



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber (NR)

Despite the commercial existence of synthetic rubbers for more than 50 years, NR is still flexing its muscles as a practically irreplaceable elastomer in a great deal of rubber products. It remains the most often used type of elastomer. In the present, transportation and engineering industries cannot survive without NR. In the tire production, tire for passenger cars is composed with NR ca. 40%; while, the heavy duty tires have NR content higher than 60%. An aircraft and earthmover tires are consisted of almost 100% NR. The use of NR in non-tire products such as belting and latex gloves has also increased in the past two decades. The current world elastomer consumption, totaling around 18 million tons per year, consists of 40% NR (solid and latex), 20% SBR (solid), 12% SBR (latex), 12% Butadiene, 5% EPDM, 2% Chloroprene, 2% Nitrile and 7% other synthetics (Budiman, 2002).

The most common source of NR is obtained by tapping the *Hevea brasiliensis* or Para rubber tree. Natural rubber latex consists of rubber hydrocarbon particles and non-rubber components suspended in an aqueous phase. A typical composition of a NR latex and dry rubber is shown in Table 2.1. The structure of NR mainly consists of over 99.99% of linear *cis*-1,4 polyisoprene as shown in Figure 2.1 (Hofmann, 1989).

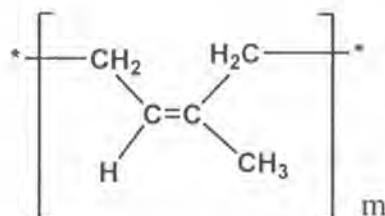


Figure 2.1 Chemical structure of NR.

Table 2.1 Typical composition of fresh latex and dry rubber (Morton, ed., 1999)

	Latex (%)	Dry Rubber (%)
Rubber hydrocarbon	36	93.7
Proteins	1.4	2.2
Carbohydrates	1.6	0.4
Neutral lipids	1.0	2.4
Glycolipids + phospholipids	0.6	1.0
Inorganic constituents	0.5	0.2
Others	0.4	0.1
Water	58.5	-

NR has a very uniform microstructure providing some very unique and important characteristics: ability to crystallize under strain (strain – induced crystallization) and very low hysteresis. NR is normally applied to products requiring high tensile strength, high resilience, excellent flexibility, high impact and tear resistance with low heat-build-up, good “green” strength and building tack (Budiman, 2002). However, the structure of NR has high unsaturation level that is susceptible to be degraded when it is exposed to heat, oxygen and ozone. This is great restriction to use NR in an outdoor application since heat and ozone are the main factors for rubber deterioration.

2.1.1 The Ageing of NR Vulcanizates

Ageing is a collective term for changes in properties of materials that occur on longer-term storage without the action of chemicals. It can lead to partial or complete degradation of a material structure. These changes can be occurred by degradation processes, fatigue processes and static crack formation (Hofmann, 1989). Basically one can differentiate the following ageing process.

Shelf ageing is basically oxidative degradation and apart from the obvious influence of oxygen. One must consider the catalytic effects of heat, light, internal and

external stresses or strains and pro-oxidant metals. The reaction of oxygen with NR causes both chain scission and crosslinking. For chain scission occurred during aging, elastomer softens and eventually may become sticky. However, most types of sulfur-cured vulcanizates initially harden and embrittle during oxidation resulting from the dominant crosslinking reactions (Hamed, 2001).

Atmospheric ageing differs from shelf ageing in that it is characterized by the attack of ozone on the rubber with different reaction mechanism (Loadman, 2008). Ozone, readily cleaves carbon-carbon double bonds in NR, even the content of ozone is only a few parts per hundred million in the atmosphere. As a result, NR exposed to ozone under strained state can quickly develops the cracking traces on the surface of rubber specimens. The severity of cracking rapidly increases if the level of applied strain is above a small threshold level.

2.1.2 The Chemical Modification of NR

NR has poor ageing properties, wet grip properties and weathering resistance. Thus, chemical modifications of NR were carried out to improve these important properties. The chemical modification can be performed either in latex, in solution or in the dry phase. Three types of chemical modification of NR can be distinguished as follows (Gelling and Porter, 1988):

1. Modifications via bond rearrangements in NR molecules: carbon-carbon cross-linking, cyclisation, *cis*, *trans*-isomerisation, depolymerisation and hydrogenation.
2. Functionalization via attachment of new chemical groups onto rubber chains through addition or substitution reactions at olefinic double bonds: chlorination, hydrochlorination and epoxidation.
3. Grafting of chains by a second polymer onto a NR backbone: graft copolymerization of vinyl monomers such as methyl methacrylate (MMA) and styrene onto NR.

2.2 Hydrogenated Natural Rubber

Hydrogenated NR (HNR) is more stable against thermal, oxidative and radiation induced degradation because its structure is highly saturated. Moreover, the structure of HNR looks like an alternating copolymer of ethylene and propylene as shown in Figure 2.2 (Hinchiranan et al., 2006). The preparation of hydrogenated products can be generally performed by using 3 methods: non-catalytic hydrogenation, homogeneous catalytic hydrogenation and heterogeneous catalytic hydrogenation. Table 2.2 shows a comparison of product yield including side reactions and the case of catalyst removal among these methods.

From the previous works, it was found that $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was the effective catalyst for hydrogenation of NR to provide a high level of hydrogenation ($> 95\%$ hydrogenation) (Hinchiranan et al., 2006). The addition of some acids and certain nitrogen containing material also showed an effect on the rate of NR hydrogenation. The results of thermal properties of HNR indicated that the thermal stability of NR increased with increasing % hydrogenation. On comparison with EPDM, it was found that decomposition temperatures of almost completely HNR were close to those of EPDM.

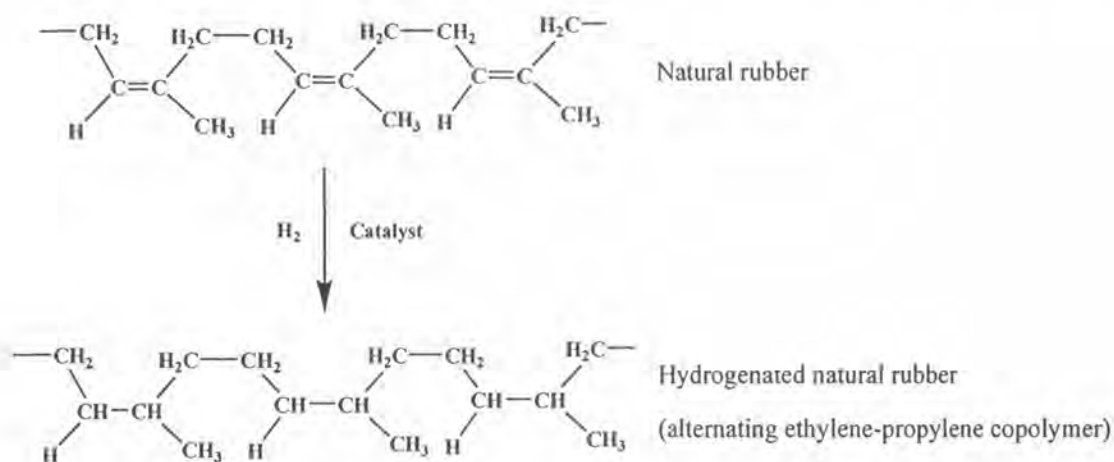


Figure 2.2 Structure of NR before and after hydrogenation (Hinchiranan et al., 2006).

Table 2.2 A comparison of hydrogenation methods for diene-based elastomers (Hashim et al., 2002)

Methods	Yield	Side reactions hydrogenated products	Catalyst poisoning and removal
Non-catalytic hydrogenation	Low hydrogenation level with (<40% hydrogenation).	Isomerisation, attachment of hydrazine fragments.	No poisoning or catalyst removal issue.
Homogeneous hydrogenation	High yield of saturated products with high hydrogenation level ($\approx 100\%$ hydrogenation).	Degradation of during operation.	Easily poisoned by impurities and difficult to be removed.
Heterogeneous hydrogenation	Yield purer products	Difficult to degrade hydrogenated products during operation. Promote the foreign groups during hydrogenation.	Possibly poisoned by impurities during catalyst preparation step.

2.2.1 Properties of HNR Vulcanizates

The mechanical properties of HNR vulcanizates with three levels of hydrogenation (20.6, 29.0 and 40.6 mol%) were reported by Ikeda et al. (2008). The the tensile properties of HNR vulcanizates with these three hydrogenation level were comparable to that of NR. With increase in the degree of hydrogenation in HNR, the stress at low stretching ratio became larger. The hydrogenation of 20.6 mol% of *cis*-1,4-isoprene units in NR did not alter the excellent tensile properties of NR. Also, dynamic mechanical properties of the vulcanizates were not much changed. The glass transition temperature of HNR vulcanizates was almost constant and almost equal with that of NR vulcanizate, in spite of the change of hydrogenation degree up to 40.6 mol%. The thermal stability of HNR vulcanizates was also better than that of NR vulcanizates.

Inoue and Nishio (2006) studied properties of 100% hydrogenation of HNR vulcanizates. On comparison with NR vulcanizate, it was found that the hardness of HNR vulcanizate was higher; while, the tensile strength and elongation at break of HNR vulcanizates tended to be lower. Vulcanized HNR at 100% hydrogenation showed a low glass transition temperature ($T_g = -43^\circ\text{C}$) and excellent abrasion resistance including good resistance to oxidation and ozonolysis ageing.

2.3 Elastomer Blends

Blends of elastomers are technological and commercial importance since they allow users to access properties of the final blends and vulcanized elastomers that are not accessible from a single commercially available elastomer alone. These potentially improve properties including chemical, physical and processing benefits. All blends show compositionally correlated changes in all of these properties compared to each component in the blends. The technology of elastomer blends is largely focused on the choice of individual elastomers and the creation of the blends to achieve a set of final properties (Datta, 2005).

2.3.1 Blends of Rubbers Containing Different Degree of Unsaturation

The classic example of blends containing rubbers with different unsaturation degree is NR/EPDM blends. NR has a higher level of unsaturation; while, EPDM is a highly saturated elastomer. The blends of NR and EPDM have been extensively studied for various applications such as tire side walls, light-colored injection-molded products and extruded profile weather-strips (Menon, Sonia and Sudha, 2006). Whilst ozone resistance has been comparatively easy to achieve in blending of NR with EPDM, the general physical and mechanical properties of rubber blends containing different degree of unsaturation are less than satisfactory. This is entirely expected that the physical properties of vulcanized rubber blends are inferior to those predicted from the properties of the component rubbers.

The main problems involving the poor properties of different unsaturation level of rubber blends are a direct result of the relative chemical reactivities of both component. NR is a highly unsaturated elastomer acting as the reactive polymer that

is very susceptible to attack by ozone; whilst, EPDM has a very low level of unsaturation resulting to a high resistance to ozone attack. In a NR/EPDM blend, such a disparity in reactivity is reflected in the relative rate of crosslinking during vulcanization. The diffusion of curatives to NR phase is normally faster than that to EPDM phase. Consequently, NR is more ready to be vulcanized than EPDM. The lower solubility of many curatives in EPDM as compared with NR further reduces the crosslink formation in the EPDM phase. Therefore, these factors give a blend having a highly crosslinked NR phase with a very poorly crosslinked EPDM phase (Cook, 1998).

2.3.1.1 Approach to Properties Improvement of NR/EPDM Blend

There have been several attempts to approach the properties improvement of the NR/EPDM blends since over the past 25 years. Generally, these approaches have sought to increase the cure rate of EPDM. Menon and Sudha (2006) studied the effect of variations in the dosage of phosphorylated cardanol prepolymer (PCP) on melt processability and physico-mechanical properties of unfilled and china-clay-filled NR/EPDM blends. The decrease in the power consumption of the mixing and activation energy of melt flow indicated an improvement of the processability of the blends in the presence of PCP possibly due to the plasticization effect of the additives in the rubbers. The increase in the tensile properties and tear strength with low crosslink density index of the vulcanizates in the presence of PCP was presumably resulted from the participation of PCP in the crosslinking reaction with the rubbers. This also promoted the better dispersion of filler particles in the rubber matrix. At 5 phr of PCP was also found to enhance the thermal stability of the vulcanizates.

Compatibility of NR/EPDM can be enhanced by the addition of a third polymeric component such as polybutadiene (BR), chlorinated rubber, chloro-sulfonated polyethylene (SPE) and polyvinyl chloride (PVC). Abou-Helal and El-Sabbagh (2005) reported that the addition of the third polymeric component into NR/EPDM blend greatly increased their compatibility resulting in the improvement of the rheological, physical and dielectric properties of the blends. Similar work was also

studied by Chang et al. (1998). They indicated that *trans*-polyoctylene rubber (TOR) melt-blended with an incompatible NR/EPDM blend showed the enhancement of homogeneity. This was induced by the encapsulation of the low viscosity component TOR onto the NR and EPDM phases during mixing and by formation of interfacial crosslinking during the vulcanization process. Fine dispersion of EPDM particles in the NR matrix achieved by the addition of TOR led to a significant increase in the ozone resistance of the NR/EPDM blend. Addition of TOR into the NR/EPDM blend also improved the dynamic properties and modulus with a slight reduction in tensile strength and elongation at break of NR/EPDM vulcanizates.

The use of dithiophosphate accelerators such as bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) with high solubility in both NR and EPDM phases could enhance the physical and mechanical properties of NR/EPDM blends obtained from a two-stage vulcanization technique as well as by judicious selection of the NR to EPDM ratio (Ghosh et al., 2001). The results exhibited the coherency and homogeneity in the blends. Thus, the cure-rate mismatch problem could be solved through the formation of rubber bound intermediates with a multifunctional additives (i.e., DIPDIS), which restricted the curative migration from lower to highly unsaturated rubber. The blend morphology as revealed by scanning electron microscope (SEM) also showed the significant improvement in physical properties of the NR/EPDM vulcanizates particularly obtained from the two-stage vulcanization technique.

All of the EPDM modification methods as described above achieves a significant improvement of the physical and mechanical properties of NR/EPDM blends. The introduction of reactive sites in EPDM enhanced the cure properties and increased the rate of vulcanization in the EPDM phase to consequently promote the higher level of crosslinking. However, it should be noted that only one of the EPDM modification procedures recorded above was achieved in an internal mixer. The reagents and conditions required for modification are hardly suitable for large scale mixing in a factory environment. The graftization of the accelerators such as bis-alkylphenoldisulphide (BAPD), dithiodicapro lactam (DTDC) and dithiodimorpholine (DTDM) has been used to modify EPDM by mixing at elevated temperatures in an internal mixer as part of a normal masterbath mixing cycle. This procedure has been

termed as “reactive mixing”. Although the crosslink densities in the modified EPDM phase in the NR /EPDM blends vulcanized by sulfur system was low, there are commensurate to increase in the modulus and tensile strength of the NR/EPDM vulcanizates (Cook, 1998).

Ray, Jha and Bhowmick (1997) and S.H. Botros (2002) also reported the modification of EPDM structure with maleic anhydride in the internal mixer at high temperature. Blending of modified EPDM with NR by subsequently dynamic vulcanization of EPDM at high temperature phase was found to improve the mechanical properties of the blend without affecting the ageing properties.

2.3.1.2 Properties of HNR/NR Blends

The cure characteristics and mechanical properties of blends consisting of HNR and NR were investigated by Hinchiranan et al. (2009). The HNR/NR blends at 50/50 wt ratio were vulcanized using various cure systems: peroxide vulcanization (PV), conventional vulcanization with peroxide (CPV) and efficient vulcanization with peroxide (EPV). The blends cured by EPV system exhibited the best mechanical properties. The hydrogenation level of HNR did not affect the tensile strength of the vulcanizates. The tensile strength of the HNR/NR vulcanizates decreased with increasing HNR content due to the higher incompatibilization. The HNR/NR vulcanizate at 50/50 wt ratio had the maximum ultimate elongation. It can be explained that the vulcanizates exhibited a synergistic effect due to the compatibility of the different morphology of HNR and NR at a ratio 50/50.

In addition, they also studied the effect of vulcanization system and blend ratio on the thermal and oxidative resistance of NR/HNR blends (Hinchiranan et al., DOI 10.1002/app.30034). It was found that the combination of peroxide and sulfur donor vulcanization (EPV system) exhibited the highest retention of mechanical properties of vulcanizates after thermal ageing. The increase in HNR content in the blends retarded the surface cracking caused by ozone as presented in Figure 2.3. The decomposition temperatures of NR and HNR phases in HNR/NR vulcanizates were not affected by the rubber blend ratio. This suggested that the

degradation pattern of HNR has no influence on another constituent. The decomposition temperature at 50% mass loss of blends increased with increasing HNR content resulting in a higher thermal stability.



Figure 2.3 Stretched surface of HNR/NR vulcanizates at various rubber blend ratios cured by EPV after exposure to ozonised air of 50 pphm ozone concentration at 40°C for 24 h: (a) HNR/NR = 50/50, (b) HNR/NR = 75/25 and (c) HNR/NR = 90/10 (Hinchiranan et al., DOI 10.1002/app.30034).

2.4 Reactive Compatibilization

A common way to improve the interfacial adhesion and mechanical properties of heterogeneous polymer blends is the addition of a small amount of a compound acting as a compatibilizing or interfacial agent. Block and graft copolymers whose segments are miscible with each polymer phase are normally employed for this purpose (Chapman and Tinker, 2003). However, such copolymers may be formed *in situ* by the addition of appropriate reactive or functional compounds during melt mixing under conditions of high temperature and shearing. This process is known as reactive compatibilization. It is technologically more versatile and economical because of the facility of developing functional polymers as compared to the synthetic processes used for the preparation of graft and block copolymers with a desired macromolecular architecture. In addition, the efficiency of reactive compatibilization to improve the interfacial adhesion is much better than that of common physical compatibilizers (Oliveira and Soares, 2003).

Several functional polymers have been developed by grafting vinyl monomers such as epoxy, maleic anhydride and acrylic acid on the main chain of commercial polymers (Liu et al., 1996, Kim et al, 2001 and Seo and Ninh, 2004).

The use of these functional polymers in blends containing polymers with various functional groups (e.g., hydroxyl, carboxyl, or amine groups) gave the resulting products with improved mechanical performance due to more uniform morphology and higher interfacial adhesion. (Liu et al., 1996, Pagnouille and Jerome, 2001 and Coltelli et al., 2006).

2.4.1 Thioacetate- and Mercapto-Modified Copolymers in Elastomer Blends

The compatibilization of rubber blends might be successfully performed by using a functionalized polymer as a reactive compatibilizer. Recently, literatures reported that diene rubbers could be compatibilized with other components with low unsaturation level by using a small amount of an appropriated mercapto-functionalized copolymer (Oliveira et al., 1999). The reactive compatibilization was based on the thiol-based group of the functionalized copolymers that reacted to the carbon-carbon double bond of the unsaturated rubber during the melt blending process. The chemical reaction between the two phases of a blend promoted an effective anchorage between the rubber phases.

Barbosa et al. (1993) introduced mercapto group along the ethylene vinyl acetate (EVA) backbone by the simple esterification reaction between hydrolyzed EVA and mercaptoacetic acid as shown in Figure 2.4. It indicated that the mercapto-modified EVA (EVASH) improved the interfacial adhesion of elastomer-based blends. For example, vulcanized and non-vulcanized blends of EVA with NR (Jansen and Soares, 1995), NBR (Jansen and Soares, 2000 and Soares and Oliveira, 2003) and SBR (Soares et al., 2001) presented the improved mechanical performance and better ageing resistance in the presence of the small amount of EVASH.

The two steps for preparation of thiol group functionalization onto EPDM structure were reported by Oliveira et al. (1999) as illustrated in Figure 2.5. The first step consisted of a free radical addition of thioacetic acid on the double bond of EPDM. The resulting thioacetate-modified EPDM (EPDMTA) was then hydrolyzed in the methanolic solution to produce EPDMSH in the second step. EPDMSH and

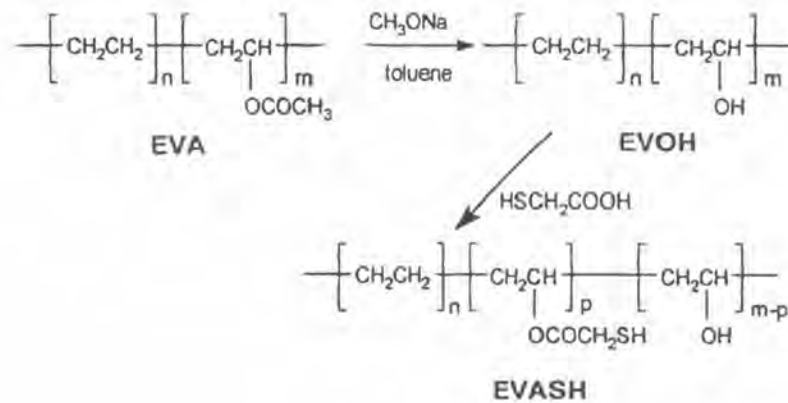


Figure 2.4 Synthetic pathways for preparation of mercapto-modified EVA (Jansen and Soares, 1996).

EPDMTA were used as the reactive compatibilizer for NR/EPDM (Sirqueira and Soares, 2006) and NBR/EPDM blends (Oliveira and Soares, 2001). For NR/EPDM blends (Sirqueira and Soares, 2003), both EPDMTA and EPDMSH acted as accelerators in the curing process resulting to the higher cure rate index with lower activation energy of vulcanization. A substantial increase in the crosslink density was also observed in EPDMSH modified blends. Both EPDMTA and EPDMSH increased tensile strength of NR/EPDM blends. However, the best performance achieved by EPDMSH probably due to the increase in the crosslink density. This could be explained that the reactive compatibilization was promoted by the reaction between mercapto groups and rubber matrix. However, the best ageing resistance was observed in EPDMTA-modified blends.

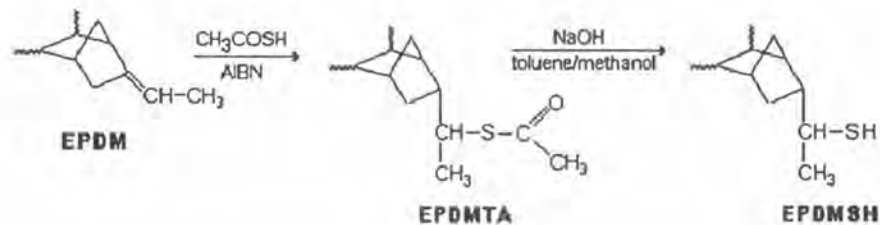


Figure 2.5 Scheme for the functionalization of EPDM (Oliveira et al., 1999).