Analysis of damage in commercial natural rubber through NMR spectroscopy

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ABSTRACT

Damage to natural rubber (NR) during processing was investigated through liquid state NMR spectroscopy. Various commercial rubbers were used in the present study such as Pale Crepe (PC), Rubber Smoked Sheet (RSS3), Technically Specific Sheet (TSS8®), Standard Thai Rubber (STR5L), and Standard Malaysian Rubber (SMR20). As-cast films of the rubbers were prepared by solution casting method and followed by purification by acetone extraction. Chemical structures of the rubbers were elucidated through ¹H, ¹³C-NMR, and DEPT spectroscopy. The ¹³C-NMR signals at 39.8 and 40.0 ppm were assigned to the *trans*-1,4-isoprene unit in the *trans-trans* and *cis-trans* sequences, respectively, while the signals at 60.8 and 64.5 ppm were assigned to C2 and C3 of an *cis* epoxy group. The *cis* epoxy groups were identified for PC, STR5L, RSS3, TSS8®, and SMR20, whereas the *trans*-1,4-isoprene units from *cis-trans* isomerization were detected for TSS8® and SMR20. The amount of these groups in TSS8® and SMR20 were higher than those in PC, STR5L, and RSS3. Mechanical properties of TSS8® and SMR20 were found to be inferior to those of PC, STR5L and RSS3. The mechanical properties depended mainly upon the damage of the samples during processing.

Keywords: commercial natural rubber, NMR, processing, isomerization, epoxidation

1. Introduction

Abnormal groups of natural rubber (NR), which form gel fraction as a crosslinking junction, prevent analysis of their structure, since the gel fraction is insoluble in deuterated solvents. The abnormal groups, i.e. epoxy groups, *trans*-1,4-isoprene units, formyl groups, cyclic ester groups (lactone) and so forth, are known to react to each other to crosslink NR molecules [1,2]. In addition, the long sequence length of the *cis*-1,4-isoprene units may be reduced, when the abnormal groups were added onto the backbone of the rubber molecules. The decrease in the long sequence length of the *cis*-1,4-isoprene units may suppress crystallization of NR on stretching, i.e. strain-induced crystallization. For instance, the presence of *trans*-1,4-isoprene units due to isomerization on the main-chain of the rubber molecules significantly decreases crystallization of NR upon stretching [3]. The suppressed crystallization on stretching may deteriorate the excellent mechanical properties of NR such as tensile strength, tear strength, permanent set and so forth. Therefore, it is necessary to decrease the amount of the abnormal groups of NR to maintain the long sequence length of *cis*-1,4-isoprene units which are responsible for the outstanding mechanical properties of NR. The abnormal groups of NR may be characterized by NMR spectroscopy after converting insoluble gel fraction to soluble fraction through two methods, i.e. physical and chemical methods, since physical and chemical crosslinking junctions are formed with the abnormal groups. The abnormal groups may be isolated after decomposition of the crosslinking junctions. One of the plausible methods to decompose the chemical crosslinking junctions is transesterification with CH_3ONa [4], whereas that to decompose the physical crosslinking junctions is addition of polar solvents [5]. Transesterification is useful for decomposition of ester linkages while the other chemical linkages formed with the abnormal groups still remain

undecomposed. In contrast, all physical crosslinking junctions are decomposed by strong polar solvents, which convert gel fraction to branched molecules. Therefore, in the present work, we use the strong polar solvents to develop a new method to analyze the structure of abnormal groups of NR.

In previous works [6,7], analysis of abnormal groups of commercial NR through NMR spectroscopy has been done with sol fraction, which was separated from the gel fraction through filtration. For instance, Farley carried out ^1H -NMR measurements for the sol fraction obtained from several commercial rubbers and found that the *trans*-1,4-isoprene unit content varied between rubber grades, suggesting that *cis-trans* isomerization of NR may be an additional source of the *trans*-1,4-isoprene unit [7]. However, *cis-trans* isomerization was not confirmed in this case due to lack of the signal corresponding to *cis-trans* isomerization in the ^{13}C -NMR spectrum. On the other hand, Eng and co-workers reported that the signal from *cis-trans* isomerization was detected for UV-degraded and masticated NR through ^{13}C -NMR spectroscopy [8]. In addition, we performed ^1H -NMR measurements for commercial rubbers, and found that, in certain cases, commercial rubbers undergo epoxidation [9]. However, whether *cis-trans* isomerization and epoxidation occur during NR processing remains ambiguous.

Epoxidation and *cis-trans* isomerization may be associated with the procedure to manufacture commercial NR [9,10]. Generally, manufacture of commercial NR involves many steps, including (1) coagulating field latex, (2) washing with water, (3) milling and sheeting, (4) drying, and (5) storing in a warehouse [11]. Among these, the drying step may result in the oxidative degradation, which introduces several abnormal groups on the rubber chain. This assumption is based on the fact that the structure of the long sequence of the *cis*-1,4-isoprene units in NR is very sensitive to

the thermal condition (*i.e.* high-temperature processing). Therefore, it is important to characterize the structure of commercial NR and to investigate the effect of the processing conditions on the abnormal groups in commercial NR.

In the present work, the appearance of abnormal groups in commercial NR and the effect on the mechanical properties were investigated. First, we characterized the commercial NR through liquid state NMR spectroscopy. Then, the effect of processing condition on the chemical structure of the rubbers was discussed with respect to the appearance of several abnormal groups. In addition, tensile strength was measured to examine the effect of oxidative degradation during processing of the rubbers.

2. Experimental

2.1. Materials

The commercial NR used in the present study were Standard Thailand Rubber (STR5L), Ribbed Smoked Sheet (RSS3), Technically Specified Sheet (TSS8®), Pale Crepe (PC), and Standard Malaysian Rubber (SMR20). SMR20, STR5L, RSS3, PC are commercially available as a bulk and TSS8® is prepared from an unsmoked sheet of NR by Von Bundit Co. Ltd, Thailand. To elucidate the influence of the drying temperature during processing, these samples were selected based on the different drying temperatures during processing. PC is usually dried for 2 – 4 days at 35 – 40 °C whereas RSS3 is dried in a smokehouse for about one week at 60 – 70 °C. Lower grade rubber (*i.e.* SMR20) is dried at a very high temperature (*i.e.*, > 100 °C) [11]. All other reagents were commercial grade.

2.2. Preparation of the rubber films

The rubber films were prepared by the solution casting method (Fig. 1). First, a commercial solid rubber was dissolved in dried toluene (1–2 w/w%) while stirring for

24 hours. Then a small amount of methanol (2–4 w/w% of the total weight of toluene solution) was added to dissolve the soft gel. The resulting solution was cast onto a petri dish and dried in a vacuum at room temperature to obtain a rubber film. The film was subsequently purified with hot acetone for 24 hours and dried in a vacuum at 30 °C for 3 days before characterization.

Fig.1. Preparation of a rubber film by the solution casting method

2.3. Transesterification

Transesterification of the acetone-extracted commercial rubbers was carried out in a toluene solution (1 w/w%) by a reaction with freshly prepared sodium methoxide while stirring at room temperature under a N₂ atmosphere for 3 hours. The resulting transesterified rubber was purified by precipitating the rubber solution using an excess (three times) methanol and dried in a vacuum at room temperature for a week.

2.4. Fourier transform infrared spectroscopy (FT-IR) analysis

The amount of fatty acid ester groups was determined based on the calibration curve prepared using a mixture of stearic acid methyl ester and synthetic *cis*-1,4-polyisoprene, Kuraprene IR10. FT-IR measurement samples were prepared by casting

a chloroform solution (2 w/w%) onto a KBr disk. The FT-IR experiments were performed by a JASCO FT-IR 410 spectrometer at 100 scans ranging from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} .

2.5. Size exclusion chromatography (SEC) measurements

The molecular weight and the molecular weight distribution of the rubbers were measured with a LC-2000 GPC, consisting of a PU-2080 JASCO pump, RI-2031 differential refractometer, and a UV-8011 UV detector. Each measurement was conducted at 30°C with a THF flow rate of 1 ml/min. The rubber solution was prepared by the dissolution of rubber into tetrahydrofuran (0.05 w/v%) and filtered through a 0.1- μm -thick membrane filter (Whatman®). Standard polystyrene (TOSOH) was used to calibrate the molecular weight.

2.6. Nitrogen content determination (Kjeldahl method)

The nitrogen content of the commercial rubber films was determined by Kjeldahl method as described in Rubber Research Institute of Malaysia Test Method B7 [12]. A mixture of rubber (0.1 g) and a catalyst (0.65 g) with a ratio of 15:2:1 (K_2SO_4 : CuSO_4 :Se) was digested with concentrated H_2SO_4 (2.5 ml) until the digested solution turned clear green. The resulting solution was distilled, and the distillate was titrated with H_2SO_4 (0.01 N) with methyl red as an indicator. The end point of the titration was determined when the color changed from yellow to light pink. A blank sample without rubber was prepared using a similar method. The equation to determine the nitrogen content is given as

$$\%N = \frac{(V_1 - V_0) \times 10^{-3} \times 0.01 \times 14}{0.1} \times 100$$

where V_1 and V_0 are the volume (ml) of H_2SO_4 for titration of the sample and blank sample, respectively.

2.7. Nuclear magnetic resonance (NMR) spectroscopy

Liquid state NMR measurements were performed with a JEOL ECA-400 FT-NMR spectrometer (JEOL, Tokyo, Japan) operating at 400 and 100 MHz for ^1H and ^{13}C , respectively. The ^1H -NMR measurements were performed in a 5-mm ϕ tube with C_6D_6 as a solvent at 50°C for 5000 scans at the pulse repetition time of 7 s with recycle delay of 4.24 s. The ^{13}C -NMR and DEPT measurements were performed in a 10-mm ϕ tube in CDCl_3 at room temperature in a JEOL EX-400 for 40000 scans at the pulse repetition time of 5 s with recycle delay of 3.79 s.

2.8. Tensile measurements

Tensile tests were conducted at room temperature using a TOYOSEIKI universal tester VG10E according to JIS K6251. Dumbbell-shaped rubbers No.7 (~1-mm thick) were subjected to the tensile test. The crosshead speed was 200 mm/min. The measurement was repeated three times for each sample.

3. Results and discussion

Fig. 2 shows the ^1H -NMR spectra for acetone-extracted PC, RSS3, STR5L, TSS8®, and SMR20. Three major signals appeared at 1.77, 2.20 and 5.29 ppm, which were assigned to the methyl (CH_3), methylene (CH_2), and methine proton (CH) of the *cis*-1,4-isoprene unit. In addition, several small signals appearing in ^1H -NMR spectra of the samples may be attributed to the signals of the abnormal groups or the non-rubber components present in NR. For instance, the signals at 3.92, 4.03, 4.08, and 4.22 ppm were assigned to the methylene proton linking the mono- and diphosphate groups of the phospholipid at the α -terminal unit as reported in the literature [13]. The signals at 2.80 and 5.63 ppm were likely due to the methylene proton ($-\text{CH}_2-\text{CH}=\text{CH}-$) and methine proton ($-\text{CH}_2-\text{CH}=\text{CH}-$) of the unsaturated fatty acids (*e.g.*, linoleic or linolenic acid), which link to the NR molecules. These signals were also observed in

the ^1H -NMR spectrum for the rubber purified from commercial high-ammonia latex, which may possess the characteristic for the rubber before undergoing processing. The signal at 2.63 ppm was assigned to the methine proton of an epoxidized isoprene unit. As previously reported, this signal could be attributed to the oxidative degradation of NR and unsaturated fatty acids [9]. In the present work, the appearance of the signal in the ^1H -NMR spectra of the samples after acetone extraction confirmed that the epoxy group was mainly present on the backbone of NR and was not a side group or associated with non-rubber impurities. This signal provides direct evidence that epoxidation occurs in commercial rubbers.

Fig.2. ^1H -NMR spectra for (a) PC-AE, (b) RSS3-AE, (c) STR5L-AE, (d) TSS8®-AE and (e) SMR20-AE

In the methyl proton region, which ranges from 1.5 to 1.8 ppm (cf Fig. 2), one signal at 1.64 ppm was found for PC, RSS3, and STR5L, whereas two signals at 1.64 and 1.67 ppm were found for TSS8® and SMR20. In the literature, the signal at 1.64 ppm was assigned to the methyl proton of the *trans*-1,4-isoprene unit in the *trans-trans* sequence and that at 1.67 ppm was assigned to the methyl protons of the *trans*-1,4-isoprene unit in the *cis-trans* sequence [8,13]. These two signals were not observed clearly in the ¹H-NMR spectra for the commercial rubbers.

The rubbers were subjected to transesterification because transesterification has been known to decompose the branching points associated with the linked fatty acid, yielding a linear chain. In Fig. 3, which shows the ¹H-NMR spectra for sol fraction of transesterified commercial NR between 1.4 and 1.8 ppm, the signals at 1.64 and 1.67 were clearly resolved. Consistent with the above assignment, the signal at 1.67 ppm was observed in ¹H-NMR spectra of TSS8® and SMR20. These results suggest that *cis-trans* isomerization occurs in TSS8® and SMR20, but not in PC, STR5L, and RSS3.

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

To confirm the assignment for ^1H -signals, we performed ^{13}C -NMR measurements for these samples in CDCl_3 (Fig. 4). The five characteristic signals for the *cis*-1,4-isoprene unit in NR appeared at 23.4, 26.4, 32.2, 125.0, and 135.2 ppm, which were assigned to C5, C4, C1, C3 and C2 of *cis*-1,4-isoprene, respectively. One signal at 39.8 ppm appeared in the ^{13}C -NMR spectra of PC, RSS3, and STR5L, whereas two signals at 39.8 and 40.0 ppm were found in the ^{13}C -NMR spectra of TSS8® and SMR20. The previous literature attributed the signals at 39.8 and 40.0 ppm to the methylene carbon of the *trans*-1,4-isoprene units in the *trans-trans* and the *cis-trans* sequences, respectively [8]. The *trans-trans* sequence may originate from the ω -terminal unit, whereas the *cis-trans* sequence may be formed from the long *cis*-1,4-polyisoprene. The signal at 40.0 ppm in the ^{13}C -NMR spectra of TSS8® and SMR20 provides conclusive evidence that *cis-trans* isomerization occurs in the cases of

TSS8® and SMR20. These findings were consistent with those from the ¹H-NMR spectra.

Fig.4. ¹³C-NMR spectra for (a) PC-AE, (b) RSS3-AE, (c) STR5L-AE, (d) TSS8®-AE and (e) SMR20-AE

In the ¹³C-NMR spectra of these samples, several small signals appeared at 60.8, 64.4, 64.5, and 69.2 ppm. As reported in the literature, the signals at 60.8 and 64.5 ppm were assigned to C2 (-C-) and C3 (-CH) of the *cis* epoxy group [14]. On the other hand, the signal at 64.4 ppm has previously been assigned to -CH₂OP in a mono- or di-phosphate group or -CH₂OCO of the glyceride structure in phospholipids at the α -terminal [15]. These four small signals in ¹³C-NMR spectrum seem to be difficult to assign correctly because of small difference in chemical shift. Therefore, it is necessary to perform DEPT measurements with various pulse sequences to determine the substituents for each carbon atom. Fig. 5 shows the DEPT spectra for STR5L-AE as an example. The signal at 64.4 ppm appeared downward in DEPT135, upward in DEPT45, and was null in DEPT90; hence, the signal was assigned to the methylene

group of a secondary carbon ($-\text{CH}_2$). In contrast, the signal at 64.5 ppm showed upward in the DEPT45, DEPT90, and DEPT135 spectra, and was assigned to the methine group of a tertiary carbon ($-\text{CH}$). Therefore, the signal at 64.5 ppm was due to C3 of an epoxy group, while the signal 64.4 ppm was from a $-\text{CH}_2\text{OP}$ or $-\text{CH}_2\text{OCO}$ group. The other signal at 60.8 ppm was attributed to a quaternary carbon because it appeared null in the DEPT45, DEPT90, and DEPT135 spectra. The remaining signal at 69.2 ppm was assigned to a secondary carbon because it shifted upward in DEPT45, null in DEPT90, and downward in DEPT135; this signal may arise from the another methylene carbon linking to the phosphate group in the glyceride structure and not a tertiary alcohol as reported in the literature [16].

Fig.5. ^{13}C -NMR spectra with pulse sequences of DEPT for STR5L-AE:

(a) DEPT45, (b) DEPT90, and (c) DEPT135

From the above assignments, the epoxy groups and *trans*-1,4-isoprene units from *cis-trans* isomerization exist on the rubber chain of commercial NR, suggesting that epoxidation and *cis-trans* isomerization occur in commercial NR. Because previous works have reported that these two reactions occur during degradation of NR [17], it

is necessary to investigate the factors that induce degradation in commercial rubbers. It is noteworthy that isomerization was found in TSS8® and SMR20 but not in PC, RSS3, and STR5L. The main difference in preparing these samples is the temperature of the drying process (i.e. TSS8®, STR5L, and SMR20 were dried between 100°C and 130°C, while PC and RSS3 were prepared at lower temperatures of 37°C and 70°C, respectively). These results imply that a high temperature may be the key factor promoting the degradation of commercial rubbers.

Fig.6. Schematic representation of oxidative degradation in commercial NR

In the present work, the formation of the epoxy group suggests commercial rubbers undergo oxidative degradation. Fig. 6 shows a schematic representation of the oxidative mechanism in commercial NR, which follows a radical route as reported in the literature [18]. Under high-temperature processing, radicals may be generated from the oxidation or degradation of lipids and subsequently incorporate oxygen in the air to form a peroxy radical species $RO_2^{\bullet}$ [19]. The peroxy radical, in turn, attacks the double bond on the rubber chain to produce a macro-radical, which then generates the epoxy group as shown in scheme (a). In the previous work, oxidative degradation of NR was reported to produce more *cis* than *trans* epoxy groups, but the *trans* epoxy

group was more favorable under a high temperature [18]. However, *trans* epoxy group was not detected on the rubbers in the current work. On the other hand, *cis-trans* isomerization is detected only in TSS8® and SMR20. As shown in scheme (b), the isomerization mechanism likely involves a radical species attacking the double bond of the *cis*-1,4-isoprene unit followed by the rotation of the macro-radical to produce *trans*-1,4-isoprene unit. Under the high temperature condition, the mobility of the polymer chain favors rotation, resulting in *cis-trans* isomerization.

The existence of the epoxy and *trans*-1,4-isoprene units from isomerization are evidence of auto-oxidative degradation in commercial rubbers. To evaluate the extent of degradation (*i.e.*, epoxidation and isomerization), the intensities of the epoxy group and *trans*-1,4-isoprene units were determined. The epoxy content ($\chi_{2.63\text{ppm}}$) and *trans* content ($\chi_{1.64-1.67\text{ppm}}$), were calculated based on the intensity ratio of the signal at 2.63 ppm for the epoxy group and 1.64-1.67 ppm for the *trans*-1,4-isoprene units, respectively, to the signal at 1.77 ppm. The equations are expressed as follows:

$$\chi_{2.63\text{ppm}} (\%) = \frac{I_{2.63\text{ppm}}}{I_{1.77\text{ppm}}/3} \times 100 \quad (1)$$

$$\chi_{1.64-1.67\text{ppm}} (\%) = \frac{I_{1.64-1.67\text{ppm}}}{I_{1.77\text{ppm}}} \times 100 \quad (2)$$

where I is the signal intensity. The subscripts represent the relevant chemical shift. Table 1 shows the values of the epoxy and the *trans*-1,4-isoprene units contents. The epoxy content and *trans*-1,4-isoprene units content were very similar. The epoxidation level of SMR20 is the highest, indicating that oxidative degradation may occur in low grades rubbers when the natural rubber is processed at a high drying temperature.

Table 1. Epoxy content and *trans* content of commercial rubbers

Sample	Epoxy content and <i>trans</i> content (%)	
	$\chi_{2.63\text{ppm}}$	$\chi_{1.64-1.67\text{ppm}}$
PC-AE	0.015	0
STR5L-AE	0.045	0.045
RSS3-AE	0.048	0.046
TSS8 ® -AE	0.036	0.037
SMR20-AE	0.075	0.084

On the other hand, the degree of *cis-trans* isomerization in commercial NR could be estimated by the intensity of the signals at 40.0 ppm ($\chi_{40.0\text{ppm}}$) to the methyl carbon signal of the *cis*-1,4-isoprene unit at 23.4 ppm as follows:

$$\chi_{40.0\text{ppm}}(\%) = \frac{I_{40.0\text{ppm}}}{I_{23.4\text{ppm}}} \times 100 \quad (3)$$

where I is the intensity of the signal and the subscripts represent the relevant chemical shift. Table 2 lists the estimated values for the intensity ratio of the signal at 40.0 ppm. As shown in the table, TSS8® had lower level of *cis-trans* isomerization than SMR20 and *cis-trans* isomerization was not detected in RSS3. In previous work, *cis-trans* isomerization was attributed to heating in a smokehouse and the drying tunnels. Fuel combustion generates combustible gases such as NO₂ and SO₂, which promote *cis-trans* isomerization in NR [7]. However, in the present work, *cis-trans* isomerization was not detected for RSS3, suggesting that *cis-trans* isomerization may be due to the processing temperature and not to combustible gases.

Table 2. Intensity ratio of the signals at 40.0 ppm to the signal at 23.4 ppm

Samples	$\chi_{40.0 \text{ ppm}} (\%)$
PC-AE	0
STR5L-AE	0
RSS3-AE	0
TSS8 ® -AE	0.042
SMR20-AE	0.163

If the epoxy group and the *trans*-1,4-isoprene units are due to degradation of these commercial rubbers, the distribution of these groups should to be inversely proportional to the molecular weight. Fig. 7 plots the *trans*-1,4-isoprene units content and epoxy group content versus the molecular weight of commercial rubbers. Both the *trans*-1,4-isoprene units content and epoxy groups content were inversely dependent on the molecular weight. The lower molecular weight, the higher the epoxy group content and the *trans*-1,4-isoprene units content. This may be explained to be due to the *trans*-1,4-isoprene unit and epoxy group are formed by oxidative degradation of NR during processing, since the low molecular weight fraction is able to be produced by chain scission of the rubber. Therefore, the existence of the epoxy group and the *trans*-1,4-isoprene unit from *cis-trans* isomerization are evidences of NR degradation.

Fig. 7. Plots of the *trans* content (◇) and the epoxy content (□) *versus* the average molecular weight of commercial rubbers

Fig.8. Stress-strain curves for (a) STR5L-AE, (b) RSS3-AE, (c) PC-AE
(d) TSS8®-AE and (e) SMR20-AE

Fig. 8 shows the stress-strain curves for STR5L, RSS3, PC, TSS8®, and SMR20 after acetone extraction, where σ and γ represent stress and strain, respectively. The stress *versus* strain for PC, STR5L, RSS3, and TSS8® increased significantly at a strain of

300% while the stress of SMR20 increased slightly at a strain of 800%. The abrupt increase in stress in a small strain region is attributed to the strain-induced crystallization of the rubbers [20]. The literature reports that the strain-induced crystallization of NR is governed by the presence of non-rubber components (*i.e.* proteins and phospholipids) and the naturally occurring network. Table 3 shows fatty acid content, nitrogen content and gel content of the rubbers. The highest stress for STR5L, RSS3 and TSS8® at strain of 300% was ascribed to the high amount of non-rubber components, *e.g.* high linked fatty acid content or nitrogen content [21,22]. Both PC and SMR20 contained similar amount of non-rubber components, however, the stress increased abruptly during straining in PC sample, while it slightly increased in SMR20 during increasing of strain until 800%. This phenomenon of stress-strain behavior in SMR20 suggests the flow of the rubber upon straining [22]. Since the fatty acid content of SMR20 was similar to that of PC, the flow of the rubber during straining of SMR20 sample may be explained by the absence of a naturally occurring network. This assumption was supported by the fact that the SMR20 film contains very little gel, *i.e.* about 6%, compared to 15.1% for PC (cf Table 3).

Table 3. Nitrogen content, fatty acid ester content and gel content of the rubber films after acetone extraction

Samples	%N	Fatty acid ester (mmol/kg-rubber)	Gel content %
PC-AE	0.276	8.4	15.1
STR5L-AE	0.408	13.5	11.1
RSS3-AE	0.345	8.5	5.2
TSS8 ® -AE	0.435	7.6	7.0
SMR20-AE	0.176	9.9	6.0

Fig. 9. Plots of the *trans* content ($\square$) and the epoxy content ($\diamond$) *versus* tensile strength of commercial rubbers

The stress at the break point of the rubbers was determined for each sample during extension. PC had the highest stress value of 8.0 MPa, whereas those of STR5L, RSS3, TSS8®, and SMR20 were 5.9, 4.9, 2.9, 2.7, and 1.6 MPa, respectively. The high stress at break of PC and STR5L may correspond to the high gel content, those were 15.1% and 11.1%, respectively. However, it seems to be difficult to explain the difference stress at break of RSS3, TSS8® and SMR20 in spite of similar amount of gel. By taking into account the degradation of the rubbers during processing, we may examine the effect of the damage of the rubbers on its mechanical properties. Fig. 9 plots the *trans*-1,4-isoprene units content and epoxy group content *versus* stress at the break of commercial rubbers. As the content of the abnormal groups increased, the stress at the break of the rubbers decreased. The lower the stress at the break of the rubbers having the higher epoxy and *trans*-1,4-isoprene unit contents may be explained to be due to the lower crystallizability. It is reasonable to hypothesize that

the crystallizability of NR is mainly due to the characteristic of the long sequence of the *cis*-1,4-isoprene units of NR [23]. The existence of the epoxy group or *trans*-1,4-isoprene on the main chain of the rubber molecules should shorten the long *cis*-1,4-isoprene sequence and consequently, reduce the tensile strength of the rubbers. Therefore, oxidative degradation is the main factor affecting the green strength of natural rubber.

4. Conclusions

Two abnormal groups, the *trans*-1,4-isoprene unit from *cis-trans* isomerization and the epoxy group, were present in the main chain of the rubber molecule as evidence from the structure characterization of various commercial NR through NMR spectroscopy. The increases in the *trans*-1,4-isoprene unit content and epoxy group content as the molecular weight decreased suggest that the low molecular weight fractions were the degradation products of NR. Consequently, the mechanical properties were inversely proportional to the amount of abnormal groups in commercial rubbers. Although epoxidation occurs in PC, RSS3, STR5L, TSS8® and SMR20, the *cis-trans* isomerization was only observed in TSS8® and SMR20. The *cis-trans* isomerization in TSS8® and SMR20 was related to the high drying temperature used to prepare commercial rubbers (*i.e.*, more than 100°C). This finding indicates that the drying temperature is an important factor inducing the degradation and consequently, the mechanical properties of commercial NR.

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Fig.1. Preparation of a rubber film by the solution casting method

Fig.2. ^1H -NMR spectra for (a) PC-AE, (b) RSS3-AE, (c) STR5L-AE, (d) TSS8®-AE and (e) SMR20-AE

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

Fig.4. ^{13}C -NMR spectra for (a) PC-AE, (b) RSS3-AE, (c) STR5L-AE, (d) TSS8®-AE and (e) SMR20-AE

Fig.5. ^{13}C -NMR spectra with pulse sequences of DEPT for STR5L-AE: (a) DEPT45, (b) DEPT90, and (c) DEPT135

Fig.6. Schematic representation of oxidative degradation in commercial NR

Fig.7. Plots of the *trans* content ($\diamond$) and the epoxy content ($\square$) *versus* the average molecular weight of commercial rubbers

Fig.8. Stress-strain curves for (a) STR5L-AE, (b) RSS3-AE, (c) PC-AE, (d) TSS8®-AE and (e) SMR20-AE

Fig.9. Plots of the *trans* content ($\square$) and the epoxy content ($\diamond$) *versus* tensile strength of commercial rubbers