Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-plated Steel Cord. Part II. Cure Time

Gyung Soo Jeon[a]; Gon Seo[b]

[a] Department of Clean Environment, Provincial College of Damyang, Chonnam, South Korea [b] Department of Chemical Technology, Chonnam National University, Kwangju, South Korea

PLEASE SCROLL DOWN FOR ARTICLE

Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-plated Steel Cord. Part II. Cure Time

GYUNG SOO JEON [a],* and GON SEO [b]

[a]Department of Clean Environment, Provincial College of Damyang, Damyang, Chonnam 517-800, South Korea; [b]Department of Chemical Technology, Chonnam National University, Kwangju 500-757, South Korea

The effect of the cure time of a rubber compound on the adhesion with brass-plated steel cord was investigated. The formation, growth and degradation of the adhesion interphase formed between the rubber compound and brass-plated steel cord was also observed as well as the formation of a weak boundary layer in the rubber near the adhesion interphase. With increase in the cure time from a fourth to four times of t_{90}, the pull-out force after vulcanization increased significantly up to one-half of t_{90} followed by a slight increase to t_{90}, and then decreased slowly with further increase in cure time. This decrease in pull-out force upon prolonged vulcanization may be explained by the severe degradation of rubber compound attached to the adhesion interphase. Also, upon prolonged vulcanization, the adhesion interphase with a rich ZnS layer may act as a barrier to copper diffusion which is required to form the adhesion interphase of copper sulfide. After thermal aging of the adhesion samples, the pull-out force decreased in comparison with that of the unaged. The decrease of pull-out force after thermal aging stemmed mainly from the decline of tensile properties after thermal aging. The adhesion after humidity aging was different from that after thermal aging. Upon increasing the cure time to one-half of t_{90}, the pull-out force increased. But a further increase in the cure time caused a decline in pull-out force. This phenomenon can be explained by the degradation of the adhesion interphase. At longer cure time, a severe growth of copper sulfide and a large amount of dezincification were observed in the adhesion interphase. At shorter cure time, a significant growth of copper sulfide in the adhesion interphase does not occur, whereas the formation a of a ZnS layer appeared after humidity aging. With increasing cure time, the formation of a weak boundary layer in the rubber near the adhesion interphase increased, resulting in the cohesive failure of the rubber layer.

---

*Corresponding author. Tel.: +82-61-380-8671, Fax: +82-61-381-9100, e-mail: gjeon@damyang.damyang.ac.kr

The proper formation of the adhesion interphase and the good physical properties of the rubber compound at optimum cure time can lead to the high retention of adhesion.

Keywords: Adhesion interphase; AES; Steel cord; Rubber compounds; Cure time

1. INTRODUCTION

Rubber-metal adhesion plays an important role in steel-belted car and truck tires where good adhesion between rubber compound and metal cord is a primary requirement to achieve a longer life of the product. During the cure process, the adhesion between brass-coated steel cord and the green rubber compound takes place through the formation of layers composed of copper and zinc sulfides and oxides [1]. The adhesion mechanism is very complex. Good adhesion depends primarily on the chemical composition and the surface structure of the brass, from which the adhesion interphase is formed, as well as the composition of the rubber compound and the cure conditions (temperature, time, pressure *etc.*).

It has been found that adhesion properties vary to a great degree depending on the condition or composition of the adhesion interphase, because copper sulfides and other sulfides and oxides of copper and zinc are formed at the interphase by the reaction of copper and zinc with sulfur, oxygen or water [2]. Since the failure may possibly occur in the rubber adhered to the interphase, the physical properties of the rubber compound have also become the dominating factor in determining the adhesion property [3,4]. Accordingly, a number of studies for the optimization of the compound composition and cure condition have been carried out to strengthen the rubber at the interphase and to form a stable adhesion interphase [1 – 8].

Also, the rubbers physical properties near the adhesion interphase are very important. Generally it is known that the crosslinking density of rubber near adhesion interphase is lower than that of bulk rubber resulting in the formation of a weak boundary layer [9]. The activated sulfur is consumed simultaneously not only in crosslinking of the rubber compound but also in the formation of the adhesion interphase during the cure process. In the rubber near the adhesion interphase, the partly deficient state of the activated sulfur occurs due to consumption of sulfur during the formation of the adhesion layer

and hindering of the diffusion of sulfur from the bulk rubber arising from the network formation of sulfur crosslinking. Therefore, adhesion failure can proceed through the weak boundary layer in rubber near the adhesion interphase.

The cure conditions affect not only the extent and rate of cross linking of rubber compound but also the degree and rate of adhesion interphase formation [10]. Generally, it is reported that the formation of the adhesion interphase is far faster than the crosslinking of rubber compounds. Prior to the scorch time, the adhesion interphase forms sufficiently. Interaction between the copper sulfide and rubber is expected to be enhanced if the sulfide grows prior to scorch time, since the rubber is still a viscoelastic liquid which is easily deformed irreversibly and enveloped by the outwardly growing copper sulfide. Subsequent crosslinking can then lock the rubber in to the interlayer. After the scorch time, because the rubber is now a viscoelastic solid, which is stiffer and more elastic, intermeshing with the growing copper sulfide may be hindered.

An excessive extension in cure time causes the adhesion to be far less than that predicted from the physical properties of the rubber. Since constitutive components and the state of the adhesion interphase vary with the cure time, it is possible that the adhesion undergoes a change although this has not yet been confirmed empirically. Investigation of the adhesion between brass-plated steel cords and rubber compounds seems relatively complex because the adhesion interphase is too thin to separate. Observation of the adhesion interphase by surface analysis of cryogenically-broken specimens using liquid nitrogen often meets difficulties to ensure enough cross-sample homogeneity and reproducibility [1, 3, 8]. However, using Auger electron spectroscopy (AES), surface analysis *via* sputtering through the brass film towards the rubber bulk of adhesion interphase, which is prepared by curing the rubber compound together with a thin brass film deposited on a glass plate, provides a full depth profile of the adhesion interphase, thus, revealing its compositional distribution [11 – 13]. Though a measurement of pull-out force and/or rubber coverage is not feasible, adhesion samples can easily be made by this procedure without such mechanical treatments as tearing or pulling-out.

Zakharov *et al.* reported the formation of a weak boudary layer in rubber near the adhesion interphase 120 μm away. This study used a

combination of swelling and cryomicrotome cutting [9]. But this method is very difficult to apply vulcanizates only 1 mm thick. Alternatively, we employed the force modulation mode of atomic force microscopy to measure the modulus of the weak boundary layer in the rubber compound near the adhesion interphase and the bulk rubber. The force modulation mode of atomic force microscopy, in which the vertical vibration amplitude of the tip was measured, as affected by the local modulus of samples, is very suitable for the measurement of local elasticity of samples [14–17]. Further, the mechanical properties are proved continuously over extended areas instead of at scattered individual points.

The present study concerns the effect of cure time (25%, 50%, 100%, 200%, 400% of t_{90} time) on the adhesion between brass-plated steel cord and rubber compounds. The physical properties of a rubber compound as well as the adhesion properties, were examined using specimens cured for a predetermined time at constant cure temperature. To observe the role of the extent of cure on the adhesion interphase by AES, vulcanization of the rubber compound and thin brass film was carried out at various cure times. Also, the extent of cure for the adhesion samples of rubber near the adhesion interphase and in the bulk rubber were measured using force modulation mode of AFM in order to confirm the magnitude of the weak boundary layer.

2. EXPERIMENTAL

2.1. Rubber Compound Preparation

A rubber compound was prepared with the basic formulation shown below:

Masterbatch components were as follows:

- natural rubber (Lee Rubber Co., Malaysia, SMR 20 100 phr,
- carbon black N330 (Lucky Co., South Korea) 55 phr,
- aromatic processing oil (Michang Co., South Korea, A#2) 3 phr,
- zinc oxide (Hanil Co., South Korea) 8 phr,
- antioxidant (Monsanto Co., USA, Kumanox-13, N-(1,3-dimethylbutyl), N-phenyl-p-phenylenediamine) 0.5 phr,

- resorcinol formaldehyde resin (Indspec Co., USA, Penacolite B-18-S) 2 phr,
- Co stearate (Tawkwang Chem. Co., South Korea, 10 wt% cobalt) 0.5 phr.

Final mixing components were as follows.

- masterbatched rubber compound,
- stearic acid (Pyungwha Co., South Korea) 1.5 phr,
- methylene donor (Cytec Co., USA, Cyrez-964, Hexamethoxy-methylmelamine 65% + SiO_2 35%) 3.0 phr,
- accelerator (Monsanto Co., USA, Santocure DZ, Dicyclohexl-benzothiazole sulfenamide) 0.6 phr,
- insoluble sulfur (Akzo Co., The Netherlands, Crystex HS OT 20) 6.0 phr.

The rubber compound was mixed following the procedures described in ASTM D3184. 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 mixed for 5 min at a rotor speed of 30 rpm and dumped at 90°C. After dumping, the batches were rolled into a sheet on a two-roll open mill (Farrel Co., model MKIII).

2.2. Measurement of Cure Rate and Vulcanizate Properties

In order to determine the cure time at 160°C, t_{90} (time required to 90% crosslinking) of the rubber compound was measured based on the rheocurve. A Monsanto Rheometer(model Rheo-100) was used to obtain then rheocurve according to ASTM D-2084. Mooney viscosity values were measured according to ASTM D-1646 using a Monsanto MV-2000.

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

2.3. Adhesion Property and Analysis of Adhesion Interphase

All adhesion samples were cured at 160°C for 25%, 50%, 100%, 200%, 400% of t_{90} time, using a cure press (Osaka Jack Co. Ltd.) at a pressure of 2.4 MPa. The cured adhesion samples were placed in a humidity chamber for 5, 10 and 15 days under the conditions of 85°C temperature and 85% relative humidity. Also, the adhesion samples were aged thermally at 90°C.

A thin brass film with a Cu/Zn ratio of 65/35 was sputtered onto a glass plate (Menzenglasser, 7.6 mm × 26 mm) using a RF Magnetron sputter for 70 sec at 2×10^{-6} Torr [12, 13, 18]. RF power was controlled to 400 W. Thickness of the thin brass film was confirmed to be 180 nm using SEM (JEOL JSM 7400). A brass-on-glass plate was sandwiched between two uncured pads of rubber compound, which were then placed in a pad mold. The depth profiles from the outer brass surface to the bulk of rubber were recorded on a Perkin-Elmer Auger spectrometer (Phi 670). A $10 \times 10 \mu m^2$ 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. Surface concentration was 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 $2 \times 2 mm^2$ was used. The sputtering rate for the brass film was determined to be 25 nm/min. However, it is difficult to determine the sputtering rate for the adhesion interphase precisely 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.

In order to investigate the variation of adhesion characteristics with cure time, pull-out force and rubber coverage of a brass-plated steel cord to the rubber compound were measured using the T-test method according to ASTM D-2229. The brass-plated steel cord (4 × 0.28) manufactured by the Hyosung T & C Co., Korea, was used. The plating weight of brass on the steel cord was 3.6 g/kg and the copper content of the brass was 63.6%. Curing and aging conditions for adhesion samples were the same as described in the preparation of the

thin brass film/rubber compound adhesion sample. Pull-out force
was determined as the maximum force exerted by the tensile tester
(Instron model 6021) on a T-test sample during the pull-out test, with
10 mm/min of crosshead speed. Rubber coverages were also noted.
Each value reported was an average of six specimens.

2.4. Extent of Cure for the Rubber Near the Adhesion Interphase Measured by the Force Modulation Mode of Atomic Force Microscopy

The extent of cure for the rubber compound near the adhesion
interphase was compared with that in the bulk using force modulation
microscopy, an extension of atomic force microscopy imaging, which
includes characterization of a sample's mechanical properties. An
AFM (Auto Probe M5 model, PSI Co., South Korea) tip was scanned
in contact with the sample for 20 μm, and a z feedback loop
maintained a constant cantilever. In addition, a signal was applied
periodically to the tip. The amplitude of cantilever modulation that
resulted from this applied signal normally varied according to the
elastic properties of the sample. The tip modulation mode was
employed. Force modulation measurements were performed with
silicon cantilevers (V-shaped, 50 μm in thickness) and a spring force
constant of 0.4 N/m. The reported radius of curvature for the tips was
10 nm. Scanning was performed at 78° with respect to the direction of
the long axis of the cantilever spring. The number of data points
analyzed was 512. The AES adhesion samples were smoothly cut in the
vertical direction of the brass plate. Two sites were chosen for analysis;
one was near the adhesion interphase, 120 μm away, and the other was
2 mm away from the adhesion interphase.

3. RESULTS AND DISCUSSION

3.1. Cure Characteristics and Physical Properties

The cure characteristics of the rubber compound were investigated at
160°C using an OD rheometer. Table I shows the cure characteristics
determined from rheocurves and the viscoelastic properties determined

TABLE I   The results of oscillating disc type rheometer and Mooney viscometer tests of the rubber compound

Oscillating disc rheometer[1]						Mooney viscometer[2]				
Time (min)			CRI	Torque (J)		Time (min)		Torque (J)		
t_2	t_{40}	t_{90}	(min^{-1})	min	max	t_5	t_{35}	initial	min	at 4 min
2.5	5.5	11.6	11.0	1.68	5.96	21.3	29.6	5.54	5.21	5.18

[1] The rubber compounds were sheared to ± 1° and 1.67 Hz at 160°C.
[2] The rubber compounds were sheared to 2 rpm at 125°C.

TABLE II   Physical properties of vulcanizates with respect to various cure times of the rubber compound

Times of t_{90}	Hardness (Shore A)	Modulus (MPa)				T.S.[1] (MPa)	E.B.[2] (%)
		5%	100%	200%	300%		
0.25	64	0.38	2.44	7.14	12.6	20.1	465
0.50	74	0.73	3.78	9.97	16.2	23.0	428
1.00	77	0.87	5.16	12.32	18.9	22.3	360
2.00	78	0.89	5.20	12.23	15.7	18.1	305
4.00	77	0.89	4.36	9.89	–	16.0	289

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

by Mooney viscometer. From the rheocurve, the t_{90} time was determined and used to calculate the cure time.

Because the objective of this study is to investigate the effect of cure time on the adhesion properties between brass-plated steel cord and rubber compound, cure time was set to be 25%, 50%, 100%, 200%, and 400% of t_{90} time. The physical properties of the rubber compound varied conspicuously as shown in Table II. With increased cure time up to the t_{90} time, hardness, modulus and tensile strength of vulcanizates increased but elongation at break decreased. These facts can be explained by the increase of crosslinking density of the rubber compounds with increasing cure time. With further increase of cure time above the t_{90} time, modulus and tensile strength decreased due to the severe reversion of the vulcanizates.

Physical properties of rubber vulcanizates aged thermally for 5 days at 90°C are summarized in Table III. The hardening of the rubber compound by aging leads to an increase in hardness and modulus. Compared with the samples before aging, tensile strength and elongation decreased; however, the tendency of these properties

TABLE III Physical properties of thermally-aged[1] vulcanizates with respect to various cure times of the rubber compound

Times of t_{90}	Hardness (Shore A)	Modulus (MPa)				T.S.[2] (MPa)	E.B.[3] (%)
		5%	100%	200%	300%		
0.25	83	1.02	8.33	–	–	12.1	141
0.50	86	1.26	10.38	–	–	10.4	102
1.00	88	1.62	–	–	–	9.5	65
2.00	88	1.48	–	–	–	9.0	59
4.00	88	1.52	–	–	–	8.3	60

[1]The tensile-test samples were thermally aged for 5 days at 105°C.
[2]Tensile strength.
[3]Elongation-at-break.

to decrease with the increase in cure time is similar to that before aging.

3.2. Adhesion Properties

Adhesion between the brass-plated steel cord and the rubber compound depends largely on the physical properties of the rubber stock adhered to the interphase as well as the stability of the adhesion interphase formed. Variation in the structure of the adhesion interphase can also alter adhesion. Pull-out force of unaged adhesion samples increased with the increase in cure time up to the t_{90} time as shown in Figure 1. Further increase in cure time decreased the pull-out force. Rubber coverage of pulled-out cord showed a maximum at the t_{90} time of cure (Fig. 2). In spite of a cure time as short as one-fourth of cure time, considerable pull-out force was found. This phenomenon supported the fact that the formation of the adhesion interphase is far faster than the crosslinking of the rubber compound.

After thermal aging, a similar trend of pull-out force with cure time is observed. Compared with unaged adhesion samples, the rubber coverages of thermally-aged adhesion samples were generally higher for the under-cured adhesion samples wereas they were lower for the optimum and over-cured adhesion samples (Fig. 3). Also, the change in the rubber coverage with thermal aging time was not the same for all the adhesion samples. The rubber coverages for under-cured adhesion samples increased with increasing thermal aging time up to 10 days. Further increase of aging time caused a decline in rubber
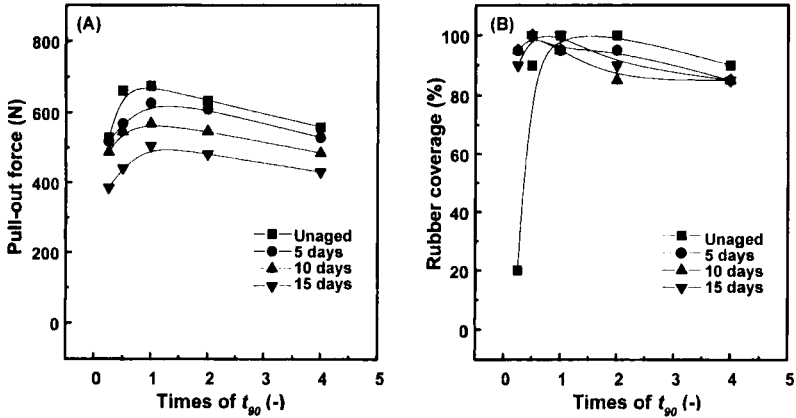
FIGURE 1 Pull-out force (A) of thermally-aged adhesion samples and rubber coverage (B) on the surface of pulled-out steel cord as a function of the cure time of the rubber compounds.
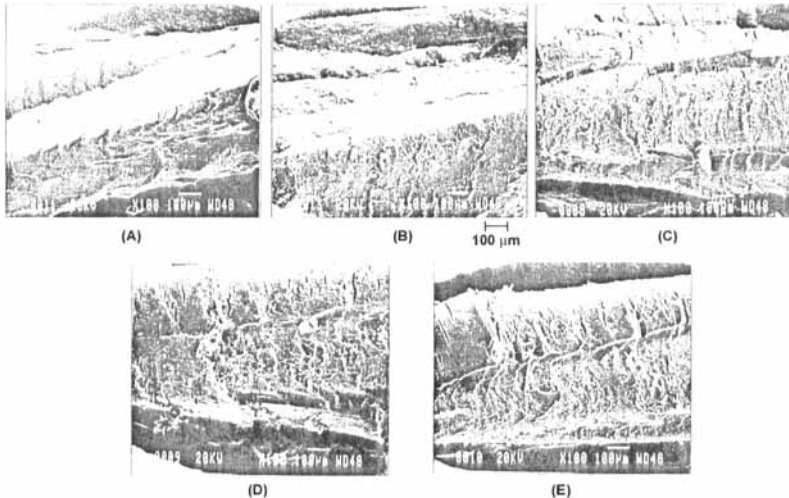

FIGURE 2 SEM micrographs of pulled-out steel cord of unaged adhesion samples with respect to the cure time: (A) 2.9 min; (B) 5.8 min; (C) 11.6; (D) 23.2 min; (E) 46.4 min.

coverage. The rubber coverages for the optimum and over-cured adhesion samples decreased with the thermal aging time; a maximum value was not shown during thermal aging periods. This phenomenon
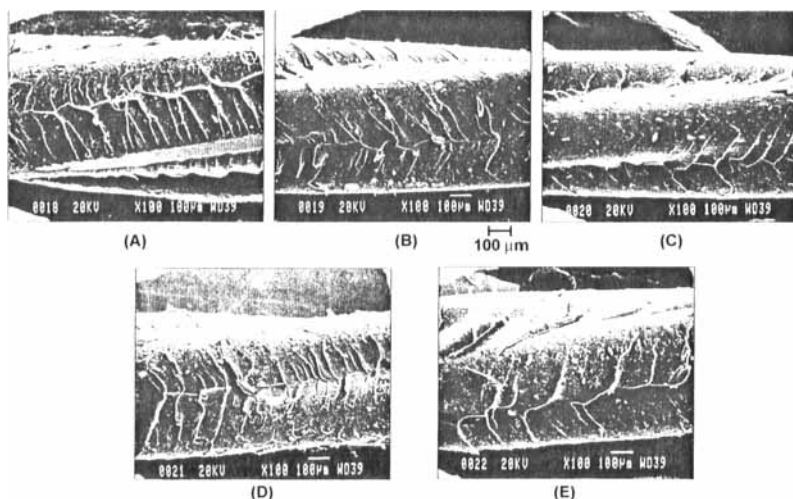
FIGURE 3   SEM micrographs of pulled-out steel cord of adhesion samples aged thermally for 15 days with respect to the cure time: (A) 2.9 min; (B) 5.8 min; (C) 11.6; (D) 23.2 min; (E) 46.4 min.

may in large part be attributable to the postvulcanization of adhesion samples. For the under-cured adhesion samples, further increase of crosslinking after thermal aging due to postvulcanization occuring during thermal aging is very useful for the enhancement of physical properties of the rubber compounds near the adhesion interphase. Further increase of aging time caused not crosslinking but reversion of rubber chains resulting in poor rubber coverage. On the contrary, the reversion of rubber chains instead of postvulcanization was dominant for the optimum and over-cured adhesion samples during thermal aging, resulting in the decrease of rubber coverage with cure time.

Adhesion properties after humidity aging showed a similar behavior to those of thermally-aged adhesion samples except for the shift of maximum pull-out force at 50% of cure time (Fig. 4). As shown in Figure 5, the attached rubber on pulled-out steel cord decreased with increasing cure time. Considering the fact that thermal aging causes adhesive deterioration *via* reduced mechanical strength of the rubber compound and humidity aging relates to the change of the adhesion interphase [14], the difference in the adhesion with cure time after humidity aging is due to the change in the adhesion interphase.
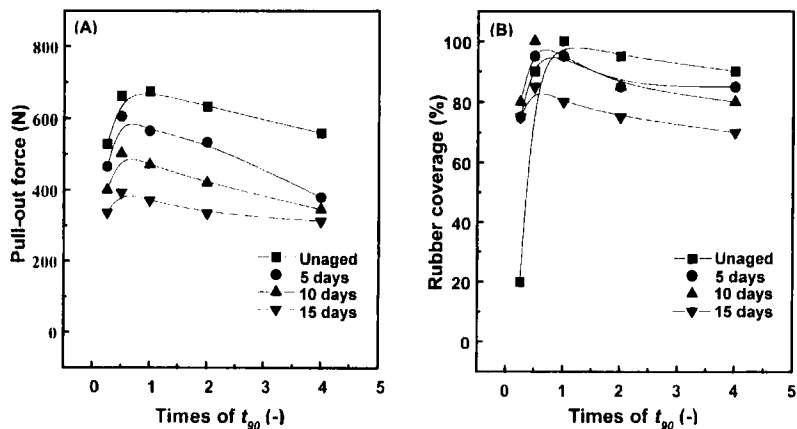
FIGURE 4   Pull-out force (A) of humidity-aged adhesion samples and rubber coverage (B) on the surface of pulled-out steel cord as a function of cure time of the rubber compounds.
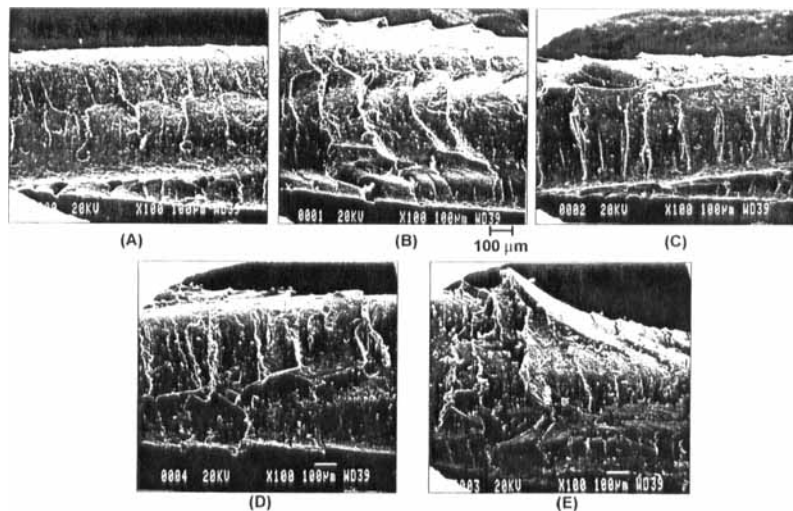

FIGURE 5   SEM micrographs of pulled-out steel cord of adhesion samples humidity aged for 15 days with respect to the cure time: (A) 2.9 min; (B) 5.8 min; (C) 11.6; (D) 23.2 min; (E) 46.4 min.

3.3. Characterizing the Adhesion Interphase

The composition and structure of the adhesion interphase between a rubber compound and a thin brass deposited film were investigated.

After curing with the same conditions as used in the preparation of the adhesion sample of rubber compound and steel cord, the distribution of copper, zinc, sulfur and oxygen at the adhesion interphase was obtained through sputtering from the brass surface to the rubber using an AES. As elaborated in a monograph by Seo [12] and Jeon *et al.* [13], unreacted brass, followed by copper, zinc, oxygen and sulfur, is detected in the adhesion interphase between the rubber compound and the thin brass film. Depth profiles of zinc and oxygen coincide well with those of copper and sulfur indicating the formation of zinc oxide and copper sulfide.

In an attempt to observe the discrepancy between adhesion interphases for different cure times, Figure 6 shows the depth profiles of sulfur and copper (upper) and that of zinc and oxygen (bottom) as a function of sputtering time. For the samples cured for 25% of t_{90} at 160°C, a shoulder peak appears at the end of the copper peak, where sulfur is detected simultaneously, suggesting the formation of copper sulfide. However, copper content seems too low for copper sulfide to
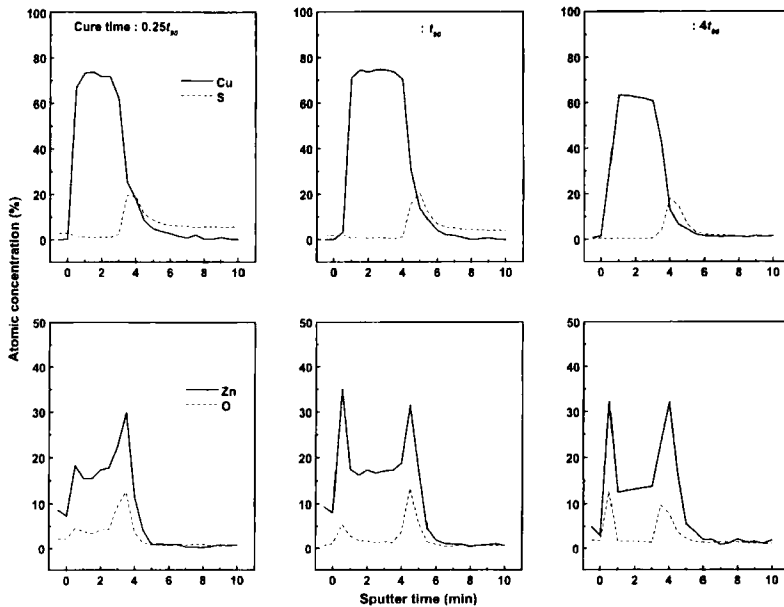

FIGURE 6 AES depth profiles of copper and sulfur (top) and zinc and oxygen (bottom) for the unaged brass-on-glass adhesion samples cured for the indicated t_{90} times.

have the structure of $Cu_{1.95}S$ as proposed by van Ooij [1]. Similarly, the depth profiles of zinc and oxygen, detected at the same sputtering time, ensure the existence of zinc oxide. Yet, because the zinc content is higher than that of oxygen, the possibility is high that a part of zinc present is in the form of zinc sulfide rather than zinc metal, ZnO, and $Zn(OH)_2$. In the depth profiles of zinc, a peak detected at the outermost surface results from the reaction of zinc, which is more readily oxidized than copper, with oxygen or sulfur *etc.*, after migrating to the surface.

The shape of those depth profiles remains similar even at the prolonged cure time up to 400% of t_{90}. However, when the cure time was increased by up to four times, depth profiles of sulfur and copper were not coincident, suggesting a portion of sulfur having structures other than copper sulfide. For the adhesion samples vulcanized for four times of t_{90} the fact that the maximum of the sulfur peak coincides well with the shoulder of the zinc peak shows the increased formation of zinc sulfide. That is, with increasing cure time, zinc sulfide forms in abundance rather than copper sulfide [18]. Copper sulfide and zinc oxide are mainly generated in the adhesion interphase between the thin deposited brass film and rubber compound cured at short cure time. However, when the cure time increases, the formation of zinc sulfide increases while copper sulfide decreases. Reactivity against sulfur is higher for copper than zinc [6]; however, sulfidation of zinc becomes relatively faster with the extension in cure time and, hence, the amount of zinc sulfide formed increases. When the cure time is as long as four times of t_{90} formation of zinc sulfide increases.

Humidity aging is a very effective way to investigate the degradation of adhesion due to the change in the adhesion interphase compared with thermal aging which induces mainly the decline of the physical properties of the rubber compound. Figure 7 shows the depth profiles of the humidity-aged adhesion interphases formed on the brass side adhered to the rubber compound. For the under-cured adhesion samples, the adhesion interphase showed no significant change compared with the unaged adhesion samples. But copper and sulfur peaks for optimum and over-cured adhesion samples were broadened with an increase in the cure time indicating the severe growth and deformation of the adhesion interphase. For the over-cured adhesion sample, the most of the zinc and oxygen disappeared. The ZnO layer
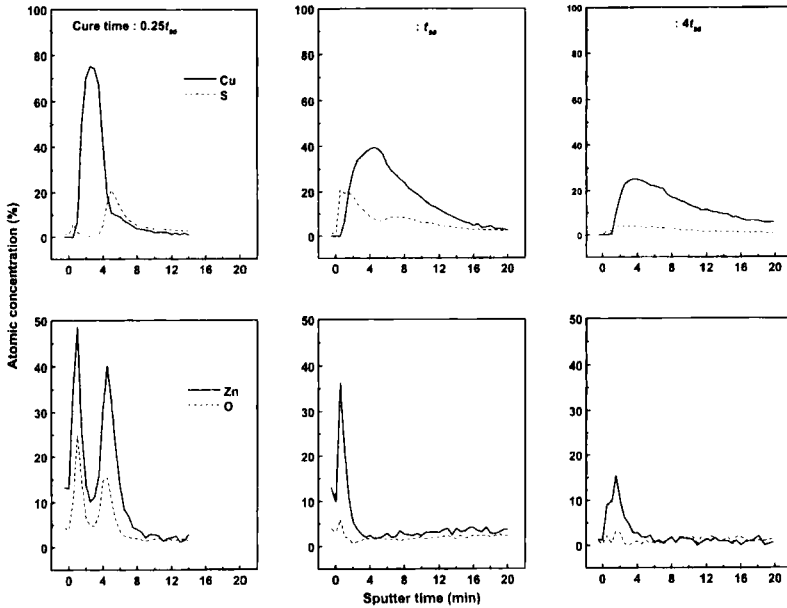
FIGURE 7   AES depth profiles of copper and sulfur (top) and zinc and oxygen (bottom) for the brass-on-glass adhesion samples cured for the indicated t_{90} times and humidity-aged for 15 days.

plays the role of a diffusion barrier of copper into adhesion interphase. As the cure time increased, a portion of the outermost ZnO reacted with the stearic acid in the rubber compound and the remaining ZnO also formed ZnS with activated sulfur in then rubber compound. Therefore, the depletion of the ZnO layer at the adhesion interphase led to the severe growth and deformation of adhesion interphase especially of copper sulfide. The humidity aging and longer cure time resulted in the occurrence of dezincification.

The difference in the extent of cure for the rubber between, the two sites is summarized in Table IV. In the cure time range of from one-fourth of t_{90} to four times of t_{90}, extent of cure of the rubber compound near the adhesion interphase was smaller than that in the bulk. The ratio of signal peak heights for near the adhesion interphase to the bulk rubber decreased with increasing cure time, indicating the severe formation of a weak boundary layer near the adhesion inter-phase by the extension of cure time. In the prematurely cured adhesion

TABLE IV Comparison of extent of cure for the rubber compound adjacent to the interphase with that away from the adhesion interphase determined by the force modulation mode of atomic force microscopy

Times	Peak Height (V),		Ratio[3]
of t_{90}	Away from interphase[1]	Adjacent to interphase[2]	(%)
0.25	1.25	1.03	82
0.50	2.81	2.25	80
1.00	3.55	2.70	76
2.00	3.81	2.71	71
4.00	4.02	2.41	60

[1] The analyzed area in the rubber was bulk rubber, 2 mm away from the adhesion interphase.
[2] The analyzed area in the rubber was near the adhesion interphase, 120 μm away from it.
[3] The ratio of average peak height for the rubber away from the interphase to that adjacent to the interphase.

samples, the peak height is small compared with the optimum and over-cured samples. This is responsible for the incomplete vulcanization of the under-cured adhesion sample. Beyond a cure time of t_{90}, however, significant decline extent of cure was also shown for the rubber near the adhesion interphase compared with that of bulk rubber. At a cure time of four times of t_{90}, the extent of cure near adhesion interphase was as much as 60% of that in the bulk. In spite of cure time as short as one-fourth of t_{90}, significant deficiency of sulfur at the adhesion interphase occurred. It is well known that the formation of the adhesion interphase occurs far faster than the rubber cure. At prolonged cure time, a large portion of sulfur near the adhesion interphase was consumed for the formation and growth of the interphase and, consequently, crosslinking in the bulk rubber occurred faster than near the adhesion interphase. Therefore a concentration gradient of sulfur through the region from near the adhesion interphase to the bulk rubber could be generated. The diffusion of sulfur into the rubber near the adhesion interphase from the bulk rubber during the cure process was effectively hindered by the crosslinking network formed during prolonged cure-time. Therefore, prolonged cure time prohibited the mass transfer of sulfur, which generally results in poor physical properties of is the rubber near the adhesion interphase, indicating one of the major reasons for lower adhesion.

The influence of humidity aging time on the adhesion interphase for the optimum and over-cured adhesion samples is shown in Figure 8 (copper and sulfur) and Figure 9 (zinc and oxygen),
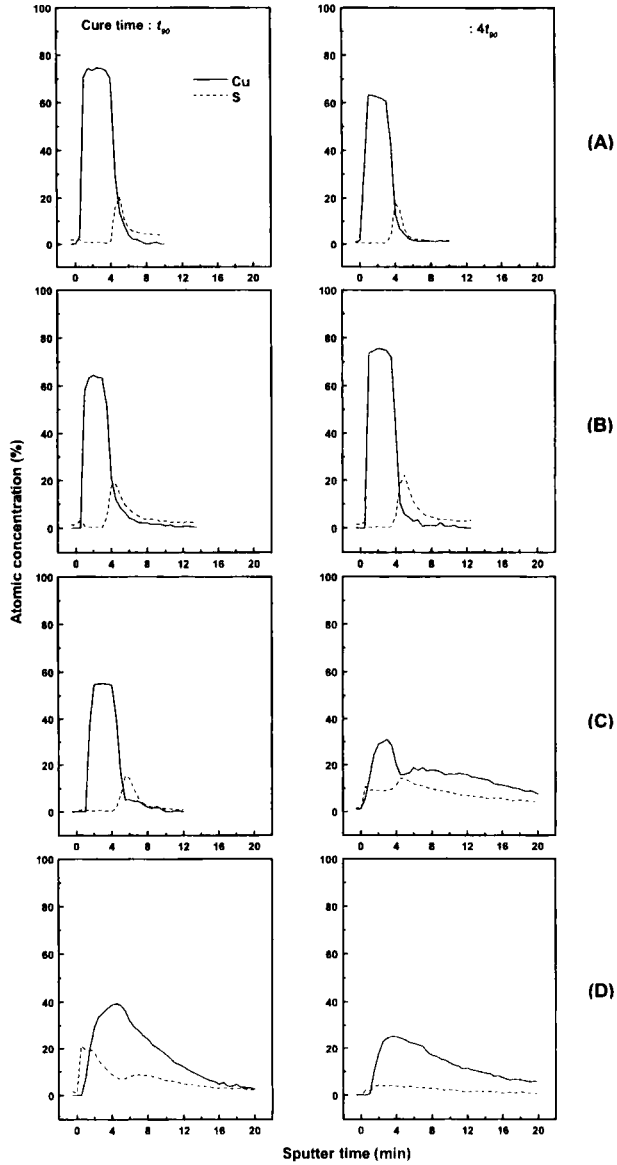
FIGURE 8 AES depth profiles of copper and sulfur for the brass-on-glass adhesion samples humidity-aged, with respect to aging time: (A) 0 days; (B) 5 days; (C) 10 days; (D) 15 days.
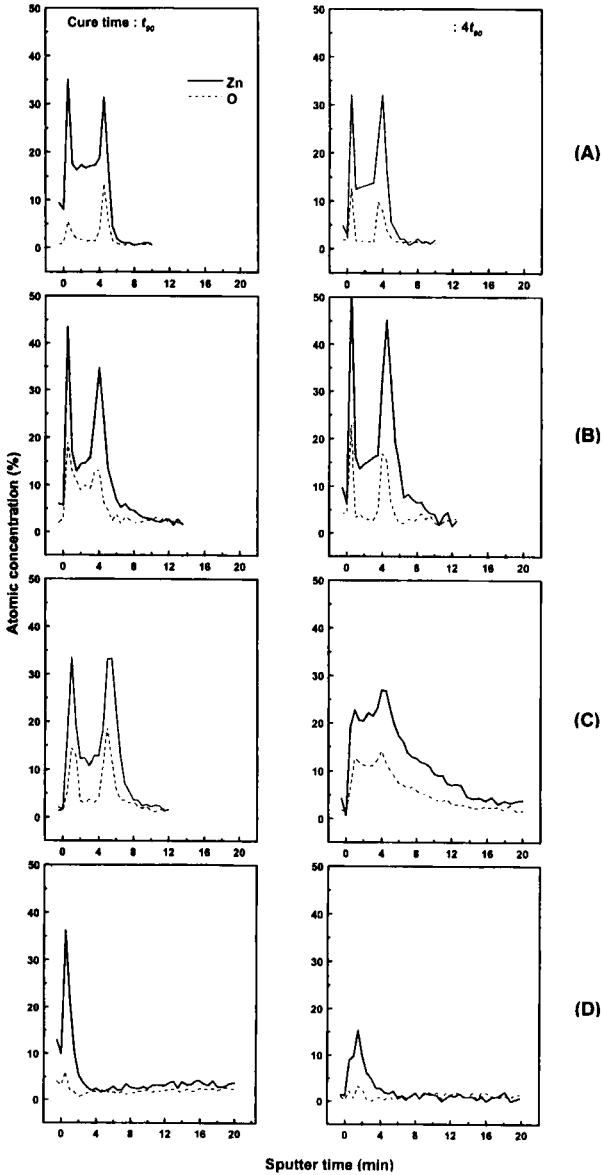
FIGURE 9 AES depth profiles of zinc and oxygen for the brass-on-glass adhesion samples humidity-aged, with respect to aging time: (A) 0 days; (B) 5 days; (C) 10 days; (D) 15 days.

respectively. As shown in Figure 8, the deformation of the adhesion interphase of copper sulfide for optimum-cure adhesion samples started in the 15th day of humidity aging, whereas that for over-cured adhesion samples started after 10 days. The over cure led to the faster deformation of the adhesion interphase. This fact was also supported in Figure 9.

3.4. Effect of Cure Time on Adhesion Properties

The influence of cure time on the adhesion properties of brass-plated steel cords embedded in the rubber compound is very large because it affects both the mechanical properties of the rubber stock and the adhesion interphase between the brass and the rubber compound. Thermal aging brings about deterioration of the adhesion, but the extent of lowering is as large as that in the tensile strength of the rubber compound.

On the contrary, residual rubber coverage reduced to 85% after 15 days humidity aging of adhesion samples cured for four times of t_{90}, and this drop in rubber coverage can not be fully explained by a lowering of the mechanical strength of the rubber vulcanizate by humidity aging. It can be attributed to the formation of an adhesion interphase that is easily disrupted by humidity aging at prolonged cure time, because extremely low rubber coverage indicates the occurrence of a rupture in the adhesion interphase. That is, a drop in rubber coverage can also result from the effect that the composition or components of the adhesion interphase vary with the cure time.

The formation of copper sulfide and zinc oxide can be confirmed with ease by the depth profiles for copper, zinc. oxygen, and sulfur obtained from the adhesion interphase between the rubber compound and the thin brass deposited film. The formation of zinc sulfide can also be inferred by comparing the composition profiles for the over cure of adhesion samples. The formation of these components varies with the cure time. Prolonged cure time accelerates the formation of zinc sulfide and, for the adhesion samples cured for four times of t_{90}, a great deal of zinc sulfide was formed to the extent that the depth profile curves of sulfur and copper were not coincident each other. A systematic study of the contribution of cure time to the adhesion or stability of zinc sulfide at the adhesion interphase has

not been reported; however, stability of the adhesion interphase was probably interfered with by the excessive formation of zinc sulfide. It is because nonstoichiometric copper sulfide contributes to the rubber adhesion [19], while the zinc oxide or zinc sulfide formed in a stable compound contributes little to the adhesion. The zinc oxide or zinc sulfide layer grown excessively is readily ruptured when the zinc metal layer is destroyed by humidity aging [18]. The effect of the overgrowth of zinc sulfide is not remarkable during thermal aging which detracts mainly from the rubber properties; however, humidity aging lowers the adhesion, especially the rubber coverage, because the metal support layer disappears due to dezincification by moisture.

The extent of cure determined by the force modulation mode of atomic force microscopy showed that the weak boundary layer of the adhesion sample near the adhesion interphase formed significantly with increasing cure time. For all adhesion samples, the extent of cure of the adhesion sample near the adhesion interphase is less than that of bulk rubber. With increasing cure time, the extent of cure for the adhesion sample near the adhesion interphase is less than that of bulk rubber. This phenomenon can be explained as follows. A long cure time causes postvulcanization in both the bulk rubber and in the rubber at the adhesion interphase. But the diffusion of active sulfur, necessary for cure, from the bulk rubber to the interphase becomes more difficult due to steric hindrance as crosslinking (postvulcanization) increases, so the extent of cure for the rubber at the adhesion interphase during a long cure time is smaller than that of rubber in the bulk, when compared with what occurs during a short cure time. Thus, a weak boundary layer is formed in the rubber near the adhesion interphase which leads to failure of adhesion.

It is rather difficult to sort out simply the effects of cure time since it affects various processes such as rubber fluidity, mass transfer rate, as well as the rate of cure reaction and formation of the adhesion interphase. Nevertheless, when samples are cured for four times of t_{90}, adhesion properties are lowered because of the decrease in the rubber strength with increasing reversion rate. In addition, adhesion, particularly rubber coverage, is lowered significantly after humidity aging because the stability of the adhesion interphase is hindered by the excessive formation of zinc sulfide in it.

4. CONCLUSIONS

Cure time has a large effect on the adhesion between a rubber compound and brass-plated steel cords because it affects both the physical properties of the rubber compound and the condition of the adhesion interphase. With the adhesion system of the rubber stock and brass-plated steel cord used in the present study, the variation in the pull-out force of the adhesion samples could be explained by the changes in physical properties, especially in the tensile strength of the rubber compound, for the specimens having a stable adhesion interphase formed during an optimum cure time. On the contrary, when the cure time was extended to as much as four times of t_{90}, rubber coverage became markedly lower because, in addition to the lessened rubber strength, the adhesion interphase is easily ruptured by humidity aging by means of which excessive zinc sulfide could be formed at the adhesion interphase, followed by dezincification. Prolonged cure time of the adhesion samples led to significant formation of a weak boundary layer near the adhesion interphase, leading to the cohesive failure of the rubber layer.

References

[1] van Ooij, W. J., *Rubber Chem. Technol.* **52**, 605 (1979).
[2] Hammer, G. E., Shemenski, R. M. and Hunt, J. D., *J. Vac. Sci. Technol. A* **12**, 2388 (1994).
[3] van Ooij, W. J., Weening, W. E. and Murray, P. F., *Rubber Chem. Technol.* **54**, 227 (1981).
[4] Ishikawa, Y., *Rubber Chem. Technol.* **57**, 855 (1984).
[5] van Ooij, W. J. and Kleinhesselink, A., *Appl. Surface Sci.* **4**, 324 (1980).
[6] Chandra, A. K., Biswas, A., Mukhopadhyay, R. and Bhowmick, A. K., *J. Adhesion Sci. Technol.* **10**, 431 (1996).
[7] Kurbatov, G. G., Beshenkov, V. G. and Zaporozchenko, V. I., *Surf. Interface Anal.* **17**, 779 (1991).
[8] Kretzschmar, T., Hummel, K., Hofer, F., Grogger, W. and Grubbauer, G., *Fresenius J. Anal. Chem.* **349**, 235 (1994).

[9] Zakharov, V. P., Sakharova, E. V., Shvarts, A. G. and Potapov, E. E., *International Polymer Science and Technology* **15**, T/6 (1988).

[10] Ozelli, R. N. and Scheer, H., *International Polymer Science and Technology* **7**, T/43 (1980).

[11] Coppens, W., Chambaere, D. and Lievens, H., *Rubbercon'87* **45A** (1987).

[12] Seo, G., *J. Adhesion Sci. Technol.* **11**, 1433 (1997).

[13] Jeon, G. S., Han, M. H. and Seo, G., *J. Adhesion* **69**, 39 (1999).

[14] Stroup, E. W., Pungor, A. and Hlady, V., *Ultramicroscopy* **66**, 237 (1996).

[15] Li, F.-B., Thompson, G. E. and Newman, R. C., *Applied Surf Sci.* **126**, 21 (1998).

[16] Munz, M., Sturm, H., Schulz, E. and Hinrichsen, G., *Composites Part A* **29A**, 1251 (1998).

[17] Kerssemakers, J. and De Hosson, J. Th. M., *Surf Sci.* **417**, 281 (1998).

[18] Lievens, H., *Kautsch. Gummi, Kunstst.* **39**, 122 (1986).

[19] Chandra, A. K., Mukhopadhyay, R., Konar, J., Ghosh, T. B. and Bhowmick, A. K., *J. Mater. Sci.* **31**, 2667 (1996).