CHAPTER I
INTRODUCTION

1.1 Dental Rubber Dam

Needs for isolation of the oral working area is rather obvious. A tooth bathed in saliva, a tongue that insists on obstructing vision, and a bleeding gingival are but a few of the obstacles that must be overcome before delicate and accurate workmanship is possible. A "Dental Rubber Dam" is the best method to control these obstacles.

The dental rubber dam is a flat thin sheet of latex / non-latex that it held by a clamp and frame that is perforated to allow the sheet to cover and protect the other teeth except the healed one. It stops things falling down the patient's throat so that they will not swallow or inhale any debris from old fillings. Whether placing a white filling or a silver filling the dentists always use a dental rubber dam unless it is impossible to get a clamp around the tooth. If they can not use a dental dam they will not place a white filling which are very sensitive to water and saliva, and if a dental dam is not used the filling will not last as long as they otherwise could. The filling may also be very sensitive after the restoration is done, and will be much more prone to recurrent decay. Silver filling is less sensitive technique and can successfully be placed without a dental dam, although they too will have a shorter usable life, and will also be susceptible to recurrent decay.

Despite its substantial value, dental rubber dams are widely used only in other countries. In Thailand, the use of dental rubber dam is limited, mainly due to none of manufacturer and the imported dental rubber dams are very expensive. Consequently, if we find material that is low price and easily available in Thailand to produce dental rubber dams, it could be sold in lower price, resulting in extensively use. More importantly, this also decreases the import of dental rubber dams, which is a means of reducing deficit balance of trade.

From the research we find that Hevea brasiliensis is not only abundantly available in Thailand but also used as material to produce dental rubber dams in foreign countries. In this thesis, we do the experiment to compound both of natural

rubber latex and deproteinized natural rubber latex for comparing the properties of finished films, to study the properties by using the three types of filler (calcium carbonate, admicelled silica and precipitated silica), to determine the relationship between the contact angle of the water drop on rubber surface and the friction of rubber surface after compounding the latex with 50% calcium carbonate, and to study the water-extractable protein concentration after compounding the latex with 10% precipitated silica. This inspiration is come from a previous work which was compounded by using fumed silica (Amder, 2000).

For these objectives, the latex will be compounded following a basic formulation for medical gloves shown in Table 1.1. The finished films are compared the mechanical properties to the dental rubber dam specification as shown in Table 1.2.

Table 1.1 Basic formulation for medical glove

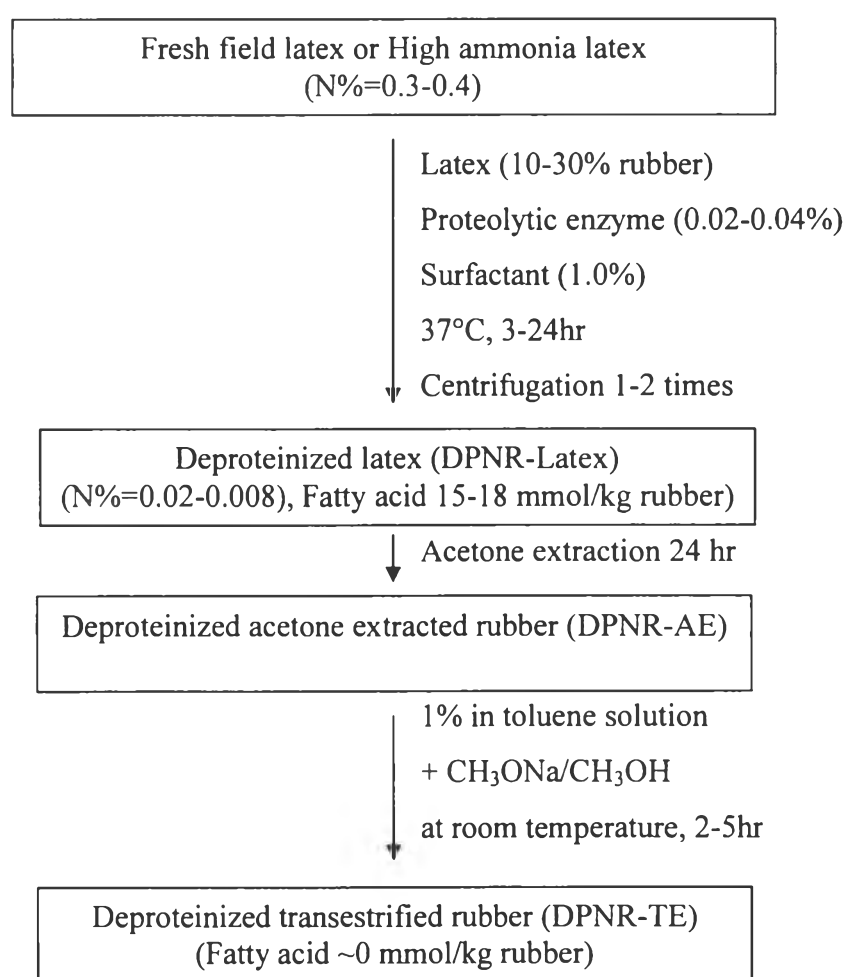|	Dry weight (g)
60% Natural rubber latex	100
10% Potassium hydroxide solution	0.5
50% Sulphur dispersion	1.5
50% Wingstay-L dispersion	1
50% Zinc diethyldithiocarbamate dispersion	1
50% Zinc oxide dispersion	1

Table 1.2 Commercial dental rubber dam specification

|	Blossom®	4D Latex®	Hygenic®
Size	5"x 5", 6"x 6"	6"x 6"	5" x 5", 6"x 6"
Thickness	0.20 mm	0.18-0.33 mm	NA*
Physical properties			
Tensile strength (min)	22 Mpa	25 Mpa	27.6 Mpa
Elongation at break (min)	700%	850%	780%
Tear strength	NA*	50 N/mm	Excellent
Hardness (Shore A)	NA*	35°	40°(plied)

NA*= not available

1.2 Deproteinization of Natural Rubber Latex

Deproteinized natural rubber (DPNR) is a new grade of natural rubber with very low nitrogen and ash contents. It is produced with a proteolytic enzyme and surfactant to reduce nitrogen content. The deproteinized rubber is further purified by acetone-extraction followed by transesterification with sodium methoxide. As shown in following chart.

Fresh field latex or High ammonia latex
(N%=0.3-0.4)

Latex (10-30% rubber)

Proteolytic enzyme (0.02-0.04%)

Surfactant (1.0%)

37°C, 3-24hr

Centrifugation 1-2 times

Deproteinized latex (DPNR-Latex)
(N%=0.02-0.008), Fatty acid 15-18 mmol/kg rubber)

Acetone extraction 24 hr

Deproteinized acetone extracted rubber (DPNR-AE)

1% in toluene solution

+ CH_3ONa/CH_3OH

at room temperature, 2-5hr

Deproteinized transestrified rubber (DPNR-TE)
(Fatty acid ~0 mmol/kg rubber)

**Figure 1.1** Deproteinization of NR-latex.

Deproteinization and transesterification can reduce the branch-points, which is occurred by the formation of branching and gel in natural rubber structure, after the removal of protein and linked fatty acid groups (Kawahara et al., 1999) as shown in figure 1.2.
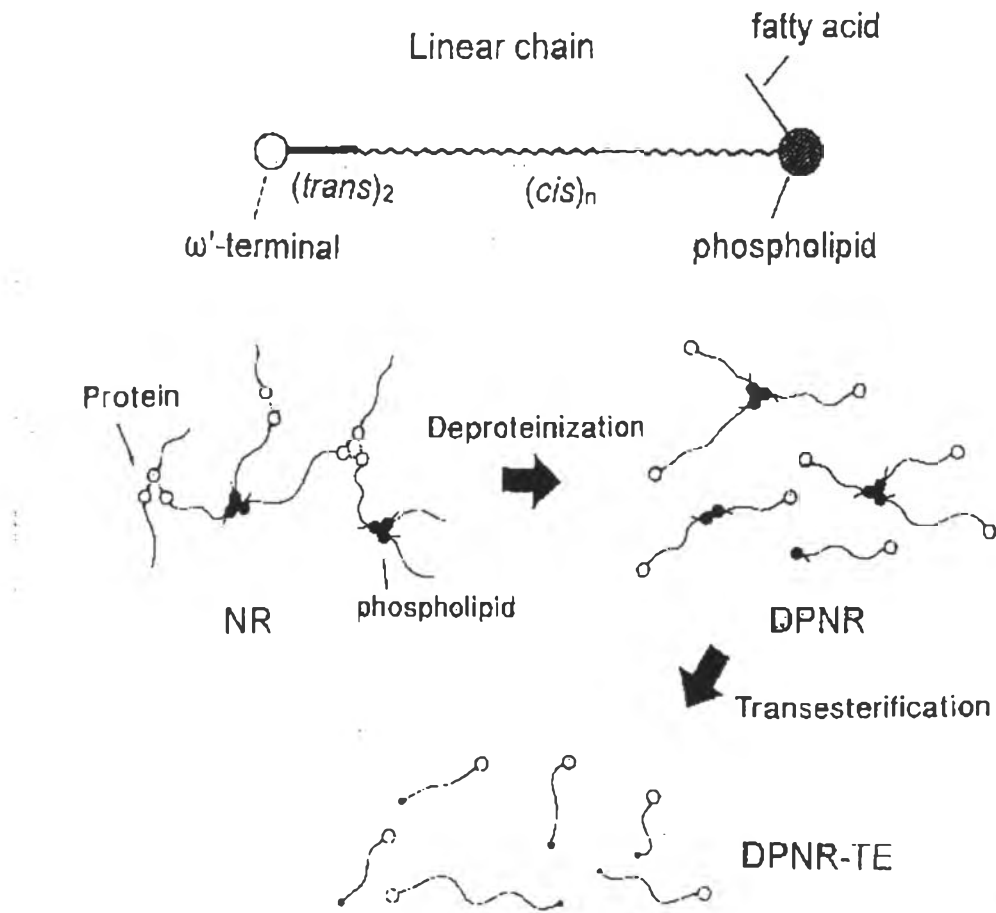
Figure 1.2 Presumed functional groups act as branch-points in natural rubber.

1.3 Silica

Silica is considered polymer of silicic acid in which the bulk structure is produced by interlinking the SiO_4 tetrahedral. At the surface, the structure terminates in siloxane groups(-Si-O-Si-) and one of the several forms of silanol groups(-Si-OH-) as shown in Figure 1.3.
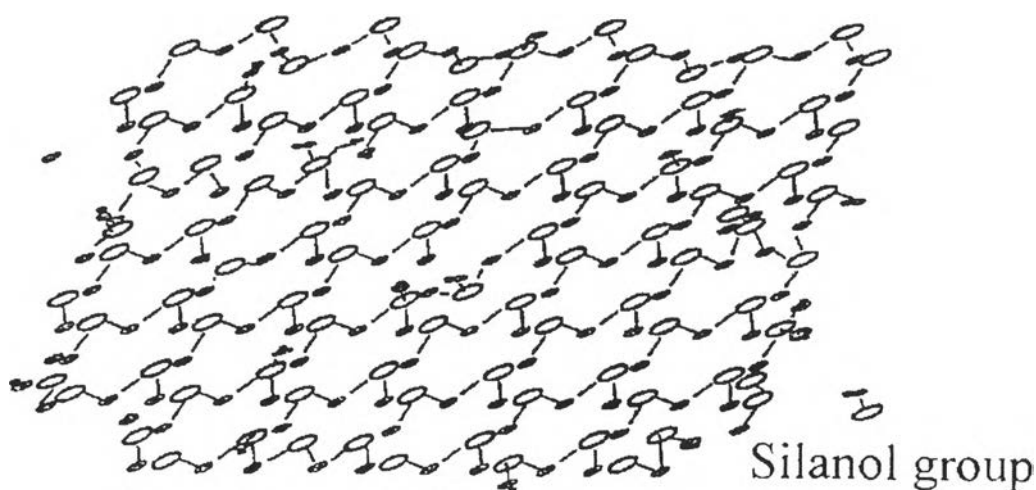

Figure 1.3 Surface chemistry of silica.

It is reinforcing filler giving compounded latex film of high tensile strength, hardness, tear strength and abrasion resistance. It is used in translucent and colored products, mechanical goods, and shoe soling. Hydrated silica retards cure and required increased dosage of accelerator or the addition of materials such as glycols or amines to promote curing.

Unfortunately, silica is hydrophilic which limits the compatibility comparing to hydrophobic rubber. Silica to silica attraction is high owing to its hydrogen bonding. As result, silica forms large aggregate and resists the flow of rubber matrix. These advantage points make rubber composite show high viscosity and the mixture is stiff. In addition, since the mixture in compatible, the properties of rubber composite will decrease instead of the expected excellent properties. Therefore, the

way to improve compatibility between silica and rubber is the addition of compatibilizer, which is compatible with both hydrophilic and hydrophobic groups, as shown in Figure 1.4.

Incompatible Mixture   **Compatible Mixture**
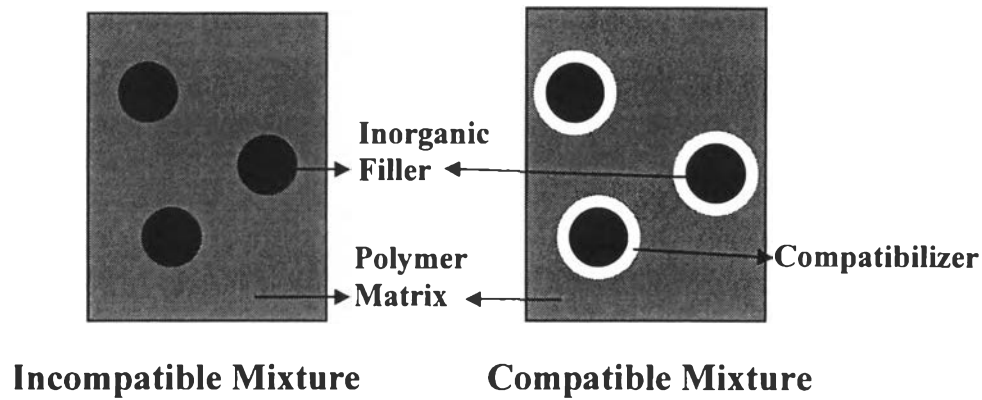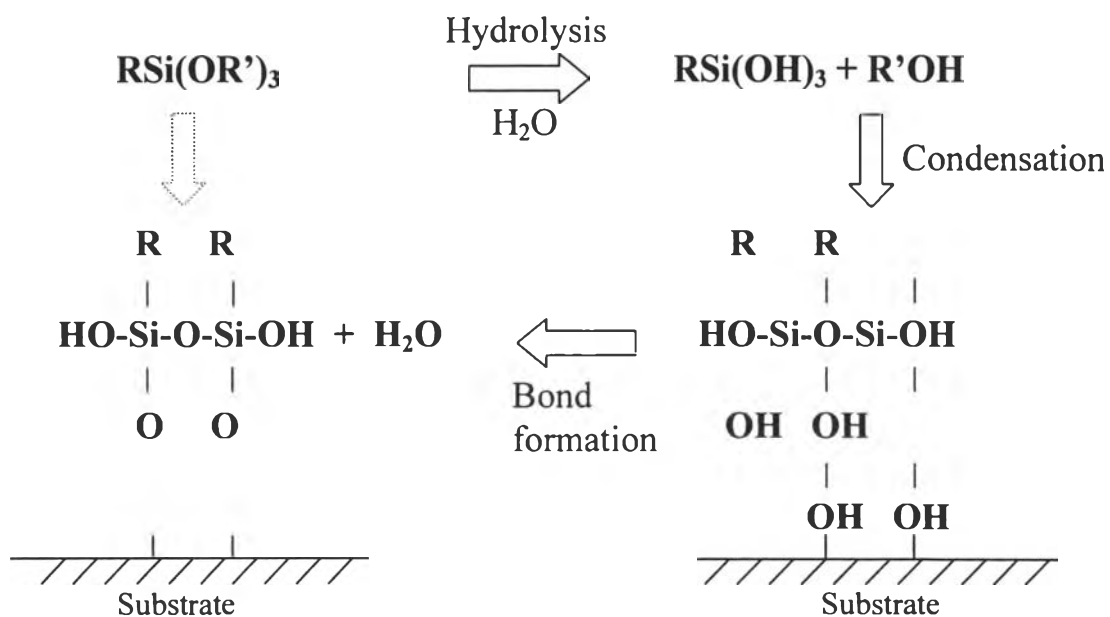
Figure 1.4 Compatibility of inorganic filler and rubber matrix.

For the silica filler, the effective compatibilizer is silane coupling agent. The silane coupling agent will bind the rubber and silica together. Thus, after treatment with silane, viscosity of the composite decreases which results in enhancing process ability, good mechanical strength and excellent properties.

1.4 Silane Coupling Agent

The simple structure of silane coupling agent is $RSiX_3$ where R is organofunctional group that is compatible and reacts with polymer matrix. X is hydrolyzed group and is usually alkoxy group or Cl. The hydrolysable group will be hydrolyzed by water and then coupled onto substance surface. The water for hydrolysis can be added from external source or may come from water at substrate surface. The reaction of silane can be described by Figure 1.5. Firstly, the alkoxy group of silane will be hydrolyzed at random to be the hydroxyl group and lose alcohol as a by-product. Then, the silane hydrolyzed is probable to condense with each other to form oligomers. After that, the silane will be coupled onto substrate surface with a loss of water. There is also a case that unhydrolyzed silane is coupling directly onto substrate surface with an elimination of alcohol.

Figure 1.5 Reaction of silane coupling agent.

The requirement of silane coupling agent for rubber is that the silane compound have the sulphur group for vulcanization across the isoprene chain. Major silane often used in rubber industry can be raised as bis[3-(triethoxysilyl)propyl]tetrasulphide (SI-69) is shown in Figure1.6.

$$C_2H_5O - Si - (CH_2)_3 - SSSS - (CH_2)_3 - Si - OC_2H_5$$

with C_2H_5O and C_2H_5O branches on the left silicon, and OC_2H_5 and OC_2H_5 branches on the right silicon.

Figure 1.6 Structure of SI-69.

In order to treat precipitated silica with the amount of silane concentration, theoretical amount of silane monolayer was calculated (Plueddemann, 1982). Surface area of silane γ-MPS [$CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$] was reported to be 120 Å^2. However, the silane Si-69 is nearly twice of the γ-MPS so the silane surface area in this case could be estimated to be 240 Å^2.

Theoretical amount of silane monolayer calculation:

The amount of silane monolayer (g)

$$= \frac{\text{surface area of silica} \times 10^{20} \times \text{molecular weight of silane}}{6.02 \times 10^{23} \times \text{surface area of silane}}$$

$$= \frac{133 \ (\text{m}^2/\text{g}) \times 10^{20} \times 539}{6.02 \times 10^{23} \times 240 \ (\text{Å}^2)}$$

$$= 0.05 \ \text{g of silane} / \text{g of silica}$$