

# Effects of rubber/filler interactions on deformation behavior of silica filled SBR systems

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## Abstract

Effect of rubber/filler interactions on the stress–strain behavior for silica filled styrene-butadiene rubber (SBR) vulcanizates were studied in relation to the chain scissions of rubber molecules during deformation. The rubber/filler interactions were controlled by the modification of silica surface using several kinds of silane coupling agents. Information on the chain scission was obtained by the electron spin resonance (ESR) measurements. The combination of ESR results and stress–strain data revealed that, at a given strain, the tensile stress increased with increasing the interfacial interactions between rubber molecules and silica surface, and simultaneously the chain scission became remarkable. Further, the degree of chain scission was closely related to the mechanical energy applied to the vulcanizates. The cyclic tests of stress–strain measurements suggested that the chain scissions contributed to the Mullins effect.

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**Keywords:** Styrene-butadiene rubber; Silica; Interfacial bonding

## 1. Introduction

It is well known that the mechanical properties of crosslinked rubber systems are enhanced by the incorporation of particulate fillers, such as carbon black and silica [1–5]. Further, such reinforcements are related to the secondary structure of filler particles (agglomerate) [6–8] and the rubber/filler interactions [9–11]. It is generally accepted that the tensile stress at a relatively large strain (> 100%) is closely related to the rubber/filler interactions. In the case of carbon black filled rubber systems, the rubber/filler interactions can be controlled by the oxidation and graphitization of carbon black surface [10,12,13]. Thus many studies have been devoted to investigate the rubber/filler interactions of carbon black filled rubber systems. Brennan et al. studied the effects of graphitization of carbon black on the stress–strain behavior of carbon black filled styrene-butadiene rubber (SBR), and reported the stress at a

large strain was enhanced by the strong chemical bonding between carbon black surface and rubber molecules [12]. Further, they suggested that the degree of chain scission of rubber molecules increased with the increase of the tensile stress. However, little information has been reported on the direct evidence of chain scission during the tensile deformation of carbon black filled rubber systems.

When rubber molecules are stretched, a carbon radical ( $-C\cdot$ ) is formed by a chain scission of rubber molecules [14–16]. Electron spin resonance (ESR) is a powerful technique to detect the carbon radical formed by the chain scission [17,18]. However, carbon black itself shows an ESR signal arisen from lone electrons in its particle [19,20]. Further, the intensity of ESR signal for carbon black is much stronger than that for the carbon radicals produced by the chain scission of rubber molecules. This suggests the difficulty of quantitative analyses of chain scissions caused by the tensile deformation of carbon black filled rubber systems.

Silica is also known as an effective filler of rubber reinforcement. Since silica does not have any radical and

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lone electrons, it does not show any ESR signals. Thus silica filled rubber systems are suitable for the investigation of chain scission of rubber molecules during the deformation. For silica filled rubber systems, the rubber/filler interactions can be controlled by the introduction of coupling agent [21–23].

In this study, silica filled SBR vulcanizates with different rubber/filler interactions were prepared by using several kinds of coupling agents. Then, the effects of rubber/filler interactions on stress–strain behavior were studied in relation to the chain scissions of rubber molecules by ESR and tensile tests.

## 2. Experimental

### 2.1. Samples

The raw rubber used was a styrene-butadiene rubber (SBR: Nipol SBR 1502,  $M_w = 4.3 \times 10^5$ ,  $T_g = -52$  °C; Nippon Zeon Co., Japan). The filler used was a precipitated silica (Nipsil AQ; Nippon Silica, Japan). Two kinds of coupling agents were used for the surface modification of silica particles. The one is a mono-functional decyltrimethoxy-silane (DS) and the other is a bi-functional bis-(triethoxysilylpropyl)-tetrasulfide (TESPT). The chemical structures of them are listed in Table 1. The reactivity of coupling agents with silanol groups on silica particles depends on the moisture content of silica particles [21,24]. In this study, as-received silica was dried at 120 °C under a reduced pressure for 12 h to control the moisture content. The moisture content of dried silica was about 2.0 wt% which was determined by thermal gravimetric analyzer. We confirmed that the moisture content of 2.0 wt% was enough to react the coupling agent with silanol groups [24].

Various kinds of composites were prepared by a mechanical mixing. The compositions of them are listed in Table 2. The conditions for the mechanical mixing were as follows; SBR was put into a Banbury mixer (Laboplastomill 50MR; Toyo Seiki, Japan) and masticated under 60 rpm at 60 °C for 1 min, then dried silica and coupling agent were mixed with masticated SBR under 60 rpm at 100 °C for 1 min. Next, zinc oxide, stearic acid and antioxidant were mixed with SBR/silica composites at 100 °C for 2 min. Finally, the masterbatch was mixed with sulfur and accelerator under 60 rpm at 60 °C for 3 min. The fill

factor of the composites at final stage was set to be 60%. The unvulcanized composites prepared by the mechanical mixing were seated on a roll mill followed by a vulcanization at 160 °C for 20 min under a pressure of 400 kg/cm<sup>2</sup>.

To prepare the samples for transmission electron microscopy (TEM) observations, the vulcanized composites were cured again in melted sulfur (~125 °C) for 36 h. The hardened compounds were easily cut into ultrathin films (< 100 nm) at room temperature by microtoming. The thin films were stuck onto the TEM grids for TEM observations.

TEM observations were also carried out for bound rubbers in unvulcanized composites. The conditions for the sample preparation were as follows; 2 g of SBR was dissolved in 150 ml of benzene. Then, the solution was mixed with 1 g of the dried silica dispersed in 100 ml of benzene and gently stirred at room temperature for 3 h. The mixture of SBR and silica was dropped on the TEM grid coated by carbon. The compound was obtained by removing the solvent from the mixture on the TEM grid at room temperature under a reduced pressure for 24 h. The compound on the TEM grid was immersed in a large amount of toluene and extraction was carried out at room temperature for 144 h. The remains on the TEM grid were the bound rubber and silica, which were used for TEM observations.

### 2.2. Measurements

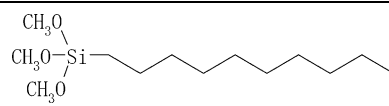
The crosslink densities of vulcanized samples ( $\nu_c$ ) were determined by the swelling method at 25 °C by using toluene.

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<sup>-1</sup>.

The ESR spectra were obtained by using an ESR spectroscopy (ES-FA200, JEOL, Japan) at a resonance frequency of 9.2 GHz. The samples for ESR measurements were prepared by the following procedure; the vulcanized sheets were cut into 1 mm × 2 mm × 30 mm. The samples were stretched by a tensile tester at room temperature up to a desired strain (IS: 10–200%) followed by an immediate ESR measurement at -100 °C. The radical concentration in the samples was obtained from a double-integration of the first derivative curves of ESR signals by using an aqueous solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl

Table 1  
Chemical structure of coupling agent

Decyltrimethoxysilane (DS)



Bis-(3-triethoxysilylpropyl)-tetrasulfide (TESPT)

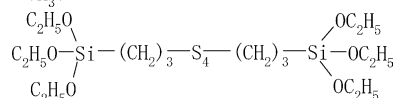


Table 2  
Compositions of silica filled SBR systems

Sample code	UM-1	UM-2	DM	TM	UF
SBR	100	100	100	100	100
Silica	50	50	50	50	–
DS	–	–	5	–	–
TESPT	–	–	–	5	–
Zinc oxide	3	3	3	3	3
Stearic acid	2	2	2	2	2
Anti-oxidant 6C <sup>a</sup>	1	1	1	1	1
Accelerator CZ <sup>b</sup>	1	1	1	1	1
Accelerator DPG <sup>c</sup>	1.5	1.5	1.5	1.5	1.5
Sulfur	1.7	2.9	1.7	1.7	1.7

<sup>a</sup> *N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine.

<sup>b</sup> *N*-cyclohexyl-2-benzothiazyl-sulfenamide.

<sup>c</sup> Diphenyl guanidine.

radical (TEMPOL) as an external standard. The *g*-value and line width were determined by using the third and fourth signals of Mn<sup>2+</sup> marker.

TEM observations were carried out by using transmission electron microscope (TEM: Hitachi H-9000 NAR Type; Hitachi) with an accelerated voltage of 200 kV.

### 3. Results and discussion

#### 3.1. The stress–strain behavior

It is well known that the stress–strain curves for silica filled rubber systems are affected by the crosslink density of rubber matrix [22,25], the size of agglomerates formed by the silica [24,26] and rubber/silica interactions [4,22]. These effects can be controlled by the contents of curing agents, the number of silanol groups on silica particles and the introduction of coupling agent.

The crosslink densities ( $\nu_e$ ) of surface modified silica filled vulcanizates (DM and TM) and unmodified silica filled vulcanizates with different sulfur content (UM-1 and UM-2) are shown in Table 3. The comparison of the data for the UM-1 and UM-2 revealed that the higher the sulfur content, the higher the  $\nu_e$  that could be obtained. It is also seen that the  $\nu_e$  was not affected by the introduction of mono-functional coupling agent (UM-1 vs. DM). The  $\nu_e$  for the TM was the highest in the samples. As shown in Table 1, the TESPT involves four sulfur atoms in one molecule which react with diene unit of SBR [22,27], leading to the increase of  $\nu_e$ .

Fig. 1 shows the stress–strain curves of the UM-1, UM-2, DM and TM. It is seen that the initial slope of the stress–strain curves were affected by the crosslink density and the

sort of coupling agents. The initial slope of stress–strain curves increased with the increase of the  $\nu_e$ , in accordance with our previous report [22]. The initial slope decreased by the introduction of coupling agents even for the TM which had the highest  $\nu_e$ . When the coupling agents were introduced on silica particles, a hydrophilic character of the particle changed into a hydrophobic one, which reduced the filler–filler interactions via reduced agglomerate size formed by silica particles, leading to the decrease of tensile modulus which is known as a Payne effects [24,27]. Fig. 2 shows TEM photographs of surface modified and unmodified silica filled vulcanizates (DM, TM and UM-1). It is clearly seen the reduction of agglomerate size by the introduction of coupling agents. This confirms that the decrease of initial slope of stress–strain curves for the DM and TM is caused by the decrease of the size of agglomerate.

At about 10% of strain, the three samples (UM-1, UM-2 and TM) showed a similar tensile stress although these samples had different  $\nu_e$ . However, the stress for the DM was quite small compared with the UM-1, UM-2 and TM. We report the effects of chemical structure of coupling agent on the stress–strain behavior of surface modified silica filled rubber composites [24]. In the case of mono-functional coupling agents, the tensile stress at a larger strain decreased with the increase of the length of alkyl chains in the coupling agents. The results suggested that the mono-functional coupling agents with long alkyl units worked as a plasticizer of rubber molecules. A similar explanation can be made for the stress–strain behavior of the DM.

At a larger strain (>20%), the tensile stress of the TM steadily increased with increasing the strain, similar to the case of carbon black filled vulcanizates [10,12]. On the other hand, the stress for the DM almost leveled off at a larger strain. A primary reaction for the difference might be

Table 3  
Crosslink densities of silica filled SBR systems

	UM-1	UM-2	DM	TM
$\nu_e \times 10^{-4} \text{ mol cm}^{-3}$	2.41	4.34	2.36	5.66

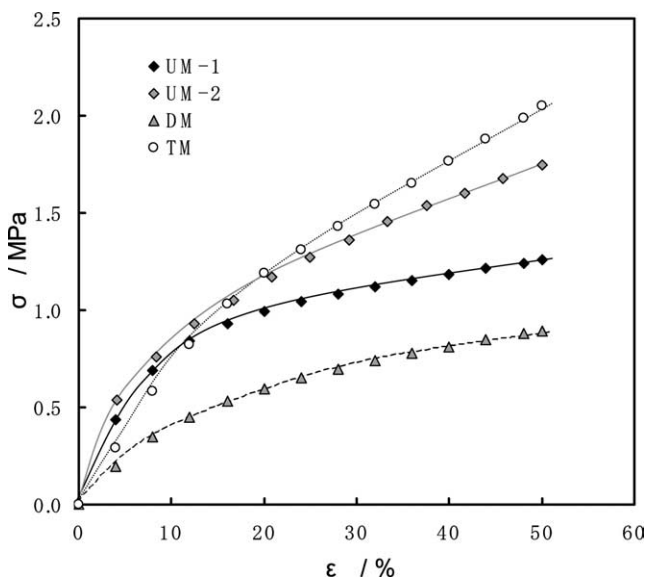


Fig. 1. Stress–strain curves for surface modified and unmodified silica filled vulcanizates.

attributed to the difference of  $\nu_c$ . In addition, we must take the interfacial bonding between silica and rubber molecules into consideration, since the TM was prepared by using bi-functional coupling agent (TESPT). It is well known that the strong interfacial bondings between carbon black and rubber matrix enhance the tensile stress at a larger strain [10,12,27]. The evidence of the interfacial bonding in the TM was also obtained by TEM observations. The samples for TEM observations were prepared by the solution mixing method as described in Section 2. Fig. 3 shows the TEM photographs for bound rubbers from surface modified silica particles. For the DM a clear boundary was recognized between each silica particle and agglomerate. In this case,

the bound rubber exists within the agglomerates [28,29]. On the other hand, for the TM, the boundary was obscure. This is due to the existence of rubber molecules on silica particles. As seen in Table 1, ethoxyl groups of TESPT react with silanol groups on silica [21,22,27]. In addition, sulfur atoms of TESPT couple with diene groups of SBR [21,22,27]. Such a chemical structure of TESPT produced a strong chemical bonding between SBR and silica, which enhanced the tensile stress at a larger strain.

### 3.2. ESR results

The unfilled vulcanizates (UF) showed a broad ESR absorption curve, even in the unstretched state. The signal intensity gradually decreased with increasing the storage time of the sample without changing the  $g$ -value and the line width at the maximum slope ( $\Delta H_{msl}$ ) and almost leveled off at one week after the sample preparation. The  $g$ -value and the  $\Delta H_{msl}$  for the absorption curve were 2.004 and 1.5 mT, respectively. The absorption curve for the sample of which storage time is one week is shown in Fig. 4(a). In unfilled SBR vulcanizates by sulfur, we can expect two kinds of radicals. The one is a sulfur radical ( $-S\cdot$ ), and the other is a carbon radical ( $-C\cdot$ ) with a  $g$ -value around 2.004. The  $g$ -value of sulfur radical is estimated to be 2.05 [30,31], which is different from the observed  $g$ -value. This means that the absorption curve obtained from the unfilled vulcanizates can be assigned to the carbon radicals. In this study, all samples were prepared by a mechanical mixing using a Banbury mixer. During the mechanical mixing, a large shear force applied to the samples, leading to the chain scission [32–34]. In SBR, the bond energy between  $sp^3$  carbon of butadiene unit ( $=CH-CH_2-CH_2-CH=$ ) is the lowest. Thus, the allyl radical ( $-C=C-C\cdot$ ) is likely to be formed by

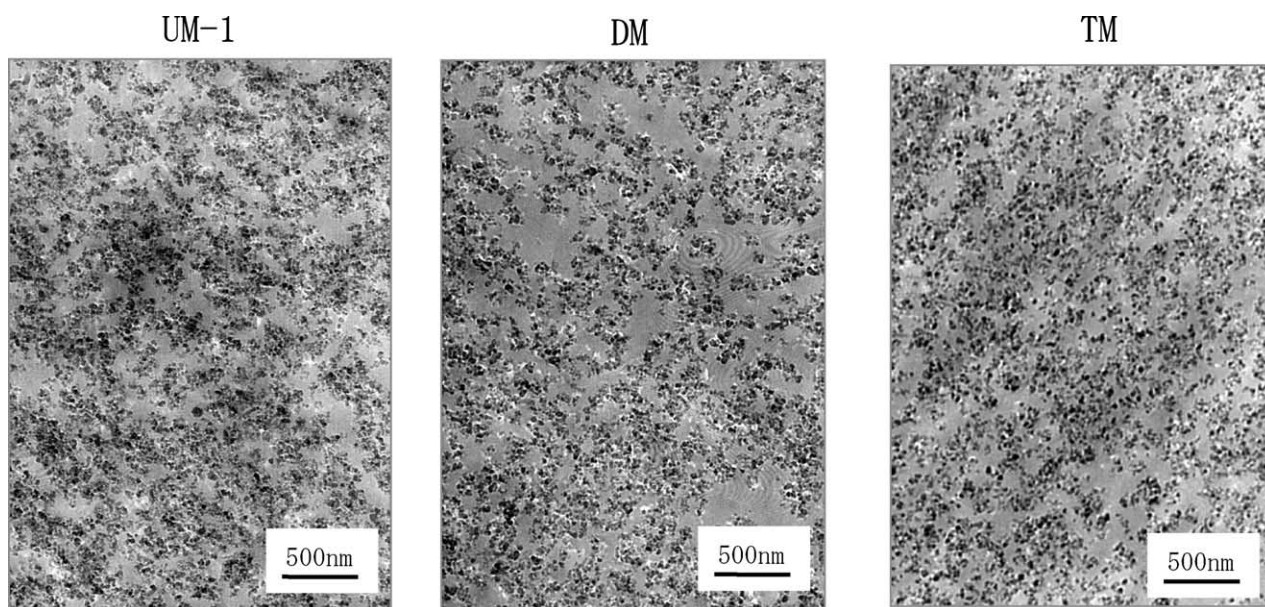


Fig. 2. TEM photographs of silica filled vulcanizates.



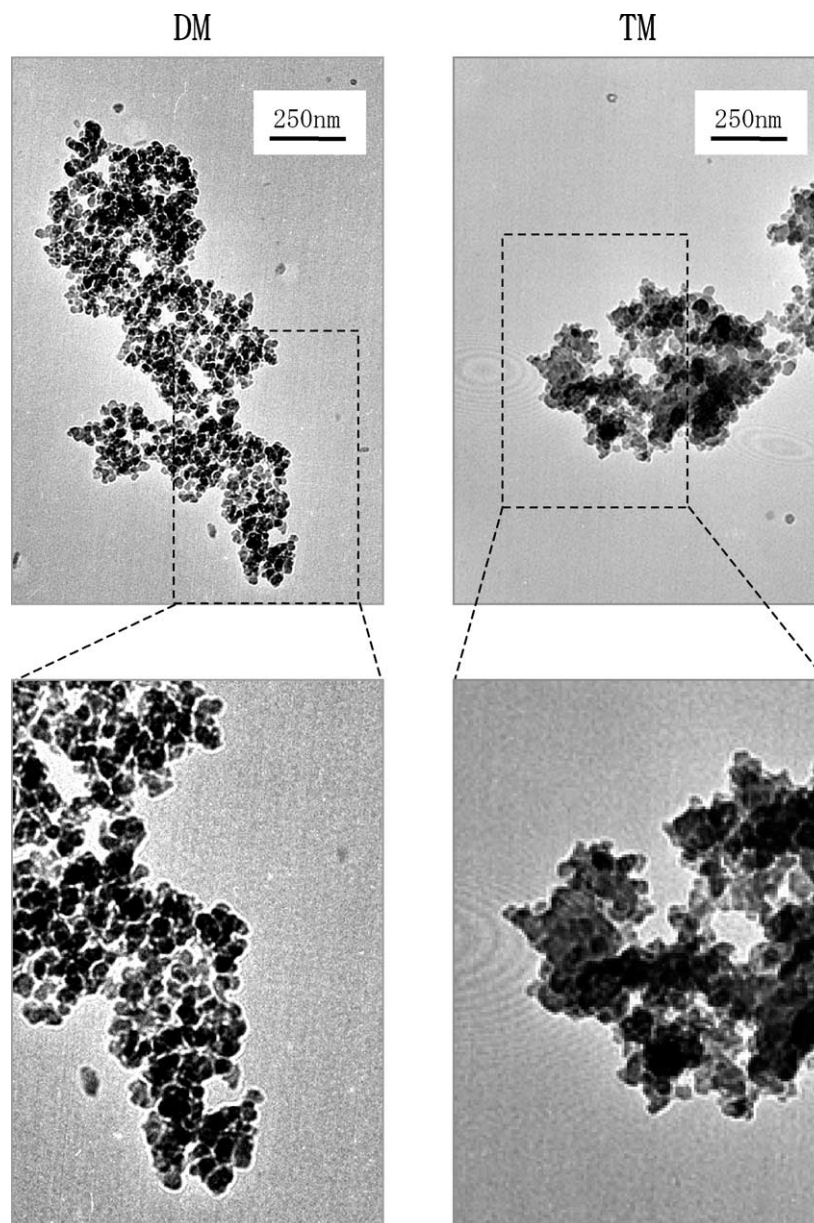


Fig. 3. TEM photographs of bound rubber from surface modified silica filled composites prepared by solution mixing method.

the chain scission. If so, the ESR signal from allyl radical should show a clear hyperfine splitting [16,35,36]. Carstensen reported that the allyl radicals in polybutadiene and polyisoprene formed at liquid nitrogen temperature were easily transformed into polyenyl radical  $-(C=C)_n-C\cdot$  during heating [35,36]. In addition, the  $g$ -value and  $\Delta H_{msl}$  for polyenyl radical are reported to be 2.004 and 1.6 mT [35, 37]. From these results, it is inferred that the absorption shown in Fig. 4(a) is assigned to the polyenyl radicals. The lifetime of allyl radicals depends on the temperature. The allyl radicals are quickly transformed into polyenyl radicals even at low temperature of  $-100\text{ }^\circ\text{C}$  [35,36]. Thus, the allyl radicals formed by mechanical mixing might quickly transform into polyenyl radicals during sample preparation.

The intensity of ESR signals for unfilled SBR

vulcanizates increased with increasing the strain (initial strain: IS, (Fig. 4(b) and (c)) without changing the  $g$ -value and  $\Delta H_{msl}$ . This suggests that the chain scissions occur during the stretching, resulting in the formation of polyenyl radicals. Since the samples were stretched at room temperature, allyl radicals formed by the chain scissions were quickly transformed into polyenyl radicals.

The first derivative ESR curves for unmodified silica filled SBR vulcanizates (UM-1) with different initial strains are shown in Fig. 5. The vulcanizates showed a broad absorption curve with the  $g$ -value of 2.004 and the  $\Delta H_{msl}$  of 1.5 mT. Further, the signal intensity increased with increasing the initial strain (IS). The  $g$ -value and  $\Delta H_{msl}$  were independent of the IS. These results were qualitatively similar to those for unfilled vulcanizates (UF) shown in

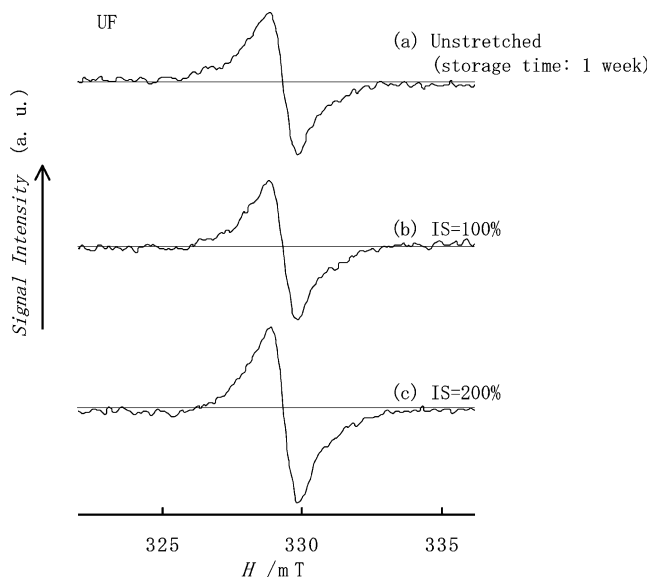


Fig. 4. ESR spectra for unfilled SBR vulcanizates (UF) with different ISs.

Fig. 4. However, the difference was that the signal intensity for unstretched samples was significantly larger for silica filled vulcanizates than for unfilled ones, although this was not recognized in Figs. 4 and 5 due to a different measurement condition such as a different amplitude of spectrometer. For the preparation of silica filled samples, the mixing torque was considerably higher than that for unfilled samples. Thus, the difference of mixing torque might induce the difference in the degree of chain scission, resulting in the difference of signal intensity between filled and unfilled samples.

The number of radicals per unit volume of vulcanizates ( $C_R$ ) was calculated by using ESR spectra as a function of

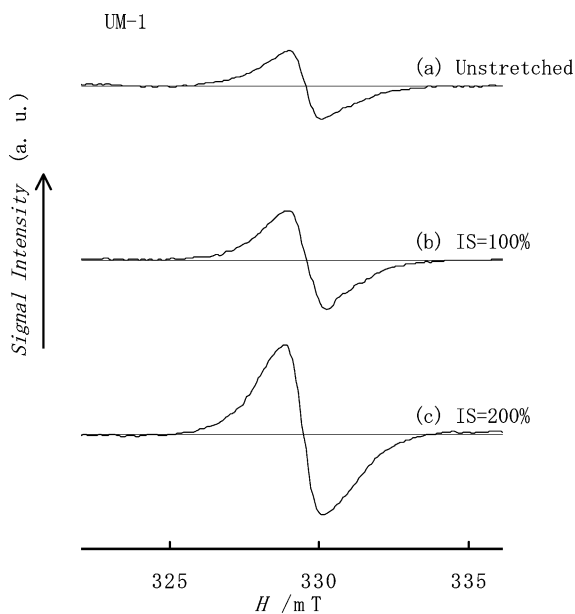


Fig. 5. ESR spectra for unmodified silica filled SBR vulcanizates (UM-1) with different ISs.

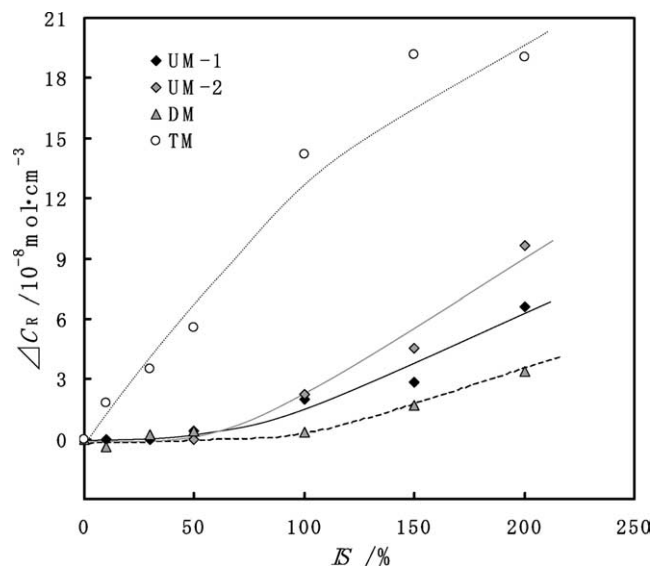


Fig. 6. Relation between the IS and the  $\Delta C_R$  for surface modified and unmodified silica filled SBR vulcanizates.

IS. Then the difference of the  $C_R$  between stretched and unstretched vulcanizates ( $\Delta C_R$ ) was calculated. Fig. 6 shows the relation between the IS and the  $\Delta C_R$  for the surface modified and unmodified silica filled vulcanizates. For the vulcanizates without interfacial bonding (UM-1, UM-2 and DM),  $\Delta C_R$  was almost zero up to 100% of IS. Above 100% of IS,  $\Delta C_R$  increased slightly with increasing the IS. Such  $\Delta C_R \sim IS$  relations for the UM-1, UM-2 and DM were quite similar to that for the UF (data not shown). At a given strain, the higher the crosslink density, the larger the  $\Delta C_R$ . Further,  $\Delta C_R$  for the DM was always the smallest. As stated, the DS works as a plasticizer due to its long alkyl chain. This might prevent the chain scission during tensile deformation. These results suggest that the increase of  $\Delta C_R$  with the IS above 100% of IS is caused by the chain scissions in the rubber matrix.

The  $\Delta C_R$  for the vulcanizate with interfacial bonding (TM) increased steadily with increasing the IS even at a small IS. These results indicate that the chain scission upon a stain is closely related to the interfacial bonding between rubber molecules and silica surface and suggest that the chain scissions occur around the fillers.

The  $\Delta C_R$  corresponds to the total number of the radicals produced during the deformation. Therefore, the  $\Delta C_R$  is likely dependent on the mechanical energy applied to the samples during the deformation rather than the tensile stress and/or strain. Thus we plotted the  $\Delta C_R$  in Fig. 7 as a function of mechanical energy ( $E$ ) calculated from the stress–strain curve. It is seen that the vulcanizates without interfacial bonding (UM-1, UM-2 and DM) show a similar relation between  $E$  and  $\Delta C_R$  even for the samples with different crosslink densities and different agglomerate sizes. It is interesting that the  $\Delta C_R$  for them is almost zero up to an  $E$  value of  $1 \text{ J cm}^{-3}$ . Above an  $E$  value of  $1 \text{ J cm}^{-3}$ ,  $\Delta C_R$  increased slightly with increasing the  $E$ . This indicates that

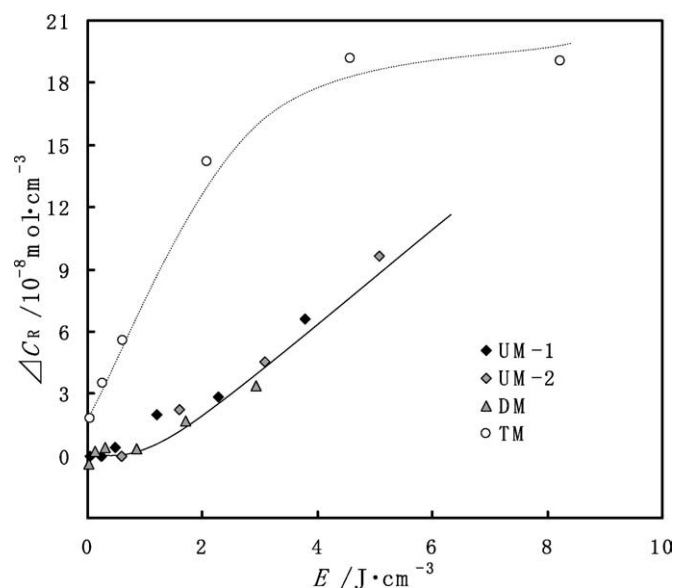


Fig. 7. The relation between the mechanical energy applied to the samples during tensile deformation ( $E$ ) and the  $\Delta C_R$  for surface modified and unmodified silica filled SBR vulcanizates.

the chain scission occurs when the mechanical energy applied to rubber molecules exceeds a certain percolation threshold. On the other hand, the  $\Delta C_R$  for the vulcanizate with interfacial bonding (TM) increased steadily with increasing the  $E$  even at a small  $E$ . Further,  $\Delta C_R$  value at a given  $E$  was much larger than that for the other samples. This means that, at a given  $E$ , the chain scission is enhanced by the introduction of interfacial bonding.

When the rubber matrix with rigid spheres is stretched, a stress concentration is built up around the spheres [38,39]. For the samples without chemical bonding between rubber matrix and the rigid sphere, the dewetting occurs at the interface between rubber matrix and the sphere during the stretching [40]. This is the case for the UM-1, UM-2 and DM. On the other hand, in the rubber matrix, which is chemically bonded to the particle (TM), small cavitations are formed near the particle by the stretching. That is, the interfacial bonding suppresses the dewetting at the interface, and enhances the build up of large stress concentration. This mechanism might lead to the increase of tensile stress, resulting in the enhancement of chain scission for the vulcanizate with interfacial bonding.

For the TM, the  $\Delta C_R$  should be almost zero up to a percolation threshold, if the rubber molecules around the silica particle form random coils, disagreement with the experimental result. This suggests that the build up of stress concentration is not enough to explain the result shown in Fig. 7. Ahagon suggests that the chain scission by mechanical deformation likely occurs around the fillers [34]. However, no direct evidence of the chain scission around the filler particle has been reported. It is well known that highly constrained rubber molecules exist around the filler particle, such as silica and carbon black [9,24,26]. The conformation of highly constrained molecules might be

rather extended state than the random coil. If so, rubber molecules around silica particle might be rather extended state, and chain scissions easily happen at a small strain. Therefore, steadily increase of the  $\Delta C_R$  at low  $E$  region is closely related the chain conformation around the fillers. For the vulcanizates without interfacial bonding, the chain scission might occur in the rubber matrix. When some rubber molecules are stretched up to an ultimate elongation state, the chain scission starts to occur.

### 3.3. Stress softening effect

As stated in a previous section, the destruction of rubber matrix of silica filled SBR vulcanizates by the chain scission of rubber molecules was detected by ESR measurements. Such destruction might influence on the tensile stress at the second stage of stretching during cyclic tensile tests. For carbon black filled vulcanizates, it is known that the tensile stress at the second stretching is always lower than that for the first stretching [25,41]. This phenomenon is called Mullins effect, and well recognized to be caused by the following mechanisms:

- Physical disentanglement of rubber molecules [42,43]
- Decrease in the interactions between rubber molecules and carbon black surface [44,45]
- Chain scission of rubber molecules [42]

These might be applicable to the silica filled vulcanizates. In order to understand the details, the effects of  $\Delta C_R$  on the stress–strain curves at cyclic tests were studied. As stated, both breakdown of agglomerates and chain scission occurred during tensile deformation of silica filled vulcanizate. Both of them might be responsible for the Mullins

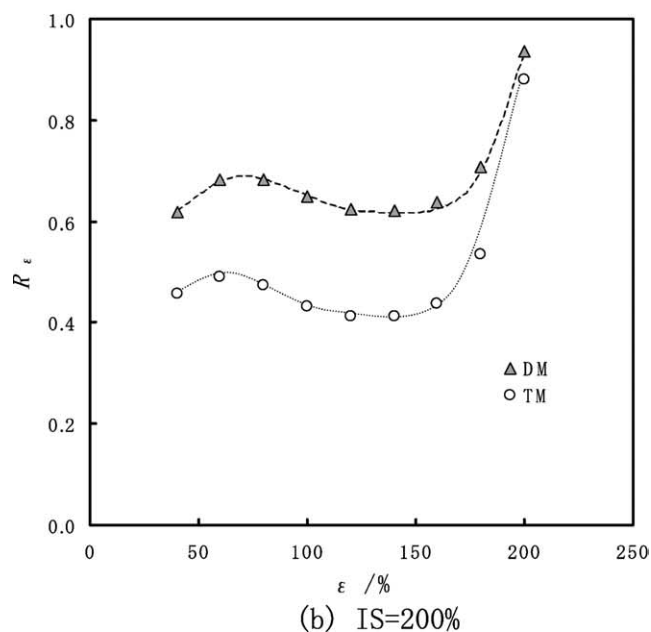
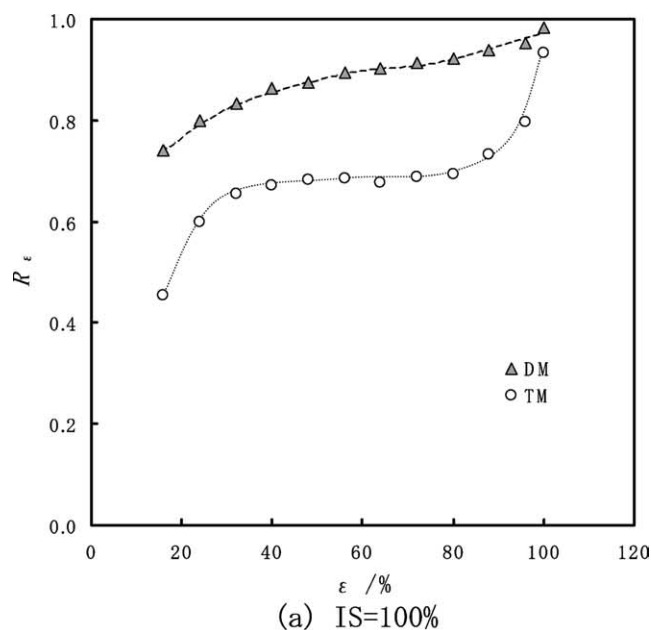


Fig. 8. Retention of stress ( $R_\epsilon$ ) as a function of strain at second stretching for surface modified silica filled composites with different ISs.

effect [42,45]. However, we can minimize the effect of breakdown of agglomerate on the Mullins effect by using the samples with smaller agglomerate size. The effects of chain scission on the Mullins effects were investigated by using the vulcanizates with small agglomerates (DM and TM). The samples were stretched up to a desired IS (first stretching) followed by a release of stress. Then, the samples were stretched again (second stretching). The ratio of the tensile stress at the first and the second stretching at a given strain (stress retention:  $R_\epsilon$ ) was calculated. Fig. 8 shows the relation between the  $R_\epsilon$  and strain at the second stretching for the samples with 100 and 200% of IS. It is

clearly seen that the  $R_\epsilon$ s for both the DM and TM were always smaller than 1.0. This means that both samples showed the Mullins effect. The Mullins effect is more prominent in the TM than in the DM. These results suggest that the Mullins effect is related to the  $\Delta C_R$ . Since the ESR measurements were carried out at  $-100^\circ\text{C}$  immediately after the first stretching, the decay of spin number might be quite small. Thus it is suggested that  $\Delta C_R$  might correspond to the number of breaking points of molecular chain produced by the first stretching. Such breaking points can not have a role to transmit the stress on draw at the second stretching, leading to the decrease of the stress on draw. This consideration is essentially similar to the model introduced by Bueche who suggested that the Mullins effect was mainly due to the breakdown of rubber/carbon black attachment [44].

#### 4. Conclusions

Silica filled SBR vulcanizates with different rubber/filler interactions were prepared by using the surface modified silicas by several kinds of coupling agents. Based on the tensile tests and ESR spectra, effects of the rubber/filler interactions on stress-strain behavior for the vulcanizates were investigated in relation to the chain scissions during the uniaxial elongation. The following conclusions were derived from experimental results:

1. The quantitative analyses of chain scission during uniaxial stretching of filled vulcanizates could be done by the utilization of silica instead of carbon black.
2. ESR results suggested that the degree of chain scission in silica filled SBR vulcanizates increased with increasing the mechanical energy applied to the samples during deformation.
3. The chemical bonding between silica and rubber molecules enhanced the chain scission during the tensile deformation of filled SBR vulcanizates.
4. The chain scission might contribute to the Mullins effect.

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