ORIGINAL ARTICLE

Mechanical properties and cross-linking structure of cross-linked natural rubber

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Molecular singularity of cross-linked natural rubber was proposed to be a significant cross-linking junction of rubber, on the basis of the assignment of nuclear magnetic resonance (NMR) signals achieved in our previous work. This molecular singularity was observed to have an important role in the most outstanding mechanical properties of the rubber, through the investigation of the relationships between the structure of cross-linking junctions and the mechanical properties of various cross-linked rubbers. The various cross-linked natural rubbers were prepared by conventional vulcanization (CV), efficient vulcanization (EV) and semi-EV (SemiEV) to have nearly identical cross-link densities. These rubbers were analyzed using solid-state NMR spectroscopy. Using ^{1}H-NMR spectroscopy, the amount of tertiary carbons linking to sulfur in the CV rubber was observed to be the same as those of the EV and SemiEV rubbers. ^{13}C-NMR spectroscopy revealed that the number of quaternary carbons linking to sulfur in the CV rubber was the largest among the rubbers. The CV rubber exhibited the best mechanical properties; hence, a cross-linking junction of quaternary carbons linked to sulfur was assigned to the molecular singularity.

INTRODUCTION

Molecular singularity is a unique concept that is characteristic of polymers. Despite being a minor component of materials, molecular singularity dominantly governs their properties. Molecular singularity is defined as a structure, such as a cross-linking junction, branching point and terminal unit, that has an extremely important role in governing the properties of the polymer. For instance, the cross-linking junctions of cross-linked rubber have been widely recognized to be one of the key factors that control mechanical properties of the rubber. However, few studies in the literature have investigated the structural analysis of the cross-linking junctions, because no suitable method to analyze the cross-linking junctions exists. It is, thus, quite important to investigate the relationship between the structure of cross-linking junctions and mechanical properties in rubber.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is known to be a powerful technique for analyzing the structure of cross-linking junctions, because the chemical shift of signals appearing after cross-linking reflects the surrounding chemical environment of the atoms in the cross-linking junctions. Previous work[1–3] on the analysis of the cross-linking junctions primary used high-resolution solid-state NMR spectroscopy, because the cross-linked natural rubber was insoluble in organic solvents as a result of the three-dimensional network formed after vulcanization and the structural heterogeneity of the cross-linking junctions. However, in the previous

work, pulse sequences applicable to analyze the cross-linking junctions of the cross-linked natural rubber were limited to one-dimensional solid-state ^{13}C-NMR spectroscopy because of high-power decoupling. Signals appearing after vulcanization were, thus, assigned using estimated values of the chemical shifts of plausible cross-linking junctions proposed by Coran.[4] Small signals at 44, 50, 57 and 64 p.p.m. of the cross-linked natural rubber were assigned to tertiary carbons linked to sulfur,[5,6] respectively.

In our recent work,[7] we developed a field-gradient fast magic-angle spinning (FMAS) probe for solid-state NMR spectroscopy. The magnetic dipole–dipole interaction of the cross-linked natural rubber was eliminated using the FMAS probe, with a rate > 20 kHz.[8–14] The field-gradient FMAS probe enabled the application of various pulse sequences, such as distortionless enhancement by polarization transfer (DEPT), attached proton test (APT) and two-dimensional correlation measurements, to solid-state NMR spectroscopy. Moreover, the field-gradient FMAS probe enabled the measurement of inverse correlations between ^{1}H and ^{13}C to detect the small signals from the small amounts of the cross-linking junctions, that is, the use of techniques such as heteronuclear multiple quantum correlation, heteronuclear single quantum correlation and heteronuclear multiple bond correlation. Refering to the results of DEPT, APT and two-dimensional correlation measurements, we assigned the signal at 44 p.p.m. to secondary carbons adjacent to carbons linked

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to sulfur and the signal at approximately 58 p.p.m. to tertiary and quaternary carbons linked to sulfur.[7] On the basis of these assignments, the cross-linking junctions of the cross-linked natural rubber were found to be not only tertiary carbons but also quaternary carbons.

Cross-linking junctions are well known to be principal units that positively govern the mechanical properties of cross-linked rubbers. For instance, a stress concentration may occur at cross-linking junctions when rubber is stretched. Therefore, cross-linking junctions are expected to be a dominant factor influencing the mechanical properties of cross-linked natural rubber. More specifically, on the basis of the precise assignments of the NMR signals, we can determine the most important structural unit to be the cross-linking junctions. In the present study, the cross-linking junctions of various cross-linked natural rubbers are analyzed by solid-state NMR spectroscopy. The relationship between the cross-linking junctions and the mechanical properties of the various cross-linked natural rubbers, which were prepared by conventional vulcanization (CV), efficient vulcanization (EV) and semi-EV (SemiEV), is investigated.

EXPERIMENTAL PROCEDURE
Preparation of rubber
The natural rubber used in this study was commercial high-ammonia natural rubber latex purchased from Golden Hope Company (Pulau Carey, Selangor, Malaysia). The total solid content and dry rubber content of the high-ammonia natural rubber latex were 62.1 and 60.7 w/w%, respectively. The dried rubber was prepared by casting the high-ammonia natural rubber latex into a thin film. The latex was dried at room temperature for 24 h and it was then oven-dried at 50 °C for another 24 h.

Preparation of compounding
The dried high-ammonia natural rubber was compounded by accelerated sulfur vulcanization systems. The formulation for compounding the rubber is given in Table 1. CV, EV and SemiEV systems were prepared to analyze the cross-linking junctions and mechanical properties.

Preparation of cross-linked rubber
The optimum time for cross-linking each of the compounded rubbers was determined by using a rotorless rheometer (RLR-4) at 150 °C. Approximately 6 g of the compounded rubber was used with a 1 ° arc (the sample oscillating arc 1 °). The time at which the rheometer torque increased to 90% of the total torque change after cross-linking the rubber was defined to be t_{90}.

Determination of cross-link density
The cross-link density of the cross-linked rubber was determined by the swelling method. The rubber was immersed in 100 ml of toluene in the dark

Table 1 Compound formulations and vulcanization characteristic of the rubber

Ingredient	CV (phr)	EV (phr)	SemiEV (phr)
NR	100	100	100
ZnO	3	3	3
Stearic acid	1	1	1
TBBS	1	1	1
TMTD	0.3	2.0	0.8
Sulfur	2.2	0.2	1.0
t_{90}[a] (min)	3.79	6.09	4.29
v[b] ($\times 10^{-4}$ mol cm^{-3})	1.86	1.45	1.67

Abbreviation: TBBS, *N-tert*-butyl-2-benzothiazole sulfonamide; TMTD, tetramethylthiuram disulfide.
[a]Optimum time for cross-linking (min).
[b]Cross-link density ($\times 10^{-4}$ mol cm^{-3}).

for a week at room temperature. The cross-link density was calculated using the Flory–Rehner equation.[15]

$$\rho_c = -\frac{1}{2V_s} \frac{\ln(1 - V_r) + V_r + \chi_1(V_r)^2}{(V_r)^{1/3} - V_r/2}$$

where ρ_c is cross-link density, V_s the molar volume of toluene (106.9 cm^3 mol^{-1} at 25 °C), χ_1 is the interaction parameter and V_r can be determined from equation below.

$$\frac{V_r^o}{V_r} = 1 - \left[3C(1 - V_r^{o^{1/3}}) + V_r^o - 1\right]\frac{\phi}{1 - \phi}$$

where V_r^0 is the rubber fraction in the swollen gel, C is the parameter for the rubber interaction ($C = 1.17$) and ϕ is the volume fraction of rubber.

Mechanical properties measurement
The tensile test was performed at room temperature using an Instron universal tensile tester (Instron model 3365, Norwood, MA, USA). Dumbbell-shaped rubbers were subjected to the tensile test, according to JIS K 6251. The cross-head speed was 200 mm min^{-1}. The thickness of the rubbers was approximately 1 mm. The measurement was repeated five times for each sample.

Structural characterization
Solid-state NMR spectroscopy was performed with a JEOL ECA400 FT-NMR spectrometer (JEOL, Tokyo, Japan) operating at 399.95 and 99.99 MHz for ^{1}H and ^{13}C, respectively. The spinning rate of the sample tube for the solid-state measurement was 18 ± 5 Hz at 323 K. The number of scans for the acquisition of spectra was 10 000 and 90 000 with a pulse repetition time of 4.2 and 2 s for ^{1}H and ^{13}C, respectively. To prepare the solid-state NMR samples, the rubbers were crushed by a cryogenic sample crusher JFC-300 (Japan Analytical Industry Co., Ltd, Tokyo, Japan) before the measurement. The crushed rubber was loaded into a sample tube and its cross-linking junctions were analyzed with a 4-mm field-gradient FMAS probe by solid-state NMR spectroscopy. The ^{1}H-NMR, ^{13}C-NMR, APT and DEPT measurements were performed at 323 K at pulse repetition times of 7 and 5 s, respectively, because the liquid-like molecular motion should be accomplished at 323 K, which was approximately 100 K higher than the glass transition temperature of natural rubber.[16] The actual temperature of the surroundings in the NMR probes was calibrated by the temperature dependence of the [207]Pb chemical shift of Pb(NO$_3$)$_2$.

RESULTS AND DISCUSSION
Figure 1 shows the solid-state ^{1}H-NMR spectra for the cross-linked natural rubbers: that is, the CV, EV and SemiEV rubbers. The major signals at 1.7, 2.1 and 5.1 p.p.m. in the spectra were assigned to the methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene units, respectively. Table 2 shows the values of the half-width and signal-to-noise ratio of the methyl proton signal at 1.7 p.p.m. for the cross-linked natural rubbers. The values of the half-width and signal-to-noise ratio for the CV rubber were nearly identical to those of the EV and SemiEV rubbers. The higher values of the half-width of the CV, EV and SemiEV rubbers, which were compared with that of unvulcanized natural rubber,[7] may be attributed to anisotropic chemical-shift distributions and residual dipole–dipole interaction due to heterogeneous mobility of the cross-linked natural rubber, for example, the fast motion of the rubber chain and the slow motion of the cross-linking junctions. As shown in Figure 1, the small signals at 3.4 and 4.2 p.p.m. were found for the three cross-linked rubbers. The signal at 3.4 p.p.m. was assigned to aliphatic ^{1}H linked to the –C-**CH**-S$_x$ group and the signal at 4.2 p.p.m. was assigned to unsaturated aliphatic ^{1}H linked to the =C-**CH**-S$_x$ group, according to our previous work.[7] The intensity of the aliphatic ^{1}H linked to the –C-**CH**-S$_x$ group (3.4 p.p.m., $\chi_{3.4\,p.p.m.}$) and the unsaturated aliphatic ^{1}H linked to the =C-**CH**-S$_x$ group (4.2 p.p.m., $\chi_{4.2\,p.p.m.}$) was estimated from the intensity ratio of the
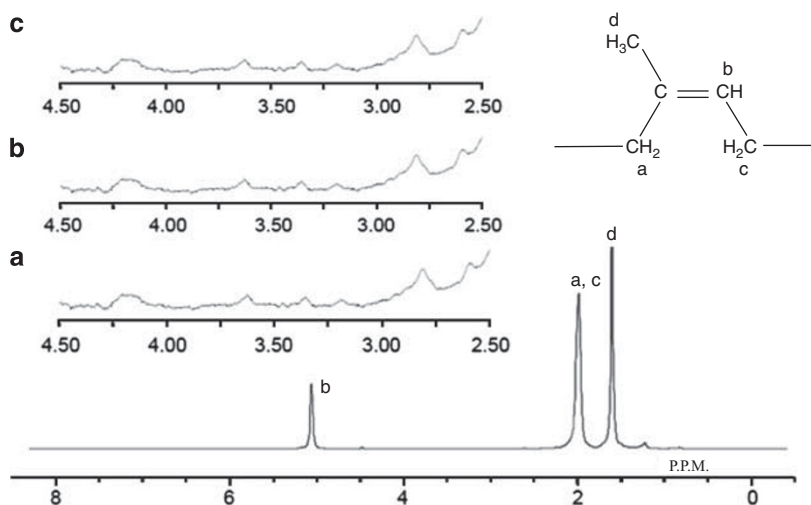
Figure 1 Solid-state ^{1}H-NMR spectra for the cross-linked natural rubbers prepared by (a) CV, (b) EV and (c) SemiEV.

Table 2 Summary of relevant parameters for the spectra shown in Figures 1 and 2

Figure	1a	1b	1c	2a	2b	2c
Samples	CV	EV	SemiEV	CV	EV	SemiEV
Signal-to-noise ratio	69 545	65 145	68 482	837	926	924
Half-width (Hz)	11.49	14.57	14.21	6.14	4.63	4.92
Time (h)	16.5	16.5	16.5	76.5	76.5	76.5

signals to the methyl proton signal at 1.7 p.p.m. as follows:

$$\chi_{3.4\,\mathrm{p.p.m.}}(\,\%\,) = \frac{I_{3.4\,\mathrm{p.p.m.}}}{I_{1.7\,\mathrm{p.p.m.}}} \times 100$$

$$\chi_{4.2\,\mathrm{p.p.m.}}(\,\%\,) = \frac{I_{4.2\,\mathrm{p.p.m.}}}{I_{1.7\,\mathrm{p.p.m.}}} \times 100$$

where I is intensity of the signal and the subscripts represent the relevant chemical shift. The estimated intensity ratio of the small signals at 3.4 and 4.2 p.p.m. to the methyl proton signal at 1.7 p.p.m. is tabulated in Table 3. The intensity of the aliphatic ^{1}H linked to the –C-**CH**-S_x group at 3.4 p.p.m. was 0.01% for the CV, EV and SemiEV rubbers, whereas that of the unsaturated aliphatic ^{1}H linked to the =C-**CH**-S_x group at 4.2 p.p.m. was 0.03% for the CV and SemiEV rubbers and 0.02% for EV rubber. These results demonstrate that the content of the small signals of the aliphatic ^{1}H linked to the –C-**CH**-S_x group and unsaturated aliphatic ^{1}H linked to the =C-**CH**-S_x group for the CV, EV and SemiEV rubbers were nearly identical to each other.

Solid-state ^{13}C-NMR spectra for CV, EV and SemiEV cross-linked natural rubbers are shown in Figure 2, with the acquisition parameters listed in Table 2. The five major signals in the spectra were assigned to the five carbon atoms of cis-1,4-isoprene units, according to the previous paper.[7] The values of half-width and signal-to-noise ratio of the signal at 24 p.p.m. for the cross-linked natural rubbers were quite similar. The narrow half-width and sufficient signal-to-noise ratio of the solid-state ^{13}C-NMR spectrum for the cross-linked rubbers implies that high-resolution was maintained for the solid-state ^{13}C-NMR spectroscopy even after cross-linking,

Table 3 Intensity ratio of the signal at 3.4 (aliphatic ^{1}H linking to –C-CH-S_x group signal) and 4.2 p.p.m. (unsaturated aliphatic ^{1}H linking to =C-CH-S_x group signal) to the signal at 1.7 p.p.m.

	Intensity of signals (%)	
Cross-linked rubber	3.4 p.p.m. (aliphatic ^{1}H linking to –C-CH-S_x group)	4.2 p.p.m. (unsaturated aliphatic ^{1}H linking to =C-CH-S_x group)
CV	0.01	0.03
EV	0.01	0.02
SemiEV	0.01	0.03

Abbreviations: CV, conventional vulcanization; EV, efficient vulcanization; SemiEV, semi-efficient vulcanization.
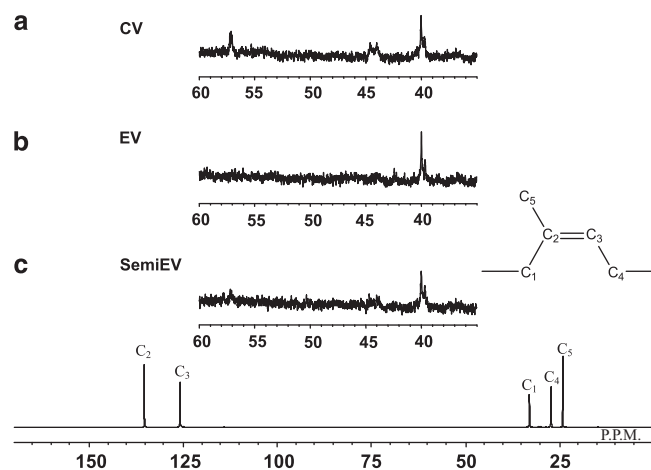

Figure 2 Solid-state ^{13}C-NMR spectra for the cross-linked natural rubbers prepared by (a) CV, (b) EV and (c) SemiEV.

because the dipole–dipole interaction between hetero-nuclei was eliminated by FMAS. This is distinguished from the very low resolution of the solid-state NMR spectrum for the cross-linked rubber reported by Klüppel[3] and Köenig.[17–19] As shown in Figure 2, the small signals at 40, 44 and 58 p.p.m. appeared in the solid-state

^{13}C-NMR spectra for the CV and SemiEV rubbers, whereas only a signal at 40 p.p.m. appeared in the solid-state ^{13}C-NMR spectrum for the EV rubber. The signals at 40 and 44 p.p.m. were assigned to C4 of the *trans*-1,4-isoprene units[20,21] and secondary carbons adjacent to carbons linking to S atom, respectively, and the signals at 58 p.p.m. were assigned to the tertiary and quaternary carbons linked to the sulfur, on the basis of our previous work.[7] This may imply that the cross-linking junctions of the CV and SemiEV rubbers were not only secondary carbon but also tertiary and quaternary carbons, whereas those of the EV rubber may contain only a small amount of quaternary carbon. The intensity of the small signals at 40 ($\chi_{40\text{p.p.m.}}$), 44 ($\chi_{44\text{p.p.m.}}$) and 58 p.p.m. ($\chi_{58\text{p.p.m.}}$) was estimated from intensity ratio of the signals to the methyl carbon signal at 24 p.p.m. as follows:

$$\chi_{40\text{p.p.m.}}(\ \%\ ) = \frac{I_{40\text{p.p.m.}}}{I_{24\text{p.p.m.}}} \times 100$$

$$\chi_{44\text{p.p.m.}}(\ \%\ ) = \frac{I_{44\text{p.p.m.}}}{I_{24\text{p.p.m.}}} \times 100$$

$$\chi_{58\text{p.p.m.}}(\ \%\ ) = \frac{I_{58\text{p.p.m.}}}{I_{24\text{p.p.m.}}} \times 100$$

where I is the intensity of the signal and the subscripts represent the relevant chemical shift. The estimated intensity ratio of the small signals at 40, 44 and 58 p.p.m. to the methyl carbon signal at 24 p.p.m. is tabulated in Table 4. The intensity of the signal at 40 p.p.m. was similar to each other (0.010%) for the CV, EV and SemiEV rubbers. This indicates that *cis–trans* isomerization occurs identically for the CV, EV and SemiEV rubbers despite the difference in the compound formulation (Table 1). In contrast, the intensity of the signals at 44 and 58 p.p.m. in the solid-state ^{13}C-NMR spectrum decreased in the CV, SemiEV and EV rubbers in order. The intensity of the secondary carbon (44 p.p.m.) and tertiary and quaternary carbons (58 p.p.m.) for the CV rubber was the highest among the three rubbers. These signals decreased for the SemiEV rubber and disappeared for the EV rubber. This implies that the amount of the quaternary carbon of the CV rubber is larger than that of the SemiEV rubber. The EV rubber may contain a small amount of the quaternary carbon as cross-linking junction.

To assign the signals, the APT and DEPT measurements were performed for the CV rubber using solid-state ^{13}C-NMR spectroscopy. Figure 3 showed the APT spectrum for the CV rubber. The APT spectrum represented downward signals at 40 and 44 p.p.m., as well as the very small upward and downward signals at approximately 58 p.p.m. Thus, we assigned the signals at 40 and 44 p.p.m. to the secondary carbons and signals at 58 p.p.m. to the tertiary and quaternary carbon. The very small upward signal at approximately

58 p.p.m. implied that the cross-linking junctions of the cross-linked rubber were composed of a very small amount of tertiary carbon.

Figure 4 shows the DEPT spectra at 45° (DEPT45), 90° (DEPT90) and 135° (DEPT135) pulses for the CV rubber. The signals at 24, 26 and 32 p.p.m. that are characteristic of methyl, C4- and C1-methylene carbons of *cis*-1,4-isoprene units were shown to be all upward in the DEPT45 spectrum, whereas they were almost nearly zero in the DEPT90 spectrum. On the other hand, in the DEPT135 spectrum, the signals at 24, 26 and 32 p.p.m. were upward, downward and downward, respectively. Thus, the pulse width determined for DEPT measurements was confirmed to be correct to assign the small signals at 40, 44 and 58 p.p.m. The small signals at 40 and 44 p.p.m. were shown to be upward in the DEPT45 spectrum, null in the DEPT90
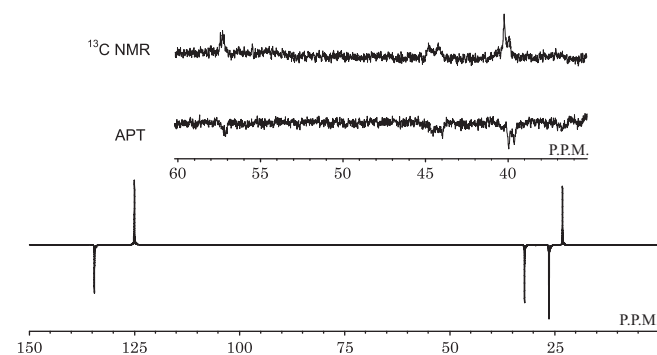

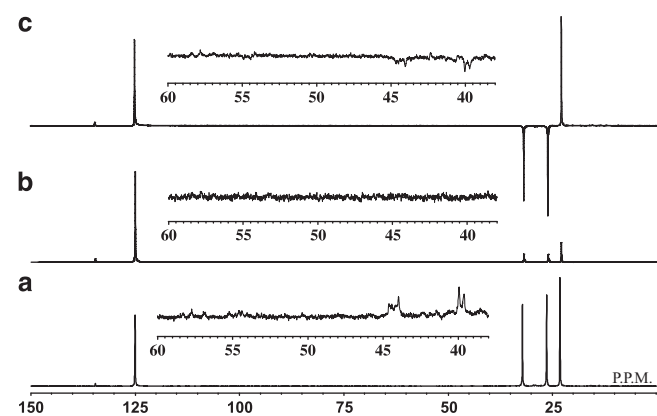**Figure 3** Solid-state ^{13}C-NMR spectrum with the APT for the CV rubber.

Figure 4 Solid-state[13]C-NMR spectra with pulse sequences of DEPT for CV rubber: (a) DEPT45, (b) DEPT90 and (c) DEPT135.

Figure 5 Stress-strain curves for (a) CV, (b) SemiEV and (c) EV rubbers.

Table 4 Intensity ratio of the signals at 40, 44 and 58 p.p.m. to the signal at 24 p.p.m.

Cross-linked rubber	Intensity of cross-linking junction signals (%)		
	40 p.p.m.	*44 p.p.m.*	*58 p.p.m.*
CV	0.010	0.005	0.005
EV	0.010	0.000	0.000
SemiEV	0.009	0.001	0.001

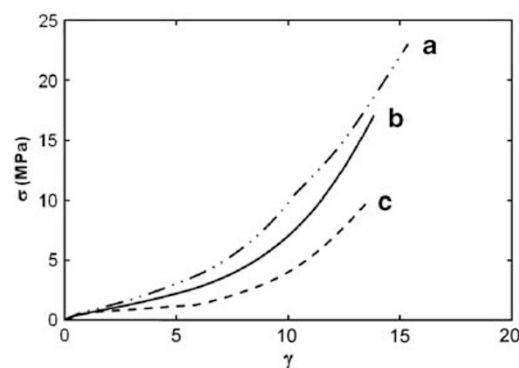Abbreviations: CV, conventional vulcanization; EV, efficient vulcanization; SemiEV, semi-efficient vulcanization.
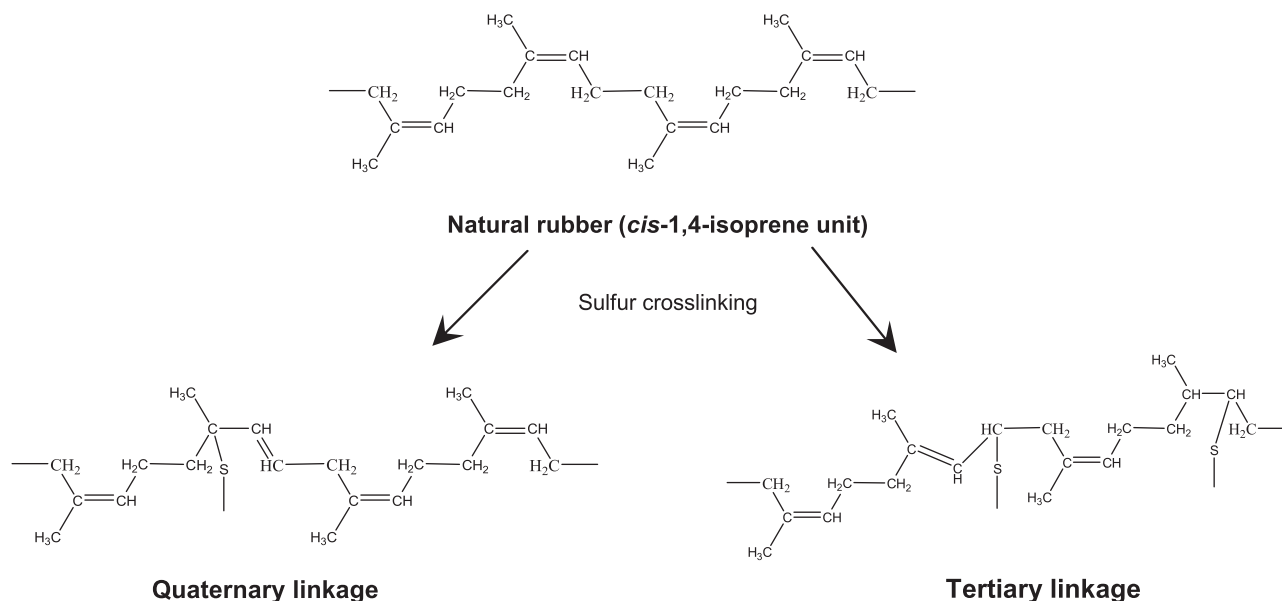
Figure 6 Possible cross-linking junctions for the cross-linked natural rubber.

spectrum and downward in the DEPT135 spectrum; hence, they were assigned to secondary carbons. In contrast, the signal at 58 p.p.m. was assigned to tertiary and quaternary carbons because of the very small upward signals in the DEPT45, DEPT90 and DEPT135 spectra.

Stress-strain curves for the CV, EV and SemiEV rubbers are shown in Figure 5, where σ represents stress and γ represents strain. The stress at strain of 1 for the CV rubber is nearly identical to that for the EV and SemiEV rubbers. This is consistent with the similarly observed values of the cross-link density of the CV, EV and SemiEV rubbers, as shown in Table 1. In contrast, the tensile strength of the three cross-linked rubbers was different, that is, the value of stress at break of the CV rubber (22.5 MPa) was the highest among the cross-linked rubbers and was reduced for the SemiEV rubber (17.0 MPa) and EV rubber (9.2 MPa). In previous work,[22] Suchiva et al.[22] reported that the improved mechanical properties of the CV rubber were due to higher concentrations of the polysulfidic cross-links rather than those of the EV rubber. Moreover, the superior mechanical properties of the CV rubber were explained to be due to differences in the mechanism of the cross-linking. The CV rubber was found to have more homogeneous network than the EV and SemiEV rubbers. However, in the present work, we found that the superior mechanical properties of the CV rubber were attributed to the quaternary carbons as the cross-linking junction.

Figure 6 shows plausible cross-linking junctions of cross-linked natural rubber. The present and previous works[7,20–21] demonstrate that the tertiary and quaternary carbons linked to sulfur may be neighbors to carbon–carbon double bonds in trans form. As shown in Figure 6, the quaternary carbon linked to sulfur at a cross-linking junction may maintain the accordion structure of natural rubber, which is a main factor in the rubber elasticity.[17] In contrast, the tertiary carbons linked to sulfur at a cross-linking junction change this configuration; hence, the accordion structure necessary for the rubber elasticity is not maintained. This result may be associated with the change in stress and strain at the break of the cross-linked rubber shown in Figure 5. The CV rubber, which possessed the quaternary carbons linked to sulfur, exhibited the highest stress and strain at break, whereas the EV rubber, which has a negligible amount of quaternary carbons linked to sulfur, exhibited the lowest. This demonstrates that the quaternary carbons

linked to sulfur are the most dominant factor for the outstanding mechanical properties of the sulfur cross-linked rubber.

CONCLUSIONS

Cross-linked natural rubbers, prepared by CV, EV and SemiEV, were fabricated to have a similar cross-link density of approximately 1.5×10^{-4} mol cm^{-3}. The intensities of the ^{1}H-NMR signals at 3.4 and 4.2 p.p.m., assigned to the tertiary carbons linked to sulfur, were found to be nearly identical for the CV, EV and SemiEV rubbers, corresponding to the similar cross-link density of the rubbers. The ^{13}C-NMR spectroscopy revealed that the intensity of the signal at 58 p.p.m. of the CV rubber was larger than that of the EV and SemiEV rubbers. The CV rubber was found to contain the largest amount of the quaternary carbons linked to sulfur at the cross-linking junction. The quaternary carbons were concluded to be the primary molecular singularity leading to the outstanding mechanical properties of the cross-linked natural rubber, because the CV rubber exhibited the best mechanical properties among the rubbers studied.

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