Elastomer
Vol. 40, No. 4, pp 284~289 (2005)

Thermal Aging Behaviors of Resole-Cured Rubber Composites

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(Received November 15, 2005, Revised & Accepted November 30, 2005)

레졸로 가교된 고무 복합체의 열노화 거동

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(2005년 11월 15일 접수, 2005년 11월 30일 수정 및 채택)

ABSTRACT : Changes of crosslink densities of resole-cured NR composites by thermal aging were studied. The thermal aging was performed at 50 - 90 ℃. The crosslink density change increased with increase of the aging temperature and then decreased. Level of the crosslink density change decreased with increase of the resole content. Increase of the crosslink density by the thermal aging was explained with the formations of new crosslinks by combination reactions of pendent groups terminated by resoles and crosslinking reactions by pendent groups having methylol or *o*-methylene quinone intermediate. And decrease of the crosslink density by the thermal aging was explained with the dissociations of the existing crosslinks having dimethylene ether linkages.

요 약 : 레졸로 가교된 NR 복합체의 열노화에 의한 가교밀도변화를 연구하였다. 노화 온도는 50 - 90 ℃였다. 가교밀도 변화는 노화 온도가 올라감에 따라 증가하다 감소하였다. 가교밀도 변화 정도는 레졸 함량이 증가함에 따라 감소하였다. 열노화에 의한 가교밀도의 증가는 레졸로 마감된 매달린 작용기들의 결합 반응과 메틸올이나 메틸렌 퀴논 중간체를 갖는 매달린 작용기의 가교 반응으로 설명하였다. 그리고 열노화에 의한 가교밀도의 감소는 디메틸렌 에테르 연결을 갖는 기존 레졸 가교의 분해로 설명하였다.

Keywords : rubber, thermal aging, resole curing, crosslink density

Ⅰ. Introduction

Crosslink type and degree of crosslink density of a rubber vulcanizate determine the physical properties such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth.[1] By increasing the crosslink density, the modulus, hardness, resilience, and abrasion resistance increase, whereas the elongation at break, heat build-up, and stress relaxation decrease. The stress relaxation, tensile strength, and resilience increase in proportion to the content of di- and polysulfides, whereas the fatigue and thermal aging resistance decrease.

In general, rubber compounds are crosslinked by the sulfur,[1-3] peroxide,[4] or resole cure system.[5] Study on resole curing was begun using NR and IIR.

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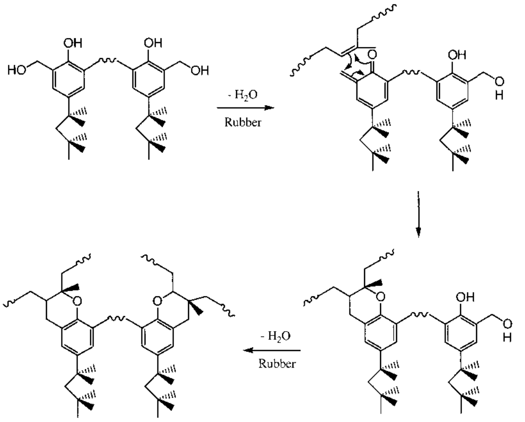


Scheme 1. Mechanism of resole curing.

Crosslinking between unsaturated elastomers and phenolic resole resins was proposed by the chroman mechanism.[6] A phenolic resole is changed to an *o*-methylene quinone intermediate by dehydration at high temperatures as shown in Scheme 1. This intermediate reacts with the double bonds of rubber to form 6-membered ring structures by a 1,4-cycloaddition.[7] In a rubber industry, SP 1045 is employed as a resin curing agent for bladder curing. SP 1045 is one of the alkylphenolic resoles and its general structure is *p-tert*-octylphenol formaldehyde resole. In the present work, thermal aging behaviors of resole-cured natural rubber (NR) composites were studied. We focused on the influence of the aging temperature and the resole content on the thermal aging behaviors.

Ⅱ. Experimental

The rubber compounds were made of NR (SMR 20), carbon black (N330), stearic acid, ZnO, HPPD, wax, and resole (SP 1045). The formulations were given in Table 1. The resole contents were varied to prepare the samples with different crosslink densities. The composites were prepared by curing at 190 ℃ for 30 min. Thermal aging was performed at 50, 60, 70, 80, and 90 ℃ for 4 and 8 days in a convection oven. Crosslink densities of the samples were measured by swelling method. Organic additives in the samples were removed by extracting with THF and n-hexane for 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the dried samples were measured, and then soaked in *n*-decane for 2 days. The weights of the swollen samples were measured. The swelling ratio was calculated as $Q = (W_S - W_u)/W_u$, where W_S and W_u are weights of the swollen and unswollen samples. In general, the reciprocal value of the swelling ratio, 1/Q, is used as crosslink density.

Table 1. Formulations (phr)

Compound No.	1	2	3
SMR20	100.0	100.0	100.0
N330	50.0	50.0	50.0
Stearic acid	2.0	2.0	2.0
ZnO	4.0	4.0	4.0
HPPD	2.0	2.0	2.0
Wax	2.0	2.0	2.0
SP 1045	5.0	10.0	15.0

HPPD: *N*-phenyl-*N′*-(1,3-dimethylbutyl)-*p*-phenylenediamine
SP 1045: *p-tert*-octylphenol formaldehyde resole resin

Ⅲ. Results and Discussion

The crosslink density increases notably with increase of the resole content. Figure 1 shows the changes of the apparent crosslink densities (1/Q) after the thermal aging. The crosslink densities after the thermal aging at 50 - 70℃, on the whole, increase except the NR composite having the resole content of 15.0 phr after the thermal aging at 50 ℃. For the thermal aging at 90 ℃, the crosslink densities after the thermal aging decrease. Changing ranges of the crosslink densities after the thermal aging at 50 - 90 ℃ are relatively small. The changing ranges of 1/Q after the thermal aging for 4 days are 0.06, 0.04, and 0.04 for the vulcanizates containing resoles of 5, 10, and 15 phr, respectively. For the thermal aging for 8 days, the changing ranges of 1/Q are 0.06, 0.06, and 0.03, respectively. The changing range decreases with increase of the

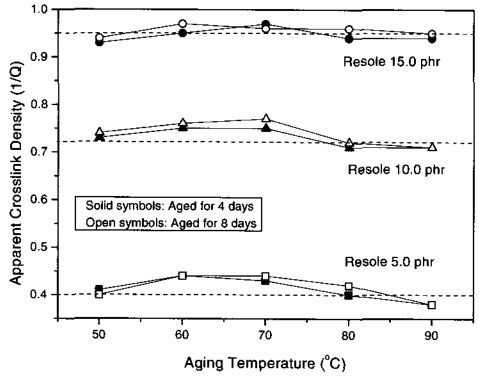


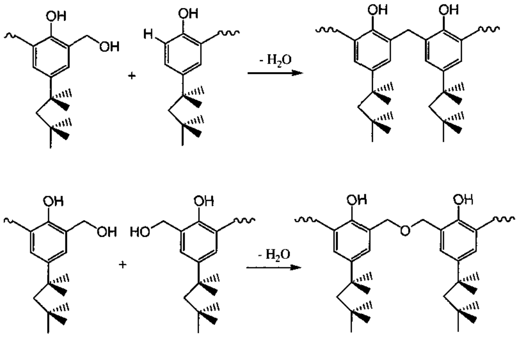
Figure 1. Variation of the crosslink density of the NR composite with the aging temperature. The squares, triangles, and circles indicate the NR composites containing the resoles of 5.0, 10.0, and 15.0 phr, respectively. The solid and open symbols stand for the aging times of 4 and 8 days, respectively. The dash lines are the apparent crosslink crosslink densities before the thermal aging.

resole content in the NR vulcanizate. The difference in the changing ranges depending on the aging time does not show a specific trend.

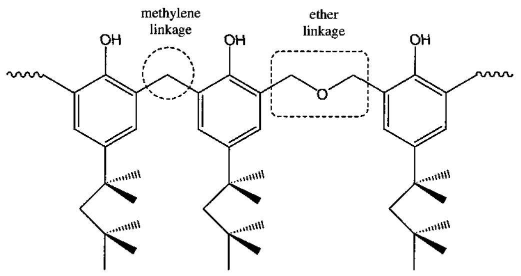
Changes of the crosslink densities of the NR composites after the thermal aging are because of the formations of new crosslinks and the dissociations of the existing crosslinks. Formations of new crosslinks lead to increase of the crosslink density, while dissociations of the existing crosslinks results in decrease of the crosslink density. Formations of new crosslinks and dissociations of the existing crosslinks simultaneously occur during aging of a cured rubber composite. When the formations of new crosslinks occur well more than the dissociations of the existing crosslinks in a cured rubber composite during aging, the crosslink density increases after the aging. On the contrary, the crosslink density increases when the dissociations of the existing crosslinks surpass the formations of new crosslinks.

For the resole-cured rubber composites, the formations of new crosslinks may be due to the pendent groups terminated by resole having a terminal of methylol or *o*-methylene quinone intermediate as shown in Scheme 1. The pendent groups having a terminal of methylol or *o*-methylene quinone intermediate can react with rubber chains to form new crosslinks. The pendent group having a terminal of methylol also reacts with another pendent group having a terminal of methylol or hydrogen to form a new crosslink as shown in Scheme 2. The resole (*p-tert*-octylphenol formaldehyde resole resin) is a series of *p-tert*-octylphenol linked with methylene or dimethylene ether as shown in Scheme 3. The methylene linkage is very stable but the dimethylene ether linkage is less stable. Thus, the ether linkage can be dissociated by thermal aging.[7-9]

Changes of the crosslink densities by the thermal aging were calculated to investigate the thermal aging behaviors in detail. The crosslink density change was obtained by dividing the difference of the crosslink densities after and before the thermal aging by the initial crosslink density. Figure 2 shows variations of the crosslink density changes with the aging temperature. By increasing the aging tem-



Scheme 2. Combination reactions of the pendent resole having a methylol terminal.



Scheme 3. Methylene and dimethylene ether linkages.

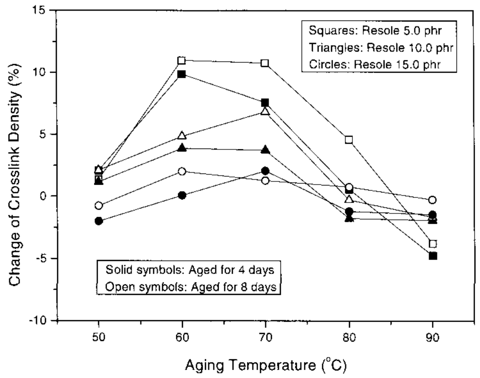


Figure 2. Variation of the crosslink density change of the NR composite with the aging temperature. The squares, triangles, and circles indicate the NR composites containing the resoles of 5.0, 10.0, and 15.0 phr, respectively. The solid and open symbols stand for the aging times of 4 and 8 days, respectively.

perature, the crosslink density change increases and then decreases. The varying level of the crosslink density change of the NR composite with lower resole content is larger than that of the NR composite with higher one. Variation ranges of the crosslink density changes after the thermal aging at 50 - 90 ℃ are 2.8 - 14.8%. The variation ranges after the thermal aging for 4 days are 14.6, 5.8, and 4.1% for the vulcanizates containing resoles of 5, 10, and 15 phr, respectively. For the thermal aging for 8 days, the variation ranges are 14.8, 8.5, and 2.8 %, respectively. The variation range decreases with increase of the resole content in the NR compound. The difference in the variation ranges with the aging time does not show a specific trend.

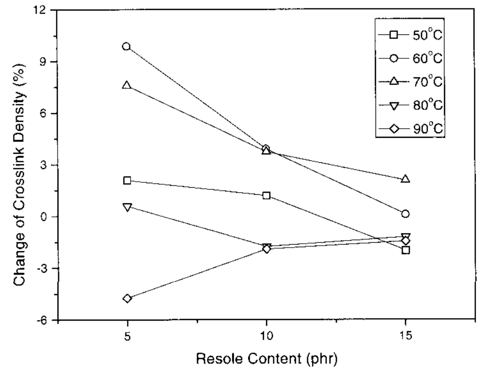


Figure 3. Variation of the crosslink density change of the NR composite after the thermal aging for 4 days with the resole content. The squares, circles, up-triangles, down-triangles, and diamonds indicate the aging temperatures of 50, 60, 70, 80, and 90 ℃, respectively.

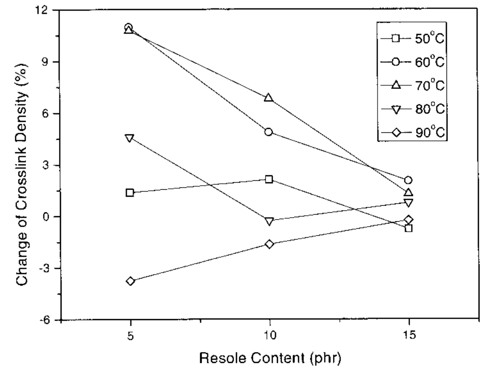


Figure 4. Variation of the crosslink density change of the NR composite after the thermal aging for and 8 days with the resole content. The squares, circles, up-triangles, down-triangles, and diamonds indicate the aging temperatures of 50, 60, 70, 80, and 90 ℃, respectively.

Variations of the crosslink density changes were plotted as a function of the resole content to investigate the influence of the resole content on the crosslink density change by the thermal aging. Figures 3 and 4 give the variations of the crosslink density change with the resole content after the thermal aging for 4 and 8 days, respectively. The variations for the aging times of 4 and 8 days show similar trends. For the thermal aging at 60 and 70 ℃, the crosslink densities increase after the thermal aging but the crosslink density change decreases as the resole content increases. For the thermal aging at 90 ℃, the crosslink densities decrease after the thermal aging and the crosslink density change increases with increase of the resole content. For the thermal aging at 50 and 80 ℃, the whole trends are generally similar to the behaviors at 60 and 70 ℃.

According to the experimental as discussed previously, we believe that the dissociation reactions of the existing resole crosslinks require more energy than the formation reactions of new resole crosslinks. Crosslinking reactions between *o*-methylene quinone intermediate of the resole and C=C double bond of NR is one of the Diels-Alder reactions. The Diels-Alder reactions can occur at relatively low temperatures.[10] But the ether linkage is relatively strong. Average bond dissociation energies of C -O, C - S, and S - S are 350, 260, and 225 kJ/mol, respectively.[11] The bond strength of the ether linkage (C-O) is much stronger than the sulfide linkages (S-S and C-S). Thus, the dissociation reactions can occur well at high temperatures.

Absolute values of the crosslink density changes become smaller as the resole content increases. This may be due to the reaction levels of crosslink formation and dissociation as well as the initial crosslink density. Initial crosslink densities (before the thermal aging) of the NR composites increases as the resole content increases. The initial crosslink densities (1/Q) are 0.40, 0.72, and 0.95 for the NR composites with the resole contents of 5.0, 10.0, and 15.0 phr, respectively. When the increments (or decrements) of the 1/Q after the thermal aging are the same, the crosslink density change (%) of the NR composite with higher resole content is smaller than that of NR composite with lower one. But, this is not the only one reason about the small absolute value of the crosslink density change of the NR composite with higher resole content because the 1/Q changing range after the thermal aging of the NR composite with higher resole content is smaller than that of NR composite with lower one. The another reason may be the numbers of the formation and dissociation reactions. Rate of the dissociation reaction will become faster and faster as the ether linkages increase. New ether linkages can be formed by combination reactions between the pendent groups having a methylol terminal as shown in Scheme 2. And the pendent groups having a methylol terminal can be also formed by dissociation of the existing ether linkage. Thus, these two reactions of the formation and dissociation reactions occur well as the resole content increases, which leads to small change of the crosslink density after the thermal aging.

Ⅳ. Conclusions

Crosslink densities of the resole-cured NR composites were decreased or increased by the thermal aging. The crosslink density change increased with increase of the aging temperature and then decreased. Crosslink density of the NR composite having lower resole content was changed larger than that of the NR composite having higher one. The crosslink densities after the thermal aging at low temperatures of 50 - 70 ℃ on the whole increased, while those at high temperature and 90 ℃ decreased. The decreased crosslink density after the thermal aging can be explained with the dissociation of the dimethylene ether linkage of the crosslinked resole.

Acknowledgements

This research has been supported by Reliability Design Technology Program (grant no. M10401000005) of Ministry of Science and Technology, Korea.

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