PREPARATION AND PROPERTIES OF NEW THERMOPLASTIC ELASTOMER BASED ON ETHYLENE VINYL ACETATE (EVA)/ NATURAL RUBBER BLENDS

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LIST OF ABBREVIATIONS

TPEs	Thermoplastic elastomers
TPOs	Thermoplastic elastomeric olefins
TPUs	Thermoplastic elastomeric urethanes
TPVs	Thermoplastic Vulcanizates
EVA	Ethylene vinyl acetate
SMR L	Natural rubber
ENR-50	Epoxidized natural rubber (50 mol% epoxidation)
PEA	Polyethylene acrylate acid
PS	Polystyrene
i-PP	Isothetic polypropylene
PP	Polypropylene
PE	Polyethylene
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
PVC	Polyvinylchloride
PCL	Polycaprolactone
PA6	Nylon 6
SMA	Styrene-maleic anhydride
OPS	Oxazoline modified polystyrene
PPE	Polyphenylene ether
EEA	Polyethylene-co-acrylic acid
EVASH	Mercapto functionalized
MAH	Maleic anhydride
ZnO	Zinc oxide
TMTD	Tetramethythiuram disulfide
CBS	N-cyclohexy benzo thiazyl sulpheamide

CV	Conventional system
EV	Efficiency system
Semi-EV	Semi-efficiency system
DCP	Dicumyl peroxide
PS-*b*-PMMA	Polystyrene-blok-polymethylmathacrylate
PS-*b*-PDMS	Polystyrene-blok-polydimethysilocane
HPB-*b*-PS	Polybutadiene-blok-polystyrene
EPDM	Ethylene-propylene diene terpolymer
IR	Polyisoprene
IIR	Butyl rubber
SBR	Styrene butadiene
NBR	Acrylonitrile butadiene rubber
CR	Chloroprene rubber
EPR	Ethylene propylene rubber
SiR	Silicone rubber
FKM	Fluroelastomer
RTR	Reclaim tire rubber
SEB	Styrene ethylene butadiene
TGA	Thermogravimetric analysis
DTG	Derivative thermogravimetry
SEM	Scanning electron microscopy
FTIR	Fourier transform infra-red spectroscopy
MEK	Methylethyl ketone

LIST OF SYMBOLS

T_g	Glass transition temperature
MW	Molecular weight
S_8	Rhombic crystal sulfur rings
M_L	Loss of mass
T_{onset}	Onset temperature
T_{max}	Maximum degradation temperature
ΔT	Difference of temperature
IDT	Initial degradation temperature
t_{onset}	Onset temperature time
σ	Tensile strength
ε	Tensile strain
E_b	Elongation at break
M100	Stress at 100% elongation
M300	Stress at 300% elongation
rpm	Rotational per minutes
˚C	Degree Celsius
min	minutes
phr	Part per hundreds rubber
Wt %	Fraction by weight
MPa	Mega Pascal
W_1	Weight before immersion
W_2	Weight after immersion

PENYEDIAAN DAN SIFAT
ELASTOMER TERMOPLASTIK BARU BERDASARKAN ADUNAN ETILENA VINIL ASETATE (EVA)/ GETAH ASLI

ABSTRAK

Penyediaan dan pencirian elastomer termoplastik baru (TPEs) yang berdasarkan adunan etilena vinil asetat (EVA)/getah asli telah dikaji. Tork adunan, morfologi, sifat-sifat tensil, sifat pembengkakan dan sifat-sifat terma seperti kajian termogravimetrik serta penuaan haba dan pengoksidaan telah dinilai. Dalam kajian bahagian pertama, penyediaan dua siri adunan tanpa pemvulkanan iaitu adunan etilena vinil asetat/ getah asli (EVA/SMR L) dan adunan etilena vinil asetat/getah asli terepoksida (EVA/ENR-50) telah disediakan. Perbandingan kesan komposisi adunan TPE kedua-dua siri adunan juga dilakukan. Kajian bahagian kedua meliputi kesan agen pengserasi seperti polietilena akrilik asid (PEA) atau ENR-50 ke atas sifat adunan EVA/ SMR L (50:50 wt/wt) telah dikaji. Kesan pemvulkanan dinamik ke atas sifat adunan EVA/SMR L juga dikaji. Keputusan eksperimen menunjukkan nilai tork campuran TPE dengan ENR-50 adalah lebih rendah berbanding dengan adunan tanpa agen pengserasi. Kecekapan pemprosesan bagi adunan EVA/ENR-50 adalah lebih baik berbanding dengan adunan EVA/SMR L disebabkan oleh sifat yang kurang likat berbanding adunan EVA/SMR L seperti ditunjuk dalalm graf kestabilan tork. Untuk adunan yang telah diserasikan, adunan EVA/SMR L dengan PEA menunjukkan nilai

tork campuran yang lebih rendah berbanding dengan pengunaan ENR-50 dalam adunan EVA/SMR L. Kesan pelinciran daripada PEA menyebabkan pemprosesan yang lebih mudah berbanding dengan pemprosesan ENR-50 dalam adunan EVA/SMR L. Dalam kajian pemvulkanan dinamik, nilai tork kestabilan meningkat dengan peningkatan kandungan sulfur. Sambung silang yang lebih banyak dihasilkan semasa pencampuran lebur dengan pemvulkanan sulfur secara dinamik. Sifat-sifat tensil seperti kekuatan tensil, M100 (tegasan pada 100% pemajangan) dan E_b (pemanjangan pada takat putus) juga meningkat dengan peningkatan komposisi EVA dalam adunan. Dalam komposisi adunan yang sama, adunan EVA/ENR-50 menunjukkan sifat tensil yang lebih baik daripada adunan EVA/SMR L. Dalam kajian kesan pengserasian, kedua-dua agen pengserasi, PEA atau ENR-50 menunjukkan peningkatan yang besar dalam sifat-sifat tensil. Sifat tensil yang lebih baik dalam adunan dengan ENR-50 adalah disebabkan oleh pelekatan antara muka yang lebih baik antara EVA dengan SMR L berbanding PEA. Imbasan elektron mikroskop (SEM) ke atas permukaan rekahan tensil menunjukkan adunan EVA/ENR-50 memerlukan tenaga yang lebih tinggi untuk menjana kegagalan katastropik berbanding dengan adunan EVA/SMR L. Dengan penambahan agen pengserasi atau pun agen sambung silang, kestabilan termal dan rintangan haba adunan ditingkatkan berbanding dengan adunan tanpa pemvulkanan. Adunan EVA/ENR-50 yang tersambung silang menunjukkan sifat kestabilan terma dan rintangan haba yang lebih baik berbanding dengan adunan EVA/SMR L.

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ABSTRACT

Preparation and properties of new thermoplastic elastomer (TPE's) based on ethylene vinyl acetate (EVA)/ natural rubber blends were examined. Mixing torque, morphology, tensile properties, swelling as well as thermal properties such as thermogravimetric study and thermo-oxidative aging were evaluated. In the first part of investigation, two series of unvulcanized blend namely, ethylene vinyl acetate/ natural rubber blends (EVA/SMR L) and ethylene vinyl acetate/ epoxidized natural rubber blends (EVA/ENR-50) were prepared and a comparative study on the effect of blend ratio on the properties of TPE was carried out. In the second part of studies, the effect of compatibilizer, i.e. polyethylene acrylic acid (PEA) or ENR-50 on properties of EVA/SMR L blend (50:50 wt/wt) were investigated. The effect of dynamic vulcanization on the properties of EVA/SMR L blend was also investigated. The experimental results indicated that mixing torque values in TPE with ENR-50 blends are lower than with SMR L blends. The processing efficiency of EVA/ENR-50 blends is better due to less viscous nature of the blend compared to EVA/SMR L blend as indicated in stabilization torque graph. For the compatibilized blend, EVA/SMR L blend with PEA displayed lower mixing torque value than ENR-50 in EVA/SMR L blend. The lubricant effect from PEA resulted

in the ease of processing in comparisons to ENR-50 in EVA/SMR L blend. In the case of dynamic vulcanization, the stabilization torque values increased with increasing sulfur content. This could be due to more crosslink were generated during melt mixing. Tensile properties like tensile strength, M100 (stress at 100% elongation) and E_b (elongation at break) also increased with increasing EVA composition in the blend. At the similar blend ratio, EVA/ENR-50 blend exhibited better tensile properties than SMR L blends. For the effect of compatibilization study, both of the PEA or ENR-50 as compatibilizer exhibited substantial improvement in tensile properties. The tensile properties in blends with ENR-50 are better due to better interfacial adhesion generated between EVA and SMR L than PEA. Scanning electron microscopy (SEM) of tensile fractured surface indicated that EVA/ENR-50 blend need higher energy to cause catastrophic failure compared to EVA/SMR L blend. The incorporation of compatibilizer as well as crosslinking agent tend to increase the thermal stability and heat resistance of the blend compared to the unvulcanized blend. For unvulcanized blend, EVA/ENR-50 blends exhibit better thermal stability and heat resistance than EVA/SMR L blends.

CHAPTER 1

INTRODUCTION

1.1 Project introduction

Blending of polymer provide means of fabricating new materials, which is combining the useful properties of all blend constituents. Thus, elastomeric rubber-plastic blends have become technologically interesting for use as thermoplastic elastomers. Thermoplastic elastomer (TPE) can have many properties of the rubber, but they can be processed as thermoplastics. They do not need to be vulcanized during fabrication of finished part. Due to its unique fabricate ability and properties, they offer designers new flexibility in applications requiring soft-touch features, seals against fluid environment, impact protection and improved ergonomics. In addition, its general reputation of light weight, recyclability or reproducibility, chlorine free as well as environmentally acceptable materials has recently attracted special interest as alternative materials for used in several of fields, such as cap and closures in house wares, sport appliances; wire and cable in automotive, electrical and electronic industries; footwear, wheels and etc (Bhowmick and Howard, 2001).

This technology and its useful properties have led to a significant number of thermoplastic elastomeric products commercialized during mid to late of 1980s (Abdou-Sabet and Patel, 1991). Some thermoplastic elastomers (TPEs), such as PP/ EPDM blends has been commercialized with trade name such as Santoprene and Geolast which posses high oil resistant of TPE and performs with the versatility of rubber properties (Huang et al., 2002). For some of the immiscible blends, with technological compatibilizations, the addition of small amount of compatibilizing agent in the blend during melts mixing could improve mechanical properties. It acts as a macromolecular surfactant and permits the formation of very small droplet of elastomer that will become small particles of vulcanized rubber when cured with dynamic vulcanization. There are limited publications concerning compatibilizing immiscible blends of TPE. Natural rubber/ HDPE are typically immiscible blends and to achieve NR/ HDPE blend with practical value, several of compatibilizers were used. The use of modified phenolic resin as a compatibilizer was improved mechanical properties of NR/ HDPE blends due to reaction that took place at unsaturated site of HDPE and methylol groups in phenolic molecules (Nakason et al, 2006). Supri and Ismail (2006) also reported, that the with use of glycidyl methacrylate (GMA) on recycle polyvinyl chloride / acrylonitrile butadiene rubber blends (GMA+ rPVC/ NBR) has improved the mechanical properties and thermal stability as well as low swelling index. On the other hand, EPDM/ nylon blends with maleic anhydride grafted EPR (MAH-g-EPR) also show better mechanical performance than other compatibilizing agent containing acid group due to better interfacial adhesion achieved (Huang et al., 2002). This again shows the beneficial effect of compatibilizer to the immiscible TPE blend.

Ethylene vinyl acetate copolymer (EVA) is obtained through chemical modification of polyethylene (PE) with vinyl acetate as comonomer which reduces the crystallinity of PE. Thus it has many characteristic of thermoplastic elastomers, which depends on percentage of vinyl acetate content. EVA provides good mechanical properties, excellent ozone resistance, good weather resistance and relatively lower material cost (Henderson, 1993 and Chantara et al., 2003). Epoxidized natural rubber (ENR) is a modified natural rubber having properties resembling those of synthetic rubber rather than natural rubber (Ismail, 2004). ENR has unique properties such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength (Bhowmick and Howard, 2001, Ismail, 2004).

There are several literatures regarding EVA blends with different types of rubbers such as nitrile rubber (NBR) (Varghese et al, 1995), natural rubber (SMR 10) (Jansen and Soares, 1996), styrene butadiene rubber (SBR) (Soares et al, 2001) and etc that having potential use in various applications such as films, footwear, tubes and hoses (Bhowmick, and Howard, 2001).

However, compatibilization as well as strong interfacial adhesion between plastic and rubber phase still remain as a major challenge in producing high performance TPE. The compatible and miscibility in a blend is not easy to achieve due to the different characteristic of each component that constitute a separate phase with low attraction force across the phase boundaries. However, some miscible blend has been reported and variously interpreted as results of specific interaction, such as hydrogen bonding, dipole-dipole interaction, ion–dipole interaction or repulsive interaction (Coleman et al, 1991). Some of the blends are also produced from chemical reaction, such as transesterification reaction and the formation of covalent bonds within the constituents of the blends (Coleman et al, 1991). Thus to improve the tensile properties of such blends, it is important to develop a proper control of phase morphology and better interfacial adhesion between the blend constituent via chemical or process approach by using compatibilizing agents or special vulcanizing technique, namely dynamic vulcanization.

In this study, preparation and properties of new thermoplastic elastomer based on ethylene vinyl acetate and natural rubber blends are investigated. EVA/ natural rubber blends are attractive because of the excellent properties of both constituent. Addition of NR to EVA increases the melt elasticity of the system (Koshy et al., 1993) and the presence of EVA as major component in the system would increase the thermal aging resistance of EVA/ NR blends (Koshy et al., 1992).

1.2 Research Objectives

The present work aims to develop a new thermoplastic elastomer based on ethylene vinyl acetate/ natural rubber blends. In this research work, new TPE's were prepared by using an internal mixer (Haake Rheomix). The main objectives of this work are:

1. To examine the effect of blend ratio, of ethylene vinyl acetate (EVA) and natural rubber (SMR L and ENR-50) on the process development, ultimate physical properties (morphological studies, swelling properties), tensile

properties (tensile strength, stiffness and toughness) as well as thermal stability (thermal oxidative aging) of the newly developed TPE.

2. To compare and to determine the optimum formulation for the blends of EVA/ SMR L and EVA/ ENR-50 blends in order to achieve a good balance of mechanical properties as well as thermal properties.

3. To determine the suitable compatibilizer for EVA / SMR L blends, which can improve the interfacial adhesion as well as enhanced the tensile properties?

4. To study the effect of the sulfur concentration on the properties of new developed TPE by dynamic vulcanization technique.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Polymer Blends

The definition of polymer blends has been described in various ways from a brief explanation to a specific one. Utracki & Favis (1989) defined polymer blend as mixture of two or more polymer or copolymer materials. Utracki (2002) stated that polymer blend as a mixture of two or more macromolecular species. Deanin (1977), in the 70's defined polymer blends as mixture of two or more polymers intimately in single continuous solid phase. The latest, Kumar and Gupta (1998) noted that polymer blends are physical mixture of two or more polymers that are commercially prepared by mechanical mixing which can be achieved through rotor-cam compounder and screw extruder.

In general, polymer blend could be derived into few types of polymer materials mixture through various type of mechanical compounding or solution mixing, for example:

- Plastic – Plastic mixture
- Rubber – Rubber mixture
- Plastic – Rubber mixture

In the development of new multiphase polymeric materials, the goal of combining the favourable properties from each of individual material is not an easy task due to low combinatorial of entropy of mixing, immiscible of blend and, etc. will give rise to two-phase system, which is mostly characterised by a coarse and unstable phase morphology and poor interfacial adhesion between the phases. The poor interfacial adhesions could also be affected by differences in material characteristic such as polar-polar and non-polar attraction, vast difference in molecular weight, amorphous or crystalline of material phase as well as the suitable blend ratio of blend composition will resulted in different compounded properties. There is number of polymer pairs that were found completely miscible to give homogeneous single phase, with properties proportional to the ratio of the two polymer in the blend,(Gabriel and George, 1999) and several of these blends were exhibited commercially importance. For example, PVC/ ENR-50 blends (Senake Perera et al., 2001), blends of polyphenylene ether with polystyrene (Liu and Baker, 1992); (Paul et al., 1988) were reported.

When two polymers are miscible down to segmental level, single homogeneous phase are formed, it will exhibit a single glass transition temperature, Tg from the compound and shows thermodynamically miscible. This will give compounder quick economical control over balance of properties for different applications. On the other hand, in practical, plastic technologists were also developed large number of polymer blends that are immiscible but very useful, combining some of the best practical properties of each polymer in the blend; they tended to use the term compatible blend. However, there are also a lot of blends which are totally immiscible and incompatible when blended together, due to differences in material characteristic (polarity, molecular weight, crystalline and etc). These incompatible blends will eventually exhibit poor properties in physically and mechanically. These problems can be solved by means of compatibilization, which consists in the modification of the interfacial properties of the blend phases by using a suitable block or graft copolymer which located at the interfacial between the phases of an immiscible blend and act as an emulsifying agent (Dedecker and Groeninckx, 1998).

For further improvement on the mechanical and thermal properties of the compatible or miscible blends by preferential crosslinking the EPDM rubber components during blending process was firstly suggested by Glasser and Cielniecki, 1988 and termed as dynamic vulcanization.

2.2 Thermoplastic Elastomer (TPE)

Thermoplastic elastomer (TPE) is a new polymer which combine the service properties of elastomer (vulcanized rubber) and also able to be process as thermoplastic. This combination of properties can be obtained through the simultaneous presence of soft elastic segments (that have high a high extensibility and low glass transition temperature, Tg) and hard segments (which have a lower extensibility, a high Tg) and there are susceptible association to crosslinking. One of the outstanding advantages of TPE is they allow rubber like article to be produce by rapid processing technique as thermoplastic industries. TPE posses many of the physical properties of rubber such as softness, flexibility and resilience (Holden et al., 1969; Campbell et al., 1978), additionally they achieve their properties by a physical process (solidification), where differ from chemical process that is showed by vulcanized rubber. Vulcanization is a thermosetting process, where is slow, irreversible and usually require heating. On the other hand, physical process of TPE is solidification via transition from a processable melt to a solid rubber-like object. Thus TPE can be processed using conventional thermoplastics processing technique such as injection moulding and extrusion. These TPE is similar to other thermoplastic materials, the scrap from the processing able to be softened and reprocess again by heating. However with this characteristic, TPE will become soft and flow when heated thus it is usually inferior to those of conventional vulcanized rubber when apply in the environment where subjected to high temperature.

TPE’s are normally not use in application such as automobile tires. Instead, most of their applications are in area which requires softness, and flexibility and also less stringent properties in high temperature, such as footwear, automotive moulded part, head lamp casing, handle of heavy duty hand tools, wire insulation and adhesives (Holden, 2000). The first commercial production of TPE began by Shell Co. in 1965 and thereafter other TPE have entered the market, these included styrene-diene block copolymer by Shell and Phillips; polyester by Du Pont and other polyurethanes (TPU’s) and polyolefin’s. Thermoplastic elastomeric olefin (TPO’s) is one of simple blend of elastomer (NR, EPDM or NBR) with a thermoplastic (PP, PE or PVC). Majority of TPO are produced in uncured manner; thermoplastic remain its own form and elastomer having little or no crosslinking, thus exhibited as two phase. Morphological investigation has showed dispersion of domain in a major continuous matrix or co-continuous of phase displayed. The interaction between component phases however could be built by either addition of agent which interact with both phase or by specific reaction between two phases. Among the different types of polymer blends, in the recent few decades, thermoplastic elastomer (TPE’s) has gained the commercial importance due to the possibility of attaining wide range of properties via blending. One obvious advantage in its production is little or no capital expenditure relative to synthesizing new polymers required, but still able to produce range of materials with properties that differ from each of single blend constituents. Among of them, blending unsaturated elastomer with ethylene vinyl acetate (EVA) copolymer seem to be a potential approach to develop rubbery material with good ozone and weathering resistance as well as good physical and mechanical properties. For example, several reported EVA-based systems that contain nitrile rubber (NBR) as unsaturated component that offer several important advantages such as excellent oil resistance, abrasion resistance and better aging resistance (Vargheses et al., 1995; Bandyopadhyay et al., 1997; Jasen and Soares, 2001 and Jasen and Soares, 2002). Although it is possible to combine the properties of two or more via blending, many of these blends are initially immiscible and incompatible thus exhibit poor mechanical properties due to lack of physical and chemical interaction across the phase boundaries and poor interfacial adhesion. This problem can be minimized by proper control of phase morphology during processing by addition of a compatibilizing agent (Jasen et al., 2003) or compatibilized by reactive processing (Xanthos and Dagli, 1991).

2.3 Compatibilization in Polymer Blends

When two or more polymers are mixing together, polyblends or polymer alloys are formed. Blending of two polymers by physical mixing is generally immiscible and incompatible, as a result low combinatorial of mixing entropy among mixing components has formed and heat of mixing polymer make the Gibbs free energy of mixing became negative (Bahadur and Sastry, 2005). Thus results a poor compatibility in blends. From phase rule and morphological point of view, immiscibility of two polymers in the blend, explains quantitatively in the extent of separate each of phase from another. This is actually not happening in pure of polymer A or polymer B, but rather in solution of A in B or solution of B in A. In general, the major phase will form continuous matrix that control most of properties and minor phase will form dispersed micro domain in the matrix and contribute certain of specific properties to the blend. Most of the dispersed domains are appear as spherical shape, where surface energy is low. When increase the attraction between phases, the size of dispersed domain tend to be decreased, and this increase practical compatibility (Liu and Truss, 1996). There are also some partial miscible between the polymers blend which correspond to different degree of miscibility and interfacial attraction. Thus, optimization on the level of phase separation, morphology and interfacial attraction are still required human intervention in optimize its balance of properties (Liu and Baker, 1992).

In practical compatibility of polymer, Polymer engineer and chemist normally control properties using physical process via physical compatibilization, technological compatibilization and chemical compatibilization.

2.3.1 Physical Compatibilization

Blending of two polymers by mechanical mixing may either form a compatible blend, which exists as a single phase or incompatible blend which exists as two phase system. Polymer chain entanglement, high viscosity of material in low processing temperature and shear rate has resulted compound difficult to flow. These are the major factors that control the compatibility in physical blend (Barlow et al., 1989; Markham, 1991). Increase processing temperature may increase or decrease thermodynamic miscibility. Increase shearing rate will decrease domain size within the limits that permitted by melt viscosity. However, extreme of shearing force especially at low temperature and high viscosity may break polymer molecules into macroradicals (A⋯A or B⋯B). Cross-combination of these radicals can then produce A – B block or grafted polymer and prepared for the later technological compatibilization. Physical compatibilization in polymer blends is mainly contributed by physical polymer chain entanglement when blended in the molten form and crystallizes during cooling (Xanthos and Dagli, 1991).

2.3.2 Technological compatibilization

Technological compatibilization of polymer blends can be produced or enhanced by simple physical addition of monomeric or polymeric material without depending any chemical reaction or chemical treatment to produce the desired properties. Addition of monomeric materials includes solvent, plasticizer, surfactant, and fillers which have been reported able to increase compatibility. Markham (1991) reported that addition of low molecular weight of polycaprolactone (PCL) as plasticizer in blend of polycarbonate (PC) and nylon 6 (PA 6) has improved the compatibility by lowering melt viscosity of PC and making it closer to the low viscosity PA 6, thus facilitating uniform melt mixing.

Another method of contributing technological compatibilization is by addition of polymeric ingredient based on the use of suitable block or grafted copolymer which are located at the interface between the phases of an immiscible blend and acted as emulsifying agent. However, this method cannot be applied for all kind of polymer blends; it is based on the in-situ formation of block or graft copolymer at the intephase due to chemically reactions during melt mixing and this method is also called reactive compatibilization (Diaz et al., 2007).

2.3.2.1 Reactive Compatibilization

Reactive compatibilization of immiscible or incompatible blend can also be performed by proper selection of blending ingredients, where third component addition is obviously miscible with one of the blend components and reactive with the other blend component. In order to fulfils these condition, the reactive copolymer normally consists of functionalized polymers of type A – C (where C is a long reactive segment or a functional group attached to the main chain); they may compatibilized a polymer pair A and B provided that C is capable of chemically reacting with B. As a result, emulsifier is produced in-situ and located at interphase, and interacts with phases via chain entanglement. High physicochemical affinity at both phases can strongly modify the morphology, interfacial adhesion, and final mechanical properties of the blends (Diaz et al., 2007). Several of researchers have reported the successful of compatibilization through reactive copolymer such as employment of styrene-maleic anhydride (SMA) as reactive compatibilizer in blend of PA-6 and acrylate rubber (woodbrey and Moncur, 1982). In the recent report of compatibilizer used, mercapto-modified copolymer in NBR/ EVA blends (Jansen and Soares, 2001), anhydride-modified copolymer in NBR/ EPDM blends (Oliveira and Soares, 2003); maleic anhydride (MAH) as compatibilizer in waste PVCw/ NBR blends (Ismail et al., 2004); mercapto-functionalized (EVASH) in polystyrene (PS)/ ethylene vinyl acetate (EVA) blends (Soares and Cario, 2005) seem to be successful compatibilizer to be used. The latest progress of polymer compatibilization on polyolefin/ polyamide mixture in one step reactive blending (Coltelli,et al., 2006) and reactive compatibilization of PE/PS via Friedel-craft reaction (Diaz et al., 2007) are showing positive approach to develop compatibilizer..

2.3.3 Chemical Compatibilization

Polymer blends are usually prepared by melt mixing process. One step mechanical process that does not involve chemical reaction are limited because not many of available basic polymer are able to perform such compatible blend in practical blending environment, thus modification of polymer during original polymerization reaction or modification after polymerization (post polymerization reaction) could be conducted in order to prepare such materials for compatibilization via block copolymerization, random copolymerization attachment of terminal functional group and control of molecular weight (Deanin and Manion, 1999).

2.3.3.1 Block Copolymerization

Block polymerization is always believed to be the most effective in producing compatibility, and experimental results are frequently proving this prediction (Paul and Newman, 1978). In fabrication of high performance thermoplastic elastomer, block polymerization always is the one to be in favour. Many of these compatibilizers were specifically prepared for use in producing polyblends, for examples, styrene-*b*-butadiene-*b*-styrene, styrene-*b*-ethylene-butylene-*b*-styrene, and chlorinated polyethylene. Careful synthesis control is able to produce maximum structure control and the most efficient compatibilization as predicted. These copolymers able to modify physical properties in the compound such as reduce crystallinity, modify glass transition temperature and improve solubility. However, polymer modification or new polymer synthesis is always difficult to control and cost of synthesis process is always high. Thus, it is not suitable to use in mass production rather than research activities. Fig. 2.1(4) shows the typical type of block copolymer.

2.3.3.2 Random Copolymerization

Random copolymer is a polymer formed when two or more different types of monomers are linked in the same polymer chain. Fig. 2.1 (3) shows possible of structural orientation of random copolymers. Major commercial examples are polyethylene ionomers, ethylene vinyl acetate copolymer, butadiene-acrylolnitrile rubber, and stryrene-acrylonitrile and styrene-maleic anhydride copolymers.

Fig. 2.1: Types and structural orientation of polymer.

2.3.3.3 Terminal Groups

In vinyl polymerizations it is possible to be use as heterofunction initiator or chain-transfer agents that attach a desired functional group to the ends of the polymer molecule. For example, PP was maleated by grafting maleic anhydride group and amine groups reacted to form amide groups, produce a graft copolymer. This was then used as a physical compatibilizer for polyblends of PP/ NBR, to produce oil resistant thermoplastic elastomer (Gaylord, 1989).

2.4 Vulcanization

Vulcanization or crosslinking is a chemical process in which the conversion of rubber molecules into three dimensional elastic network by formation of crosslink. Natural rubber compounds can be vulcanized in all common processes such as, hot air with or without pressure, steam, hot press, transfer moulding, injection moulding, molten salt bath, hot air tunnel, high frequency radiation and etc (Hofmann, 1989). Vulcanization or crosslinking of rubber could be performed by sulfur system and non-sulfur system (peroxide or other special vulcanizing agent or high energy irradiation system). Sulfur vulcanization system was first founded by Charles Goodyear in

Springfield, Massachusetts in 1841, where sulfur reacts with natural rubber to produce materials which do not brittle when hot or sticky. Properties of vulcanized rubber are found great interest from technological point of view, where the combination of high tensile strength with a high rebound elasticity, good low temperature flexibility, excellent dynamic properties as well as low heat build-up. They are found useful and have beaten the properties of synthetic IR in several applications.

2.4.1 Improvement of properties by vulcanization

In practical vulcanizates, average molecular weight (MW) is about 4,000 to 10,000. Vulcanization of rubber is irreversible process, similar to thermoset materials in plastics industry. By introducing crosslinking to rubber, physical properties of rubber change from thermoplastic to elastic state. As more crosslinking are formed, strength and elasticity of vulcanized rubber increased. Fig. 2.2 shows the effect of vulcanization on some properties of vulcanized.

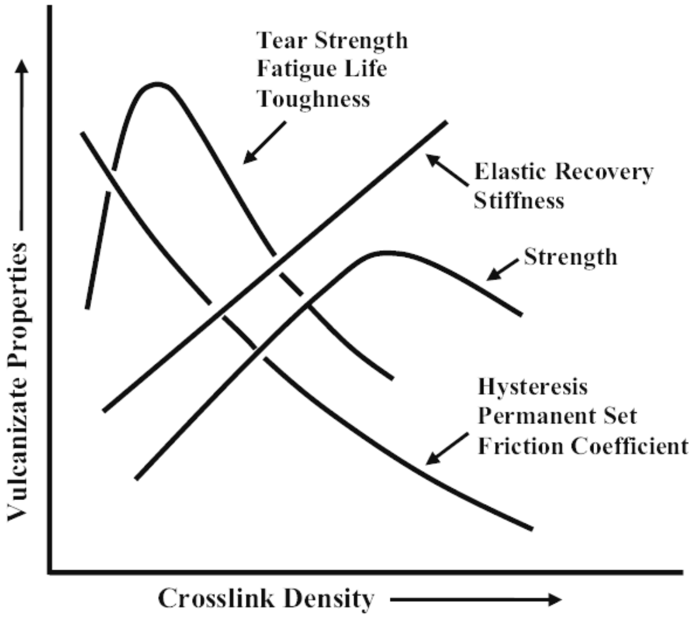


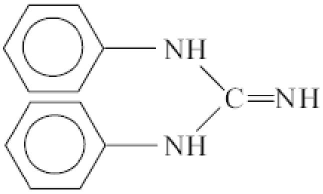
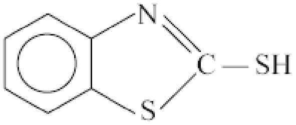
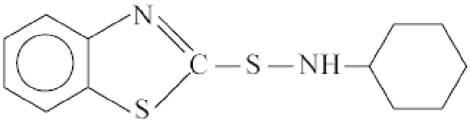
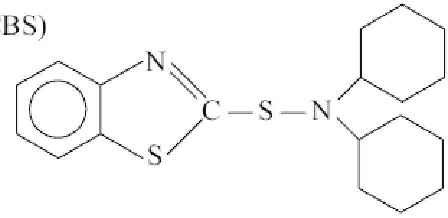
Fig. 2.2 : Vulcanizate properties in the function of the crosslinking density.

The physical and mechanical properties such as tensile strength, modulus, hardness, tear strength and fatigue life as well as toughness are changed after vulcanization, and these changes are majority influenced by crosslink density from vulcanization. In unvulcanized elastomer, when stressed, chain may readily slide pass one another and disentangle, thus fracture occur at low stress without breaking chemical bonds. Whereas in vulcanized elastomer, the produced crosslinking have increased molecular weight by create branched molecules, a broader molecular weight distribution. As a result, more chain entanglement has created and increases tensile strength. As crosslinking continue to increase, a three dimensional network are formed and gel point are reached. The fracture of these gels could not occur without breaking any chemical bonds, thus strength at gel point are considerably higher. The gel in the compound also could not be dissolved by solvent. However, these properties do not show further increase with continuous increase of crosslinking. When a vulcanized elastomer is deform by external stress, part of the external energy exerted is stored elastically in the chain, and the balance of the energy is dissipated through molecular motions thus less chemical chain is break. On the other hand, at high level of crosslink, molecular chain motion has been restricted; this will tighten molecular network and making it unable to dissipate the external energy that was exerted. Hence, chemical chain is relative easy to break. As a result, an optimum of crosslink level must be well control in such a way that must be high enough to prevent failure viscous flow (scorch), but must low enough to prevent brittle failure.

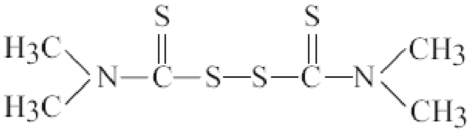
2.4.1.1 Sulfur Vulcanization additives: (Activator and accelerator)

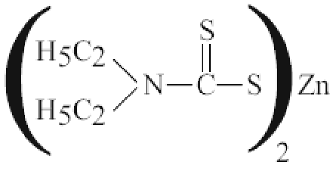
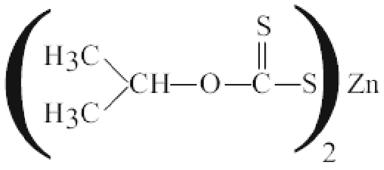
Conventional sulfur crosslinking is quite inefficient and requires long curing time. In this unaccelerate sulfur crosslink rubber, only 40 to 55 of sulfur atom are combined to the rubber. This structure contains polysulfide linkages, dangling sulfur fragments and acrylic sulfides. Many of sulfurs are not involved in crosslinking thus such networks are unstable and have poor aging resistance. For that reasons, commercial sulfur vulcanization with use special additive to accelerate curing, and it is termed as activator and accelerator. Activator used is normally a metal oxide (ZnO) and a fatty acid (stearic acid), that create soluble zinc ion when reacted with accelerator to form rubber soluble complex, and enable them to react with sulfur in producing crosslinking. Accelerator, tetramethythiuram disulfide (TMTD) is well known as effective accelerator, they also can be used as sulfur donor who can provide primarily mono- and disulfide crosslinks. Typical accelerators used in diene rubber (Fath, 1993) are shown in Table 2.1.

Table 2.1: Typical of accelerator used with sulfur for vulcanization of diene rubber

Type and example	**Chemical formula**	**Comments**
Guanidine		
- Diphenyl guanidine (DPG)		Medium-speed accelerator- now largely used in conjunction with other accelerators. Strong synergism with MBT
Thiazole		
- Mercaptobenzothiazole (MBT)		MBT and its derivatives form the dominant group of accelerators used with dienes. MBT is powerful but tends to be scorchy.
Sulphenamide		
- N-cyclohexyl benzo thiazyl sulphenamide (CBS)		Delayed actions semi-ultra accelerator. Widely used.
- N, N-dicyclohexyl benzo thiazyl sulphenamide (DCBS)		

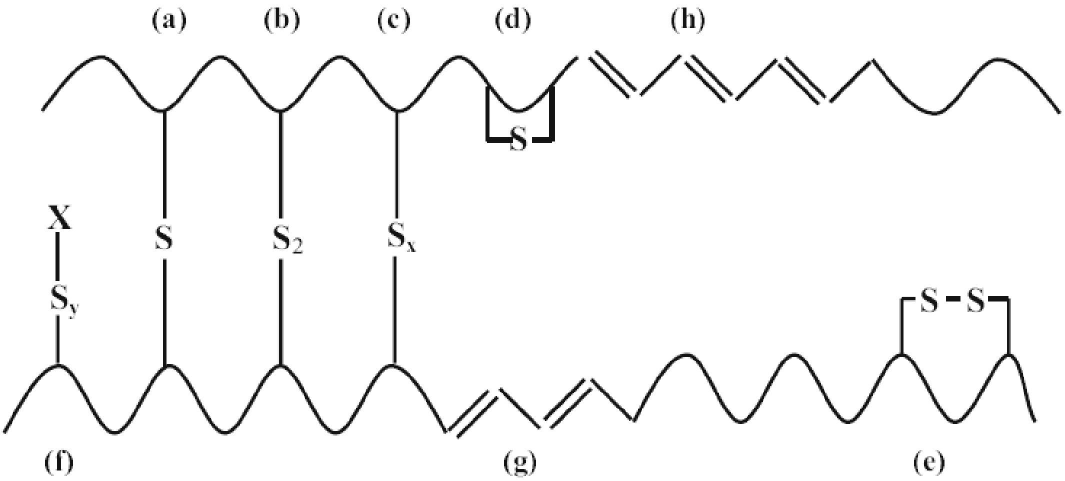
Thiuram

- Tetramethyl thiuram disulfide (TMTD)		Ultra-accelerator. Also vulcanizing agent.

Dithiocarbamate		
- Zinc diethyl dithiocarbamate (ZDC or ZDEC)		Ultra-accelerator. This and other dithiocarbamates usually too fast for dry rubber technology. Used in latex work.
Xanthate		
	Zinc isopropyl xanthate (ZIX)	Ultra-accelerator

2.4.1.2 Sulfur Crosslink structures in vulcanization

Sulfur vulcanization on natural rubber requires temperature that is high enough to initiate the vulcanization process. Normally is achieved by heating at 100˚C to 180˚C. Sulfur vulcanization generates crosslinked intramoleculer chains and modify to rubber backbone (Porter, 1968). There are mono-, di- and polysulfide crosslinks (a, b, and c respectively) as shown in Fig. 2.5. There are also other sulfidic crosslink structures that might happen such as cyclic monosulfide, cyclic disulfide, and pendant sulfide group terminated by accelerator moieties and conjugated diene and tri-ene units.



(a) Mono-sulfidic crosslink
(b) Di-sulfidic crosslink
(c) Poly-sulfidic crosslink
(d) cyclic mono-sulfidic crosslink
(e) cyclic di-sulfidic crosslink
(f) Pendent sulfide groups terminated by accelerate moieties.
(g) conjugated diene unit
(h) Conjugated tri-ene unit

Fig. 2.5: Structural features of an accelerated sulfur vulcanizate of natural rubber.

2.4.1.3 Crosslinking efficiency by sulfur vulcanization

Crosslinking efficiency in sulfur vulcanization is referring to number of crosslink formed per sulfur atom that reacts. In practice, the optimum degree of crosslinking depends on level of sulfur over activity of the accelerator, its molecular weight, presence of organic or inorganic activator and types of accelerator used. There is generally 3 types of system used in NR, which are conventional system (CV) that contain more sulfur level than accelerator, efficient system (EV) that contain higher accelerator level than sulfur and semi-efficient (semi-EV) that laid between CV and EV (Chung et al., 2002).

In conventional system (CV), ratio of the weight of sulfur to accelerator is about 1.0 – 1.5, where 1.5 – 2.5 phr of sulfur with 1.0 – 0.5 phr accelerator. Crosslink that formed will contain higher sulfur atoms, most of the crosslink formed are in polysulfide and disulfide and minority in monosulfide. On the other hand, efficient system (EV) requires sulfur level about 0.5 – 1.2 phr and 1.5 – 2.5 phr accelerator level to achieve the similar crosslink density but in low sulfur content. In semi-EV system, weight ratio of sulfur to accelerator about 0.4 – 1.5, the network formed is intermediate in structure and thermal stability and reversion resistant vulcanizate is expected to be between CV and EV systems (Chung et al., 2002).

2.4.2 Non-sulfur Vulcanization

Sulfur vulcanization is suitable to be used in unsaturated rubber which consist covalent bond in the chemical structure. Saturated rubber such as silicon rubber shows inefficient when cure in sulfur system. Peroxides are another type of curing agent, where no covalent bond from carbon are require for crosslink, thus this cure system are suitable to use for saturated elastomer (Elliott and Tidd, 1973). The presence of peroxide in the blend produce reactive radicals upon decomposition at elevated temperature via exothermic reaction that is beneficial in rubber compound. Dicumyl peroxide (DCP) produce rapid cure under typical vulcanization temperature, which is used to vulcanize saturated polymer such as polypropylene (Ho et al., 1990). DCP also reported to be useful curing agent in dynamic vulcanization accompanied with PP/EPDM blends by (Ha et al., 1986 and sariapanahi et al., 2002).

Another type of non-sulfur vulcanization used is Crosslinking by irradiation. At present, the most two common type of irradiation used in industrial are gamma and e-beam, where gamma is mainly facilities from cobalt-60. The advantages of using gamma rays include, deep interpenetrating of ray sources, simple technology and low down time (Halls, 1991). However, still the E-beam machine plays a significant role in the processing of polymeric materials, and different of energy level and machine design are available (Berejka, 1993 and Boaler, 1991). This method also applicable to some polymers that lacking of reactive functional group that induce crosslinking process. Radiation crosslinking of polymer foams has been reported to be having commercial value for automotive cushions, heat insulation, buoyancy product for marine use, and sport goods (Cardoso, et al., 1998; Tokuda and Kemmotsu, 1995 and Ghazali et al., 1999).

2.5 Dynamic Vulcanization

Dynamic vulcanization has been extensively applied to the vulcanization of soft rubber phase that is blended with rigid thermoplastic. This curing process is carried out under high shearing force and above the melting point of thermoplastic. The temperature used must be sufficiently high to initiate crosslinking and vulcanization is completed during blending process. During dynamic vulcanization, polymeric chains from rubber phase and thermoplastic phase will become interconnect and converting