

CHAPTER I

INTRODUCTION

1.1 Natural Rubber

Natural rubber latex is most commonly harvested from *Heavea brasiliensis* tree consisting of rubber and nonrubber dispersed in an aqueous serum phase. Freshly tapped natural rubber latex is a whitish fluid of density between 0.975 and 0.980 g/ml, pH from 6.5 to 7.0 and surface free energy from 40-45 ergs cm⁻². Latex coagulates on exposure to air because bacteria in the air react with enzyme in latex, thus lowering the pH of latex to the point where the latex coagulation occurs. To avoid the problem, latex is preserved with ammonia. Being a natural product, the composition of fresh latex varies between wide limits. The following figures are typical: total solid content (TSC) 36%, dry rubber content (DRC) 35%, protein substances 1-1.5%, resinous substances 1-2.5%, ash up to 1% and water ad.100%.

These substances are distributed between three principal phases: the rubber particles, the aqueous phase, and the lutoid phase. The rubber phase contains 96% weight rubber hydrocarbon which is cis-1,4-polyisoprene, 1% weight protein substances, and 3% weight lipid substances. Trace metals,

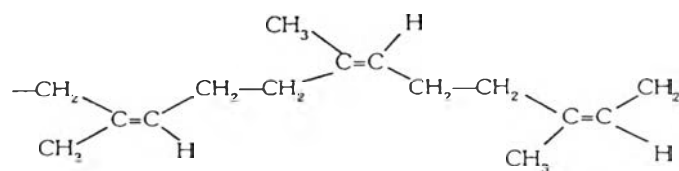


Figure 1.1 Structure of cis-1,4-polyisoprene.

notably magnesium, potassium and copper, are also associated with the rubber particles to an aggregate extent of approximately 0.05%. The rubber particles are stabilized by an adsorbed layer of protein and phospholipid.

The aqueous phase or serum phase is a dilute aqueous solution of density 1.02 g/ml. The serum contains different chemical species including carbohydrates, proteins and amino acid of which α -globulin and hevein known as principal ones, enzymes, and nitrogenous bases.

The lutoid phase is bottom yellow fraction from centrifugation of fresh latex at low speed. Lutoid particles contain small quantities of soluble protein, insoluble protein as well as phospholipid. The presence of carotenoid pigments in nonrubber particles gives natural rubber its yellow color.

Fresh latex is typically transformed to be dry rubber and concentrated latex. Fresh latex is concentrated to about 60% dry rubber content mostly by centrifugation because it is economical to transport over large distance and it tends to be more uniform in quality.

Concentrated latex is processed to a variety of products such as dipped goods (surgeons' gloves, dentists' gloves, household gloves, balloons, condoms, and tubing), adhesives, carpet industry, foam products, thread, and so on.

Unvulcanized natural rubber is soft, easily deformed, tacky when hot, and hard and rigid when cold. Although, after vulcanization, it possesses the excellent tensile strength, tear resistance, fatigue resistance, low creep and low heat build-up, it still has residue tack.

1.2 Tack

Tack (Hamed, 1981) is described for the ability of two materials to resist separation after bringing their surfaces into contact for a short time under light

pressure. Autohesion or autohesive tack is coined for two similar materials whereas adhesive tack is coined for two dissimilar materials.

Many investigators have discussed the mechanism of tack. When two surfaces come into intimate molecular contact, interdiffusion of chain across the interface takes place and the bond formed can resist high stress before rupture. The bond formed is ascribed to van der Waals forces by Bostrom (1953) and Forbes and Meleod (1958), but Voyutskii and Magolina believe that the said bond is established by diffusion.

Wool (1984) considers the tack in terms of dynamics and statics of random-coil chains by using molecular dynamics model based on deGennes theory of reptation. In this model, amorphous bulk materials consist of linear random-coil configuration of the chain. As illustrated in Figure 1.2, the chain is in its initial tube at $t=0$. Then the chain, acting by Brownian motion, diffuses

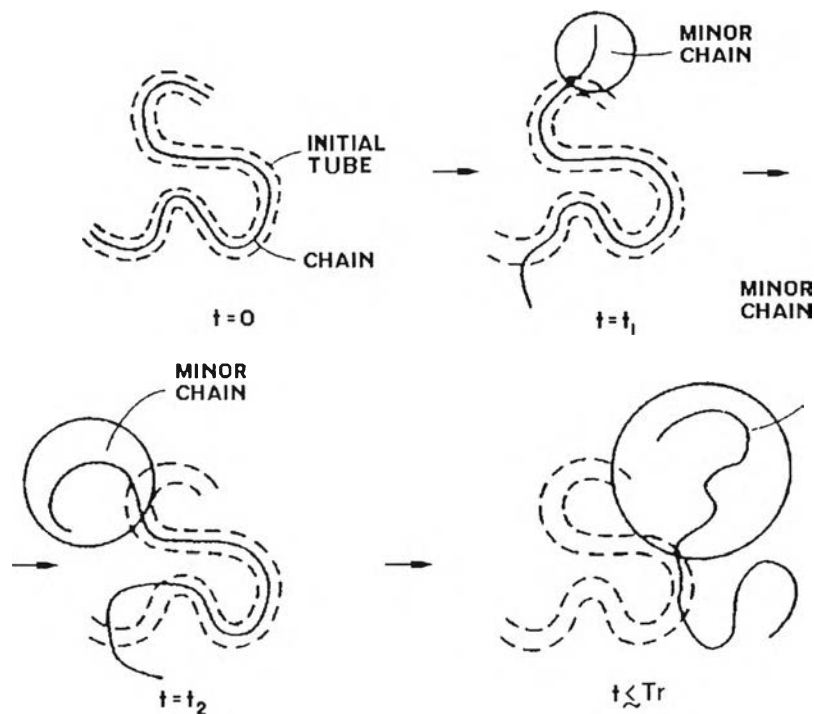


Figure 1.2 The reptation model for a random-coil chain.

back and forth in the tube at $t=t_1$ and chain ends can move to any direction away from the tube.

The chain escaping from the initial tube is so called the minor chain. At $t=t_2$, the minor chain increases further in length and finally it has escaped from its original tube or configuration.

This theory is applied to describe the molecular interdiffusion at the interface. Figure 1.3 shows the interdiffusion process at the only one side of the interface for convenience. At $t=0$, molecular contact is achieved at the interface. Thus as time is infinity, complete interpenetration and reentanglement are achieved.

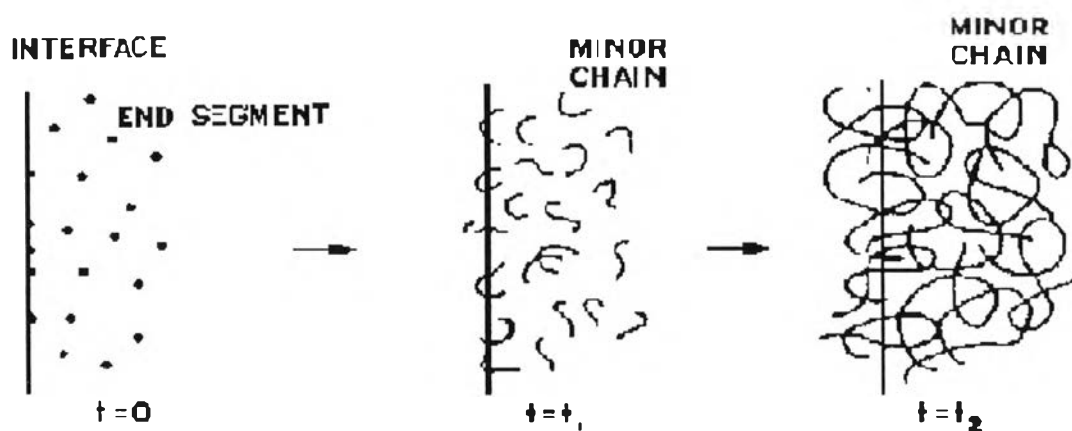


Figure 1.3 The interdiffusion process at an interface in term of the behavior of the minor chains.

Natural rubber is one elastomer exhibiting tack because it flows readily under a compressive force, hence interdiffusion of polymeric chains across the interface is usually formed. Due to its crystallization with elongation, it then forms bond that is capable of resisting high stress before rupture. So strain crystallizing material like natural rubber displays tack easier than amorphous rubber. Noncrystallizable chain must interdiffuse enough to become entangled with other chains before it will significantly resist the

separation. On the other hand, strain crystallizing natural rubber need less interdiffusion to form a tack bond.

Many investigators have studied various effects on tack strength. Tack value depends on following factors:

1. Bulk properties of the material
2. Surface (geometry and aging)
3. Compression (force, time, temperature, and direction of the force)
4. Separation (speed, temperature, and direction of the force).

Tack strength increases with increasing compression pressure and time. Effect of temperature gives two opposite directions. The movement of the macromolecular segments is enhanced with raising the temperature during the compression period. On the other hand higher temperature during the separation process decreases the force measured.

When measured with higher speed of separation, tack strength increases because the rubber does not have time to flow. Consequently, the molecular chains have no time to disentangle and must be broken. Oxidation of the surface is to be detrimental to tack, i.e., destroying tack, relying on kind of material.

1.3 Polydimethylsiloxane

Polydimethylsiloxane (PDMS), shown in Figure 1.4, is one member of semiorganic polymers built up of long chains of alternate silicon and oxygen atoms. Being formed by either condensation of silanols or by hydrolysis of organyloxysilanes with functional (e.g. halogens, amino, etc.) substituents, PDMS is the basic polymer for a series of different products varying from oils to elastomers.

In oil form, it consists of linear polydimethylsiloxane macromolecules with a molecular weight in the range of 4000-25000. It is produced from

dimethyldichlorosilane or a mixture of methane and phenylchlorosilane which is continuously hydrolyzed by mixing with dilute hydrochloric acid. The viscosity of silicone oil is controlled by the ratio of hexamethyldisiloxane to dimethyl dimethoxysilane (or other suitable silane) employed.

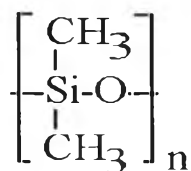


Figure 1.4 Structure of polydimethylsiloxane.

PDMS is colorless, odorless, nontoxic and physiologically inert. In addition, because of low intermolecular forces, it has low activation energy for viscous flow, high compressibility, and small change of viscosity with temperature. Other important property is resistant to not only oxidation, but also a wide variety of chemicals.

Many derived products, e.g., emulsion, greases, coatings have been developed for diversified applications in the food, medical, electronic, cosmetic and other industries.

1.4 Glove Manufacture

Natural rubber latex gloves are at first introduced by William Halstead in 1890. Dipping process, shown in Figure 1.5, involves essentially the immersion of a former, which is made from porcelain or glass, and cleaned by acid wash to remove calcium carbonate and corn starch residues as well as by alkali wash to remove extractable protein residues into coagulant to give an even layer of chemical coating onto the former. Then the former is immersed into suitably compounded latex, followed by slow withdrawal in such a way to obtain a uniform latex depositing on the former. The thickness of the

deposit may be reinforced with subsequent coating. The process is completed by drying, leaching and, if necessary, vulcanizing the deposit.

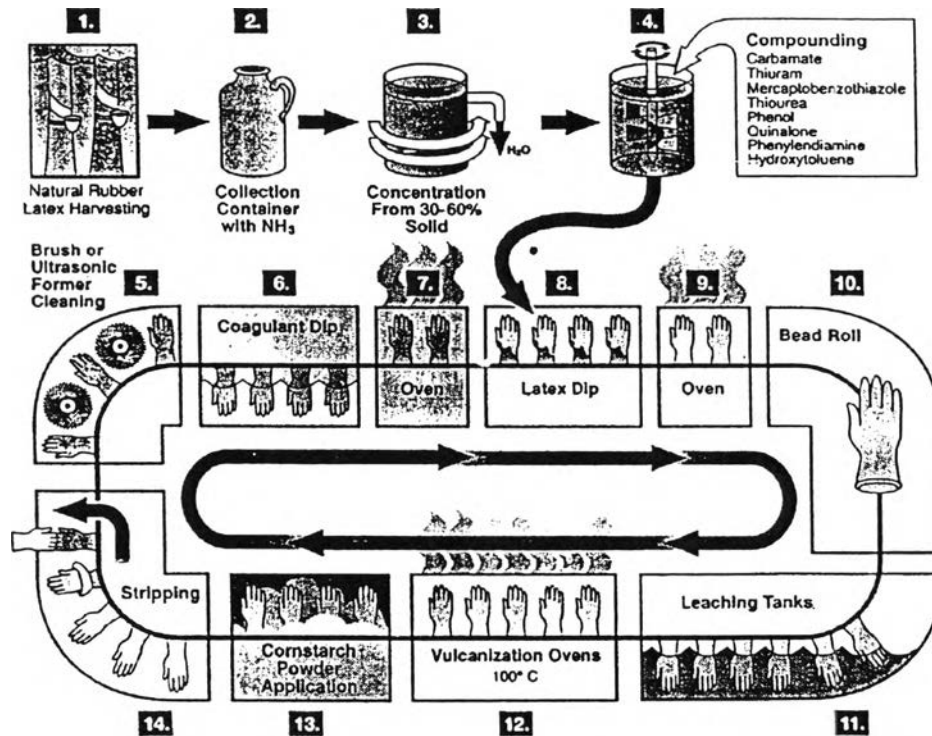


Figure 1.5 Rubber glove manufacture. (Source: Hamann, C. P. (1993) Natural rubber latex protein sensitivity in review, *American Journal of Contact Dermatitis*, 4(1), 7)

Generally, vulcanizates produced from natural rubber latex tends to have surface friction and surface with a degree of residual tack. Additionally, the vulcanizate surfaces exhibit poor lubricity with respect to dry and damp surfaces. A high coefficient of friction and a degree of residual tack are distinct disadvantages in those applications where vulcanizate surfaces must slide on another surfaces. This is particularly important in the use of medical gloves, such as examination gloves and surgeon gloves.

To enhance the lubricity with respect to dry and damp surfaces, conventional approach is to treat surface with a fine powder such as talc and

starch. However it is understood that powder can interfere and contaminate for the application in surgical and industrial field. Furthermore, for sensitive individuals, the powder can cause allergy or be a hand irritant because it can absorb and release some of the naturally occurring proteins from the latex.

Many attempts have been made to produce powder-free gloves. One approach is to chemically treat the surfaces of rubber with halogen species such as chlorine, bromine or fluorine. Although this treatment imparts temporary slipperiness, it results in a poor aging resistance such as discoloration and oxidation. Another common practice to prevent autohesion is to treat with silicone oil, which is non-allergic material and overcome poor aging resistance. However it can reduce the need of the powder to only one third. Other methods have entailed coating the rubber surface with other polymers such as hydrogel or polyurethane which renders a lower coefficient of friction to the surface.

To reduce tack and surface friction in natural rubber, it is desirable to compound a small amount of a low molecular weight non-tacky oligomer with natural rubber latex and prepare powder-free natural rubber vulcanizate. The oligomer employed is poly(dimethylsiloxane). The assumption of the function of oligomer is that it will preferentially segregates and moves towards the surface and eliminates tack entirely. Then properties involving autohesive strength, mechanical properties, surface morphology will be measured.