

Characterization of Structure and Composition of Vietnam Commercial Natural Rubber

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Abstract

Characterization of chemical structure and determination of composition of Vietnam commercial natural rubbers (CNR) were carried out to investigate the relationship between structure and properties of natural rubber. Five different grades of CNRs used are SVR10, SVR5, SVR3L, SVRCV50 and SVRCV60. The CNRs films were prepared by solution casting technique following by acetone extraction. The structure of the samples was investigated by ¹H-NMR spectroscopy and FT-IR spectroscopy. It is found that epoxidation occurred in SVR5 and SVRCV50 and isomerization occurred in SVR5, SVR10, SVRCV50 and SVRCV60, but not in SVR3L. The nitrogen content, fatty acid ester content and gel content of the rubbers are similar, except SVR10 with lowest nitrogen content and SVRCV50 with the lowest gel content. The mechanical strength of SVRCV50 is the poorest and SVR10 is the strongest. The mechanical properties depend on the damage of the rubbers and gel content.

Keywords: Vietnam commercial natural rubber, ¹H-NMR, epoxidation, gel content, non rubber components

1. Introduction

Natural rubber (NR) is made from the latex of *Hevea Brasiliensis* and consists of ca. 94% cis-1,4-polyisoprene (94%) and ca. 6% non-rubber components such as fatty acids and proteins. These non-rubber components are assumed to interact with ω-terminal and α-terminal groups of the polymer to form naturally occurring crosslinking junctions. Both hydrocarbon polymer and non-rubber compositions are believed to contribute to the superior mechanical properties of NR [1].

In previous work [2], the chemical structure of NR has been reported to be damaged after NR undergoes processing procedure from NR latex into solid commercial NR. This is due to the highly reactivity of C=C double bonds in cis-1,4-isoprene units during heating, irradiating, and so forth. Besides, the degradation of some non-rubber components may also occur resulting in the destruction of the naturally occurring network of NR. These effects may be concerned with the significant damage in the properties of NR.

The effect of processing conditions, such as temperature and drying time, onto the damage of commercial NR may be investigated through NMR spectroscopy, since the oxidative and thermal degradations of NR during high-temperature drying are known to generate several abnormal groups in NR

molecules. In previous works [3-6], some abnormal groups were found in commercial NR. For instance, the *trans*-1,4-isoprene units, generated by *cis-trans* isomerization, were found for several commercial NRs through ¹H-NMR spectroscopy, as reported by Farley [7]. In addition, the epoxy groups were found for the commercial NR through ¹H-NMR spectroscopy as reported by Chaikumpollert [3]. These suggest that *cis-trans* isomerization and epoxidation of NR take place under a certain condition during drying: probably, relatively high temperature to dry the rubber.

In the present work, we use five different grades of Vietnam commercial NRs to investigate the relationship between structure and properties of commercial NR. First, structure characterization of the rubbers is carried out by NMR spectroscopy to identify the changing in the chemical structure. Then, the composition of non-rubber components such as protein content, fatty acids content will be determined through the analytical method described elsewhere. Finally, the structure and composition of Vietnam CNRs will be discussed related to mechanical properties.

2. Experiments

2.1 Materials

Five Vietnam commercial natural rubbers were provided by Dong Phu rubber company. They are Standard Vietnam Rubbers grade 5 (SVR5), grade 10 (SVR10), grade 3L (SVR3L), grade constant viscosity 50 (SVRCV50) and grade constant viscosity

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60 (SVRCV60). These CNRs were used as received without further treatment. Toluene, chloroform, acetone, and acetic acid were purchased from Merck. Methyl stearate was purchased from Nacalaise Techque, Japan. IR rubber was provided from Zeon Corporation, Japan.

2.2 Preparation of rubber film

Rubber films were prepared by solution casting method as depicted in Figure 1. The commercial NRs were cut into small pieces and dried for 1 day at 50°C. The appropriate amount of dried toluene (stored with molecular sieve one day before use) and a small amount of acetic acid were used to dissolve the rubber. The rubber film was obtained after casting the solution onto petri-dish until dried. The rubber film was further purified by acetone extraction to get acetone-extracted film.

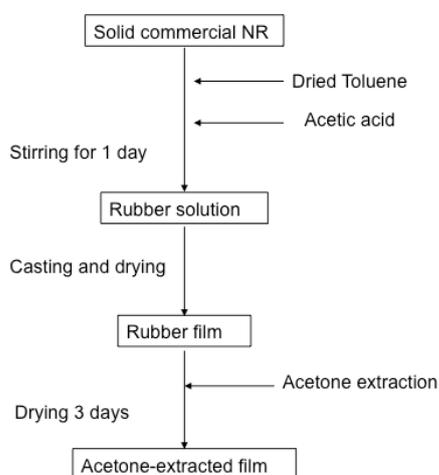


Fig.1. Solution casting procedure to prepare rubber film from solid rubbers

2.3 Characterization

Nitrogen content

Protein content is estimated through the nitrogen content. Measurement of nitrogen content using Kjeldahl method is described in the reference [8]. Rubber sample of 0.1 g and 0.65 g catalysis mixture (K_2SO_4 : $CuSO_4$: $Se = 15:2:1$) was digested with 2.5 ml H_2SO_4 (98 wt.%) until green homogenous solution was obtained. The solution afterward was subjected to steam distillation and captured in H_3BO_3 2 wt.%. The distillate was titrated with H_2SO_4 0.01N until the indicator (methyl red) changing from yellow to light pink.

FT-IR analysis

FT-IR analysis was carried out to determine the fatty acid ester content. This measurement is performed with a JASCO FT-IR 4600 spectrometer from 400 cm^{-1} to 4000 cm^{-1} at room temperature with

a resolution of 4 cm^{-1} . Fatty acid ester content is quantified through calibration curves made from five mixtures of stearic acid methyl ester and synthetic cis-1,4-isoprene, Kuraprene IR10. The intensity ratios of absorption peak at 1740 cm^{-1} to peak at 1640 cm^{-1} was plotted versus amount of stearic acid methyl ester in IR rubber.

Before running the FT-IR measurement, the sample was dissolved in chloroform 2 wt.%, then casted onto KBr disk until dried. The number of scans for the measurement is 100 scans for all samples to obtain the qualified spectrum.

Gel content

Gel content was determined by swelling method. About 0.04 g rubber sample was immersed in 40 ml dried toluene for a week in the dark. The sol fraction was removed through centrifugation and the gel fraction was coagulated with methanol and dried for a week. The gel content is determined from weight of dried gel and weight of initial rubber sample as shown below:

$$\text{Gel content (wt.\%)} = \frac{\text{Weight of dried gel}}{\text{Weight of initial rubber}} \times 100$$

Mechanical properties

Tensile strength of commercial natural rubbers was measured using a Tokyo Instron 5300 at room temperature. Rubber samples were cut into pieces using dumbbell-shaped no.7 according to JIS K6251. The thickness of the films is controlled about 1 mm. The crosshead speed of the measurement is 200 mm/min, in which each sample was measured three times, repeatedly.

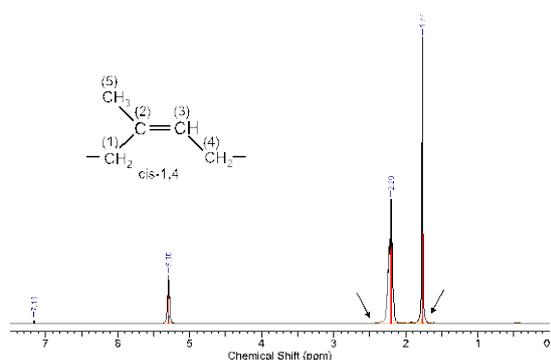
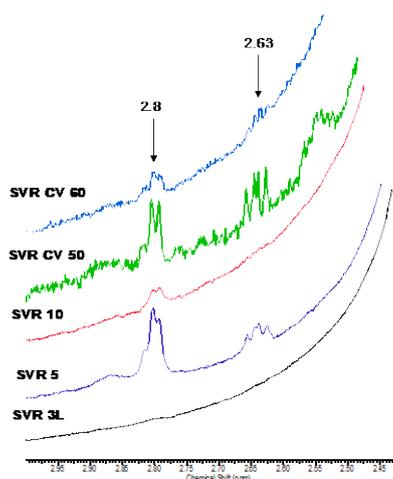
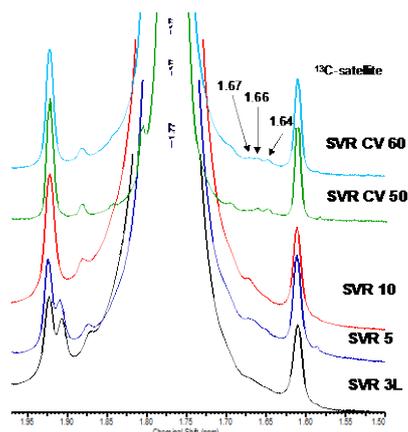
NMR spectroscopy

1H -NMR spectrum was recorded in a JEOL FT-NMR 400 spectrometer. Approximately 15 mg of rubber sample was dissolved in C_6D_6 at 50°C for 1 week. The measurement was run at 50°C for 5000 scans in order to obtain the highest signal to noise (S/N) ratios. The chemical shift was adjusted to benzene proton of C_6D_6 at 7.16 ppm as a reference.

3. Results and discussion

3.1 1H -NMR spectra

Figure 2 exhibits the 1H -NMR spectra for commercial natural rubber. Three major signals for methyl proton, methylene protons and methine proton appeared at 1.77 ppm, 2.2 ppm and 5.30 ppm, respectively. This demonstrated that the typical feature in the structure of commercial natural rubber is preserved during processing.

Fig.2. ¹H-NMR spectra of CNRsFig. 3. Expanded ¹H-NMR spectra of CNRs from 1.5 to 1.95 ppm and from 2.45 to 2.95 ppm

The small signals close to 1.7 ppm and 2.6 ppm were expanded and displayed in Figure 3. As can be seen, the signals at 1.67, 1.66 and 1.64 ppm are assigned to methyl protons of *trans*-1,4-isoprene in *cis-trans* and *trans-trans* sequence, respectively [2]. The arisen of signal at 1.67 ppm implies that the sample underwent isomerization. It could be concluded that all rubber samples are isomerized, except SVR3L. Another two signals at 2.63 and 2.8 ppm are assigned to methyl protons of epoxy

group in poly *cis*-1,4-isoprene backbone and in unsaturated fatty acid ester, respectively. The signal at 2.8 ppm appeared in the spectra of all samples, but the signal at 2.63 ppm appeared in only SVR5 and SVRCV50. This confirms that SVR5 and SVRCV50 were epoxidized during processing.

The *epoxy* content and *trans* content are calculated from the following equations and the values were given in Table 1.

$$\chi_{2.63 \text{ ppm}} (\%) = \frac{I_{2.63 \text{ ppm}}}{I_{1.77 \text{ ppm}} / 3} \times 100$$

$$\chi_{1.64-1.67 \text{ ppm}} (\%) = \frac{I_{1.64-1.67 \text{ ppm}}}{I_{1.77 \text{ ppm}}} \times 100$$

Table 1. *Trans* content and *epoxy* content determined by ¹H-NMR spectroscopy

Sample name	<i>Trans</i> content (%)	<i>Epoxy</i> content (%)
SVR5	0.040	0.045
SVR10	0.042	0
SVR3L	0.016	0
SVRCV50	0.028	0.015
SVRCV60	0.018	0

3.2 FT-IR analysis

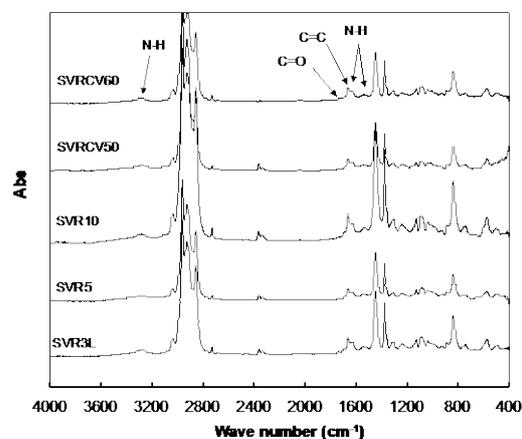


Fig. 4. FT-IR spectra of five commercial NRs

Figure 2 presents FT-IR spectra for acetone-extracted films of SVR5, SVR10, SVR3L, SVRCV50 and SVRCV60 ranging from 400 to 4000 cm^{-1} . The absorption peaks at around 3280, 1624 and 1540 cm^{-1} were characteristic peaks for N-H stretching vibration of proteins. On the other hand, the absorption peak at 1730 cm^{-1} was assigned to C=O bond of fatty acid ester and the absorption at 1664 cm^{-1} is characteristic of C=C bond in *cis* 1,4-polyisoprene. It indicates that

the commercial NRs contains mostly proteins, fatty acid ester as similar as in the NR latex. The intensity of absorption peak at 1730 cm^{-1} represents amount of fatty acid ester. The higher the intensity, the higher amount of fatty acid ester. Therefore, the fatty acid ester content of commercial NR can be calculated from the intensity ratios of 1730 cm^{-1} to 1664 cm^{-1} .

In the present work, the calibration curve was made by using five mixtures of methyl stearate and IR rubber with the concentrations are 10, 20, 30, 40 and 50 mmol/kg rubber and plots of intensity ratios 1730 and 1664 cm^{-1} versus ester concentrations is shown in Figure 5.

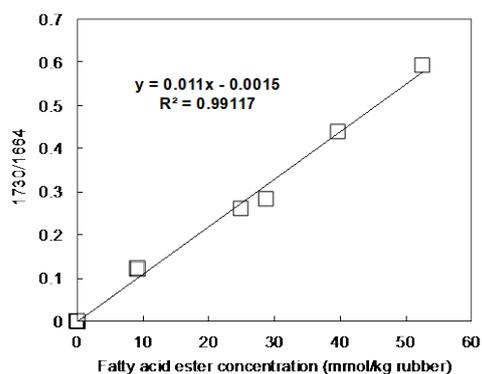


Fig. 5. Calibration curve for determination of fatty acid ester content

From the graph, we obtain the linear equation: $y=0.011x-0.0015$ with R^2 is 0.99117. Then, we calculated the fatty acid ester contents and they were presented in Table 2. The fatty acid ester content of the rubbers is similar to each other, approximately 7 mmol/kg rubber. It demonstrated that the coagulation process during processing may not affect the fatty acid ester content of solid commercial rubbers.

3.3 Non-rubber compositions and gel content

Compositions of CNRs, that is nitrogen content, fatty acid ester content and gel content were listed in the Table 2. SVR5 contain the highest gel content. SVRCV50 contains the lowest gel content and SVR3L and SVRCV60 have the similar amount of gel. The presence of the gel in the rubber films suggests the existence of the physical gel in which they dissipate in mixture of toluene and polar solvent and they reform after drying. This physical gel may be proportional to nitrogen content since the physical crosslinking junctions is supposed to form by the interaction of proteins with NR molecules at ω -terminal group.

3.4 Mechanical properties

Stress-strain curves for the acetone-extracted films were shown in Figure 6. The mechanical strength

of SVRCV50 is the lowest among the five samples with the stress at break around 0.07 MPa and the strain at break about 250%. This is because of both degradation and low gel content of SVRCV50 in comparison with other samples. On the other hand, SVR3L sample has the highest mechanical properties with the stress at break of 1.7 MPa and strain at break of 771%. This is probably due to the fact that SVR3L is not damaged during processing.

Table 2. Non-rubber compositions and gel content

Sample name	Non-rubber compositions		Gel content (wt.%)
	Nitrogen content (wt.%)	Fatty acid ester content (mmol/kg rubber)	
SVR5	0.445	7.3	7.6
SVR10	0.212	5.4	4.4
SVR3L	0.354	6.2	6.9
SVRCV50	0.350	7.5	2.8
SVRCV60	0.342	7.7	6.5

Table 3. Stress at break, strain at break and stress at a strain of 1 of commercial NR

Sample name	Stress at break (MPa)	Strain at break (%)	Stress at a strain of 1 (MPa)
SVR5	0.67	536	0.36
SVR10	1.22	794	0.41
SVR3L	1.70	771	0.357
SVRCV50	0.07	252	0.118
SVRCV60	0.74	590	0.373

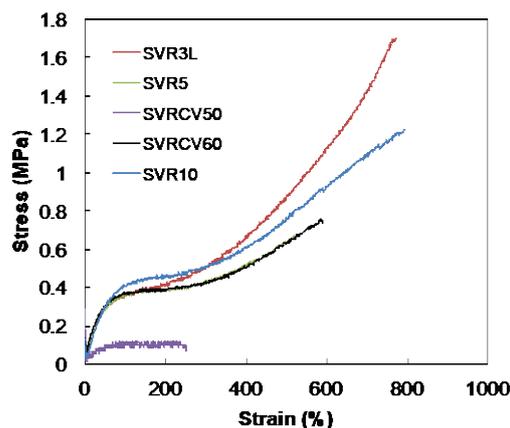


Fig. 6. Stress-strain curves of acetone-extracted films of SVR10, SVR5, SVR3L, SVRCV50 and SVRCV60

Table 3 provides the value of stress and strain at break as well as the stress at a strain of 1 for all the

rubbers. In previous work [9], the stress at a strain of 1 was reported to depend on the nitrogen content. However, in this work, SVR10 has the highest stress at a strain of 1 despite lowest nitrogen content (0.212%). This contradiction is probably due to the deformation of rubber network related to proteins due to the degradation of SVR10 during processing.

4. Conclusion

The results in this work demonstrated that the isomerization occurred in SVR5, SVR10, SVRCV50, SVRC60 and the epoxidation occurred in SVR5 and SVRCV50 sample. The SVR3L sample without degraded during processing possesses the best tensile strength. On the other hand, SVRCV50 sample is drastically damaged and therefore the mechanical properties are the poorest. The physical gel of the rubbers is quite low compared to that of NR latex. The mechanical properties of commercial NRs are believed to depend on the damage of the rubber during processing and insignificantly depend on the non-rubber components.

Acknowledgments

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