

2.2 The effect of non-rubber components, such as, protein and long chain fatty acid ester on storage hardening and elucidation of the mechanism of the branching and gel formations.

Fresh natural rubber (FNR) was prepared by casting freshly tapped NR latex on to a glass plate followed by drying under reduced pressure. Deproteinized NR (DPNR) was prepared by incubating fresh latex with 0.04% w/v proteolytic enzyme and 1% w/v sodium dodecyl sulphate (SDS) at 37°C for 24 h followed by centrifugation twice. Transesterification of FNR was carried out by mixing 1% w/v toluene solution of the rubber with freshly prepared sodium methoxide at room temperature for 2.5 h under N₂ atmosphere. The resulting solution was precipitated with methanol and precipitate was dried under reduced pressure.

The six test pieces were cut from the double sheet with the Wallace punch. The thickness of test pieces was between 3.2-3.6 mm. These were divided into two sets of three; one set of each for the plasticity tests before and after accelerated storage hardening. The accelerated storage hardening test was carried out by using standard test pellets of the rubber samples dried in preheated (to 60°C, a 30 min) desiccators. Then, phosphorus pentoxide (P₂O₅), sodium hydroxide (NaOH), silica gel, and distilled water were placed in each of the preheated desiccators. The desiccators were placed in the oven at 60°C at various times, *i.e.*, 1, 3, 6, 10, 22, 33, and 48 h. The change in plasticity value (ΔP) was used as representative data to indicate the change in accelerated storage hardening. This can be expressed as follows:

$$\Delta P = P_H - P_0$$

Where P_H is the median plasticity value of three storage hardening test pieces, P_0 is the median plasticity value of three non-storage hardening test pieces, and ΔP is the difference in plasticity units between P_H and P_0 .

The gel content was determined by dissolving small pieces of rubbers, which was sampling in five different positions for one sample, in dried toluene to give a concentration of 0.1 % weigh by volume (w/v) and kept in the dark without shaking or stirring for one week at room temperature. The rubber solution was centrifuged at 8,500 rpm for 20 minutes to separate the gel. The precipitated gel fraction was recovered and dried at 50°C and weighed to calculate the gel content.

The degree of crosslinking of NR was determined by the solvent equilibrium swelling method. The modified Flory-Rehner equilibrium swelling equation was used for determining the molecular weight of the primary chain segment between crosslinks (M_c) as follows:

$$V = \frac{1}{2} M_c = - [\ln(1-V_r) + V_r + \chi V_r^2] / [\rho_r V_0 (V_r^{1/3} - V_r/2)]$$

Where V is the crosslink density per gram of rubber, M_c is molecular weight between crosslinks, V_r is the volume fraction rubber, χ is the Huggins interaction constant, ρ_r is the density of rubber, V_0 is the molar volume of solvent, and ρ_s is the density of solvent. The volume fraction (V_r) was calculated from the reciprocal of the degree of swelling;

$$V_r = 1 / (1+Q)$$

Where
$$Q = \frac{(\text{weight of sol in network})}{(\text{weight of network})} \times \frac{\rho_r}{\rho_s}$$

2.3 Preparation of hypoallergenic natural rubber latex

Appropriate reaction conditions were studied for the decomposition of proteins in NR by saponification of latex with NaOH. The effect of concentration of NaOH, reaction time and reaction temperature was analyzed from a viewpoint of residual nitrogen content and stability of latex during the saponification reaction. Field latex (FL-latex) and high ammonia latex (HA-latex), provided by Thaitex Co., were diluted to 30% DRC and incubated with NaOH (1-7 %w/v) in the presence of a surfactant (Triton X-100, 0.2 %w/v) at 50-70 °C for 1-7 hrs. Decomposed protein in saponified latex was washed by centrifugation. Cream of saponified latex was dispersed in distilled water to make 30% DRC and then coagulated by 10%w/v formic acid. The resulting rubber was washed and dried at 50°C for 2 days. Nitrogen of saponified NR was determined.

The nitrogen content was analyzed by a Nitrogen Analyzer (Leco instrument, FP 528) with the sensitivity of 0.001%. High purity oxygen (99.99%) and helium gases (99.99%) were used as the combustion and carrier gas, respectively.

3. ผลที่ได้รับ (Results)

3.1 Investigation of the factor controlling the physical change of various zones of special commercial grade natural rubber during keep under ambient condition.

STR 5L and STR XL showed increase in gel content and Mooney viscosity. On the contrary, STR CV showed lower gel content and constant Mooney viscosity. However, PRI value of STR CV was highest comparable to those of the other samples. From these three kinds of samples, STR 5L rubber after storage for one year showed the largest inconsistency in processing properties such as PRI, P_0 and Mooney viscosity. For the various zones of rubber sample after keeping, the gel content of outer zone of STR XL and STR 5L had lower value than the other zones. These might be due to the oxidative degradation occurred on the outer zone of NR bale. This zone was easily attacked with O_2 and ozone. On the other hand, the gel content of STR CV showed the same value in all of parts. It may be due to the hydroxylamine reacted at aldehyde group in rubber samples and the crosslink reaction would be inhibited.

3.2 The effect of non-rubber components, such as, protein and long chain fatty acid ester on storage hardening and elucidation of the mechanism of the branching and gel formations.

Storage hardening was significantly increased in the case of FNR, CFNR, and DPNR when accelerated under low humidity conditions. On the other hand, storage hardening did not proceed in the case of TENR and DPTE-NR. The fatty acid ester groups the most importance role in causing gel formation and storage hardening of rubber under low humidity, and proteins have no effect on the

storage hardening of rubber. The molecular weight between the crosslinks of gel fractions of the sample after the storage hardening test was about 10^4 and high in gel content. This implies that the crosslinks structure of samples after stored under low humidity conditions is composed of hard gel or chemical crosslinks between the rubber chains. It can be concluded that storage hardening in FNR, CFNR, and DPNR rubbers should be due to the crosslinking reaction between the active functional groups containing fatty acid ester groups that might be linked to rubber chains and some chemical crosslinks between the rubber chains. There is no hardening of rubber samples under high humidity conditions. The plasticity index of TENR and DPTE-NR with increased storage time showed negative ΔP . This indicates that the storage hardening of any kind of the rubber samples was inhibited under high humidity.

3.3 Preparation of hypoallergenic natural rubber latex

Saponification of latex was carried out with various reaction conditions of temperature (50, 60, 70°C), concentration of NaOH (1, 3, 5, 7 %w/v), and reaction time (1, 3, 5, 7 hrs). In the saponification, NaOH can react with proteins in the latex to decompose into short-chain peptides. The decomposed compounds will dissolve in water phase and be removed by centrifugation. In this experiment, the saponified HA-latex was centrifuged to remove decomposed oligopeptides and to find an appropriate condition for getting the nitrogen content less than 0.02%.

The nitrogen content of the rubber from starting material (HA-latex) 0.268% decreased to 0.019-0.020% after saponification with 7% NaOH at 70°C for 1-7 hrs. The reaction at 3% and 5%

NaOH showed a similar tendency as 7%. The reaction at 50 °C was not strong enough to decompose proteins at a level of the nitrogen content lower than 0.03%. The nitrogen content decreased rapidly at the initial stage of reaction and slowly at 3-7 hrs for most of the reaction conditions. This may be due to the slow decomposition of proteins on the surface of rubber particles or the difficulty of removing very small amounts of decomposed proteins by centrifugation. Although the use of high concentration of NaOH and higher reaction temperature gives the rubber of low nitrogen content, these conditions could cause coagulation of the latex during saponification which will result in stopping the saponification reaction.

4. งานที่จะทำต่อในอนาคต (Future works)

- 4.1 Elucidation of the mechanism of branching formation and storage hardening in natural rubber.
- 4.2 Preparation of hypoallergenic natural rubber by saponification reaction.

5. ผลงานจากงานวิจัย

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5.2 การเสนอผลงานมีจำนวน 4 ครั้ง ดังนี้

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