



## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Natural Rubber

Natural rubber (NR) is mainly obtained from the latex of *Hevea Brasiliensis* tree. The chemical structure of NR has been known as *cis*-1,4-polyisoprene as shown in Figure 2.1 (Morton, 1973). In addition, NR consists of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. The non rubber components include proteins, sugars, alcohols, fatty acids and small amounts of mineral substances. Its composition varies according to the clones of rubber, age of rubber tree and tapping method (Blackley, 1977).

##### 2.1.1 Properties of NR

NR vulcanizates have excellent physical and mechanical properties for serving as a general purpose elastomers. It has high tensile strength, tear strengths, resilience, abrasion resistance and very low heat build-up (Hofmann, 1989). Even after vulcanization, the NR still has carbon-carbon double bonds in the polymer chain. Therefore, it is susceptible to weather, oxygen and ozone resulting to chain scission. This causes the rubber to be softer and weaker (Thavornyutikarn, 1999). Also, NR vulcanizates have poor resistance to swell in the presence of non-polar organic solvents, oil and fuels due to the non-polarity of NR structure. For these reasons, many effort have been applied to improve the properties of NR to be used in wider applications.

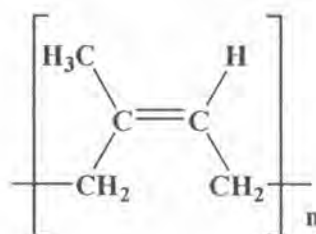


Figure 2.1 Natural rubber or *cis*-1,4-polyisoprene (Morton, 1973).

## 2.2 Properties Improvement Methods for NR

There are two important methods to improve or modify the properties of NR: blending NR with other polymers including both plastics and rubbers (Thavornytikarn, 1999) and chemical modification of NR structure.

### 2.2.1 Blending Method (Sroysom, 1999)

NR is normally blended with other synthetic rubbers (SR) having some properties which cannot be found in NR. For example, NR is blended with ethylene-propylene-diene rubber (EPDM) to improve weathering resistance, or with butadiene rubber (BR) to increase abrasion resistance. NR is also blended with nitrile rubber (NBR) to improve oil and fuel resistance of NR phase with better mechanical properties of NBR phase in the blend. This method is more favorable and economical than the development of new rubber. However, successful blend technology requires a sound scientific basic.

### 2.2.2 Chemical Modification Method (Sroysom, 1999)

The properties of NR can also be improved via chemical modification of its molecular structure due to the presence of carbon-carbon double bonds in its repeating unit. The chemical modification of NR can be achieved by one of the following methods:

- Changing the structure or geometry of NR molecules with introducing some new materials.
- Attaching to the NR structure with some functional chemical groups having specific physical characteristics or chemical reactivities.
- Grafting short or long chains of a different polymer types onto the NR backbone.

## 2.3 Chemical Modification of NR

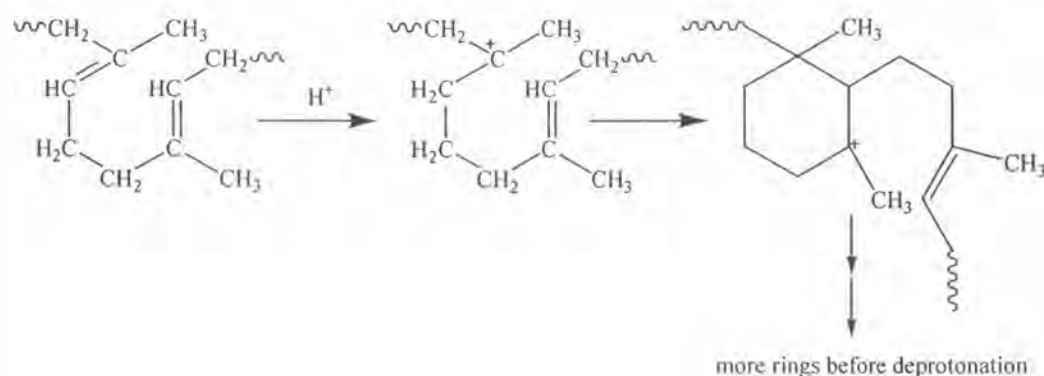
Chemical modifications of NR have been a subject of long interest. There are reviewed below.

### 2.3.1 Cyclization (Subramaniam, 1988: 762-86 cited in Thavornyutikarn, 1999)

Cyclized rubber is obtained by treating the rubber with strong protonic acid or Lewis acids. Cyclization is believed to proceed via the carbenium ion mechanism as shown in Figure 2.2 (Thavornyutikarn, 1999). Cyclized NR is a brittle resin, powder, hand sheet or crepe. It has higher density (sp. gr. = 0.96-0.99) with softening point (90-130°C) and lower solution viscosity than those of NR (sp. gr. = 0.91,  $T_g = -68\text{ }^\circ\text{C}$ ). Actual properties values are depended on the degree of cyclization. Cyclized and partially cyclized NR have been used for shoe soles, hard moulding, corrosion-resistant surface and printing ink. However, they have been mostly replaced by copolymers, e.g., cyclized synthetic *cis*-1,4-polyisoprene.

### 2.3.2 Hydrogenation (Bhowmick and Stephens, 2001)

Complete hydrogenation of NR gives an alternating copolymer of ethylene and propylene. Scheme of NR hydrogenation is indicated in Figure 2.3.



**Figure 2.2** Scheme of cyclization of NR (Subramaniam, 1988: 762-86 cited in Thavornyutikarn, 1999).



**Figure 2.3** Scheme of hydrogenation of NR (Bhowmick and Stephens, 2001).

The NR hydrogenation can be carried out by using catalysts and hydrogen gas passed through NR dissolved in organic solvents. Catalyst systems may be conveniently classified into four groups: metal and supported metal catalysts, noble metal catalysts, organo-metallic systems and diimide generators. Hydrogenated NR (HNR) is more crystalline and has a slightly higher glass transition temperature than that of NR. The HNR vulcanizates with high hydrogenation degree show higher ozone resistance.

**2.3.3 Halogenation** (Subramaniam, 1988: 762-86 cited in Thavornyutikarn, 1999)

Chlorination, one of halogenated rubber types, has been extensively studied. The reaction is complex and may include addition, substitution, cyclization, crosslink and degradation. Chlorinated rubber is not flammable and highly resistance to organic chemicals. A fully chlorinated product is more stable than a partially chlorinated one. It can be applied in printing inks, chemicals and heat resistant surface coating.

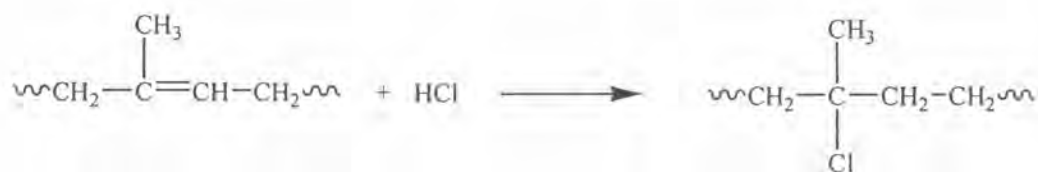
**2.3.4 Hydrohalogenation** (Bhowmick and Stephens, 2001)

Hydrogen chloride is added into NR to give a hydrochloride rubber. The addition follows the Markonikov's rule, but it is also accompanied by some cyclization. Hydrohalogenation of NR is shown in Figure 2.4. Hydrochloride rubber has high crystallinity and it is also a tough semi-elastic material which can be used as a packaging film and a rubber-to-metal adhesive. This kind of hydrochloride rubber is normally produced in a powder form which is unstable. For the hydrochloride rubber with low degree of crystallinity, it shows the elastic properties with higher stability to

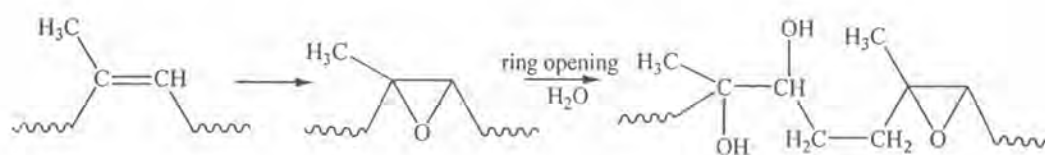
heat and bases. However, this hydrochloride rubber with low crystalline content becomes more brittle material at room temperature. Consequently, it has not been commercially produced.

**2.3.5 Epoxidization** (Subramaniam, 1988: 762-86 cited in Thavornyutikarn, 1999).

NR can be epoxidized by peracids. The epoxidation process rapidly occurs via opening the strained epoxy ring as shown in Figure 2.5. This ring opening reaction is carried out in the presence of hydrogen ions under high reaction temperatures. The epoxidized NR (ENR) is an elastic material with higher density than NR. After epoxidation, the glass transition temperature ( $T_g$ ) of ENR linearly increased by  $1^\circ\text{C}$  for every mole percentage of epoxidation resulting the reduction of resilience and air permeability with higher hysteresis. However, the wet traction of ENR is better. The epoxy groups also increases the polarity to enhance the to hydrocarbon oil resistance. ENR can be potentially applied in engineering components, inner liners of tubeless tyres, oil seals and tire treads.



**Figure 2.4** Scheme of hydrohalogenation of NR (Bhowmick and Stephens, 2001).



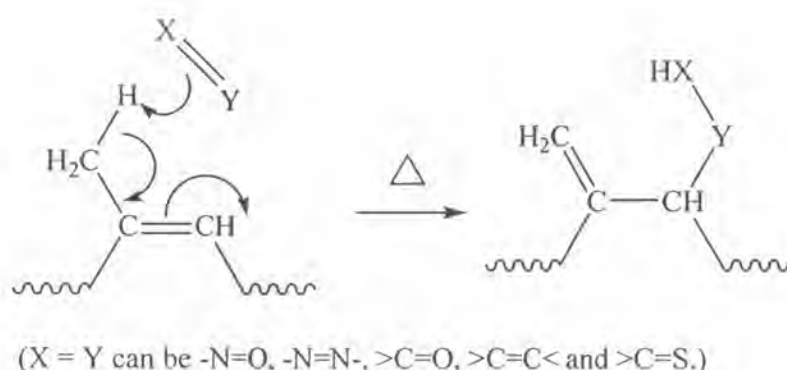
**Figure 2.5** Scheme of epoxidation of NR (Subramaniam, 1988: 762-86 cited in Thavornyutikarn, 1999).

### 2.3.6 Ene Reaction (Bhowmick and Stephens, 2001)

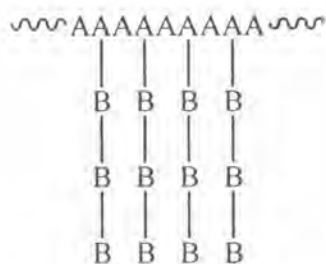
The general ene reaction with NR represented in Figure 2.6 involves both of the direct reaction between molecules and the reaction. This is not related to active species such as ions and free radicals which act as intermediates. The ene reaction applied to NR leads the concept of rubber-bound antioxidants. The initial stage of the ene reaction involves the reaction between the rubber and a nitroso compound. Nitrosoarenes give a hydroxylamine as a main product. Such antioxidants are not leached during washing or solvent treatment. Thus, it may be useful for a rubber tread for garments. However, this process has not been exploited because of the formation of coloured by-products.

### 2.3.7 Graft Polymerization

Graft copolymerization of NR and vinyl polymers is prepared by polymerization of a monomer initiated by free radicals or attachment of a polymer to the rubber backbone. The backbone and the branches polymers may be homopolymer or copolymers with different chemical nature or composition. The simplest case of graft copolymer can be represented by the following structure as shown in Figure 2.7, where A and B are two different monomers. The properties of graft copolymer are different from a random copolymer (ABABABAB) or a physical mixture consisting of two homopolymers from  $(A)_n$  and  $(B)_n$  (Odian, 2004).



**Figure 2.6** Scheme of ene reaction of NR (Bhowmick and Stephens, 2001).



**Figure 2.7** Model of graft copolymer (Odian, 2004).

Normally, there are two methods to synthesize graft copolymers. (Chansook, 2001):

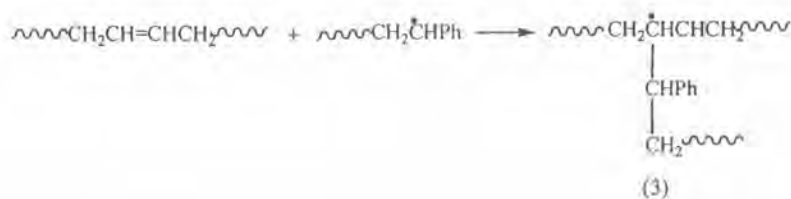
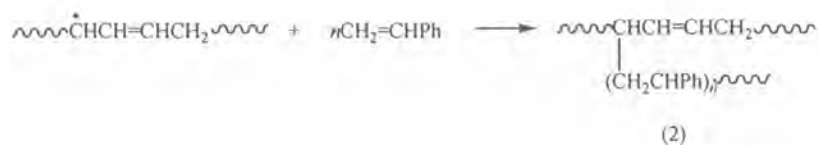
1. The side chain polymer can be directly linked by a suitable chemical reaction to the backbone polymer.
2. The backbone polymer can be initiated to occur active sites such as free radicals or ions to be used for polymerization of suitable monomers resulting the side chain polymer.

### 2.3.7.1 Radical Graft Polymerization.

The radical graft polymerization can be carried out by various methods such as chain transfer and copolymerization, ionizing radiation, redox initiation and living radical polymerization.

#### (a) Chain Transfer and Copolymerization (Odian, 2004)

The chain transfer reaction is the most well recognized and extensively studied for free radical polymerization. For the graft polymerization of polystyrene (PS) onto polybutadiene (PB) (Figure 2.8), the radicals on PB (1) are formed through chain transfer from PS radicals to PB. The resulting product (2) consists of polystyrene grafted on the backbone of 1,4-poly-1,3-butadiene. Polymer radicals are also formed by attacking on a polymer chain by primary radicals from an initiator. In addition, the carbon-carbon double bonds in 1,4-poly-1,3-butadiene are also grafted by the PS radicals initiated via chain transfer as shown in a product (3).



**Figure 2.8** Scheme of chain transfer reaction (Odian, 2004).

### (b) Ionizing Radiation

The ionizing radiation has been widely used to produce chemically active polymers for adsorption and separation processes (Lee, Bondar and Han, 2007). The irradiation of NR in the presence of vinyl monomers primarily leads to a synthesis of graft copolymers, but some block copolymers are always occurred. The ionizing radiation can be carried out in solution, emulsion or suspension. The monomers used in this process can be applied as liquid with or without a diluent or as vapor. The rubber may be pre-irradiated in the absence of air to produce free radicals for later monomer addition. However, the life of these radicals is short. Irradiation at very low temperature makes a possibility to use the trapped radicals technique for a variety of natural and synthetic rubbers. The graft polymer in the latex form is generally favored due to its simplicity. Thus, it can be seen that the graft copolymerization of vinyl monomers such as MMA, ST, ACN and vinyl chloride (PVC) onto NR has been done in this way.

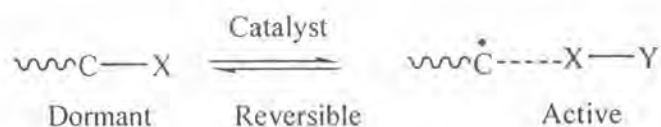


### (c) Redox Initiation

Redox initiator is an efficient method for graft polymerization. The redox reaction relates to both inorganic and organic components. An advantage of redox initiation is that radical production occurs at reasonable rate for wider range of temperature (273-323 K), which is depended on the particular redox systems (Odian, 2004). For example, Arayaprane et al. (2002) studied the graft copolymerization of ST/MMA monomer mixture at 50/50 (%W/W) onto NR latex using cumene hydroperoxide/sodium formaldehyde sulfoxylate dehydrate/ethylenediamine tetraacetic acid (EDTA)-chelated  $Fe^{2+}$  as a redox initiator. The effects of the process factors such as the amount of initiator, emulsifier, and chain-transfer agent, monomer-to-rubber ratio (M/R) and temperature on the grafting efficiency (GE) and grafting level (GL) were reported. It was found that the formation of graft copolymers occurred on the surface of latex particles. It was implied that the graft copolymerization was a surface-controlled process.

### (d) Living Radical Polymerization (Thavornytikarn, 1999)

Free radical polymerization is a chain-growth addition of a vinyl monomer involving four reaction steps, i.e., initiation, propagation, chain transfer and termination. In the last steps, it is related to chain-breaking process which a growing polymeric chain becomes a dead chain. Free radical polymerization has innate side reactions such as intermolecular radical coupling reactions, disproportionation reactions and chain transfer reactions yielding a polymer with uncontrolled molecular weight and ill-defined structure. Such a less controlled reaction is overcome by a rapid progress in living radical polymerization that can control molecular weights and molecular weight distributions of resulting polymers. The living free radical polymerization typically consists of initiation and propagation steps, while the chain-breaking processes are absent. The common feature of these polymerization relates to reversible and rapid equilibrium between activated and dormant species as illustrated in Figure 2.9. The terminal covalent bonds in the dormant species can be dissociated by heat, radiation or transition metals to produce active growing radical species.



**Figure 2.9** Scheme of living radical polymerization (Subramaniam, 1988: 762-86 cited in Thavornnyutikarn, 1999)

### 2.3.7.2 Initiation System

The different initiator systems have been extensively used to prepare graft copolymerization of vinyl monomers onto NR in recent years as follows:

#### (a) Thermal Decomposition of Initiators (Odian, 2004)

The thermal or hemolytic dissociations are widely used to generate radicals to initiate polymerization for both commercial process and theoretical studies. The number of different chemicals used as thermal initiators is rather limited. Normally, the thermal initiators should have bond dissociation energies in the range of 100-170 kJ mol<sup>-1</sup>. Several different types of peroxy compounds are widely used. There are acyl peroxides such as acetyl and benzoyl peroxides, alkyl peroxides such as cumyl and tert-butyl peroxides, hydroperoxides such as tert-butyl and cumyl hydroperoxides and persters such as tert-butyl perbenzoate. Aside from the various peroxy compounds, the main other class of compound extensively used as initiators is the azo compounds. 2, 2'-Azobisisobutyronitrile (AIBN) is most important member of this class of initiators.

For example, Qu et al. (2002) studied the graft copolymerization of ST and ACN onto EPDM via free radical polymerization. The graft NR was prepared by solution polymerization in n-hexane/benzene using benzoyl peroxide (BPO) as an initiator. The influence of the polymerization conditions such as reaction time, initiator concentration, EPDM content and ST/ACN (W/W) on the grafting properties was investigated. The ST/ACN was kept constant at 3.0, which was close to the azeotropic point of copolymerization of ST and ACN. The graft NR structure analyzed by FTIR spectroscopy showed the absorption band at 2,238 cm<sup>-1</sup> attributed

to the stretching vibration of  $C\equiv N$ . It was also found the absorption bands at 760-700  $\text{cm}^{-1}$  which were the characteristic peaks of monosubstituted benzyl ring. Therefore, ST and ACN monomers were grafted onto the molecular chain of EPDM. In addition, the thermal property of the graft NR was studied using programmed thermogravimetric analysis (TGA). The results showed that the initial decomposition temperature and the maximum weight loss rate temperature of graft NR were 405 and 450°C, respectively. Thus, the graft NR has a good heat resistant properties near EPDM (450°C) and also better than acrylonitrile-butadiene-styrene copolymer (419°C).

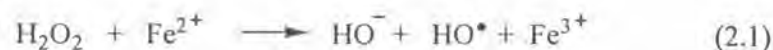
### (b) Persulphate Initiator System (Chansook, 2001)

In aqueous solutions, the persulphate ion is known as a strong oxidizing agent. It can be used either alone or with activators. The reaction proceeds via a free radical mechanism involving the decomposition of persulphate by using heat or reducing agents to produce sulphate radical.

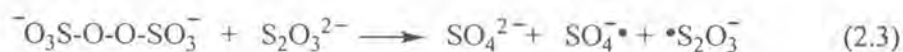
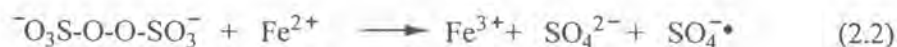
### (c) Redox Initiator System (O dian, 2004)

The redox initiations are normally used for graft copolymerization such as:

- Peroxide with combination of a reducing agent is a common source of radicals. For example, the reaction of hydrogen peroxide with ferrous ion generates  $\text{HO}^\bullet$  as illustrated in eq. 2.1.



- The combination of various inorganic reductants and inorganic oxidizing agents to promote the radical polymerization as shown in eq. 2.2 and 2.3.



Kochthongrasamee et al. (2006) studied the effect of redox initiator on graft copolymerization of MMA onto NR. Three initiator systems such as cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), tert-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ( $K_2S_2O_8$ )/sodium thiosulfate ( $Na_2S_2O_3$ ) were used for initiating graft polymerization in latex form. The optimum condition for each redox initiator system on the graft copolymerization of MMA onto NR was investigated. The results showed that CHPO/TEPA gave the maximum grafting efficiency with high content of graft product and high percentage of monomer conversion. The CHPO was more effective than TBHPO and  $K_2S_2O_8$  for grafting MMA onto NR. Due to the significant difference initiator efficiency between monomer-swollen NR and the aqueous phase, the grafting properties were indeed affected. It was expected that the radical concentration from CHPO/TEPA on the NR particles was higher than that from TBHPO and  $K_2S_2O_8$ , since TBHPO/TEPA was soluble in both organic and aqueous phases, while  $K_2S_2O_8$ / $Na_2S_2O_3$  was only soluble in the aqueous phase. Thus, CHPO/TEPA was an appropriate redox initiation system for grafting of MMA onto NR in latex form.

#### **(d) Ionizing Radiation (Chansook, 2001)**

The irradiation of organic macromolecules predominantly leads the formation of free radicals. The two available radiation sources are Co-60, which is commonly used in the radiation plants, and Cs-137. The Co-60 sources is relatively cheaper with 5.25 years of useful half life.

#### **2.4 Introduction to Polymer Blends**

In some applications, users generally require materials having some properties from one polymer and other properties from different ones. Instead of synthesize a new polymer with all desired properties, the blend of different polymers having required properties is more practical and economical. In general, a miscible blend of two polymers exhibits the combination properties obtained from those polymers (Fayt, 1985).

### 2.4.1 Preparation Method of Polymer Blends

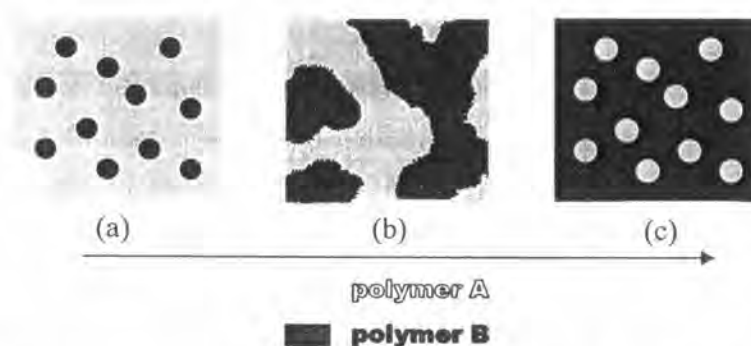
There are many methods to make polymer blends such as mechanical blending, mechano-chemical blending, latex blending and chemical blending (Malcolm,1999). Mechanical method is mostly used in industry because of its convenience for large scale production.

### 2.4.2 Effect of Factors on Morphology of Blends

Morphology of polymer blends plays an important role to determine the final physical properties. The morphology of polymer blends is normally depended on the following factors:

#### 2.4.2.1 Polymer Proportion (Fayt, 1985)

For an immiscible blend from two polymers (polymer A and polymer B), the smaller amount of polymer B indicated as little spherical globs is separated and dispersed in the larger phase of polymer A (continuous phase) as presented in Figure 2.10a. Thus, polymer B is called as the dispersed phase. On the other hand, when the content of polymer B increases, it acts as continuous phase and polymer A is dispersed in the polymer B (Figure 2.10c). For the partially miscible blend containing higher content of polymer B, the spherical globs of polymer B become larger and they partially join together with the continuous phase to form co-continuous as shown in Figure 2.10b.



**Figure 2.10** Relative amount of polymer B in the immiscible blend (Fayt, 1985).

#### **2.4.2.2 Polymer Viscosity**

Polymers with lower viscosity tend to form continuous phase whereas one with higher viscosity can be formed as dispersed phase. Moreover, the difference in viscosity between each polymeric component also affects morphology of blends (Corish, 1974).

#### **2.4.2.3 Blending Method**

There are many methods to blend different polymers such as mechanical blending, mechano-chemical blending, latex blending, chemical blending and solution blending (Malcolm, 1999). Each method generates different shear forces resulting the dissimilarity of morphology of the blends. Usually, the size of dispersed polymer is reduced with increasing mixing time and severity of mixing. Furthermore, types of mixing instrument must be considered because it provides the different shear stress and polymer flow rate during mixing process (Hess, Scott and Callan, 1967).

### **2.5 Rubber-Rubber Blends**

#### **2.5.1 Introduction of Blends (Huffman, 1989)**

NR can be readily blended with a great number of non-polar rubbers. The blends of NR with SBR, BR or some NBR content, are technically exploited. It is found that some properties of SBR are transferred to NR or from NR to the SBR. During mixing process, it is important to masticate NR for reducing its viscosity same as that of blend partners. Otherwise, it is impossible to achieve a miscible blending of the components. The appropriate vulcanization system is also the main factor to meet the properties requirement of each blend partner. This is a problem for NR/SBR blends which have quite different cure properties same as the EPDM/NR blends.

### **2.5.2 Problem of Blends (Sroysom, 1999)**

Due to the high molecular weight and chain length of rubber molecules, rubber blends are usually immiscible. Therefore, the major problem of rubber blends is heterogenesis with consisting of one rubber phase dispersed in the matrix of the second rubber acting as the continuous phase. The size of the dispersed phase varies from 0.5  $\mu\text{m}$  depending on the nature of the blended rubbers, rubber viscosities and blending method as well as mixing conditions. The blending of two different rubbers normally causes the unbalance distribution of curing agents, fillers and other rubber chemicals due to the different solubilities of rubber chemicals or fillers in different rubber phase. Processing procedure also affects the distribution of fillers and rubber chemicals in each rubber phase.

### **2.5.3 NR/Synthetic Rubber Blends (Hofman, 1989)**

The blending of NR with synthetic rubbers (SR) is the cheapest method that is used to improve physical and mechanical. It also promotes the easier process for serving economical purpose. According to SR having different characteristics, blending NR with disparate SR normally gives the rubber products with distinctive properties.

#### **2.5.3.1 NR/CR Blend**

Polychloroprene (CR) has excellent resistance to ozone, weathering and heat aging with good mechanical properties. It also has good resistance to mineral oil, aliphatic hydrocarbons and greases. Thus, blends of NR with CR are used in automotive product, driving belts, conveyor belts, adhesives, fabric coating and bridge pads

### 2.5.3.2 NR/SBR Blend

Styrene-butadiene rubber (SBR) is an elastomeric copolymer consisting of butadiene (67-85%) and styrene (15-33%). It has good abrasion resistance and good aging stability. It is also blended with NR to produce passenger tires and numerous applications including pneumatic tires, wires, gaskets and cable insulation.

### 2.5.3.3 NR/EPDM Blend

Ethylene-propylene diene rubber (EPDM) has high resistance to ozone as well as ultraviolet radiation. It can be extended by the addition of mineral oils. Therefore, blending NR with EPDM is used as a material for the face seals of industrial respirators and automotive paint spray.

### 2.5.3.4 NR/NBR Blend (Hofman, 1989)

Acrylonitrile-butadiene rubbers or nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile. Individual grades of nitrile rubber differ by the content of acrylonitrile in the range from 18 to 50% (Franta, 1989). The chemical structure of NBR is shown in Figure 2.11.

The polarity of NBR becomes greater with increasing acrylonitrile content to provide higher oil resistance. The thermal stability of NBR is quite good and it also exhibits high abrasion resistance. However, ozone and weathering resistance of NBR is poor. The properties of conventional NBR are presented in Figure 2.12.

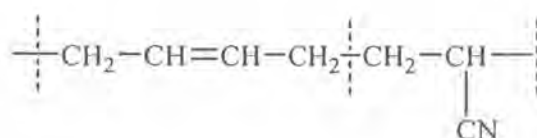
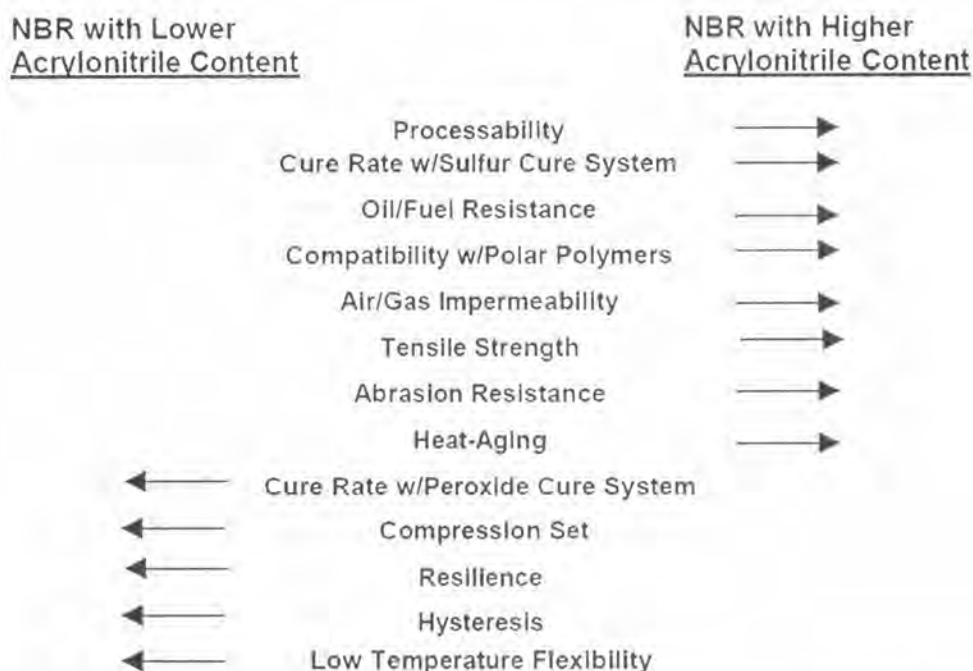


Figure 2.11 NBR structure (Hofman, 1989).





**Figure 2.12** Summary of common properties of conventional NBR polymer( Franta, 1989).

For NR/NBR blends, it is expected that NBR can improve oil and fuel resistance of NR and NR in the blend should enhance mechanical properties of NBR. Due to the difference in polarities of NR and NBR, properties of NR/NBR blends can be improved by the addition of a small amount of other compounds, i.e., block or graft copolymers used as compatibilizers to increase their compatibility.

In general, there are two main techniques for improving the compatibility of blends.

1. Addition of a third component, i.e., compatibilizers such as copolymer and low molecular weight polymer such as liquid NR (LNR) (Dahlan, Zarman and Ibra 2002).

2. Functionalization process, i.e., a graft copolymer formed during mixing process (Xanthos and Dagli, 1991).

Application of NR/NBR blends involves the production of automotive transmission belts, hoses, oil seals, valve and piping gaskets and printer's rolls.

## 2.6 Compatibilization (Folkes, 1993)

Generally, melt mixing process of two polymers produces a material that is weak and brittle. The low deformation modulus may follow an approximately linear mixing rule, but the ultimate properties do not follow this rule due to the presence of stress concentrations and weak interfaces between the dispersed phase and a matrix. The process of bridging to enhance the mechanical properties by addition of a third component, or by *in situ* chemical reaction is called as compatibilization. In most cases, the compatibilizer possibly affects the final products such as

- a) Reduction of the interfacial tension during melt mixing resulting to a finer dispersed phase.
- b) Increase in the adhesion at phase boundaries giving the improved stress transfer with strengthening the interface in the solid state.
- c) Stabilization of the dispersed phase by reducing the rate of domain coalescence during melts processing and annealing.

The method of compatibilization can be divided into four categories.

### 1. Thermodynamic miscibility

This method is a main idea to produce commercial blends. The miscibility between polymers can be explained by a balance of enthalpic and entropic contributions to the free energy of mixing. The change of free energy ( $\Delta G$ ) during mixing is written as shown in eq. 2.4

$$\Delta G = \Delta H - T\Delta S \quad (2.4)$$

where H is enthalpy, S is entropy and T is temperature. For spontaneous mixing,  $\Delta G$  must be negative as presented in eq. 2.5

$$\Delta H - T\Delta S < 0 \quad (2.5)$$

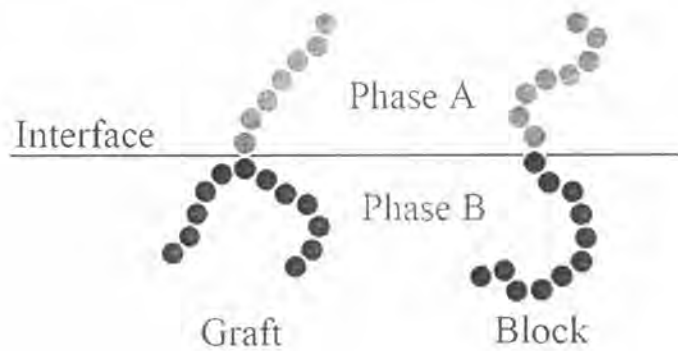
The entropy of polymers is almost zero. This inferred that mixing is the exothermic process, whereas, endothermic mixture is missible at high mixing temperatures.

## 2. Addition of block or graft copolymers

The addition of block or graft copolymers has been widely studied to enhance the compatibilization of blends. The block and graft copolymers containing chemically identical segments to the blend components can be applied as compatibilizers to increase the miscibility between the copolymer segments and the corresponding blend component. This provides the resulting polymer blends having desired structure and molecular weight. Normally, the copolymer used as the compatibilizers for blending preferably locates at interface of the blends as illustrated in Figure 2.13. The better dispersion and adhesion in the blends resulted from the addition of the compatibilizers improves mechanical properties of the blends. However, the finest dispersion may not be necessary to the blends to yield desired properties. The optimum size of dispersion phase must be related to the required end-use properties of the blend.

## 3. Addition of functional polymers

The addition of functional polymers as the compatibilizations has been described by many researchers. The polymer structure in the blends is modified to have functional (or reactive) units for increasing the affinity for other components. The modification via functionalization may be achieved in a reactor or during an extrusion-modification process. For the grafting reaction, the graft copolymerization of maleic anhydride or similar compounds onto polyolefins produces pendant carboxyl groups having the ability to form chemical linkages with polyamides via their terminal amino groups. Functionalized polymers (usually maleic anhydride or acrylic acid-grafted polyolefins) are commercially available with acceptable cost for using as compatibilizers for the polymer blends.



**Figure 2.13** Schematic diagram showing locations of block and graft copolymers at phase interfaces (Folkes, 1993).

#### 4. Reactive blending

The blend components with modified their structure having reactive sites can form crosslink during melt mixing process without the addition of another compatibilizer. The example materials used in reactive blending process are graft or block copolymers to generate the *in situ* crosslink formation by following various reaction mechanisms:

- Mechanical chain scission and recombination of polymer induced by high shear force during processing.
- Chemical bonding reaction between reactive functional groups initiated by radical initiator.
- Interchanging reaction on the polymer backbone obtained from condensation polymerization.

These reactions may be occurred either in batch-type melt mixers or continuous processing equipment (such as single or twin screw extruders). However, disadvantages of these methods are high operating cost and their chemically linked structure is difficult to be recycled.

## 2.7 Literature Reviews

Oommen et al. (1999) studied the dynamic mechanical and thermal properties of NR/PMMA blends by the addition of graft copolymer of PMMA on NR (NR-g-PMMA). Dynamic mechanical and thermal analysis (DMA) was used to observe the effect of graft copolymer acted as a compatibilizer on the heterogeneous NR/PMMA blends. The storage modulus increased with increasing the compatibilizer contents. This indicated the improvement of adhesion between the polymer components in the blends. The addition of compatibilizer reduced the size of dispersed phase resulting in the higher storage modulus. The interpenetration degree of NR and PMMA at the interface was analyzed by calculating the entanglement density from DMA studies. Thermogravimetric analysis showed the higher thermal stability of the blend, which was slightly improved by the addition of the graft copolymer. The compatibilized blends exhibited a considerable improvement in the mechanical properties compared to the uncompatibilized ones.

Ismail et al. (2001) studied the curing characteristics and mechanical properties of NBR/NR blends prepared by using a Brabender at 60°C. The results indicated that the scorch time and the optimum cure time increased with increasing NBR contents in NBR/ENR50 and NBR/SMRL blends. In NBR/ENR50 blends, the increase in the content of NBR enhanced the maximum elastic torque, torque difference and viscous torque. However, it was observed the opposite results for NBR/SMRL blends in terms of maximum elastic torque and torque difference. The tensile strength and elongation at break of the blends gradually decrease with increasing the NBR contents.

Prasassarakich et al. (2001) investigated the graft copolymerization of ST and ACN onto NR prepared by an emulsion polymerization using potassium persulfate as an initiator. The optimum condition was 1.5 parts by wt of initiator concentration under 3.1 bar of N<sub>2</sub> pressure at 70°C for 8 h. In addition, the mechanical properties of blends containing graft NR and styrene-acrylonitrile copolymer (SAN) were also studied. It was observed that this graft product could be used as an impact modifier for SAN. The suitable ratio of graft NR to SAN for giving the blend with high mechanical performance was 20/80 by wt.

Okieimen et al. (2002) reported graft copolymerization of ACN and MMA monomer mixture onto crump NR. It was found that the amount of ACN monomeric units incorporated into the polymer was lower than ACN content in the feed. The miscibility of the NR-*g*-polyacrylonitrile-*co*-PMMA/poly(vinyl chloride) (PVC) blends was studied by viscometry, differential scanning calorimetry (DSC) and phase contrast microscopy. The results showed the semimiscible morphology for these blends.

Nah et al. (2002) studied the influence of the addition *trans*-polyoctylene rubberm (TOR) on the physical properties and phase morphology of NR/NBR blends. It was found that the increase in TOR contents enhanced hardness, tensile modulus and resilience of the blends; whereas, their tensile strength and elongation at break tremendously decreased. When TOR was added to 50/50 NR/NBR blends, TOR mostly located in the NR phase and some TOR content was positioned at the interfaces between the NBR and NR phases.

Zeng et al. (2004) studied the graft copolymerization of ST and ACN onto ethylene-propylene-diene terpolymer (EPDM) in *n*-heptane/toluene using benzoyl peroxide as an initiator. The reaction variables, such as reaction temperature, initiator concentration, rubber content, solvent component and reaction time significantly affected the monomer conversion, grafting ratio and grafting efficiency. The optimum condition was carried out by using ST/ACN as 3/1 by wt in heptane at 40/60 by volume with 50% EPDM concentration initiated by  $3.38 \times 10^{-3}$  M of BPO concentration at 80°C for 20 h. TEM micrographs showed the good miscibility of SAN/AES blends and the AES with high rubber content was an effective toughening agent for SAN. When the EPDM content of the blend reached to 15 wt%, a sharp brittle-to-tough transition was occurred. The toughening mechanism was caused by the crazing initiation from rubber particles and shear deformation of the SAN matrix.

Arayapranee et al. (2004) studied the physical and mechanical properties of PVC/NR-*g*-(ST-*co*-MMA) blends. The copolymerization of MMA and ST onto NR was carried out by emulsion polymerization by using redox initiator to provide an impact modifier for PVC. It was found that the impact strength of blends

increased with increasing the content of graft NR in the blends. The results from dynamic mechanical analysis (DMA) showed that NR-g-(ST-co-MMA) had partial compatibility with PVC. The scanning electron micrograph (SEM) also confirmed a shift from brittle failure to ductility with increasing the amount of graft copolymer in the blends. Thus, it could be concluded that NR-g-(ST-co-MMA) was an effective impact modifier for increasing the impact strength of PVC.

Suriyachai et al. (2004) reported the graft copolymerization of glycidyl methacrylate and ST onto NR latex. The graft NR were synthesized via emulsion polymerization using redox initiator. The graft NR could be used as a compatibilizer for NR/PMMA blend. The fracture surfaces of NR/PMMA blend examined by SEM exhibited good adhesion upon the addition of graft NR. A good compatibility of NR/PMMA blends was obtained at 5-10 phr of graft NR content. The morphology of the blends showed good interfacial adhesion upon the addition of graft NR.

Hinchiranan et al. (2007) studied properties of modified acrylic sheet improved by the addition of graft NR. The modification of NR by graft copolymerization with MMA and ST was synthesized by emulsion polymerization initiated by potassium persulfate. The results showed that the impact resistance, tensile strength and elongation at break of the modified acrylic sheet increased with increasing the amount of graft NR in the range of 0.5–4 parts. From the stress-strain behavior, the characteristics of the modified acrylic sheet shifted from brittle to ductile materials when the amount of graft NR increased.