CURING CHARACTERISTICS, MECHANICAL PROPERTIES AND MORPHOLOGY OF SURFACE MODIFIED MONTMORILLONITE FILLED NATURAL RUBBER NANOCOMPOSITES

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LIST OF ABBREVIATIONS

NR	Natural Rubber
ENR	Epoxidized Natural Rubber
ENR 50	50 % Epoxidized Natural Rubber
SMR L	Standard Malaysian Rubber L
IR	Synthetic Polyisoprene
BR	Polybutadiene Rubber
CRI	Cure Rate Index
PRI	Plasticity Retention Index
ASTM	American Society of Testing and Materials
RRIM	Rubber Research Institute of Malaysia
CBS	*N*-cyclohexyl-benzothiazole-2-sulphenamide
IPPD	*N*-isopropyl-*N*'-phenyl-*p*-phenylenediamine
ZnO	Zinc Oxide
Phr	Parts per hundred parts of rubber
CR	Chloroprene Rubber
EPDM	Ethylene Propylene Diene Rubber
NBR	Nitrile Rubber
OC	Organoclay
ODA	Octadecylamine Ammonium Chloride
DDA	Dodecyl Ammonium Chloride
CEC	Cation Exchange Capacity
CB	Carbon black
MMT	Montmorillonite

SBR	Styrene Butadiene Rubber
ABS	Acrylonitrile butadiene styrene
PP	Polypropylene
POM	Polyoxymethylene
TGA	Thermogravimetric analysis
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

LIST OF SYMBOLS

Na^+	Natrium ion
K^+	Kalium ion
Mg^{2+}	Magnesium ion
Fe^{2+}	Ferrous ion
Li^+	Lithium ion
T_g	Glass Transition Temperature
M_H	Maximum Torque
t_2	Scorch time
t_{90}	Cure time
λ	X-ray Wavelength
θ	Angle of Diffraction
d	Interlayer Spacing
M100	Modulus at 100 % Elongation
M300	Modulus at 300 % Elongation
E_b	Elongation at break
Q_f/Q_g	Filler-rubber Interaction

CIRI-CIRI PEMATANGAN, SIFAT-SIFAT MEKANIK DAN MORFOLOGI KOMPOSIT NANO GETAH ASLI TERISI MONTMORILLONITE TERUBAHSUAI PERMUKAAN

ABSTRAK

Komposit nano getah asli telah disediakan dengan menggunakan ‘Standard Malaysian Rubber’ (SMR L), montmorillonite yang bersifat organofilik (tanah liat organo) dan pengisi hybrid hitam karbon/tanah liat organo. Komposit nano SMR L telah disediakan melalui teknik pencampuran dengan menggunakan penggiling bergulung dua. Seterusnya komposit nano tersebut telah disambung-silang dengan menggunakan sistem pemvulkanan sulfur separa cekap. Komposit nano getah asli terepoksida (ENR 50) (50 % mol pengepoksidaan)/tanah liat organo telah disediakan untuk tujuan perbandingan. Kesan pembebanan tanah liat organo sehingga 10 bsg (bahagian per seratus getah) terhadap kelakuan sambung-silang, sifat-sifat mekanikal, kekerasan, pembengkakan dan kestabilan termal komposit nano SMR L dan ENR 50 telah dikaji. Masa skorj dan masa pematangan menurun manakala nilai tork maksimum dan indeks pematangan meningkat apabila pembebanan tanah liat organo meningkat dalam komposit nano SMR L. Komposit nano ENR 50 pula mempamerkan masa skorj dan masa pematangan yang lebih pendek, indeks pematangan yang lebih rendah tetapi nilai tork maksimum yang lebih tinggi. Kekuatan tensil bagi kedua-dua jenis komposit nano meningkat hingga pembebanan tanah liat organo yang tertentu (4 bsg untuk komposit nano SMR L dan 6 bsg untuk komposit nano ENR 50). Apabila pembebanan tanah liat nano ditingkatkan lagi, kekuatan tensil menurun. Pemanjangan takat putus semakin menurun dengan pembebanan tanah liat organo bagi ENR 50 manakala mencapai nilai optimum pada pembebanan 4 bsg bagi sistem SMR L. Seperti yang dijangkakan kekerasan dan modulus tensil meningkat dengan peningkatan pembebanan tanah liat organo. Ujian pembengkakan menunjukkan bahawa interaksi getah-pengisi adalah lebih baik dalam komposit nano ENR 50 yang seterusnya membawa kepada peningkatan yang lebih baik dalam sifat-sifat mekanikal komposit nano ENR 50 berbanding komposit nano SMR L. Kestabilan termal komposit nano SMR L adalah lebih baik berbanding kestabilan termal komposit nano ENR 50. Ujian penyerakan sinar 'X-ray' (XRD) dan mikroskopi transmisi electron (TEM) membuktikan kewujudan struktur tanah liat nano yang terinterkalasi dan tereksfoliasi. Kedua-dua struktur nano ini bertanggungjawab ke atas peningkatan sifat-sifat komposit nano. Mikrograf daripada mikroskopi pengimbasan electron (SEM) menunjukkan tanah liat nano telah menukarkan mekanisme kegagalan komposit nano di dalam kedua-dua matrik. Dalam pada itu, peningkatan kekuatan tensil, pemanjangan takat putus dan kestabilan termal berlaku apabila 2 bsg tanah liat nano dan 8 bsg hitam karbon digunakan. Ini adalah kerana kesan sinergistik kedua-dua pengisi.

CURING CHARACTERISTICS, MECHANICAL PROPERTIES AND MORPHOLOGY OF SURFACE MODIFIED MONTMORILLONITE FILLED NATURAL RUBBER NANOCOMPOSITES

ABSTRACT

Natural rubber (NR) nanocomposites was investigated by using Standard Malaysian Rubber (SMR L) grade, organophilic modified montmorillonite (organoclay) and carbon black/organoclay as hybrid filler. The NR nanocomposites were prepared by melt mixing on a two roll mill and cured using a sulfur semi efficient vulcanization system. For comparison purpose, epoxidized natural rubber (50 mol % epoxidation), ENR 50/organoclay nanocomposites were produced as well. The effects of organoclay with different filler loading up to 10 phr on curing characteristics, mechanical properties, hardness, swelling behavior and thermal stability of SMR L and ENR 50 nanocomposites were studied. In term of curing characteristics, both scorch time and cure time reduced, whereas the maximum torque and cure rate index increased with the incorporation of organoclay. ENR 50 nanocomposites showed shorter scorch time, cure time and lower cure rate index but higher maximum torque values. The tensile strength of both NR nanocomposites increased up to certain filler loading (4 phr for SMR L and 6 phr for ENR 50) and then decreased. Elongation at break continuously decreased for ENR 50 compounds and achieved an optimum at 4 phr for SMR L nanocomposites. As expected, the hardness and the tensile modulus increased with increasing organoclay loading. Swelling test indicated that ENR 50 nanocomposites had the higher filler-rubber interaction. The improvement in mechanical properties of ENR 50 nanocomposites is better as compared to SMR L nanocomposites. The thermal stability of SMR L nanocomposites was better enhanced by adding organoclay than that of ENR 50 nanocomposites. X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed the existence of intercalated and exfoliated structure of organoclay, which resulted in the improved mechanical properties. Scanning electron microscopy (SEM) manifested the addition of organoclay has transformed the failure mechanism of both rubber nanocomposites. For the carbon black/organoclay hybrid nanocomposites, the enhanced properties such as tensile strength, elongation at break and thermal stability were observed at 2 phr of organoclay and 8 phr of carbon black. This has been attributed to the synergistic effect of both fillers.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Addition of an inorganic component to polymers leads to improvements in various physical and mechanical properties. These improvements are the result of a complex interplay between the properties of the individual constituent phases: the polymer, the filler, and the interfacial region. Filler morphology such as the particle size, structure, and aspect ratio (length/diameter) have a large influence on the physical performance of the polymer composites (Joly et al., 2002).

Recently, considerable research interest is focused on nanocomposites prepared by incorporation of layered silicate of natural or synthetic origin in various polymers. The term polymer layered silicate nanocomposites describes a class where the reinforcing phases, in shape of platelets, has only nano level dimensions. Due to their nanometer phase dimensions, nanocomposites possess unique properties typically not share by their conventional microcomposites counterparts, and therefore offer new technology and business opportunities. Polymer nanocomposites exhibit significant improvement in physical and mechanical properties in relation to the polymer host (Giannelis, 1996; Alexandre & Dubois, 2000; Ray & Okamoto, 2003). The addition of nanolayered silicates can increase the stiffness and strength with a minimal loss in ductility and impact resistance, decrease the permeability and swelling in solvents, enhance the abrasion, flame resistance and thermal endurance. These substantial improvements are obtained at very low silicate content (Pinnavaia, 1983).

A wide variety of particulate fillers are used in the rubber industry to improve and modify the mechanical and physical properties of elastomeric materials. The reinforcement of rubbers is expressed by enhancement of modulus, failure properties (tensile and tear strength), and abrasion of resistance of the vulcanizates (Arroyo, 2003). Carbon black is one of the most common reinforcing fillers use in rubber compounding since the beginning of the XX century. Due to special particle dimension, shape and its special interaction with polymer matrices with physical and chemical bonding, carbon black is able to produce an excellent nano-reinforcing effect that greatly enhances the mechanical properties of the bare polymer or rubber (Cataldo, 2007). However, its polluting nature, the monotonous black color of the rubber material, its dependence on petroleum and it often reduces the processability of rubber compounds, especially at high volume loadings caused researchers to develop other satisfying reinforcing agents instead (Zhang et al., 2000).

Clays and clay minerals such as montmorillonite, saponite, hectorite, etc, are cheap natural raw materials that have been widely used for many years as filler for rubber and plastic to reduce polymer consumption and cost. Clay is comprised of silicate layers having a 1 nm thick planar structure and 200-300 nm in the lateral dimension. Because of the agglomeration of these particles, their low surface activity and these mineral fillers are not compatible with polymer matrix, their reinforcing effect is poor (Arroyo et al., 2003). Organophilic modification improves the compatibilization between the surface of the clay and the hydrophobic polymer matrix and thus polymers penetrate more easily into the layer galleries. The resulting organophilic clay (organoclay) can well be dispersed in the polymer exploiting the shear stress field created by the mixing equipment.

While organoclays have been extensively used in various thermoplastics and thermosetting polymer, much less attention has been paid to the elastomer as matrices (Kader et al., 2006; Arroyo at al., 2007; Cataldo, 2007). There are various methods to prepare rubber/layered silicate nanocomposites, including in situ polymerization intercalation (Zilg et al., 1999), solution intercalation (Vu et al., 2001, Liang et al., 2005), melt intercalation (Arroyo et al., 2003; Varghese et al., 2004; Wu et al., 2004; Arroyo et al., 2007) and latex compounding (Wang et al., 2000; Kader et al., 2006). Among them, melt intercalation is the simplest method and considered as the most effective route for the preparation of clay-nanocomposites (Alexandre & Dubois, 2000; Ray & Okamoto, 2003).

Although natural rubber (NR) is known to exhibit numerous outstanding properties, such as high tensile strength due to the ability to crystallize under strain, high resilience, excellent flexibility and resistance to impact and tear, low heat-build-up, reinforcing fillers are usually added into NR in most cases in order to gain the appropriate properties for specific applications. Organoclay may become suitable substitute as filler in applications where carbon black and silica are currently dominant or combine with them to produce hybrid reinforcement for natural rubber.

In this work, the organoclay used was a nanomer I.30T. It was a surface modified montmorillonite mineral, which was added to natural rubber matrices to produce rubber/organoclay nanocomposites. The effect of this organoclay on the vulcanization behavior, mechanical properties, and thermal stability of NR/organoclay hybrid was investigated to determine the potential of this filler to improve the properties of NR vulcanizates.

1.2 Objectives of Study

In this research, the preparation and properties of NR/organoclay nanocomposites were studied using two types of natural rubber i.e. SMR L and ENR 50. The melt compounding method was used to produce the nanocomposites. The main aim of this research can be divided into three categories:

- To determine the effect of organoclay loading on the properties of organoclay filled SMR L nanocomposites.
- To study the effect of organoclay on the properties of organoclay filled ENR 50 nanocomposites as compared to SMR L nanocomposites.
- To investigate the effect of carbon black/organoclay loading ratio on the properties of SMR L nanocomposites.

For each part of this research, the curing characteristics, mechanical properties (tensile strength, elongation at break, tensile modulus at 100 % and tensile modulus at 300%), hardness, swelling behavior and thermogravimetric analysis (TGA) were carried out. In addition, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were also conducted to characterize the NR/organoclay nanocomposites.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Rubbers (Elastomers)

The term rubber (elastomer) is used to describe vulcanized polymeric materials, whose glass transition temperature is sub-ambient and, amongst other properties, has the ability to be extensively and on release of stress, return to its original length (Heinisch, 1966). The common characteristics of elastomers are their elasticity, flexibility, and toughness. Beyond these common characteristics, each rubber has its own unique properties, often requiring additives to achieve the appropriate behaviors. It is customary when discussing the formulation of rubber compounds to classify the additives by the function they serve. Rubber compounding ingredients can be categorized as: vulcanizing or crosslinking agents, processing aids, fillers, antidegradants, plasticizers and other specialty additives (Hamed, 2001).

The rubbers in the marketplace are of two main types: crosslinking system and thermoplastic elastomer. Most of the commonly used rubbers are polymeric materials with long chains, which are chemically crosslinked during the curing process. This type of elastomer cannot be reshaped, softened, melted nor reprocessed by subsequent reheating, once formed (Hamed, 2001, Walker, 1988). They absorb solvent and swell, but do not dissolve; furthermore, they cannot be reprocessed simply by heating. The molecules of thermoplastic rubbers, on the other hand, are not connected by primary chemical bonds. Instead, they are joined by the physical aggregation of parts of the molecules into hard domains. Hence, thermoplastic rubbers dissolve in suitable solvents and soften on heating, so that they can be processed repeatedly. In many cases thermoplastic and thermoset rubbers may be used interchangeably. However, in demanding uses, such as in tires, engine mounts, and springs, thermoset elastomers are used exclusively because of their better elasticity, resistance to set, and durability (Hamed, 2001).

The commercial natural rubber (NR) is obtained from latex produced almost exclusively from the tree Hevea brasiliensis, which are grown in plantation around the world (Mark, 1989). NR is a nearly perfect type of raw material source. Natural rubber (NR) is a linear polymer with repeat units being isoprene (C_5H_8), its sub-ambient glass transition temperature is about -70^{0}C and its specific gravity is 0.93 at 20^{0}C. It crystallizes when stretched or stored at temperatures below 20^{0}C due to its regularity of structure. Temperature and type (grade) of natural rubber are factors which influence this rate of crystallization (Barlow, 1988). Natural rubber is the only true hydrocarbon polymer found in nature. Unstretched rubber has no regular X-diffraction patterned is therefore, amorphous. However, stretched rubber has an orderly crystalline-like X-ray diffraction pattern. Analysis of the pattern indicates that rubber has either an all *cis* or *trans* configuration depending upon its sources as shown in Figure 2.1. Common rubber has *cis* configuration (Billmeyer, 1971).

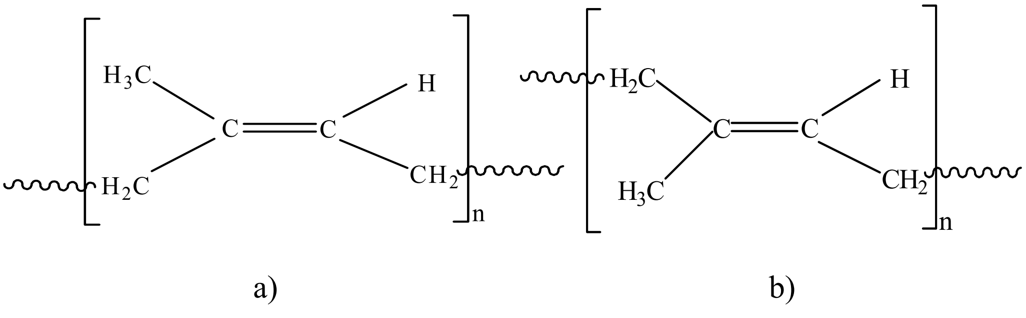


Figure 2.1 (a) *cis*-1, 4-polyisoprene, (b) *trans*-1, 4-polyisoprene (Billmeyer, 1971).

NR compounds usually contain peptizers, carbon black or non-black fillers or both, zinc oxide, fatty acids, processing aids, plasticizers, antioxidants, antiozonants, protective waxes and vulcanizing ingredients (usually sulphur, low sulphur or nonelemental sulphur vulcanizing systems; less frequently peroxides). NR can be blended with other diene rubbers such as synthetic polyisoprene (IR), Styrene-butadiene rubber (SBR) and polybutadiene (BR) (Nagdi, 1993).

Fillers and curing agents largely control the technical properties of rubber compounds. Sulphur is the most widely used curing agent for rubber, due to its ability to produce good properties. When it is used together with an accelerator and activator at elevated temperatures, thermally stable covalent bonds are formed between the elastomer chains at the carbon–carbon double bonds. This improves the properties of rubber vulcanisates. Nasir and Teh (1988) investigated the effects of the various types of crosslinks, including sulfur-based systems on the physical properties of NR. They reported improvement in tensile strength as a function of crosslink density.

NR vulcanizates have high tensile strength over a wide hardness range. The high strength is due to crystallization of the polymer chain at high strains enabling NR to be used in unfilled compounds. Furthermore, NR vulcanizates have the highest resilience of all elastomers (except BR), which is responsible for very low heat buildup. Further advantages include low compression set and stress relaxation, good electrical insulation and good resistance to abrasion, tear and fatigue.

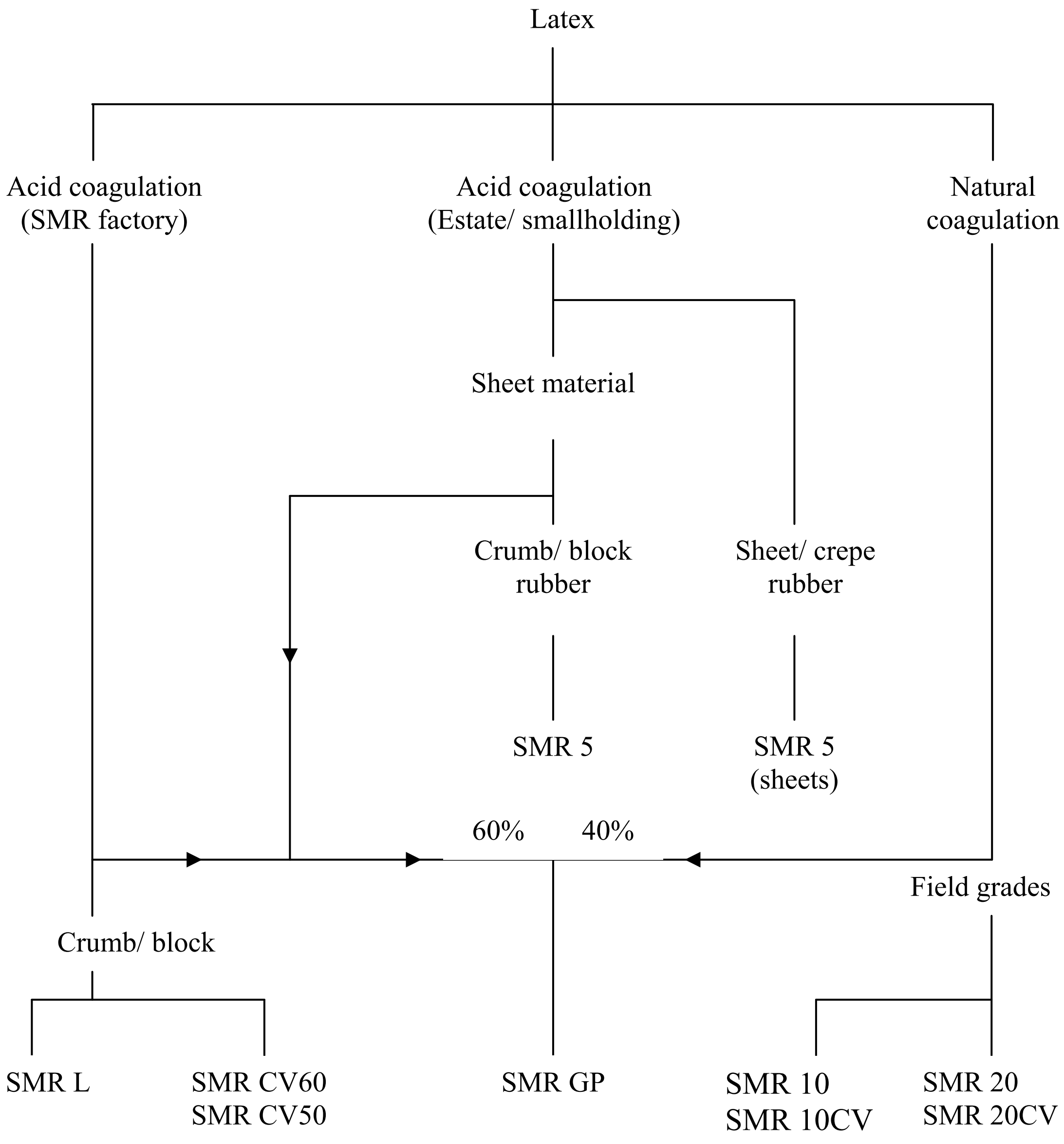
NR can be compounded for continuous use at 90^0C and for intermittent periods up to 100^0C. The vulcanizates remain flexible at temperature down to -55^0C without adding plasticizers. However, they tend to crystallize readily when stored for long periods at low temperatures. Like other unsaturated elastomers, NR vulcanizates are susceptible to attack by atmospheric ozone. However, the ozone and weather resistance can be improved by blending with a saturated rubber such as ethylene-propylene rubber (EPDM) or by incorporating antiozonants and protective waxes in the compound. NR vulcanizates are not resistant to petroleum-based oils and fuels but they can be used with a wide range of organic and inorganic chemicals, such as nonpetroleum-based automotive brake fluids, silicone oils and greases; glycols; alcohols; water; and nonoxidizing aqueous solutions of acids, alkalis and salts (Nagdi, 1993).

NR is the only rubber available for many years that has been the subject of intensive development and today it remains as the best choices for many applications that require low heat buildup such as large tires, passenger car tires, vibration mounts, springs and bearings. Other products include hoses, conveyer belts, gaskets, seals, rolls, rubberized fabrics, elastic bands and pharmaceutical goods (Nagdi, 1993).

2.1.1 SMR L

SMR (Standard Malaysian Rubber) are natural rubbers graded by technical specifications, not by the conventional visual standards. The introduction of the Standard Malaysian Rubber (SMR) scheme in 1965 marked a turning point in the whole approach to production and marketing of natural rubber. The scheme was so successful that it led to the adoption of an international scheme for Technically Specified Rubber (TSR). These schemes led to fewer grades, all with guaranteed specifications relating to quality and packed in small polyethylene wrapped bales (33.3 kg) for easy transport, storage, and factory handling. TSR production is different to conventional rubber production. Figure 2.2 gives an example of the SMR scheme with the relationship between source materials and grades (Fulton and Thorpe, 1996).

Based on SMR specification scheme, natural rubber has been classified by referring to dirt level, ash level, nitrogen level, volatile level matter, Lovibond color, P_0/PRI where P_0 is Wallace plasticity and PRI (Plasticity Retention Index). SMR L was classified based on the Lovibond color. SMR L is a color-specified rubber with a range limit of two Lovibond units within a production lot. The light amber color is produced by selecting clones with a low carotenoid content. After collection, the field latex is preserved with a mixture of ammonia and boric acid and subsequently treated using 0.05% sodium metabisulphite to inhibit enzymic darkening. The latex is coagulated by addition of formic acid and allowed to mature for up to 12 hours. The resulting coagulum is processed into crumb form, followed by hot air drying at 100^0C for about 5 hours. The dried crumbs are cooled to 60 °C and compressed into standard bales of 33.3 kg and wrapped in polyethylene. Table 2.1 summarizes the specification scheme for SMR L (Fulton and Thorpe, 1996).



Grades of Standard Malaysian Rubber

Figure 2.2 Processing routes by which raw materials are converted into the various grades of Standard Malaysian Rubber (Fulton and Thorpe, 1996)

Table 2.1 SMR L properties and specifications (Fulton and Thorpe, 1996)

Parameters	**Value**
Dirt retained on 44µ aperture (max), % wt	0.02
Ash content (max), % wt	0.50
Nitrogen (max), % wt	0.60
Volatile matter (max), % wt	0.80
Wallace rapid plasticity (P_0), min	30
Plasticity Retention Index (PRI), min, %[b]	60
Lovibond color:	
Individual value (max)	6.0
Individual range (max)	2.0

[b] Special producer limits and related controls are also imposed by RRIM to provide safeguard.

2.1.2 Epoxidized Natural Rubber (ENR)

Natural rubber (NR) has a number of its disadvantages: some of its engineering properties, such as its resistance to oils and solvents, air permeability and wet skid are quite poor. These properties can be improved greatly by the modification of NR by means of epoxidation, using an organic peracid directly or produced in situ (Heping et al. 1999). Epoxidized natural rubber (ENR) is a rubber that has properties which resemble those of synthetic rubbers rather than natural rubber. The epoxidized natural rubber (ENR) has epoxy groups that are randomly distributed along the chain backbones, which gives it increased polarity and higher glass transition temperatures (T_g). The increased polarity is of particular interest in the present context since it frequently facilitates reinforcement by fillers without the need for coupling agents (Baker & Gelling, 1979).

ENR is a derivative of natural rubber produced by chemical modification. The chemistry of epoxidizing unsaturated compounds employing peroxyacids is well documented in the literature and has been applied to NR to produce a range of ENRs. Currently, 50 percent mol of epoxidized natural rubber (ENR 50) is commercially available, and other epoxidation levels can be manufactured on request. As the natural rubber is expoxidized, its chemical and physical properties change according to the extent to which the mole percentage of modification is introduced. ENR 50 has comparable oil resistance and air permeability to some of the speciality synthetic elastomers. ENR has high tensile strength like NR, they undergo strain induced crystallization same as NR. In addition, a high degree of reinforcement is obtained with silica fillers, even in the absence of a coupling agent (Gelling, 1996). An X-ray study of ENR gum vulcanizates has confirmed that the strain crystallization does indeed occur. The crystallization percentage remains practically constant up to 50-percentage of mol epoxidation. However, beyond 50 percentage of mol epoxidation, there is a sharp reduction in degree of crystallinity (Colin, 1981).

2.2 Rubber Compounding

The production sequence in the rubber manufacturing industry can be defined into three stages: mixing (mastication and compounding), forming, and curing. A general rubber formulation is given in Table 2.2.

Table 2.2 A general rubber formulation (Nagdi, 1993)

	Parts per hundred parts of rubber
Crude rubber	100
Filler	50
Softener	5
Antioxidant	1
Stearic acid	1
Zinc oxide	5
Accelerator	1
Sulfur	2

Each of ingredients has a specific function, in either processing, vulcanization or end use of the product. The various ingredients may be classified according to their specific function in the following groups:

- Fillers (carbon blacks and non-black fillers)
- Plasticizers or softeners (extenders, processing aids, special plasticizers)
- Age resistors or antidegradants (antioxidants, antiozonants, special age resistors, protective waxes)
- Vulcanizing ingredients (vulcanizing agents, accelerators, activators)
- Special-purpose ingredients (coloring pigments, blowing agents, flame retardants, odorants, antistatic agents, retarders, peptizers).

2.2.1 Mixing

The polymers, fillers, processing aids, vulcanizing ingredients, and other additives, which the compounder has decided on, have to be mixed together. The two basic machines for this process are the two-roll mill and the internal mixer.

Prior to mixing of natural rubber, there is the mastication step. The reduction of viscosity and increase of plasticity of natural rubber and some synthetic rubbers brought about by mechanical milling and working have both advantages and disadvantages. The advantages lie in the ability to reduce molecular weight and viscosity so as to render the material more easily processable; the disadvantage is that processing involving mechanical working of the mix reduces molecular weight and hence the modulus of the vulcanizate .

The mixing of the ingredients into rubber often involves a compromise. High viscosity promotes high shear, which is required to break up filler aggregates; low viscosity assists wetting of the particles, which is essential to achieve uniform modulus and other properties. It has been said that the quality of the final product is made in the mill room or mixing department because it is there that a uniform and high level of dispersion and consistent rheological properties must be produced in the batches of mixed compounds (Blow, 1971)

2.2.2 Forming

After mixing, the green stock generally requires forming (shaping) into blanks of suitable dimensions. At this stage the stock will retain the shape imposed on it because it is predominantly plastic (Nagdi, 1993). Although alternative methods of shaping exist, the majority of products are produced by combined shaping and vulcanization operation known as moulding. Three distinct types of moulding are used – compression, transfer and injection. For each, a steel or aluminum mould having a cavity of the product shape required is heated to the vulcanization temperature (140-200^{0}C). The differences arise in the method of introducing the unvulcanised rubber into the mould.

In compression moulding, a hydraulic press having heated platens is utilized. A shape and weighed charge of rubber is introduced into the mould which is then reassembled and placed between the platens of the press. The force generated by the press closing the mould causes the rubber to flow to the form of the cavity and ensures that the expansion of volatiles within the rubber mix are contained until dimensional stability is achieved. The vulcanization time is dependent upon temperature, size of product and their heat transfer.

Transfer moulding may involve the heated hydraulic press used for compression moulding. The principle is the same in both instances; the mould cavity is closed before the moulding operation starts, the rubber is then introduced into a secondary cavity adjacent to the shaped product-forming cavity and is transferred by hydraulic ram pressure to the primary mould cavity through channels known as runners. The advantage of this system is twofold; the rubber received considerable fractional heating in transfer, shortening the vulcanization time; and metal inserts used in rubber to metal bonding may be positively located. The majority of engineering rubber components is produced by this method. Injection moulding is an extension and improvement of transfer moulding, allowing more precise control of material temperature during injection (which is similar to transfer) and thus allowing the further reduction of vulcanization times (Freakly & Payne, 1978)

2.2.3 Curing

After the green stock has been formed to the desired shape, it needs to be converted to an elastic material. This can be achieved by the vulcanization process, which usually takes place under pressure at elevated temperature, using different techniques, such as: press vulcanization, open vulcanization, continuous vulcanization and cold vulcanization. Chemically, the process involves insertion of cross-links between polymer macromolecules through the action of vulcanizing ingredients. Without these chemical bonds no improvements in the physical properties of the rubber mix can occur. It is quite probable that the crosslinks tie the macromolecules together in such a way that the whole mass becomes a single molecule. The cross-linking of rubber is also referred to as curing, because it is a process whereby a raw material is converted into a useful product (Nagdi, 1993). When rubber is vulcanized, sulfur molecules crosslink the polymer strands. That cross-linking helps hold rubber products together and allow them to resume their original shape after stretching (Freakley & Payne, 1978).

2.3 Vulcanizing Ingredients

Vulcanizing agents are chemicals which are incorporated in order to insert cross-linking between the polymer chains when the compounded stock is heated to an appropriate temperature. A cross-linking is formation of chemical bonds between polymer chains to give a network structure. The main purpose of vulcanization is to convert the essentially plastic raw rubber into an elastic and dimensionally stable material and also to render its physical properties temperature independent to a greater extent while making it insoluble in liquids which would have dissolved the unvulcanized rubber (Freakly & Payne, 1978). The type of cross-linking agent required will vary with the type of rubber used; however, they can usually be grouped in the following categories:

- Sulfur and related elements: the most common agent used is sulfur, as it enters into reactions with the majority of the unsaturated rubber to produce vulcanizates. In addition, two other elements in the same periodic family, namely selenium and tellurium, are capable of producing vulcanization. Selenium and tellurium are used in place of sulfur where excellent heat resistance is required. They generally shorten cure time and improve some vulcanizate properties.

- Sulfur-bearing chemicals: accelerators and similar compounds can be used as a source of sulfur for the vulcanization of natural and styrene-butadiene rubbers in recipes using very small amount of elemental sulfur.

- Nonsulfur vulcanization: most nonsulfur vulcanization agents belong to one of three groups: metal oxides, difunctional compounds, and peroxides. Carboxylated nitrile, butadiene, and styrene-butadiene rubbers may be crosslinked by the reaction of zinc oxide with the carboxulated groups on the polymer chains. This involves the formation of zinc salts by neutralization of the carboxylate groups. Other metal oxides are also capable of reacting in the same manner. Certain difunctional compounds form crosslinks with rubbers by reacting to bridge polymer chains into three-dimensional networks. Organic peroxides are used to vulcanize rubbers that are saturated or do not contain any reactive groups capable of forming crosslinks. This type of vulcanization agent does not enter into the polymer chains but produces radicals which form carbon-carbon linkages with adjacent polymer chains (Morton, 1973).

2.3.1 Accelerators

The function of an accelerator is to increase the rate of vulcanization. Accelerators can cut the vulcanization time from hours to minutes or seconds at high temperatures; and at lower temperatures the vulcanization time may be reduced from months to hours or minutes. This reduction is of a great importance as this result in very high production rates and reduction in capital investment. The main reason for using accelerators is to aid controlling the time and/or temperature required for vulcanization and thus improves properties of the vulcanizate. The reduction in the amount of time required for vulcanization is generally accomplished by changing the amounts and/ or types of accelerators used (Morton, 1973). At one time, basic oxides such as lime, litharge, and magnesia were widely used as accelerators. Today, accelerators are almost always organic compounds containing either nitrogen or sulfur or both. Very few accelerators, knows as sulfur donors, such as tetramethylthiuram disulphide, can be used as vulcanizing agents without the addition of elemental sulfur. According to speed of action, accelerators are sometimes described as slow, moderately fast, fast and ultra accelerators (Nagdi, 1993).

2.3.2 Activators

These components are used to increase the vulcanization rate by activating accelerators so that it performs more effectively. It is believed that they react in some manner to form intermediate complexes with the accelerators. The complex thus formed is more effective in activating the sulfur present in the mixture, thus increasing the cure rate. Accelerators are grouped as follows:

- Inorganic compounds (mainly metal oxides): zinc oxide, red lead, white lead, magnesium oxide, alkali carbonate, etc. Zinc oxide is the most common and it is often used in combination with a fatty acid to form a rubber-soluble soap in the rubber matrix.

- Organic acids: are normally used in combination with metal oxides; they are generally high molecular weight monobasic acids or mixtures of the following types: stearic, oleic, lauric, palmitic, etc.

- Alkaline substances will increase the pH of a rubber compound and in most instance increase the cure rate. As a rule of thumb, in the majority of recipes, any material which makes the compound more basic will increase the cure rate since acidic materials tend to retard the effect of accelerators (Morton, 1973).

2.3.3 Antioxidants

Antioxidants design to inhibit oxidative and ozone-caused deterioration, but ultraviolet light protectors and antiflex agents are included as well. The results of oxidative attack depend on the polymer, like NR, become soft and sticky. Ozone attack is manifested by cracking at the surface perpendicular to the stress. In the selection of antioxidant, the following factors must be considered: type of protection desired, chemical activity, discoloration, staining and cost. IPPD is one of the most popular antioxidant being used in compounding; the chemical structure is shown in Figure 2.3.

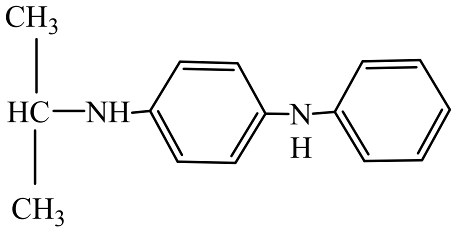


Figure 2.3 *N*-isopropyl-*N*'-phenyl-*p*-phenylenediamine (IPPD) (Roff & Scott, 1971)

2.3.4 Special-Purpose Ingredients

Certain ingredients are added for special purposes, but these ingredients are not normally required in the majority of rubber compounds. Examples include coloring pigments, blowing agents, flame retardants, odorants, antistactic agents, retarders and peptizers.

Coloring pigments are substances added for coloring nonblack rubber goods. It is important to note that only the nonstaining grades of crude rubbers, age resistors, accelerators and other ingredients should be used for colored compounds. Coloring pigments are usually divided into two groups: inorganic or mineral pigments and organic dyes.

Blowing agents are gas-generating chemicals that are necessary for manufacturing sponge and microporous rubber products. Suitable agents that are capable of releasing gas during the vulcanization period include sodium bicarbonate, ammonium carbonate and certain nitrogen-bearing compounds. The released gas brings about a cellular or spongelike structure.

Flame retardants are chemicals added to reduce the flammability of the end product. Materials used extensively for this purpose include, for example, chlorinated hydrocarbons, certain phosphates and antimony compounds. Odorants or odor improvers are strongly scented substances added in very small amounts (about 0.1 phr) that are capable of masking the characteristic odor of some rubber compounds or imparting a scent. Vanillin is frequently used for this purpose.

Antistatic agents are sometimes added to reduce the accumulation of dust or dirt on the surface of the elastomeric part during service and also to minimize the possibility of sparking resulting from discharge of accumulated static electricity. Typical antistatic agents include certain esters, fatty amines and amides. Retardants are substance used to reduce the tendency of a rubber mix to scorch, that is, to avoid premature vulcanization during factory processing. Peptizers are compounding ingredients used in small proportions to accelerate the softening o crude rubber under the influence of mechanical action, generally induced on open roll mills or in internal mixers (Nagdi, 1993).

2.4 Fillers

Since the early days of the rubber industry, fillers in the form of fine particulates have been used in rubber compounding. Particulate fillers are usually divided into two groups, inert fillers and reinforcing fillers. Inert fillers are added to the rubber to increase the bulk and reduce costs. In contrast, reinforcing fillers such as carbon black and silica are incorporated in the rubber to enhance the mechanical properties, to change the electrical conductivity, to improve the barrier properties or to increase the resistance to fire and ignition (Alexandre & Dubois, 2000, Nugay & Erman, 1999). Reinforcement of elastomeric compounds, defined as the simultaneous enhancement of the elastic modulus and the elongation at break, by addition of particulate filler, is probably one of the most important phenomena in material science and technology. The increase in stiffness imparted by the filler particles involves a hydrodynamic effect, which depends on the filler volume fraction, but the occlusion of rubber by the aggregate and the rubber trapped within the filler agglomerates may increase the effective filler volume. On the other hand, the shape factor (anisometry) also contributes to the increase in moduli (Bokobza & Chauvin, 2005).

The performance of filler in the rubber matrix is governed by its characteristics, such as the particle size and concentration, particle shape, surface activity, degree of interactions with rubber matrix and structure of the particle agglomerates (Siriwardena et al., 2001, Bokobza & Rapoport, 2001). One of the most important parameters is the average particle size, as shown in Figure 2.4. Particles larger than 10^3nm do not have reinforcing capabilities (at best) or have a detrimental action, and generally increase viscosity by a mere hydrodynamic effect.

Reinforcement is readily obtained with sizes smaller than 100 nm but particle structure appears as a more decisive factor. Two classes of minerals have been found to offer significant reinforcing capabilities are carbon black and silica.

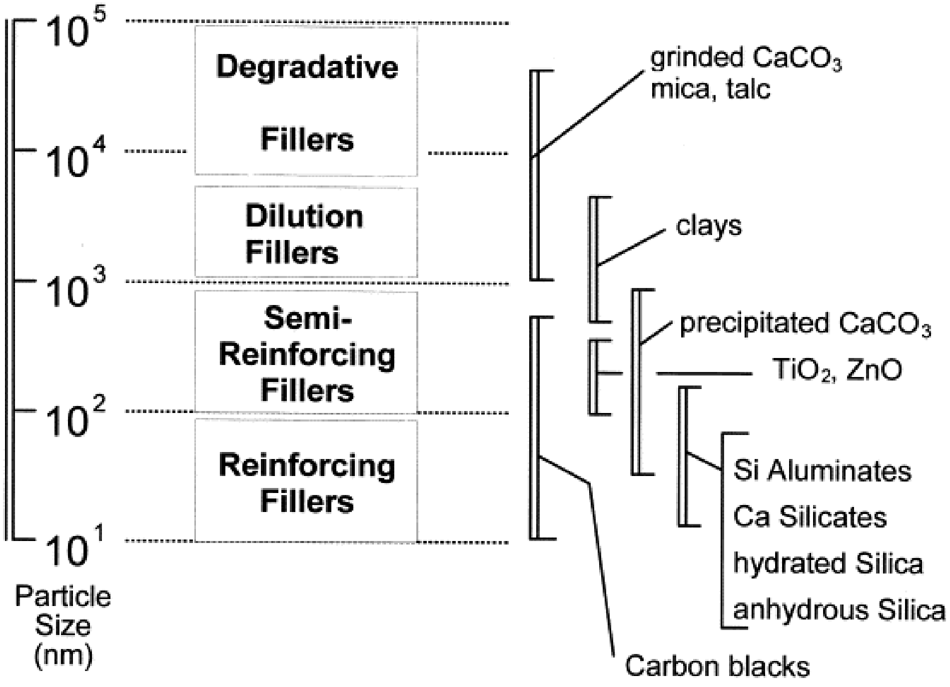


Figure 2.4 Classification of fillers according to average particle size (Leblanc, 2002)

Increasing the area of contact between rubber matrix and filler particles seems to be the most important factor in providing a strong reinforcement effect. The interfacial contact area between rubber matrix and filler is controlled by the size of filler particles and filler volume fraction. The degree of bonding between rubber matrix and filler particles is a key factor in determining the degree of elastomer reinforcement (Moshev & Evlampieva, 2003).

2.4.1 Carbon Black

Carbon black (CB) is the most extensively used reinforcing filler in rubber compounds, since the discovery of colloidal carbon black reinforcing qualities in 1904 (Blow, 1971). CB is an amorphous carbon of semi-graphitic structure which, when compounded with rubbers, increases the tensile strength, modulus, abrasion and tear resistance of vulcanizates. Carbon blacks have the smallest particle size of any industrial commodity. The CB used to reinforce rubbers has a particle size that ranges between 1 and 500 nanometers (Semaana et al., 2001).

The structure of carbon black is schematically shown in Figure 2.5. The primary dispersable unit of carbon black is referred as an "aggregate," which is a discrete, rigid colloidal entity. It is the functional unit in well-dispersed systems. The aggregate is composed of spheres that are fused together by covalent bonds (Mark, 2004 a). Carbon black particles diameters are less than 20 nm in some of furnace CB grades and up to few hundred nanometers in the thermal CB, whilst the carbon black aggregate dimensions fall in range of 100 nm to a few micrometers (Rogers, 2004).

The incorporation of carbon black with high surface area in an elastomer results in a high level of reinforcement and higher tensile strength, tear strength, and abrasion resistance, but also results in a compound with high hysteresis, high cost, and one which is more difficult to mix and process (Evans, 1981). The dramatic improvement in properties such as tensile strength, modulus, tear strength, and abrasion resistance when carbon black is added to elastomers has motivated much research into the mechanisms of such reinforcement. There are likely both chemical and physical interactions between carbon back and the rubber matrix, resulting in