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Characterization of commercial natural rubber purified with transesterification

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Abstract

Highly purified commercial natural rubbers were prepared and characterized to elucidate the effect of processing condition on structure characteristic of the rubbers. In the present study, various commercial rubbers, i.e. Pale Crepe (PC), Ribbed Smoked Sheet (RSS3), Technically Specified Sheet (TSS8®), Standard Thailand Rubber (STR5L) and Standard Malaysian Rubber (SMR20) were purified by acetone extraction and transesterification (TE) to prepare highly purified commercial rubbers (TE-NR). The resulting TE-NRs were characterized by nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and size exclusion chromatography (SEC). Epoxy group was found for PC, STR5L, RSS3, TSS8® and SMR20 and *trans*-1,4-isoprene unit from *trans*-1,4-isoprene units from *cis-trans* isomerization was found for TSS8® and SMR20 from the assignments of ^{1}H-NMR signals. This result implies that the degradation, that is epoxidation and isomerization, took place during the processing of commercial rubbers. The damage of commercial natural rubbers was investigated with respect to its molecular weight.

Keywords. Commercial rubber, transesterification, NMR, epoxidation, isomerization.

1. INTRODUCTION

Natural rubber (NR) obtained from *Hevea brasiliensis* is widely known to be a strategic material which exhibits outstanding mechanical properties such as high resilience, a low heat build-up and high dynamic properties; since it possess the unique molecular characteristic. The characteristic of NR includes not only its homogeneous macromolecular structure of high *cis*-1,4-isoprene content (99.8%) but also its inherent branching structure formed by non-rubber components such as proteins and phospholipids at two terminal ends, *i.e.* α- and ω-terminals, which are completely distinguished from synthetic rubber [1, 2]. These characteristics may be modified under very harsh condition of processing from NR latex to commercial solid rubbers, since many sides reactions, *i.e. cis-trans* isomerization, epoxidation, chain scission, have been possible to occur during high-temperature processing [3]. As a result, several abnormal groups were introduced into rubber chain, *i.e.* aldehyde group, epoxide group, *trans*-1,4-isoprene unit and so forth and the presence of these abnormal groups plays an important role in controlling the properties of commercial NR. However, few studies in the literature have provided direct evidence to confirm the occurrence of these reactions and subsequently the presence of these abnormal groups in commercial NR.

In the previous works, structural characterization of several kinds of commercial rubbers was carried out by using ^{1}H-NMR spectroscopy after the rubbers were purified with acetone extraction [4]. It is found that some degradation products containing epoxy group were removed by acetone extraction. These compounds may originate from the fatty acids exist in NR. To perform precisely structural analysis, the purification of NR should be carried out more extensively, that is the combination of acetone extraction and transesterification, since transesterification is one of the methods to remove the fatty acid linking to NR. The removal of linked fatty acids by transesterification also accompany with the decrease in branching points which are formed via the interaction between the rubber molecules and non-rubber components [5]. In the case of natural rubber, it is difficult to observe small signals due to abnormal group because of very high molecular weight. Therefore, the low molecular weight fraction should be more favorable for structural characterization. In the present work, transesterification will be performed and sol fraction of the rubbers will be separated and subjected to be characterized by NMR spectroscopy.

In the present work, we performed the structural characterization of various rubbers grades prepared by different manufacturing processes which are currently used in rubber industry. The rubbers used in the present work are crepe, sheet and block rubbers provided from several countries. The changes in molecular structure were discussed in the relation to processing condition and thermal property of resulting products.

2. EXPERIMENTAL

2.1. Materials

The commercial NR used was SMR20, STR5L, RSS3, and PC which were commercially available as a bulk. TSS8® was prepared from the unsmoked sheet of the natural rubber by Von Bundit Co. Ltd, Thailand. STR5L, RSS3, TSS8® and PC are produced directly from field latex and processed in a strictly controlled procedure in Thailand. Other grade such as SMR20 is prepared from non-smoked sheet, cup lump or a mixture of the two. PC is usually prepared by coagulation of diluted latex with $NaHSO_3$ followed by washing extensively with water before drying for 2-4 days at 35-40 °C. On the other hand, RSS3 dried in the smoked house for about one week at 60-70 °C. For other rubber grades, the coagulation was made directly or automatically without any chemical and followed by drying at very high temperature, more than 100 °C. All reagents used were commercial grades.

2.2. Purification of samples

The samples were purified by soxhlet extraction in hot acetone for 40 hours to remove free fatty acid and impurities. Transesterification of commercial dry rubber was carried out in toluene solution 1 w/w% by reaction with freshly prepared sodium methoxide (CH_3ONa) and stirring at room temperature under N_2 atmosphere for 3 hours. The resulting transesterified rubber was purified by precipitation of the rubber solution using the triple excess of methanol and then dried under vacuum at room temperature for a week.

2.3. Fourier transformed infrared spectroscopy

A sample for FT-IR measurement was prepared by casting 2 w/w% chloroform solution onto a KBr disk. The measurement was performed by a JASCO FT-IR 4100 spectrometer at 100 scans ranging from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.4. Size exclusion chromatography

Measurement of molecular weight and molecular weight distribution of the rubber were made with RI-8012 differential refractometer and UV-8011 UV detector. The measurement was made at 30 °C with the flow rate of tetrahydrofuran (THF) at 1 ml/min. The rubber solution was prepared by the dissolution of rubber into THF at a concentration of 0.05 w/v% and filtered through a 0.1 μm-pore size membrane filter (Whatman®). Standard Polystyrene (TOSOH) were used for the calibration of the molecular weight

2.5. Nuclear magnetic resonance spectroscopy

NMR measurement was performed with a JEOL ECA-400 FT-NMR spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz for ^{1}H-NMR. The ^{1}H-NMR measurements were performed in the C_6D_6 solvent in 5 mm tube at 50 °C for 5000 scans. The repetition time is 7 s and the chemical shift was referred to benzene in benzene-d_6.

3. RESULTS AND DISCUSSION

3.1. FT-IR analysis

Figure 1 shows FT-IR spectra for transesterified commercial NR, *i.e.* PC-TE, STR5L-TE, RSS3-TE, TSS8®-TE and SMR20-TE, ranging from 1200 to 3500 cm^{-1}. The absorption peaks of C=O bonds due to fatty acids at 1730 cm^{-1} was almost disappeared, demonstrating that most of the fatty acid esters were removed through transesterification with sodium methoxide (CH_3ONa) in toluene solution. It is worthy of note that the absorption bands at 3280, 1624 and 1540 cm^{-1}, which attributed to stretching vibrations of N-H, amide I and amide II, respectively, in proteins still remain after transesterification. Transesterification is very useful for decomposition of the chemical linkages formed by phospholipids association with linked fatty acid, but not disturbing the physical linkages association with the proteins at ω-terminal unit. Therefore, it is not surprising that proteins remain in commercial NR after transesterification.

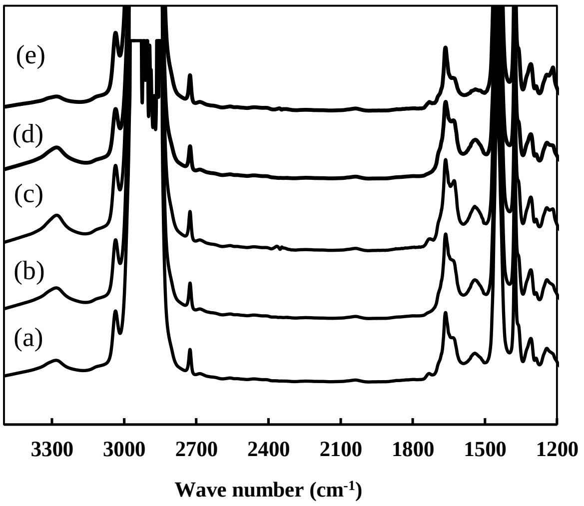

Fig. 1: FT-IR spectra for (a) PC-TE, (b) RSS3-TE, (c) STR5L-TE, (d) TSS8$^{®}$-TE and (e) SMR20-TE

3.2. NMR analysis

Sol fractions of the transesterified commercial NR were separated from the gel fraction and subjected to NMR measurement. Figure 2 shows ^{1}H-NMR spectra for the sol fraction of PC-TE, RSS3-TE, STR5L-TE, TSS8$^{®}$-TE and SMR20-TE. Three major signals appeared at 1.77, 2.20 and 5.29 ppm were assigned to methyl (CH_3), methylene (CH_2) and methine proton (CH) of *cis*-1,4-isoprene units, respectively. The characteristic signals due to the phospholipid in NR, which is expected to resonate at around 4 ppm were not observed in these ^{1}H-NMR spectra [6]. This suggests that sol fraction of transesterified commercial NR contains no phospholipid groups at the α-terminal unit, which confirmed that it was removed completely via transesterification.

On the other hand, several signals appeared from 3.2 to 3.6 ppm may be assigned to the alcohol terminal after the conversion of ester linkages through transesterification. It is worthy of note that the signal at 2.63 ppm was assigned to methine proton of an epoxidized isoprene unit as reported in our previous literature [4]. The existence of this signal after transesterification demonstrating that epoxy group existed in a linear rubber chain. This evidence implies that the epoxidation occurred during processing of NR.

Figure 3 shows expanded ^{1}H-NMR spectra for these transesterified commercial NR in methyl proton region ranging from 1.2 to 2.4 ppm. A signal at 1.64 ppm appeared for PC-TE, RSS3-TE and STR5L-TE whereas two signals appeared at 1.64 and 1.67 ppm for TSS8$^{®}$-TE and SMR20-TE. The signals at 1.64 and 1.67 ppm were assigned to methyl protons of *trans*-1,4-isoprene units in *trans-trans* sequence and that in *cis-trans* sequence, respectively. The first signal was originated from the biosynthesis pathway of NR, however, the later resulted from *cis-trans* isomerization. This implies that *cis-trans* isomerization was taken place during the processing of TSS8$^{®}$ and SMR20.

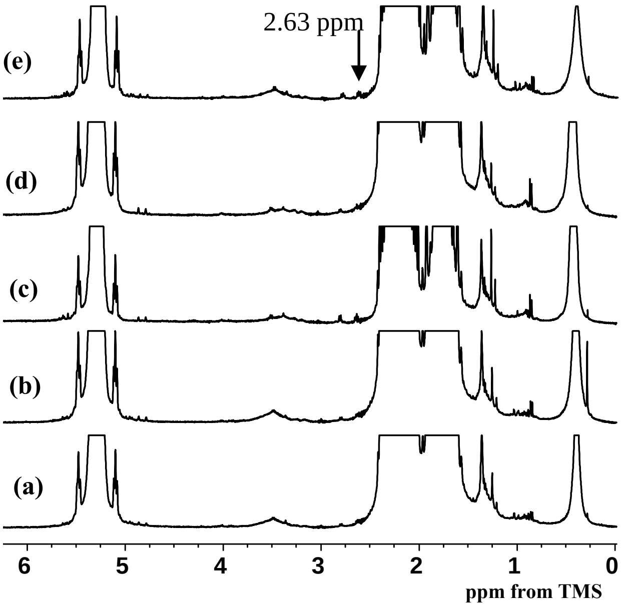

Fig. 2: ^{1}H-NMR spectra for sol fraction of (a) PC-TE, (b) RSS3-TE, (c) STR5L-TE, (d) TSS8$^{®}$-TE and (e) SMR20-TE

The degree of epoxidation and *cis-trans* isomerization, were determined from the intensity of the signals at 2.63 and 1.67 ppm, respectively, *versus* the signal at 1.77 ppm as follows:

$$\chi_{2.63ppm}(\%)=\frac{I_{2.63ppm}}{I_{1.77ppm}/3}x100 \quad (1)$$

$$\chi_{1.67\ ppm}(\%)=\frac{I_{1.67\ ppm}}{I_{1.77\ ppm}}x100 \quad (2)$$

Table 1: Degree of epoxidation and isomerization

Samples	$\chi_{2.63\ ppm}$ (%)	$\chi_{1.67\ ppm}$ (%)
PC-TE	0.009	0
STR5L-TE	0.015	0
RSS3-TE	0.015	0
TSS8®-TE	0.009	0.007
SMR20-TE	0.024	0.022

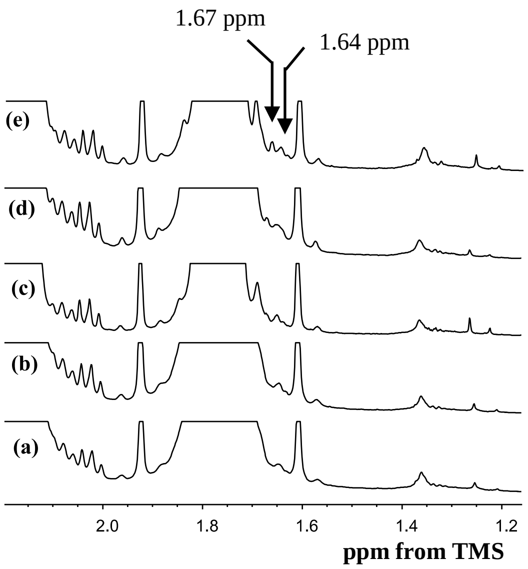

Fig. 3: Expanded ^{1}H-NMR spectra for sol fraction of commercial NR (a) PC-TE, (b) RSS3-TE, (c) STR5L-TE, (d) TSS8®-TE and (f) SMR20-TE.

In the previous work, the epoxidation and *cis-trans* isomerization have been found to occur as side reactions during oxidative degradation of NR. The NMR analysis of commercial NR in the present work gives conclusive evidence to confirm the occurrence of epoxidation and *cis-trans* isomerization during processing of commercial NR. This suggests that the degradation of TSS8® and SMR20 was more severe than that of PC, STR5L, and RSS3. The high temperature may be responsible for the damage of TSS8® and SMR20. The molecular weight of the rubbers was taken into account since the degradation of NR also affects the molecular weight.

3.3. SEC analysis

Figure 4 shows SEC curves for the rubbers after transesterification and the value for number average molecular weight (M_n), the weight average molecular weight (M_w) were shown in table 2. The molecular weight of commercial rubbers showed a great variation among the rubbers.

The appearance of the peak at low M_w region may be explained to be due to the decomposition of branched molecules to linear molecules. The MWD curves with the bimodal distribution and have been ascribed to be due to the branching structure of NR. This characteristic does not disappear even after transesterification as observed in the previous work [7]. From the data, we can conclude that the lower molecular weight, the more severe damage during processing.

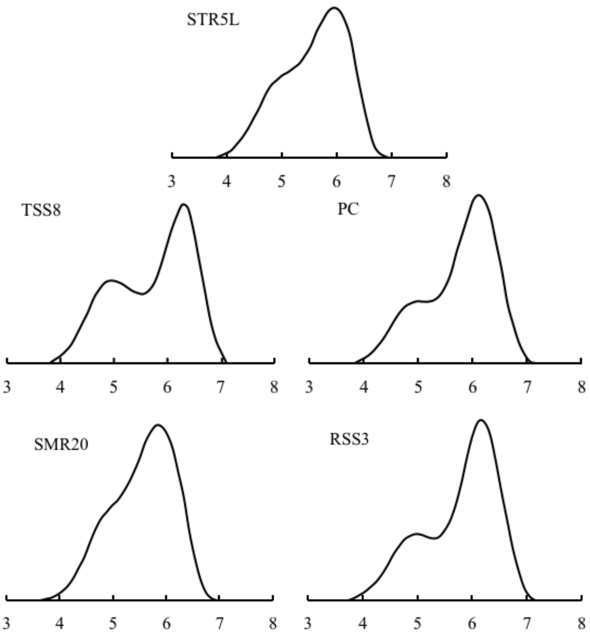

Fig. 4: Molecular weight distribution of STR5L-TE, TSS8®-TE, PC-TE, SMR20-TE and RSS3-TE

Table 2: Molecular weight of the rubbers

Samples	M_n×10^5 (g/mol)	M_w×10^6 (g/mol)
PC	1.71	1.26
STR5L	1.43	0.80
RSS3	1.60	1.39
TSS8®	1.37	1.43
SMR20	1.37	0.74

4. CONCLUSION

The commercial NR was found to be degraded after rubber processing at high temperature that is more than 100 °C. The rubber was concluded to be epoxidized and isomerized under that severe condition resulting in introduction of epoxy group and *trans*-1,4-isoprene units into rubber chain. The appearance of these groups may be concentrated on the low molecular weight fraction, suggesting that the low molecular weight may be formed by the degradation of the rubbers.

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