

Influence of Filler and Cure Systems on Thermal Aging Resistance of Natural Rubber Vulcanizates Under Strained Condition

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ABSTRACT: Aging and decomposition of polymer based articles are influenced by various environmental factors. Hence, it is important to research the various factors precisely to interpret the aging mechanism. This study deals with the tensile set properties of natural rubber (NR) vulcanizates with different reinforcing and cure systems after thermal aging. The tensile set increased with increasing both the aging temperature and aging period. Thermal aging resistance and tension set was enhanced by increasing the cure accelerator content in the sample. The carbon black-filled NR vulcanizates showed better thermal aging resistance than the silica-filled ones. It was found that silane coupling agent enhanced the thermal aging resistance

of the silica-filled NR vulcanizates. The experimental results could be explained by the cross-link density change and also from the consumption of the antidegradants due to thermal aging. The permanent tension set and cross-link density were increased as the aging temperature and aging time were increased. The filler and cure systems were found to influence on the surface morphologies of the thermally aged samples. The cross-link density change was a key factor of the changes of tension set. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3074–3081, 2010

Key words: NR compound; tension set; thermal aging; filler system; cure system

INTRODUCTION

Aging and decomposition of polymer is influenced by various environmental factors. Hence, it is important to understand these various factors to interpret precisely the aging mechanism. The various factors include progress in oxidation reaction, exhaustion of antioxidants in the compound, changes in polymer morphology, the catalyst residue, and consecutive reactions of chain scissions, which are promoted for a period when exposed to heat or ultraviolet rays.¹ It is very important to analyze the aging properties of rubber articles, because it helps to predict the service lifetime. Currently, the aging characteristics of elastomeric materials could be traced out by

measuring the mechanical properties after thermal aging. However, there is seldom information available about the chemical changes of materials after being aged. Some researchers verified the changes that occur in cross-linking network of elastomeric materials after being aged.^{1–3} Some researchers have also tried to explain the specific reasons about the aging of elastic articles.

Cross-link type and cross-link density of a rubber vulcanizate affect the mechanical properties such as modulus, hardness, elasticity, tensile strength, and elongation at break. In sulfur cross-linking system, stress relaxation, tensile strength, and elasticity are improved by increasing cross-link density, whereas fatigue and aging resistance decreased.⁴ Sulfur cross-links such as S–S and C–S bonds are less stable compared with C–C bond. Moreover, polysulfides cross-links are much less stable than mono- and disulfide cross-links.^{4–7} During the aging, there is a possibility of the cross-link density change by dissociation of these existing cross-links and formation of new cross-links.^{8–11}

Silica has been widely used in manufacturing various rubber compounds including tires. However,

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TABLE I
Formulation of Rubber Compounds (phr)

Compound No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SMR CV60	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Z175	40	40	40	40	40	40	40	40	40	40	–	–	–	–	–
Si69	–	–	–	–	–	3.2	3.2	3.2	3.2	3.2	–	–	–	–	–
N220	–	–	–	–	–	–	–	–	–	–	40	40	40	40	40
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	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	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	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	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.0	1.4	1.8	2.2	2.6	1.0	1.4	1.8	2.2	2.6	1.0	1.4	1.8	2.2	2.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4

there are seldom studies focusing on the thermal aging properties, which can be a measure of service life of the final product. In this work, a comparison has been made on the properties of thermally aged natural rubber (NR) compounds with different reinforcing systems such as silica, silica/silane coupling agent, and carbon black. Influence of the cure systems on NR compounds after aging was also investigated. Tensile set, change in cross-link density, surface morphology changes, and exhaustion of anti-degradants in the NR compounds were examined.

EXPERIMENTAL

The NR of grade SMR-CV60 was used in this study. The reinforcing fillers used in the study were silica (grade: Z175) and carbon black (grade: N220). The remaining components were comprised of ZnO, stearic acid, wax, *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD), *N*-tert-butyl-2-benzothiazole sulfinamide (TBBS), and sulfur. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT, Si69) was used as a silane coupling agent. The detailed formulations of the compounds are listed in Table I. The compounds 1–5 were silica-filled NR compounds without Si69, the compounds 6–10 were silica-filled NR compounds containing Si69, and the compounds 11–15 were carbon black-filled NR compounds. Five cure systems of TBBS/sulfur ratio = 1.0/1.4, 1.4/1.4, 1.8/1.4, 2.2/1.4, and 2.6/1.4 were employed in this study.

The NR was mixed with the compounding ingredients, except the curatives, in an internal mixer (Haake Rheocord 9000 series, selstr., Germany) at a temperature of 150°C and speed of 60 rpm for 10 min. The compounded rubber was then mixed with the curatives in a two-roll mill (8422, Farrel Co, SA) according to the procedure in ASTM D 3182 and D 3184. In the compound containing a silane coupling agent, the compounding ingredients (except curatives) and silane coupling agent (Si69) were mixed in the same internal mixer under the same conditions mentioned above.

The tensile set experiments were carried out as follows (Fig. 1): First, the samples were cut in the dimensions of 70 mm length and 5 mm width (2 mm thickness). Second, the sample was stretched to a strain of 100%. Third, the strained samples were aged at 60, 80, and 100°C for 10, 20, and 30 days in a natural convection oven. Finally, the applied strain was removed and then measured the permanent deformation which could not be recovered. The tension set (*TS*) was calculated by the eq. (1);

$$TS = \frac{(L_r - L_0)}{(L_e - L_0)} \times 100 \quad (1)$$

where L_0 , L_e , and L_r are the initial, 100% extended, and released lengths.

To figure out the changes in cross-link densities due to thermal aging, the specimens before and after aging were immersed in tetrahydrofuran (THF, Fisher Scientific, Seoul, Korea) for 72 h and in *n*-hexane (Sigma Aldrich, Kyunggi-do, Korea) for 24 h at room temperature to extract the free organic materials in the sample. The weight of specimen was measured after drying for 24 h in a vacuum oven at

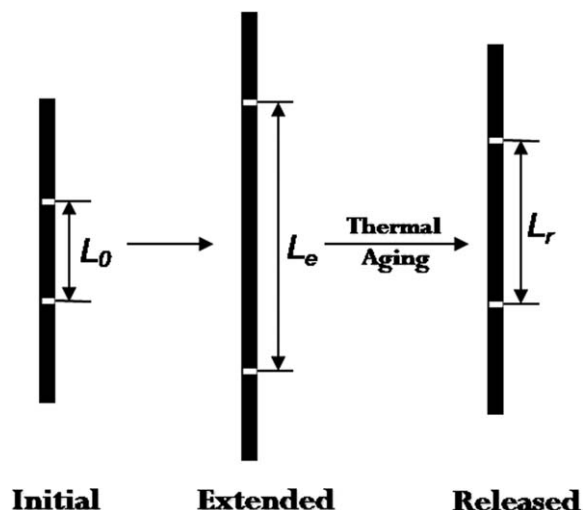


Figure 1 Schematic of tension set experiment.

25°C. The organic free extracted sample was immersed in *n*-decane (Sigma Aldrich, Kyunggi-do, Korea) for 48 h at room temperature. After that, the weight of the swollen sample was measured. The swelling ratio (Q) was calculated by the equation;

$$Q = \frac{(W_s - W_u)}{W_u} \quad (2)$$

where W_s and W_u are the weights of the swollen and unswollen samples. In general, the reciprocal swelling ratio ($1/Q$) can be used as the apparent cross-link density.

The changes in surface morphology of the thermally aged rubber compounds were investigated using Stereoscopic Zoom Microscope. The surface morphology of the swollen sample (in THF for 24 h) was observed under swelling condition. Remained antidegradants in the sample before and after aging were extracted using THF for 5 h at 70°C and the residue of antioxidants was estimated using gas chromatography (Acme 6000M GC, Young Lin Instrument, Anyang, Korea). HP-5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 μ m film thickness) was used. Injector and detector temperatures of GC analysis were 250°C.

RESULTS AND DISCUSSION

Regardless of the reinforcing systems, the permanent deformation was generally increased, when the condition of thermal aging was getting harsh (aging at higher temperature for longer time). However, under the same aging conditions, the permanent deformation was decreased by increasing the content of cure accelerator. Figure 2 shows the results of permanent deformation based on tension set as a function of aging temperature. At 60°C and 80°C, the Si69-contained silica-filled compounds and the compounds reinforced with carbon black showed similar levels of permanent set. However, the silica-filled samples without Si69 showed higher permanent deformations. As some of curatives are adsorbed by silanol groups on the silica surface, the cross-link density may be lower than the other two reinforcing systems.¹²⁻¹⁴ Moreover, silica and NR are highly incompatible to each other. In the case of silica treated with a silane coupling agent, the silane coupling agent played an important role to improve the compatibility between silica and rubber matrix through a strong interface between them. Therefore, the silica-filled sample containing silane coupling agent showed an improved thermal stability compared with that of the silica-filled sample without a silane coupling agent.^{12,13,15}

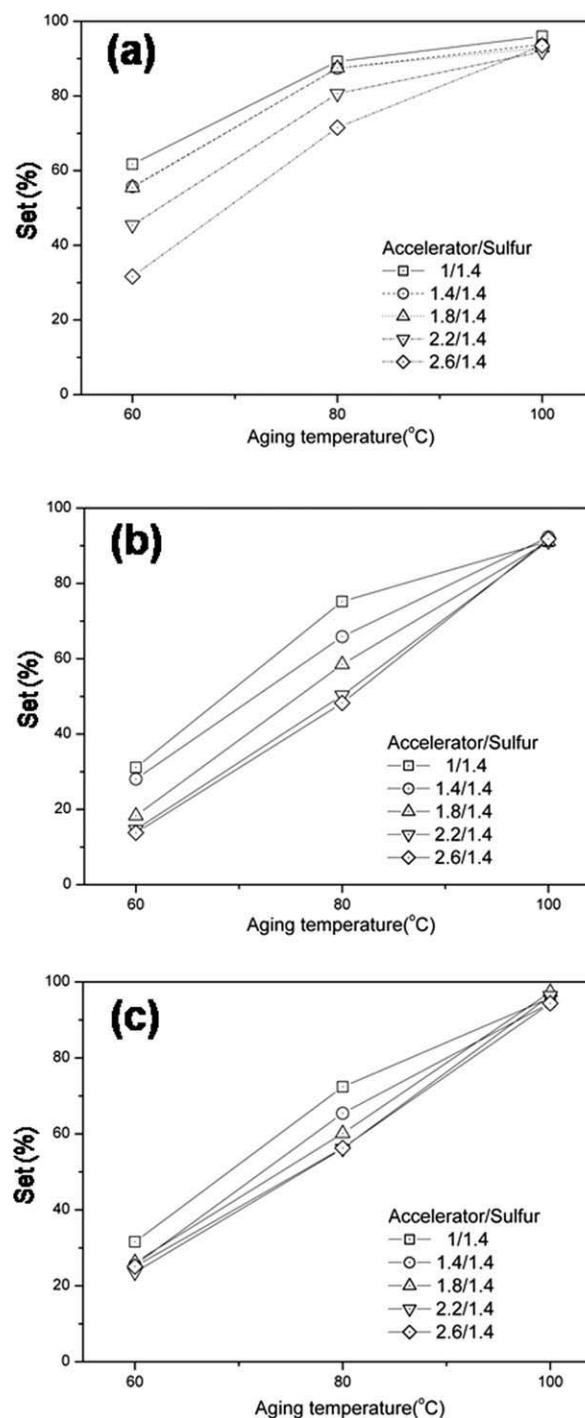


Figure 2 Variation of tension set as a function of aging temperature for (a) silica-filled samples without Si69, (b) silica-filled samples containing Si69, and (c) carbon black-filled samples.

As the cure accelerators to sulfur ratio was increased, the permanent tension set was decreased. The observed trend was similar regardless of reinforcement type and aging temperature. This is possibly because of the type of cross-link network formation. When the content of cure accelerator is getting higher, mono and disulfides types of cross-links

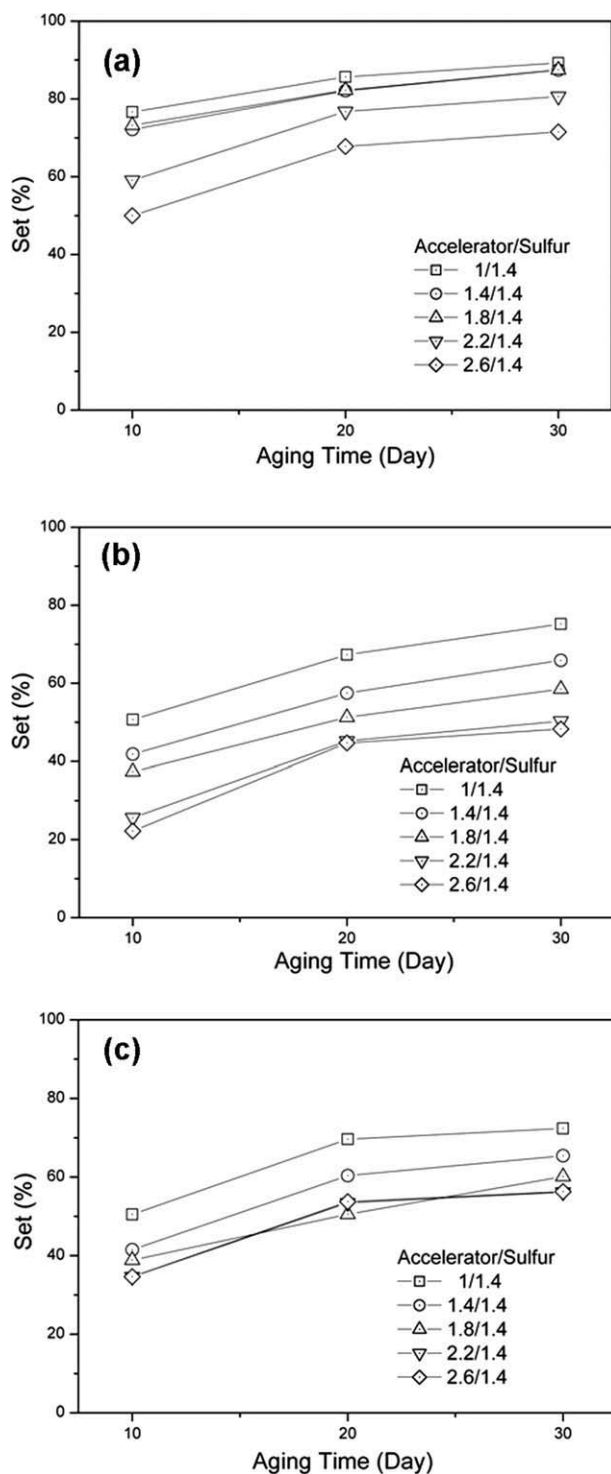


Figure 3 Variation of tension set as a function of aging time, (a) silica-filled samples, (b) silica-filled samples with Si69, and (c) carbon black-filled samples. (Aging temperature = 80°C).

were preferred to form rather than the polysulfide cross-links.^{4-7,16} Hamza¹⁷ and Cunneen and Russell¹⁸ have suggested that the sulfide bond is quite sensitive to oxidation, so it can be easily aged compared with other chemical bonds. Bhowmick and De¹⁹

have verified that the number of polysulfide links decrease after deformation of main chain of NR. These previous experimental results support our experimental findings in this study. Overall, as the aging temperature was increased, the permanent tension set increased. However, at 100°C where the aging was extremely severe, 90% of permanent deformation occurred regardless of amount of cure accelerator.

Figure 3 shows the results of permanent deformation in tension as a function of aging period at 80°C. The tension set increased with increase in aging time at a particular temperature. At similar aging times, the silica-filled samples without Si69 showed higher permanent set than the other two reinforcement systems. This shows that the silica-filled samples without Si69 have lower thermal stability. In the case of silica filled compounds with Si69 and carbon black compounds, a similar value of tension set was observed. However, at higher level of cure accelerator system, the silica-Si69 reinforcing system showed a considerably lower tension set. This again indicates that the silane coupling agent enhanced the thermal resistance of the rubber compounds. Figure 4 shows the variation of tension set as a function of accelerator/sulfur ratio at different temperatures and at different periods. The tension set decreased with increase of accelerator/sulfur ratio. This may be because of the decrease in polysulfidic cross-link formation, which is easily broken by heating.

The tension set were also found to be influenced by the cross-link density changes. Moreover, the change in cross-link density might be related with the permanent set as the rubbers were being aged. The level of cross-link density change increased with increase of the aging temperature, as shown in Figure 5. In the specimen with lower cure

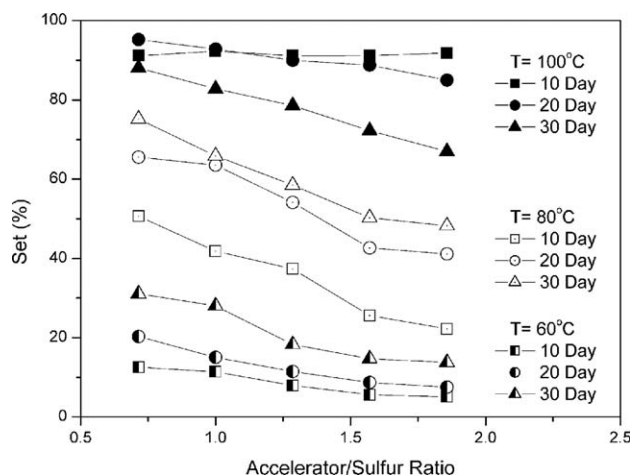


Figure 4 Variation of tension set as a function of cure accelerator/sulfur ratio for silica-filled samples containing Si69. (At different temperatures and times).

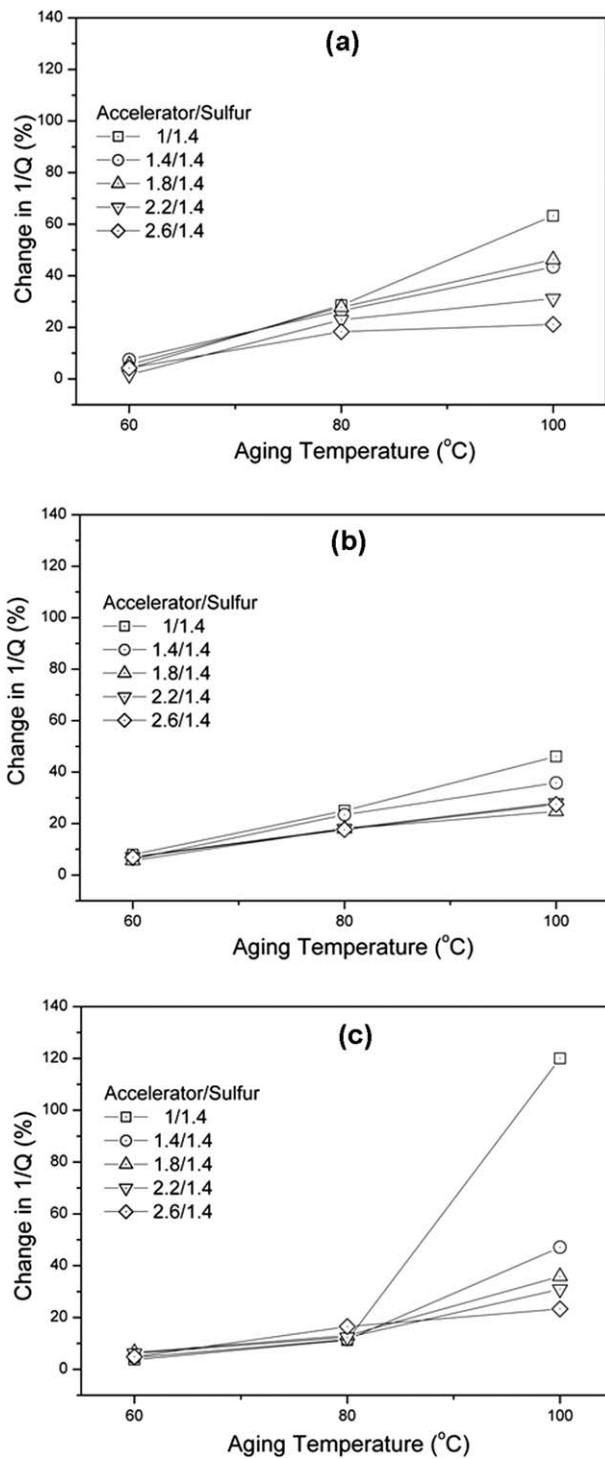


Figure 5 Variation of cross-link density ($1/Q$) change as a function of aging temperature, (a) silica-filled samples, (b) silica-filled samples with Si69, and (c) carbon black-filled samples. (Aging period = 30 days.).

accelerator content where the ratio of sulfur to accelerator is higher, more polysulfide linkages were formed and there were a lot of free sulfurs. Polysulfides can be easily dissociated and rearranged to mono or disulfides. Free sulfurs, which are not engaged in the cross-linking reactions, can join in

the formation of new cross-links by thermal aging, and they can cause the increase of cross-link density.^{4-6,11-14,16} It was found that for a particular reinforcing system, change in the degree of cross-link density decreased with increase in accelerator content in sulfur accelerator system. The thermal stability of the specimen with higher content of cure accelerator seems to be responsible to more stable

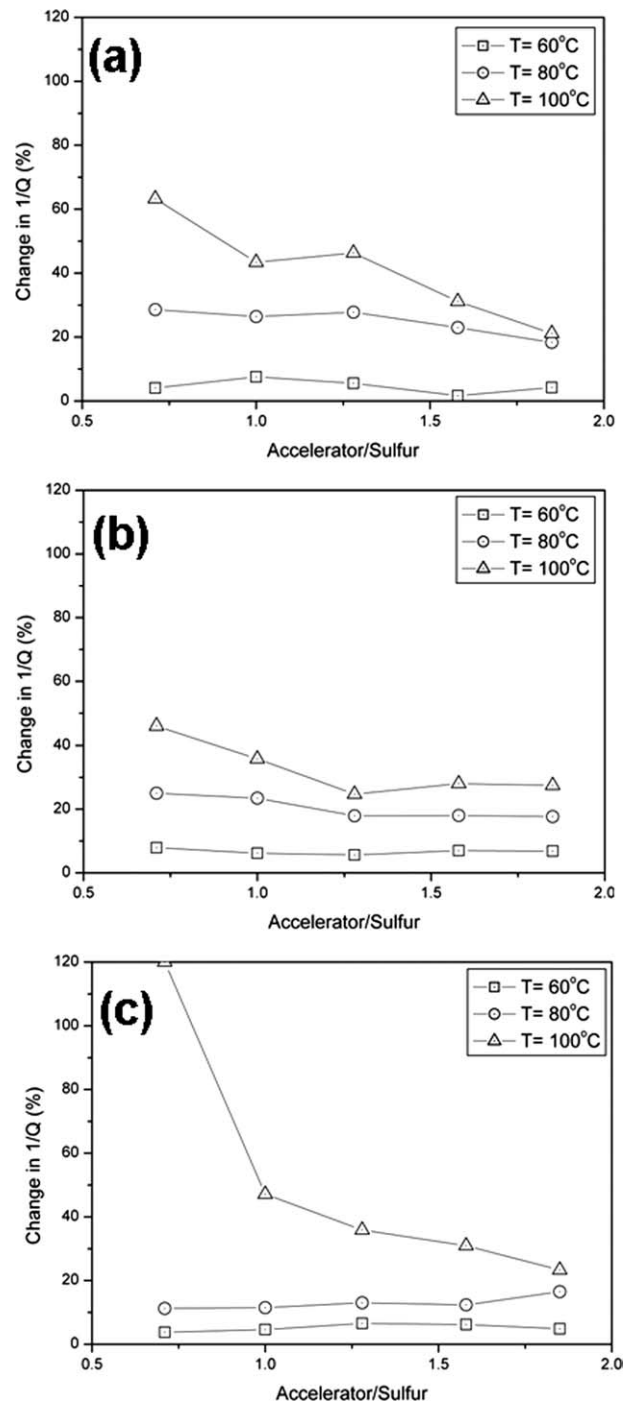


Figure 6 Variations of cross-link density ($1/Q$) change as a function of cure accelerator/sulfur ratio for (a) silica-filled composites, (b) Si69-treated silica-filled composites, and (c) carbon black-filled composites.

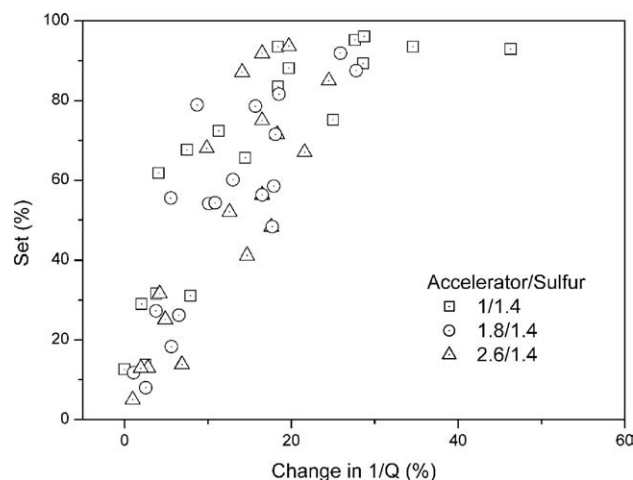


Figure 7 Variations of tension set as a function of cross-link density change for the silica-filled composites without Si69, silica-filled composites containing Si69, and carbon black-filled composites at three different aging temperatures of 60, 80, and 100°C. (Squares, circles, and triangles indicate the accelerator to sulfur ratio: 1/1.4, 1.8/1.4, and 2.6/1.4, respectively.)

cross-linking networks composed of mono and disulfides.

Figure 6 shows the variations of cross-link density ($1/Q$) change versus the cure accelerator/sulfur ratio. The degree of the cross-link density change increased with increase in aging temperature. At the lower aging temperature (60°C), the cross-link density change was not varied much depending on the accelerator/sulfur ratio. However, the changes in cross-link density at higher temperature (100°C) of aging decreased with increasing the accelerator content. The change was quite noticeable for the carbon black-filled sample. At high temperature (100°C) of aging and lower cure accelerator/sulfur ratio, the cross-link density changes of the carbon black-filled samples were considerably larger than those of the silica-filled ones. For the silica-filled samples at 80°C and 100°C aging, the cross-link density changes of the samples containing Si69 were lower than those of the samples without Si69.

The variation of tension set was plotted with the cross-link density change to figure out any general

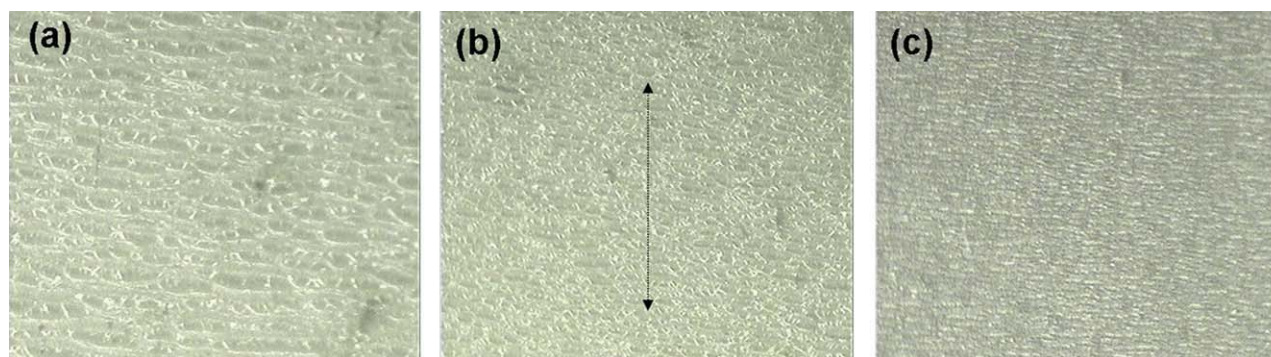


Figure 8 Surface morphologies of swollen samples with different filler systems, (a) silica-filled composite without Si69 (Compound No. 1), (b) silica-filled composite containing Si69 (Compound No. 6), and (c) carbon black-filled composite (Compound No. 11). The samples were aged at 60°C for 20 days. The ratio of accelerator to sulfur was fixed by 1/1.4. (The arrow indicates the strain direction of the specimen). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

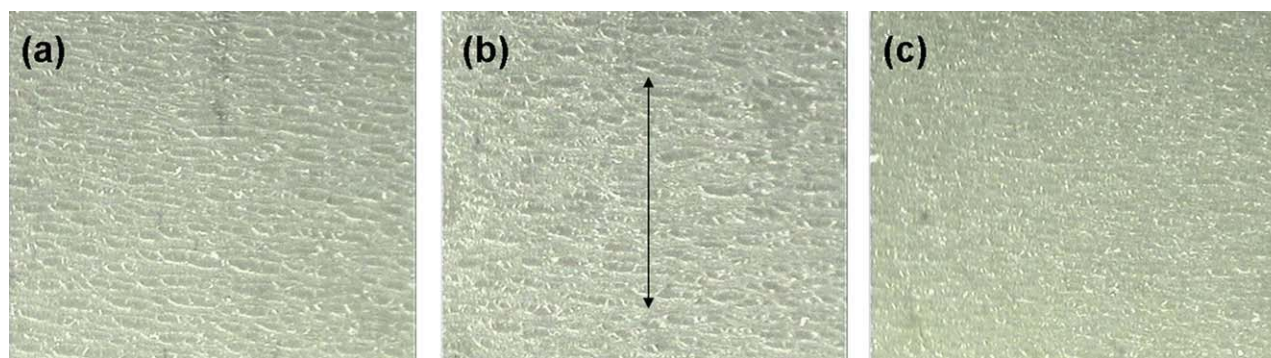


Figure 9 Surface morphologies of swollen silica-filled samples with the different cure systems of (a) low cure accelerator content (Compound No. 1), (b) medium cure accelerator content (Compound No. 3), and (c) high cure accelerator content (Compound No. 5). The samples were aged at 60°C for 10 days. (The arrow indicates the strain direction of the specimen). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

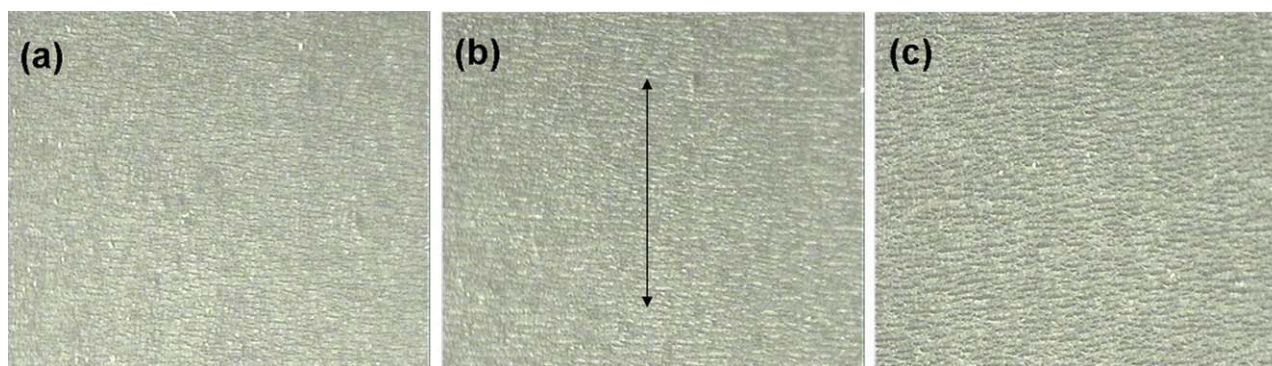


Figure 10 Surface morphologies of swollen carbon black-filled samples (Compound No. 11) after aging at 100°C for (a) 10 days, (b) 20 days, and (c) 30 days. (The arrow indicates the strain direction of the specimen). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

relationship between them (Fig. 7). The tension set was notably increased close to 90% as the cross-link density change was increased to around 30% and then the tension set was leveled-off giving constant values of 90%. This result leads to a conclusion that the cross-link density change is a key factor of the tension set and there is a critical level of cross-link density change leading to a constant tension set level.

In an attempt to compare the surface cracks of the aged samples, the aged specimen was immersed in THF for 24 h and the surface morphology of the swollen sample was observed with a stereoscopic microscope. Figure 8 shows the surface morphologies of the samples aged at 60°C for 20 days. The surface cracks were clearly visible after swelling in the solvent. The silica-filled sample without Si69 was swollen more, because its cross-link density was lower than those of the silica-filled sample containing Si69 and carbon black-filled ones. The silica-filled sample containing Si69 and carbon black-filled sample showed similar morphologies. Figure 9 shows different morphologies according to the cure accelerator contents under same aging conditions. In the specimen with high content of cure accelerator, the crack size was relatively smaller than those of the specimens with low cure accelerator content. This morphologies support the previous results that the cross-link density is more stable for higher accelerator content. The morphology changes depending on the aging time were presented in Figure 10. As the aging time is increased, the surface crack was increased. It was found that, all the cracks observed in this study were formed in the perpendicular direction to the strain after swelling.

Wax and HPPD were added to the rubber compounds as antidegradants. Amounts of antidegradants remained in the sample after thermal aging were measured with GC. Figure 11 shows, the variation of the residual HPPD amounts in the silica-filled samples containing Si69 after thermal aging at

100°C with the aging time. The amount of HPPD remained in the sample was linearly decreased by increasing the aging time irrespective of the cure accelerator/sulfur ratios. The sample with higher cure accelerator content had larger amount of the residual HPPD than the samples with lower ones. Figure 12 shows the variation of the residual HPPD and n -C₂₈H₅₈ of wax in the samples with the aging temperature. HPPD plays a role of radical scavenger, whereas wax makes a physical barrier on the surface of a rubber article. A conventional wax (a mixture of normal alkanes) of n -C₂₈H₅₈ was used in this study. The residual amount of the antidegradants (wax and HPPD) in the sample was decreased with increasing the aging temperature irrespective of the filler systems, and the decreasing speed was much higher for HPPD than wax. This possibly indicates that the HPPD contributes more to protect the rubbers from aging than wax. The amount of the residual HPPD in the silica-filled compound containing Si69 was larger than in the other filler systems. Amounts of

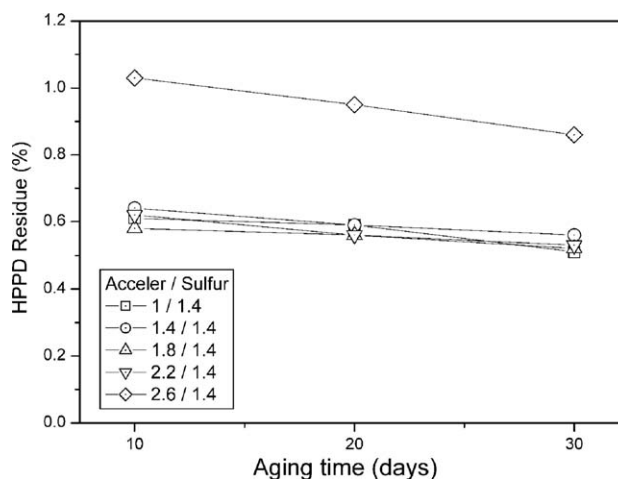


Figure 11 Amounts of HPPD remained in the silica-filled samples containing Si69 (Compound No. 6–10) after thermal aging at 100°C.

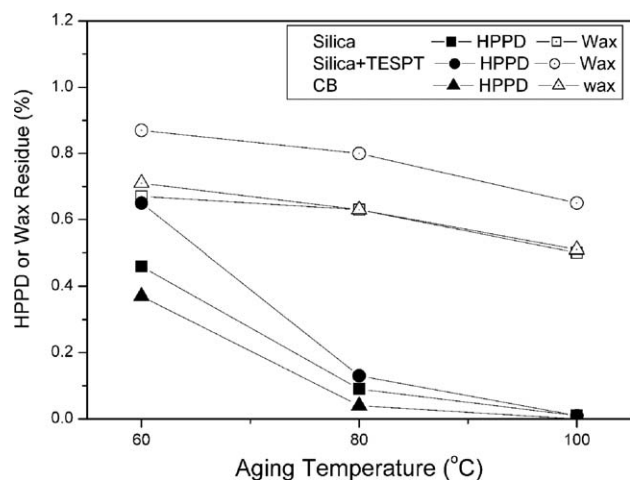


Figure 12 Amounts of antidegradants remained in the samples (Compound No. 5, 10, 15). The cure accelerator/sulfur ratio was 2.6/1.4. The wax was n-C28H58.

the residual HPPD in the carbon black-filled compounds were smaller than in the silica-filled ones. This is because of strong interactions between silanol groups on the silica and amine groups of HPPD.^{20,21} The strong interactions of antidegradants with filler particles cause a slower migration of antidegradants to the surface.

CONCLUSIONS

Thermal aging of NR compounds have been carried out with special focus on the types of reinforcing and cure systems. As the aging temperature and aging time was increased, the permanent deformation (tension set) and cross-link density of the NR compounds increased irrespective of the reinforcing systems. The silica-filled specimens without Si69 were permanently deformed more than the silica-filled specimens containing Si69 and carbon black-filled specimens. The thermal stability was improved for compounds with higher cure accelerator content.

Surface morphology could explain the cross-link density change by thermal aging and the surface crack formation increased with increase in aging temperature and aging time. For an antioxidant incorporated system, the consumption of HPPD contributed more aging resistance to rubber than wax. There is a linear relationship between the tension set and cross-link density change in the range below ~ 30%, and the tension set stayed constant with further increase of cross-link density change. Thus, the cross-link density change was a key factor to monitor the tension set behavior during thermal aging.

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