



CHAPTER II

LITERATURE REVIEW

2.1 Natural Rubber

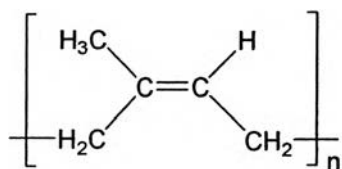
Natural rubber latex is naturally obtained from the milk liquid (latex) of various plants in more than 1,000 species; however, the important commercial source of natural rubber is the tree *Hevea brasiliensis*, which was found in Brazil (Dupont *et al.*, 1976). The production of natural rubber is starting from natural rubber latex, which is collected by tapping from *Hevea* rubber trees. The latex is a colloidal suspension of rubber particles in an aqueous serum phase. The fresh natural rubber latex or fresh latex obtained consists of a suspension of 20-40% dry rubber and 5-10% non-rubber contents. The non-rubber components are consisting of 1-2% proteins and phosphoproteins, 2% resins, 1% fatty acids, 1% carbohydrates, and 0.5% inorganic salts (Greve, 2003). The component depends on the age of rubber and tapping method (Hofmann, 1989). These non-rubber constituents are postulated to be the causes for outstanding properties of natural rubber.

After excluding from trees, the natural rubber particles in latex maintain the colloidal system covered by proteins and phospholipids layers with anionic charge repulsion. After a certain time, the rubber particles demonstrate partial coagulation resulting from the decomposition of proteins by bacteria and enzymes under air exposure during the storage in ambient. Therefore, the treatment of the latex to prevent the coagulation of rubber particles needs to be done by adding the preservative agent such as ammonia solution (~0.7% v/v) after collection of the latex by tapping (Hofmann, 1989). The concentration of latex is important to reduce the volume of latex for lower transportation cost and can be done by centrifugation, evaporation, and creaming. These processes increase the natural rubber latex concentration up to 60%.

The composition of natural rubber consists of carbon and hydrogen under the monomeric structure of C_5H_8 or isoprene unit connected to each other in head-to-tail arrangement. The double bond in isoprene units is known to be in the *cis* configuration corresponding to *cis*-1,4 isoprene units as shown in Scheme 2.1. In the

rubber latex, the polymer exists as microparticles with an average size of 0.15-3.0 μm .

Scheme 2.1 Chemical repeating unit of natural rubber



2.2 Coagulation

The most of natural rubber latex is further processed to solid rubber via coagulation process. As the surface of rubber particles is covered with negatively charged phospholipids, coagulation is an effective way to induce the aggregation of rubber particles by neutralizing the surface charge. Generally, coagulating agents in the uses for rubber are acids, such as acetic or formic acid, or salts, such as sodium silicofluoride.

Normally, the latex is diluted with water to a solid content concentration of 15-20% before coagulation. The addition of the dilute solution (0.5%) of formic acid or acetic acid brings the coagulation of rubber. The charge on colloidal surfaces is usually a function of the pH. The surface of rubber particles is covered by proteins in the serum. This protein layer prevents the aggregation of ionic rubber particles in the latex. At high pH, colloids tend to be negatively charged, while at low pH they are in positively charged (Greve, 2003). The preferable condition for latex coagulation is under the pH range of 5.1 to 4.8, i.e., at the isoelectric point. Then, the rubber and most of non-rubber fractions are obtained as bulky coagulum and separated from the serum fraction containing water soluble non-rubber components. This acidified coagulation is simple; however, it shows the disadvantage of the green environment and the steps of washing rubber. Thus, acidic process needs additional treatment to avoid pollution (Loykulnant *et al.*, 2007). As the ecologically friendly material becomes an issue of material development on these days, an alternative material is indeed needed.

2.3 Flocculation

Flocculant can be classified into inorganic, natural organic and synthetic organic ones. The examples of inorganic flocculants are iron (III) chloride, alum and sodium aluminate. The group of natural organic flocculants is water-soluble starch, alginates, gelatin, and chitin-chitosan. For polymeric flocculants, typically, they are synthetic water-soluble macromolecules with charges such as nonionic, anionic and cationic flocculants, for example, polyacrylamide, poly(sodium acrylate), and polyethylenimine.

Flocculation is a process of bringing between small particles and flocculant to perform larger particles, so-called 'floc'. The interaction between polymeric flocculant and small particles is proposed in two mechanisms. The first, polymer must have a charge opposite to that of colloidal particles. The excess of polymeric flocculant provide long range electrostatic attraction of other particles. The second, a few segments of the polymer can be attached to the surface of particle to form bridging (Burkert and Hartmann, 2003).

Recently, the use of flocculation in rubber latex treatment has been developed for synthetic rubber. For example, Verezhnikov *et al.* (2001) reported the use of poly-*N,N*-dimethyl-*N,N*-diallylammonium chloride as cationic flocculant to separate styrene-butadiene rubber from latex. The copolymer performs the re-stabilization of system by recharging of particle surface. The addition of acid in the system is a way to accelerate the phase separation after flocculation. Verezhnikov *et al.* (2002) clarified that the molecular weight of poly-*N,N*-dimethyl-*N,N*-diallylammonium chloride at 172 , 62 and 16 kDa rarely shows the positive effect on rubber recovery.

Shatalov *et al.* (2003) reported the flocculation of synthetic rubber latex using homopolymer of *N*-vinylcaprolactam and water-soluble copolymers of *N*-vinylcaprolactam and *N*-vinylimidazoles. They found that copolymers exhibit stronger flocculating power than homopolymer.

Verezhnikov *et al.* (2004) showed the use of water-soluble polymeric ammonium salts of *N,N*-dimethylaminoethyl methacrylate and mineral acids in

flocculating butadiene-styrene latex flocculation. The flocculation performance decreases with the acidity of solution.

At the present time, approaches to improve the separation of natural rubber from rubber latex are still needed. The treatment using acid coagulant generates the problems of acid odors, consumption time, washing, and even obstructs the continuous process. The separation of rubber out of latex as short as a single minute followed by washing with small amount of water is an ideal scheme. Based on this view point, the use of flocculant instead of coagulant can be considered as an alternative choice (*See 2.8 Development of Chitin-Chitosan as Flocculant*).

2.4 Compounding of Natural Rubber

Natural rubber has many advantages on the rubber properties such as high structure stability with high elasticity, very good cold flexibility, and excellent dynamic properties. The major use of natural rubber uses is tires, in which various layers have to be welded to each other (Hofmann, 1989 and Greve and Threadingham, 2003).

Fillers in rubber technology can be classified into carbon black and mineral fillers. Carbon black is used for reinforcement, improved abrasion resistance, weathering, resilience and dynamic properties and reduced hysteresis. For mineral fillers, they are used to modify electrical properties, to improve the resistance for heat, flame, tear and moisture, and to reduce the volume cost of compound (Johnson, 2001).

At the present time, natural rubber has been developed to a certain level that the requirement of fillers is not only the physical and mechanical properties any more but also the consequent functions or the unique properties of the product. For example, Michelin Company succeeded in using silica to substitute carbon black and achieve the unique appearances. One of the weak points of carbon black is the treatment after use. In these days, most of rubber wastes, especially tires end up with landfill which remains nondegradable in the environment. Tire pyrolysis is an alternative choice to recover carbon resources, especially alkyl-based oil. However, the combustion of carbon black generates acid and smoke to the atmosphere.

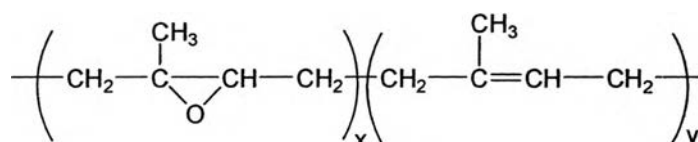
Currently, the polymeric composite materials filled with nanosized rigid particles (inorganic or organic) have received much attention due to the possibility to drastically change the physical and mechanical properties. The ultimate goal of nanocomposites is a desired enhancement of mechanical, barrier, thermal, and/or other properties relative to the original polymer matrix, even at very low contents of nanofillers. In the case of natural rubber, the requirements for fillers or additives are (i) the environmental friendly additives for ecologically environmental product, (ii) light weight for the ease of use and energy saving in the case of tire product, and (iii) nano-scaled particles for the sake of effective reinforcement.

2.5 Modified Natural Rubber

Natural rubber has been modified in many different ways mainly by chemical modification methods. The degree of modification can vary from a few percent to complete modification of the rubber chain resulting to physical properties.

The most well known types of modification are epoxidation, hydrogenation, chlorination, cyclization and etc. The modification highly affects physical properties of natural rubber to be suitable for many applications. For example, epoxidized natural rubber (ENR) consisting of isoprene units and epoxidized isoprene units (Scheme 2.2) is obtained from chemical modification of natural rubber by treating with peracid such as peracetic acid and performic acid (Bradbury and Perera, 1988). The epoxidization provides the unique properties, for example, oil resistance, low gas permeability, high damping, and good wet grip (Zurina *et al.*, 2006). It also gives an increase in polarity and glass transition temperature. The increase in polarity induces compatibility either between rubber and rubber or between rubber and plastic blending (Yew *et al.*, 2005).

Scheme 2.2 Chemical repeating unit of ENR



Ismail *et al.* (1997) studied the effect of filler content and size on mechanical properties of oil palm wood flour (OPWF) reinforced epoxidized natural rubber (ENR) composites. An increase in OPWF content resulted in the reduction of tensile strength and elongation at break, while it increased the tensile modulus, tear strength and hardness. In addition, the smaller OPWF size showed higher tensile strength, tensile modulus and tear strength.

Teh *et al.* (2004) studied the nano-composites containing natural rubber as a matrix, ENR as compatibilizer, and organophosphoric layered clay (organoclay) as fillers. They found that ENR improved the dispersion of organoclay resulting from the polar-polar interaction between ENR and organoclay.

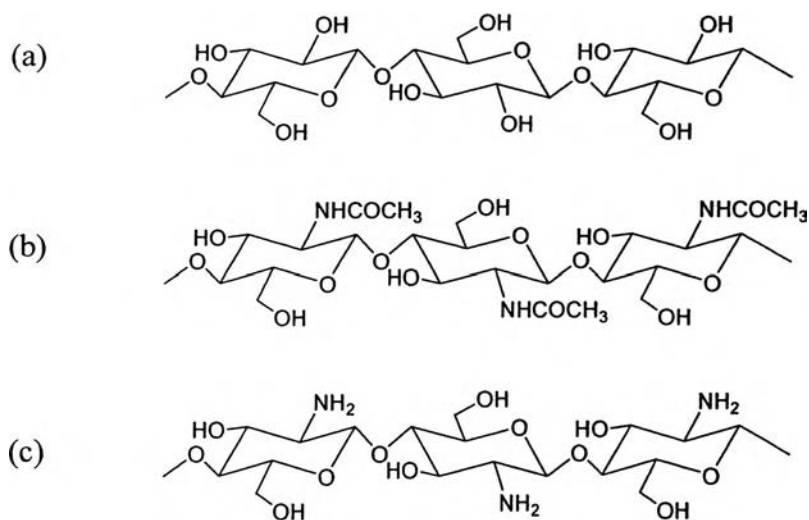
Arroyo *et al.* (2006) reported the use of ENR as compatibilizer for natural rubber composites with organo-montmorillonites. They found that the exfoliated nanocomposites have been successfully developed to achieve homogeneous dispersion of ENR. The exfoliated nanoclay layers are mostly located at NR/ENR interphase. The improvement of physical and mechanical properties was related to the homogeneous exfoliated structure.

2.6 Chitin-Chitosan: the Structure and Unique Properties

Chitin, poly- β -(1 \rightarrow 4)-N-acetyl-D-glucosamine, is the second most abundant naturally occurring amino polysaccharide next to cellulose. The chemical structure is similar to cellulose, but it is an amino polysaccharide having acetamide groups at the C-2 positions instead of hydroxyl groups. It is widely found in the shells of crustacean and insects. Chitosan, poly- β -(1 \rightarrow 4)-D-glucosamine, is highly advantageous for providing biological functions and for conducting modified reactions resulting from the presence of amino groups more than 70% in chitin. In general, chitin and chitosan units are distributed in random (Scheme 2.3).

Utilization of the materials and derivatives prepared from chitin and chitosan is in various fields including medicine, pharmacology and the food industry as a result of their biological activity, biocompatibility and biodegradability in combination with its low toxicity.

Scheme 2.3 Chemical structures of (a) cellulose, (b) chitin, and (c) chitosan



Considering the chemical structure of chitin and chitosan, many specific properties can be described as shown below.

a) Hydroxyl Groups. In the repeating unit, two hydroxyl groups are existed. The primary hydroxyl group is located at C-6 and the secondary hydroxyl is placed at C-3. Normally, the primary hydroxyl group is more reactive than the secondary one. Thus, the most chemical reactions are performed at C-6. These hydroxyl groups inform hydrophilicity to chitosan chains and exhibit the inclusion properties. As a result, it forms inclusion and/or a host-guest compound with ions or molecules, which is suitable for the use as flocculant or removal metal in industrial waste water treatment. The lone pair electrons of oxygen atom also forms complex with many metal ions types, i.e. Ca^{2+} , Ni^{2+} , etc. (Nishi *et al.*, 1987) and initiates the antimicrobial properties.

b) Amino Group. Chitin-chitosan is more reactive than cellulose and can be chemically modified, since it has the reactive primary amino group. Moreover, a lone pair electron of nitrogen atom interacts with ions and metal cations or accepts the proton to be protonated species. The use as a flocculants is also based on the interaction of amino group with inorganic species, soil, mud, etc. to accelerate the precipitation. This brings the application to waste water treatment (Peniche-covas *et al.*, 1987). It is important to note that the amino group can be protonated in the

presence of proton species providing positively charged polymer ($-\text{NH}_3^+$) as a cationic polymer. Thus, the protonation of amino group causes the electrostatic attraction of anionic compounds, such as metal anions or anionic dyes (Guibal, 2004), and also induces the ionic bond formation between the positively charged amino group and negative charged microorganism cell-wall, resulting in the growth inhibition of bacteria and virus (Kendra and Hadwiger, 1984).

c) Acetamide Group. The functions of acetamide group are almost similar to those of amino group, while acetamide group is rather inert for the chemical reaction. The strong hydrogen bond network comes from the acetamide group initiating to have the high crystallinity of chitin. As a result, chitin shows poor solubility in almost all usual organic solvents.

d) Pyranose Ring. Chitin-chitosan consists of pyranose ring either as *N*-acetyl-D-glucosamine or D-glucosamine. The glucosamine is reported for the detoxification and the combining with fatty acid for lowering cholesterol (Muzzarelli, 1996). Chitin-chitosan oligomers are known as activator for tissue growth and as fibroblast functions for reconstruct collagen leading to an effective wound recovery. The activity of chitin-chitosan imparts the biocompatibility (Richardson *et al.*, 1999), bioactivity (Dumitriu *et al.*, 1989), and non-toxicity (Rao and Sharma, 1997) under the structure of pyranose ring with *N*-acetyl-D-glucosamine or D-glucosamine.

e) Glycoside Linkage. Both chitin and chitosan are biodegraded in nature (Majeti and Kumar, 2000). The glycoside linkage or glucosidic bond (C-O-C) provides biodegradability via enzymatic hydrolysis such as chitinase, chitosanase, and lysozyme leading to chain degradation.

2.7 Modifications of Chitin-Chitosan

Considering the chemical structure of chitin-chitosan, the high molecular weight and strong inter- and intra-molecular hydrogen bond network provide the limitation of chitin-chitosan applications due to the lack of solubility and chemically inert. However, chitosan (degree of deacetylation more than 70%) can be solublized in dilute acid such as 1% of acetic acid. For chitin, it can be dissolved in N,N-

dimethylacetamide (DMAC)-LiCl (Cho *et al.*, 2000 and Einbu *et al.*, 2004), hexafluoro-acetone, and hexafluoro-2-propanol (Kurita, 2001). The developments of chitin-chitosan by either nanomerterization to provide materials in nano-scale or functionalization on chitin-chitosan to obtain water-soluble chitin-chitosan were studied to improve for using in many advance applications such as medicine, pharmacology, the food industry.

2.7.1 Water-Soluble Chitosan

The $-NH_2$ group at the C-2 positions gives the specific reaction to chitosan (Rinaudo, 2006). As chitin-chitosan is lacking of the solubility in common solvents, the functionalization at either $-NH_2$ or $-OH$ group is an effective way to obstruct inter and intra hydrogen bond resulting in solubility for bioactivity applications. The examples of water-soluble chitin-chitosan are follow:

Chitin- and chitosan-grafted copolymer

The hydrophilic group of poly(ethylene glycol)-aldehyde (PEG-aldehyde) provides Chitosan-PEG conjugation, partially acetylated chitosan-PEG, and chitin-PEG, which are water-soluble. The solubility depends on not only the degree of grafting but also molecular weight of PEG (Sugimoto *et al.*, 1998). Furthermore, water-soluble chitin-PEG hybrid was obtained by the acetylation of chitosan-PEG hybrid.

Trimethylchitosan ammonium

Domard *et al.* (1986) prepared trimethylchitosan ammonium which is the quaternization of chitosan. The reaction was done by using methyl iodide in sodium hydroxide resulting to cationic polymer of chitosan to achieve water-soluble in all practical pH range.

O- and N-carboxymethyl chitosan

The carboxymethylation on chitin-chitosn provides a water-soluble in a large range of pH. Dung *et al.* (1994) prepared *N*-dicarboxymethylated derivatives with a substitution of 95%. This derivative can be completely dissolved in water.

In 1994, Muzzarelli *et al.* achieved the water-soluble of *N*-carboxymethyl chitosan by using glyoxylic acid in equimolar with amino group of chitin-chitosan.

Chen and Park (2003) reported the use of monochloroacetic acid to introduce carboxymethyl group on chitin-chitosan at -OH to achieve *O*-carboxymethyl chitosan which is soluble in water.

2.7.2 Nanometerization

In recent years, nano-scale materials have received much attention to use in various fields such as electronic, biomedical, cosmetic and material applications due to its attraction characteristics, for example, high surface area and significant mechanical performance (Huang *et al.*, 2003). In order to achieve materials in nano-scale, nanometerization can be done via physical and chemical treatments. In the physical treatments, grinding, emulsion processing and electrospinning were applied to provide materials in nano-scale. The materials were treated by chemical such as acid and base for either depolymerization or size reduction.

2.7.2.1 *Nanomaterizations via Physical Treatments*

Physical treatments are useful for materials which can be dissolved either in water or organic solvent.

In 2004, Min *et al.* produced the chitin nano-fibrous matrix by using electrospinning process. Chitin was depolymerized by gamma irradiation to improve its solubility before electrospinning. 1,1,1,2,2,2-hexafluoro-2-propanol (HFIP) was used as a spinning solvent. The broad fiber diameter distribution obtained, the most of the fiber diameters are less than 100 nm.

In 2008, Chen *et al.* prepared collagen–chitosan complex nano-fibers. Their blends were dissolved in the mixture of 1,1,1,3,3,3-hexafluoroisopropanol (HFP) and Trifluoroacetic acid (TFA). The formation of nanofiber was achieved by using electrospinning experiments.

2.7.2.2 *Nanomaterizations via Chemical Treatments*

The treatment with a chemical reagent is the way to reduce the size of materials from miliscale to nanoscale.

Cellulose chains are self-assembled into microfibrils which are amorphous regions as defect regions in cellulose. The micro-fibrils can be modified to short micro-crystals by acid hydrolysis. This procedure can be used to

prepare highly crystalline particles called “microcrystalline cellulose” or “cellulose whisker” which forms colloidal in aqueous suspensions. The cellulose whiskers obtained are rod-like shape particles and the dimensions depend on the cellulose origin.

In 1998, Dong *et al.* prepared a cellulose whisker by sulfuric acid hydrolysis of cotton fibers and studied the effect of preparation chitin whiskers (time, temperature, and ultrasound treatment). The decrease in cellulose whiskers length depended on hydrolysis time. Characterization of cellulose whiskers was performed using different techniques such as transmission electron microscopy (TEM).

In 2001, Paillet and Dufresne found that the purification step of chitin with 3N hydrochloric acid has to be optimized in order to remove remaining proteins and to take the advantage by favoring the formation of a rigid chitin formation, so-called “chitin whiskers”.

2.8 Development of Chitin-Chitosan as Flocculant

The development of cationic polyelectrolytes flocculation for waste water treatment is for the goal of protecting and preventing environment. Polysaccharides are important natural polymers in term of the abundance and the biodegradability. In recent years, chitin-chitosan is highlighted as cationic polyelectrolytes and possibility to use as a flocculant.

Ashmore and Hearn (2000) studied on chitosan as nontoxic flocculant with various degrees of deacetylation to evaluate the flocculation of model latex particles. Chitosan requires acidic condition to act as cationic polyelectrolyte and to retain their solubility. They found that chitosan showed enhancement of flocculation rate by “charge patch” mechanism. The efficiency reduced with the degree of deacetylation resulting from the more rigid chain of chitosan with high molecular weight.

Divakaran and Pillai (2002) studied on the effectiveness of chitosan in removing water turbidity due to the suspension of river slit. The effectiveness of flocculant was found to be depended on pH and concentration. The optimal pH for

flocculation is around 7 to initiate flocs. They found that the quality of water was improved as compared to the conventional alum-lime method.

Laue and Hunkeler (2006) prepared a polymer chitosan grafted with quaternary ammonium cationic monomers. The polymer obtained accelerated the agglomeration. The long-chain branches and rigid nature of backbone provided more extended conformation with a higher charge density in solution. They found that the chitosan obtained showed strong bridging and/or charge patch mechanism in the flocculation mechanism.

Chaikumpollert demonstrated the use of chitosan chloride for creaming the skim natural rubber latex. Based on this background, the present work aims to develop chitosan-based material for the use as a flocculant. Here, the requirements are; (i) cationic charge to neutralize negatively charged natural rubber particles, (ii) miscibility with natural rubber to enhance the flocculation, (iii) water solubility for the washing out of the separated rubber, and (iv) environmental friendly so as to overcome the limitation of acid coagulant.

2.9 Development of Chitin-Chitosan as Biofillers

The additives or fillers used for polymers and rubber are concerned mainly on the physical and mechanical properties. As the requirement of environment of environmental friendly becomes a main issue for novel materials. Various types of green fillers and additives have been proposed.

Nair and Dufresne (2003) prepared nanofiller based on chitin-chitosan materials blending with natural rubber. The chitin whisker was simply achieved from acid hydrolysis of chitin. They modified chitin whiskers as nanofiller in rubber bio-nanocomposites. They found that whiskers formed a rigid network to be governed by a percolation mechanism. The existence of rigid chitin network provided the improvement in swelling in an organic solvent medium and the blend system depended on the sample preparation condition. They also extended the work to study the mechanical properties. The mechanical properties improved with chitin whisker incorporation resulting from three-dimensional chitin network formed as hydrogen bonding. The surface of chitin whisker was successfully modified by using different

coupling agents, namely, phenyl isocyanate (PI), alkenyl succinic anhydride (ASA), and 3-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI). The chemical treatment improved the adhesion between fillers and rubber matrix. However, the mechanical properties decreased as a consequence of the partial or total destruction of the three-dimensional network of chitin whiskers.

2.10 Points of the Present Work

The present work stands on the development of chitin-chitosan for novel applications in the rubber industry. The first part (CHAPTER III) focuses on the modification of chitin-chitosan to get water-soluble derivatives, i.e., chitosan-hydroxybenzotriazole (CS-HOBt), chitosan-acetate (CS-Acetate), carboxymethyl chitosan (CM-CS), and Iodo-chitosan (Iodo-CS). The main objective of this part is to develop chitosan as a biodegradable flocculant for rubber separation from the natural rubber latex colloidal suspension.

The second part focuses on the development of chitin-chitosan as biodegradable nanofillers for rubber bio-nanocomposites. Chapter IV shows a novel approach of preparing chitosan nanoscaffold from chitin whisker via microwave technique. This simple but effective process reduces the treating time as well as the possibility of large scale production.

Chapter V and VI concentrates on the bio-nanofiller chitosan. Here, nano-scaled chitosan, as fillers for epoxidized natural rubber (ENR) are demonstrated. The work covers the mixing process and the evaluation of the rubber reinforced with nanomaterial chitosan. The work shows the mechanism how to control the morphology the physical and mechanical properties of ENR blend.