HALLOYSITE NANOTUBES/NATURAL RUBBER (HNTs/NR) NANOCOMPOSITES: PREPARATION AND PROPERTIES

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By

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DECLARATION

I declare that the content presented in this dissertation is own my work which was done at Universiti Sains Malaysia unless onformed otherwise. This dissertation has not been previously submitted for any other degree.

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ACKNOWLEDGEMENT

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LIST OF SYMBOLS

Symbol	Description
%	Percentage
°C	Degree Celsius
Al_2O_3	Alumina (aluminium oxide)
$CaCO_3$	Calcium carbonate
cm	Centimeter
cpm	Cycles per minute
dNm	Deci Newton Meter
Eb	Elongation at break
Fe_2O_3	Iron (III) oxide
g	Gram
K_2O	Potassium oxide
Kc	Kilocycles
lb	Pound
M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
MgO	Magnesium oxide
M_H	Maximum torque
mm	milimeter
mm/min	Millimeter per minute
Na_2O	Sodium oxide
-NH-	Amine
-OH	Hydroxyl group
Pd-Au	Palladium-Aurum

phr	Part per hundred rubber
SiO_2	Silica (silicon dioxide)
t_{90}	Cure time
t_{s2}	Scorch time
T_5	Decomposition temperature at 5% weight loss
T_{10}	Decomposition temperature at 10% weight loss
T_{20}	Decomposition temperature at 20% weight loss
T_{30}	Decomposition temperature at 30% weight loss
T_{40}	Decomposition temperature at 40% weight loss
T_{50}	Decomposition temperature at 50% weight loss
T_{80}	Decomposition temperature at 80% weight loss
TiO_2	Titania (titanium dioxide)
wt %	Weight percentage

LIST OF ABBREVIATION

Abbreviation	Description
ASTM	American standard testing and materials
BKF	2, 2 methylene-bis-(4-methyl-6-tert-butylphenol)
BR	Polybutadiene rubber
CB	Carbon black
CBS	N-cyclohexyl-2-benzothiazole sulfenamide
CEC	Cation-exchange capacity
CNT	Carbon nanotubes
C.V.	Continuous vulcanization processes
CV	Conventional vulcanization systems
DPG	Diphenyl guanidine
EPC	Easy processing furnace
EV	Efficient vulcanization systems
ENR	Epoxidized natural rubber
ENR 25	Epoxidized natural rubber with 25% mol of epoxy
ENR 50	Epoxidized natural rubber with 50% mol of epoxy
EPDM	Ethylene-propylene-diene
FEF	Fast extruding furnace
FTFT	Fatigue-to-Failure Tester
FT	Fine thermal
HAF	High abrasion furnace
HMF	High modulus furnace
HNTs	Halloysite nanotubes
IR	Polyisoprene

ISAF	Intermediate SAF
J.I.S	Japanese industrial standard
LNR	Liquid natural rubber
MBT	Mercaptobenzothiazole
MBTS	Dibenzothiazyl disulfide
MMT	Montmorillonite
MT	Medium thermal
NR	Natural rubber
OENR	Oil-extended natural rubber
PET	Polyethylene terephthalate
PPD	Para-phenylenediamine
PRI	Plastic retention index
RRIM	Rubber Research Institute Malaysia
SAF	Super abrasion furnace
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscope
Semi-EV	Semi-efficient vulcanization systems
SMR	Standard Malaysian Rubber
SRF	Semi-reinforcing furnace
TBBS	N-tert-Butyl-2-benzothiazole sulfenamide
TGA	Thermogravimetric analysis
TPG	Triphenyl guanidine
TSR	Technically specified grades
ZnO	Zinc oxide

NANOKOMPOSIT TIUBNANO HALLOYSITE/GETAH ASLI (HNTs/NR): PENYEDIAAN DAN SIFAT-SIFAT

ABSTRAK

Kajian ini tertumpu tentang kesan pelbagai pembebanan HNTs terhadap sifat-sifat nanokomposit getah asli. Siri (1), HNTs diisi di dalam dua jenis getah asli iaitu tidak diubahsuai dan ubahsuai yang masing-masingnya dinamai SMR L dan ENR 50. Dalam Siri (2), kajian mengenai penggantian separa HNTs dengan karbon hitam (CB) sebagai pengisi hibrid di dalam getah asli dikaji. Akhir sekali dalam Siri (3), kajian mengenai perbezaan jenis kaedah pencampuran iaitu kaedah pencampuran mekanikal dan larutan telah dibezakan. Sistem pemvulkanan konvensional (CV) telah dipilih dalam kajian ini dan penggiling bergulung dua makmal digunakan untuk proses pencampuran. Sifat-sifat yang dikaji dalam kajian ini termasuk ciri-ciri pematangan, sifat-sifat mekanikal, peratusan pembengkakan, hayat fatig, kestabilan termal dan sifat-sifat morfologi getah asli yang diisi oleh HNTs. Mosanto Moving Die Rheometer (MDR) dengan suhu 150°C telah digunakan untuk menentukan ciri-ciri pematangan nanokomposit. Dalam Siri (1), kekuatan tensil optimum nanokomposit HNTs/SMR L dan HNTs/ENR 50 dicapai dengan 20 phr. Kestabilan termal meningkat dengan penambahan HNTs di dalam kedua-dua nanokomposit. Dalam Siri (2), kekuatan tensil, modulus tensil, dan kestabilan termal nanokomposit meningkat. Dalam Siri (3), nanokomposit kaedah pencampuran larutan menunjukkan kekuatan tensil, modulus tensile dan hayat fatig yang lebih tinggi pada mana-mana pembebanan HNTs. Amnya, imej SEM menunjukkan pembebanan HNTs yang rendah boleh tersebar secara seragam di dalam matrik tetapi penyebaran yang teruk dan kurang memuaskan telah diperhatikan pada pembebanan HNTs yang lebih tinggi.

HALLOYSITE NANOTUBES/NATURAL RUBBER (HNTs/NR)

NANOCOMPOSITES: PREPARATION AND PROPERTIES

ABSTRACT

This research focused on the effect of various HNTs loading on the properties of natural rubber nanocomposites. Series (1), HNTs filled in two types of natural rubber i.e., unmodified and modified natural rubber namely SMR L and ENR 50 respectively were investigated. In Series (2), the study of partial replacement of HNTs with carbon black (CB) as hybrid fillers was studied. Lastly in Series (3), the study regarding different type of mixing methods i.e., mechanical and solution mixing methods were compared. Conventional vulcanization (CV) system has been selected in this research and laboratory two-roll mill was used for mixing process. The studied properties in this research includes curing characteristics, mechanical properties, swelling percentage, fatigue life, thermal stability and morphological properties of HNTs filled natural rubber. Mosanto Moving Die Rheometer (MDR 2000) with temperature at 150°C was used to determine curing characteristics for nanocomposites. In Series (1), optimum tensile strength of HNTs/SMR L and HNTs/ENR 50 nanocomposites was achieved with 20 phr. Thermal stability increased with addition of HNTs in both nanocomposites. In Series (2), tensile strength, tensile modulus and thermal stability of nanocomposites increased. In Series (3), solution mixing method nanocomposites showed higher tensile strength, tensile modulus and fatigue life at any HNTs loading. Generally, the SEM images showed that lower HNTs loading can be dispersed uniformly in matrix but bad and poor dispersion was observed at higher HNTs loading.

CHAPTER 1

INTRODUCTION

1.1   Introduction

The discovery regarding the reinforcement effect in rubber properties by adding certain additives called filler can be considered the most important finding in rubber technology after the discovery of vulcanization process. This turned natural rubber vulcanizates into more desirable properties. Basically, it is started with the usage of zinc oxide (ZnO) for its color at the early years of 20th century and in the same time it is discovered that ZnO also showed their reinforcement potential (Ciullo and Hewitt, 1999). Then, continued with the usage of carbon black (CB). Up until now, CB still the most important filler in industry (Mouri, 2001) and ZnO still being used in rubber compound since it is accidently found that ZnO is suitable used as activator (Ciullo and Hewitt, 1999).

Afterward, the studies continued with introduction of nonblack filler into rubber compound. Generally, the addition of nonblack filler is to produce white or light colored products which cannot be produced by using CB. The most three nonblack fillers that widely used are calcium carbonate ($CaCO_3$), clay and precipitated silica which also showed improvement in rubber properties (http://www.rtvanderbilt.com/NonBlackFillers.pdf).

Many researchers show great interest to investigate potential of other materials which may have possibility to act as filler as good as CB or silica in rubber compounds. Therefore, wide varieties of materials generally from renewable

resources such as agricultural waste, recycled products, and also from mineral resources or from other resources have been investigated tremendously for this purpose. For examples, rice husk ash (Ismail et al., 1998), oil palm fiber (Ismail et al., 1997) or starch (Wu et al., 2009) from agricultural waste while recycled polyethylene terephthalate (PET) bottles (Nabil et al., 2011) from recycled products and various types of clay such as montmorillonite (MMT) (Joly et al., 2002), kaolin (Yahya et al., 2009), bentonite (L'alikova et al., 2010) from mineral resources has been used lately. These materials not only limited in rubber composites but also in other polymer matrixes.

Then recently, considerable attempt has been expanded in rubber nanocomposites studies due to revolution from micro-sized filler to nano-sized fillers. The switch using micro-sized filler to nano-sized filler due to several advantages displayed by nano-sized filler filled rubber. Some of the advantages of nanocomposites are improvements in the mechanical properties, heat stability, flame retardance, gas-barrier properties, abrasion resistance, and solvent resistance (Wu et al., 2001). It can be related to high aspect ratio and the dispersion of filler in nano-dispersion where it can be expected better interfacial between filler and rubber which is fundamentally different compared to microcomposites (Maiti et al., 2008). Besides, reinforcement is possible at very low loading of fillers (< 10 wt %) if compared to conventional filler composites, which require much larger quantities (Teh et al., 2004a).

Currently, nanoclay loaded rubber nanocomposites is one of fast growing development which has been studied in various fields of study for examples in

mechanical, thermal or electrical purposes. Clay minerals are potential nanoscale additives because of their layers consisting of 1 nm thick planar structures (Kato et al., 2006). Toyota group is the first group who utilized silicate layered clay namely montmorillonite (MMT) in polyamide compound and demonstrated significantly increased in modulus, tensile strength and heat distortion temperatures (Ismail et al., 2008). The result obtained made other researchers eagerly to explore more about MMT and similar materials in natural rubber properties.

1.2   Problem statement

It is well known that natural rubber is the most popular rubber being used in industry due to their unique properties. Usually, natural rubber is loaded with fillers to modify the properties of rubber vulcanizate, to reduce cost of production or to impart the color.

In this work, HNTs is loaded into natural rubber since no details works has been done. Rooj et al. (2010) only show basic information about the addition of HNTs inside natural rubber. Thus, this study is important to know in more details about the possibility affect of HNTs loading towards natural rubber properties.

However, some of limitation suffered by natural rubber is due to non-polar nature property. Natural rubber showed weakness in making good interaction with filler due to this reason. Thus, epoxidized natural rubber with 50% mol of epoxy is used as matrix for a comparison with unmodified natural rubber. The polar property in ENR 50 is expected to interact with HNTs and consequently show positive effect in the properties of HNTs/ENR 50 nanocomposites. Sadequl et al. (1999) observed

CB and silica filled ENR 25 matrix able to show better interaction than CB or silica filled natural rubber where the tensile strength of ENR composites is higher than natural rubber composites but the fatigue life of natural rubber composite is higher than ENR 25 composites.

Various studies investigated the effect of hybrid fillers in natural rubber composites. This is to investigate the possibility of synergism effect by well known reinforced filler and new fillers. Recently, hybrid polymer nanocomposites containing layered silicate and with well-known reinforced filler gained huge attention. For example, Chattopadhayay et al. (2010) used CB/organoclay hybrid filler in ENR 25 nanocomposites. It is found that the addition CB/organoclay with ratio 20:15 show synergistic effect reflected in their dynamic mechanical and tensile properties.

Filler dispersion is one of the critical factors that influence the properties of final rubber composites. Hence, the mixing process plays the most important step in determine good dispersion of filler inside rubber matrix. Generally, there are several types of mixing methods such as melt mixing, solution mixing, and also in situ mixing methods that commonly used. Besides melt mixing, solution mixing is the easiest mixing methods and usually been chosen by many researchers in order to obtain better filler dispersion in rubber composites. Ismail et al. (2010a) studied two types of mixing methods for carbon nanotubes (CNT)/natural rubber nanocomposites. From this study, they concluded that solution mixing method can exhibited better mechanical properties than nanocomposites prepared by mechanical mixing method due to well dispersed of CNT in natural rubber matrix for solution

mixing method. Lopez-Manchado et al. (2004) compared the properties of organoclay-natural rubber nanocomposites prepared by mechanical and solution mixing where they obtained similar trend as reported by Ismail et al. (2010a).

1.3   Research objectives

This research is study about the effect of various HNTs loading on properties of natural rubber. Then, it is expanded into several parameters. The main objectives of this research are:

1. To compare and investigate the effect of HNTs loading on properties of different types of rubber matrix which is between SMR L and ENR 50.

2. To investigate the effects of HNT/CB hybrid fillers in natural rubber nanocomposites.

3. To study the effect of different mixing methods to prepare HNTs filled natural rubber nanocomposites.

1.4   Scope of research

The scope of this research is summarized in Figure 1.1. In this figure, the preparation to produce natural rubber nanocomposites filled with HNTs starts with the preparation of filler. The next step is mixing procedure by using external mixing methods, laboratory two-roll mill. Then, the uncured samples are tested by Moving Die Rheometer (MDR 2000) to determine the curing characteristics of samples. After that, the cure times obtained were used in compression molding. Next step is to examine and study the properties of filled natural rubber in tensile properties, swelling percentage, fatigue life and also thermal stability. Lastly, the morphological

properties of tensile and fatigue fractured surface is investigate by scanning electron microscope (SEM). Then, overall results are analyzed and discussed.

HNTs preparation
(sieved and dried)

↓

Mixing process
(two-roll mill)

↓

Curing test
(Monsanto Moving Die Rheometer, MDR 2000)

↓

Compression molding
(hot press)

↓

Testing:
- Tensile properties,
- Swelling percentage,
- Fatigue life,
- Thermal stability

↓

Scanning Electron Microscope (SEM):
- Tensile,
- Fatigue fractured surface
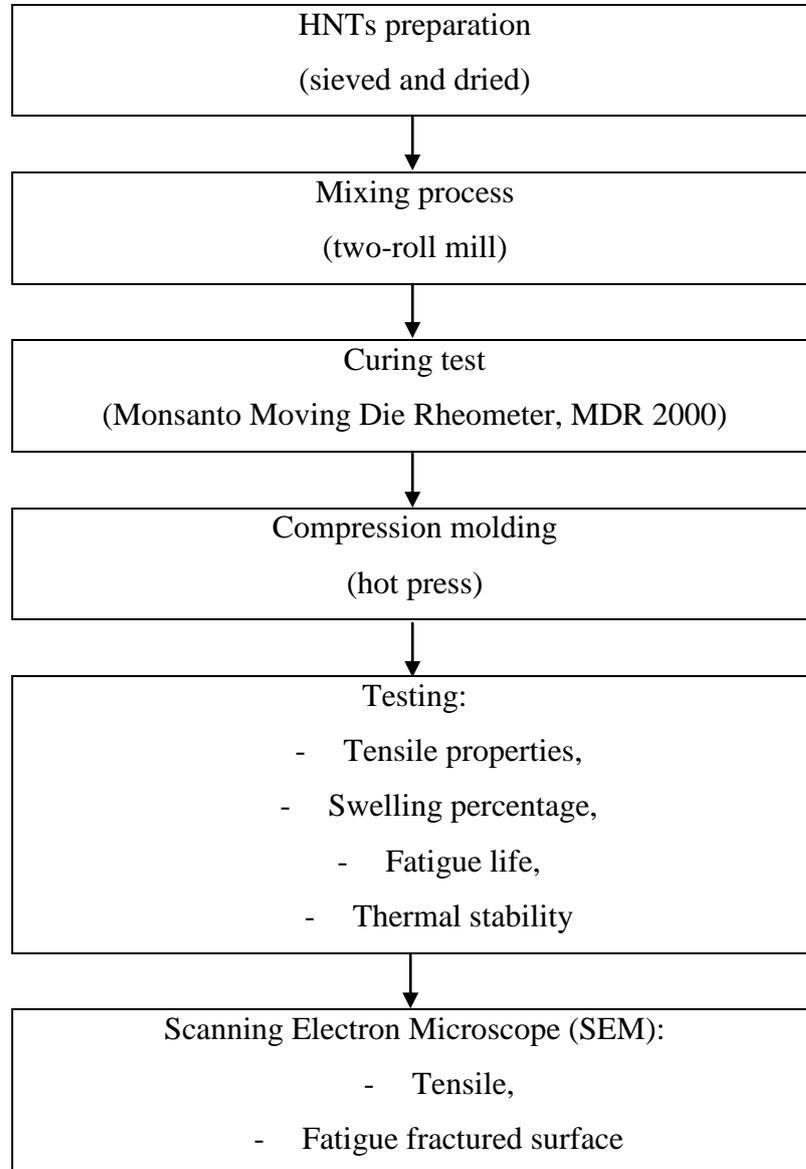
Figure 1.1 Summary for scope of research in this study.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction to rubber

There are many definitions for rubber can be found. Term of elastomers also come along when it's regarding about rubber. Basically, term 'rubber' originally meant the materials obtained from the rubber tree Hevea brasiliensis while elastomer is preferred term for vulcanized rubber (Nagdi, 1993). Generally, Lesko (2008) explained that rubbers and elastomers are materials that return to their original shape after being stretched to several times their length.

However, in more details, rubber and elastomer can be differentiated on the basis of how long a deformed material requires to return to its approximately original size after deforming force is removed and by its extent of recovery (Rosato et al., 2000). Rubber is defined as a material that is capable of recovering from large deformation quickly and forcibly, and which in its modified state, retracts within one minute, to less than 1.5 times its original length after being stretched at room temperature to twice its length and held for one minute before release. An elastomer is defined as a macromolecular material which, at room temperature, is capable of recovering substantially in shape and size after removal of deforming force, with no time is given for full recovery (Lesko, 2008).

Based on the general definition, various materials which show similar behavior just aforementioned can be classified into two main groups, i.e., natural and synthetic rubber (Chandrasekaran, 2007). Natural rubber is polyisoprene extracted

from Hevea brasiliensis (Ciesielski, 1999). While, synthetic rubber may be defined as one built up by chemical means from various substances, and possessing all the chemical and physical properties of natural rubber (Wright, 1908).

Natural rubber exhibits a set of properties which unequalled by synthetic rubber such as higher elasticity, strain-induced crystallization, low heat build-up and also high tack and green strength. High elasticity of natural rubber is owing to it's crystallize ability under strain (100% cis- and associative structure). Strain-induced crystallization is largely due to the stereochemical regularity of macromolecules (natural rubber: 100% cis as shown in Figure 2.1) and such crystallization is reversible, with crystallite disappearing when stretching stops. Moreover, natural rubber is the elastomers with the lowest heat build-up making it unavoidable for dynamical applications with high strain and high frequencies such as tires subjected to heavy strains. Furthermore, high inherent tack and green strength are the most important aspects of processablity of natural rubber. The mechanism responsible for high green strength is strain crystallization which it not active in the bond formation stage and hence does not interfere with contact and interdiffusion, but rather develops upon stretching. High tack of natural rubber is attributed to its great ability to flow under compressive load and its high green strength (Mathew, 2007).
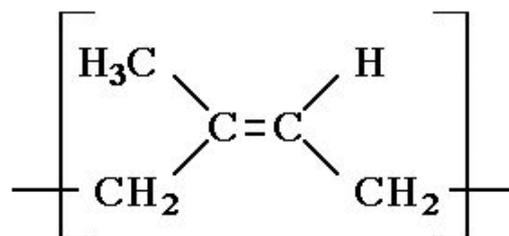
Figure 2.1: General chemical structure of cis-1, 4-polyisoprene (natural rubber).

The exploration of natural rubber expends all the applications in the human necessities. Initially, natural rubber has been used in production of tires widely and any kind of rubber applications. But then, there are many attempts to produce synthetic rubber in order to replace natural rubber. Synthetic rubber production is started during the World War I in German due to inadequate natural rubber from the tropical regions where it produced. Similarly, the massive American effort of World War II was driven by the shortage of natural rubber and accelerated when the Japanese take control of Asian plantation areas (Henderson, 1987).

Currently, synthetic rubber has been conquered around 60% market share of the world's total consumption. The introduction of synthetic rubber has also capped the increase in the prices of natural rubber but reduced the volatility of price fluctuation (Lim, 2004). This definitely due to better properties of synthetic rubber compared than natural rubber. For instance, polyisoprene (IR) is an excellent choice when processing is important while tack and green strength are not critical. IR is gaining favor in medical applications as replacement for natural rubber to eliminate the dangers of patients suffering allergic reactions to the natural proteins and impurities found in natural rubber. Ethylene-propylene-diene (EPDM) is the most widely used when superior resistance to ozone is required. Besides, EPDM also can be highly loaded with low-cost filler, including clays, silica, and carbon black (CB) and talc (School, 2001).

However, due to increase the awareness of renewable and environmental friendly resources caused renewed interest in the development of modified natural rubber (Mathew, 2007). This is because synthetic rubber is obtained from the

petroleum refineries as a by product (Brahman, 2002). Generally, rubber can be produced from petroleum because both are members of vast chemical family of hydrocarbons – carbon and hydrogen in combined form (Dherer, 1942). Thus, exploration modified natural rubber as new choice to replace synthetic rubber is begin.

2.1.1   Natural rubber

There are two generic classifications of natural rubber, the crepes and sheets, and the technically specified grades (TSR) (Day, 2001). The conventional forms of natural rubber, the crepes and sheets, are graded according to the "Green Book", which sets out the International Standards of Quality and Packing for Natural Grades. Grading is by visual examination and is based on the presence or absence of extraneous foreign matter (dirt), bubbles, uniformity and intensity of color, mold and rust spots, and so on. Low dirt content generally reflected for better technological properties but most of the other visual criteria have no technological basis (Subramaniam, 1987).

The introduction of TSR by Standard Malaysian Rubber (SMR) scheme in 1965 is a major step forward in providing natural rubber to guaranteed specifications (Elliot, 1979). TSR are different from crepes and sheets in several aspects, most noticeably in weight of TSR rubber supplied which is in 75 lb bales rather than 250 lb blocks. Moreover, TSR is not graded visually, but by chemical test (Day, 2001). The advantages of TSR include assurance of quality for important technical parameters, consistency in quality, and minimum space for storage and clean and

easy to handle packing (Mathew, 2001). Important TSR grades are shown in Table 2.1 (Rodgers and Waddell, 2005).

Table 2.1: Technical Grades of Natural Rubber (Rodgers and Waddell, 2005).

Property	SMR L	SMR CV	SMR 5	SMR 10	SMR 20	SMR 50
Dirt (% maximum)	0.05	0.05	0.05	0.10	0.20	0.50
Ash (% maximum)	0.60	0.60	0.60	0.75	1.00	1.50
Volatile matter (%)	0.80	0.80	0.80	0.80	0.80	0.80
Nitrogen (%)	0.60	0.60	0.60	0.60	0.60	0.60
Plasticity	30.00	-	30.00	30.00	30.00	30.00
[1]PRI, %	60.00	60.00	60.00	50.00	40.00	30.00
Color index	6.00	-	-	-	-	-
Mooney Viscosity	-	60.00	-	-	-	-

[1] PRI: Plastic retention index

As can be seen in Table 2.1, all grades show lowered limit for nitrogen and volatile matter. The volatile matter is limited to a maximum 0.80% which is an assurance that the rubber is adequately dried and this should be reduce, if not eliminate, the occasional bale that is found contain wet patches, which has been a sporadic problem in the past. Plasticity retention index (PRI) is a measure of raw-rubber oxidisability, high values indicating greatest resistance to oxidation (Elliot, 1979).

2.1.2 Epoxidized natural rubber (ENR)

Modified natural rubbers can be done by physical and/or chemical means which resulted in several suitable forms for specific processes and applications. These included viscosity-stabilized rubber, thermoplastic natural rubber, oil-extended natural rubber (OENR), epoxidized natural rubber (ENR), graft copolymers and chlorinated rubber and liquid natural rubber (LNR) (Kurian and Peter, 2007). Modified natural rubber products have attained some applications such as chlorinated

rubber is used as an adhesive for metal to rubber bonding and for chemically resistant paints while ENR is the most attractive from both a technical and economic point of view (Feldman and Barbalata, 1996).

The most important modification of natural rubber is perhaps ENR. ENR can be produced by epoxidizing natural rubber in the latex stage by reaction with formic acid and hydrogen peroxide. It may called as ENR 10, ENR 25, and ENR 50 which contain 10 mole %, 25 mole % and 50 mole %, respectively, of epoxide groups (Subramaniam, 1987). Commercially, there are two forms of ENR available in market which is ENR 25 and ENR 50 (Liu, 1999). General structure of ENR is shown in Figure 2.2 (Karak, 2009).
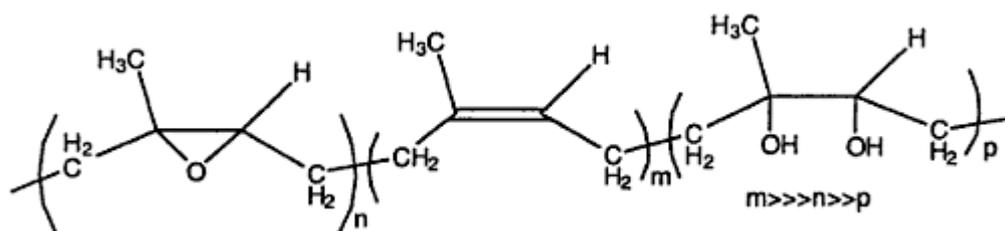
Figure 2.2: General chemical structure of epoxidized natural rubber (ENR) (Karak, 2009).

The modification of natural rubber by replaced unsaturated backbones with epoxy groups progressively shows improvement in certain properties. ENR has unique set of properties which offering high strength, due to ability to undergo strain crystallization, along with increased glass transition temperature and solubility parameters. These properties are reflected as increased oil resistance, enhanced adhesive properties and a high degree of damping and reduced gas permeation (Gelling, 1991).

Besides that, filled ENR has been popular research subject due to the versatility of ENR to accept numerous types of fillers. For instance, silica filled ENR has show significant improvement in tensile and tear strength without using coupling agent (Mohd Ishak and Bakar, 1995).

2.2   Rubber compound

Traditionally, a typical manufacturing sequence comprises mixing, forming, and vulcanizing in the rubber manufacturing industry. The compounding of rubber products starts with the choice of elastomers, filler (filler or extending), crosslinking chemical, and various additives which, when mixed together, will provide a compound with the desired properties and performance (Ciullo and Hewitt, 1999). Table 2.2 shows the proportions of various ingredients for most rubber products where the base rubbers are considered as 100 parts by weight (Chandrasekaran, 2007).

Table 2.2: Various ingredients in rubber compounds (Chandrasekaran, 2007).

Ingredient	Parts per hundred rubber (phr)
Base rubber or blend of rubbers	100.00
Vulcanizing agent (sulfur)	0.50 – 40.00
Accelerator	0.50 – 5.00
Activator	1.00 – 5.00
Antioxidant	0.50 – 2.00
Reinforcing fillers, carbon black, and minerals	25.00 – 200.00
Processing oils	0.00 – 25.00
Inert fillers	25.00 – 200.00
Coloring additives	1.0 – 5.00

2.2.1   Mixing process

Mixing is defined as a process which reduces the composition nonuniformity or inhomogeneity of a mixture of two or more components (Gupta, 1998). In general, four unit processes are involved in mixing process, each requiring separate

consideration; mastication, incorporation, dispersion and distribution (Nakajima, 2000). The first step in rubber compounding is mastication or polymer "breakdown" (Ciullo and Hewitt, 1999). During mastication, natural rubber chains break, resulting in a substantial decrease of molecular weight (Nakajima, 2000). The viscosity of natural rubber must be reduced to produce good mixing and processing (Martin, 1997).

Then, incorporation is a process where filler particles become included inside the rubber. The rubber fills the voids space and cavities in the filler agglomerate where rubber-particle complex acts as a single deformable unit under the application of shear in mixing equipment. Dispersion is a process where filler such as carbon black pellets and their fragments, agglomerates are broken down to the primary units called aggregates. If the filler particles do not get incorporated into the rubber matrix, its dispersion cannot be achieved. Distribution corresponds to mixing in the usual sense except that it is homogenization on the macro-scale (Nakajima, 2000).

These steps are accomplished essentially trough the application of very high shear force and pressure through a specific design of mixers (Gupta, 1998). The most common equipment used for mixing process are two-roll mills, internal batch mixers, continuous mixers, extruders or combination thereof (Melotto, 1997).

Definite time, temperature range and sequence schedule are important factors when using two roll mill as mixer. Besides, the space between the rolls is increased at intervals to maintain a constant bank. In addition, powders that drop into the mill tray are swept to the front by the operator and added back to the mix. During the

mixing operation, cutting and blending is carried out in order to obtain a thorough and uniform dispersion of the ingredients in the rubber mix (Nagdi, 1993).

2.2.1 Forming

After mixing, the compounded rubber is plastic and is now ready to be formed into a shape for vulcanization. The most common process is by molding under pressure in a heated molding such compression, transfer and injection molding (Thomas and Stephen, 2010). The other methods are extrusion or calendering.

In compression molding, mixed compound is added in the form of slabs directly into a mold, which is subsequently closed to shape the desired part. In injection molding, a rubber strip is fed into a chamber or reciprocating screw which meters and injects the rubber compound into a mold. Transfer molding combines features of both (White, 1995). Extrusion is used to form final product in the case of hoses, tubes and profiles, and many tire components are extruded before being built into a tire. The extruder itself has two main functions: to pump the rubber compound through the barrel and to generate enough pressure in the process to force the material through a die to give the required cross-sectional shape. Calendering machines are used to produce continuous sheets from rubber compounds, sometimes incorporating reinforcing materials such as textile or wire cord, and for impregnating or coating fabrics with compound (Johnson, 2001).

2.2.2 Vulcanization

Sulfur vulcanization takes places in three stages: induction, curing and reversion or overcure (Martin-Martinez, 2002). Induction period is the time elapsed

before crosslinking starts. Sufficient delay or scorch resistance in needed to permit mixing, shaping and forming, and flowing in the mold before vulcanization. Scorch resistance is usually measured by the time at a given temperature required for the onset of crosslink formation as indicated by an abrupt increase in viscosity (Coran, 2005). At the second stage, cure time is the time required for the compound to reach a state of cure where the desired balance of properties has been attained. When a compound is cured beyond the point where its balance of properties has been optimized it becomes overcured. For most elastomers, overcure means the compound becomes harder, weaker and less elastic (Hewitt, 2007).

During vulcanization, the changes may occur is long chains of rubber molecules become crosslinked by reactions with the vulcanization agent to form three-dimensional structures where soft, weak plastic-like material transform into strong elastic product. In addition, rubber loses its tackiness and becomes insoluble in solvents and is more resistant to deterioration which normally caused by heat, light, and aging processes (Stephens, 1987).

Stephens (1987) outlined eight significant methods for vulcanization techniques which are compression molding, transfer molding, injection molding, open cure, continuous vulcanization processes (C.V.), cold vulcanization, high-energy radiation and microwave vulcanization. However, there are three important variants of the methods: compression, transfer and injection where compression mold is the most widely used. Basically, the vulcanizing process applied heat at an elevated temperature for a given time to cure the product so it takes up a shape in mold (Ma et al., 2009).

2.3 Compounding ingredients

As aforementioned, rubber products greatly depend on the types of rubber used as matrix. However, the properties of rubber products also can be modified through appropriate selection of compounding ingredients. Careful selection of compound ingredients may show major impact in final properties. Hence, various functions of compounding ingredients are required such as activator, accelerator, vulcanization agent, antidegradant, and miscellaneous ingredients.

2.3.1 Vulcanization agents

Materials that are able to form crosslinks between polymer chains may be generally classified as vulcanizing agents (Datta and Ingham, 2001). Vulcanization converts a substance that is plastic and moldable into one that is flexible and elastic (Ciullo and Hewitt, 1999).

There are several types of vulcanization system used in rubber industry dependent on the rubber used. Vulcanization agent can be grouped into two main groups: sulfur and related elements and nonsulfur vulcanization. Sulfur exists in two forms, rhombic and amorphous (or insoluble). Rhombic form is normally used for vulcanization where it exists as a cyclic (ring) structure composed of eight atoms of sulfur while the amorphous form is actually polymeric in nature; it is a metastable high polymer. In addition, two other elements in the same periodic family as sulfur, namely selenium and tellurium also capable of producing vulcanizations (Stephens, 1987).

For sulfur system, there are three main systems in terms of the usage of sulfur in the vulcanized network namely conventional (CV), efficient (EV) and semi-efficient (Semi-EV) vulcanization systems as shown in Table 2.3 (Datta, 2001). For EV system, low or even zero level of sulfur with high level of accelerator and possibly a sulfur donor is used. In this system, resultant natural rubber vulcanizates has a high proportion of mono- and disulphide crosslinks and low degree of main-chain modifications giving high resistance to thermal and oxidative ageing. While the conventional system show natural rubber vulcanizates with high proportion of main-chain modifications. This gives poor resistance to thermal and oxidative ageing (Rodger, 1979). High sulfur level and low accelerator concentration used in CV system forming polysulfidic crosslinks in natural rubber vulcanizates and thermally unstable and readily oxidized. However, have better fatigue resistance. In Semi-EV system, which are intermediate between EV and CV system, are a compromise between resistance to oxidation and required product fatigue performance (Rodgers and Waddell, 2005).

Table 2.3: CV, Semi-EV and EV vulcanization systems 3 (Datta, 2001).

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
CV	2.0 - 3.5	1.2 – 0.4	0.1 – 0.6
Semi-EV	1.0 – 1.7	2.4 – 1.2	0.7 – 2.5
EV	0.4 – 0.8	5.0 – 2.0	2.5 – 12

Generally, sulfur is the most commonly used as curing agent for unsaturated rubber, particularly for diene rubbers such as natural rubber, styrene-butadiene rubber (SBR), polybutadiene, nitrile, polychloroprene, and polyisoprene and not suitable for saturated rubber. While, alternate curing system is required for elastomers with chemically saturated backbones because they cannot be crosslinked with sulfur (Ciullo and Hewitt, 1999). The system used for saturated elastomer is

called nonsulfur vulcanization agents. Most nonsulfur vulcanization agents belong to one of three groups: metal oxides, difunctional compounds or peroxides (Stephens, 1987).

2.3.2 Activators

The rate at which sulfur reacts with unsaturated polymer can be accelerated by activators: a metal oxide plus fatty acid. The most common combination is zinc oxide (ZnO) and stearic acid, with the fatty acid solubilizing the zinc in the elastomers. Zinc oxide is inorganic activator (lead and magnesium oxides are alos used, but less often), while stearic acid is the organic activator (To, 2001). It is believed that the sulfur reacts, in the presence of metal, as a cation at the double bond. This results in charged and uncharged polysulfides, the latter of which could form free radicals. Metal activated vulcanization will proceed more rapidly than crosslinking by sulfur alone, but still too slow for most production purposes. The metal oxide/fatty acid is, in practice, used not to activate the sulfur itself, but to activate the organic compounds used as vulcanization accelerators (Ciullo and Hewitt, 1999). In other words, activators help accelerators in vulcanization process (Chandrasekaran, 2007).

2.3.3 Accelerators

Accelerators are products which increase both the rate of sulfur crosslinking in a rubber compound and crosslink density (Rodgers and Waddell, 2005). This indicates function of accelerator not only to speed up the vulcanization, but also to increase the efficiency of vulcanization by encouraging useful mono- and disulphide crosslinks to form, rather than to waste sulfur in forming ineffective polysulfide

crosslinks and cyclic structures (Alger, 1997). The choice of accelerator will affect the scorch (premature vulcanization) safety, the cure rate, and the length and number of crosslinks which form (Ciullo and Hewitt, 1999).

There are many accelerators available which has been grouped into several classes. Accelerators may be classified in several ways: inorganic or organic, acidic or basic, by chemical types or by speed of the cure, giving rise to the terms slow, medium, semi-ultra and ultra (Datta, 2001).

Most accelerators fall into one of eight groups: aldehydeamines, thioureas, guanidines, thiazoles, sulfenamides, dithiocarbamates, thiurams and xanthates (Rodger and Waddell, 2005). Accelerator in the same group may exhibit similar or different speed of cure. For instance, diphenyl guanidine (DPG) and triphenyl guanidine (TPG) are in the same group but DPG show medium accelerator while TPG show slow accelerator activity. Mercaptobenzothiazole (MBT) and dibenzothiazyl disulfide (MBTS) from thiazoles group also act differently where MBT show semi-ultra accelerator while MBTS exhibit semi-ultra (delayed action) accelerator (Ghosh, 2002).

2.3.4 Antidegradants

An antidegradant is a compounding material used to retard deterioration caused by oxidation, ozone, light or combinations of these (Ciesielski, 1999). Unsaturated elastomers such as NR, SBR, polybutadiene rubber (BR), nitrile rubber and neoprene usually need antidegradants. This is because unsaturated elastomers containing unsaturated bonds with allylic or tertiary benzylic hydrogen atoms are

somewhat reactive and more prone to degradation. The degradative results may due to chain scission which caused loss of physical properties, or increased in stiffness and hardness due to extra crosslinking formation, or catastrophic failure in fatigue cracking during dynamic flexing and/or surface cracking and crack growth when rubber is under stress particularly when stretched either under static or dynamic conditions (Ignatz-Hoover, 2001).

There are two main classes of antidegradants used in rubber which are antioxidants and antiozonants. Antioxidants belong to the class of compounding ingredients known as protective agents, responsible to remove free radicals which are generated by the interaction of oxygen and the polymer at elevated temperature (Simpson, 2002). Oxidation is a cyclic free radical chain process that proceeds by two mechanisms: chain scission of the polymer backbone causes softening and weakening while radical-induced crosslinking causes hardening and embrittlement. For instance, chain scission is the primary mechanism in natural rubber while crosslinking is predominant with styrene-butadiene rubber (SBR) (Ciullo and Hewitt, 1999). Hence, the addition of antioxidant acts either by interrupting chain reactions or by preventing free-radical formation (Fishbein, 1983). The chemical structure of 2, 2 methylene-bis-(4-methyl-6-tert-butylphenol) (BKF) is shown in Figure 2.3.
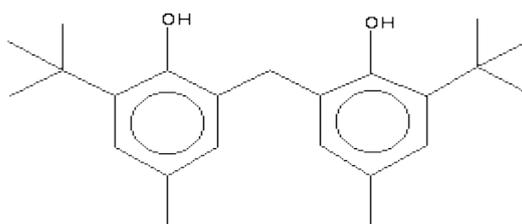

Figure 2.3: Chemical structure of 2, 2 methylene-bis-(4-methyl-6-tert-butylphenol) (BKF).

Antiozonants is an ingredient to protect rubber compound against the deteriorating influence by ozone, the function of antiozonants is not limited to protection against ozone attack, but also give high protection against oxidative and thermal degradation, and against fatigue failure (flex cracking) (Simpson, 2002). The most widely accepted class of antiozonants is derivatives of para-phenylenediamine (PPD) and general structure is shown in Figure 2.4 (Birdsall et al., 1991).
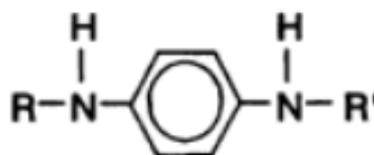

Figure 2.4: General structure of para-phenylenediamine (PPD).

2.4 Fillers

The use of fillers in rubber products is nearly as old as the use of rubber itself (Ciullo and Hewitt, 1999). Wide variety of fillers is added into rubber matrix in order to modify the properties of rubber. It can be to improve cured physical properties, reduce cost, and/or impart color to the rubber products (Waddell and Evans, 2001).

Fillers can be divided into three main groups; reinforcing, semi-reinforcing or non-reinforcing fillers (Sae-Oui et al., 2009). Reinforcing fillers are ingredients added which increase stiffness, hardness, strength of rubber and its resistance to abrasion, cutting and tearing. Their effect in rubber is not chemical but physical depending mainly on the fineness and the homogeneous dispersion in rubber. Carbon black, zinc oxide, magnesium carbonate, silica and China clay belong to the reinforcing class of filler (Chandrasekaran, 2010). Semi-reinforcing filler is a particulate material that is able to increase tensile strength and tear strength but does

not improve abrasion resistance (Skelhorn, 2003). Fillers that only lead to small increases in viscosity of the compound, cause deterioration of the mechanical properties of the vulcanizates, and do not exhibit any reinforcing action are called non-reinforcing or inactive fillers (e.g., calcium silicate, chalk powder, etc) (Kim et al., 2011).

Filler properties that have the most influence on rubber processing and vulcanization are particle size, surface area and character, and structure (Arayapranee and Tempel, 2008). Generally, smaller particulate filler impart greater reinforcement. Besides, particle with a high aspect ratio has higher reinforcement than a more spherical one (Wagner, 2011). Polymer-filler bonding can be physical or chemical interaction. These interactions such carbon black in rubber lead to formation of high modulus compound even in the absence of coupling agent which is a very clear indicator that polymer-filler bonding has taken place. Particle shape may provide further changes in reinforcement. Overall, the effect on reinforcement is relatively small. Particle complexity has more pronounced effect on processing behavior than on reinforcement and provides important benefits in this area (Skelhorn, 2003).

2.4.1   Halloysite nanotubes (HNTs)

Clay minerals may be liberated by the breakdown of geological mudstones and clays. However, in natural soils, most are the products of chemical weathering. Clay minerals are composed of hydrated aluminium, iron or magnesium silicates that are combined in complex crystalline structures. The main building blocks of the clay minerals have been portrayed as layers of silica tetrahedral, involving silicon cations and 4 oxygen anions and aluminium octahedra involving 6 hydroxyl or oxygen

anions and cations of aluminium, or sometimes magnesium, calcium etc (Haigh, 2000).

Clay minerals, on the basis of their crystalline arrangement, can be divided into three main groups. It is observed that more or less similar engineering properties are exhibited by all clay minerals belonging to a particular group. The group of minerals and the most important clay minerals in each of these groups can be seen in Table 2.4 (Ranjan and Rao, 2007).

Table 2.4: Clay minerals (Ranjan and Rao, 2007).

Name of mineral and group	Structural formula
Kaolin group	
a) Kaolinite	$(OH)_4.Al_4Si_4O_{10}$
b) Halloysite	$(OH)_4.Al_4Si_4O_{10}.4H_2O$
Montmorillonite group	
Montmorillonite	$(OH)_4.Al_4Si_4O_{20}.nH_2O$
Illite group	
Illite	$(OH)_4K_y(Si_{g-y}Al_y)(Al_4.Mg_6.Fe_4.Fc_6)O_{20}$

As can be seen in Table 2.4, halloysite is one of clay in kaolin group just like kaolinite. Halloysite is defined as two layered aluminosilicates, chemically similar to kaolin, which has predominantly hollow tubular structure in the submicron range. Interlayer water in HNTs is one of the most important features distinguish HNTs from kaolinite (Du et al., 2010). The physical appearance of HNTs is very similar to that CNTs, but the cost of HNTs is much lower (Ng et al., 2011). Figure 2.5 show typical schematic diagram for HNTs. Beside, HNTs may exist in two forms. Firstly, may exist as hydrated halloysite with basal spacing (d_{001}) of 10Å. However, due to interlayer water weakly held, so that halloysite (10Å) can readily transform to halloysite (7Å) which also known as methahalloysite (Yuan et al., 2008).