Improvement of Properties of Silica-Filled Natural Rubber Compounds Using Polychloroprene

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ABSTRACT: Because silica has strong filler–filler interactions, a silica-filled rubber compound is characterized by a poor dispersion of the filler. Properties of silica-filled natural rubber (NR) compounds were improved using polychloroprene (chloroprene rubber [CR]). The bound rubber content of the compound increases and the filler dispersion is also improved by adding CR to the compound. Physical properties such as modulus, tensile strength, abrasion, and crack resistance are improved by adding CR. Elongation at break of the vulcanizates containing CR is longer than that of the vulcanizate without CR, although crosslink density of the former is higher than that of the latter. The improved physical properties are attributed to the good dispersion of silica by adding CR. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2609–2616, 2002

Key words: silica-filled compounds; natural rubber; polychloroprene; filler dispersion

INTRODUCTION

Because silica has a number of hydroxyl groups on the surface,[1] which results in strong filler–filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black–filled one. The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Given that the silica surface is acidic, it especially forms strong hydrogen bonds with basic materials. The adsorption of curatives by silica results in delay of the scorch time and reduction of the crosslink density of a silica-filled rubber compound. In general, a silane coupling agent such as bis(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface.[1–4]

Polychloroprene (chloroprene rubber [CR]) is used for oxidation-resistant, oil-resistant, and heat-resistant elastomers.[5,6] CR has a structure similar to that of natural rubber (NR, polyisoprene). CR and NR are homopolymers of chloroprene (CH_2=CCl—CH=CH_2) and isoprene (CH_2=CCH_3—CH=CH_2), respectively. The chlorine on CR is an electron-rich group, so one can expect that it will make a hydrogen bond with the silanol group. In this work, the influence of CR on properties of silica-filled NR compounds was studied by adding 3.0–15.0 parts per hundred rubber (phr) of CR to silica-filled NR compounds. The study was focused on improvement of filler dispersion by adding CR.

EXPERIMENTAL

The silica-filled NR compounds were made of NR, CR (0.0–15.0 phr), silica, a silane coupling agent, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Neoprene W of Du Pont Co. (Wilmington, DE) was used as CR. Z 175 (pH = 6.9,

Table I   Formulations (phr)

	Compound					
	1	2	3	4	5	6
SMR CV60[a]	100.0	97.0	94.0	91.0	88.0	85.0
Neoprene W[b]	0.0	3.0	6.0	9.0	12.0	15.0
Z 175[c]	60.0	60.0	60.0	60.0	60.0	60.0
Si 69[d]	4.8	4.8	4.8	4.8	4.8	4.8
Stearic acid	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
HPPD[e]	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
TBBS[f]	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4

[a] SMR CV 60: standard Malaysian rubber with constant viscosity of 60.

[b] Neoprene W: polychloroprene of Dupont Co.

[c] Z 175: silica (Kofran Co., Korea).

[d] Si 69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) (Degussa Co., Germany).

[e] HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (Kumho-Monsanto Co., Korea).

[f] TBBS: *N-tert*-butyl-2-benzothiazole sulfenamide (Kumho-Monsanto Co., Korea).

BET = 175 m^2/g) of Kofran was used as silica. The formulations are given in Table I.

Mixing was performed in a Banbury-type mixer at a rotor speed of 40 and 30 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80°C for the MB and FM stages, respec-

tively. The MB compounds were prepared as follows. (1) The rubbers were loaded into the mixer and premixed for 0.5 min. (2) The silica and silane coupling agent were compounded into the rubbers for 2.0 min. (3) The cure activators and antidegradants were mixed for 1.5 min and the compounds were discharged. The FM compounds
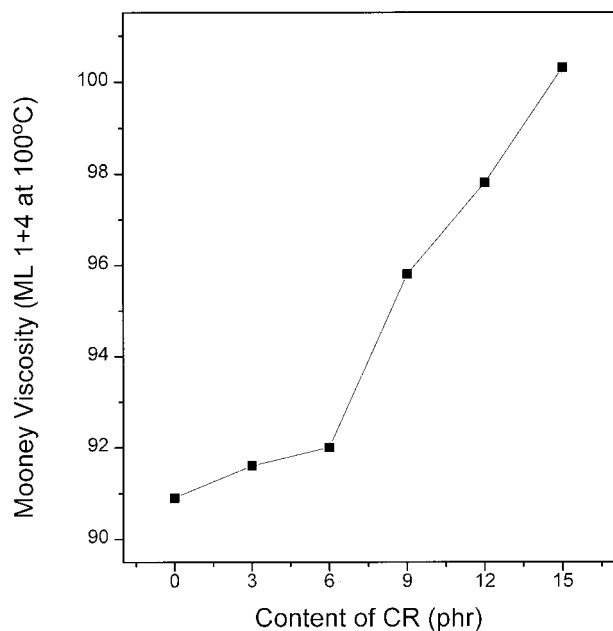

Figure 1   Variation of Mooney viscosity of the FM compound with the content of polychloroprene in the compound.
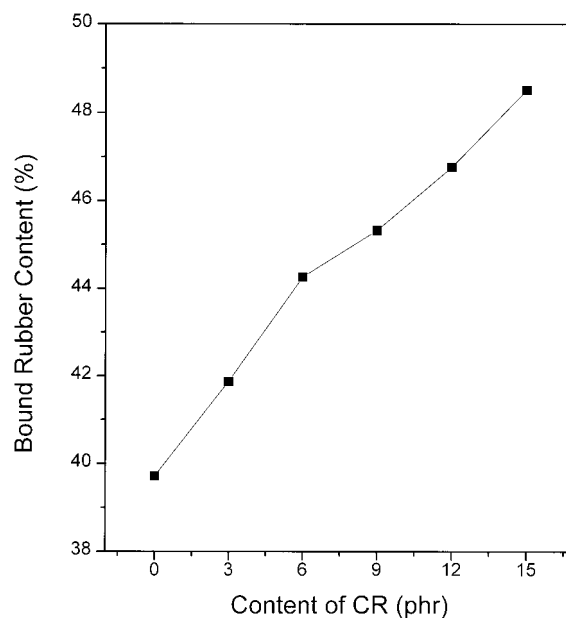

Figure 2   Variation of bound rubber content of the FM compound with the content of polychloroprene in the compound.
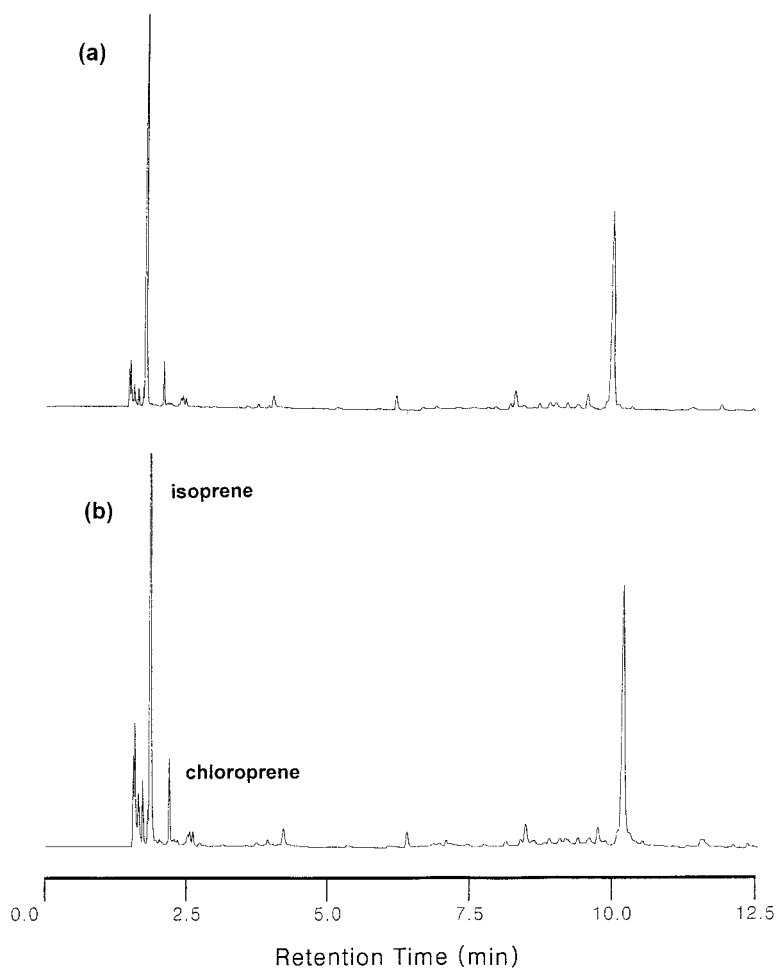
Figure 3 Pyrolysis-GC chromatograms of compounded rubber (a) and bound rubber (b) of compound 5.

were prepared by mixing the curatives with the MB compounds for 1.5 min.

Viscosities and Mooney cure times of the compounds were measured using an MV 2000 viscometer of Alpha Technologies. The contents of bound rubber were determined by extraction of unbound materials such as ingredients and free rubbers with toluene for 7 days and *n*-hexane for 1 day and drying for 2 days at room temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated. Composition of the bound rubber was determined using pyrolysis gas chromatography (pyrolysis-GC). The analysis conditions for the pyrolysis-GC were described in detail elsewhere.[7]

The vulcanizates were prepared by curing at 160°C for 20 min. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021; Instron, UK). Abrasion loss was measured according to ASTM 2228 with a Pico abrasion tester of BF Goodrich for 80 cycles. Flex cracking resistance was measured with a DMFC tester (FT-1503, 300 cpm). To investigate the influence of thermal aging on the physical properties, the vulcanizates were thermally aged for 3 days at 90°C.

RESULTS AND DISCUSSION

Mooney Viscosity and Bound Rubber

The Mooney viscosity increases as the CR content increases, as shown in Figure 1. The Mooney viscosity increases slightly as the CR content increases from 0.0 to 6.0 phr, after which it increases significantly. The difference in the

Mooney viscosities between the compounds containing CR of 6.0 and 0.0 phr is about 1 MU but that between the compounds containing CR of 15.0 and 6.0 is about 8 MU. The increase of Mooney viscosity with increase in the CR content may be attributable to the increase of the bound rubber content. Mooney viscosity increases with increase of the bound rubber content.[8,9] The bound rubber content increases with increasing CR content in the compound (Fig. 2). The increment is about 0.6% per 1.0 phr of CR. This implies that CR is more compatible with silica than with NR.

The rubber composition of the bound rubber was measured with a pyrolysis-GC. The compounded rubbers were used as reference samples to determine the CR content of the bound rubber. Figures 3(a) and 3(b) give pyrograms of compounded rubber and bound rubber of compound 5. The important pyrolysis products are isoprene and chloroprene, which correspond to the peaks at 1.8 and 2.1 min, respectively. The isoprene and chloroprene are formed from NR and CR, respectively. As shown in Figure 3, the relative peak intensity of chloroprene of the bound rubber (3.5%) is higher than that of the compounded rubber (1.7%). The CR contents of the samples
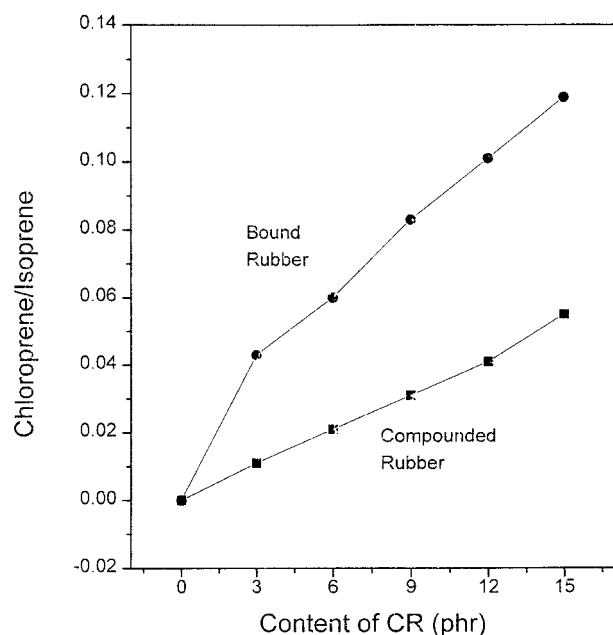

Figure 4 Variation of the peak intensity ratio of chloroprene and isoprene peaks as a function of the polychloroprene content in the compound. Rectangles and circles indicate compounded rubber and bound rubber, respectively.

Table II Compositions of Bound Rubber

	Compound					
	1	2	3	4	5	6
CR content of the bound rubber (%)	0	12	17	23	28	33

were determined using the relative peak intensities of chloroprene and isoprene in the pyrolysis-GC chromatograms. Figure 4 shows variation of the peak intensity ratio of chloroprene and isoprene with the CR content. The chloroprene/isoprene ratio increases linearly with an increase of the CR content. The variation of the chloroprene/isoprene ratio for the compounded rubber is fitted well to a linear equation, which has the curve-fitting equation of $y = 0.00357x - 0.00029$, with a correlation coefficient of 0.998. From the curve-fitting equation for the compounded rubber, CR content in the bound rubber was calculated, the results of which are summarized in Table II. The CR content of the bound rubber is much higher than that of the compounded rubber by more than a factor of 2. This implies that CR is much more compatible with silica than with NR. This may be attributable to the high electronegativity of chlorine. The hydrogen atom of the silanol of silica has a locally positive charge and chlorine of the CR has a locally negative charge. Thus, silanol groups of the silica can readily make hydrogen bonds with chlorines of the CR, as shown in **Scheme 1**.

Dispersion of Silica

To investigate the CR effect on dispersion of silica, the degree of silica dispersion was investigated by optical microscopy. Figure 5 gives the photographs of the vulcanizates for compounds 1, 3, and 5 (magnification ×1000). The vulcanizate without CR has a very poor dispersion of silica. Figure 5(a) shows that silica agglomerates are clustered. Sizes of the silica agglomerates in the vulcanizate without CR are larger than those in the vulcanizates containing CR. For the compounds containing CR, silica agglomerates are not clustered and silica is dispersed to some extent. This can be explained by the adsorption of CR on the silica. The CR adsorbed on the silica surface reduces the filler–filler interactions, so that the silica is dispersed well into the rubber.

Figures 5(b) and 5(c) are the photographs of the vulcanizates with the CR contents of 6.0 and 12.0 phr, respectively. A comparison of the level of the filler dispersion reveals that the former is better than the latter.

Cure Characteristics

Cure times of the compounds were investigated with the Mooney test at 125°C. The t_5 (Mooney scorch time), t_{35}, and Δt (cure rate index) were obtained. The t_5 and t_{35} mean the times taken for the viscosity to reach from the minimum point to increases of 5 and 35 MU, respectively. The Δt is the difference between the t_{35} and t_5. The reciprocal of the Δt is used as a cure rate. The greater the value of Δt, the slower the cure rate. The t_5 value increases with increase in the CR content. This can be explained by the difference in the number of reaction sites on the rubbers. A sulfur crosslinking reaction occurs on allylic carbon. The numbers of the allylic carbons on the isoprene and chloroprene repeat units are 3 and 2, respectively. Thus, it needs longer time to begin the crosslinking reaction as the CR content increases. The t_{35} value also increases with increase in the CR content. This is also attributed to the number of the reaction sites on the rubbers. Variation of the Δt with the CR content does not show a specific trend.

Delta torque is the difference between the maximum and minimum torques. Because the torque in the rheograph starts to increase by formation of crosslinks, the delta torque is very closely re-
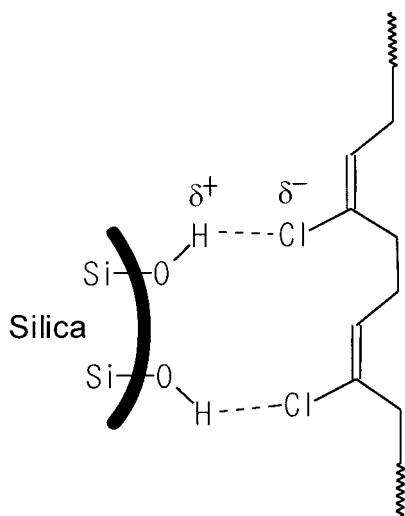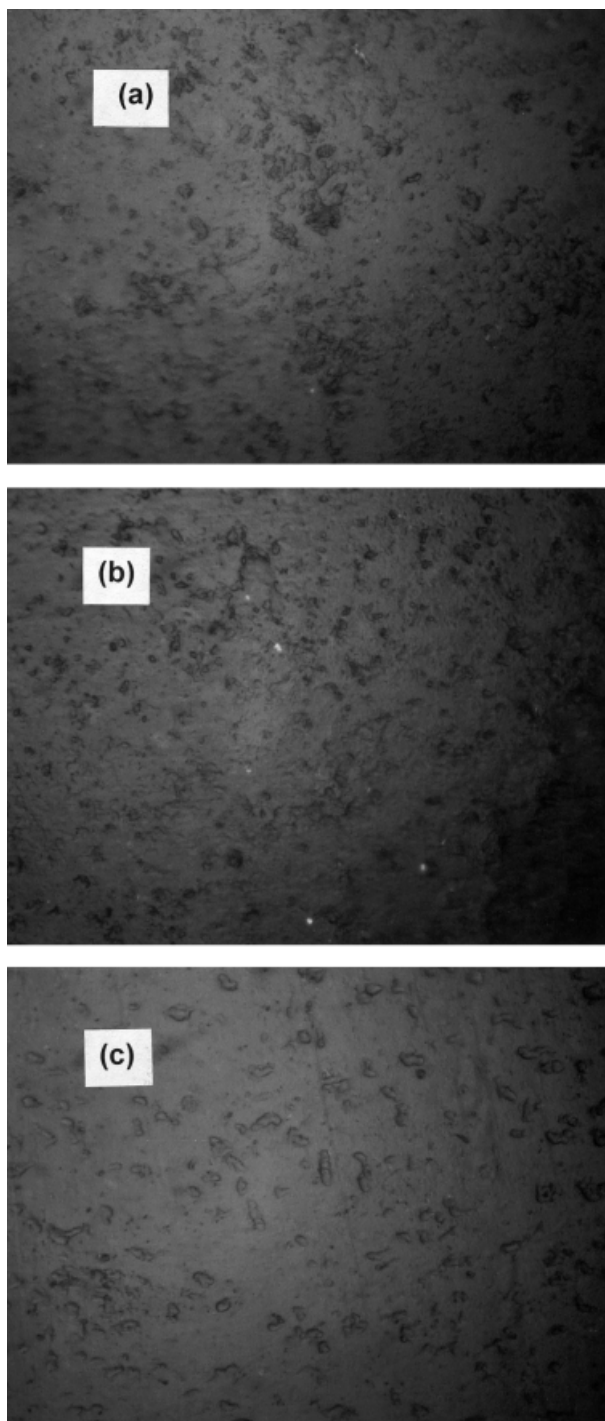

Figure 5 Photographs of the vulcanizates 1 (a), 3 (b), and 5 (c), obtained using an optical microscope (×1000).

lated to the crosslink density.[13–15] The greater the delta torque, the higher the crosslink density. The delta torque was obtained from the rheograph at 160°C (Table III). The delta torques of the compounds containing CR, on the whole, are

Scheme 1

Table III   Cure Characteristics

	Compound					
	1	2	3	4	5	6
Mooney test at 125°C						
t_5 (min)	23.87	27.60	28.80	31.47	33.73	34.93
t_{35} (min)	32.13	36.53	37.73	40.00	42.13	43.07
Δt (min)	8.26	8.93	8.93	8.53	8.40	8.14
Delta torque (N · m) obtained from the rheograph at 160°C	2.96	2.94	3.07	3.05	3.04	3.11

higher than that of the compound without CR. This may be attributable to reduction of the curative adsorption on the silica surface by adding CR. Given that CR is more compatible with silica than with NR, the silica surface is more covered with CR in the compound. Thus, the amount of curatives adsorbed on the silica surface is reduced by adding CR.

Physical Properties

Physical properties of the vulcanizates such as hardness, tensile strength, elongation at break, and modulus were measured before and after the thermal aging for 3 days at 90°C. Variation of the hardness with the CR content is negligible, as shown in Figure 6. After the thermal aging, the hardness increases remarkably, more than 10%. This is ascribed to the increased crosslink density after the thermal aging. Crosslink densities of the vulcanizates before and after the thermal aging were measured by the swelling method. Organic additives in the samples were removed by extracting with THF and n-hexane, each for 2 days, and they were dried for 2 days at room temperature. The weights of the organic material–extracted samples were measured. They were soaked in n-decane for 2 days and the weights of the swollen samples were measured. The swelling ratio was calculated: $Q = (W_s - W_u)/W_u$, where W_s and W_u are the weights of the swollen and unswollen samples, respectively. The reciprocal swelling value $1/Q$ is used as the crosslink density.[13] The results for the $1/Q$ are summarized in Table IV. The value of $1/Q$ is increased by about 30% after the thermal aging.

The tensile strengths of the vulcanizates having CR are higher than that of the vulcanizate without CR (Fig. 7). This is because the crosslink densities of the vulcanizates containing CR are higher than that of the vulcanizate without CR.

In general, the tensile strength of a rubber vulcanizate increases with an increase of the crosslink density.[14] After the thermal aging, the tensile strength decreases because the elongation at break is decreased. The elongation at break decreases remarkably after the thermal aging, as shown in Figure 8. The difference in the elongation at break before and after the thermal aging is about a factor of 2. The elongations at break of the vulcanizates containing CR are longer than that of the vulcanizate without CR, although the crosslink density of the vulcanizate increases by adding CR. This is a surprising result. In general, elongation at break of a rubber vulcanizate with a
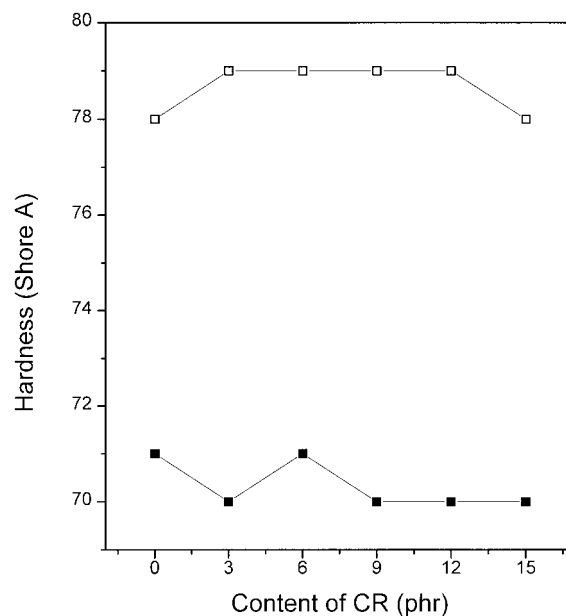

Figure 6   Variation of the hardness with the content of polychloroprene in the compound. Closed and open symbols indicate before and after aging for 3 days at 90°C, respectively.

Table IV   Reciprocal Swelling Ratio (1/Q)

	Compound					
	1	2	3	4	5	6
Before the thermal aging	1.108	1.132	1.177	1.242	1.265	1.321
After the thermal aging	1.390	1.444	1.500	1.596	1.722	1.674

high crosslink density is shorter than that of a rubber vulcanizate with a low crosslink density. This may be attributed to the good dispersion of silica by CR. The filler dispersion is improved by adding CR, as discussed previously.

Figure 9 illustrates the variation of the modulus with the CR content. The modulus increases with increasing CR content. This is also explained with the crosslink density. The crosslink density, on the whole, increases with an increase in the CR content. The modulus increases significantly after the thermal aging. The 200% modulus after the thermal aging is higher than the 300% modulus before the aging. This is ascribed to the remarkable increase of the crosslink density after the thermal aging, as shown in Table IV.

The crack growth–resistance property is improved by adding CR (Table V). The crack size of the vulcanizate without CR is about twofold greater than that of the vulcanizates containing CR. This may be the result of the filler dispersion. In general, the crack-resistance property is improved by improving the dispersion.[15] The wear property is also improved by adding CR. The amount of the abrasion loss, on the whole, decreases with an increase of the CR content. This may be the result of the filler dispersion and crosslink density. The silica dispersion is improved and the crosslink density increases by adding CR. Richmond[16] studied the influence of dispersion on abrasion and reported that a vulcanizate with a good filler dispersion had a better wear property than that with poor filler dispersion.
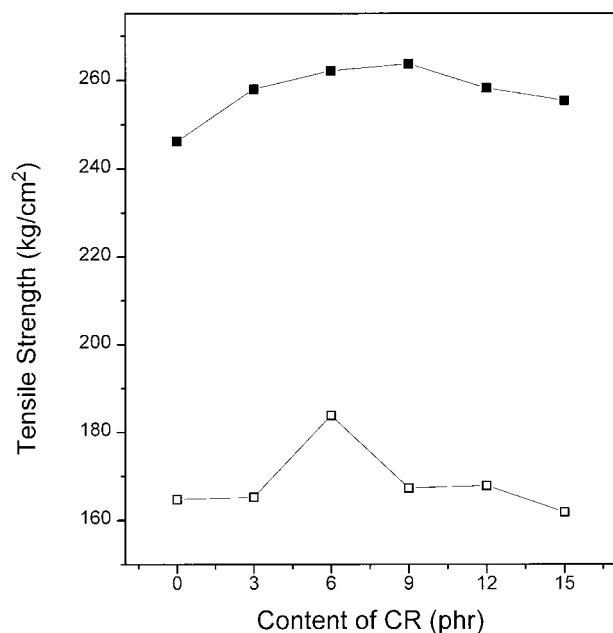

Figure 7   Variation of the tensile strength with the content of polychloroprene in the compound. Closed and open symbols indicate before and after aging for 3 days at 90°C, respectively.
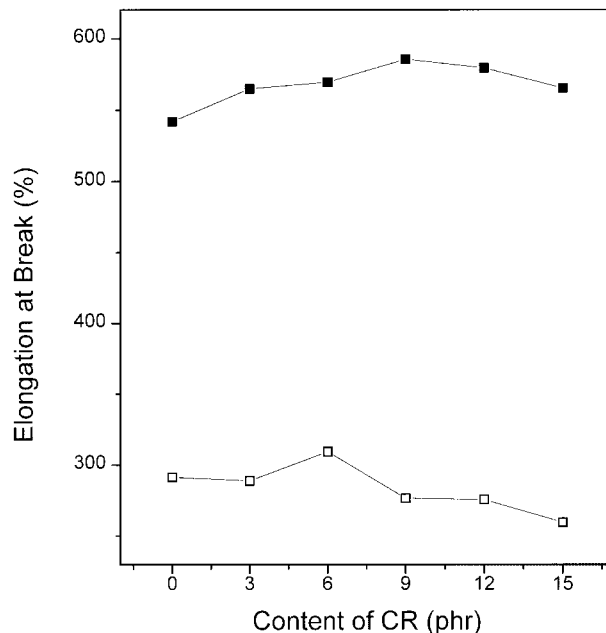

Figure 8   Variation of the elongation at break with the content of polychloroprene in the compound. Closed and open symbols indicate before and after aging for 3 days at 90°C, respectively.

CONCLUSIONS

By adding CR to the silica-filled NR compounds, dispersion of the filler is improved. The delta torques of the compounds containing CR are higher than that of the compound without CR. However, the Mooney scorch time increases with increasing CR content because the isoprene unit of NR has more allylic carbons than the chloroprene unit of CR. The tensile strength increases and the elongation at break becomes longer by adding CR. This is attributed to the increased crosslink density and the good filler dispersion of the vulcanizates containing CR. Improvement of the silica dispersion by adding CR leads to the increased crack-resistance and wear properties. From the results for the Mooney viscosity and physical properties before and after the thermal aging, it is concluded that the recommended CR content is about 6 phr.
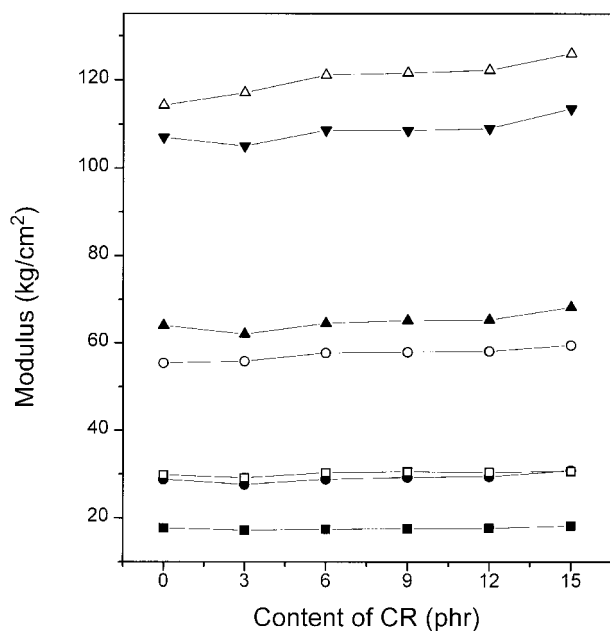

Figure 9 Variation of the modulus with the content of polychloroprene in the compound. Closed and open symbols indicate before and after aging for 3 days at 90°C, respectively. Rectangles, circles, up-triangles, and down-triangles stand for 50, 100, 200, and 300% strains, respectively.

Table V   Crack and Abrasion Tests

	Compound					
	1	2	3	4	5	6
Dematia flex-cracking test (60,000 cycles) Crack size (mm)	13.1	7.2	5.4	5.7	5.9	5.3
Abrasion loss (mg)	43.5	43.0	39.0	36.5	38.0	33.5

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