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CHARACTERIZATION AND PROPERTIES OF EPOXIDISED NATURAL RUBBER (ENR-50) / ETHYLENE VINYL ACETATE (EVA) BLENDS

by

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Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

This work is dedicated to my beloved husband and children for their endless love, patience and support. My parents for their love and encouragement.

My husband and children

MD. KAMARUDIN, NUR FATIHAH, MUHAMMAD SOLIHIN

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LIST OF SYMBOLS

T_g	Glass transition temperature
T_m	Melting temperature
ΔH_f	Heat of fusion
X_c	Degree of crystallinity
phr	Part per hundred rubber
php	Part per hundred polymer
rpm	Revolution per minute
ºC	Degree Celsius
wt %	Weight percentage
kGy	Kilo Gray

LIST OF ABBREVIATION

ABS	Acrylonitrile butadiene styrene
CP	Chloroprene rubber
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
ENR	Epoxidized natural rubber
EPDM	Ethylene propylene diene terpolymer
EVA	Ethylene vinyl acetate
HIPS	High impact polystyrene
HVA-2	N,N-m phenylene dimaleimide
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
PAA	Polyacrylic acid
PB	Polybutadiene
PBA	Polybutyl acrylate
PE	Polyethylene
PEA	Polyethylacrylate
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SBR	Styrene butadiene rubber
TGA	Thermogravimetrc analysis
TMPTA	Trimethylolpropane triacrylate
TPE	Thermoplastic elastomer
TPGDA	Tripropyleneglycol diacrylate
TPO	Thermoplastic elastomer olefins
TPV	Thermoplastic vulcanizates
XPCL	Carboxylated poly (Є-caprolactone)
MBS	N-Oxydiethylene benzothiazole-2-sulphenamide
TMTD	Tetramethylthiuram disulphide
CTP	N-(Cyclohexylthio)phthalimide

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LIST OF PUBLICATIONS & SEMINARS

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1.2 M. Zurina , H. Ismail, and C. T. Ratnam, Characterization of irradiation-induced crosslink epoxidize natural rubber / ethylene vinyl acetate (ENR-50/EVA) blend., *Polymer Degradation and Stability*, 91,2723-2727, 2006

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PENCIRIAN DAN SIFAT-SIFAT ADUNAN GETAH ASLI TEREPOKSIDA (ENR-50) / ETILENA VINIL ASETAT (EVA)

ABSTRAK

Kesan komposisi adunan, pemvulkanan dinamik, radiasi alur elektron dan gabungan radiasi serta agen sambung silang ke atas sifat-sifat adunan getah asli terepoksida/ etilena vinil asetat (ENR-50/EVA) telah dikaji. Pemvulkanan dinamik disediakan menggunakan Sulphur dan Dikumil peroksida (DCP) sebagai agen sambung silang sementara trimethylolpropane triacrylate (TMPTA), tripropyleneglycol diacrylate (TPGDA) dan N,N-m pehylenebismaleimide (HVA-2) adalah agen sambung silang yang dipilih untuk digunakan bersama radiasi. Adunan disediakan dengan menggunakan pencampur dalaman Haake Rheomix Polydrive R600/610 pada suhu 120ºC dan kelajuan rotor 50 rpm. Sistem adunan meliputi komposisi yang berbeza iaitu 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 ENR-50/EVA. Keputusan menunjukkan sifat-sifat tensil dan kestabilan terma meningkat dengan peningkatan komposisi EVA disebabkan oleh sifat-sifat EVA yang lebih baik berbanding ENR-50. Sifat-sifat mekanikal dinamik menunjukkan adunan adalah serasi untuk semua komposisi. Sementara, pemvulkanan dinamik telah meningkatkan kekuatan tensil, sifat-sifat terma dan kandungan gel. Keputusan ini mematuhi teori yang menyatakan bahawa pembentukan sambung silang meningkatkan kekusutan molekul di dalam fasa getah, pembentukan fasa getah yang lebih kecil akibat sambung silang, membaiki kestabilan morfologi dan seterusnya meningkatkan sifat-sifat adunan tersebut. Walaubagaimanapun, dalam kes DCP, selain daripada pembentukan sambung silang dalam fasa getah, pemutusan rantai juga berlaku pada EVA. Dengan mengenakan radiasi alur elektron ke atas adunan ENR-50/EVA (50/50) pada dos yang berbeza iaitu 20,40,60 dan 100 kGy telah meningkatkan sambung silang adunan. Sambung silang yang dipengaruhi oleh radiasi meningkat dengan peningkatan dos radiasi dan

menyebabkan peningkatan pada sifat-sifat tensil, sifat-sifat terma dan keserasian adunan. Penggunaan agen sambung silang seperti TMPTA, TPGDA dan HVA-2 telah meningkatkan lagi sambung silang ini dan menyebabkan peningkatan dalam kekuatan tensil, sifat-sifat terma dan sifat-sifat mekanikal dinamik. TMPTA didapati paling berkesan dalam meningkatkan sambung-silang yang dipengaruhi oleh radiasi.

CARACTERIZATION AND PROPERTIES OF EPOXIDISED NATURAL RUBBER (ENR-50) / ETHYLENE VINYL ACETATE (EVA) BLENDS

ABSTRACT

The effect of blend ratio, dynamic vulcanization, electron beam irradiation and the combination of irradiation and crosslinking agent on the properties of epoxidised natural rubber/ ethylene vinyl acetate (ENR-50/EVA) blends were investigated. The dynamic vulcanization were prepared using sulphur and dicumyl peroxide (DCP) as crosslink agent, while trimethylolpropane triacrylate (TMPTA), tripropyleneglycol diacrylate (TPGDA) and N,N-m pehylenebismaleimide (HVA-2) were crosslinking agents chosed to combined with irradiation. Blends were prepared by melt mixing in an internal mixer, Haake Rheomix Polydrive R600/610 at temperature and rotor speed of 120ºC and 50 rpm respectively. Blend systems were covering various compositions viz. 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 of ENR-50/EVA. Results showed that the tensile properties and thermal stability increased with the increases in EVA content due to it superior properties than ENR-50. Results on dynamic mechanical properties revealed that the blend was compatible at all blend ratios. Meanwhile, dynamic vulcanization has increased tensile strength, thermal properties and gel content. These findings follow the theory stated that the formation of crosslinking increases the molecular entanglement in the rubber phase. Formation of finer vulcanized rubber particles due to the presence of crosslinks improved stability of the morphology and subsequently increased the blend properties. However, in the case of DCP, apart from the crosslinking formation in rubber phase, the chain scission has also developed on ethylene vinyl acetate (EVA). The introduction of electron beam irradiation on ENR-50/EVA (50/50) blends at different dosage viz. 20,40,60 and 100 kGy has enhance the irradiation-induced crosslinking. Irradiation-induced crosslinking increased with increase in irradiation dose and lead to the improvement in tensile

properties, thermal properties and compatibility of the blend. The incorporation of crosslinking agents such as TMPTA, TPGDA and HVA-2 has further enhanced the irradiation-induced crosslinking and lead to the improvement of tensile strength, thermal and dynamic mechanical properties. TMPTA was found to be the most effective in promoting irradiation-induced crosslinking of ENR-50/EVA blends.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Polymer blending was recognized in the last few decades as the most promising way to prepare new material with tailored individual properties. Polymer blend are defined as a mixture of two or more polymers or copolymers. Blending of existing commodity or engineering polymers often can be implemented more rapidly and it is less expensive than realization of new polymer chemistry including development of monomer synthesis and polymerization technology. Extensive studies have been carried out in the area of polymer blend. This study includes rubber-rubber blend, rubber-plastic blend and plastic-plastic blend.

A thermoplastic elastomer (TPEs) is a relatively new class of polymer blend. TPE can be prepared by mixing a thermoplastic and elastomer under high shearing action using standard plastic machinery above melting temperature of thermoplastic. It can be processed in the molten state as a thermoplastic and which has many of the performance characteristic of a thermoset rubber (Harper, 1992).

The great variety of commercially available elastomer and thermoplastics offers huge opportunities for blending of TPEs. There are many combination of elastomer and thermoplastic which are commercially available nowadays. Among them are the combination of EPDM rubber with PP (Synnott et al., 1990), EPDM with EVA (Mishra et al., 1998a; Mishra et al., 1998b) blend of NBR with PVC (Watanabe, 1990), blend of NBR with EVA (Jansen & Soares, 2001) and blend of SBR with EVA (Radhakrishnan et al., 2004). Other than synthetic rubber, natural rubber and it derivatives also been used in rubber plastics blend such as NR and ENR. Among them are NR/PP blend (Elliott, 1990), NR/PE blend (Choudhury et al., 1990), ENR/PVC blend (Varughese and

De, 1989; Ratnam et al., 1999; Umaru, 1993), ENR/PMMA (Nakason et al., 2004) and etc.

Currently Malaysian Rubber Board produces ENR with the trade name Epoxyprene. Two grades are available, namely ENR-25 and ENR-50, with 25, and 50 mol % epoxidation, respectively. However the market and applications for ENR found to be limited. Thus attempts are being made to diversify the usage and application of this rubber, especially in advanced engineering field. As mention earlier, blending with other polymer is the easiest and the cheapest way to tailor the properties of ENR and at the same time reduces the material cost. Furthermore, the presence of oxirane group in ENR was found to be effective in causing specific interaction with a second polymer (Kallitsis and Kalfoglou, 1989).

Ethylene vinyl acetate copolymers (EVA) are randomly structured polymers, which offer excellent ozone resistance, weather resistance, and excellent mechanical properties (Doak, 2004). EVA is chosen to be blended with ENR-50 because of its excellence properties and halogen-free thermoplasticity. It is hoped that the blends of EVA and ENR will lead to the production of halogen-free materials, which may suit many applications that are currently dominated by plasticized PVC and the modification on the processing will enhance the tensile properties, thermal properties and compatibility of ENR-50/EVA blend.

The main aim of blending rubber with thermoplastic (TPE), is to develop a compound with low specific gravity, as well as meeting high resilience, strength and modulus requirement. However, one of the decisive factors governing the properties of the multi-component polymer is phase separation behaviour (compatibility between the phases). This might due to the lack of adhesion between the component polymers, which make it difficult to produce blends with the desired properties by simple blending. Many researches have been carried out in the field of miscibility and compatibility of

ENR blends. Kallitsis and Kalfouglou (1989) investigated the compatibility behaviour of ENR at two different degrees of epoxidation with hydroxyl-containing polymeric resins. Mallick et al. (1993) studied on the compatibility of polyacrylic acid (PAA) and ENR. Margaritis and Kalfouglou (1987) studied on the miscibility of ENR at two level of epoxidation (25 and 50 mol%) with polyvinyl chloride.

Within a short period, this area of research has undergone rapid diversification. It ranges from the use of coupling agent, chemical modification of immiscible polymers to foster miscibility and compatibilization which facilitate the production of polymer alloy. One of the latest blending technique, referred to as reactive blending, exploit both physical and chemical means. All this has been done in order to produce a new range of polymer blend with it own speciallity.

1.2 Objective and Organization of the Thesis

1.2.1 Objective

The main objective of this study is to investigate the possibility of producing a new thermoplastic elastomer material from the blend of epoxidised natural rubber (ENR-50) and ethylene vinyl acetate (EVA). The studies on the effect of blend ratios and some process modification such as dynamic vulcanization (with sulphur and dicumyl peroxide), electron beam (EB) irradiation and irradiation with the existence of crosslinking agent/coagent (TPGDA, TMPTA and HVA-2) on the characteristic and properties of ENR-50/EVA blend will be evaluated.

The activities of this work are:

- To study the process development of ENR-50/EVA blends at different blend ratios. This is important since the process development gives the information on the effect of blend ratios and different additives used on the processability of the blends.

- To measure the tensile properties of ENR-50/EVA blends in order to assess the performance of the end product.
- To determine the dynamic mechanical properties of ENR-50/EVA blends in order to gather the information of the viscoelastic behavior of the materials and at the same time, determine the glass transition temperature (T_g) of blend materials which could be correlate with the degree of crosslinking and compatibility of the blends.
- To determine the morphology and measure the degree of crosslinking through gel content of ENR-50/EVA blends, which is the factors that influence the tensile properties, dynamic mechanical properties and thermal properties of the blends.
- To evaluate the thermal stability of ENR-50/EVA blends. This thermal behavior is important since the degradation is a major problem in the development of the materials and the service life temperature is important to determine the suitable application for these blend materials.

1.2.2 Organization of the Thesis

There are eight chapters in the thesis and each chapter gives information related to the research interest.

- **Chapter 1** contain the introduction of the thesis. It is covers a brief introduction about research background, a problem statement, objective of the project and organization of the thesis.
- **Chapter 2** contain the review of the literature. It is covers the fundamental of polymer blends and thermoplastic elastomer and also a general overview about the process modification on the polymer blends.

- **Chapter 3** contain the information about the materials specification, equipment and experimental procedures used in this study.
- **Chapter 4** discusses the effect of blend ratios on ENR-50/EVA blend.
- **Chapter 5** discusses the effect of different curing system on the dynamically vulcanized ENR-50/EVA blend.
- **Chapter 6** discusses the effect of different irradiation dose on the irradiation-induced crosslink of ENR-50/EVA blend.
- **Chapter 7** discusses the effect of TMPTA and TPGDA on the irradiated ENR-50/EVA blend.
- **Chapter 8** discusses the effect of HVA-2 on the irradiated ENR-50/EVA blend.
- **Chapter 9** concludes the above findings and assessment was made to evaluate the achievement of the objectives.

CHAPTER 2
LITERATURE REVIEW

2.1 Polymer Blends

Polymer blend constitute of 36 wt% of the total polymer consumption, and their pertinence continues to increase. About 65% of polymer alloy and blend are produced by polymer manufacturer, 25% by compounding companies and the remaining 10% by the transformer (Utracki, 2002)

In general polymer blend can benefit in term of: (i) Providing materials with full set of desired properties at the lowest price. (ii) Extending the engineering resins performance. (iii) Improving specific properties. (iv) Offering the means for industrial and/or municipal plastics waste recycling. Blend also benefits manufacturer by offering: (i) Improved processability, product uniformity, and scrap reduction. (ii) Quick formulation changes. (iii) Plant flexibility and high productivity. (iv) Reduction of the number of grades that need to be manufactured and stored. (v) Inherent recyclability, etc. (Utracki, 2002)

2.1.1 Definition

Utracki (1990) defined polymer blend as a mixture of at least two polymers or copolymer. Later, Utracki (2002) defined polymer blend as a mixture of at least two macromolecular substances, polymer or copolymer, in which the ingredient content is above 2 wt%. Kumar and Gupta (2003) termed polymer blend as a physical mixtures of two or more polymers and are commercially prepared by mechanical mixing, which is achieved through screw compounders and extruders. On the other hand Paul and Newman (1978) defined polymer blend as a means of combining the useful properties of different molecular species, but blend allow to be done through physical rather than chemical means. From overall definition, we can conclude that polymer blend is a

mixture of two or more homopolymer or copolymer, obtained through various processes and technique.

2.1.2 Method of Blending

In plastic processing the terms mixing, blending and compounding have different meanings. Mixing indicates the physical act of homogenization, blending usually indicates preparation of polymer blend and alloys, while compounding is the incorporation of additives into polymeric matrix, viz. antioxidants, lubricants, pigments, fillers, or reinforcements (Utracki and Shi, 2002).

Polymer blend, in general has been prepared commercially by melt mixing, solution blending and latex blending.

2.1.2 a) Melt Mixing

Melt mixing technique is an easy and economical way of blending different polymers to avoid problems of contamination, solvent or water removal and etc. Mixing can be accomplished on heated roll mills. However, this is not very practical since the plastic have high melting points. Mixing on an open mill in air at elevated temperatures induces oxidative degradation. Internal mixers, mixing extruder, and twin-screw extruder are more efficient and their use gives less oxidative degradation. An internal mixer is a batch mixer, whereas a twin-screw extruder is a continuous mixer (Coran, 2001).

2.1.2 b) Solution Blending

Due to the experimental difficulties in mixing and measuring highly viscous polymer blends, it is a frequently laboratory practice to attain intimate mixing by dissolving the two polymers in a common solvent then drying them. However, the morphology of polymer alloy and blend prepared by solvent casting depends on the solvent, temperature, time, concentration and etc (Utracki, 1990).

2.1.2 c) Latex Blending

The latex blends were used either directly, for example, as paint, adhesives or sealants, or they were spray dried or palletized. Spray drying has been the most frequently used method. Since emulsion polymerization was able to produce either a fine dispersion of homo or copolymer, or alternatively large drop aggregates, comparable to those generated in suspension polymerization. The latex blending offered not only a wide range of composition but also diverse morphologies. The disadvantage of the latex blending was high content of contaminants such as emulsifiers, residuals of the initiators, chain transfers, stabilizers and etc (Utracki and Shi, 2002).

2.1.3 Classification of Polymer Blends

Polymer blends can be classified in various ways using different indicators such as compatibility (compatible and incompatible blends), production methods (mechanical blend or chemical blends), nature of polymer architecture (block and graft polymers), number of constituent polymers (binary blends, ternary blends and etc) and the types of constituent polymers. Based on the latest parameter, polymer blends can be broadly classified into three main groups as follows: i) rubber-rubber blends, ii) plastic-plastic blends and iii) rubber-plastic blends (TPE) (Susantha, 2002).

The important of rubber-rubber blends become manifest when we realize that nearly every major rubber component in a tire constitutes a blend of two or more of these rubbers, Styrene butadiene rubber (SBR), Natural polyisoprene rubber (NR), Synthetic polyisoprene rubber (IR), Polybutadiene rubber (BR), Butyl rubber (IIR) and Ethylene propylene rubber (EPDM or EPM). The reasons of producing rubber-rubber blend are: (a) the compound cost may be lowered, (b) easy fabricated in the complex shaping, forming and building operations, (c) the final product performance can be modified beneficially (McDonel et al., 1978).

Polyolefin form the largest group of commercial thermoplastic. They constitute a group of polymer of complex macromolecular structure, wide molecular weight distribution that are diverse in shape, substantial short and long chain branching and high crystallinity. Their density is the lowest among polymers and strongly influences performance characteristics. The characteristic of plastic-plastic blend are: exellent dielectric properties, water repellence, nonpolarity, high melt viscosities that respond weakly to temperature change but strongly to shear rate or stress changes, high melt elasticity and melt strength. Most of the studies on plastic-plastic blending used in production of films, profiles and containers, molding and insulation and jackets for cables.(Plochocki, 1978).

Rubber-plastic blend or known as thermoplastic elastomer (TPE) blends is a relatively new class of polymer that are processable as a melt at elevated temperature but exhibit properties similar to a vulcanized elastomer at use temperature. Thermoplastic elastomer blends exhibit stress-strain characteristics that fall between the low modulus crosslink elastomers (curve c Figure 2.1) and the high modulus yielding materials that undergo a high degree of plastic deformation (curve b, Figure 2.1) (Kresge, 1978).

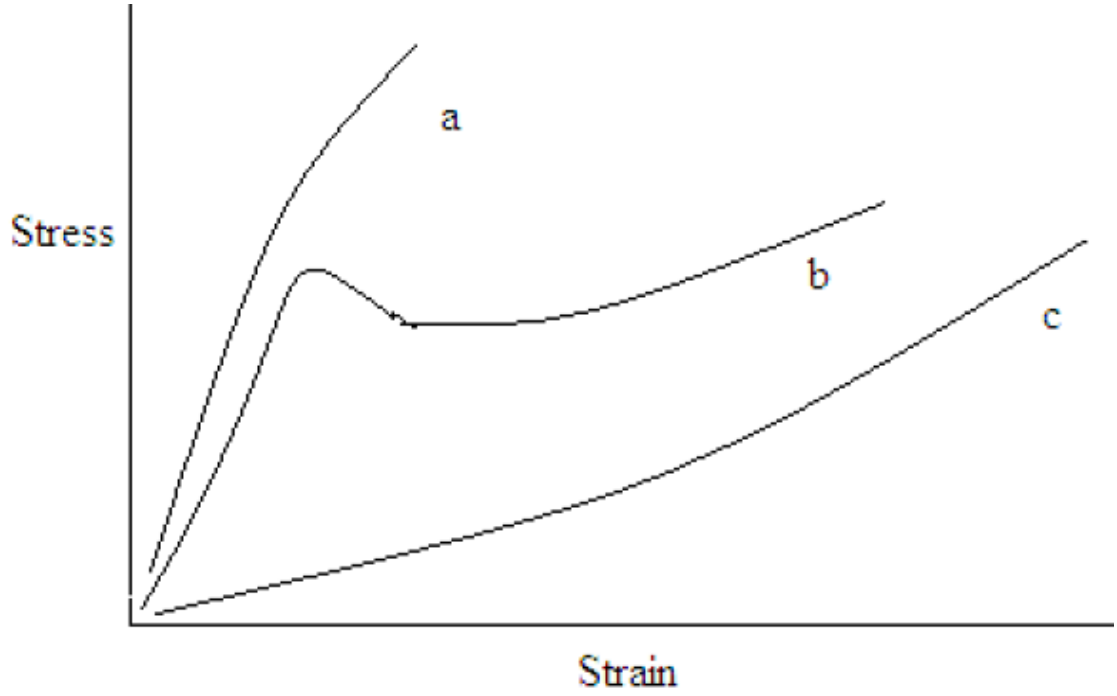


Figure 2.1: Three typical types of stress-strain curves: a) high modulus plastic, b)high modulus with yielding and poor recovery on return cycle, c)low-modulus rubbery (Kresge, 1978).

2.2 Thermoplastic Elastomer (TPEs) Blends

TPE form a relatively new class of materials, which possess the processing characteristics of plastics and the physical properties of vulcanised elastomers simultaneously. They need no separate vulcanisation step. Scrap and rejects of these materials can be recycled without significant inferior effect on the properties and hence show the environmentally friendly behaviour. TPEs are capable of being molded like thermoplastics in injection moulding and extrusion at suitable processing temperatures. They have a measure of resilience, recovery and flexibility associated with vulcanised elastomers at the normal service temperature (Walker and Rader, 1988; De and Bhowmick, 1990). Some advantage and disadvantage of TPEs are summarized in Table 2.1.

Table 2.1: Advantages and disadvantages of TPEs (De and Bhowmick, 1990; Harper, 1992).

	Advantages
1	Processing is simpler and involves fewer steps (little or no compounding steps).
2	Shorter fabrication cycles, which are on order of seconds compared to the several minutes long vulcanisation and fabrication cycle of thermoset rubber.
3	Improved quality of the articles, due to higher level of compositional consistency.
4	Low energy consumption due to fewer and simple processing steps.
5	Recyclability of scraps and rejects.
6	Reduction of significance of environmental problems associated with above (5).
7	Improvement in dimensional stability.
8	Lower specific gravity than comparable thermoset rubber containing various additives such as fillers (valid only for unfilled TPEs).
9	Economic benefits associated with all above advantages.
	Disadvantages
1	Unfamiliar technology and processing equipments to most of thermoset processors, though the technique is familiar to thermoplastic processors.
2	Drying requirement, before moulding.
3	Limited number of low hardness TPEs.
4	Melting at elevated temperatures.

The TPEs discussed here is mainly focused on TPEs prepared by melt mixing, other types of TPEs and their developments are also summarised in order to distinguish them from melt mixed TPEs. TPEs can be categorised into five major classes (Harper, 1992). They are:

1. Thermoplastic polyurethanes (TPUs)

2. Styrenic block copolymers (SBS)

3. Elastomeric alloy

4. Copolyester (COPs)

5. Polymer blends (i) rubber-polyolefin blends (TPOs)

(ii) thermoplastic vulcanisates (TPVs)

The first four groups of TPEs are based on block polymers consist of elastomer and thermoplastic components and exist as two distinct phases which are, however, chemically bonded. The end blocks of thermoplastic agglomerate into plastic dominants, which are then dispersed in a continuous rubber phase. However, the production of TPEs of first four groups involves with complex chemistry compared with TPEs obtained from simple melt mixing of elastomer and plastics.

2.3 Thermoplastic Elastomer Olefins (TPOs).

The blending of two or more polymers has gained considerable importance in recent years because the blend may give rise to certain properties that cannot be attained by other means or from individual components. Thus thermoplastic elastomer can be prepared by mixing a thermoplastic (such as PP, PE or PVC) and an elastomer (such as EPDM, NR, ENR or NBR) under high shearing action. Besides having low cost, these blends have certain advantages over other types of TPEs. In This class, the desired properties can be achieved by suitable selection of both rubber and plastics and their ratio in the blend. For example, thermoplastic blends of hardness ranging from 60 Shore A to 60 Shore D can be prepared by adjustment of the plastic and rubber components. Since the properties are derived from the phase structure and crystallinity of the plastics, the properties can be manipulated by variation of the above parameters. Moreover, preparation of these blends is carried out by using standard plastic machinery at a high temperature (above melting point of the plastics). The

properties are also affected by introduction of filler, crosslinkers, interfacial agents, etc (Bowmick & De, 1990)

2.3.1 Thermoplastic

Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled. Thermoplastic polymers can be repeatedly softened by heating and then solidified by cooling, a process similar to the repeated melting and cooling of metals. These behaviors occur due to the non existing chemical crosslinking in this polymer. Most linear and slightly branched polymers are thermoplastic. All the major thermoplastics are produced by chain polymerization (Progelhof & Throne, 1993; Crawford, 1981). The examples of thermoplastic polymers are PE, PP, PS, PET and etc.

2.3.1 a) Ethylene Vinyl Acetate (EVA)

The large number of PE usage is the results of the enormous number of variations possible in the molecular structure of homopolymers and polar copolymers. Polar copolymers usually exhibit lower crystallinity and yield strength. They are used for application requiring flexibility, toughness, stress-cracking resistance and adhesion to coatings, co-extruded film and laminates. One of the PE copolymer is the one containing vinyl acetate known as ethylene vinyl acetate (EVA).

Crystallinity in EVA copolymer is low, but not density (0.922-0.943 g/cm^3), because the vinyl acetate (VA) groups increase the density of the amorphous phase. Copolymer containing up to 20 wt% of VA are used in various extrusion and molding applications. Copolymer containing 2-5% VA behave similarly to PE, but have better clarity, higher impact strength, better low temperature flexibility and lower heat seal

temperatures. Copolymer containing 7.5-12% VA have still greater flexibility, higher puncture resistance and exceptional impact strength. They are used in high performance film applications. Copolymer containing 15-18% VA are now available and some are almost rubbery in nature (Doak, 2004).

Ethylene vinyl acetate copolymers (EVA) are randomly structured polymers which offer excellence ozone resistance, weather resistance and excellence mechanical properties (Doak, 2004). Ethylene vinyl acetate (EVA) is one of the widely used polymers for cable insulates. It is also frequently used as a long-lasting-life plasticizer to improve the mechanical and processing properties of PVC. EVA is available as a plastic, thermoplastic elastomer, and rubber depending on the vinyl acetate (VA) content in the copolymer. EVA containing 28% VA is a thermoplastic elastomer, and 50% VA is a rubber (Shifeng et al., 2004). Figure 2.2 shows the unit structure of EVA.

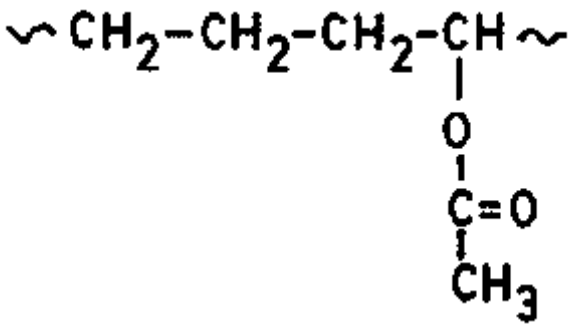


Figure 2.2: Unit structure of EVA (Dutta et al., 1996).

The incorporation of VA in the ethylene chain imparts flexibility, toughness and clarity as compared to LDPE. Other important features include toughness at low temperature and intrinsically good processability. Because of these important properties, EVA copolymers have found several applications in sheeting, wire and

cable coating, flexible tubing, shoe soles and food packaging. They also represent a good partner for polymer blends as an impact modifier.

Beside their good properties, EVA copolymer can be easily converted into compatibilizing agents for EVA based polymer blends. Chemical modification of preformed polymers may be very profitable when functional groups are already present along the backbone. The presence of acetate groups facilitates the generation of free radical along the backbone, which enables promotion of grafting reactions in the presence of several monomers. Such graft copolymers can be prepared in situ during the blend preparation. Chemical modification of EVA by introducing a functional group that can act as a chain transfer agent is another elegant pathway for the synthesis of EVA-based graft copolymer (Souza et al., 1999).

2.3.2 Elastomer

Terminology of elastomer is defined by Fisher in 1939 as a natural or synthetic product that can be vulcanized, where it shows elastic behavior after crosslinked and could be stretch at least double the original length at room temperature and will return to original length after release it (Heinisch, 1966). Elastomers are rubbery polymers that can be stretched easily to several times their unstretched length and which rapidly return to their original dimensions when the applied stress is released. Elastomers are crosslinked, but have a low cross-link density. The polymer chains still have some freedom to move, but are prevented from permanently moving relative to each other by the crosslinks. To stretch, the polymer chains must not be part of a rigid solid. An elastomer must be above its glass transition temperature, T_g, and have a low degree of crystallinity (http://www.lasalle.edu/academ/chem/ms/polymersRus/Resources/Classification.htm#thermoplastics, 2000).

2.3.2 a) Epoxidised natural Rubber

Epoxidised natural rubber (ENR) is a derivative of natural rubber produced by chemical modification. It was not until the mid 1980s that pure samples of ENRs were prepared and their properties fully recorded (Gelling, 1999). The mechanical properties of natural rubber (NR) are generally superior to those of synthetic rubbers. However, NR cannot compete with the specialty synthetic elastomers with regards to such properties as gas permeability and oil resistance. The epoxidation reactions established criteria for the chemical modification of NR, which lead to the development of clean Epoxidised natural rubber (ENR). These new polymer have improved oil resistance and decrease gas permeability, whilst retaining many of the properties of NR and also exhibiting some novel features.

Table 2.2: Typical properties of ENR and SMR L (Ismail, 2004).

Properties	SMR L	ENR 10	ENR 25	ENR 50
Glass transition temperature, T_g (ºC)	-69	-60	-45	-25
Specific gravity	0.93	0.94	0.97	1.03
Mooney viscosity, $M_{L,\ 1+4}$ (100ºC)	50-70	90	110	140

The epoxide content of ENR-25 and ENR-50 is within 1-2% of the quoted values as determined by a combination of elemental oxygen analysis and proton nuclear magnetic resonance (NMR). The distribution of epoxide groups along the polymer backbone determine the physical properties of the ENR concerned. The epoxide group sequences of both ENR-25 and ENR-50 have been measured by NMR spectroscopy and the observed sequences agree with those calculated for a totally random epoxidation. Epoxidised NRs are thus randomly Epoxidised cis-1, 4-polyisoprenes.

Both ENR-25 and ENR-50 have mooney viscosities in the range 75-90 on production. Epoxidation of NR increases the polarity, and thus the solubility of ENR depends on the level of epoxidation and the nature of the solvent. For every 1 mol% epoxidation, the glass transition temperature (T_g) increases by approximately 1ºC thus ENR-25 has a T_g of -47ºC and ENR-50 a T_g of -22ºC. ENR vulcanizates show that these materials undergo strain cryatallization. Beyond 50 mol% epoxidation rapid decrease strain crystallization was observed. The polarity of ENR increases with rise in epoxide content. At high epoxidation levels, these materials become more resistant to hydrocarbons but their resistance to polar solvents decreases (Baker & Gelling, 1987).

The epoxide groups in ENR have also been investigated as routes to new crosslinking systems and rubber bound antidegradants and as intermediates for further chemical modification (Gelling, 1999). Figure 2.3 shows the structure of epoxidised natural rubber (ENR).

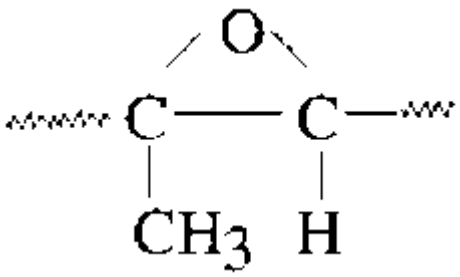


Figure 2.3: Structure of Epoxidised Natural Rubber (ENR) (Ratnam et al., 2001b).

2.4 Thermoplastic Vulcanisates (TPVs)

This type of TPE is produced by dynamic vulcanization, defined as the process of intimate melt mixing of a rubbery polymer and a thermoplastic to vulcanize the rubbery polymer and thus generate a TPE with properties closer to those of a thermoset rubber than those of a comparable unvulcanized composition. Upon melt mixing of the thermoplastic and rubbery polymers under high shear, the less viscous

thermoplastic will tend to become the continuous phase with the more viscous rubber dispersed in it. The dispersed rubber particles will be vulcanized, forming a three dimensional polymer network within each particles, and become trapped since they cannot recombine into larger aggregates (Rader, 1988; Coran, 2001).

The morphology of the TPV is best understood as a dispersion of very small, highly crosslink elastomer particles in a continuous phase of hard thermoplastic (Figure 2.4). The size of the elastomer phase particles is a key to the performance of the TPV. As the size of these particles decreases, the ultimate tensile properties of the TPV increase. The second key to TPV performance is the degree of crosslinking of soft elastomeric phase. Highly crosslinking the elastomeric phase gives good properties and allows the TPV to capture many of the application previously devoted to a thermoset rubber (Rader, 1988).

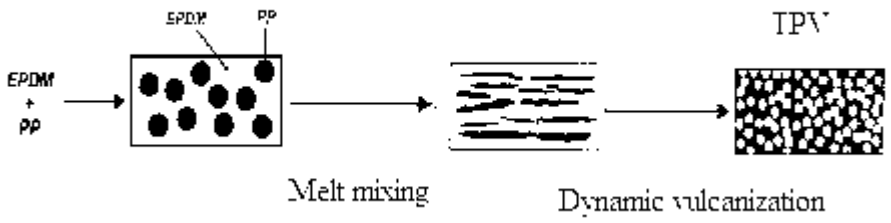


Figure 2.4: Phase Morphology of TPV (Katbab et al., 2000)

2.4.1 Dynamic Vulcanization

Dynamic vulcanization is the process of vulcanizing the elastomer during its melt mixing with molten plastic. Dynamic vulcanization is a route to new thermoplastic elastomers which have properties as good or even in some cases better than those of block copolymer. Elastomer and thermoplastic is first melt mixed. After sufficient melt mixed in the internal mixer to form well mixing blend, vulcanizing agents (curatives, crosslinker) are added. Vulcanization then occurs while mixing continues. The more rapid the rate of vulcanization, the more rapid the mixing must be to ensure good

fabricability of the blend composition. It is convenient to follow the progress of vulcanization by monitoring the mixing torque or mixing energy requirement during mixing (Coran, 1987; Coran, 2001).

The change in morphology that occurs during dynamic vulcanization is Schemeally represented in Figure 2.5. During dynamic vulcanization, a co-continuous morphology may be transferred to a matrix and dispersed phase morphology, there may be some possibility of phase inversion, or the crosslink rubber phase may become finely and uniformly dispersed in the plastic matrix. During the process of dynamic vulcanization, the viscosity of the rubber phase increases because of crosslinking and the rubber domains can no longer be sufficiently deformed by the local shear stress and are eventually broken down into small droplets (John et al., 2003).

There is much commercial interest in dynamic vulcanization since the introduction of proprietary product (e.g. SANTOPRENE thermoplastic elastomer) prepared by the dynamic vulcanization of blends of olefin rubber with polyolefin resin. If the elastomer particles of such a blend are small enough and if they are fully vulcanized, then the properties of the blend are greatly improved. Examples of the improvements are as follows (Coran, 1987):

1. Reduced permanent set,
2. Improved ultimate mechanical properties,
3. Improve fatigue resistance,
4. Greater resistance to attack by fluids (hot oil),
5. Improved high temperature utility,
6. Greater stability of phase morphology in the melt,
7. Greater melt strength and
8. More reliable thermoplastic fabricability

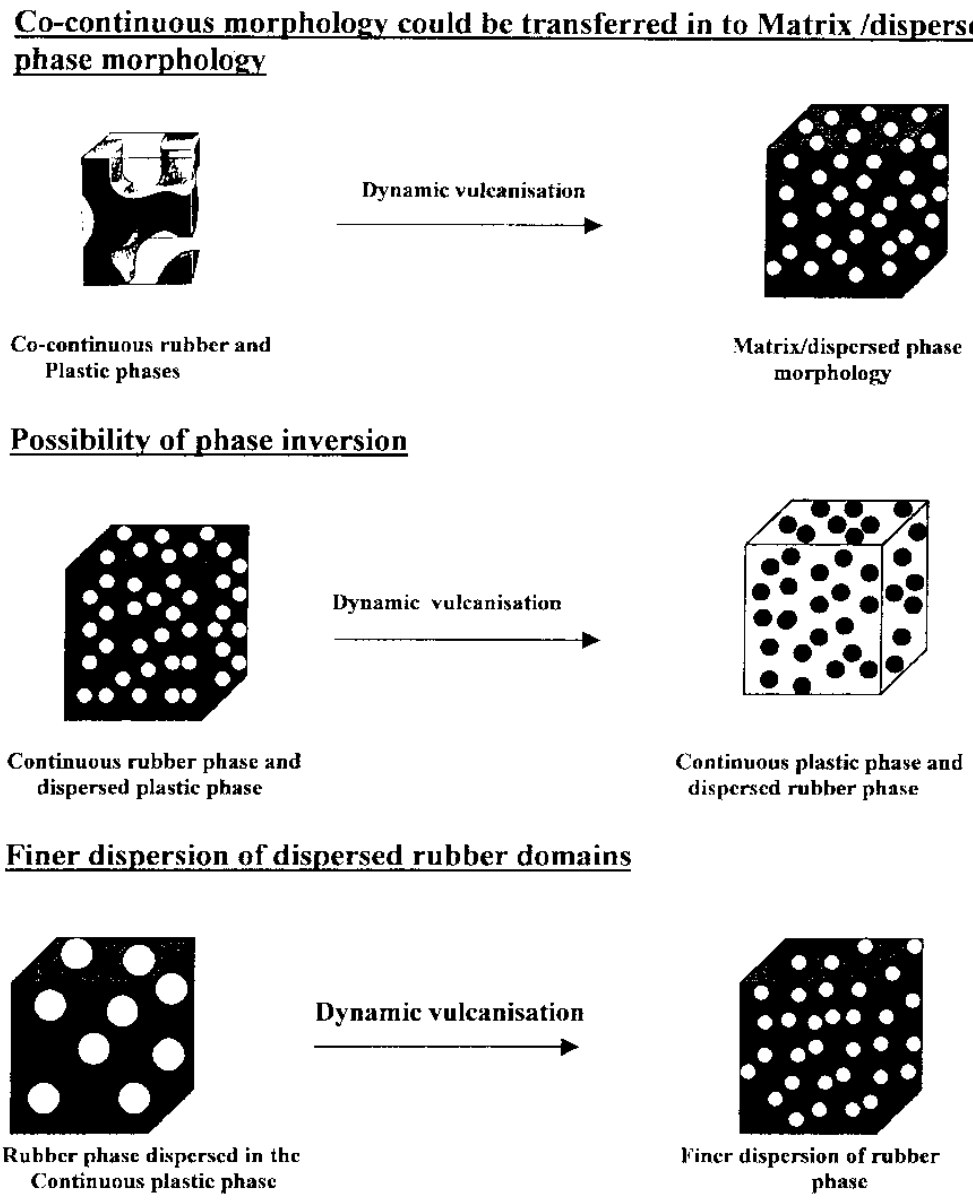


Figure 2.5: Scheme representation of dynamic vulcanization (John et al., 2003)

In short, dynamic vulcanization can provide compositions which are very elastomeric in their performance characteristics. However, these same thermoplastic vulcanizate compositions can be rapidly fabricated into finished parts in thermoplastic processing equipment. The best elastomer thermoplastic vulcanizates are those in which the surface energies of the plastic and elastomer are matched. When the entanglement molecular length of the elastomer is low and when the plastic is 15-30% crystalline.

2.4.2 Sulphur vulcanization

Sulphur was the first agent used to vulcanize the first commercial elastomer, natural rubber (NR). Accelerated sulphur vulcanization is suitable for the following types of elastomer (Rodger, 1979):

1. General purpose - natural rubber (NR), synthetic isoprene rubber (IR), polybutadiene rubber (BR), styrene/butadiene rubber (SBR).
2. Speciality – Nitril rubber (NBR), butyl rubber (IIR), chloro butyl rubber (CIIR), bromo butyl rubber (BIIR) and ethylene/propylene/diene modified rubber (EPDM).

Table 2.3: The basic recipe for the sulphur vulcanization system (Rodger, 1979)

Ingredient	Amount
Zinc oxide	2-10 phr
Stearic acid	1-4 phr
Sulphur	0.5-4 phr
Accelerator	0.5-10 phr

phr-parts per 100 parts of rubber

Table 2.3 shows the basic recipe for the sulphur vulcanization system. Zinc oxide and stearic acid comprise the common activator system where the zinc ions are made soluble by salt formation between the acid and the oxide. The part of the vulcanization system that offers the most opportunity for variation is the sulphur level and type and level of organic accelerator. Accelerated sulphur vulcanization is thought to proceed by the following steps:

1. The accelerator reacts with sulphur to give monomeric polysulphide of the type Ac-S_x-Ac, where Ac is an organic fragment derived from the accelerator. Certain initiating species may be necessary to start the reaction, which then appears to be autocatalytic.

2. The polysilphides can interact with rubber to give polymeric polysilphides of the type rubber-S_x-Ac. During this reaction, the formation of mercaptobenzothiazole (MBT) was observed when an accelerator derived from MBT had been used. When MBT itself is used, it first disappears, and then appears during the formation of rubber polysulphides.
3. The rubber polysulphides then react, either directly or through a reactive intermediate, to give crosslink or rubber polysulphides of the type rubber-S_x-rubber.

In general accelerated sulphur vulcanization can be divided into three systems depending on the relative amount of sulphur, activators and accelerator used. These systems are known as conventional vulcanization (CV), Semi-efficient vulcanization (Semi-EV) and efficient vulcanization (EV) (Table 2.4).

Table 2.4: Sulphur vulcanization system (Ismail & Hashim, 1998).

System	Amount sulphur (phr)	Amount accelerator (phr)	E value
CV	2.0-3.5	1.0-0.5	8-25
Semi-EV	1.0-2.0 (or sulphur donor)	2.5-1.0	4-8
EV	0.3-1.0 (or sulphur donor)	6.0-2.0	1.5-4

E value is defined as total amount of sulphur atom in one crosslinked that have been produced. The lower E value shows the more efficient of sulphur as a crosslink agent. Semi-EV or EV type cure systems have been found to be the most satisfactory for ENR. Examples of such systems ere recorded in Table 2.5.

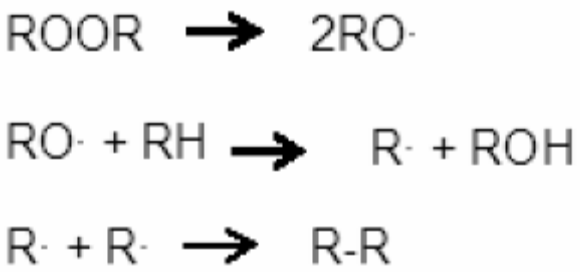
Table 2.5: Compounding formulation for ENR (Baker & Gelling, 1987)

	Semi-EV (phr)	EV (phr)	
ENR	100	100	100
Base	0.3-5		
Filler		As required	
Aromatic oil	5	5	5
Zinc oxide	5	5	5
Stearic acid	2	2	2
Antioxidant	2	2	2
Sulphur	1.5	0.3	0.8
MBS	1.5	2.4	3.0
TMTD	-	1.6	-
CTP	0.2	0.2	0.2

2.4.3 Peroxide vulcanization

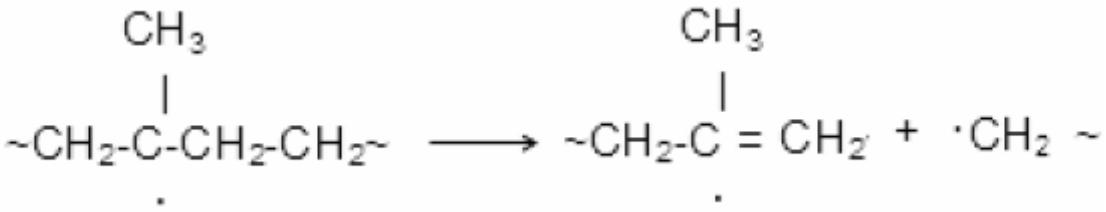
The use of organic peroxide as crosslinking agents for natural rubber was first investigated by Ostromislensky, who used benzoyl peroxide, in 1915. However, it is only since dicumyl peroxide (DCP) become available that this method of vulcanization has been employed commercially (Elliott, 1979). DCP is today the most used peroxide for crosslinking of polyolefin.

Peroxide (ROOR) form reactive radicals under the influence of heat. They decompose in accordance with a first-order reaction. In presence of the polymer the peroxide radicals abstract hydrogens from the hydrocarbon chain. By combination of alkyl radicals, carbon-carbon crosslinks are formed as in Scheme 2.1. Where ROOR is an organic peroxide, RH, represents polymer and R-R represents crosslinked polymer.

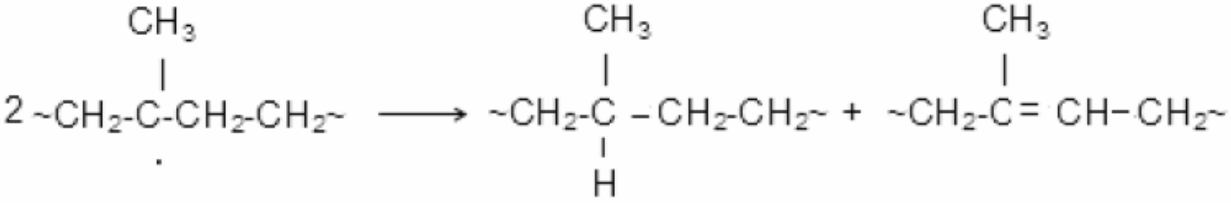


Scheme 2.1: The mechanism of peroxide vulcanization (Elliott, 1979; Sultan & Borealis, 1996).

The polymer radicals formed by hydrogen abstraction will, in addition to the combination reaction, also undergo a number of side reactions. The most important are, beta-scission (chain cleavage) (Scheme 2.2), disproportionation (Scheme 2.3), intermolecular recombination (ring formation) (Scheme 2.4), recombination with radicals originating from peroxide decomposition (Scheme 2.5) and reaction with antioxidants (Scheme 2.6). The chain cleavage reaction takes place particularly at the methyl branch points, but also at secondary radicals, specially at high temperatures (Sultan & Borealis, 1996).



Scheme 2.2



Scheme 2.3