Korean J. Chem. Eng., **15**(3), 317-323 (1998)

IMPROVING ADHESION PROPERTIES BETWEEN RUBBER COMPOUND AND BRASS-PLATED STEEL CORD BY THE ADDITION OF EPOXIDIZED NATURAL RUBBER TO RUBBER COMPOUND

Gyung Soo Jeon, Min Hyeon Han* and Gon Seo†**

Department of Chemical Technology, Provincial College of Damyang, Chonnam 517-800, South Korea
*Kumho Tire Co. & Ltd., R&D Center, Kwangju 506-040, South Korea
**Department of Chemical Technology, Chonnam National University, Kwangju 500-757, South Korea
(*Received 5 January 1998 • accepted 10 April 1998*)

Abstract – The adhesion between a rubber compound containing epoxidized natural rubber (ENR) and a brass-plated steel cord was studied to shed light on the role of ENR for the improvement of adhesion. The addition of ENR in the rubber compound caused cure rate to decrease, and as ENR loading increased, modulus and hardness increased while tensile strength and elongation at break decreased. An improvement of adhesion was obvious with low loading of ENR at the range of 2 phr, while an adverse effect was observed with higher concentrations of 10 phr. Since the ratio of sulfur to copper at the interphase of the rubber compound/brass film adhesion sample increases with increased ENR loading up to 2 phr, the acceleration of sulfide formation by ENR could be proven. Adequate curing of rubber and the formation of high-molecular layer at the interphase by addition of small amount of ENR improve adhesion. However, the toughening of the rubber caused by the addition of larger amounts of ENR degrades the adhesion due to the poor physical properties of the rubber compound.

Key words : Adhesion Interphase, Rubber-to-Brass Bonding, Adhesion Promoter, AES, Depth Profile, Epoxidized Natural Rubber

INTRODUCTION

Brass-plated steel cord is typically used to reinforce tire belts and carcasses to improve the durability of their structure. The brass plating on the cord reacts with the sulfur present in the rubber compound during the tire curing process, forming an adhesion interphase between the rubber and the steel cord. Therefore, a thick and stable interphase is essential for good adhesion.

Copper and zinc sulfides, and oxides and hydroxides of copper and zinc are formed at the adhesion interphase by the reaction of brass with sulfur, oxygen and water in the rubber compound [van Ooij, 1977; van Ooij and Kleinhesselink, 1980]. This demonstrates the chemical complexity of the adhesion interphase, which varies with the composition of the rubber compound and brass as well as the curing conditions [van Ooij, 1978; van Ooij et al., 1981]. Adhesion becomes weak when the thickness of the copper sulfide layer is insufficient, but excessive formations of copper sulfide and zinc oxide also bring about cohesive failures. Severe proliferation of copper sulfide and zinc oxide into the rubber also leads to poor adhesion [Hammer et al, 1994]. A depth profile measured by surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) gives information about the adhesion interphase [van Ooij, 1977; van Ooij and Kleinhesselink, 1980; Kurbatov et al., 1991a,b; Hammer et al., 1994]. Adhesion samples prepared by letting rubber compound react with thin brass film deposited on glass are useful in obtaining homogeneous and reproducible depth profiles, compared to mechanically broken rubber compound-steel cord samples [Coppens et al., 1987; Seo, 1997].

Many studies for stable adhesion have thus already been carried out regarding the optimal rubber composition [Ishikawa, 1984] and curing conditions, as well as copper content and brass plating thickness [Haemers and Mollet, 1978]. Since activated sulfur is involved not only in the crosslinking of rubber but also in the formation of the adhesion interphase, adhesion is strongly dependent on curing conditions (time and temperature) and on the amount and species of the sulfur activating additives (sulfur, accelerator, activator, cobalt salt, resin systems etc.). Cobalt salt is used as an adhesion promoter to accelerate the activation of sulfur at the interphase by inducing the formation of an adequate copper sulfide layer, thus making better adhesion possible [Barker, 1981; van Ooij and Biemond, 1984b; Seo et al., 1990]. However, an adverse effect is observed for rubber compounds with high levels of cobalt salt, or after humidity aging, due to the formation of an excessive copper sulfide layer which induces cohesive failure [Jeon et al., 1998]. Hence, an organic adhesion promoter which loses its potency after curing would more effective in reducing adhesion loss.

ENR was introduced as an adhesion promoter by Boscott and Lehrle [1990], but almost nothing has been so far reported about its role in enhancing adhesion between rubber com-

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[†] To whom all correspondence should be addressed.
E-mail : gseo@orion.chonnam.ac.kr

pound and brass-plated steel cord. Also, Seo et al., have reported that poly (glycidyl methacrylate), an epoxy derivative, improves not only physical properties of vulcanizate [1993], but also adhesion properties between rubber compound and brass-plated steel cord [1992]. Thus, it would be helpful for the design of adhesion promoters to verify the function of ENR at the adhesion interphase.

The aim of this study is to show how ENR acts as an adhesion promoter. The effects of ENR on adhesion between rubber compound and brass-plated steel cord were examined based on the formation and degradation of the adhesion interphase from depth profiles of rubber compound/brass film samples.

EXPERIMENTAL

1. Stock Preparation

The ENR, Epoxyprene-50 (R.R.I.M., Malaysia), was used for the preparation of seven rubber stocks with different amounts of ENR. Fig. 1 shows the IR spectra of natural rubber and ENR. A medium intensity symmetric stretching vibration band at about 1,250 cm^{-1} and a medium intensity asymmetric band between 950 and 815 cm^{-1} indicate the presence of epoxide group in ENR.

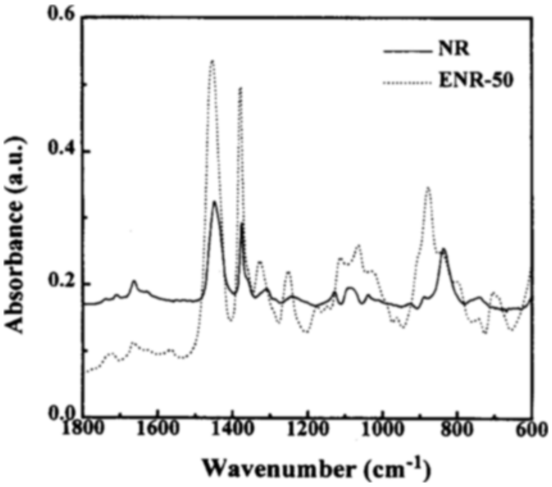

Fig. 1. IR spectra for natural rubber and epoxidized natural rubber.

Formulations for masterbatches and final mixed compounds are given in Table 1. The loading amounts of ENR were 0, 1, 2, 4, 8, 10 and 20 phr. All the rubber compounds were mixed as described in ASTM D-3184 using an internal mixer (Banbury Mixer model 82, Farrel Co., U.S.A.). Ingredients for masterbatch were mixed for 10 min at a rotor speed of 40 rpm and dumped at 150 °C. After the masterbatch was cooled down to room temperature, the final mixing components were added and blended for 5 min at 30 rpm and dumped at 90 °C. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co., U.S.A.).

Rheocurves were recorded using a Monsanto Rheometer 100 at 160 °C. T_{90} time and maximum torque were obtained from those rheocurves. Mooney viscosity was also measured by Monsanto MV-200 machine according to ASTM D-1646.

Hardness of the vulcanizate was measured using a Shore A durometer according to ASTM D-2240, and tensile properties were determined by a tensile tester (model 6021, Instron, U.S.A.) as described in ASTM D-412.

2. Adhesion Test

By the procedure described in ASTM D-2229, specimens for T-test were cured at 160 °C on a cure press. Curing was maintained 5 min longer than T_{90} time. Brass-plated steel cord (4×0.28) manufactured by Hyosung T&C Co., Korea was used. The plating weight of the brass was 3.6 g/kg and the copper content 63.6 %. For humidity aging, specimens were placed in a humidity chamber at 85 °C under 85 % relative humidity for 5, 10 and 15 days. Thermal aging was performed at 90 °C.

Table 1. Rubber compound recipe

Material	Trade name	Manufacturer	Contents (phr)
Masterbatch			
NR	SMR-20	Lee Rubber Co., Malaysia	variable
ENR	Epoxyprene-50	R.R.I.M., Malaysia	variable
Carbon black	N330	Lucky Co., Korea	55
Processing oil	A#2	Michang Co., Korea	5
Activator	ZnO	Hanil Co., Korea	10
Antioxidant	Kumanox-RD[1]	Monsanto Co., U.S.A.	1
Bonding agent	Manobond 680C[2]	Rhone Poulenc Co., France	0.4
Bonding agent	B-18-S[3]	Indspec Co., U.S.A.	2
Final Mixing			
Activator	Stearic acid	Pyungwha Co., Korea	1.5
Bonding agent	Cyrez-964[4]	Cytec Co., U.S.A.	3
Accelerator	Santocure MOR[5]	Monsanto Co., U.S.A.	0.7
Sulfur	Crystex HS OT20	Akzo Co., The Netherlands	5

1) 2,2,4-trimethyl-1,2-dihydroquinone
2) Cobalt boroacylate, Co 23 wt%
3) Resorcinol formaldehyde resin
4) Hexamethoxymethylmelamine 65 %+Hisil-233 35 %
5) 2-(Morpholinothio)-thiobenzothiazole

Pullout force was determined as the maximum force exerted by the tensile tester on a T-test adhesion sample during pullout test, with 10 mm/min of crosshead speed. Rubber coverage was also noted. Each value reported was an average of six specimens. Scanning electron microscopy (SEM, JEOL JSM 7400) was used to investigate the fracture mode of adhesion.

3. Observation of Depth Profile of Adhesion Interphase

A thin brass film with the Cu/Zn ratio of 70/30 was sputtered onto a glass plate (Marienfeld, Germany, 75×25 mm) using an RF Magnetron sputter for 120 sec at 2×10^{-6} Torr. RF power was controlled to 250 W. The thickness of the film was confirmed to be 150 nm by SEM (JEOL JSM 7400).

A brass-on-glass plate was sandwiched between two uncured pads of each rubber compound, which were then placed in a pad mold. Curing and aging conditions for rubber compound/brass film samples were kept the same as in the preparation of T-test specimens.

Depth profiles from the outer brass surface to the rubber bulk were recorded on an Auger electron spectroscope (Perkin-Elmer Phi 670). An area of 10×10 mm^2 surface was examined at a potential of 5.0 keV, a current of 0.03 mA and an incident angle of 30° to the specimen. Surface concentrations were determined from the Auger peaks of detected elements with compensation for their sensitivities at every 0.5 min. Data were collected in dE N(E)/dE mode using a lock-in amplifier with a 20 ms time constant and an analyzer modulation of 6 eV peak-to-peak. A sputter gun with an argon ion beam rastered on 2×2 mm^2 area was used for the depth profiling. The sputtering rate for the brass film was determined to be 25 nm/min. It is difficult however to determine precisely the sputtering rate for the adhesion interphase because it includes various chemical components with variable concentrations. Therefore, sputtering time instead of absolute depth was used to indicate the depth of the adhesion interphase in this paper.

RESULTS

1. Physical Properties of ENR-blended Rubber Compounds

Cure rates for the rubber compounds were varied with the degree of ENR loading as indicated in Table 2. The T_{90} value was constant up to 2 phr and increased with increasing ENR content over 2 phr, whereas the T_2 value decreased slightly. Therefore the cure rate index (CRI), calculated from T_{90} and T_2 values, decreased with the addition of ENR. Maximum torque increased with increases in ENR loading, indicating higher crosslinking density.

Time-dependent viscosity changes in green compounds at 125 °C are shown in Table 3. With increasing ENR loading, the T_5 value indicating the onset of scorch time decreased, and viscosity deduced from torque increased steadily except for the rubber compound containing 20 phr of ENR.

The physical properties of unaged vulcanizates are summarized in Table 4. Hardness and modulus increased with the addition of ENR. Tensile strength and elongation at break decreased monotonously with ENR loading. Compared with unaged vulcanizate, modulus increased but tensile strength became smaller upon thermal aging (Table 5).

2. Adhesion Properties of ENR-contained Rubber Compound

Pullout force and rubber coverage for the adhesion samples

Table 2. The result of oscillating disc type rheometer[1] with respect to ENR content in rubber compounds

ENR content	Time (min)		CRI	Torque (J)	
(phr)	T_2	T_{90}	(min^{-1})	min	max
0	2.5	10.1	13.2	1.67	6.58
1	2.4	10.1	13.0	1.74	6.47
2	2.3	10.1	12.8	1.75	6.58
4	2.4	10.5	12.3	1.88	6.71
8	2.2	10.7	11.8	1.83	6.98
10	2.2	12.5	9.7	1.84	7.21
20	2.1	17.5	6.5	1.63	7.75

[1] The rubber compounds were sheared to 1° and 1.67 Hz at 160 °C.

Table 3. The result of Mooney viscometer test[1] with respect to ENR content in rubber compounds

ENR content	Time (min)		Torque (J)		
(phr)	T_5	T_{35}	initial	min	at 4 min
0	15.2	23.1	6.97	5.48	5.64
1	14.5	21.7	7.47	5.84	6.01
2	14.1	21.1	7.50	5.91	6.04
4	14.7	21.1	8.13	6.27	6.54
8	13.3	19.7	7.93	6.21	6.41
10	13.5	19.3	8.00	6.54	6.61
20	10.5	17.5	7.04	5.88	5.71

[1] The rubber compounds were sheared to 2 rpm at 125 °C.

Table 4. Physical properties of vulcanizates with respect to ENR content in rubber compounds

ENR content	Hardness	Modulus (MPa)			T.S.	E.B.
(phr)		100 %	200 %	300 %	(MPa)	(%)
0	79	5.50	13.0	19.8	23.6	370
1	81	5.84	13.1	19.7	21.3	335
2	82	6.16	13.3	19.8	21.0	324
4	84	6.76	13.9	20.1	20.6	311
8	86	6.96	13.9	20.0	21.1	322
10	88	8.48	15.3	–	17.8	246
20	91	10.84	–	–	14.3	148

Table 5. Physical properties of vulcanizates after thermal aging[1] with respect to ENR content in rubber compounds

ENR content	Hardness	Modulus (MPa)			T.S.	E.B.
(phr)		50 %	200 %	300 %	(MPa)	(%)
0	88	7.10	–	–	7.22	51
1	90	7.88	–	–	8.77	62
2	91	8.10	–	–	9.04	58
4	93	9.55	–	–	9.39	47
8	95	9.91	–	–	10.11	50
10	97	–	–	–	11.92	30
20	99	–	–	–	13.86	8

[1] The tensile-test samples were thermally aged for 5 day at 105 °C.

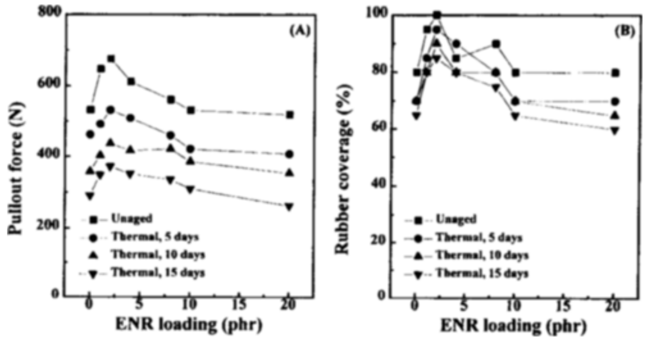

Fig. 2. Adhesion properties of ENR loaded rubber compounds. Humidity aging : 85 °C and 85 % relative humidity for 15 days.

containing ENR with brass-plated steel cord before and after humidity aging are shown in Fig. 2. There were considerable increases in pullout force and rubber coverage with ENR loading. In fresh samples without aging, pullout force increased abruptly up to 2 phr of ENR, and then decreased slowly. Rubber coverages followed the same trend as pullout force. Though pullout force and rubber coverage decreased in part after humidity aging, the enhancement in the adhesion with ENR loading at low levels was significant. After aging for 15 days, pullout force increased with ENR loading up to 2 phr. Beyond this loading level, pullout force decreased slightly. The pullout force for the sample loaded with 20 phr of ENR, either unaged or after humidity aging, was similar to that of ENR-free compounds. Rubber coverage showed complex behaviors for ENR loading and humidity aging time. For the adhesion samples subjected to 5 days humidity aging, rubber coverage was constant regardless of ENR loading. However with increased humidity aging time, rubber coverage increased considerably with ENR loading to 2 phr, but over this loading level rubber coverage decreased.

The enhancement of adhesion properties by the addition of ENR was also observed after thermal aging as shown in Fig. 3. The trend for pullout force with thermally aged adhesion samples with ENR loading was similar to that of humidly aged adhesion samples. So was the rubber coverage on the pulled-out steel cord. Rubber coverage on thermally aged samples increased dramatically with the addition of ENR up to 2 phr, but over this level of ENR loading rubber coverage decreased. This improved rubber coverage in ENR loaded adhesion samples suggests that fracture occur predominantly at the rubber layer instead of the adhesion layer.

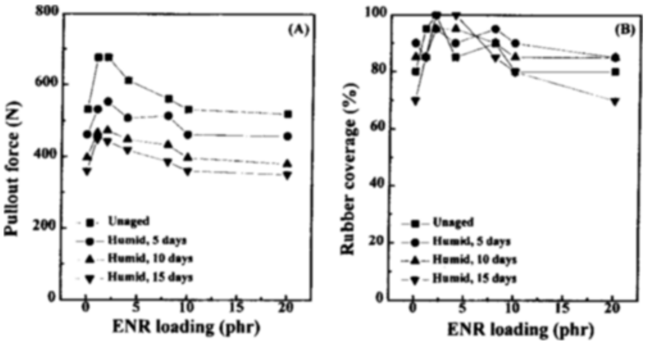

Fig. 3. Adhesion properties of ENR loaded rubber compounds. Thermal aging : 90 °C for 15 days.

To summarize ENR loading enhances adhesion properties at low loading levels, below 2 phr. The enhancement in pullout force and rubber coverage is diminished with higher loadings of ENR such as 10 and 20 phr. These findings suggest that the contribution of ENR loading to good adhesion is significant with low loading. The disappearance of such enhancement with higher loading indicates the presence of two contrary contributions, positive and negative, of ENR to adhesion. At high loading, the negative contribution of ENR outweighs the positive enhancement observed at low loading.

3. Characterization of Adhesion Interphases

Such adhesion properties as pullout force and rubber coverage varied with the loading level of ENR. Since adhesion properties depend primarily on the adhesion interphase, it is reasonable to interpret the difference in the adhesion behaviors through observation of the adhesion interphase. On this point of view, the structure and state of the adhesion interphase between ENR loaded rubber compound and the thin brass film deposited on glass plates were investigated.

Fig. 4 shows the depth profiles of the unaged adhesion interphase prepared using brass film and the rubber compound with various ENR concentrations. On the outer surface for 1 min of sputtering, carbon, zinc, copper and oxygen were detected. Since zinc has a high affinity for oxygen, the concentration of zinc at the outer surface is high compared to the that of copper due to migration of zinc to the surface. Carbon on the outer surface is thought to arise from partial contamination. A constant ratio of copper to zinc is observed at the region of sputtering time from 1 to 3 min, indicating that the brass layer has not reacted. Copper content decreased after sputtering of 3 min. After sputtering of 4 min, a peak showing sulfur content was observed. Peaks of zinc and oxygen were observed after sputtering of 3-5 min. After sputtering of 6 min, the concentrations of copper, zinc, oxygen and sulfur diminished and that of carbon increased very rapidly, indicating the rubber bulk. This depth profile is a typical adhesion interphase between rubber compound and brass film [van Ooij, 1984a; Seo, 1997]. The facts that the peaks of zinc and oxygen were observed on the brass layer and those of copper and sulfur were observed on rubber layer accord well with van Ooij's mechanism, in which adhesion is built up through the penetration of copper sulfide to the rubber bulk.

The schematic shapes of the adhesion interphase are almost the same even when the loading amount of ENR is changed from 0 to 20 phr. But the relative concentrations of sulfur and copper at the interphase vary with ENR concentration. With increasing ENR up to 2 phr in the adhesion sample, the ratio of sulfur to copper increased. But the ratio did not change noticeably in the range from 4 to 20 phr of ENR loading. The ratio of zinc to oxygen increased with ENR loading.

This suggests that ENR accelerates the formation of sulfide at the adhesion interphase with low loading of ENR. At the adhesion interphase for the ENR loading of 2 phr, sulfur concentration is quite high compared to the concentration of copper, indicating the concomitant formation of zinc sulfide.

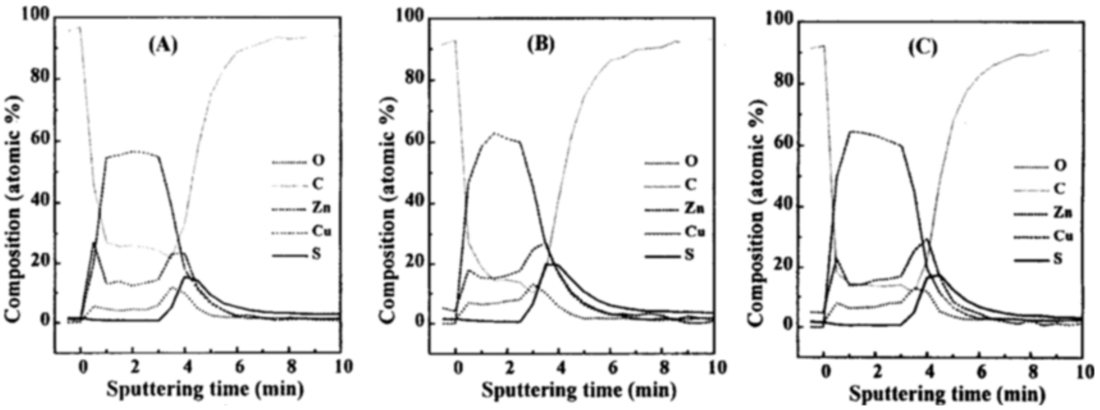

Fig. 4. Depth profiles of the adhesion interphase for unaged rubber compound/brass film with respect to ENR loading.
(A) 0 phr, (B) 2 phr, and (C) 20 phr.

The fact that peaks of zinc became larger whereas those of oxygen remain constant with increasing ENR loading also supports the large formation of zinc sulfide. Usually copper is more concentrated than zinc on the rubber side [Seo, 1997], but the zinc peak in the rubber compound with 20 phr of ENR shifts toward the rubber side beyond the copper peak. Furthermore, the considerable discrepancy between copper and sulfur peaks for the rubber with 20 phr of ENR is a result of the remarkable formation of zinc sulfide.

The adhesion interphase grows and spreads widely after humidity and thermal aging because additional copper and zinc sulfides and oxides are formed, and they penetrate into the rubber bulk. Therefore, it is not usual to observe distinct structure in the adhesion interphase after long aging treatments.

Fig. 5 shows the depth profiles of the humidity aged adhesion interphase prepared using a brass film and rubber compound with various ENR loadings. The adhesion interphase for ENR-free rubber is diminished after 15 days of humidity aging, but those for ENR containing rubber remain intact. Compared to the adhesion interphase before aging, the intensity of the zinc peak for humidity aged adhesion samples with 2 phr of ENR increased. Though the sulfur peak after 15 days of humidity aging was large for the rubber compound with 2 phr of ENR, there was no remarkable change in sulfur peaks as a result of humidity aging. The changes in oxygen peaks with humidity aging are not significant for ENR contained rubber.

This indicates that the adhesion layer grows and penetrates the rubber significantly in a humid atmosphere for ENR-free rubber due to the lack of adhesion stability. With the addition of ENR, the structure of the adhesion interphase was maintained even after 15 days of humidity aging, resulting in an improvement of adhesion stability. With increasing ENR loading up to 2 phr, zinc and sulfur peaks become larger, while there is no considerable change in oxygen peaks. Usually the content of zinc oxide increases with humidity aging. The excessive growth of zinc oxide during humidity aging is inhibited by ENR loading. When 20 phr of ENR was added, the change in the adhesion interphase with humidity aging was very small. Brass layer was still remained. The sulfur peak was small compared to that of 2 phr loaded ENR adhesion sample. The influence of ENR on the adhesion interphase of humidity aged adhesion samples would be related to the improvement of adhesion stability, and the decrease in the sulfur peak for rubber with high loadings of ENR might be the cause of the enhancement of adhesion properties by low loadings of ENR.

The depth profiles of the thermal aged adhesion interphase prepared using a brass film and the rubber compound with various ENR loadings are shown in Fig. 6. A small portion

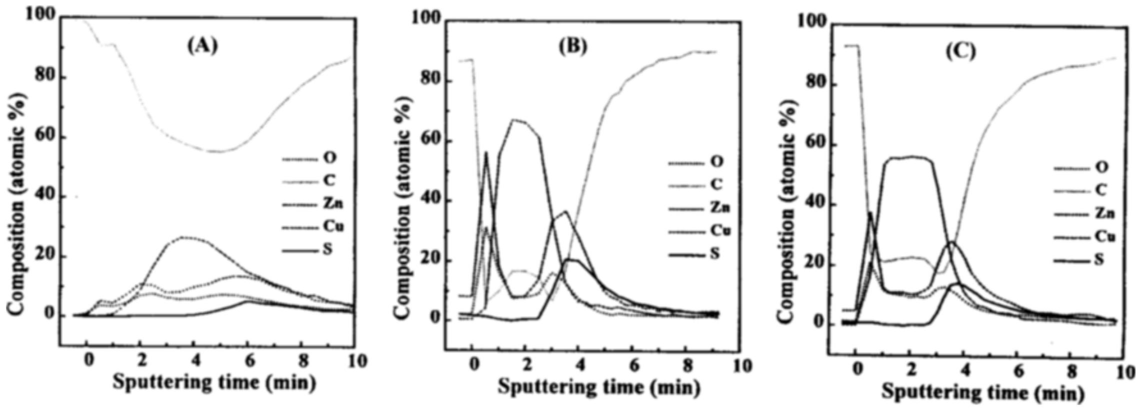

Fig. 5. Depth profiles of the adhesion interphase for humidity-aged rubber compound/brass film with respect to ENR loading.
(A) 0 phr, (B) 2 phr, and (C) 20 phr. Humidity aging; 85 °C and 85 % relative humidity for 15 days.

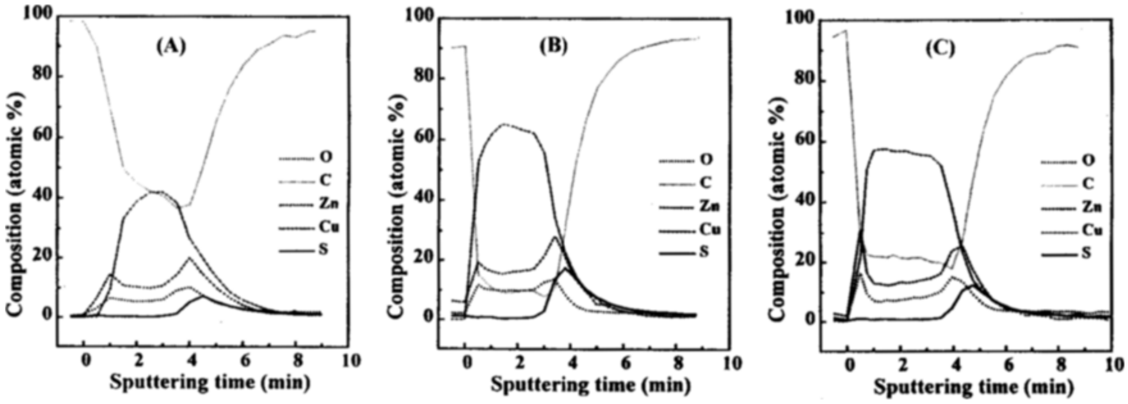

Fig. 6. Depth profiles of the adhesion interphase for the thermal-aged rubber compound/brass film with respect to ENR loading. (A) 0 phr, (B) 2 phr, and (C) 20 phr. Thermal aging; 95 °C for 15 days.

of the adhesion interphase was still retained after thermal aging even for ENR-free rubber. The adhesion interphase was nicely maintained after 15 days of thermal aging for ENR loaded rubber. The intensity and width of the sulfur peak did not change noticeably compared to the adhesion interphase before aging. The shapes of the profiles after thermal aging were similar to the adhesion interphase after humidity aging, but the magnitude of the changes with thermal aging was relatively small.

DISCUSSION

With increasing the loading amount of ENR in the rubber compound, cure rates decreased and the optimum cure time increased. Slow cure rates for ENR loaded rubber compound are induced by the reaction of activating sulfur with the epoxy group of ENR. On the other hand, some of the epoxy groups in ENR react with the double bond of the other rubber molecule, contributing the high crosslinking density. The increase in the crosslinking density of the cured rubber after ENR loading could be verified from the increase in modulus and the decrease in tensile strength and elongation at break with increasing loading level of ENR.

The adhesion properties were improved by ENR loading in the rubber compound, and this enhancement was significant at low concentrations. However, when the ENR loading became as high as 10 phr or more, the enhancement disappeared. This improvement in the adhesion with ENR loading was also observed after thermal and humidity aging.

The schematic shapes of the unaged adhesion interphase obtained from various rubber compound/brass film samples were similar regardless of the amount of ENR loading. But the concentrations of sulfur and zinc at the interphase were, depending on the amount of ENR and aging, quite different. Copper sulfide and zinc oxide were major components at the interphase of the ENR-free rubber compound and they increased concomitantly with aging treatment [Lievens, 1986; van Ooij et al., 1991]. The excessive growth of these materials induced cohesive failure, resulting in the degradation of adhesion properties. On the other hand, rubber compounds containing ENR showed high stability at the adhesion interphase. The adhesion interphase was retained even after thermal and humidity aging. No meaningful change in the adhesion interphase was observed for rubber with 20 phr of ENR. The improvement of the adhesion stability is obvious for ENR loaded rubber, as can be seen from the depth profiles shown in Fig. 4, 5 and 6.

The magnitude of sulfur peaks at the adhesion interphase for ENR loaded rubber varied with the loading level. Sulfur peaks increased up to 2 phr of ENR and decreased for higher loading of ENR. The non-coincidence between copper and sulfur was large for rubber containing 2 phr of ENR. The zinc peak was extraordinarily large for the rubber containing 2 phr of ENR after humidity aging. On the other hand, there was no significant difference in oxygen peaks even after humidity aging.

Though the changes in the constituents at the adhesion interphase with loading level of ENR and aging treatments were very complex, but they can be explained by the way ENR controls curing rates and the rate of sulfide growth. The restriction of mass transfer by a highly crosslinked network might be accepted as one of plausible explanation. The migration of vulcanizing ingredients to the adhesion interphase decreases as curing progresses, limiting the formation of sulfide. Therefore, the slower curing caused by ENR loading results in the sufficient formation of copper sulfide at the adhesion interphase, improving adhesion. But for rubber with high loadings of ENR, excessive crosslinking density due to the incorporation of epoxy groups inhibits the steady supply of vulcanizing ingredients to the adhesion interphase. Thus the growth of copper sulfide dwindles with increased loading of ENR, inducing poor adhesion. This restriction of mass transfer by ENR might be similar to bonding systems consisting of resin and methylene donors forming protective layers of high molecular weight near to the adhesion interphase to improve its stability [Seo, 1997]. Thus the only considerable enhancement of adhesion properties occurred at low loadings of ENR, when the negative effects of rubber hardening caused by higher loadings of ENR were not significant.

The abundance of zinc sulfide at the adhesion interphase for the rubber with 2 phr of ENR also contributes to adhesion stability against humidity aging, because the reactivity of zinc sulfide to water is low compared to that of zinc oxide. In addition, the capture of water by the epoxy group in ENR may contribute to inhibit dezincfication at the adhesion interphase. Though these explanations on the increased stability of the adhesion interphase by ENR loading are plausible, more systematic studies will be required for quantitative confirmations.

The action of ENR in controlling curing rate and material migration by ENR loading is most important for understanding how ENR acts as an adhesion promotor. The optimum formation of sulfides and the stability of the adhesion interphase seem to be controlled by ENR, resulting in the enhancement of adhesion at low loadings. However, higher loadings of ENR result in rubber hardening and the deficient formation of sulfides at the adhesion interphase. The degradation of rubber properties at high loadings outweigh the enhancement observed at low loadings, eliminating the positive contribution of ENR to adhesion. These results support the use of ENR as an adhesion promotor without adverse effects at low loadings, to help a sufficient adhesion interphase develop, and to suppress its excessive growth.

CONCLUSION

There was significant enhancement of the adhesion between rubber compound and brass-plated steel cord with the addition of ENR to the rubber compound with low levels such as 2 phr. The optimum formation of sulfides and the improvement of the adhesion interphase were considered plausible causes for the enhancement. The hardening of rubber with greater amounts of ENR, inducing the degradation of rubber properties, is the cause of the negative contribution. Thus there was considerable enhancement of adhesion with the addition of low loadings of ENR since, in small amounts, its negative contribution of rubber hardening was not significant.

ACKNOWLEDGMENTS

The authors wish to thanks Dr. Kim, Y. M., Dr. Han, S. H. and Lee, J. H. at Advanced Analysis Center in Korea Institute of Science and Technology (KIST) for analysis of adhesion interphase samples using Auger Electron Spectroscope.

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