PREPARATION, CHARACTERIZATION AND PROPERTIES OF ORGANOCLAY FILLED NATURAL RUBBER NANOCOMPOSITES.

by

RAJA NAZRUL HAKIM BIN RAJA NAZRI

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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
TGA	Thermogravimetric analysis
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

LIST OF SYMBOLS

Na^+	Sodium ion
K^+	Potassium ion
Mg+	Magnesium ion
Fe^+	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	Rubber-filler interaction

PENYEDIAAN, PENCIRIAN DAN SIFAT - SIFAT NANOKOMPOSIT GETAH ASLI TERISI ORGANO-TANAH LIAT.

ABSTRAK

Kajian tentang nanokomposit menggunakan getah asli “Standard Malaysian Rubber” (SMR L) bersama pengisi organo-tanah liat yang bersifat organofilik telah dijalankan. Nanokomposit SMR L telah disediakan melalui teknik pencampuran dengan menggunakan penggiling bergulung dua. Seterusnya nanokomposit telah disambung – silang dengan menggunakan sistem pemvulkanan konvensional. Nanokomposit getah asli berpengisi silika (Vulkasil S) disediakan untuk tujuan perbandingan. Kesan pembebanan organo-tanah liat sehingga 10 bsg (bahagian per seratus getah) terhadap kelakuan sambung – silang, sifat – sifat mekanikal, pembengkakan dan kestabilan termal nanokomposit SMR L telah dikaji. Masa skorj dan masa pematangan menurun manakala nilai tork maksimum meningkat apabila pembebanan organo-tanah liat meningkat dalam nanokomposit SMR L. Nanokomposit berpengisi silika mempamerkan masa skorj dan masa pematangan yang lebih panjang dan nilai tork maksimum yang lebih rendah. Kekuatan tensil bagi nanokomposit SMR L berpengisi organo-tanah liat meningkat hingga pembebanan 8 bsg. Pemanjangan takat putus semakin meningkat dengan pertambahan pembebanan organo-tanah liat. Perbandingan dibuat nanokomposit SMR L berpengisi silika dan didapati kekuatan tensil, pemanjangan takat putus yang dicapai adalah lebih rendah berbanding dengan nanokomposit SMR L berpengisi organo-tanah liat. Nanokomposit ENR 50 menunjukkan masa skorj dan masa pematangan yang lebih pendek apabila dibandingkan dengan nanokomposit SMR L. Kekuatan tensil bagi kedua – dua jenis nanokomposit meningkat hingga pembebanan organo-tanah liat pada 8 bsg. Kemudian apabila ditingkatkan lagi, kekuatan tensil menurun. Nanokomposit ENR 50 mempunyai pemanjangan takat putus yang lebih rendah berbanding nanokomposit SMR L. Kesan penambahan asid stearik ke atas sifat – sifat fizikal nanokomposit SMR L dikaji. Penggunaan kandungan organo-tanah liat yang optimum telah ditetapkan iaitu pada 8 bsg. Nanokomposit SMR L mempamerkan masa skorj dan masa pematangan yang lebih panjang dengan pertambahan kandungan asid stearik. Kekuatan tensil pula menunjukkan peningkatan yang optimum pada 7.5 bsg dan seterusnya menurun bila pembebanan asid stearik ditambah. Kesan pemanjangan takat putus pula menunjukkan peningkatan dengan pertambahan pembebanan asid stearik. Kesan penambahan getah asli tergraf malik anhidrida (MANR) terhadap nanokomposit SMR L dibuat. Pembebanan MANR telah ditetapkan pada 6 bsg. Masa skorj dan masa pematangan yang lebih pendek dengan MANR bila dibandingkan tanpa MANR. Kekuatan tensil meningkat ke tahap optimum iaitu 8 bsg sebelum ia menurun dengan pertambahan bebanan pengisi. Peningkatan sifat – sifat lain seperti pemanjangan pada takat putus dan modulus tensil juga telah didapati dengan MANR. Kestabilan termal nanokomposit SMR L adalah tinggi dengan MANR. Nanokomposit SMR L organo-tanah liat kemudiannya telah diuji dengan ujian pembelauan sinar X (XRD), penskanan elektron mikroskopi (SEM) dan ujian transmisi electron mikroskopi (TEM). Didapati bahawa organo-tanah liat telah berjaya diserakkan dengan sempurna di dalam nanokomposit SMR L.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF ORGANOCLAY FILLED NATURAL RUBBER NANOCOMPOSITES.

ABSTRACT

The research on natural rubber (NR) nanocomposites using “Standard Malaysian Rubber” (SMR L) grade with organophilic montmorillonite clays was undertaken. SMR L nanocomposites were prepared by melt mixing on a two roll mill and cured using a sulphur conventional vulcanization system. Silica/NR nanocomposites were used as comparison. The effects of organoclay with different filler loading up to 10 phr on curing characteristics, mechanical properties, hardness, swelling behaviour and thermal stability of SMR L nanocomposites were studied. Both scorch time and cure time were reduced and the maximum torque increased with the increased loading of organoclay in SMR L nanocomposites. Silica filled NR nanocomposites exhibit longer scorch time, cure time and decreased maximum torque values. The tensile strength of NR nanocomposites increased up to 8 phr loading and then decreased with increasing organoclay loading. Elongation at break continuously increased with increased organoclay loading. Comparison is made with silica filled NR nanocomposites and it shows that the tensile strength and elongation at break of silica filled NR nanocomposites are much inferior than organoclay filled NR nanocomposites. ENR 50 nanocomposites exhibit shorter scorch and cure time when compared to SMR L nanocomposites. The tensile strength of both the nanocomposites increased to an optimum of 8 phr organoclay loading. When organoclay loading was increased, tensile strength drops slightly. When compared between the two nanocomposites, ENR 50 nanocomposites have lower value of elongation at break. The effect of stearic acid on properties of natural rubber nanocomposites was studied. The optimum organoclay content was fixed at 8 phr. SMR L nanocomposites display longer scorch and cure time with the increased amount of stearic acid. Tensile strength increased to an optimum of 7.5 phr and then drops slightly with increased stearic acid loading. However, elongation at break increased with increased loading of stearic acid. The effect of increased organoclay loading with the presence of maleated natural rubber (MANR) in SMR L nanocomposites was studied. MANR content was capped at 6 phr. Shorter scorch and cure time was achieved with the presence of MANR when compared to SMR L nanocomposites without MANR. Tensile strength increased to an optimum of 8 phr before it reduced slightly. Improvements of mechanical properties such as elongation at break and tensile modulus was also observed with MANR. Thermal stability of SMR L nanocomposites with MANR is excellent. Organoclay filled SMR L nanocomposites are then subjected to X – ray diffraction test (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) test. It has been proven that organoclays intercalated and exfoliated within SMR L nanocomposites.

CHAPTER 1
INTRODUCTION

1.1 Polymer Nanocomposites

1.1 Introduction

The term ‘‘advanced composite’’ means specifically this combination of very discrete elements (particles/fibres) within a matrix designed to hold the reinforcements together. This type of composite combines the extreme strength and stiffness of the particles and, owing to the presence of the matrix, shows much greater toughness than would otherwise be obtainable. In many cases, the dimensions of one of the phases of a composite material are small, say between 10nm and a few micrometers, and under these conditions that particular phase has properties rather different from those of the same material in the bulk form. When the microstructural scale falls in the range of a few nanometers, such a material is referred to as a ‘‘nanocomposite.’’ (Mortensen, 2007).

Polymer nanocomposites are defined as having two parts i.e. a polymeric material (e.g., elastomers, thermoplastics or thermosets) and a reinforcing nanoscale material (nanoparticle). The nanoparticle aforementioned must have at least one dimension in one billionth of a meter (10^{-9} m) *(*Ke and Stroeve, 2005). Various researches have proven that polymer nanocomposites show major improvements in mechanical properties, gas barrier properties, thermal stability, fire retardancy and other areas. There are many factors that can be attributed to the polymer nanocomposite properties i.e. synthesis methods such as melt compounding, solvent blending, in-situ polymerization, and emulsion polymerization, polymer nanocomposite morphology vis-à-vis types of nanoparticles and their surface treatments, polymer matrix such as crystallinity, molecular weight, polymer chemistry, and whether it is elastomers, thermoplastic or thermosets.

Polymer nanocomposites are not a straightforward proposition as it deemed to be. Improvement of property related to polymer nanocomposites properties such as improved mechanical properties i.e. tensile strength, stiffness, toughness, improved gas barrier properties, improved dimension stability and higher chemical resistance comes at the expense of several processing difficulties such as increased processing difficulties due to higher viscosity, optical issues and also costly raw material and higher wear to processing equipments.

A wide variety of particulate fillers are used in the rubber industry to improve or 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 et al., 2003).

Clays and layered silicates can be classified as magadiite, bentonite, kaolinite, montmorillonite, clay saponite, sepiolite, vermiculite, talc, hectorite, attapulgite, fluoromica, illite, and chlorite. Nanoclays comprised of silicate layers having a 1 nm thick planar structure and 200 -300 nm in the lateral dimension. Due to agglomeration of these particles, their low surface activity and incompatibility issues with polymer matrix, their reinforcing effect is poor. Surface modifications via cation exchange reactions resolve the compatibilities issues between the surface of the clay and the hydrophobic polymer that have plagued hydrophilic clays. (Koo, 2006)

Natural rubber is the most important material and most widely used in expansive applications. Natural rubber has high strength as a gum vulcanizates (cured, low hardness rubber, containing no fillers) but materially it is soft and has low dimension stability (easily deformed). Inherent weather resistance provided by the raw gum elastomer is poor. Ozone attack is of most concern for thin products and those that are subjected to stretching in service. Electrical insulation is very good and, like all elastomers, is dependent on compounding. Dilute mineral acid (although not oxidizing acids such as nitric) and dilute base resistance is good. Solvents follow the polarity rule, thus resistance to petroleum oils is poor while resistance to alcohols (such as ethanol and methanol) and ketones (such as methyl ethyl ketone (MEK) and acetone) is much better. (Ciesielski, 1999)

Nonetheless, rubber technologists use fillers and various additives to modify these inherent disadvantages of natural rubber. The choice and level of filler loading depends principally on the particular product and its final vulcanizates desired properties.

In the past decade though, polymer-clay nanocomposites have generated excitement from both the industry and academia because it has demonstrated remarkable improvements in materials properties at very low clay loading (up to 10 wt.%) when compared to pristine polymer or conventional composites. Nanocomposites constitute a new class of material having nano-scale dispersion, typically 1-100 nm, of the filler phase in a given matrix. The outstanding reinforcement of nanocomposites is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase (up to 750 m^2/g). The nanolayers have much higher aspect ratio than typical microscopic aggregates. Mineral clays which can be dispersed as silicate nanolayers of high aspect ratio are attractive for polymer reinforcements. Polymer-clay nanocomposites have shown drastically enhancements in mechanical properties (modulus and strength), thermal properties (heat resistance and flammability), barrier properties, and biodegradability of the pure polymer.

For this work, nanomer I.30T manufactured by Nanocor Inc. was chosen. It is a type of surface modified montmorillonite clay. This then will be added with natural rubber and epoxidized natural rubber to produce rubber / organoclay nanocomposites. The effects of organoclay on curing, mechanical and thermal stability properties will be investigated to gauge the potential of this filler as potential replacement for commercial fillers.

1.2 Problem Statement

Polymer-clay nanocomposites that exhibit improvement in properties are typically made up of functionalized polymers such as polyamides and epoxy. This can be due to the affinity of these polymers to form chemical interactions between the organic cation present in the nanoclay silicate layers with their respective functional groups. Nano-sized clay silicates filler is still considered as cutting edge materials in the advanced material industry, which has yet to be adopted widely. It has been published many times over that compounding polymers with inorganic material including organoclay can improve the mechanical, barrier and thermal properties of the resultant polymer composites (LeBaron *et al.,* 1999).

Malaysia as being the leader in natural rubber innovations and technology, should take the initiative in embracing nanotechnology in developing new and innovative natural rubber applications. Advantages of using natural rubber rather than synthetic rubber as the main matrices for the nanocomposites include excellent dynamic properties, high resilience, relatively low cost, low hysteresis and fatigue resistance which is comparable and sometimes exceed synthetic specialty rubbers. Natural rubber also possesses superior green strength and tack properties that no other rubber can emulate or surpass. It also exhibits superior tensile properties as it is capable of strain-induced crystallization (Alger, 1989).

For this research work, the potential of organoclay is investigated by comparing it to silica which is an established commercial filler. NR/organoclay nanocomposites are prepared and mechanical properties, thermal properties and curing characteristics and the morphology of the vulcanizates will be studied.

Since NR does not possess polar groups in its backbone, NR/organoclay nanocomposites are prepared by using functionalized natural rubber i.e. epoxidized natural rubber (ENR 50) as the rubber matrix. These nanocomposites will then be studied on its mechanical properties, thermal properties and curing characteristics and the morphology of the vulcanizates.

Montmorillonite clays (MMT) exhibit many interesting structural features including exchangeable interlayer cations, hydroxyl groups on the edges of clay platelets and a high aspect ratio and small dimensions of the invidual layers. However, the pristine silicate surface is generally too hydrophilic to be compatible with natural rubber. To render MMT useful, clay modifications has to be made. Generally, there are two objectives for clay modification i.e. to weaken the polar interaction between adjacent layers thus increasing the distances between MMT layers and to enhance the affinity/compatibility between natural rubber and MMT. Pre-treatment of MMT with stearic acid will be done and later NR/organoclay nanocomposites will be prepared with the modified MMT thereof. These nanocomposites will then be studied on its mechanical properties, thermal properties and curing characteristics and the morphology of the vulcanizates.

Significant improvement in blend properties can usually be achieved by the addition of a suitable compatibilizer that was mostly polymer functionalized with maleic anhydride (MA). Maleic anhydride grafted natural rubber (MANR) will be prepared and used as compatibilizer in NR/organoclay nanocomposites. . These nanocomposites will then be studied on its mechanical properties, thermal properties and curing characteristics and the morphology of the vulcanizates.

1.3 Objectives of Study

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

- To compare organoclay with respect to silica on properties of natural rubber nanocomposites.
- To compare organoclay filled epoxidized natural rubber nanocomposites against organoclay filled natural rubber nanocomposites.
- To investigate the effect of stearic acid on properties of natural rubber nanocomposites.
- To investigate the effect of maleated natural rubber on properties of natural rubber 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%), swelling behaviour 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

Elastomers are hydrocarbon polymeric which is defined based on the property of extensibility, or stretching. The definition of an elastomer is a polymeric material which at room temperature can be stretched to at least twice its original length and upon immediate release of the stress will return quickly to approximately its original length. As indicated above, the major distinguishing characteristic of elastomers is their great extensibility and high-energy storing capacity. Also, because of their capacity for storing energy, even after they are strained several hundred percent, virtually complete recovery is achieved once the stress is removed (Brady et al., 2003).

Elastomers are useful and diverse substances that easily form various rubbery shapes. Many industries rely on parts made from elastomers, especially automobiles, sports equipment, electronics, electrical equipment, and assembly line factories. Another criterion is that, unlike thermoplastics that can be repeatedly softened and hardened by heating and cooling without substantial change in properties, most elastomers are given their final properties by mastication with fillers, processing aids, antioxidants, curing agents, and others followed by vulcanization (curing) at elevated temperatures that cross‑links the molecular chains and causes them to be thermosetting systems (Gooch, 2007).

The advantages of NR over other synthetic rubber are its outstanding green strengths and excellent natural tack properties. Apart from that, NR also has good mechanical properties, vis ã vis tensile strength and extensibility, elasticity and low hysteresis in the important low strain region of the stress-strain curve, hence low heat build up and good creep properties (Blow and Hepburn, 1982). The excellent mechanical strength can be attributed to the ability of NR to undergo strain-induced crystallization in which realignment of the polymer chains takes place at high strain. (Brydson, 1989).

However, NR tends to crystallize readily when stored for long periods at low temperatures. Like other unsaturated elastomers, NR vulcanizates are susceptible to attack by atmospheric ozone. Conversely, 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 (Gent, 2001). To date, the most effective antiozonants are secondary alkyl-aryl-p-phenylenediamines such as N-isopropyl-N-phenyl-p¬phenylenediamine (IPPD) (Brydson, 1989).

NR vulcanizates are not resistant either to petroleum-based oils and fuels but they can be used with a wide range of organic and inorganic chemicals, such as non-petroleum based fluids, silicone oils and greases, glycols, alcohols, water and non-oxidizing aqueous solutions of acid, alkalis and salts (Gent, 2001).

NR is generally considered to be the best of the general-purpose rubbers, meaning those characteristics suitable for a broad application. With NR, compounds can be produced over a wider stiffness range than any other materials. NR is used predominantly in tyre manufacturing (Rosato et al., 1991). For tyre manufacturing, the bulk of natural rubber is compounded with other elastomers to produce blends and thereby obtaining the desired mechanical properties. The natural rubber content in tread compounds can range from 10 phr, when it has been added to improve processing qualities, to 100 phr, as when it is used in commercial radial truck tyres for good hysteresis and tear strength. Other polymers typically blended with natural rubber are polybutadiene (BR) for resistance to abrasion and fatigue, styrene butadiene rubber (SBR) for traction and stiffness, butyl rubber (IIR) and halobutyl rubber (CIIR, BIIR) for enhanced tyre traction performance, and synthetic polyisoprene (IR) for processing qualities. Tyre sidewalls are typically 50:50 blends of natural rubber and polybutadiene for resistance to fatigue, cut growth, and abrasion (Rodgers, 2004).

Natural rubber compounds also tend to find use in covers of high-performance conveyor belts where a similar set of performance parameters such as those of a tyre tread compound are found (Mark et al., 2005). NR is also a significant choice for slurry pump lines and impellers as well as for tank linings due to its good abrasion resistance and relative low cost (Ciesielski, 1991).

2.1.1 Natural Rubber (NR)

It is estimated that there are more than 2000 species of trees, shrubs, or vines from mostly tropical and also temperate climate regions that produces milky fluid that congeals when exposed to air or known as latex from which natural rubber or a closely related material can be obtained. Nevertheless, latex from the trees of Hevea Brasiliensis is the only important commercial source of natural rubber. (Blow and Hepburn, 1982)

NR is a hydrocarbon consisting solely of carbon and hydrogen with an empirical formula of C_5H_8 with high molecular weight polymer of isoprene (Stern, 1982). Structurally, cis-polyisoprene is a highly stereoregular polymer with CH_3 group at the alpha terminal and three to four trans units at the omega end of the molecule (Fig. 2.1). Molecular weight distribution of Hevea Brasiliensis rubber shows considerable variation from clone to clone, ranging from 100,000 to over 1,000,000. Natural rubber has a broad bimodal molecular weight distribution. The polydispersity or ratio of weight-average molecular weight to number-average molecular weight, M_w/M_n, can be as high 9.0 for some variety of natural rubber. This tends to be of considerable ignificance in that the lower molecular weight fraction will facilitate ease of processing in end product manufacturing, while the higher molecular weight fraction contributes to high tensile strength, tear strength, and abrasion resistance (Rodgers, 2004).

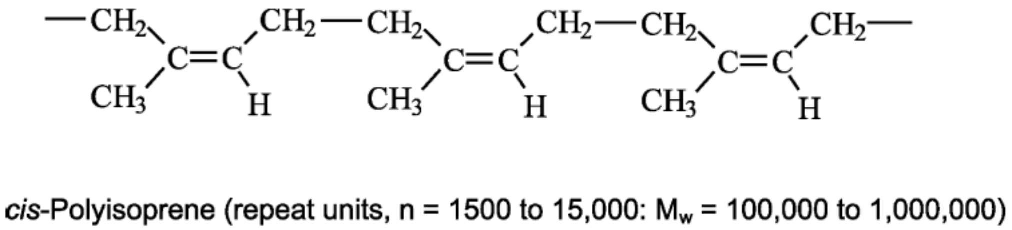

Figure 2.1 – Straight chain polymer structure of cis – 1, 4 polyisoprene (Rodgers, 2004)

Natural rubber is obtained from the Hevea Brasiliensis tree by cutting a thin slice of the tree bark with a tapping knife. A downward cut from left to right and at about a 20 – 30^0 angle to the horizontal plane is made to a depth approximately 1.0 mm from the cambium. Latex then exudes from the cut and can flow from the incision into a collecting cup. This process is called tree-tapping. Latex occurs in the trees in the form of particles suspended in a protein-containing serum. About two to three hours after tree-tapping, the latex collected from the trees are then added with stabilizers (ammonia) to prevent premature coagulation, and brought to a factory or smallholder central processing centre. The tapped latex consists of 30 – 35% rubber, 60% aqueous serum, and 5 – 10% other constituents such as fatty acids, amino acids and proteins, starches, sterols, esters, and salts. Some of the non-rubber substances such as lipids, carotenoid pigments, sterols, triglycerides, glycolipids, and phospholipids can influence the final properties of rubber such as its compounded vulcanization characteristics and mechanical properties. (Blow and Hepburn, 1982)

Residual latex continues to flow slowly for several hours after the initial collection. The leftover latex is not collected immediately and is being left to coagulate in the collection cup. These are then called cup lump. A small amount of latex coagulates as thin film on the tapping cut to form tree lace. These coagulated materials, known as field or natural coagulum, constitute about 15 to 20% of the total crop and are collected on the next day .

At the processing centre, the latex is first sieved and blended. Field latex is either concentrated to turn it into latex concentrate, or it is deliberately coagulated and processed into dry rubber. (Ciesielski, 1991).

Natural rubber is available in six basic forms i.e. sheets, crepes, technically specified sheet rubber, technically specified block rubber, preserved latex concentrates and mechanically or chemically modified specialty rubbers (Rodgers, 2004). Among these six types, the first four are in a dry form and represent nearly 90% of the total NR produced in the world. In the commercial market, these three types of dry NR are available in over 40 grades, consisting of ribbed smoked sheets; air-dried sheets; crepes, which include latex-based and field coagulum–derived estate brown crepes and remilled crepes; and TSR in block form. Among the three major types, crepes are now of minor significance in the world market, accounting for less than 75,000 tonnes per year. Field coagulum grade block rubbers have essentially replaced brown crepes except in India. Only Sri Lanka and India continue to produce latex crepes. (Fulton and Thorpe, 1996). Figure 2.2 presents a simplified schematic of the process followed in the production of natural rubber.

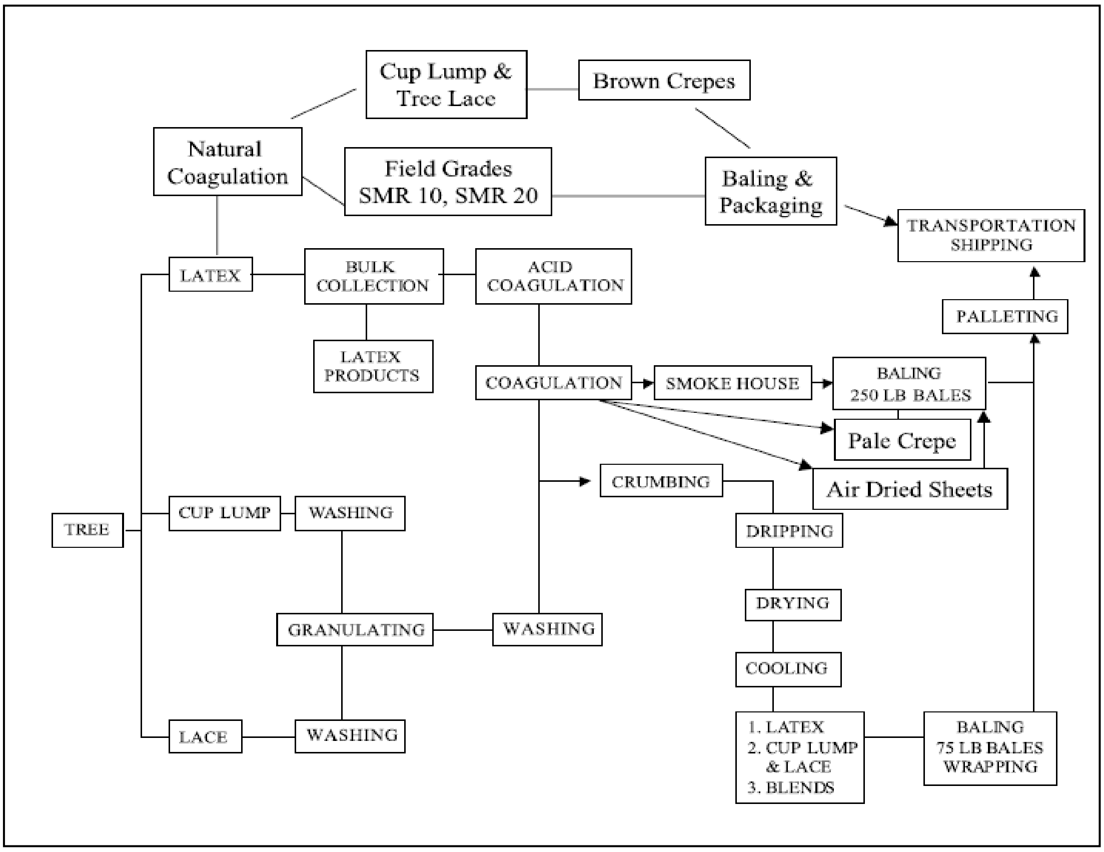

Figure 2.2 - Schematic of the natural rubber production process. (Rodgers, 2004)

SMR L

The International Standards Organization (ISO) first published a technical specification (ISO 2000) for natural rubber in 1964. Based on these specifications, Malaysia introduced a national Standard Malaysian Rubber (SMR) scheme in 1965, and since then all the natural rubber–producing countries have started production and marketing of technically specified rubbers based on the ISO 2000 scheme. Technically specified rubbers are shipped in ‘‘blocks,’’ which are generally 33.3 kg bales in the international market and 25.0 kg in India. All the block rubbers are also guaranteed to conform to certain technical specifications, as defined by the national schemes or by ISO 2000 (Table 2.1).

The nomenclature describing technically specified rubbers consists of a three- or four-letter country code followed by a numeral indicating the maximum permissible dirt content for that grade expressed as hundredths of 1%. In Malaysia, the TSR is designated as Standard Malaysian Rubber (SMR). (Fulton and Thorpe, 1996)

Table 2.1 – Technically Classified Rubbers Defined in ISO 2000 (Rodgers, 2004)

Property	**TSR CV**	**TSR L**	**TSR S**	**TSR 10**	**TSR 20**	**TSR 50**
Dirt content, max, wt%	0.05	0.05	0.05	0.1	0.2	0.5
Ash content, max, wt%	0.6	0.6	0.5	0.75	1	1.5
Nitrogen content, max, wt%	0.6	0.6	0.5	0.6	0.6	0.6
Volatile matter, max, wt%	0.8	0.8	0.8	0.8	0.8	0.8
Initial Wallace Plasticity P_0, min		30	30	30	30	30
Plasticity retention index (min)	60	60	60	50	40	30
Color, max, lovibond units		6				
Mooney viscosity	60 ± 5					

SMR L is a light-coloured rubber. This colour specified rubber has a value limit of 6.0 Lovibond units with a range of 2.0 Lovibond units within the production lots. (Rodgers, 2004). In achieving the light amber colour of SMR L, it is produced by selecting clones with low carotenoid acid and the use of appropriate preservatives to prevent darkening by the action of enzymes. (Fulton and Thorpe, 1996). Field latex that has been collected is then preserved with ammonia or a mixture of ammonia and boric acid. About 0.05% of sodium-metabisulphite is added soon after bulking to prevent enzymic darkening. The latex is coagulated without dilution at a pH value of 5 using formic acid. The coagulum is left to mature for 6 - 12 hours and then converted to granular form and the crumbs are then dried. The dried crumbs are cooled to 60^0C and compressed into standard bales of 33.3 kg and wrapped in polyethylene (Blow and Hepburn, 1982).

2.1.2 Epoxidized Natural Rubber (ENR)

As mentioned above, natural rubber has a number of disadvantages especially an uncontrolled oxidation of natural rubber which is detrimental to its physical properties. Oxidation reactions take place readily at unsaturated groups in polymers and are often referred to collectively as epoxidation; however, oxidation under controlled conditions can lead to useful products such as the epoxidized natural rubber introduced by the Malaysian Rubber Producers Association (Mark et al., 2005).

Epoxidized natural rubber (ENR) is a chemically modified form of natural rubber whose vulcanizates properties is designed to closely resemble those of some of the specialty synthetic rubbers (Baker et al. 1987). The epoxidized natural rubber has epoxy groups that randomly distributed along the chain backbones, which gives it increased polarity and higher glass transition temperature (T_g). The increased polarity is of particular interest because it easily offers better reinforcement by fillers without the need for coupling agents. (Baker and Gelling, 1979).

The chemistry of epoxidation of unsaturated compounds is normally carried out by employing acetic or formic acids, either pre-formed or generated in situ to epoxidized NR latex. The in situ formation of ENR is illustrated in Figure 2.3.

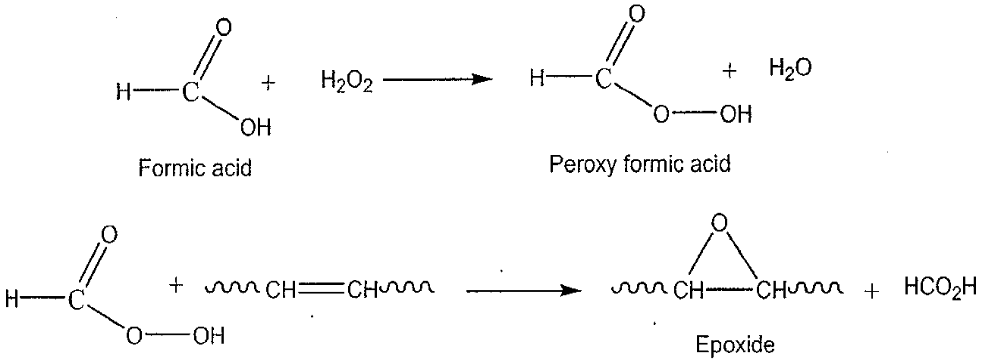

Figure 2.3 – Formation of ENR (Hourston and Tabe, 1996)

This aqueous based epoxidation reaction is a two phase system in which formic acid and hydrogen peroxide react to form peroxy formic acid. The peroxy formic acid then act as an epoxidation agent then diffuses into NR latex particles to form epoxidized natural rubber. Epoxy groups are randomly distributed along the polymer chain. Calcium stearate is required as a stabilizer. (Gelling, 1996). The epoxidation reaction with peroxy acids is stereospecific and thus ENR retains the stereoregularity all-cis-1, 4-configuration of NR with epoxide groups randomly situated along the polymer backbone. (Hourston and Tabe, 1996). Currently, 25 percent mol of epoxidized natural rubber (ENR 25) and 50 percent mol of epoxidized natural rubber (ENR 50) are available commercially. Other epoxidation levels can be manufactured on request. As the natural rubber is epoxidized, its chemical and physical properties changed according to the extent to which the mole % of modification is introduced (Mark et al, 2005).

Comparing with natural rubber, ENR has comparable high tensile strength to NR. This can be due to their ability to undergo strain induced crystallization identically as NR (Mark et al, 2005). 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 (Morton, 1987).

Additionally, ENR has unique properties such as good oil resistance (ENR 50 is comparable to polychloroprene), low gas permeability (equivalent to that of butyl rubber), wet grip and rolling resistance coupled with high strength. The properties of ENR vulcanizates are largely determined by three factors: the ability to strain crystallize, the increase in the glass transition temperature and solubility parameter with the extent of epoxidation (Gelling, 1996).

2.2 Rubber Compounding

Processing is termed as the complete sequence used in industry to convert raw rubber into a useful rubber product. There are usually three steps: mixing, forming / shaping and vulcanizing.

The mixing stage is generally understood as the mastication and compounding of the rubber compound. The reason for mixing is to incorporate the compounding ingredients into the rubber and distribute it as uniformly as possible within the rubber compounds. With NR, it may be necessary to add a preliminary stage: in which NR on its own or with the addition of peptizers is subjected to a shearing process to reduce its viscosity prior to mixing.

The forming or shaping stage came subsequently after mixing. This is to ensure that the rubber compounds mixed are converted or processed into the shape and form of the final finished products. Most of the time, shaping and vulcanization stage is carried out as one operation. Lastly, vulcanization process takes place. Vulcanization is the heating of the shaped article to cause cross linking to take place. This then will produce useful elastic products by means of cross linking agents. The vulcanized rubber product made then to has meet various physical properties such as hardness, modulus, tear strength, abrasion resistance etc.

Materials used in dry rubber compounding can be classified into eight major categories, namely: rubber, processing aids, curing agents, accelerators, activators, antidegradant, fillers, miscellaneous ingredients which include retarder, inhibitors, pigments and blowing agents. In conclusion, Table 2.2 shows the materials required for compounding, the functions of the materials and the common proportions used in rubber compounding.

Table 2.2 - A general rubber formulation (Blow and Hepburn, 1982)

Material Property Required	Compounding Ingredient Function	Common Proportions
Non thermoplastic properties i.e. Elastic behaviour	<u>Basic Additive</u> Crosslinking or vulcanization reagents. Reaction catalysts or accelerators.	Parts by weight 1 -3 0.5 - 3
Protection from degradation by O_2, O_3	Antidegradants i.e. antioxidant additives	1 - 4
Ability to design for a specific stiffness or hardness	Use of fillers especially small particles size powders: Examples are carbon blacks, silicas, calcined clays.	10 - 100
Processability i.e. shaping before crosslinking	Processing Aids: Oils, Waxes, Soaps etc.	1 - 10
Adhesion to textile, metal, ceramic etc. substrates	Integral bonding additives and surface treatments	2 - 10
Colour changes	Pigments as organic Pigments as inorganic	0.1 – 3.0 5 - 20
Cost Reduction	Extender fillers, Depolymerized reclaimed rubber, Ground vulcanized rubber	10 – 200 10 – 100 5 - 50
Cellular structures	Blowing agents e.g. organic, inorganic	0.5 – 2.0 ; 5 - 30
Reduced fire hazard (self extinguishing)	Flame retardants e.g. phosphates, antimony salts, halogenated organics, borates (Antimonytrioxide and chlorinated wax – common for NR)	1 - 20
Magnetism	Magnetic inorganic salts e.g. iron oxides	5 - 100
High energy radiation absorption	High energy absorbers e.g. heavy metal salts, lead oxides	10 - 100
Electrical insulation	Non conductive ingredients e.g. mineral fillers, hydrocarbon oils	5 – 50
Electrical anti-static	Anti-static additives, polar esters, soaps; small amount of black	0.1 – 2.0
Electrical conductivity	Conductive ingredients e.g. carbon black, metal particles and their salts	10 - 50
Bacteria resistance	Fungicides e.g. chlorinated phenols.	0.5 – 5.0

2.2.1 Mixing

Compounding—that is, mixing together a variety of components such as different polymeric materials, solid, and liquid additives, sometimes accompanied by a chemical reaction—is often used to produce a polymeric material with new and improved properties. In fact, compounding actually offers a far less expensive and more practical route for creating a wide variety of new, improved products than the development of chemically new polymers (Tadmor, 2006). The objectives of mixing are to obtain uniformed ingredients with good dispersion of each ingredient and to produce consistent batches which are uniform in viscosity and in degrees dispersion. The two basic machines for this process are the two-roll mill and the internal mixer.

Rubber mixing is a partly physical, partly chemical process. For mixing, there are two stages i.e. the mastication and compounding of the rubber compound. The purpose of mastication is to reduce the viscosity and increase the plasticity of natural rubber and some synthetic rubbers brought about by mechanical milling. Decrease in viscosity for rubber is also achieved by heat generated through rubber shearing between rubber – rubber and rubber – mixing machine. This directly will improve the processability of the material for nest stage. The purpose of compounding is to incorporate, dissolute or partially dissolute and physically disperse compounding ingredients and reduce their particle size (Long, 1985).

Mixing should be optimized with respect to time, temperature, and energy. Compound viscosity should be reduced only to that level which allows acceptable processing in the ongoing manufacturing stages. Uniform distribution and optimum dispersion of all compounding materials should be achieved, and the influence on scorch time has to be minimal and/or controllable. If possible, the tackiness of the compound should be controlled. Both excessive sticking to the machines and bagging on the mill due to a lack of stickiness must be avoided (Rodgers, 2004).

2.2.2 Forming

Rubber compound that has been put through the mixing stage generally requires some kind of forming or shaping into blanks of suitable dimensions before it can be vulcanized. At this stage the stock will retain the shape imposed on it because it is predominantly plastic (Gent, 2001). Ideally rubber compounds should have a smooth surface, uniform shrinkage, and freedom from blisters. Last but not least, bloom should be avoided. The majority of products are produced by combined forming or shaping and vulcanization operation known as moulding. Three most widely used moulding methods are compression, transfer and injection moulding. A steel or aluminium 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 unvulcanized rubber into the mould (Hofmann, 1989).

For compression moulding, a pair heated platens mounted on hydraulic press is used. A shape and weighed of rubber blanks is inserted into the mould which is then reassembled and placed between the platens of the hydraulic press. The heat and compression force generated by the hydraulic press causes the rubber to flow and takes shape according to mould. The compression force generated by the hydraulic press also helps to contain the expansion of volatiles within the rubber mix until dimensional stability of the rubber mix is achieved. The vulcanization time is highly dependent upon this three factors i.e. temperature, size of product and their heat transfer (Long, 1985).

For transfer moulding, the heated hydraulic press is used is similar as in used in 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 (Morton, 1987).

For injection moulding, it is a bit more complicated compared to compression and transfer moulding. Processing cycle wise, it involves automatic feeding, heating and plasticization of a rubber mix and its high pressure in measured quantity, through a narrow orifice into a tightly closed mould in which vulcanization takes place (Long, 1985).

The advantage of this type of machine is in the heat generated by thermal conduction through the mechanical work done by the screw. Heat can be carefully regulated by the screw speed, back pressure and barrel temperature. As the screw plasticizes, the rubber mix progresses along the retractable screws and fills up the required preset volume in front of the screw. This volume of rubber mix is then injected into the mould. Heat is generated as the mix is forced through the mould gates (Blow and Hepburn, 1982).

2.2.3 Vulcanization

After the rubber compound has been formed into the desired shape, it needs to be converted to an elastic material. This is achieved through subjecting the rubber compounds through vulcanization process, which usually takes place at a high temperature under elevated pressure, using different techniques, such as press vulcanization, open vulcanization, continuous vulcanization and cold vulcanization. Chemically, this process is about introducing crosslinks between polymer macromolecules through the action of vulcanizing ingredients. Without these chemical bonds, no improvements in the physical properties of the rubber mix can take place. The crosslinks tie the macromolecules together in such a way that the whole mass becomes a single interconnected three dimensional molecule. When rubber is vulcanized, sulphur molecules crosslink the polymer strands. This crosslinking reaction helps to strengthen the vulcanizates and allows it to retain its natural elastic disposition that is their ability to undergo large elastic deformations, that is, to stretch and return to their original shape in a reversible way (Morton, 1987).

2.3 Vulcanizing Ingredients

There are various vulcanization systems available to cure natural rubber. The two commonly used systems are the sulphur vulcanization system and peroxide curing system.