

Influence of Polymer–Filler Interactions on Retraction Behaviors of Natural Rubber Vulcanizates Reinforced with Silica and Carbon Black

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ABSTRACT: In general, silica-filled rubber compounds contain a silane coupling agent to improve the filler dispersion and polymer–filler interactions. The silane coupling agent modifies the silica surface and makes crosslinks between the rubber and the silica. Influence of the modification of silica on the retraction behaviors of natural rubber (NR) vulcanizates reinforced with silica and carbon black was studied. Variation of the retraction behaviors of NR vulcanizates with filler composition was also investigated. The vulcanizates containing the silane coupling agent were recovered faster than those without the silane coupling agent. The recovery difference between the vulcanizates without and with the silane coupling agent increased with increased

silica content. For the vulcanizates containing the silane coupling agent, the retraction behaviors were nearly the same, irrespective of filler composition. But, for the vulcanizates without the silane coupling agent, the vulcanizate was recovered more and more slowly as the silica content increased. The experimental results are explained with the polymer–filler interactions, modification of silica surface, and formation of crosslinks between silica and rubber. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 691–696, 2006

Key words: rubber; silicas; vulcanization; retraction behaviors; silane coupling agent

INTRODUCTION

Carbon black and silica are the most popular reinforcing agents in rubber compounds.^{1–7} Silica has a number of hydroxyl groups (silanol, Si–OH), which results in strong filler–filler interactions and adsorption of polar materials by hydrogen bonds.^{6,8} Since intermolecular hydrogen bonds between silanol groups on the silica surface are very strong, it can aggregate tightly.^{7,9} This property can cause a poor dispersion of silica in a rubber compound. In general, a silane coupling agent such as bis(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve filler dispersion and to prevent adsorption of curatives on the silica surface.^{10,11} TESPT reacts with silanol on the surface of silica and a siloxane bond is formed. The silane molecule bound to the silica surface can react with a rubber molecule to form a crosslink between silica and rubber.

Rubber materials have been widely used for vibration damping. The low glass transition temperature (T_g) property leads to use of vibration damping at low temperature. A rubber material has a recovery prop-

erty that allows it to return to its original shape from deformation.^{12–14} Hergenrother and Doshak¹⁵ measured the tensile retraction of SBR compounds filled with different carbon blacks. Yun and Kim¹⁶ studied the influence of filler content, curative, and plasticizer on the retraction behaviors.

Since a silane coupling agent modifies the silica surface and makes crosslinks between silica and rubber, it affects polymer–filler interactions and the mobility of rubber chains in a rubber vulcanizate. Retraction behaviors can be also affected by treatment with the coupling agent. In the present work, we studied the influence of polymer–filler interactions on the retraction behaviors of rubber vulcanizates using natural rubber (NR) vulcanizates reinforced with silica and carbon black. In general, polymer–filler interactions of silica-filled rubber compounds are improved by treatment with a silane coupling agent. Variation of the retraction behaviors of NR vulcanizates with filler composition of carbon black and silica was also investigated.

EXPERIMENTAL

NR compounds reinforced with silica and carbon black were made of NR (SMR CV60), silica (Z175), carbon black (N220), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Si69 from Degussa (TESPT) was

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TABLE I
Formulations (phr)

Compound No.	W1	W2	W3	W4	C1	C2	C3	C4
SMR CV60	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N220	40.0	30.0	20.0	10.0	40.0	30.0	20.0	10.0
Z175	0.0	10.0	20.0	30.0	0.0	10.0	20.0	30.0
Si69	0.0	0.0	0.0	0.0	1.2	1.2	1.2	1.2
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

SMR CV60, standard Malaysian rubber with viscosity of 60 MU; N220, carbon black; Z175, silica; Si69, silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT); HPPD, *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine; TBBS, *N*-*tert*-butyl-2-benzothiazole sulfenamide.

used as a silane coupling agent. The total filler content was 40 phr and the filler compositions were carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr. The compounds without the silane coupling agent (compound Nos. W1–W4) and the compounds containing the silane coupling agent (compound Nos. C1–C4) were prepared. The formulations are given in Table I.

Mixing was performed in a Banbury-type mixer at a rotor speed of 40 and 25 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80°C for MB and FM stages, respectively. The MB compounds were prepared as follows: (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The fillers and silane coupling agent were compounded into the rubber for 2.0 min. (3) The cure activators and antidegradants were mixed for 2.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

The vulcanizates were prepared by curing at 160°C for 30 min. The sample dimension for the temperature retraction (TR) test was 50 mm length, 2 mm width, and 2 mm thickness. The TR test according to the ASTM D1329 with a TR tester ET01 from Elastocon was performed as follows: (1) The sample was strained by 50% and kept in a low-temperature chamber (about -75°C) for 30 min. (2) The elongated sample was released and the temperature was increased at 1°C/min. (3) Variation of the recovery with the temperature was measured. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021). Tan δ of the vulcanizates was measured according to the procedure in ASTM D2231-87 with a Qualimeter Eplexor 150N from Gabo.

RESULTS AND DISCUSSION

The TR test was started at -75°C and finished at the temperature of 90% recovery. Retraction behaviors of

the vulcanizate without the silane coupling agent were compared with those containing the silane coupling agent. Figures 1–4 show the differences in retraction behaviors of the vulcanizates without and containing the silane coupling agent. The vulcanizates begin to recover at -65 to -60°C. The recovery rates slow slightly around -40°C and become notably fast above -10°C. The vulcanizates containing the coupling agent (circles in Figs. 1–4) are recovered faster than those without the coupling agent (squares in Figs. 1–4). The recovery difference between the vulcanizates without and containing the silane coupling agent appears clearly above -60°C. The slopes (from -60 to -20°C) for the vulcanizates containing the silane coupling agent are steeper than those without the silane coupling agent. The slope difference, on the whole, becomes greater as the silica content increases. Let the 10% recovery be R_{10} . For the vulcanizates without the silane coupling agent, the temperatures at R_{10} (T_{10}) are -53.5, -53.3, -50.8, and -52.2°C for the

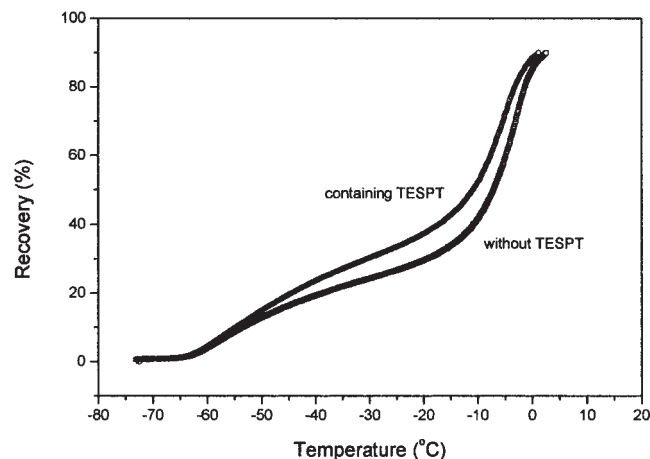


Figure 1 Recovery curves of vulcanizates with filler composition of carbon black/silica = 40/0 phr. Squares and circles indicate the vulcanizates without and containing TESPT, respectively.

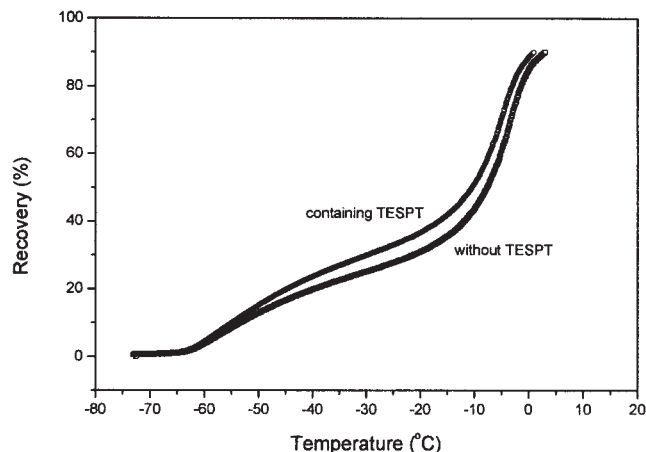


Figure 2 Recovery curves of vulcanizates with filler composition of carbon black/silica = 30/10 phr. Squares and circles indicate the vulcanizates without and containing TESPT, respectively.

vulcanizates with filler compositions of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively. For the vulcanizates containing the silane coupling agent, the T_{10} 's are -54.8 , -54.9 , -54.8 , and -54.7°C , respectively. These values are lower than their glass transition temperatures (T_g). The T_g 's obtained from the rheovibron test are -46 to -50°C . Thus, we can say that the vulcanizates begin to recover at lower temperatures than their T_g 's. The vulcanizates containing the silane coupling agent start to recover faster than those without the silane coupling agent. The vulcanizates containing the silane coupling agent also reach the R_{10} faster than those without the silane coupling agent. The T_{90} 's of the vulcanizates without the silane coupling agent are $+2.6$, $+3.0$, $+6.7$, and $+9.8^\circ\text{C}$ for vulcanizates with filler compositions

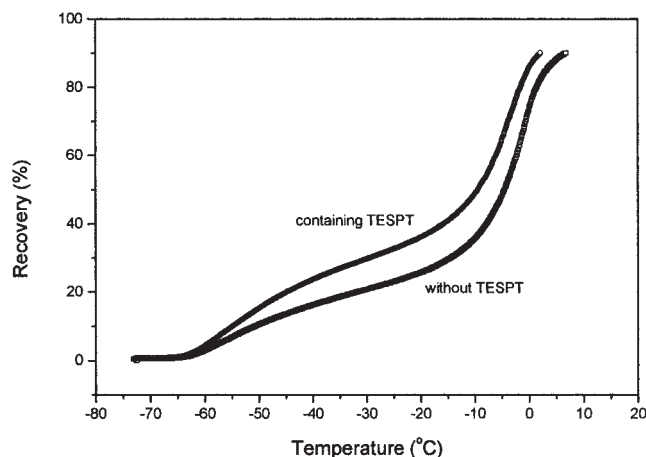


Figure 3 Recovery curves of vulcanizates with filler composition of carbon black/silica = 20/20 phr. Squares and circles indicate the vulcanizates without and containing TESPT, respectively.

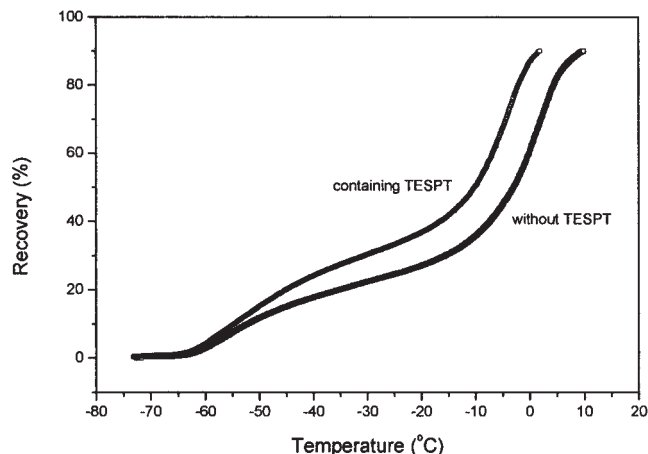


Figure 4 Recovery curves of vulcanizates with filler composition of carbon black/silica = 10/30 phr. Squares and circles indicate the vulcanizates without and containing TESPT, respectively.

of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively. The T_{90} 's of the vulcanizates containing the silane coupling agent are $+1.2$, $+1.0$, $+2.1$, and $+1.9^\circ\text{C}$, respectively.

The faster retraction behaviors of the vulcanizates containing the silane coupling agent can be explained with the stress applied to the elongated sample. Moduli of the vulcanizates containing the silane coupling agent are much higher than those of the vulcanizates without the silane coupling agent, as listed in Table II. The higher moduli of the vulcanizates containing the silane coupling agent are due to the higher crosslink density and formation of crosslinks between the silica and rubber. Crosslinks between the silica and rubber are formed by TESPT, as discussed previously. Crosslink densities of the vulcanizates containing the silane coupling agent are higher than those of the vulcanizates without the silane coupling agent by 7–16%. Delta torque, the difference between the maximum and minimum torque in the rheograph, was used as the crosslink density. Since the torque in the rheograph starts to increase by formation of

TABLE II
Physical Properties of the Vulcanizates

Compound No.	W1	W2	W3	W4	C1	C2	C3	C4
Hardness (Shore A)	58	55	57	54	63	61	57	58
100% Modulus (kg/cm^2)	19.1	17.2	15.7	11.8	26.3	25.1	20.7	16.9
300% Modulus (kg/cm^2)	92.3	81.2	64.7	38.3	124.1	121.9	100.1	74.2
Tensile strength (kg/cm^2)	298.9	250.3	252.9	184.5	295.7	317.3	290.0	252.9
Elongation at break (%)	604	570.2	626.1	647.3	541.2	573.9	578.8	598.9

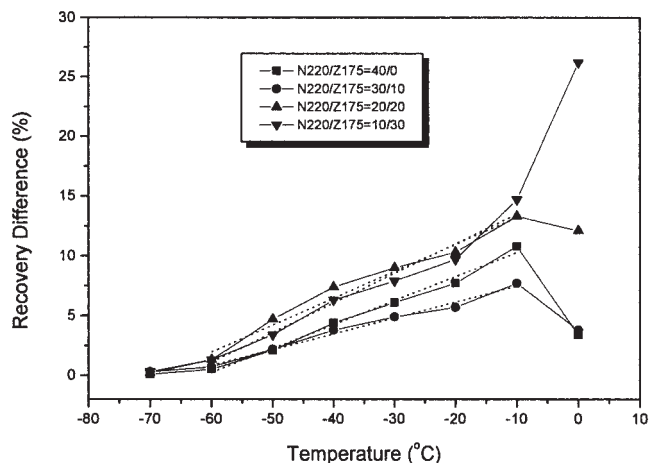


Figure 5 Variation of the recovery difference as a function of temperature. Squares, circles, up-triangles, and down-triangles indicate vulcanizates with filler composition of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively.

crosslinks, the δ torque is very closely related to the crosslink density.^{17,18} Samples were elongated by the same strain rate of 50% but the stresses were applied at different levels. When a sample has higher crosslink density, higher compatibility of rubber with filler, and more crosslinks between rubber and filler, the applied stress will be larger at the same strain rate. The larger stress will lead to faster return to its original form. The vulcanizates containing the silane coupling agent have higher crosslink density, higher compatibility of rubber with filler, and more crosslinks between the rubber and filler than those without silane coupling agent.

The temperature versus the recovery difference (Fig. 5) and the recovery versus the temperature difference (Fig. 6) were plotted to compare the differences of the retraction behaviors in detail. The recovery differences increase continuously below -10°C with increased temperature, irrespective of the filler composition (Fig. 5). The plots of Figure 5 in the range from -60 to -10°C show good linear relations. The curve fitting equations in the range were calculated and are listed in Table III. The level of recovery difference increases with increased silica content when excepting the vulcanizate filled with only carbon black from the four vulcanizates. This may be due to the increased differences in polymer–filler interactions by modification of the silica surface and in the crosslinks between rubber and silica. The silane coupling agent modifies the silica surface and forms crosslinks between rubber and silica, as discussed previously. Figure 7 shows SEM images of the vulcanizates. Filler dispersion of the vulcanizate containing the silane coupling agent is better than that without the silane coupling agent. For the vulcanizates with the filler compositions of carbon black/silica = 40/0, 30/10,

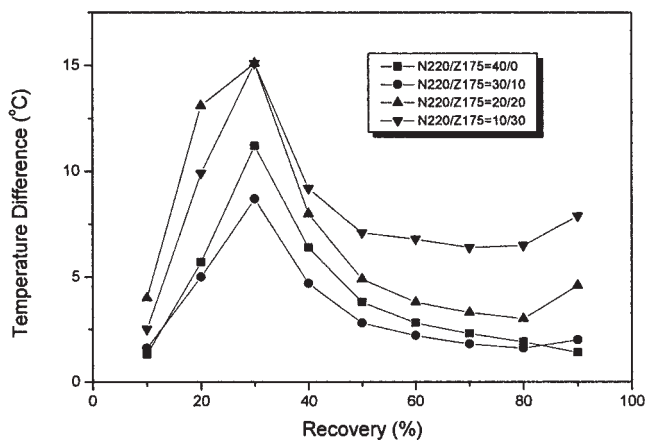


Figure 6 Variation of the temperature difference as a function of recovery. Squares, circles, up-triangles, and down-triangles indicate vulcanizates with filler composition of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively.

and 20/20 phr, the recovery differences increase until -10°C with increased temperature and then decrease (Fig. 5). For the vulcanizate with filler compositions of carbon black/silica = 10/30 phr, the recovery difference increases with increased temperature and notably increases above -20°C .

Figure 6 shows the variation of temperature difference with recovery. The temperature differences increase until 30% recovery and then decrease. Figure 6 shows that the temperature to reach to a certain recovery is lower for the vulcanizate containing the silane coupling agent than for that without the silane coupling agent. This can be also explained with the polymer–filler interactions and crosslink densities, as discussed previously. The temperature difference, on the whole, increases with increased silica content. The temperature differences at the R_{10} are 1.3, 1.6, 2.5, and 4.0°C for the vulcanizates with filler compositions of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively. The temperature differences at the R_{90} are 1.4, 2.0, 4.6, and 7.9°C , respectively.

Figure 8 shows variation of the retraction behaviors of the vulcanizates without the silane coupling agent with filler composition. The vulcanizates with filler

TABLE III
Curve Fitting Equations for the Plot of Temperature versus Recovery Difference with the Linear Region from -60 to -10°C in Figure 5

Filler composition (phr) (carbon black/silica)	Curve fitting equation	Correlation coefficient (r)
40/0	$y = 0.200x + 12.27$	0.995
30/10	$y = 0.133x + 8.83$	0.994
20/20	$y = 0.224x + 15.51$	0.989
10/30	$y = 0.250x + 15.97$	0.984

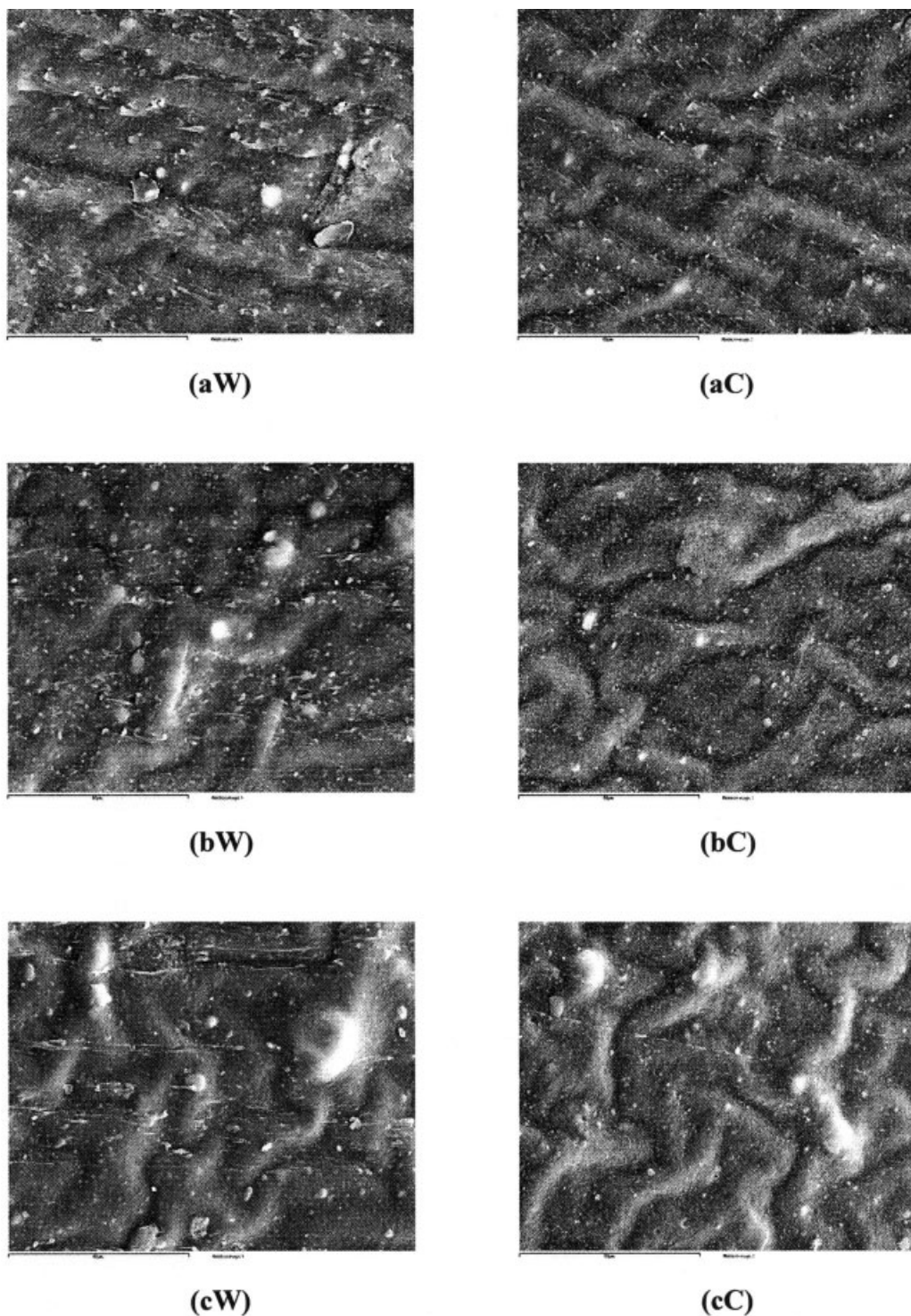


Figure 7 SEM images of vulcanizates with filler compositions of carbon black/silica = 30/10 phr (a), 20/20 (b), and 10/30 phr (c). “W” and “C” are the vulcanizates without and containing the silane coupling agent.

compositions of carbon black/silica = 40/0 and 30/10 phr show similar retraction behaviors. Recovery on the whole becomes slower as silica content increases and recovery difference is larger as temperature increases. Recoveries at -60°C are 4.0, 3.7, 3.0, and 2.9% for the vulcanizates with filler compositions of carbon

black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively. Recoveries at 0°C are 85.0, 84.7, 73.7, and 60.6%, respectively. The T_{90} also becomes higher from $+2.6$ to $+9.8^{\circ}\text{C}$ as the silica content increases from 0 to 30 phr. This can be also explained with the polymer-filler interactions and crosslink densities. Since silica

has many silanol groups, it is not compatible chemically with NR. Thus, the polymer–filler interactions of silica with NR are much poorer than those of carbon black with NR. The crosslink density also becomes lower as the silica content increases, since silica adsorbs the curatives.

For the vulcanizates containing the silane coupling agent, there are no big differences in retraction behaviors with filler composition, as shown in Figure 9. This may be due to the modified silica surface. By modification of silica with the silane coupling agent, the polymer–filler interactions of silica and rubber are improved and crosslinks between the rubber and silica are formed. This will reduce the difference in the whole polymer–filler interactions of rubber with carbon black and silica, which also leads to reduced difference in the retraction behaviors with filler composition and shows similar retraction behaviors.

CONCLUSIONS

Influence of the polymer–filler interactions on retraction behaviors of rubber vulcanizates was investigated using NR vulcanizates reinforced with silica and carbon black. The recovery rates of the vulcanizates containing the silane coupling agent were faster than those without the silane coupling agent. This was due to the polymer–filler interactions, crosslinks between the rubber and silica, and increased crosslink densities. The recovery differences between the vulcanizates without and containing the silane coupling agent increased with increased silica content. This was be-

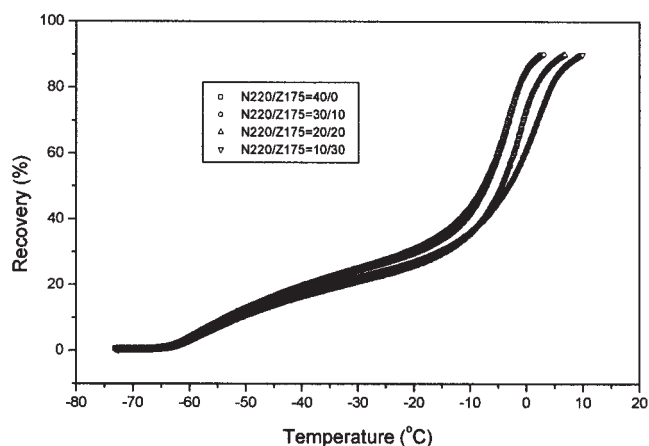


Figure 8 Recovery curves of vulcanizates without TESPT. Squares, circles, up-triangles, and down-triangles indicate vulcanizates with filler composition of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively.

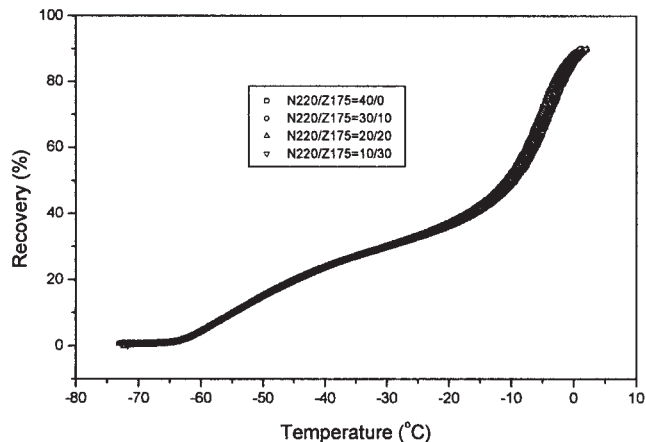


Figure 9 Recovery curves of vulcanizates containing TESPT. Squares, circles, up-triangles, and down-triangles indicate vulcanizates with filler composition of carbon black/silica = 40/0, 30/10, 20/20, and 10/30 phr, respectively.

cause the differences in the polymer–filler interactions and crosslinks between the rubber and silica became larger. The vulcanizates containing the silane coupling agent showed similar retraction behaviors irrespective of filler composition. But, the vulcanizates without the silane coupling agent showed slower retraction behaviors with increased silica content.

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