Effects of Cure Levels on Adhesion Between Rubber and Brass in the Composites Made Up of Rubber Compound and Brass-Plated Steel Cord

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(*Received 10 September 2002 • accepted 16 January 2003*)

Abstract−The adhesion between rubber compound and brass-plated steel cord of rubber-brass composites with different cure levels was investigated in relation to the formation and growth of their adhesion interphase examined with AES spectroscopy. The optimum-cured adhesion sample showed a maximum pullout force, but the pullout forces of samples under-cured and over-cured were low. The adhesion property of under-cured adhesion samples enhanced with humidity aging due to further curing of rubber and supplementary growth of the adhesion interphase. Cure level exhibiting good adhesion was discussed based on the composition and structure of the adhesion interphase and the crosslinking density of the rubber layer attached to the interphase.

Key words: Adhesion Interphase, Brass-Plated Steel Cord, Rubber Compound, Cure Level, AES

INTRODUCTION

The adhesion between rubber compound and metal has been widely applied in various industries. A typical case is adhesion of rubber compound with brass-plated steel cord in tire production, providing a sufficient mechanical strength and stability to endure the weight of the car itself and its huge loads. Sulfides and oxides of copper and zinc formed through the reaction between the brass and the rubber compose an adhesion interphase, establishing the adhesion [Kurbatov et al., 1991; Hammer, 2001]. Since formation rates of these components at the adhesion interphase largely vary with the cure temperature and time, a cure level of composites is important for their adhesion properties. Under-cured composites cured at low temperature or for short time show poor adhesion due to an insufficient formation of the adhesion interphase as well as a low crosslinking density of rubber. On the contrary, long time cure at high temperature brings about over-cure. Excessive growth of the adhesion interphase also results in poor adhesion because of the cohesion failure in sulfides and oxides layers [van Ooij, 1979; Holtkamp et al., 1995]. The poor physical property of over-cured rubber lowers adhesion strength because of the cohesion failure in rubber layer. Therefore, a number of studies for the optimization of the cure conditions for rubber-brass composites as well as the composition of rubber compounds have been carried out to strengthen the adhered rubber to the brass surface and to form a stable adhesion interphase [Fernando et al., 2000; Jeon and Seo, 2001a, b]. The improvement of the production rate of tire by shortening cure time by raising cure temperature also activates the study on the effect of cure conditions on adhesion.

The composition and structure of the adhesion interphase, as mentioned above, are important for the adhesion property, but reports on direct experimental observations about the interphase are rare. Since an extremely thin adhesion interphase is located between the cured rubber and the brass, the isolation of the interphase from the rubber or the brass must accompany severe damage of its structure and composition. Thin brass films deposited on glass are useful in studying the structure of the adhesion interphase formed by the reaction of rubber with brass, but they do not provide any adhesion strength to correlate those of real rubber-brass composites [Seo, 1997; Jeon et al., 1999]. Insertion of a filter paper between rubber compound and brass-plated steel cord, however, is effective in preparing samples for the adhesion interphase without any mechanical shock [Persooner et al., 1994; Jeon and Seo, 2001c]. Since chemicals except large rubber molecules can migrate through the holes of filter papers, the change occurring on the brass surface during curing process provides valuable information about the surface reactions among copper, zinc, sulfur, and oxygen. On the other hand, a partial loss of sulfides and oxides at the adhesion interphase is inevitable while preparing the adhesion samples by inserting filter paper, because cured rubber is essential for holding the interphase. Therefore, this preparation method is not suitable for obtaining samples for quantitative analysis of the adhesion interphase, but it is useful in conducting a qualitative inspection. High simplicity and reproducibility of sample preparations are effective in inspecting the variation of the adhesion interphase caused by cure levels of composites, especially in terms of the contents of its components.

The present study focuses on the effects of the cure levels, under-cure, optimum-cure, and over-cure on the adhesion between rubber compound and brass-plated steel cord. Cure temperature and time were adjusted to obtain various cure levels of the composites. Adhesion property of embedded cords in rubber compound was discussed in relation to the deduced adhesion interphase from AES analysis of filter paper-inserted adhesion samples.

EXPERIMENTAL

1. Preparation of Rubber Compound

Table 1. Composition of rubber compound prepared

Material	Trade name	Manufacturer	Content (phr[7])
Masterbatch			
Natural rubber	SMR-20	Lee Rubber Co., Malaysia	100
Carbon black	N351	Lucky Co., Korea	55
Processing oil	A#2	Michang Co., Korea	5
Activator	ZnO	Hanil Co., Korea	10
Antioxidant	Kumanox-13[1]	Monsanto Co., USA	1
Adhesion promoter	B-18S[2]	Indspec Co., USA	3
Adhesion promoter	Cobalt stearate[3]	Rhone Poulenc Co., France	1
Final mixing			
Activator	Stearic acid	Pyungwha Co., Korea	1
Accelerator	MOR[4]	Monsanto Co., USA	0.6
Sulfur	Crystex HS OT 20[5]	Akzo Co., The Netherlands	5
Adhesion promoter	Cyrez-964[6]	Cytec Co., USA	3

[1]N-(1,3-dimethyl-butyl) N-phenyl-p-phenylenediamine. [2]Resorcinol formaldehyde resin. [3]Cobalt 10 wt%. [4]2-morpholinothio benzothiazole sulfenamide. [5]Insoluble sulfur. [6]65% Hexamethoxymethylmelamine with 35% silica. [7]Parts per hundred of rubber.

A rubber compound with the basic formulation was prepared (Table 1). The rubber compound was mixed in accordance with the procedures described in ASTM D3184-80. Mixing was carried out in two stages using an internal mixer (Farrel Co., Banbury Mixer model 82) with a capacity of 1.2 kg batch weight. All the masterbatch components were mixed for 10 min at a rotor speed of 40 rpm and discharged at 150 °C. After the masterbatch compound was cooled to room temperature, the final mixing components were added. Then the final mixing compound was mixed for 5 min at a rotor speed of 30 rpm and dumped at 90 °C. The final mixed rubber compound was rolled into a sheet on a two roll open mill (Farrel Co., model MKIII).

2. Measurement of Cure Rate and Physical Properties

Rheocurves of the prepared rubber compound were recorded with a Monsanto Rheometer (model Rheo-100) in the temperature range from 130 °C to 170 °C with an interval of 20 °C following the procedure described in ASTM D-2084. A Shore A durometer was employed to measure the hardness of vulcanizates according to ASTM D-2240. Tensile properties of vulcanizates described in ASTM D-412 were determined from stress-strain curves recorded using a tensile tester (Instron model 6021).

3. Adhesion Test

Adhesion samples are composed of brass-plated steel cord (3× 0.30 mm) and the rubber compound. Five T-test adhesion samples with different cure levels were prepared by changing temperature and time for the cure of these composites. The plating weight of brass on the brass-plated steel cord manufactured by the Kiswire Co. Korea, was 3.6 g/kg, and the copper content of the brass was 63.6%. According to the procedure described in ASTM D-2229, the adhesion samples were cured with a cure press (Osaka Jack Co. Ltd.) under the pressure of 2.4 MPa. Under-cured adhesion samples were cured at 130 °C for 20 min and at 150 °C for 5 min. Optimum-cured adhesion samples were obtained by curing at 150 °C for 20 min. In addition, cure conditions such as 150 °C and 80 min and 170 °C and 20 min were employed to prepare over-cured adhesion samples. Cure times were selected based on t_{90} time at 150 °C: 20% of t_{90} time for the under-cure, 100% for the optimum-cure,

and 400% for the over-cure. In order to investigate the effect of humidity aging on the adhesion, the cured samples were placed in a humid chamber adjusted at 85 °C and 85% relative humidity for 15 days.

Pullout force was determined as the maximum force exerted by the tensile tester on a T-test sample during the pullout test at 10 mm/ min crosshead speed. Rubber coverage, defined as a percentage of the surface covered by rubber, was also measured with an interval of 5% by the naked eye [Jeon and Seo, 2001a]. Each value reported was an average of six samples.

4. Investigation of Adhesion Interphase

Samples for the investigation of the adhesion interphase were prepared by inserting a filter paper (pore size 5 μm, catalog No. 14250, Millipore Co., USA) between the rubber compound and the brass-plated steel cords as described in our previous paper [Cho et al., 1999; Jeon and Seo, 2001c]. Cure conditions of the samples for the adhesion interphase were the same as those for the preparation of the T-test adhesion samples. By removing the rubber block adhering on filter paper from the cord, the adhesion samples, which reacted with rubber compounds, were obtained.

The depth profiles from the adhesion interphase to bulk brass were recorded on a Perkin-Elmer Auger electron spectrometer (Phi 670). A 10×10 μm² area of the surface was examined with 5.0 keV of Ep, 0.03 μA of Ip, and an incident angle of 30° to the specimen. Compositions of the exposed surface were measured 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. For the depth profiling, a sputter gun with an argon ion beam rastered at 2×2 mm² was used. The sputtering rate for the brass film was determined to be 25 nm/min. The determination of the sputtering rate for the adhesion interphase, however, was difficult because it included various chemical components with variable concentrations. Therefore, in this paper, sputtering time was used to indicate the depth of the adhesion interphase instead of absolute depth.

RESULTS AND DISCUSSION

Table 2. Cure characteristics of rubber compound determined using an oscillating disc type rheometer[1]

Cure temperature (°C)	Time (min)			CRI[2] (min⁻¹)	Torque (J)	
	t_2	t_{40}	t_{90}		min.	max.
130	3.5	39.6	54.8	1.9	1.8	5.0
150	2.2	10.8	20.0	5.6	1.7	5.9
170	1.3	3.2	6.1	20.8	1.5	5.4

[1]The rubber compound was sheared to $\pm 1°$ and 1.67 Hz.
[2]Cure rate index (CRI) $= 100/(t_{90} - t_2)$.

1. Cure Characteristics and Physical Properties of Rubber Compound

The cure rate of the rubber compound increases as the cure temperature increases, but the reversion rate of cured rubber also increases at elevated temperature. Table 2 shows exponential decrease in t_2 and t_{90} times with the rising cure temperature. The cure rate index at 170 °C was high by about 10 times compared to that at 130 °C. Minimum and maximum torques observed in the cure process change in an opposite direction according to the cure temperature. An improvement of rubber fluidity at high temperature lowers the minimum torque, while the increase in cure temperature enhances the cure rate to achieve high torque because of the high crosslinking density of rubber. The simultaneously enhanced reversion rate at higher temperature, however, reduced the crosslinking density. As a result, the highest maximum torque was obtained at a moderate temperature of 150 °C.

The physical properties of the rubber compound cured with different conditions are shown in Table 3. At the cure temperature of 150 °C, hardness and modulus of vulcanizates increased with the increasing cure time, but their elongation at break decreased. Their

maximum tensile strength was obtained from the optimum-cured vulcanizate. Further increase of cure time caused a decrease in tensile strength as a result of the reversion, which induces a breakage of crosslinked rubber network. At the under-cure condition such as lower cure temperature or shorter cure time, poor tensile strength of vulcanizates was obtained because of the low crosslinking density of rubber compound. On the other hand, tensile strength and elongation at break of over-cured vulcanizates were low despite their high modulus, because the hardening of vulcanizates due to long-time cure lowers their tensile properties.

2. Variation of the Adhesion Property with Cure Level

The adhesion samples with different cure levels showed different adhesion properties as shown in Table 4. The optimum-cured adhesion sample, either unaged or humidity aged, exhibits the highest pullout force among the under-cured and over cured adhesion samples. The rubber coverages of under-cured adhesion samples at unaged state are lower at 55% and 60%, but those of over-cured adhesion samples are higher at 90%. Both the pullout force and rubber coverage of under-cured adhesion samples increased with humidity aging. On the other hand, rubber coverages of over-cured adhesion samples remained constant, while their pullout forces decreased with humidity aging.

The temperature and time for the optimum-cure of the rubber-brass composite were selected to achieve 90% cure of the rubber compound. This condition reflects only the proper crosslinking density of the rubber compound, not the extent of adhesion interphase formed. The importance of the physical property of rubber compound in adhesion was proven by the fact that the highest adhesion property of the composites was obtained at the optimum-cured adhesion sample. Since weak rubber easily departs from the adhesion interphase during the pullout test, under-cured adhesion samples with the rubber of low modulus and tensile strength exhibit low rub-

Table 3. Physical properties of vulcanizates with different cure levels

Classification	Cure condition		Hardness (Shore A)	Modulus (MPa)			T.S.[1] (MPa)	E.B.[2] (%)
	Temp. (°C)	Time (min)		100%	200%	300%		
Under-cure	130	20	63	2.02	4.88	12.9	17.2	442
	150	5	61	1.89	4.53	11.6	16.4	485
Optimum-cure	150	20	73	4.09	7.83	17.4	18.2	376
Over-cure	150	80	75	3.46	7.83	-	13.1	298
	170	20	76	3.22	7.25	-	12.2	263

[1]Tensile strength.
[2]Elongation-at-break.

Table 4. Unaged and humidity aged[1] adhesion properties of adhesion samples with different cure levels

Classification	Cure condition		Pullout force (N)		Rubber coverage (%)	
	Temp. (°C)	Time (min)	Unaged	Humidity-aged[1]	Unaged	Humidity-aged
Under-cure	130	20	215	302	55	90
	150	5	246	296	60	90
Optimum-cure	150	20	470	427	90	90
Over-cure	150	80	425	389	90	90
	170	20	347	350	90	90

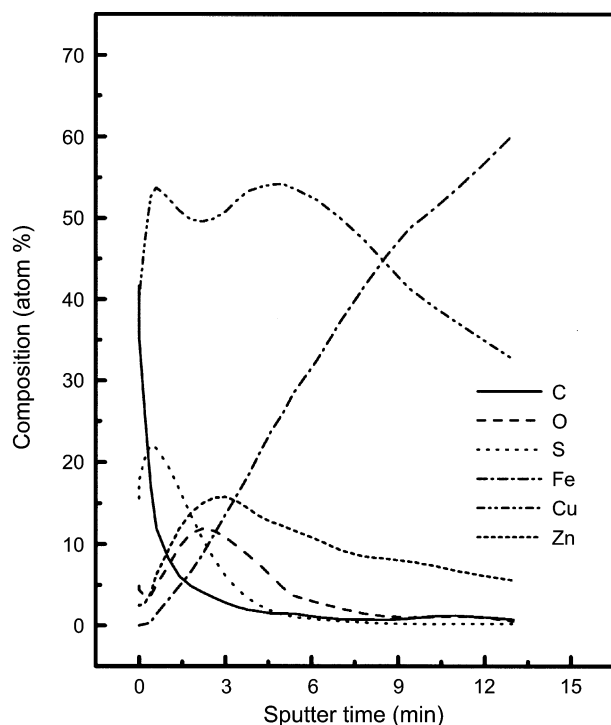[1]Humidity aging for 15 days at 85 °C and 85% relative humidity.

Fig. 1. AES depth profiles of C, O, S, Fe, Cu and Zn for adhesion interphase between rubber compound and brass-plated steel cord cured at 130 °C for 20 min.

ber coverage as well as low pullout force. Over-cured adhesion samples also showed adhesion properties lower than the optimum-cured adhesion sample. Deterioration of rubber network by exposure to high temperature for long time resulted in a significant decrease in the pullout force of over-cured adhesion samples, although their rubber coverages still remained as high as 90%.

3. Characterization of Adhesion Interphase

Adhesion interphase between rubber compound and brass-plated steel cord is generally composed of sulfides and oxides of copper and zinc. Fig. 1 shows depth profiles of copper, zinc, sulfur, oxygen, carbon, and iron obtained from an adhesion sample prepared by inserting a filter paper to investigate the adhesion interphase. Depth profiles were calculated from AES spectra recorded with sputtering from the brass surface to the steel core. The coincidence in profiles of different species such as copper and sulfur or zinc and oxygen suggests the formation of copper sulfide or zinc oxide, respectively. Since the inserted filter paper prevents a direct contact of rubber with the brass surface, depth profiles obtained reveal only the reactions between the brass and migrated chemicals from the rubber compound.

The outer surface of the brass was contaminated with carbon, but the carbon peak was rapidly diminished with sputtering. Copper sulfides and zinc oxides the main components of the adhesion interphase were located beneath the carbon layer. The contents of copper and zinc were still high after 5 min sputtering even though those of sulfur and oxygen were negligible, indicating the presence of non-reacted brass. Iron content gradually increased from the brass surface, not by stepwise, suggesting an unevenness of steel cord surface. The difference in the amount of brass plated on the steel surface from site to site caused some ambiguity in the interpreta-

tion of surface analysis results.

From these depth profiles of several species, we can confirm a typical structure of an adhesion interphase proposed in the literature [Kurbatov et al., 1991; Hammer, 2001; Jeon and Seo, 2001a, b]: the copper sulfide layer forms on the rubber side and the zinc oxide layer locates on non-reacted brass. The content of each component varies with cure temperature or time, but the fundamental structure of the adhesion interphase of rubber-brass composites remained unchanged unless the cure condition was extraordinary. This simple structure of adhesion interphase, therefore, is useful to interpret the variation of adhesion property with cure temperature and time in terms of the stability of the adhesion interphase and physical property of rubber adhering on the interphase.

Fig. 2 shows the depth profiles of copper, sulfur, zinc, and oxygen in the adhesion samples cured at different temperatures. The depth profiles obtained from the adhesion sample cured at 130 °C, as mentioned before (Fig. 1), show the basic structure of the adhesion interphase. In addition, the large difference in the contents of copper and sulfur (upper) indicates that only a small part of copper of the brass forms copper sulfide. On the other hand, a small difference in the contents of zinc and oxygen (lower) suggests that most of zinc converts to zinc oxide or zinc hydroxide. The large amount of non-reacted brass indicates that only a small amount of the brass forms the adhesion interphase at low temperature.

The cure temperature altered depth profiles of four elements at the adhesion interphase. Although copper sulfide and zinc oxide commonly formed at the interphase in this cure temperature range, the depth profiles obtained were too complex to be explained by only the further formation of sulfide and oxide with rising temperature. With the sample cured at 130 °C cured sample, non-reacted brass remained beneath these materials. On the other hand, oxygen content exceeds zinc content from the depth profiles of adhesion samples cured at 150 °C, indicating that all of zinc reacted with oxygen and formed zinc oxide. Part of oxygen must exist in the interphase copper oxide as well as in zinc oxide. Furthermore, the disappearance of the first peak of copper at the outer surface and the shift of the maximum position of zinc content to the surface indicate a partial loss of the weak layer formed at the interphase. The rapid formation of copper sulfide and oxide at elevated temperature brings about a sufficient formation of adhesion interphase, but its partial loss is due to the absence of rubber.

However, the depth profiles obtained from the adhesion sample cured at 170 °C are considerably different. A large, broad sulfur peak on the outer surface and the disagreement in the zinc and oxygen profiles suggest the formation of zinc sulfide and copper oxide. Rapid formation of zinc sulfide at elevated temperature suppresses the formation of copper sulfide and zinc oxide, resulting in different adhesion property [Jeon et al., 1999; Jeon and Seo, 2001a].

The variation of depth profiles with cure temperature can be summarized as follows: 1) the formation of the adhesion interphase is not sufficient at low cure temperature, 2) at moderate cure temperature, copper sulfide and oxide are simultaneously formed, and some of them are removed at departing step, and 3) the formation of zinc sulfide as well as copper sulfide is clear at 170 °C.

Cure time also affects the formation of the adhesion interphase. Fig. 3 shows the depth profiles obtained from the adhesion samples cured at 150 °C for different cure times. Formation of copper
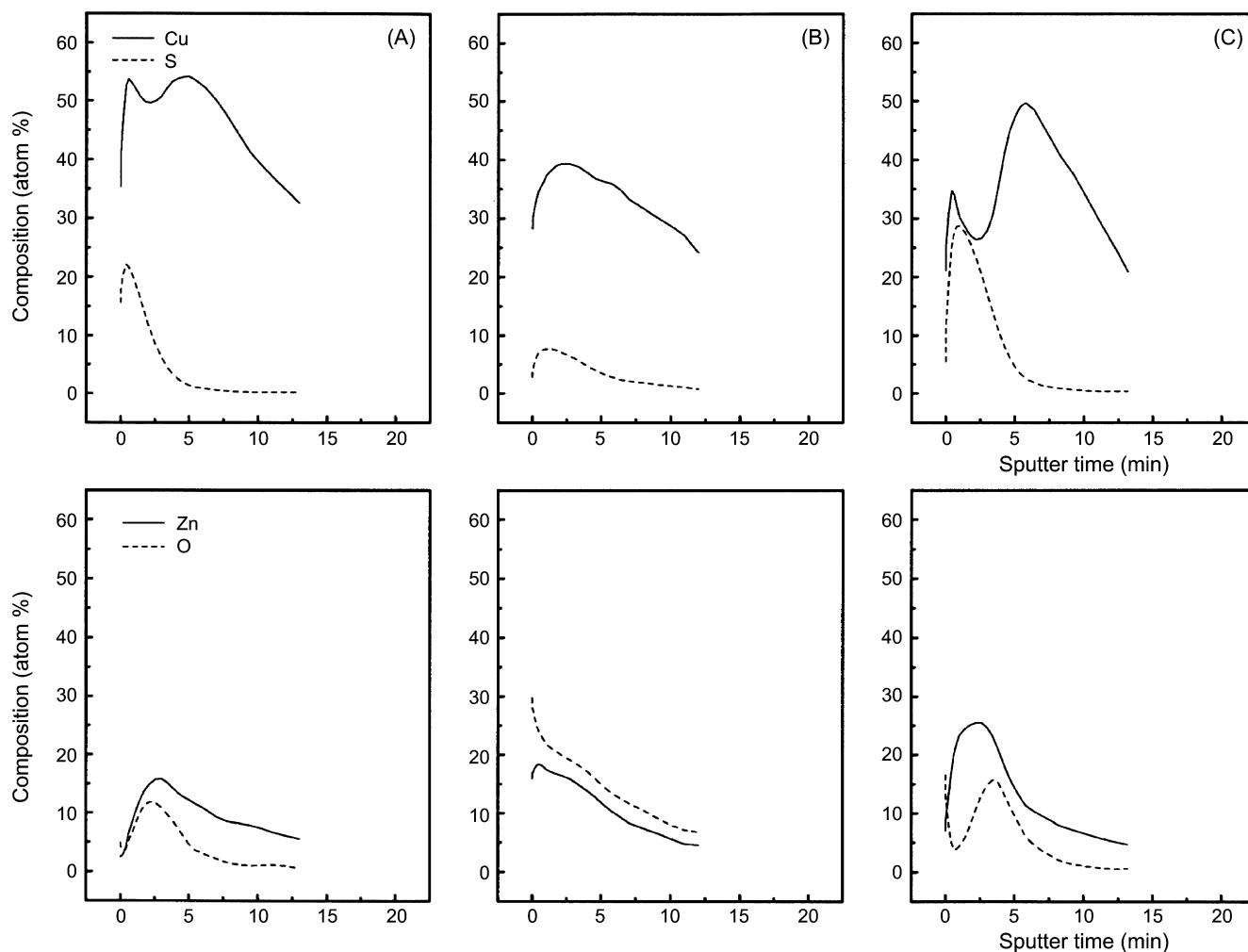
Fig. 2. AES depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) from adhesion interphase between rubber compound and brass-plated steel cord cured for 20 min at different cure temperatures.
(A) 130 °C, (B) 150 °C, and (C) 170 °C

sulfide was not evident in the sample cured for 4 min, while small amount of zinc oxide was formed on the outer surface. Too short cure time brings about an insufficient formation of adhesion interphase. As mentioned before (Fig. 2), the depth profiles from the optimum-cured adhesion sample could be explained in terms of the sufficient formation of sulfide and oxide of copper and their partial loss. The further increase in cure time continues the formation reaction of sulfides and oxides of copper and zinc at the interphase. Since these materials are weak, especially oxides of zinc and copper, their excessive growth results in a partial loss at the surface.

4. Effect of Cure Level on the Adhesion

The pullout force of the optimum-cured adhesion sample was higher than those of both the under-cured and over-cured adhesion samples. Rubber coverages of the under-cured adhesion samples were lower than that of the optimum-cured adhesion sample, while the rubber coverages of the over-cured adhesion samples were not low. Both pullout forces and rubber coverages of the under-cured adhesion samples increased with humidity aging. On the other hand, the pullout forces of the over-cured adhesion samples decreased with humidity aging, while rubber coverage did not decrease.

Effects of cure levels on adhesion between rubber and brass in

the composites made up of rubber compound and brass-plated steel code seem to be too complex to derive a clear explanation. However, the change in the adhesion property with the cure level can be related to the difference in the adhesion interphase and the rubber property of the composites. Poor adhesion of the under-cured samples is attributed to the insufficient formation of the adhesion interphase and weak tensile property of rubber compound caused by low cure temperature and short cure time. The further growth of the adhesion interphase as well as the enhancement of crosslinking density during humidity aging improves their adhesion properties. On the other hand, the over-cured adhesion samples show a decrease in their pullout forces after humidity aging without any decrease in their rubber coverages. The deterioration of rubber properties during humidity aging causes cohesion failure in the rubber layer, lowering only pullout force.

CONCLUSION

The adhesion between rubber compound and brass-plated steel cord varied considerably with its cure level, because cure temperature and time determine the physical property of rubber and the for-
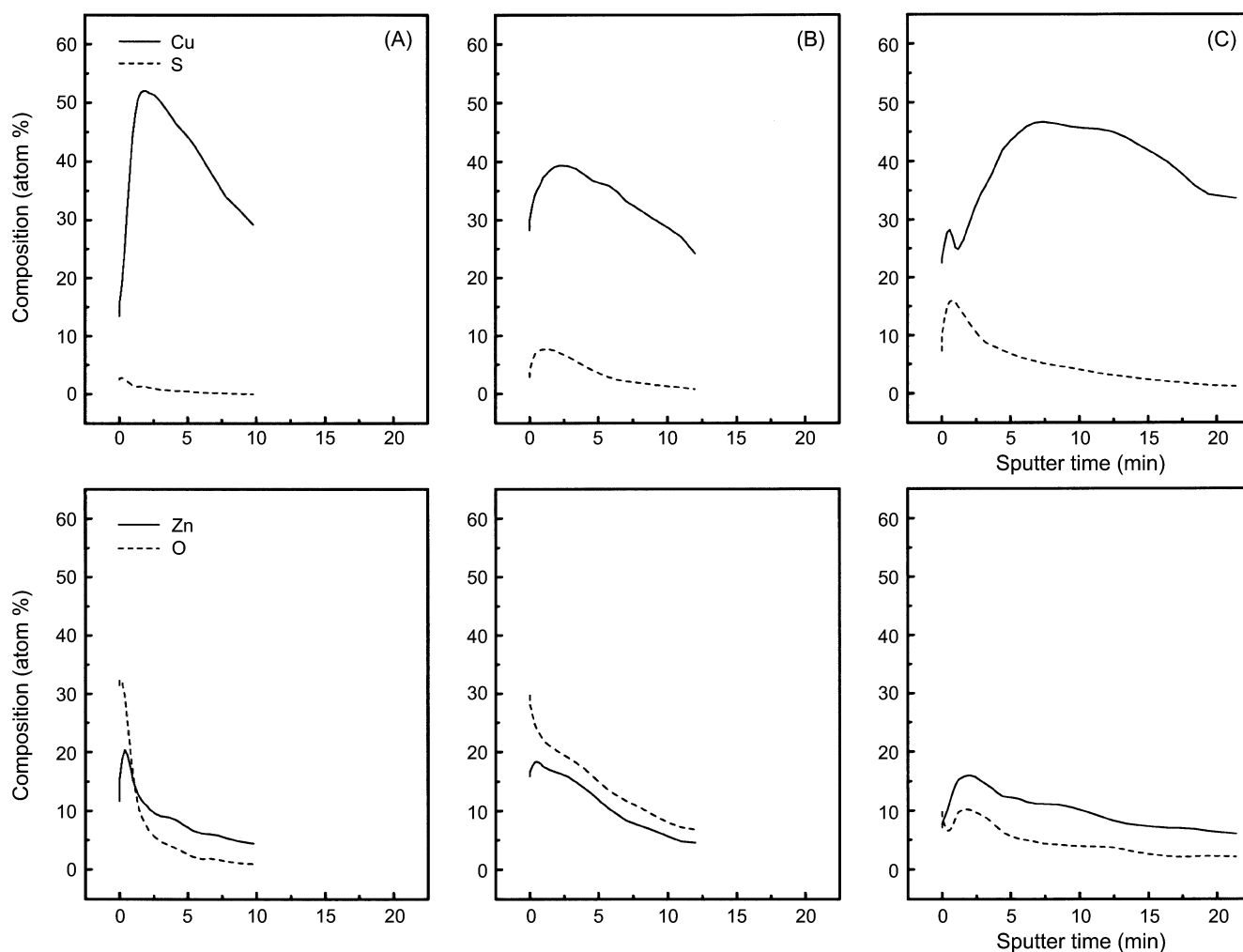
Fig. 3. AES depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) from adhesion interphase between rubber compound and brass-plated steel cord cured at 150 °C with different cure times.
(A) 4 min, (B) 20 min, and (C) 80 min

mation of adhesion interphase. Poor adhesion of the under-cured adhesion samples was attributed to the insufficient growth of the adhesion interphase as well as weak rubber property. The optimum-cure adhesion sample showed the highest pullout force among the under-cured and over-cured samples because the cure time was enough to achieve the sufficient growth of the adhesion interphase and proper crosslinking density of rubber. Compared to the crosslinking of rubber network, rapid formation of copper sulfide at the adhesion interphase emphasizes the importance of rubber property in adhesion.

ACKNOWLEDGMENT

REFERENCES

Cho, P. L., Jeon, G. S., Ryu, S. K. and Seo, G., "Adhesion between Rubber Compound and Copper-Film-Plated Steel Cord," *J. Adhesion*, **70**, 241 (1999).

Fernando, M. S. D., Cudby, P. E. F. and Cook, S., "The Influence of Moulding Temperature on the Strength of Natural Rubber to Metal Bonded Joints," *Kautsch. Gummi, Kunstst.*, **53**, 194 (2000).

Hammer, G. E., "A New Look at the Steel Cord-Rubber Adhesive Interphase by Chemical Depth Profiling," *J. Vac. Sci. Technol. A*, **19**, 2846 (2001).

Holtkamp, D., Elschner, A., Muller, G. and Pieroth, M., "Novel Model System to Study the Influence of Rubber Compound Formulation on the Structure and Composition of the Rubber-Brass Interphase," *Surf. Interface Anal.*, **23**, 155 (1995).

Jeon, G. S., Han, M. H. and Seo, G., "Enhancing Adhesion Properties between Rubber Compound and Brass-Plated Steel Cord by Incorporating Silica into Rubber," *J. Adhesion Sci. Technol.*, **13**, 153 (1999).

Jeon, G. S. and Seo, G., "Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-Plated Steel Cord. Part I. Cure Temperature," *J. Adhesion*, **76**, 201 (2001a).

Jeon, G. S. and Seo, G., "Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-Plated Steel Cord. Part II. Cure Time," *J. Adhesion*, **76**, 223 (2001b).

Jeon, G. S. and Seo, G., "Promotion Effect of a Chlorotriazine Deriva-

tive on the Adhesion Between Rubber Compounds and a Brass-Plated Steel Cord," *J. Adhesion Sci. Technol.*, **15**, 689 (2001c).

Kurbatov, G. G., Beshenkov, V. G. and Zaporozchenko, V. I., "AES and Factor Analysis Study of Cord-Oxidized Brass Layers and Rubber-to-Brass Interface Chemical Composition," *Surf. Interface Anal.*, **17**, 779 (1991).

Persooner, P., De Volder, P. and De Gryse, R., "The Influence of Cobalt on the Oxysulfidation of Brass," *Solid State Commun.*, **92**, 675 (1994).

Seo, G., "Stabilizing the Adhesion Interphase between Rubber Compound and Brass Film by the Addition of Resorcinol Formaldehyde Resin to the Rubber," *J. Adhesion Sci. Technol.*, **11**, 1433 (1997).

van Ooij, W. J., "Fundamental Aspects of Rubber Adhesion to Brass-Plated Steel Tire Cords," *Rubber Chem. Technol.*, **52**, 605 (1979).