, L. B. and Calvert, W. C., *Ind. Eng. Chem.*, **19**, 1033 (1927).

Brydson, J. A., '*Rubber Chemistry'*, Applied Science Publishers Ltd., Essex, UK, 66 (1978).

Bueche, F., *J. Appl. Polym. Sci.,* **4** 107 (1960).

Burfield, D. R, Lim, K. L. and Law, K. S , *J. Appl Polym. Sci*, **29,** 1661 (1984).

Cain, M. E., Knight, G. T., Lewis, P. M. and Saville, B., *J Rubb Res Inst. Malaya*, **22** (3), 289 (1968).

Campbell, D. S and Tinker, A. J., *Polymer*, **25**, 1146 (1984).

Carswell, T. S and Nason, H. K., "*Symposium on plastics,* " *ASTM Spec. Tech publ.* **59**, 72 (1944).

Chaki, T. K., *Indian J Nat Rubb. Res* , **5** (1 & 2), 221, (1992).

Chang, M. C. O., Thomas, D. A. and Sperling, L H , *J. Appl. Polym. Sci* , **34**, 409 (1987).

Chen, C., Dong, L. and Yu, P., *Eur. Polym, J* , In Press, Corrected Proof, (2006),

Chen, H. and Chen, J , *J. Appl. Polym. Sci.*, **50**, 495-501 (1993).

Chou, Y. C and Lee, L. J, *Polym. Engineering and science*, **35 (12),** 976 (1995).

Chou,, Y. C and Lee, L J, in *Interpenetrating Polymer Networks*, Eds , Klempner, D., Sperling, L. H and Utaracki, L A , *Adv Chem Series,* 239, Am. Chem Soc., Washington, D.C. (1993).

Claramma, N. M , Mathew, N. M. and Thomas, E. V., *Inter. J. of Radiation Applications and Instrumentation, part C Radiation physics and Chemistry*, **32** (2), 87 (1989).

Clegg, D. W. and Collyer, A A , *"Polymeric Materials*", The Institute of Materials, London (1993).

Colclough, T , *Trans. Inst. Rubber Ind.*, **38,** T11 (1962).

Coleman, M. M., Serman, C. J. and Painter, P. C , *Macromol* , **20**, 226 (1987).

Cooper, W. and Vaughen, G., *J. Polym. Sci* , **34,** 670 (1959).

Coran, A Y., *Rubb. Chem. Technol* , **61**, 281 (1988).

Coran, A.Y. and Patel, R., *Rub Chem. Tech* , **56**, 1045 (1993).

Cowie, J. M. G., *Polymers: Chemistry and Polymer Physics of Modern Materials* 2nd Edn., Blackie Academic & Professional, London (1991)

Cuadrado. T. R., Borrajo, J., William, R. J. J., *J. Polym. Sci. Part B Polymer physics*, **26** (8) 1735-49 (1988).

Čulin, J., Šmit. I., Andreis, M , Veksli,Z., Anžlovar, A and Žigon,M., *Polymer*, **46** (1), 89 (2005).

Cunneen, J. I and Higgins, G. M. C , Chapter 2 of *The Chemistry and Physics of Rubber-like Substances*, Ed. L. Bateman, Wiley Science, New York (1963).

Cunneen, J. I. and Shipley, F. W., *J. Polym. Sci* , **36**, 77 (1959).

Cunneen, J. I , Moore, C. G. and Shephard, B , *J. Appl Polym. Sci* , **3** (7),11 (1960).

D'Auzac, Jacob, J. L. and Crestine, H , *Physiology of rubber tree latex*,C. R. C. Press, Inc, Florida (1989).

Dafader, N C., Haque, M. E., Akhtar, F. and Ahmad., M. U., *Radiation physic and chemistry*, **75** (1), 168 (2006).

Dahlan, H. M. Ph D. Thesis, Univ. Kebangscan, Malaysia (1988).

Dahlan, H. M , Zaman, M. D. K., Ibrahim A , *Radia Phys and Chem*. **64**, 429 (2002).

Dannenberg, E M., *Rubber Chem Technol* , **48**. 410 (1974).

Das, A., Sinha, S and Gangopadhyay, T., *Eur. Polym J.*, **29** (1), 57 (1993).

Das, B. and Gangopadhyay, T., *Eur.Polym J* , **28**, 867 (1992).

Davies, C , Wolfe, S., Gelling, I. R and Thomas, A. G., *Polymer*, **24**, 107 (1983)

de Gennes, P. G , *"Reptation of a polymer chain in the presence of fixed obstacles," J Chem Phys* **55**, 572 (1971)

Decker, C , Xuan, H. Le. and Viet, T. V., *J Polym. Sci.* Part A, **33**, 2759 (1995)

DiMauro, P. J., "Characterisation of Polymer and Compound Properties using Monsanto MV and MDR 2000", (Private communication).

Dinsmore, R. P , *Rubb Age*, **78**, 99, (1955).

Djomo, H, Widmaier, J. M. and Meyer, G. C, *Polymer*, **24**, 1415 (1983).

Donatelli, A. A , Sperling, L H., Thomas, D. A., *J. Appl Polym. Sci.*, **21**, 1189 (1977).

Donatelli, A , Sperling, L. H. and. Thomas, D. A , *Macrmol.*, 9(4), 676 (1976)

Dannenberg, E. M , *Rubber Chem Technol.*, **48**. 410 (1974).

Eastmond, G. G and Smith, E. G., *Polymer*, **18**, 244 (1977).

Eastwood, E., Viswanathan, S , O'Brian, C. P., Kumar, D. and Dadmun, M. D., *Polymer*, **46**, 3597 (2005)

Egbon, S H O and Fagbuli, M ., *Eur. Polym. J.*, **24**, (11), 1041 (1988).

Ehabé, E , Bonfils, F., Aymard, C., Akinlabi, A K. and Beuve, J. S., *Polymer Testing*, **24** (5), 620 (2005).

Elmér, A. M. and Janasch, P., *Solid State Ionics*, **177**, 573 (2006).

Erbil, C., Kazancıoglu, E. and Uyanık, N., *Eur Polym J*, **40** (6), 1145-(2004).

Eskina, M. V., Khachafurov, A. S , Krentsel, L. B. and Litmanovich, A. D., *Eur. Polym J*, **26** (2), 181 (1990).

Fahrenholtz, S R. and Kwei, T. K., *Macromol*, **14**, 1076 (1981).

Farmer, E. H., *Rubb Chem. Technol*, **15**, 765 (1942).

Farmer, E. H., *Rubb Chem. Technol*, **16**, 769 (1943).

Felisberti, M., Freitas, L.L. and Stadler, R., *Polymer*,**31**, 1441 (1990)

Fernandes, A. C., Barlow, J. W., Paul, D. R., *J Appl. Polym Sci.*, **32**, 5481 (1986).

Fernandez, A. M. Ph. D. Thesis, Lehigh Univ. Bethlehem, PA (1984).

Fındık, F., Yılmaz, R. and Koksal, T., *Materials & Design* **25** (4), 267 (2004).

Firsch, H L , *Rubber. Chem. Technol.*, **45**, 1442 (1972)

Firscher, H L.,US Patent 1, 605, 180 (1926).

Flory, F. J , Rabjohn, N. and Mc Schaffer, *J Polym. Sci.*, **4**, 435 (1949).

Flory, P. J. and Rehner, J., *J Chem Phys*, **11**, 512 (1943)

Fradkin, D G , Foster, J. N., Sperling, L. H , Fradkin, D. G. and Thomas, D.A , *Rubb Chem. Technol.*, **59**, 255 (1986).

Frisch, H. L, Klempner, D , Yoon, H. K and Frisch, K. C., *Macromol.*, **13**, 1016 (1980)

Frisch, H. L. and Hus, Y., *Macromol* , **22**, 91 (1989).

Frisch, H. L., Klempner, D. and Frisch, K. C , *J. Polym Sci , Polym. Phys* , **7** (11), 775 (1969).

Frisch, H L , Xu, Q. and Zhou, P., *Polym Gels Network*, 2(3/4) 257 (1994).

Gan, L. H. and Ng, S. C., *Eur. Polym J* , **22**, 573 (1986).

Gan, S. N. and Hamid, Z. H., *Polymer*, **38** (8), 1953 (1997)

Gan, S. N., Burfield, D. R , *Polymer*, **60**, 1903, (1989).

Gehman, S. D , Field, J. E., *J Appl Phys.*, **10**, 564 (1939).

Gelling, I. R. and Porter, M , "*Natural Rubber Science and Technology*" (Eds , Roberts, A. D.), Oxford Univ. Press, 359 (1988)

Gelling, I. R., *J Nat. Rubb. Res* , **6** (3), 184 (1991).

Gelling, I. R., Morrison, N. J., *Rubb Chem Technol.*, **88**, 243 (1985)

Gelling, I. R., *Proc. Inter Rubber Technol , Conf,* Penang (1988).

Gent, A N., Liu, G L and Mazurek, M., *J Polym. Sci* , Part B, **22**, 271 (1974)

George, S , Neelakanthan, N. R., Verughese, K. T. and Thomas, S., *J Polym Sci Polym. Phys* **35**, 2309 (1997).

Ghosh, P., *J Polym Sci , Macromol. Rev* , **5**, 195 (1971).

Gillick, J G. and Waddell, W. H., (to the Good Year Tire and Rubber Co.), U. S. 4, 824, 692, (April, 1989).

Gladisher, G. P. and Leplyanin, G. V., *Viskomol Soedin,* **A9**, 2438 (1967).

Goh, S. H , Srow. K S., and Lee, S. Y., *Eur Polym. J* , **27** (9), 921 (1991).

Golub, M A., Fuqua, S. A. and Bhacca. N. S , *J. Am Chem Soc.*, **84**, 4981 (1962)

Golub, M. A., *J. Polym. Sci* , **25**, 373 (1957)

Green, M. S and Tobolsky, A V., *J. Chem Phys* , **14**, 80 (1946).

Hand book of Rubber Culture and Processing, Eds , Peries, O S. and Fernando, D. M., Caxton Printing, (1983)

Harnes, C. D , *Untersuchungen uber denaturlichen und kunstlichen. Springer.*, Berlin (1919).

Harun, M. G. and Kassim, R. F. M., *J App. Polym Sci.*, **49** (1993).

Hashim, A. S and Kohjiya, S , *Paper presented at the 6th Annual Discussion Meeting of the society of Rubber Industry*, Osaka, Japan, December (1992)

Hashim, A. S. and Kohjiya, S , *Sonderdruck aus'Kautschuk Gummi. Kunststoffe*, 3/93, 210 (1993).

Hashim, A , kawabata, N N. and Kohjiya, S , *J. Sol Gel Sci. and Technol.*, **5**, 211 (1995a).

Hashim. A. S , Kohjiya, S and Ikeda, Y., *Polymer International*, **38**, 111 (1995).

He, X., Widmaier, J. M. and Meyer, G. C, *Polym. Internat*, **32**,295 (1993b)

He, X., Widmaier, J. M , Herz, J. E. and Meyer, G. C., *Polymer*, **33**, (2) 364 (1989).

He, X , Widmaier, J. M , Herz, J. E. and Meyer, G C., *Polymer*, **33**, (4) 866 (1992).

Hebant, C , Devic, C., and de Fay, E , *Rev. Gen. Caoutch Plast.*, **614**, 97 (1981).

Heinen, W., Resenmoller, C. H., Wenzel, C R., Gront, H. J M. de , Lurtenburg, J. and van Duin M., *Macromol*, **29**, 1151 (1996).

Henning, U., Moslein, E. M., Arreguin, B. and Lynen, F., *Biochem* **333**, 534 (1961).

Hepper, C. M. and Audley, B. G., *J Biochem,*. **114**, 379 (1969).

Hermant, I , Damyanidu, M. and Meyer, G. C., *Polymer*, **24**, 1419 (1983).

Herna´ndez, R., Pe´rez, E., Mijangos, X. and Lo´pez, D., *Polymer*, **46**, 7066 (2005).

Hill, A J. T., Perera, M. C S., Pomery, P. J. and Toh, H K., *Polymer*, **41**, 9131 (2000).

Hill, D. J. T., Perera, M. C. S. and Pomery., P. J., *Polymer*, **39** (21), 5075 (1998)

Hoffmann, H. M. R., *Angew. Chem Int Edn.*, **8** (8), 556 (1969).

Honquan Xie, Private communication (1993)

Hou, X. and Siow, K. S., *Polymer*, **42**, 4181(2001).

Hourston D. J. and Romaine, J , *J. Appl Polym Sci.*, **39**, 1587 (1990).

Hourston, D. J. and McClusky, J. A , *J. Appl. Polym. Sci.*, **30**, 2157 (1985).

Hourston, D. J. and McClusky, J A , *J. Appl. Polym. Sci.*, **31**, 645 (1986).

Hourston, D. J. and Romaine, J., *Eur. Polym J* , **25**, 695 (1989).

Hourston, D. J. and Romaine, J., *J. Appl Polym Sci* , **43**, 2207 (1991).

Hourston, D. J. and Zia, Y *J Appl Polym Sci* **29** (1984), p. 629.

Hourston, D J. and Zia, Y., *J. Appl Sci* , **28**, 3849 (1983)

Hourston, D J., Song, M., Hammiche, A., Pollock, H. M. and Reading, M., Polymer, **38**, 1 (1997)

Hourston, D J. and Satgurunathan, R., *J. Appl. Polym Sci*, **29**, 2969 (1984).

Hseieh, K. H , Han, J. L., Yu, C. T. and Fu, S. C. *Polymer*, **42** (6), 2491 (2001).

Hsieh, K. H., Hung, W. Y., Liao, D C., and Kao, S. C., *J. Appl. Polym Sci*, **57**, 319 (1995).

Huang, C , Kuo, S , Lin, F , Wang, C , Hung, C. J. and Chang, F., *Polymer,* In Press, Corrected Proof, (2006).

Huang, J. and Zhang, L , Polymer, 43 (8), 2287 (2002).

Huelck,V., Thomas, D. A. and Sperling, L. H., *Macromol.,* **5**, 348 (1972)

Hur, T., Manson, J. A. andSperling, L. H., *J Polym Sci, Part B, Polymer Physics,* **27**, 2251 (1989).

Indukuri, K. K. and. Lesser, A. J., *Polymer,* **46** (18), 7218 (2005).

Iniesta- Jaén, J., Pastor-Blas, M. M., Mahiques-Bujanda, M M , Martin-Martinez, J. M. and Dillard, J.G , *J. Adhesion Science and Technology*, **13** (8), 903 (1999)

Inoue, T., Soen, T., Hashimioto, T., and Kawai, H. *Macromol* , **3**, 87(1970).

Ismail, H. and Suzaimah, S , *Polymer Testing,* 19 (8), 879 (2000).

Janarathanan, V. and Thyagarajan, G., *Polymer*, **33** (17), 3593 (1992)

Jayawardena, S., Reyx, D , Durand, D. and Pinazzi , C. P., *Macromol. Chem* , **185,** 2089 (1984).

Jehl, D.,Widmaier,J. M and Meyer, G. C., *Eur. Polym J.*, **19,** 597 (1983)

Jeon, H. K , Zhang, J. and Macosko, C. W., *Polymer,* **46** (26), 12422 (2005)

Jha, A and Bhowmick, A. K., *Rubb Chem. Technol.*, **70,** 798 (1997).

Jia, D. M , You, C. J., Wu, B and Wang, M Z , *Int Polym Process*, **3** (4); 205 (1988).

Jiang, M., Cao, X and Yu, T , *Polymer*, **27**, 1923 (1986)

Jin, S R and Meyer, G C , *Polymer* , **27**, 592 (1986)

Jin, S. R., Widmayer, J. M. and Mayer, G. C., *Polymer*, **29**, 346 (1988).

Jin, S. R., Widmayer, J. M. and Mayer, G. C., *Polymer*, **29**, 346 (1993).

Johnston, J. A., Racusen, D. A. and Bonner, *J, Proc. Nat. Acad Sci.*, **40,** 1031 (1954)

Jones, K. J., Kinshott, I., Reading, M , Lacey, A. A , Nikolopoulos, C. and Pollock, H. M , *Thermochimica Acta*, **304/305**, 187 (1997)

Kadir, A , *Int. Proc Rubb. Conf,* 214 (1975).

Kadir, A., *Rubber forum*, 10th-14th Sept, 110 (1990).

Kalkar, A, K., and Parkhi, P. S., *J. Appl Polym. Sci*, **57**, 233 (1995).

Kambour, R. P., Bendler, J T , and Bopp, R. C., *Macromol* **16,** 753 (1983)

Kaplan, M. L., Kelleher, P. G., Bebbington, G. H. and Hartness, R. L., *J. Polym Sci ,Polym. Lett. Ed.*, 11, 357 (1973).

Katz, J. R., *Naturwiss.*, **13**, 411 (1925)

Keskkula, H., Turley, S. G. and Boyer, R. F., *J Appl Polym Sci* , **15**, 351 (1971).

Kim, H. I., Pearce, E. M., Kwei, T. K., *Macromol* , **22**, 3374 (1989).

Kim, J., Kang, P. S and Chang-Sikha, *Reactive and functional polymers*, **64** (3), 151-156 (2005).

Kim, S. C., Klempner, D. and Frisch, K. C., *J. Polym. Sci* , **21**, 1289 (1977).

Klempner, D., Frisch, H. L. and Frisch, K. C., *J. Elastoplast*, **3** (1), 2 (1971).

Klinklai, W., Kawahara, S., Mizumo, T., Yoshizawa, M., Sakdapipanich, J. T., Isono, Y. and Ohno, H., *Eur Polym. J.,* **39** (8), 1702 (2003),

Knight, G. T. and Pepper, B., *Tetrahedron*, **27**, 6201 (1971).

Kobryner, W. and Banderet, A., *J. Polym. Sci.,* **34,** 381 (1959).

Kohjiya, S and Hashim, S , *Proc. Inter. Workshop on Green Polymers*, 4-8, Bandung-Bong, Indonesia (1996).

Kohjiya, S., Katoh, A., Shimanuki, J., Hasegawa, T. and Ikeda, Y., *Polymer,* **46** (12), 4440 (2005).

Kohjiya, S., Murakami, K., Ito, S , Tanahashi, T. and Ikeda, Y., *Rubb. Chem. Technol ,* **74** (1), 16 (2001).

Koklas, S. N. and Kalfoglou, N. K , *Polymer*, **33** (1), 75(1992).

Kolthoff, I. M, Lee, T. S. and Maris, M. A., *J. Polym Sci , Polym. Chem Ed ,* **2,** 206, 220 (1973).

Krause, S. J., in *Polymer Blends*, Academic, New York, Vol. 1 (1978).

Krause, S. J., *J. Macromol. Sci. Rev. Chem.*, C7, 2, 251 (1972)

Kumar, C. R , Fuhrmann, I.. and Karger-Kocsis, J., *Polymer deg and stability* **76** (1), 137 (2002).

Kumar, H , Kumar, A. Siddaramaiah, *Polym Deg And Stability*, **91** 1097 (2006).

Kumnuantip, C and Sombatsompop, N., *Material letters*, **57** (21), 3167 (2003).

Lamb, D , Anstey, J. F., Fellows, C. M ,. Monteiro, J. M. and Gilbert, R. G., *Biomacromolecules*, 2 518 (2001)

Latif, F , Aziz, M , Katum, N., Ali, M M. and Yahya, M Z , *J Power Sources*, xxx, xxx (2006)

Lattimer, R P and Windig, K. M. S.W. and Meuzelaar, H L. C., *Journal of Analytical and Applied Pyrolysis*, 8, 95 (1985).

Lee, D S. and Kim, S. C. *Macromole ,* **17,** 2193 (1984a).

Lee, D. S. and Kim, S C. *Macromole ,* **17,** 2222 (1984b).

Lee, D. S. and Kim, S. C. *Macromole.*, **17**, 268 (1984c).

Lee, D. S. and Kim, S. C., *Macromole* , **18**, 2173 (1985)

Lee, D. S., Kang, W. K., An, J. H. and Kim, S. C , *J Membrane science,* **75**, 15 (1992).

Lehrle, R. S. and Willis, S L , *Polymer,* **38** (24), 5937 (1997).

Leila, L. Y. and Cristina, T. A , Chiaki, A., *Polymers for Advanced technologies*, **4**, 490 (1990).

Lemieux, E., Teyssie, Ph., Jerome, R., and Prud"homme, R E., *Macromol* , **21**, 2148 (1988).

Lenka, S , Nayak, P. L and Basak, A., *J. Polym Sci. Part A Polym Chem Ed.,* **24**, 3139 (1986)

Lenka, S , Nayak, P. L , Das, A. P. and Mishara, S. N., *J. Appl Polym. Sci.*, **30**, 429 (1985).

Li, B.Y , Bi, X. P., Zhang, D. H. and Wang, F. S.,. *in Advances in interpenetrating polymer networks*, **1**, Eds., Klempner, D. and Frisch, K.C., Technomic, Lancaster (1994).

Li, D., Liu, Z., Han, B. Song, L., Yang, G. and Jiang, T., *Polymer,* **43** (19), 1 5363 (2002).

Liau, W. B. and Cheng, K C *Polymer,* **39** (24), 6007 (1998)

Liau, W. B., *Polymer,* **40**, 599 (1999).

Lin, M. and Lee, S , *Polymer*, **38**, 53 (1997).

Lipatov, Y. S, Grigoryeva, O. P, Kovernik, G. P., Shilov, V. V. and Sergeyeya, L. M, *Makromol Chem.* **186**, 1401 (1985)

Lipatov, Y. S. and Sergeeva, C. M , *Russ. Chem Rev* , **45** (1), 63 (1967).

Lipatov, Y. S., Alekseeva, T. T., Kosyanchuk, F., Rosovitsky, V. F. and Babkina, N V., *Polymer,* **40** (25), 7083 (1999)

Lipatov, Y. S , Sergeyeva, L M , Karabanova, L V., Rosovitskii, V. F., Skiba, S. I. and. Babkina, N. V., *Polymer Science U S S R.,* **30** (3), 651 (1998).

Lipatov, Yu S , Shifrin, V. V. and Vasilenko, O. I., *Polymer Science U.S S R.,* **29** (7), 1538 (1987).

Liucheng, Z., Xiucuo, Li , Tianchang, L. and Xiongyan, Z., Gaofenzi Cailiao kexue Yu Gongcheng., 8 (4), 76 (1992).

Liucheng, Z., Xiucuo, Li., Tianchang, L., *Hebei Gongxueyuan xuebao*, 18 (4), 20 (1989)

Lloyd, D. G , *Materials and Design,* **12** (3), 139 (1991).

Lu,.S; Pearce, E. M and Kwei, T K, *Polymer*, **36**, 2345 (1995).

Luch, D., Yeh, G. S. Y., *J Macromol. Sci. Phys.*, **B97,** 121 (1973)

Lye, P. H. and Toh, K. H , *J. Polym. Sci , Polym lett Ed.*, **22**, 327 (1984)

Lynen, F. and Henning, U , *Angew Chem.*, **72**, 820 (1960)

Lynen, F., Eggerer, H., Henning, U. and Kessel, *J., Angens-Chem* , **70**, 738 (1958).

McCallum, J. R. and Smith, J. S. G., *Eur. Polym J* , **36**, 491 (2000)

Machado, A. V. and. van Duin, M., *Polymer,* **46** (17), 6575 (2005).

Mairs, J. A. and Todd, J., *J Chem Soc.*, **386** (1932).

Manson, J. A and Sperling, L. H., *Polymer blends and composites*, Plenum Press, NY, (1976).

Marvel, C S., Clearke, K. G , Inskip. H. K., Taft, W. K. and Labbe, B. G., *Ind Engeng. Chem* , **45** (9), 2090 (1953).

Mathew, A P., Packirisamy, S and Thomas, S , *Polym. Deg Stability*, **72** 423 (2001)

Mathew, A. P., Packirisamy, S , Radusch, H. J. and Thomas, S , *Eur. Polym J.*, **37** (9), 1921 (2001).

Mathew, A.P. and Thomas, S , *Mat. Lett* , **50** 154 (2001).

Mattson, B and Stenberg, B., *J Appl Polym Sci* , **50**, 1247 (1993).

McCrum, N. G., *J. Polym Sci.*, **34,** 355 (1959a).

McCrum, N. G., *Macromol. Chem*, **34**, 50 (1959b)

McCrum, N. G.., *J Polym Sci* , **27**, 555 (1958)

McNeill, I. C. and Ćoskun , M , *Polym Deg And Stability*, **23** (2), 175-183 (1989).

Medalia, A I and Kraus, G., *Science and Technology of Rubber*, Academic Press, New York (1994).

Mengnjoh, P C and Frisch, H. L., *J. Polym Sci, Part A Polym Chem*, **27**, 3363 (1989).

Menon, C. C. and Kapur, S. L, *J Appl Polym. Sci.*, 1, 372 (1959).

Merrett, F. M , *J Polym. Sci* , **24**, 467 (1957).

Millar, J R., *J. Chem Soc* , 1311 (1960).

Min, K. E , Chiou, J. S , Barlow, J W., and Paul, D. R , *Polymer*, **28**, 1721 (1987).

Min, T. I., Klein, A., El-Aasser, M S and Vanderhoff, J W., *J. Polym Sci , Polym. Chem.*, Edn., **21**, 2845 (1983)

Mishara, V., Du Prez, F., Gosen, E , Goethals, E. J. and Sperling, L. H , *J. Appl. Polym. Sci* , **58**, 331 (1995).

Mishra, V and Sperling, L. H , *Polym Mat Sci Eng. (Prepr)*., **72** 122, 124 (1995)

Mishra, V , Du Prez , F. E., Goethals, E. J. and Sperling L. H , *J. Appl. Polym Sci.*, (1994).

Misra, B. N. and Kaul, J , *Ind J. Chem* , **22**, 601 (1983).

Misra, B. N., Kaul, J , *Indian J Chem.*, 21A, 922 (1982).

Mitchell G R., *Polymer.*, **25**, 1562 (1984).

Modulated Temperature Differential Scanning Calorimetry, Theoratical and Practical Applications in Polymer Characterisation, Eds , Reading, M. and Hourston, D. J., Springer (2006)

Mohanty, S., Nando, G. B., Vijayan, K. and Neelakanthan, N. R , *Polymer*, **37** (24), 5387 (1996).

Moir G. F. J., *Nature* (London), 184, 1626 (1959).

Momose, A. A., U. S. 4, 597, 108 (July, 1986).

Morin, A., Djomo, H. and Meyer, G. C., *Polym. Eng. Sci.*, **23**, 394 (1983).

Morton, M., Haely, J. C., *Polym. Prepr.*, **8**, 1569 (1967).

Morton, M., McGrath, J. E. and Juliano, P. C., *J Polym Sci.*, **26** C, 99 (1969).

Mullins, L. and Tobin, N. R., *Rub. Chem. Technol.*, **30**. 555 (1957).

Murayama, T., *Dynamic Mechanical Analysis of Polymer Materials*, Elsevier, Amersterdam (1978).

Nair, P. D , Jayabalan, M. and Krishnamurthy, V. N., *J Polym. Sci , Part A, Polymer Chemistry*, **28**, 3775 (1990).

Nakagawa, T., Yoshida, M. and Kidokoro, K., *J Membrane Science*, **52** (3), 263 (1990)

Nakason, C., Kaesaman, A. and Supasanthitikul, P., *Polymer testing*, **23** (1), 35 (2004).

Nakason, C., Panklieng, Y. and Kaesaman, A , *J. Appl. Polym Sci.*, **92**, 3561 (2004)

Natural Rubber Science and Technology, Ed Roberts, A D , Oxford Science Publications (1988)

Nayak, P. L., Basak, A., *J Appl Polym. Sci* , **32**, 4271 (1986)

Nevissas, Widmaier J. M. and Meyer, G. C., *J Appl. Polym Sci.*, **36**, 1467 (1988).

Ng, S C. and Gan, L. H , *Eur. Polym. J.*, **17**,1073 (1981).

Nogues, P., Dawans, F , *Macromol. Chem.*, **182**, 843 (1981).

Okubo, M., Katsuta, Y. and Matsumoto, T., *J Polym Sci. Polym. Lett Edn* , 20, 45 (1982) .

Okwu, U. N. and Okieimen, F. E., *Eur Polym. J* , **37**, 2253 (2001).

Okwuand, U. N and Okieimen, F. E., *Eur Polym J.*, **35**, 1855 (1999).

Oliveira, P. C. de., Oliveira, A. M de, Garcia, A , Barboza, J. C. de. S , Zavaglia, C. A. de C , Santos, A M , *Eur Poly. J.* **41**,1883 (2005).

Oommen, Z and Thomas, S , *Polym Bull.*, **31**, 623 (1993)

Oommen, Z , Thomas, S. and Nair, M. R. G., *Polym Eng. Sci.*, **36**, 151 (1996).

Oommen, Z., Thomas, S , Premalatha, K. C. and Kuriakose, *J. Polym. Sci , Part B* , **38** (22), 5611 (1997)

Pagnoulle, C. and Jérôme, R., *Polymer*, **42** (5), 1893 (2001).

Pandit, S.B., Kulkani, S. S. and. Nadkarni, V. M., *Macromol* , **27**, 4595 (1994).

Panzel, N., Meyer, G and Weill, G., *Polymer,* **36** (12), 2323 (1995)

Panzel, N , Meyer, G C. and Well, G , *Polymer*, **34**, 2495 (1993).

Patsis, A , Xiao, H. X., Frisch, K. C. and Al-khatib , *J. Coat, Technol.*, **58**, 743, 41 (1986).

Patterson, D J. and Koeing, J. L., *Macromol. Chem* , **188**, 2325 (1987)

Paul, D R , and Barlow, J W., *Polymer*, **25**, 487 (1984).

Pazonyi, T. and Dimitrov, M., *Rub. Chem. Technol.*, **40**, 1119 (1967).

Perera, M. C. S. and Rowan, C. C., *Polymer*, **41**, 323 (2000).

Perera, M. C. S , *J Appl Polym. Sci.,* **39**, 749 (1990)

Perera, M C. S , *J. Polym Sci , Part B, Polym Physics*, **37**, 1141 (1999)

Phinyocheep, P. and Duangthong, S., *J. Appl. Polym Sci.*; **78** (8), 1478 (2000)

Pillai, V. B., and Francis D. J., *Indian Jounal of Eng and Mat Sci* , **1** , 355 (1994).

Pillai, V. B , Ph D. Thesis, Univ. of Cochin, India (1995).

Pinnazi, C., Chentat, R. and Pautrat, R (1962) *Revue gen Caoutchouc,* **39** (12), (1951).

Pinnazi, C., Danfard, J C. and Pautrat, R., *Proc. Nat. Rubb. Res. Conf. Kuala Lumpur*, 551, (1960).

Powell, P. C , *Engineering with polymers*, **13** (1983).

Predeep, P., Najidha, S., Sreeja, R. and Saxsena, N. S., *Nuclear Instruments and Methods in Physics Research*, B, 240,850 (2005).

Pummerer, R , Ebermeyer, G. and Gerlach, K , Ber., **64**, 809 (1931)

Qi, H. J and Boyce, M. C., *Mechanics of Materials,* 37(8), 817 (2005).

Qipeng, G., *Eur Polym J* **26** (12), 1333, (1990a).

Qipeng, G., *Polym. Commun.* **31**, 217 (1990b).

Rabjohn, N., *J. Am Chem Soc* ,**70**, 1181 (1948)

RABRM Intelligence Division Report ID 5307, (1951).

Rahman, H. A., M. Phil. Thesis , University of Loughborough, United Kingdom (1990).

Ramesan, M. T., *Reactive and Functional Polymers*, **59** (3), 267 (2004)

Ramesan, M. T., Rosamma, A. and Khanh, N. V., *Reactivity and Functional Polymers*, **62**(1), 41-50 (2005).

Rao, G. R., Castiglioni, C., Gussoni, M., Zerbi, G. and Martuscelli, *Polymer*, **26** , 811 (1985).

Rattanasom, N., Poonsuk, A. and Makmoon, T., *Polymer Testing*, **24** (6), 728 (2005)

Razzak, M. T., Otsuhata, K , Tabata, Y., Ohashi, F. and Takeuchi, A., *J Appl. Polym Sci.*, **36**, 645 (1988).

Razzak, M. T , Otsuhata, K , Tabata, Y., Ohashi, F. and Takeuchi, A., *J. Appl. Polym. Sci* , **38**, 829 (1989).

Razzak, M. T , Tabata, Y., Otsuhata, K., *Radiat Phys Chem.* 42,(1-3), 57 (1993)

Reading, M , Elliott, D. and Hill, V. L., *10th ICTAC August* 24-28 (1992), *J , Thermal Analys.*, **40**, 949 (1993).

Reichenbach, J. K. W., Sornero, L J., Fitzgerald, J. J , *Macromol* , **27**, 1338 (1994).

Ribelles, J. L. G , Pradas, M. M., Dueñas, J. M. M. and Cabanilles, C. T., *J. Non Crystalline Solids,* **307-310**, 731(2002)

Richardson, M J.,"Thermal Analysis," Bevington, A., '*In Comprehensive Polymer Science, Polymer Characterization*, Pengamion Press, 1, 867 (1989).

Riess, G , Kohler, J., Tournut, C , and Banderet, A. *Makromol, Chem* , **58**, 101(1967).

Rigbi, Z., *Adv Polym. Sci* , **36**, 21 (1980).

Ritzenthaler, Reydet, E. G. and Pascault, *Polymer*, **41**, 6375 (2000)

Roberts, G E. and white, E. F. T , *In The Physics and Glassy Polymers*, Ed. Hooward, R N., New York, Wiley, 173 (1973).

Roberts, J. S. and Skinner, H. A , *Trans. Faraday Soc.*, **45** 339 (1949).

Roland, C.M. and Lee, G F , *Rubb. Chem Technol* , **63**, 554 (1990).

Romaine, J , Ph. D. Thesis, Uni. Lancaster, United Kindom (1988).

Rosowsky, A , *In Heterocyclic Compounds with three and four membered rings, Part1"*, Interscience Publishers, NY, (1964).

Rouf, C., Derrough, S., Andre, J. J., Widmaier, J. M. and Meyer G C., *In "Interpenetrating Polymer Networks"*, Eds , Klempner, D., Sperling, L. H. and Utaracki, L.A., ACS Books, Washington, DC (1994).

Rouilly, A.., Rigal, L. and Gilbert, R. G , *Polymer,* **45**, 7813 (2004)

Roux, C., Pautrat, R , Cheritat, R. and Pinazzi, C., *Compt. Rend.*, **258**, 5442 (1964)

Saffer, A and Johnson, B. l., *Ind. Eng Chem*, **40**, 538 (1948).

Salomon, G., Chr. Van der Schee, A., Ketekar, J. A. and van Eyk, B. *J, Disc Faraday Soc.*, **9**, 291 (1950); *J Polym Sci.*, **14**, 181 (1954).

Sánchez, M. S., Ferrer, G. G. Cabanilles, C. T., Dueñas, J. M. M., Pradas, M M Ribells, J. L. G , *Polymer*, **42**,10071 (2001).

Sang, S. T. M , *J Rubb Res. Inst Malaya*, **26** (2), 48 (1978).

Santos, M. and Guthrie, J. T., *Mat Sci. and Eng , R. Reports*, (50), 3, 31,79 (2005).

Sayigh, A. A. R., Tucker, B , Ulrich, H., US S. Pat. No 3, 652, 599 (1970).

Schneider, M , Pith, T. and Lambla, M , *Toughening of Plastics-III*, 571, (1994).

Scriven, E F. V , Azides and Nitrenes. Academic Press., New York (1984).

Sefton, M. V. and Merrill, E. W , *J. Appl. Polym. Sci* , **20**, 157 (1976).

Shanmugharaj, A. M , Kim, J. K. and Ryu, S. H., *Applied surface science index* 252 (16), 5714 (2006).

Shelton, J. R. and McDonald, E. T., *Proc. Int Rubb Conf* , Washington DC, 596 (1959).

Sheu, H R., EL-Aasser, M S. and Vanderhoff, J W., *J Polym Sci , Part A, Polym. Chem. Edn.*, **28**, 629 (1990).

Shi, D., Yang, J., Yao, Z., Wang, Y , Huang, H., Jing, W., Yin, J. and Costa, G., *Polymer,* **42**, (13), 5549 (2001).

Schneider, M , Pith, T. and Lambla, M., *Toughening of Plastics-III*, 571 (1994).

Shibayama, K. and Suzuki, Y , *Rubber Chem Tech* , **40**, 476, (1967)

Shimomura, Y., White, J. L and Spruiell, J. E , *J. Appl. Polym. Sci.*, **27**, 3553 (1982).

Shucai, Li.,Yunming, Li. and Jimin,Wu, *Gaofenzi Cailiao Kexue Yu Gongcheng* **7**(4),44 (1991)

Shukla, S. R. and Athalye, A. R., *J. Appl. Polym. Sci.*, **48**, 1877 (1993)

Singh, S, Ghiradella, H. and Frisch, H. L, *Macromol.*, **23**, 375 (1990).

Solt, G. S., British Patent 728, 508, (1955)

Song, M., Hourston, D. J., Reading, M., Pollock, H. M. and Hammiche, A., *J. Thermal Analysis and Colourimetry,* **56**, 991 (1999).

Song, M., Pollock, H. M., Hammiche, A., Hourston, D. J. and Reading, M , Polymer, **38**, 503 (1997).

Song, Mo and Long, F., *Eur Polym. J ,* **27** (9), 983 (1991).

Sperling L. H , *Interpenetrating Networks: An Overview, Adv. In Chem Ser* Eds Klempner, D , Sperling, L. H. and Utrcki, L. A., **239**, 3 (1994).

Sperling, L. H. and Friedman, D W , *J. Polym Sci* , A-2 (7), 425 (1969).

Sperling, L. H. and Mishra, V., *Polymers for Advanced Technologies, Rev. Article,* 197, (1996).

Sperling, L H., *'in Multi-component Polymer materials'* Eds., Paul, D. R. and Sperling, L. H , *ACS 211, Amer. Chem. Soc.*, Washington D. C. (1986)

Sperling, L H., Chiu, T. W., Gramlich, R. G. and Thomas, D. A., *J. Paint Technol* , **46**, 47 (1974).

Sperling, L. H., *Contemporary Topics in Polymer Science, Current status*, 6, 665, (1989).

Sperling, L. H., *Encyclopedia of Poly Sci. and Tecnol.*, **15**, Ed. Bikales, N. M , Wileys & Sons, NY, (1971).

Sperling, L. H., *Interpenetrating Polymer networks and Related Materials*, Plenum, New York (1981)

Sperling, L H , *Introduction to Physical Polymer Science*, 2nd Edn , John Wiley & Sons Inc., New York (1992).

Sperling, L. H., *Polymer News*, **12**, 332, (1987)

Sperling L H , Thomas, D. A ,US Patent 3, 833, 404, (1974)

Spurlin, H. M., US. S. Pat. No. 3, 754, 973 (1971).

Staudinger, J. J. P., Hutchinson, H. M., U. S Patent 2, 539, 377, (1951)

Stephen, R, Jose, S., Joseph, K., Thomas, S and Oommen, Z., *Polym Deg and Stability,* xx, 1e9 (2006)

Sulekha, P. B., Joseph, R., Madhusoodanan, K. N. and Thomas, K. T., *Polym. Deg and Stability,* **77** (3), 403 (2002),

Suma, N., Joseph, R. and Francis, D J , *Kautsch. Gummi. Kunstat*, **43**, 1095 (1990).

Suzuki, Y., Frijimoto, T., Tsunodo, S and Shibayama, K. J., *Macromol. Sci Phys*, **17**, 787 (1980).

Svorcik, V., Rybka, V , Volka, K , Hnatowicz, V , Kvitek, J.and Seidl, P. *J Appl. Phys.B* , **31**, 287 (1992)

Tangpakdee, J., Mizokoshi, M , Endo, A. and Tanaka. Y , *Rub Chem. Technol.*, **71**, 795 (1998)

ten Brinke, G., Karasz, F. E. and MacKnight, W. J , *Macromol.*, **16**, 1827 (1983).

Thakur, M., *Macromole*, **21**, 661 (1998)

Thaler, W. A. and Franzus, B., *J. Org. Chem.*, **29**, 2226 (1964).

Toki, S., Sics, I , Ran, S., Liu, L., Hsiao, B. S , Murakami, S., Senoo, K. and Kohjiya, S., *Macromolecules*, **35**, 6578 (2002).

Tung, C. J. and Hjsu, T. C., *J. Appl Polym Sci*, **46**, 1759 (1992).

Utracki, L. A., *Adv Chem Ser.*, **239**, 77 (1994).

Vainio, T., Hu, G., Lambla, M. and Seppala, J., *J Appl. Polym Sci.*, **61**, 843 (1996).

Vancaeyzeele, C , Fichet, O., Boileau, S., Teyssie, D., *Polymer*, **46** (18), 6888 (2005).

Vancaeyzeele, C., Fichet, O., Laskar, J, Boileau, S and Teyssié, D., *Polymer* **47** (6) 2046 (2006).

Vernekar, S. P., Sabne, M. B., Patil, S. D , Patil, A. S., Idage, S. B., Avadhani, C. V. and Sivaram, S., *J. Appl. Polym Sci* , **44,** 2107 (1992)

Vorenkamp, E. J., ten Brinke, G., Meijer, J. G., Jager, H. and Challa, G., *Polymer*, **26**, 1725, (1985).

Waddell, W. H., Evans, L. R , Gillick, J. G and Shuttleworth, D., *Rubb Chem, Technol*, **65**, 687 (1992).

Wang Geng-Chao, Cui Hai-wei, Fang Bin, Z. Zhi-Ping, J.Appl.Polym Sci, 44,1165 (1992).

Wang, J. and Roland, C. M., *Polymer*, **46** (12), 4160 (2005).

Wang, P ,Tan, K L., Ho. C. C., Khew, M. C., Kang, E. T., *Eur polym J* , **36** 1323 (2000),.

Wang, S. H., Zawadzki, S., Akcelrud, L., *J Polym. Sci Part B Polym Phys* **38** (22), 2861 (2000).

Warley, R. L. and. Halladay, J. R , *Polymer Testing* **24** (6), 678 (2005).

Williams, D. H. and Fleming, I , *Spectroscopic Methods in Organic Chemistry*, 4th Edn., McGraw Hill Book Company (1989).

Wolf, D. E., Hoffman, C. H., Aldrich, P. E , Skeggs, H. R., Wright, L. D. and Folkers, K., *J Am. Chem. Soc* , **79**, 1486 (1957).

Woo, E. M. and Wu, M. N., *Polymer*, **37** (12), 2485 (1996).

Xantos, M. and. Dagli, S. S , *Polym. Eng. And Sci* , **31**, 92 (1991).

Xiao, H Q., Zhang, C. X. and Guo, J. S., *In Interpenetrating polymer networks*, (Eds , Klempner, D., Sperling L H. and Utracki L. A,, ACS Books, Washington D. C. (1994).

Xiao, H. X, Frisch, K C and Frisch, H L , *J. Polym Sci Polym. Chem. Ed.*, **22**, 1035 (1984).

Xiao, H X., Frisch, K. C and Frisch, H. L , *J. Polym Sci. Polym Chem. Ed*, **21**, 2547 (1983).

Xuan, H. Le and Decker, C., *J. Polym. Sci. Part A, Polym Chem,*, **31**, 769 (1993).

Yan, M., *Reactive and Functional Polymers*, **45**, 137 (2000).

Yeo, J. K.,. Sperling, L. H. and Thomas, D. A , *Polymer,* **24** (3), 307 (1983).

Yucai, Ke., Zhao, S , Zengpu, C. *Gaofenzi xuebao*, (6), 250 (2-5), 656, (1992).

Yusof, A. M. M , Ph. D. Thesis, University of Loughborough, United Kingdom (1999)

Zeng, M., Zhang, L. and Kennedy, J. F., *Carbohydrate Polymers* , **60**, 399 (2005).

Zhou, P. and Frisch, H. L , *J Polym Sci Part A. Polym. Chem.*, **31**, 3479 (1993).