



## CHAPTER I INTRODUCTION

Natural rubber latex is obtained from the tree *Hevea brasiliensis* and present as a colloidal suspension of natural rubber particles in aqueous serum. In freshly tapped natural rubber latex, the rubber particles are enrobed in a continuous monolayer (Dupont *et al.*, 1976) of negatively charged phospholipid-protein complex providing the stability for the colloidal system. By simply adding positively charged reagent into the colloidal system, the phase separation, so-called “coagulation” gradually occurs resulting in the ease of separation of rubber particles as a coagulum out of the rubber latex.

In general, coagulation of natural rubber latex has been done by adding an acid such as formic acid or sulfuric acid. Some salts, for example sodium silicofluoride, are also reported as precipitating agents functioning at pH 5.1-4.8 (Greve, 2003). As the acidic coagulation of latex is simple and cheap, it is widely used as a primary step to prepare rubber crumbs and sheets from the latex. However, the acid waste needs additional treatment to avoid pollution (Loykulnant *et al.*, 2007).

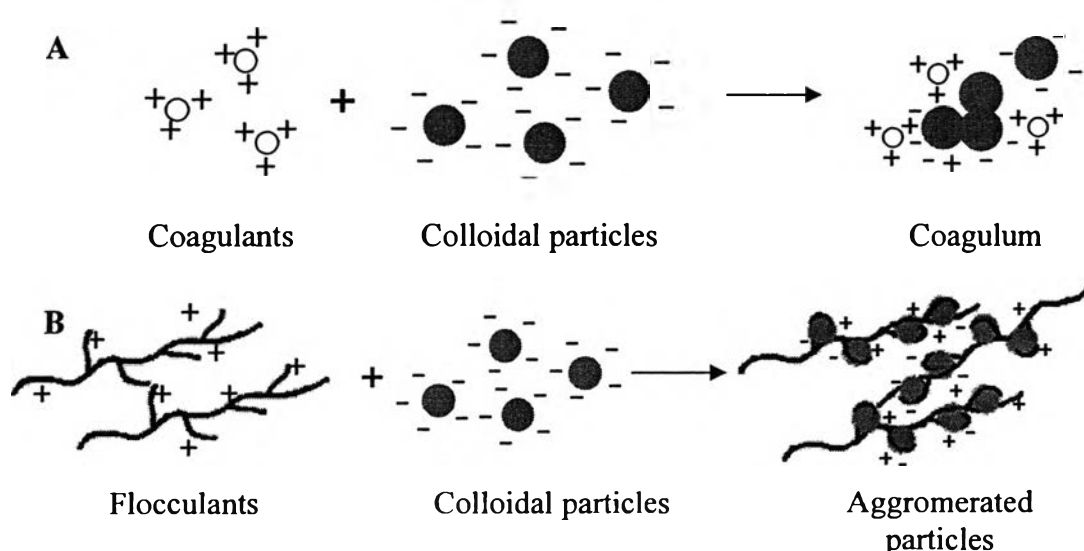
In the current years, an understanding of environmental problems has brought to the needs of ecological materials. In the rubber industry, the development of a novel method of coagulating rubber latex to substitute the use of acid is a topic on an expectation. “Flocculation” is a concept of applying polymer with ionic properties to initiate the interaction between micrometer sized particles in aqueous media resulting in the phase separation or precipitation (Burkert and Hartmann, 2003). In the case of rubber latex, the fact that the rubber particles in latex are surrounded by a membrane with anionic charge, the flocculation is an alternative way to separate rubber using cationic polymer (Shatalov *et al.*, 2003 and Verezhnikov *et al.*, 2005). FLOERGER® is a commercial flocculant, based on polyacrylamide copolymer, to assemble suspension particles in waste water, metal particles, pulp fibers, etc. into aggregates in order to be efficiently separated from the water. This is useful for mines, paper mills, and other industries ([www.snf-group.com/Flocculants.html](http://www.snf-group.com/Flocculants.html)). Copolymer of acrylamide and 2-

[(methacryloyloxy)ethyl]trimethylammonium chloride is an example of cationic flocculant using for decolorization, which is the interaction between sulfonic group in dye molecules and quaternary ammonium of flocculant (Shen *et al.*, 2006). Although the concept of using an ionic polymer as a flocculant is another choice to separate ionic colloidal suspension, the degradability after used is the point to consider (Wang, *et al.*, 2008). On this viewpoint, an environmentally friendly biodegradable flocculant is an ideal.

In the case of natural rubber latex, the flocculants have to meet the following requirements; (i) the biodegradability so as the polymer after use will not be remain in the environment, (ii) the effectiveness which allows us to use only in small amount and will not be the problems in elimination from the coagulum, (iii) the water solubility which enables the simple step of washing thoroughly by water to exclude the polymer from the aggregated particles, and (iv) the availability and the cheapness so that the flocculation treatment will not affect to the price of rubber.

The schematic illustration of coagulation and flocculation is shown in Scheme 1.1. In general, coagulants are small molecules those especially acids, whereas flocculants are polymer with ionic charge. The significant difference between the coagulation and flocculation is the mechanism of the aggregation of rubber particles in NR latex. The coagulation gives a hard coagulum due to the slow aggregation, whereas only small amount of flocculation initiates aggregation rapidly of microparticles via charge-charge interaction of polymer and rubber particles (Burkert and Hartmann, 2003).

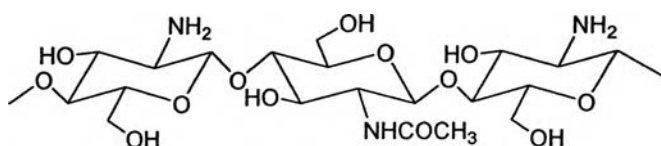
**Scheme 1.1** (A) Presumed coagulation and (B) flocculation processes



Considering the requirements of flocculant mentioned above, a biodegradable natural product of chitin-chitosan is one of the ideal polymers. Chitin-chitosan (Scheme 1.2) is the second most abundant naturally occurring polysaccharide next to cellulose, which can be found in the crustacean and insect shells as well as the cell walls of fungi and algae. The structure of chitosan is a copolymer between  $\beta$ -(1-4)-2-acetamido-2-deoxy- $\beta$ -D-glucose and  $\beta$ (1-4)-2-amino-2-deoxy- $\beta$ -D-glucose. This aminopolysaccharide covers bio-physico-chemical specific properties of biocompatibility, biodegradability, and non-toxicity including the high viscosity, the thermal stability and the cationic properties.

One of the limitations of chitin-chitosan is its insoluble property in most of the solvents including water as chitin-chitosan forms strong inter- and intra-molecular hydrogen bonds. The increase in solubility is possible in aqueous acids due to the protonation at the amino groups, which obstructs the hydrogen bond network. In order to overcome the poor solubility of chitin-chitosan for advanced applications, various chemical modifications have been proposed at the hydroxyl and amino groups to achieve organo-soluble or water-soluble chitin-chitosan. Typical examples are *N*-phthalolyl chitosan, (Nishimura *et al.*, 1991), carboxymethyl chitin (CM-chitin), and carboxymethyl chitosan (CM-chitosan) (Chen and Park, 2003).

**Scheme 1.2** Structure of chitin-chitosan



It is important to note that the amino group on chitosan chain demonstrates a cationic polyelectrolyte to initiate agglomeration of anionic particles. This brings the possibility to use it as a biodegradable flocculant (Pinotti *et al.*, 1997, Divakaran and Pillai, 2001 and 2002, Roussy and Guibal, 2007, Wang, 2008, and Zeng *et al.*, 2008). Mishra *et al.* (2008) reported the use of chitosan grafted with *N*- vinyl formamide as a flocculant for removing metal ions in water treatment.

The fact that the raw material is available in Thailand, is also an attractive point to develop this material for practical usage. There, the essential point to be considered is the derivatization of chitosan to be water soluble ones. As chitin-chitosan is under the inter- and intramolecular hydrogen bond network, it is difficult to dissolve in most solvents. The derivatization of chitin to chitosan with percent deacetylation more than 80 brings chitosan be soluble in acids. Modification of chitosan with carboxylate salts as seen in the case of *N,O*-carboxymethyl chitosan is a good way to bring water solubility to chitosan. Based on the above mentioned points, chitosan is a potential material to develop as a flocculant for NR.

The development of rubber for environmental friendly materials is not only related to the rubber latex purification to remove allergenic proteins and mal-odor, but also the additives for rubber compounding. In most cases, rubber has to be compounded with various chemicals including reinforcing materials to manufacture the products. There, additional fillers such as carbon black have seen in the case of tire in automotive products. However, carbon black may produce eye irritation and carbon monoxide and carbon dioxide are generated after combustion to cause pollution. Silica is also considered as fillers with unique properties on the white color and hydrophilicity. The limitation of silica is about the high density as compared to the carbon black. Considering the waste treatment after use of rubber products, especially, tires, the landfill and pyrolysis are only choices which also generate the environmental problem.

Based on this viewpoint, the renewable resources based fillers; especially natural fibers are the most potential materials (Carvalho *et al.*, 2003 and Lu *et al.*, 2004). Therefore, the materials obtained from renewable resources have been paid much attention and been extensively studied as biofillers. The advantages of natural fillers are their low density which functions in light weight, renewable character which is environmental friendly and the reasonable price (Ismail *et al.*, 1997).

Previously, Nair and Dufresne (2003) proposed the use of biofiller in nano-scale, especially the chitin whisker. The physical and mechanical properties of natural rubber improved after incorporating with chitin whisker. The reinforcement of whisker depended on their rigid three-dimensional network formation and the high

specific surface area, resulting in the strong interactions such as hydrogen bond between the whiskers (Kvien, *et al.* 2005).

Arroyo *et al.* (2007) reported that organoclay provides exfoliated structure by adding epoxidized natural rubber as dispersing agent. Epoxidized natural rubber (ENR), is a random copolymer of isoprene units and epoxidized isoprene units, which can be obtained from the natural rubber treated with peracid such as peracetic acid and performic acid (Bradbury and Pereral, 1988). The copolymer exhibits the unique properties such as, oil resistance, low gas permeability, high damping, and good wet grip (Zurina *et al.*, 2006). The extent of epoxidation unit gives an increase of polarity and glass transition temperature. The increased polarity is important when we consider the reinforcement by fillers with a good interaction between fillers and polymer matrix.

In the past, Phongying *et al.* (2007) succeeded in preparing chitosan nanoscaffold by simply deacetylating chitin whisker. This material is attractive in term of the fibrous network and the hydrophilicity appropriate for ENR. The expectation on ENR with chitosan nanoscaffold biocomposites is about the changes in toughness, swelling, including the factors related to the dispersibility of chitosan nanoscaffold in ENR matrix.

The present dissertation, thus, focuses on the possibility of the application of chitin-chitosan in rubber technology. The first part concentrates on the development of water-soluble chitosan derivatives as a flocculant for coagulating natural rubber latex (CHAPTER III). The second part is about the application of microwave technique to prepare a large-scale chitosan nanoscaffold from chitin whisker including a comparative study between conventional treatment and microwave one to conclude the effectiveness of the microwave system (CHAPTER IV). The work extends to the use of chitosan as a nano-biofiller in rubber (CHAPTER V and VI).