

ESR Study of Silica-Filled SBR with Different Rubber/Filler Interactions

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ABSTRACT: Silica-filled styrene-butadiene rubber (SBR) unvulcanizates and their vulcanizates with different rubber/filler interactions were prepared by using several kinds of coupling agents. Tensile tests and electron spin resonance (ESR) measurements were carried out for both unvulcanized and vulcanized samples to get information on the effects of filler/rubber interactions on the breakdown of carbon-carbon (C-C) linkages in SBR and carbon-sulfur (C-S-C, C-S-S-C) linkages at the cross-linked points between rubber and sulfur by a tensile force.

The combination of ESR results and stress-strain data suggested that with increasing the mechanical energy applied to the samples by the stretching, the carbon-sulfur linkages around silica particles were broken first, followed by the breakdown of carbon-sulfur and C-C linkages in the rubber matrix. The assignment of ESR spectrum was also discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1385-1392, 2008

Key words: ESR; silica; SBR; interactions; stretching

INTRODUCTION

When a filled rubber vulcanizate is stretched, a stress distribution appears in the system because the filled rubber vulcanizates have multicomponent structure depending on the mobility of rubber molecules. With increasing the restriction of chain mobility, the stress on draw should increase. The development of multicomponent structure has been explained by the interactions between fillers and rubber molecules as well as the network structure of rubber molecules produced by the vulcanization. Brennan and Jermyn suggest that, the higher the tensile stress on drawing, the larger the degree of chain scission of rubber molecules that can be expected.¹ This suggests that the degree of chain scission by the tensile force is closely related to the multicomponent structure of filled rubber systems.

We reported the ESR results for the stretched silica-filled styrene-butadiene rubber (SBR) vulcanizates.^{2,3} At a given strain, the tensile stress on draw and radical concentration increased by the introduction of coupling agent such as bis(triethoxysilyl propyl)-tetrasulfide (TESPT). Ethoxyl groups of TESPT react with silanol groups on silica particles. In addition, sulfur atoms in TESPT couple with diene groups of SBR. Such chemical structure of TESPT produced a chemical bonding between SBR and silica through TESPT, which might enhance the

increases of tensile stress and breakdown of chemical linkages. The stretched vulcanizates showed only one resonance line of which g -value and the line width at the maximum slope (ΔH_{msl}) were 2.004 and 1.5 mT, respectively. In SBR, the binding energy between sp^3 carbon of butadiene unit is the lowest. Thus, the allyl radical ($-C=C-C$) is likely to be formed if the breakdown of chemical linkages happened in SBR. In that case, the ESR spectrum from allyl radical should show a clear hyperfine splittings.⁴⁻⁶ However, Carstensen reported^{5,6} that the allyl radicals in polybutadiene and polyisoprene formed at liquid nitrogen temperature were easily transformed into polyenyl radical ($-(C=C)n-$) during heating. In addition, the g -value and ΔH_{msl} for polyenyl radical are reported to be 2.004 and 1.6 mT.^{5,7} Although the breakdown of carbon-sulfur linkages was also taken into consideration for vulcanized samples, we could not observe the ESR signal with the g -value of around 2.02-2.05 which was assigned to the sulfidic radicals.⁸⁻¹⁰ Thus, we concluded in our previous study^{2,3} that the ESR spectrum for the stretched silica-filled SBR vulcanizates was responsible for the polyenyl radicals. This means that the increased radical concentration by the introduction of TESPT can be explained by the enhancement of chain scission of rubber molecules.

As described, the vulcanized silica-filled SBR with TESPT has the carbon-sulfur linkages around the silica particles. Such linkages also exist in the rubber matrix of the vulcanizates. The mobility of rubber molecules around silica might be highly constrained compared with that in the rubber matrix.³ Therefore,

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TABLE I
Chemical Structure of Coupling Agents

Agent	Structure
TESPT	$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \diagdown \\ \text{C}_2\text{H}_5\text{O} - \text{Si} - (\text{CH}_2)_3 - \text{S}_4 - (\text{CH}_2)_3 - \text{Si} - \text{OC}_2\text{H}_5 \\ \text{C}_2\text{H}_5\text{O} \diagup \end{array}$ <p style="text-align: center;">Bis-(3-triethoxysilylpropyl)-tetrasulfide</p>
VS	$\begin{array}{c} \text{CH}_3\text{O} \diagdown \\ \text{CH}_3\text{O} - \text{Si} - \text{CH}=\text{CH}_2 \\ \text{CH}_3\text{O} \diagup \end{array}$ <p style="text-align: center;">Vinyltrimethoxysilane</p>
MS	$\begin{array}{c} \text{CH}_3\text{O} \diagdown \\ \text{CH}_3\text{O} - \text{Si} - \text{CH}_3 \\ \text{CH}_3\text{O} \diagup \end{array}$ <p style="text-align: center;">Methyltrimethoxysilane</p>

the chain scissions occur preferentially around the interfacial regions between fillers and rubber molecules at a small strain, followed by the scission in the rubber matrix at a larger strain. The binding energy for carbon-sulfur (C-S-C) and sulfur-sulfur (C-S-S-C) linkages has been estimated to be smaller than that for carbon-carbon (C-C) linkage.¹¹ Thus, it is reasonable to speculate that the C-S-S-C and/or C-S-C linkages are broken first followed by the breakdown of C-C linkage in the SBR vulcanizates. This suggests that the effects of breakdown of C-S-S-C and C-S-C linkages on the increase of the radical concentration must also be taken into consideration, although we failed to detect the ESR spectrum assigned to the sulfidic radicals⁸⁻¹⁰ in the previous work.^{2,3}

The ESR study for the unvulcanized silica-filled rubbers certainly gives us useful information on the effects of vulcanization on the ESR spectra by comparing the results with those for vulcanized samples.

In this study, ESR measurements were carried out for the stretched silica-filled SBR unvulcanizates with different interfacial interactions between silica and SBR by using several kinds of coupling agents.¹² The results were compared with those for vulcan-

ized samples to discuss on the effects of vulcanization on the ESR results of silica-filled SBR.

EXPERIMENTAL

Samples

The raw rubber used was a SBR (Nipole SBR 1502, $M_w = 4.3 \times 10^5$, $T_g = -52^\circ\text{C}$, Nippon Zeon, Japan). The silica used was a precipitated silica (Nipsil AQ, Nippon Silica, Japan). Three kinds of coupling agents were used for the surface modification of silica particles. The chemical structure of the coupling agents are shown in Table I. The reactivity of coupling agents with silanol groups on silica particles depends on the moisture content of silica particles.^{13,14} Thus, as-received silica was dried at 120°C under a reduced pressure for 12 h to reduce the moisture content of silica particles.

Composites were prepared by a mechanical mixing. The composition of them is listed in Tables II and III. The conditions for the mechanical mixing were as follows: SBR was put into a Banbury mixer (Labo plastomill 50 MR, Toyo Seiki, Japan) and masticated under 60 rpm at 60°C for 1 min, then dried

TABLE II
Compositions of Silica-filled Unvulcanizates

Sample code	UN	U-AQ	U-VS	U-MS	U-TESPT
SBR1502	100(phr)	100(phr)	100(phr)	100(phr)	100(phr)
Silica	-	30	30	30	30
VS	-	-	3	-	-
MS	-	-	-	3	-
TESPT	-	-	-	-	3

phr, weight per hundred rubber.

TABLE III
Compositions of Silica-Filled SBR Vulcanizates

Sample code SBR1502	V-AQ 100(phr)	V-VS 100(phr)	V-MS 100(phr)	V-TESPT 100(phr)
Silica	30	30	30	30
Zinc oxide	3	3	3	3
Stearic acid	2	2	2	2
Accelerator (Cz) ^a	1	1	1	1
Accelerator (DPG) ^b	1.5	1.5	1.5	1.5
Sulfur	1.7	1.7	1.7	1.7
VS	–	3	–	–
MS	–	–	3	–
TESPT	–	–	–	3

phr, weight per hundred rubber.

^a *N*-cyclohexyl-2-benzothiazyl-sulfenamide.

^b Diphenyl guaidine.

silica and coupling agent were mixed with masticated SBR under 60 rpm at 100°C for 1 min. The unvulcanized composites prepared by the mechanical mixing were seated on a roll mill at 60°C which was used for measurements. For the preparation of vulcanized samples, SBR/silica composite prepared by the mechanical mixing was mixed with zinc oxide, stearic acid, and antioxidant at 100°C for 2 min. Then the master batch was mixed with sulfur and two kinds of accelerators (Cz and DPG) under 60 rpm at 60°C for 3 min. The seated composites were vulcanized at 160°C for 30 min under a pressure of 400 kg/cm².

Measurements

Measurements of stress–strain curves were carried out on a tensile tester (IM-20ST, Intesco, Japan) at room temperature (24°C). The strain rate was 3.0 min^{−1}.

The ESR spectra were obtained at −100°C by using a JEOL (Tokyo, Japan) ES-FA 200 X-band (9.2 GHz) spectrometer with 100 kHz field modulation and with a JES-VT-100X variable temperature accessory. The samples for the measurements were prepared by the following procedure: both vulcanized and unvulcanized sheets were cut into strips with the size of 1 mm × 2 mm × 30 mm. The strips were stretched by a tensile tester at room temperature up to a desired initial strain (IS) in the range of 10–200%, followed by a release of tensile stress (pre-stretched sample). Then the prestretched samples were cut into small strip with a length of 15 mm to get a similar value of filling factor of ESR cavity. Each small strip was put into an ESR test tube, followed by the immediate quenching in liquid nitrogen to minimize the change in the number of radicals produced by the tensile deformation. The quenched sample with test tube was transferred to the precooled (−100°C) ESR cavity, followed by the measurements.

The *g*-value and the radical concentration of the samples were determined by the following procedure. First of all, ESR measurement was carried out for the sample at room temperature to determine the magnetic field at the center of resonance line. Then the measurement was done for the external standard involving Mn²⁺. The Mn²⁺ showed six resonance lines. Among them, the third and fourth resonance lines of which *g*-values were 2.034 and 1.981 were used to determine the *g*-value of the sample. The *g*-values of Mn²⁺ were put into the data processor equipped with the ESR spectrometer. The resonance frequency determined by the frequency counter equipped with the spectrometer was also fed into the data processor automatically. Then data processor calculated the *g*-value of the sample. The value of magnetic field at the center of resonance line was almost the same for all samples. In addition, the value was almost constant between room temperature and −100°C. From these results, the *g*-value for all the samples was determined to be 2.004.

Calculation of the radical concentrations for the samples at −100°C was carried out by using an aqueous solution of 4-hydroxy-2,2,6,6-tetramethyl piperidinoxyl radical (TEMPOL). A double integration of the first derivative curve of ESR signal at room temperature from the TEMPOL with a known radical concentration was used as a standard. Because the signal intensity from the TEMPOL at −100°C was too weak to use a quantitative analysis.

RESULTS AND DISCUSSION

Stress–strain behavior of unvulcanizates

Figure 1 shows the stress–strain curves at room temperature for unvulcanized silica-filled SBR with

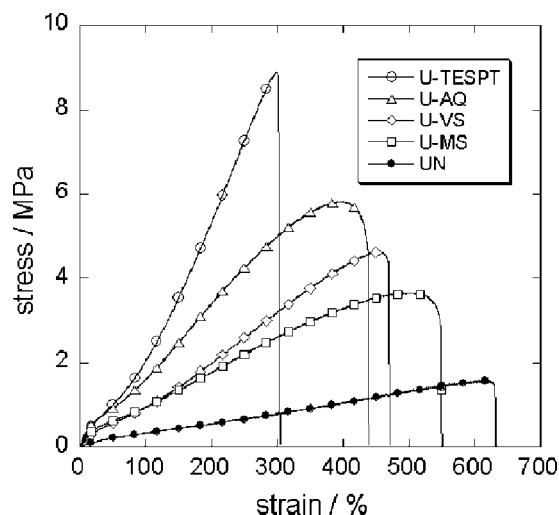


Figure 1 Stress–strain curves at room temperature for silica-filled SBR unvulcanizates.

TABLE IV
Tensile Properties of Unvulcanizates and Vulcanizates

	Tensile modulus (MPa)	Strength at break (MPa)	Elongation at break (%)
U-AQ	3.28	5.80	438.0
U-VS	2.30	4.62	469.0
U-MS	1.23	3.58	545.5
U-TESPT	2.00	8.88	302.5
V-AQ	5.52	135.0	926.0
V-VS	2.21	118.5	745.5
V-MS	2.20	131.0	770.5
V-TESPT	5.19	147.0	664.0

different kinds of coupling agents. The tensile modulus, strength at break, and elongation at break were evaluated from the stress–strain curves, and the results are shown in Table IV. The tensile modulus was determined from the initial slope of stress–strain curves at a low strain (0.5%). It is seen that the initial slope, stress at a larger strain, and the elongation at break were dependent on the sort of coupling agent. We studied the reaction of coupling agent with silanol groups on the silica surface in the rubber matrix, and found that the mixing of rubber with silica and coupling agent at 100°C for 1 min was enough to proceed the reaction of silanol groups with methoxy and ethoxy groups in the silane coupling agent.¹³ In this study, the conditions for the mixing of SBR with silica and coupling agent were similar to those for the previous work.¹³ Thus, it is reasonable to infer that the surface of silica particles was modified by the coupling agent in the rubber matrix.

The initial slope corresponds to the tensile modulus of the samples. The tensile modulus of unvulcanized silica-filled rubber systems has been correlated with the dispersion of silica in the rubber matrix and silica/rubber interactions.^{13,14} The initial slope for the U-MS and U-VS was smaller than that for the sample without coupling agent (U-AQ). By the reaction of coupling agent with silanol groups on silica particles, the hydrophilic character of silica changed into hydrophobic one, which reduced the silica–silica interactions via reduced agglomerate size formed by silica particles in the rubber matrix, leading to the decrease in the tensile modulus of silica-filled SBR unvulcanizates.

At a larger strain (>200%), the tensile stress for the U-TESPT increased steadily with increasing the strain, similar to the case of carbon black-filled rubber composites.^{1,15} On the other hand, the increase was less for the U-VS and U-MS as well as without coupling agent (U-AQ). The stress–strain behavior of the filled rubber vulcanizates is affected primarily by two factors: the one is the crosslink density, and the other is the interactions between filler and rubber molecules. For unvulcanized system, the crosslink is

formed by the physical entanglement of rubber molecules which should be almost constant in all samples. Thus, the primary reason for the observed differences might be attributed to the difference of interactions between fillers and rubber molecules. Ethoxy groups of TESPT react with silanol groups, and sulfur atoms in TESPT might partly react with diene groups of SBR during mixing, although the mixing temperature of 100°C was slightly lower than the optimum vulcanization temperature. In that case, rubber molecules and silica were connected through TESPT, resulting in the formation of strong interfacial interactions between silica and SBR. On the other hand, both VS and MS are monofunctional coupling agents. Although they can react with silanol groups on silica particles, there is no functional group which can react with SBR. It is well-known that the strong interfacial interactions between carbon black and rubber matrix enhance the tensile stress at a larger strain.^{1,15,16}

The monofunctional coupling agent with alkyl groups such as VS and MS might work as a plasticizer for rubber molecules, which induced the slippage of rubber molecules at a larger strain, leading to the rather small increase of stress with further increase of strain. The tensile stress at a break is slightly larger for the U-VS than for the U-MS. Although we cannot expect a direct chemical reaction between SBR and VS, the results suggest that the interactions between VS and SBR are larger than those for MS and SBR. The possibility of the reactivity between VS with SBR was examined by infrared spectroscopy measurements. However, we could not get information on the chemical interaction between vinyl groups in VS and SBR. The difference of hydrophobic character between VS and MS might be taken into consideration to explain the difference of stress–strain behavior at a larger strain between U-MS and U-VS.

Stress–strain behavior of vulcanizates

Figure 2 shows the stress–strain curves at room temperature for the vulcanized silica-filled SBR with different coupling agents. The tensile properties were also evaluated from the stress–strain curves, and the results are shown in Table IV. We can see the effects of vulcanization on the stress–strain behavior of filled rubber systems by comparing Figure 2 with Figure 1. The elongation at break and the stress at a larger strain were greatly increased by the vulcanization. The stress at a larger strain was the smallest for the sample without coupling agent (V-AQ), although the unvulcanized sample (U-AQ) showed a rather large stress (Fig. 1). As shown in Table III, all the samples were vulcanized under a similar condition (sulfur and accelerator contents, vulcanization tem-

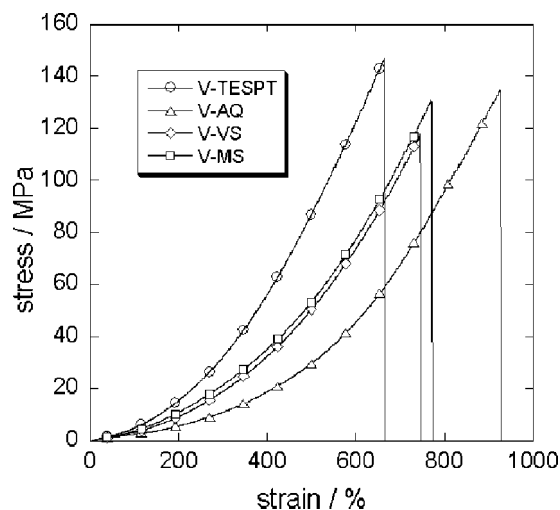


Figure 2 Stress-strain curves at room temperature for silica-filled SBR vulcanizates.

perature and time). However, the silanol groups on silica particles are acidic, which have an ability to absorb an accelerator with a basic character, leading to the decrease in the efficiency of vulcanization. For the samples with coupling agents, the silanol groups are partly covered with the coupling agents, which reduce the possibility to absorb the accelerator. As a result, the efficiency of vulcanization is higher for the samples with coupling agent than for without coupling agent. Thus, the difference of stress at a larger strain can be partly correlated with the difference in the efficiency of vulcanization. It is interesting that all the samples showed a similar strength at break around 120–150 MPa, although the strength for the unvulcanized samples was greatly affected by the sort of coupling agent. The results suggest that the stress distribution around the elongation at break for the vulcanized samples is different from that for unvulcanized samples. This will be discussed further in the next section.

ESR results

The first derivative ESR spectra at -100°C for the U-VS and U-TESPT having different initial strains (ISs) are shown in Figures 3 and 4. All the samples showed a broad resonance line with the g -value of 2.004 and the line width at the maximum slope (ΔH_{msl}) of 1.5 mT. The intensity of resonance increased with increasing the IS without changing the g -value and ΔH_{msl} . The unstretched sample (IS = 0) also showed a resonance. During the sample preparation by the mechanical mixing, small amounts of radicals were produced by the breakages of rubber molecules, since the mixing torque was considerably increased by the incorporation of silica into the rubber.

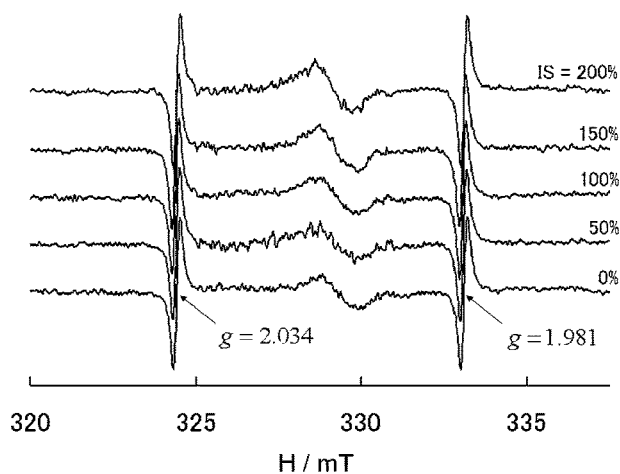


Figure 3 ESR spectra at -100°C for the U-VS having different ISs.

The signal intensity decreased with time without changing the g -value as well as the ΔH_{msl} and almost leveled off at 1 week after the sample preparation. Thus, the stretched samples were prepared by using the unstretched one which was stored in a vacuum oven at room temperature for a week.

When the ESR measurements for the stretched samples were carried out at room temperature, the signal intensity decreased with increasing the storage time which corresponded to the time difference between sample preparation and ESR measurements. The decrease of signal intensity with the storage time became less prominent when the storage temperature of stretched samples and measurement temperature were below the glass transition temperature of SBR (approximately -5°C). Thus, the ESR measurements were carried out at -100°C for the samples just after the stretching at room temperature. The details are described in the Experimental section.

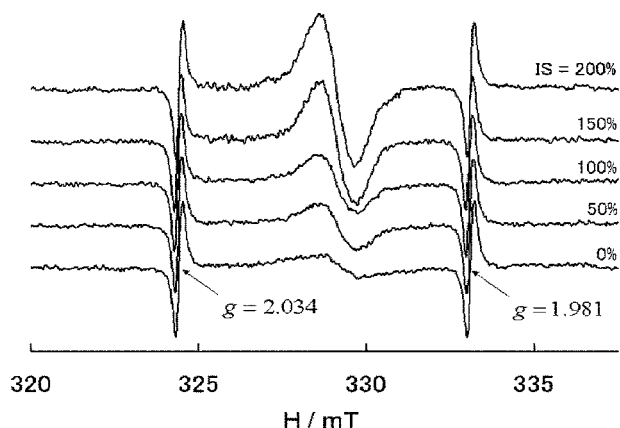


Figure 4 ESR spectra at -100°C for the U-TESPT having different ISs.

The number of radicals per unit volume of samples (C_R) was calculated from the double integration of the first derivative ESR spectra at -100°C . The sample volume in the ESR cavity was calculated from the sample size. The area of double integration of the first derivative ESR curve from the TEMPOL with a known radical concentration at room temperature was used as a standard. Thus, the absolute value of the radical concentrations for the samples at -100°C might be slightly different from those shown in this article. However, the difference had little effects on the qualitative discussion on the relation between radical concentration and strain. Because ESR measurements for all samples were carried out at a constant temperature of -100°C . The radical concentration produced by the stretching (ΔC_R) was calculated by the subtraction of radical concentration (C_R) for the unstretched sample from the C_R for the stretched sample.

Figures 5 and 6 show the relation between IS and ΔC_R for unvulcanized and vulcanized silica-filled samples with different coupling agents. As the signal intensities for the unvulcanizates were weak compared with those for the vulcanized samples, the error range of ΔC_R for the unvulcanizates was not small. However, the following results can be seen that for the U-VS, U-MS and without coupling agent (U-AQ), the ΔC_R was almost zero up to the IS of 100%, followed by the gradual increase with the increase of the IS.

The ΔC_R for the U-TESPT showed a stepwise increase with increasing the IS. It should be noted that the increase of ΔC_R with the IS was observed even at a small IS where the other samples showed no increase of ΔC_R . Around 100% of IS, the ΔC_R increased discontinuously where the ΔC_R for the other samples started to increase. These results were

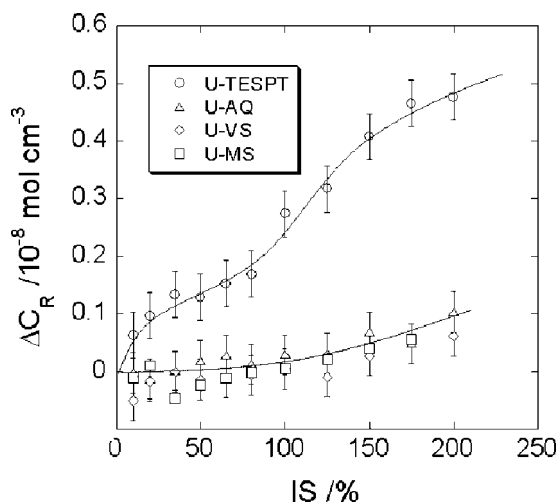


Figure 5 Relation between the IS and ΔC_R for the unvulcanizates.

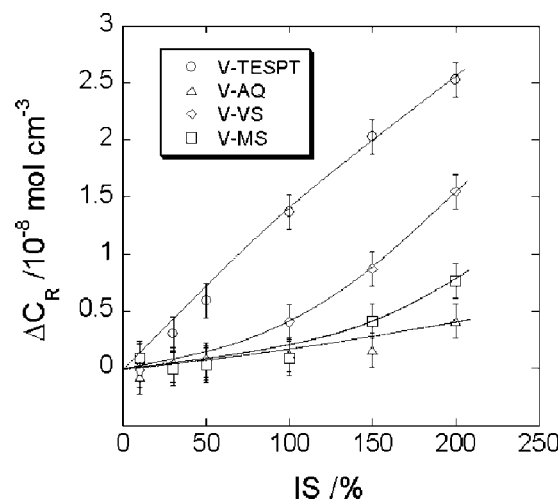


Figure 6 Relation between the IS and ΔC_R for the vulcanizates.

compared with those for the vulcanized samples shown in Figure 6 to evaluate the vulcanization effects. It is clear that the ΔC_R at a larger strain for the vulcanizates is more than four times larger than that for unvulcanizates. As seen in Figures 1 and 2, the stress at a given strain is extremely increased by the vulcanization. This is reasonable since an effective network structure was formed by the vulcanization which suppressed the chain slippage during tensile drawing. Therefore, at a given IS, the stress applied to the molecular chains was higher for vulcanizates than for unvulcanizates. Further, V-TESPT showed a continuous increase of ΔC_R with IS, which is different from the result for U-TESPT. The difference will be discussed later.

The ΔC_R corresponds to the total number of radicals produced by the stretching. Therefore, the ΔC_R is likely dependent on the mechanical energy applied to the samples during stretching rather than the tensile stress and/or strain. Thus, in Figures 7 and 8, the ΔC_R for both unvulcanizates and vulcanizates are plotted as a function of mechanical energy (E) calculated from the stress-strain curves. For the U-VS and U-MS and without coupling agent (U-AQ), the ΔC_R was almost zero up to around the E value of 0.5 J/cm^3 , followed by a small increase of ΔC_R with a further increase of E . On the other hand, for the U-TESPT, a two-step increase of ΔC_R with E can be seen, similar to the case of ΔC_R -strain relation.

As shown in Figure 1, the stress at a given strain for the U-VS was slightly larger than that for the U-MS. However, we could not find any notable difference between the U-VS and U-MS in Figure 7. This might be due to the quite small value of ΔC_R for each sample. When monofunctional coupling agent with alkyl groups such as VS and MS was intro-

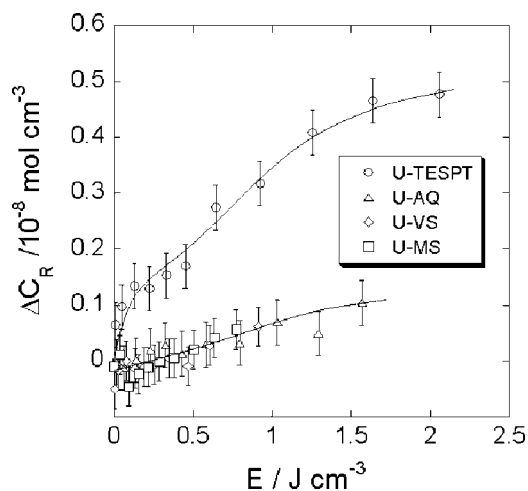


Figure 7 Relation between the mechanical energy (E) and ΔC_R for the unvulcanizates.

duced into the unvulcanized sample, they might act as a plasticizer of rubber molecules. In that case, a chain slippage occurs during the stretching of unvulcanized samples, which suppresses the efficient chain extension, resulting in the low value of ΔC_R .

For the vulcanized samples (Fig. 8), it is clearly seen that the ΔC_R at a given E is more than four times larger than that for unvulcanized samples. This is reasonable since the stress at a given strain for the vulcanized samples was more than four times larger than that for unvulcanized samples (see Figs. 1 and 2). The comparison of Figure 8 with Figure 7 revealed some interesting facts. The first is that the ΔC_R for both unvulcanizates and vulcanizates (except for U- and V-TESPT) was almost zero up to about 0.5 J/cm^3 . The results for the unvulcanizates indicate that the breakdown of C—C linkages is negligible up to around 0.5 J/cm^3 . However, the U-TESPT showed an increase of ΔC_R even below 0.5 J/cm^3 , further, the increase was more prominent in the vulcanized sample (V-TESPT).

As described, TESPT involves four sulfur atoms in one molecule which can react with diene unit in SBR. For unvulcanized sample, the mixing temperature of 100°C was slightly lower than the optimum vulcanization temperature; however, a high level of stress on draw as shown in Figure 1 suggests that a part of diene unit was coupled with sulfur in TESPT even in the unvulcanized sample (U-TESPT). On the other hand, for the vulcanizates, the vulcanization was carried out around an optimum vulcanization temperature of 160°C . Thus, a high level of coupling between diene unit in SBR and sulfur in TESPT might be achieved around the silica particles when vulcanization proceeded in the rubber matrix. These suggest that C—S—C and/or C—S—S—C linkages formed by the coupling agent and SBR around the

silica particle exist in both U-TESPT and V-TESPT, and the concentration of the linkages is higher for V-TESPT than for U-TESPT. The mobility of rubber molecules around silica might be constrained compared with that in the rubber matrix due to the development of chemical bonding between SBR and silica through the TESPT.³ At a given strain, the stress for highly strained SBR molecules is larger than that for unstained molecules. In addition, the binding energy for C—S—C and C—S—S—C linkages is lower than that for C—C one.¹¹ From these results and discussion, it is inferred that the radicals produced by the low mechanical energy ($< 0.5 \text{ J/cm}^3$) are responsible for the breakdown of carbon-sulfur linkages. In this case, the ESR spectrum with the g -value of 2.004 can be assigned to carbon and sulfidic radicals. It is reported that sulfidic free radicals show an ESR spectra with the g -value of 2.02.⁸ In this work, however, we could not observe the corresponding resonance line. The vulcanization mechanism for rubber-sulfur-accelerator systems is not simple.^{9,10} In this work, we used the combination of *N*-cyclohexyl-2-benzothiazyl sulfonamide (Cz) and diphenyl guanidine (DPG) as accelerators instead of tetramethylthiuram disulfide (TMTD). We observed an ESR signal with the g -value of 2.003 when the Cz was heated up to 100°C . On the other hand, TMTD itself showed an ESR signal with the g -value of 2.02 at 100°C (data not shown). At present we have no direct information to draw the conclusion that the sulfidic radicals contribute to the ESR spectra for the vulcanized samples. However, it is true that the breakdown of the carbon-sulfur linkages was induced by the low mechanical energy less than 0.5 J/cm^3 (U-TESPT) which showed the ESR signal with the g -value of 2.004. This consideration is also supported by the fact that at a larger mechanical energy, the ΔC_R at a given E is larger for vulcanizates

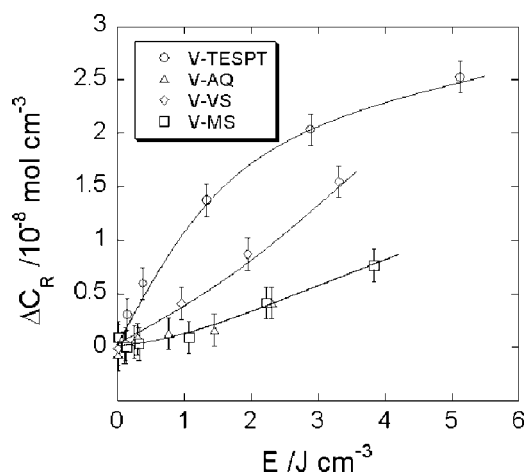


Figure 8 Relation between the mechanical energy (E) and ΔC_R for the vulcanizates.

than for unvulcanizates, since large amounts of C—S linkages exist in the vulcanizates.

The second interesting fact is that the ΔC_R for the U-TESPT showed a stepwise increase with the increase of E , however, the V-TESPT showed a continuous increase of ΔC_R with E . As discussed, the C—S linkages are formed around the silica particles for both unvulcanized (U-TESPT) and vulcanized (V-TESPT) samples, further, the C—S linkages are easily broken by a small mechanical energy less than 0.5 J/cm^3 . However, the C—S linkages are nothing in the rubber matrix of U-TESPT although the V-TESPT has large amounts of C—S linkages in the rubber matrix. At a larger E , the C—C linkages in SBR might be broken, however, the amount is quite small, because the increase of ΔC_R at a larger E is small for the unvulcanizates. On the other hand, for the vulcanizates, both C—S and C—C linkages in the rubber matrix are broken by the larger E . As a result, the radical concentration for the V-TESPT increased continuously with increasing the mechanical energy.

The third is that the ΔC_R for the V-VS was larger than that for the V-MS although the difference was negligible for the unvulcanized state. The VS has chemically active vinyl groups. During the vulcanization process the vinyl groups can react with sulfur, and simultaneously diene groups in SBR react with sulfur. In fact, the swollen tests revealed that the crosslink density for V-VS was about 5% larger than that for V-MS. In V-VS, the C—S linkages which are broken by a relatively small mechanical energy are formed around silica particles. However, the amounts might not be large enough to increase the tensile stress because the stress–strain behavior of V-VS was similar to that for V-MS. This is a reason why the V-VS showed a relative large value of ΔC_R compared with V-MS.

CONCLUSIONS

Silica-filled SBR unvulcanizates and their vulcanizates with different rubber/filler interactions were prepared by using several kinds of coupling agents.

Based on the results of tensile tests and ESR measurements, the following conclusions were derived:

1. The ESR spectra with the g -value of 2.004 are responsible for both breakdowns of the C—C linkages in SBR and carbon–sulfur linkages between TESPT and SBR as well as SBR and sulfur.
2. At room temperature, more than 0.5 J/cm^3 of mechanical energy seems to be necessary to break the C—C linkages in SBR.
3. However, the carbon–sulfur linkages around silica particles were broken by the small mechanical energy less than 0.5 J/cm^3 .
4. The minimum energy necessary to break the carbon–sulfur linkages seems to depend on the mobility of SBR molecules. With increasing the mechanical energy, the linkages around the highly constrained SBR molecules which exist around silica particles break first, and then the breakdown occurs in the highly mobile SBR phase which exists in the rubber matrix.

References

1. Brennan, J. J.; Jermyn, T. E. *Rubber Chem Technol* 1967, 40, 817.
2. Suzuki, N.; Ito, M.; Yatsuyanagi, F. *Polymer* 2005, 86, 1622.
3. Suzuki, N.; Ito, M. *J Soft Mater* 2005, 1, 1.
4. Mead, W. T.; Porter, R. S.; Reed, P. E. *Macromolecules* 1978, 11, 56.
5. Carstensen, P. *Makromol Chem* 1970, 135, 219.
6. Carstensen, P. *Makromol Chem* 1971, 142, 131.
7. Ohonishi, S.; Ikeda, Y.; Nitta, S. *J Polym Sci* 1960, 41, 503.
8. Gardner, D. M.; Frankel, G. F. *J Am Chem Soc* 1956, 78, 3279.
9. Coleman, M. M.; Shelton, J. R.; Koenig, J. L. *Rubber Chem Technol* 1973, 46, 957.
10. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 45, 563.
11. Ossefort, Z. T. *Rubber World* 1959, 140, 69.
12. Goerl, U.; Hunsche, A.; Mueller, A.; Koban, H. G. *Rubber Chem Technol* 1997, 70, 608.
13. Suzuki, N.; Yatsuyanagi, F.; Ito, M.; Kaidou, H. *J Appl Polym Sci* 2002, 86, 1622.
14. Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. *Polymer* 2001, 42, 9523.
15. Dannenberg, E. M. *Rubber Chem Technol* 1986, 59, 512.
16. Lin, C. J.; Hergenrother, W. L.; Alexanian, E.; Bohm, G. G. A. *Rubber Chem Technol* 2002, 75, 865.