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Influence of Initial States of Test Sheets on Adhesion of NR/NR, BR/BR, and NR/BR

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시험편의 초기 상태가 NR/NR, BR/BR, 그리고 NR/BR 접착에 미치는 영향

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ABSTRACT : Adhesion of NR and BR composites with different initial states of precured or uncured conditions was studied. Adhesion between the NR and BR sheets as well as adhesion between the same rubber sheets was investigated. Adhesion forces of the uncured/uncured specimens were larger than those of the cured/uncured and cured/cured ones. The cured/cured samples and uncured NR/cured BR specimen were fully peeled out by the peel test. When one sheet was broken during the peel test, the sheet having the higher crosslink density was broken irrespective of the rubber types. Adhesion forces of the same rubber sheets were higher than those of the different ones and adhesion force of the cured NR/uncured BR sample was higher than that of the uncured NR/cured BR one. The experimental results were explained with the crosslink density and interdiffusion of rubber chains.

요 약 : 초기 상태를 선가황 혹은 미가황으로 다르게 한 NR과 BR 복합체 간의 접착에 대해 연구하였다. 동일한 고무인 NR/NR과 BR/BR 간의 접착뿐 아니라 이종 고무 간의 접착인 NR/BR의 접착도 조사하였다. 미가황 시트 간의 접착력이 선가황/미가황 시험편과 선가황/선가황 시험편보다 우수하였다. 선가황/선가황 시험편과 미가황 NR/선가황 BR시험편은 완전 박리가 일어났다. 박리 시험 중 파단이 일어난 경우, 고무의 종류에 상관없이 두 개의 시트 중에 가교밀도가 높은 곳에서 끊어졌다. 이종 고무 간의 접착력보다는 동종 간의 접착력이 더 우수하였으며, 선가황 NR/미가황 BR의 접착력이 미가황 NR/선가황 BR의 경우보다 더 컸다. 실험 결과는 가교밀도와 고무 사슬의 계면간 확산으로 설명하였다.

Keywords : adhesion, NR, BR, crosslink density, interdiffusion

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Ⅰ. Introduction

Formation of elastomer-to-elastomer adhesion can be described with three steps of wetting, inter-diffusion of rubber chains, and co-crosslinking between the sheets.[1] Self-adhesion (or called autohesion) of elastomers is a time-dependent behavior. Rubber chains diffuse across the interface and chain entanglements and homogenization occur. Crosslinking of the joined polymers leads to the formation of a three dimensional network in the bulk material. When some rubber chains have crossed the interface, they can be covalently bonded to the opposite network.

Blend of two types of rubber has been used for the preparation of new materials with desirable properties absent in the each component rubber. Natural rubber (NR) is blended with synthetic rubber to improve physical and chemical properties. The useful polymer-polymer combination is linked by intermolecular forces such as van der Waals forces or dipole moments and exhibits sufficient thermodynamic compatibility. Saad and El-Sabbagh[2] studied compatibilities of NR with synthetic rubbers such as styrene-butadiene rubber (SBR), polybutadiene rubber (BR), and ethylene-propylene-diene rubber (EPDM), acrylonitrile-butadiene rubber (NBR), and chloroprene rubber (CR) by measuring permittivity and dielectric loss and reported that the NR/SBR and NR/BR blends were compatible while the NR/EPDM, NR/NBR, and NR/CR blends were incompatible.

In the present work, we studied adhesion behaviors of NR/BR sheets depending on the initial states of rubber composites. The uncured and cured rubber composites were used as the initial sheets. Adhesion between the same rubber sheets was also investigated to help understanding the adhesion behaviors of NR/BR. Experimental results for the peel test to measure the adhesion force were explained with the crosslink densities and diffusion of rubber chains through the interfacial region.

Ⅱ. Experimental

The NR and BR compounds were made of rubber (SMR20 or BR01, 100.0 phr), carbon black (N330, 50.0 phr), zinc oxide (4.0 phr), stearic acid (2.0 phr), *N*-phenyl-*N′*-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD, 2.0 phr), wax (2.0 phr), *N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS, 1.5 phr), and sulfur (1.5 phr). The compounds had the same formulations except the rubber type. Mixing was performed in a two roll mill at a roll speed of 18 rpm. The MB compounds were prepared as follow. (1) The rubber was loaded into the two roll mill and preheated for 4.0 min. (2) The carbon black was compounded into the rubber for 10.0 min. (3) The cure activators (ZnO and stearic acid) and anti-degradants (HPPD and wax) were mixed for 6.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives (TBBS and sulfur) with the MB compounds for 5.0 min. The sheet was cut with the dimension of 140× 140 mm^2 and 2 mm thickness.

For the peel test specimens of the same rubber compounds (NR/NR or BR/BR), three type specimens of uncured/uncured, cured/cured, and uncured/cured couples were prepared. The precured sheet was prepared by curing at 160 ℃ for 6.0 and 8.0 min for the NR and BR compounds, respectively, in a press mold (2×140×140 mm^3) since the NR compound had faster optimum cure time than the BR one. The peel test specimens were prepared as follow. (1) Two sheets of paper were inserted between the two rubber sheets in the middle of the rubber sheet and half of the two rubber sheets was attached as shown in Figure 1. (2) The combined rubber sheet was vulcanized at 160 ℃ for 6.0 and 8.0 min for the NR and BR specimens, respectively, in a press mold (4×140×140 mm^3). (3) The inserted papers were removed. For the peel test specimens of NR/BR, four type specimens of uncured/uncured, cured/cured, uncured NR/cured BR, and cured NR/uncured BR couples were prepared by curing at 160 ℃ for 8.0 min.

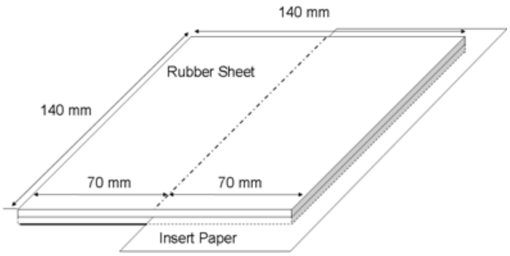

Figure 1. Sample preparation for the adhesion test.

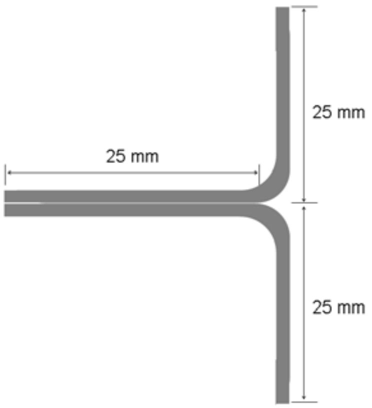

Figure 2. Specimen for peel test with 10 mm width.

Dimension of the peel test specimen was 10×50 mm with the adhesive boundary at the center of the sample. The peel test was performed with DUT-500CM of Daekyung Engineering Co. of Korea and the head speed was 50 mm/min (Figure 2). Crosslink density of the each sheet was measured by swelling method. Organic additives in the sample 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 weight of the organic materials-extracted sample was measured. It was soaked in toluene for 2 days and the weight of the swollen sample was measured. The swelling ratio (Q) was calculated by the equation of $Q = (W_s-W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples. In general, the reciprocal swelling ratio (1/Q) was used as the apparent crosslink density. Experiments were carried out three times and they were averaged.

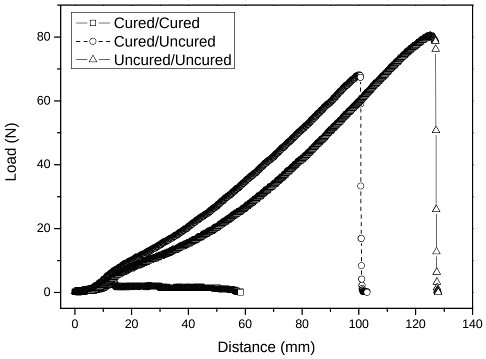

Figure 3. Stress-strain curves for the peel test of the NR/NR specimens. Squares, circles, and triangles indicate the cured/cured, cured/uncured, and uncured/uncured combinations, respectively.

Ⅲ. Results and Discussion

Figure 3 gives the stress-strain curves obtained from the peel test of the NR/NR adhesion specimens. The cured/cured specimen was fully peeled out while the uncured/uncured and cured/uncured specimens were broken before peeling out. For the cured/uncured sample, the broken side is always the precured sheet. This can be explained with the difference in the stiffness of the two sheets. The precured sheet is stiffer than the uncured one since it is doubly vulcanized. The peel test was performed by pulling out the both side and the each sheet got bent at 90° as shown in Figure 2. The bending stress can be more applied to the stiffer sheet.

As expected, the adhesion force of the uncured/uncured sample is higher than the others and the cured/cured specimen shows very low adhesion force. The adhesion forces were summarized in Table 1. Mechanical strength of adhesion between two rubber sheets is directly proportional to the degree of interfacial interlinking.[3] For the uncured/uncured specimen, rubber chains diffuse across the interface and crosslinking reactions in the interfacial region will occur during the vulcanization. We expected that the adhesion force of the cured/uncured sample is much lower than that of the

Table 1. Adhesion forces (N).

	Cured NR	Cured BR	Uncured NR	Uncured BR
Cured NR	1.8	0.8	66.2	31.2
Cured BR	-	1.4	13.6	27.8
Uncured NR	-	-	74.6	39.2
Uncured BR	-	-	-	41.8

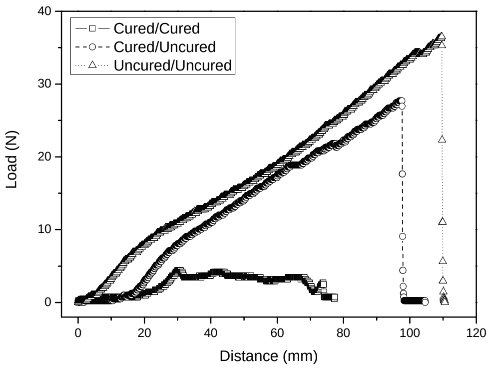

Figure 4. Stress-strain curves for the peel test of the BR/BR specimens. Squares, circles, and triangles indicate the cured/cured, cured/uncured, and uncured/uncured combinations, respectively.

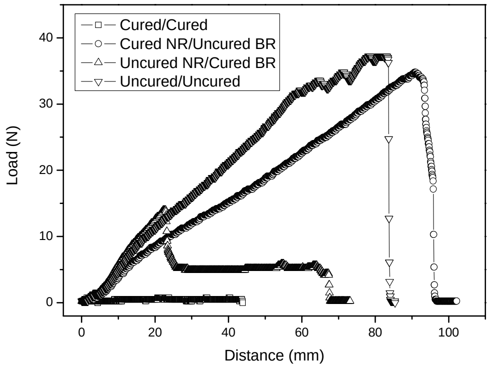

Figure 5. Stress-strain curves for the peel test of the NR/BR specimens. Squares, circles, up-triangles, and down-triangles indicate the cured/cured, cured NR/uncured BR, uncured NR/cured BR, and uncured/uncured combinations, respectively.

uncured/uncured one. However, the cured/uncured specimen has relatively high adhesion force as shown in Figure 3. This means that interdiffusion of rubber chains in the interfacial region of the cured/uncured specimen actively occurs during the vulcanization.

The BR/BR specimens also show the same trend as the NR/NR ones (Figure 4). The cured/cured specimen was fully peeled out and the others were broken before peeling out. The precured sheet is also always broken for the cured/uncured sample. The precured sheet is stiffer than the uncured one since apparent crosslink density (1/Q) of the former is higher than that of the latter. The 1/Qs of the precured and uncured sheets are 1.52 and 1.36, respectively. Stiffness of a rubber vulcanizate is a proportional property to the crosslink density.[4] The adhesion force of the uncured/uncured sample is higher than the others and the cured/cured specimen shows very low adhesion force as shown in Figure 4. The adhesion forces of the BR/BR specimens are much lower than those of the NR/NR ones as shown in Table 1. This implies that interdiffusion of materials in the interfacial region for the NR/NR samples more actively occur than for the BR/BR ones.

Adhesion property of the NR/BR specimen is varied with the initial states of the two rubber sheets as shown in Figure 5. The cured/cured specimen was fully peeled out and the uncured NR/cured BR specimen was also fully peeled out. All the uncured/uncured and cured NR/uncured BR specimens were broken in the BR sheet. These experimental results are very interesting. The fully peeling out of the uncured NR/cured BR sample indicates that NR chains in the uncured sheet can not diffuse into the precured BR sheet whereas the experimental results of the uncured NR/BR cured specimen means that BR chains in the uncured sheet can diffuse into the precured NR sheet. For the the uncured/uncured and cured NR/uncured BR specimens, the 1/Q of the BR sheet is higher than that of the NR sheet irrespective of the initial states. The 1/Qs of the NR and BR sheets for the uncured/uncured sample are 1.05 and 1.25, respectively, and those for the cured NR/uncured BR one are 1.06 and 1.48, respectively.

This means that the broken side depends on the stiffness including crosslink density.

Adhesion force of the cured NR/cured BR specimen is much lower than that of the cured/cured samples with the same rubber sheet. For the uncured/uncured specimens, the adhesion force of the NR/NR is much higher than those of the BR/BR and NR/BR. For the cured/uncured samples, the adhesion force of the NR/NR is also higher than the others. The adhesion force of the cured NR/uncured BR sample is much higher than that of the uncured NR/cured BR one as listed in Table 1. This can be also explained by the crosslink density. The cured/uncured sample of the BR sheets and the cured NR/uncured BR specimen were broken in the BR sheet while the uncured NR/cured BR sample was fully peeled out. The 1/Qs of the BR sheets for the uncured NR/cured BR, cured BR/uncured BR, and cured NR/uncured BR specimens are 1.61, 1.52, and 1.48, respectively. The specimen composed of the sheet with the higher crosslink density shows lower adhesion force than that with lower one.

Let us consider the big difference in the adhesion behaviors of the cured NR/uncured BR and uncured NR/cured BR specimens as discussed previously. NR and BR compounds having sulfur cure systems show different cure characteristics. In general, NR compound has faster cure rate than a BR one while the former has lower crosslink density than the latter.[5] For the uncured/cured specimens, interdiffusion of rubber chains will occur from the uncured sheet to the cured one during the vulcanization. In order for some rubber chains to diffuse across the interfacial region, the precured sheet having lower crosslink density is more favorable than that having higher one because the less the crosslink density is the more the flexible (or loose) region in the interface is. Since a rubber vulcanizate with lower crosslink density has more loose area, solvent swelling ratio is larger compared to that with higher crosslink density. Crosslink densities of the BR sheets are much higher than those of the NR ones as discussed above. Therefore we can say that the precured BR sheet with higher crosslink density protects the interdiffusion of NR chains from the uncured NR sheet to the cured BR one whereas that the precured NR sheet with lower crosslink density accepts the interdiffusion of BR chains from the uncured BR sheet to the cured NR one. This leads to the difference in the adhesion behaviors of the NR/NR, BR/BR, and NR/BR specimens.

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References

1. F. Ruch, M. O. David, and M. F. Vallat, "Adhesion in EPDM joints: Role of the interdiffusion mechanism on interfacial co-crosslinking", *J. Polym. Sci. B: Polym. Phys.*, **38**, 3189 (2000).
2. A. L. G. Saad and S. El-Sabbagh, "Compatibility studies on some polymer blend systems by electrical and mechanical techniques", *J. Appl. Polym. Sci.*, **79**, 60 (2001).
3. A. N. Gent, "The role of chemical bonding in the adhesion of elastomers", *Int. J. Adhesion Adhesives*, **1**, 145 (1980).
4. N. J. Morrison and M. Porter, "Temperature effects on the stability of intermediates and crosslinks in sulfur vulcanization", *Rubber Chem. Technol.*, **57**, 63 (1984).
5. S.-S. Choi, "Cure characteristics of carbon black-filled rubber compounds composed of NR, SBR, and BR", *Elastomer*, **35**, 215 (2000).