CHAPTER II

LITERATURE SURVEY

2.1 Structure, Properties, and Applications of Natural Rubber

Natural rubber is the product from the rubber tree (Hevea brasiliensis). The original form of NR is a colloidal dispersion of rubber particles in an aqueous medium. After coagulation at the low pH by adding some acids, the solid state NR is obtained. Raw NR always contains a certain amount of impurities, which depend somewhat on sources and processing conditions as shown in Table 2.1.

Table 2.1 Composition of raw NR.

Composition	wt %
Rubber hydrocarbon	89.30 - 92.30
Proteins	2.50 - 3.50
Moisture	2.50 - 3.50
Ash	0.15 - 0.50

The rubber hydrocarbon of NR comprises over 99.99 wt% of linear cis-1,4-polyisoprene. The cis-1, 4-isoprene unit is shown in the Figure 2.1.
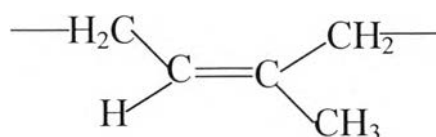

Figure 2.1 Structure of the cis-1,4-isoprene unit.

After vulcanization, NR vulcanizates possess several unique properties namely high tensile strength with high rebound elasticity, good low temperature flexibility, low heat buildup, and excellent dynamic properties. Moreover, its insulation property and impermeability to gases and water make it indispensable in many applications.

Although soft NR vulcanizates with high tensile strength can be produced without any filler, for most applications, fillers are still necessary to attain specific properties and to reduce cost of production

2.2 Structure, Properties, and Applications of Clay

Clay, a mineral from soil, consists of silicate layers held together by weak ionic forces. Generally, it can be classified into many types according to differences in structures and compositions such as talc, micas and smectite. Among several types of clays, the smectite one is usually used as a filler in polymer composites because of its reinforcing property and economic reason.
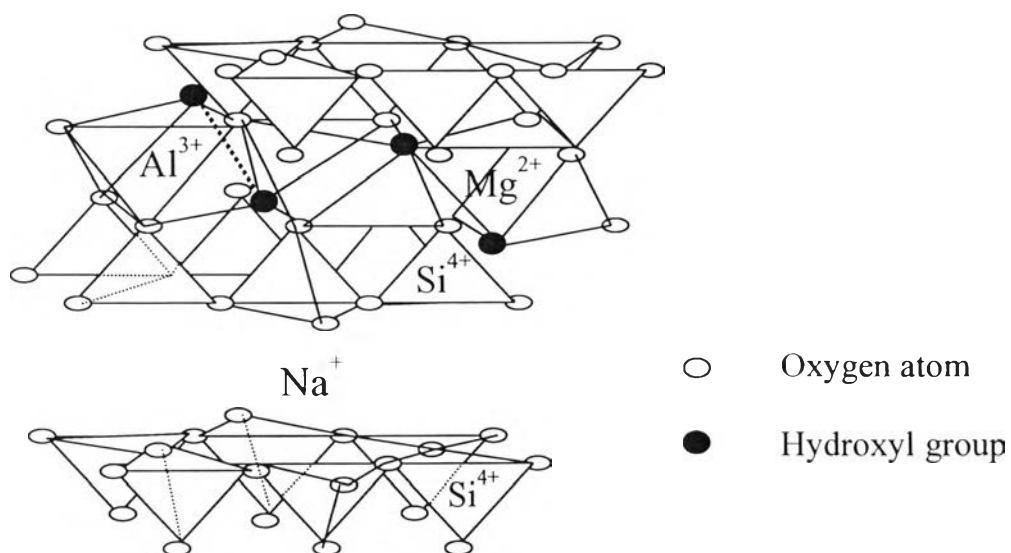

Figure 2.2 Structure of the layered silicate.

Smectite clay, shown in Figure 2.2, is a group of material composed of silicate layers whose individual layer constitutes of the octahedral structure of one sheet of metal oxide sandwiched between the tetrahedral structure of two sheets of SiO_4. These three sheets combined together to be a silicate layer by sharing oxygen atoms at the edges between sheets. The isomorphic substitutions within metal oxide sheets with the lower valency species give the silicate layer slightly negative charges, and it is counterbalanced by interlayer cations namely Na^+ and K^+.

Montmorillonite (MMT), used in this work, is one of the most familiar clays in the smectite family normally applied to polymeric matrix nanocomposites. Ideal formulas of clays in a smectite group were illustrated in Table 2.2. In the case of MMT, two-third of octahedral sites is occupied by Al^{3+} while the rest belong to Mg^{2+}. The nonstoichiometry, therefore, brings about negative charges on the silicate layer which are compensated by Na^+. Because of its inclination to absorb moisture, a hydrated form of Na^+ is always found in nature.

Table 2.2 Ideal formulas of smectite clays.

Subgroup	Species	Ideal Formula
Saponites	Saponite	$Na_{0.6}[Mg_6(Al_{0.6}Si_{7.4})O_{20}(OH)_4]$
	Hectorite	$Li_{1.6}[(Li_{1.6}Mg_{4.4})Si_8O_{20}(OH)_4]$
	Fluorohectorite	$Li_{1.6}[(Li_{1.6}Mg_{4.4})Si_8O_{20}F_4]$
Monmorillonites	Montmorillonite	$Na_{0.6}[(Mg_{0.6}Al_{3.4})Si_8O_{20}(OH)_4]$
	Beidellite	$Na_{0.9}[Al_4(Al_{0.9}Si_{7.1})O_{20}(OH)_4]$

The unique properties of Na-montmorillonite (Na-MMT) that make it most popular to be employed in polymeric matrix nanocomposites are its

high ionic exchangeability and its ability to be swollen by suitable materials after modification with organic cations.

2.3 Polymeric Matrix Nanocomposite

Composites are a class of material that combines two or more outstanding characteristics of each component together in order to achieve particularly desired properties. In general, the properties of polymeric matrix composites always depend not only on the size of component phase but the dispersion in polymer matrix as well. Therefore, nanocomposites are designed and synthesized by using silicate layers as the inorganic phase because of their ability to break down into nanoscale dimension and disperse well in a continuous polymer matrix. However, polymer-layered-silicate composites can be categorized into three groups according to the dispersion behavior of silicate layers as shown in Figure 2.3.
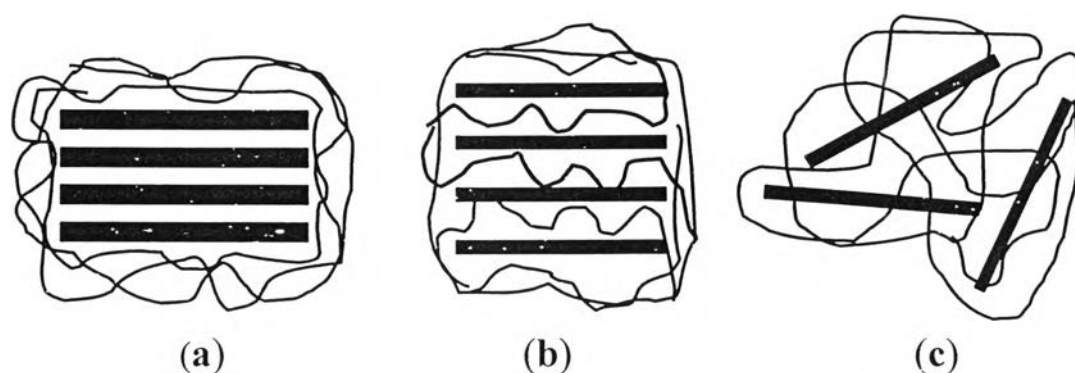

(a)   (b)   (c)

Figure 2.3 Types of polymer-layered-silicate composites: (a) conventional composite, (b) intercalated nanocomposite, (c) exfoliated nanocomposite.

Firstly, conventional composites compose of silicate tactoids with the silicate layers aggregated in the unintercalated form. Consequently, discrete phases usually take place because of no penetration of polymer molecules

into layered silicate phase. Secondly, intercalated nanocomposites are formed by the intercalation of polymer molecules into the spaces between silicate layers, resulting in the more or less definite structure. Lastly, exfoliated nanocomposites normally occur at a quite low content of silicate layers. In this type of nanocomposites, there is no any correlative distance between silicate layers, which reflects the extreme separation of silicate layers.

Polymer-layered-silicate nanocomposites can be prepared through both modified and unmodified silicate layers, which are determined by thermodynamic properties and additional techniques used in a particular system. Giannelis et al. (1996) synthesized polyethyleneoxide (PEO) nanocomposite by melt intercalation process. He also found that unmodified Na-MMT could be intercalated into the interlayer gallery of unmodified Na-MMT by heating the mixture at 80 $^{\circ}$C. XRD data exhibited the increase in the basal spacing of Na-MMT. Additionally, improvements in mechanical properties and conductivity of PEO-Na-MMT nanocomposite were also reported. Not only was PEO used to prepare nanocomposites with unmodified MMT but also an epoxy-MMT nanocomposite was synthesized by Lee and his colleagues (1997) by means of emulsion polymerization. Moreover, they proposed that the possibility of polymer intercalation in emulsion system depended on the sizes of monomer-containing micelles. In addition, Noh et al. (1999) suggested that by sonicating Na-MMT in a heterogeneous monomer/water system before following with emulsion polymerization resulted in the styrene-acrylonitrile copolymer (SAN)-Na-MMT nanocomposite.

Although unmodified Na-MMT can be used to prepare nanocomposites, it seems to be suitable only to polymers that have polarity to some extent. Besides, the resulting nanocomposites always fall in an intercalated type, not an exfoliated one. Consequently, Na-MMT has to be

organically modified to render it organophilic before dispersing in the matrix of polymer. Pinnavaia et al (1996) used alkylamines as modifying agents, and prepared epoxy nanocomposites by in-situ polymerization. They ruled out that the length of hydrocarbon part in the structure of alkylamines determined wheather the resulting nanocomposites could be exfoliated ones or not. Moreover, their results also suggested that tensile strength and modulus of exfoliated nanocomposites were much higher in rubbery state than in the glassy counterpart.

In addition to epoxy, nanocomposites in the matrices of elastic polyurethane and silicone, and polyimide were studied by Wang (1998), Long (1998), and Tyan (1999) respectively. In the case of elastic polyurethane, the increase in basal spacing upon curing was reported. Besides, especially in the last case, p-phenylenediamine was used to prepare a reactive organoclay that provided functional groups to react with dianhydride end groups of poly(amic acid), forming the irreversible swelling.

Though several elastic polymers had been already investigated in the nanocomposite manner, natural rubber, a very versatile material, has not been studied by anyone. So, it is very interesting to persue the idea of nanocomposite in this one of the most plentiful materials in the world.