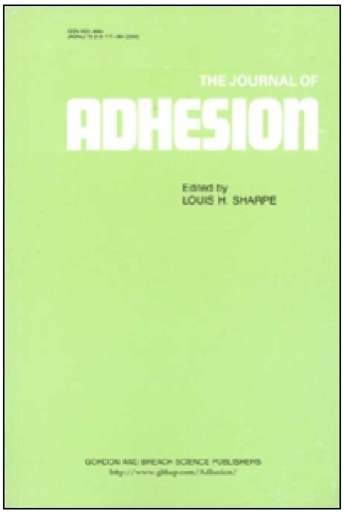

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# Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-plated Steel Cord. Part I. Cure Temperature

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# Influence of Cure Conditions on the Adhesion of Rubber Compound to Brass-plated Steel Cord. Part I. CureTemperature

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The effect of the cure temperature of rubber compound on the adhesion with brass-plated steel cord was investigated in conjunction with the formation, growth and degradation of the adhesion interphase formed between the rubber compound and brass-plated steel cord. With increasing cure temperature from 130°C to 190°C, the pull-out force after cure decreased linearly. This decrease in adhesion force at higher temperature may be explained by the limitation of the mass transfer of vulcanizing agents into the adhesion interphase and/or rubber compound near the adhesion interphase, resulting in a deficiency of sulfur due to the fast cure of the rubber compound which significantly retards the diffusion of vulcanizing chemicals. Also, at a high temperature, an adhesion interphase with a ZnS-rich layer, which may act as a barrier to copper diffusion for the formation of the adhesion interphase of copper sulfide, was formed. 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 the tensile properties after thermal aging. The adhesion property after humidity aging was completely different from that after thermal aging. With increase in the cure temperature to 160°C, the pull-out force increased. But further increase in the cure temperature caused a decline in pull-out force. This phenomenon can be explained by the degradation of the adhesion interphase. At lower cure temperatures, a severe growth of copper sulfide and a large extent of dezincification were observed in the adhesion interphase. At higher cure temperatures, a significant growth of copper sulfide in the adhesion interphase appeared. The proper formation of the adhesion interphase and good physical properties of the rubber compound at a moderate cure temperature can result in high retention of adhesion properties.

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*Keywords*: Adhesion interphase; AES; Steel cord; Rubber compounds; Cure temperature

## 1. INTRODUCTION

Brass-plated steel cord embedded in rubber compounds provides, through the adhesion between them by the reaction of copper in brass with sulfur in rubber during the curing process, increased mechanical stability for tires. Adhesion properties, however, 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 [1]. Since the failure may possibly occur by the rubber adhered to the interphase, the physical properties of the rubber compound have also become the dominating factor in determining the adhesion properties [2, 3]. Accordingly, a number of studies for the optimization of the compound's composition and cure condition have been carried out to strengthen the rubber at the interphase and to form a stable adhesion interphase [1 – 7].

As the degree and rate of reaction for the adhesion interphase formation and crosslinking of compounds vary with the cure temperature and time, the adhesion properties of the rubber compound change. Decreasing the cure time and increasing the cure temperature for better productivity encounters limitations such as the deterioration of adhesion and physical properties of rubber compounds. Rapid cure reaction resulting from elevated vulcanization temperature leads to reversion and increasing heterogeneity of the rubber compound [8].

An excessive rise in cure temperature causes the adhesion property to be far less than that predicted from the physical property of the rubber. Since constitutive components and state of the adhesion interphase vary with the cure temperature, it can be anticipated that the adhesion property will undergo a change, although this has not yet been confirmed empirically.

Investigation of the adhesion property 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, 2, 7]. 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, showing its compositional distribution [9–11]. 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.

The influence of cure temperature on the adhesion property depends partly on the diffusion rate of the crosslinking agent of the rubber compound into the adhesion interphase. The diffusion limitation of crosslinking agent of the rubber compound leads to the formation of a weak boundary layer of rubber near the adhesion interphase which is the principal reason for cohesive failure in the rubber layer. Zakharov *et al.* reported the formation of a weak boundary layer near the adhesion interphase, 120 μm away. This study used a combination of solvent swelling and cryomicrotome cutting [12]. But this method is very difficult to apply to a vulcanizate only 1 μm thick. Alternatively, we employed the force modulation (FM) technique of atomic force microscopy (AFM) to measure the extent of cure for the rubber near the adhesion interphase and bulk rubber. The force modulation 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 [13–16]. Further, the mechanical properties are proved continuously over extended areas instead of at scattered individual points.

The present study concerns the effect of cure temperature 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 at a predetermined cure time and temperature derived from a rheocurve. In addition, vulcanization of the rubber compound in contact with a thin brass film was carried out at various temperatures to observe by AES the role of cure temperature on the adhesion interphase. Also, the extents of cure of adhesion samples of rubber near the adhesion interphase and in the bulk rubber were measured using the force modulation technique of

AFM. From these observations, the reason why the adhesion property decreases greatly at a very high temperature was considered and discussed.

## 2. EXPERIMENTAL

### 2.1. Rubber Compound Preparation

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

Masterbatch components were as follows:

- natural rubber (Lee Rubber Co., Malaysia, SMR 20) 90 phr,
- butadiene rubber (Kumho Petrochem. Co., South Korea, BR-01) 10 phr,
- carbon black N351 (Lucky Co., South Korea) 45 phr,
- aromatic processing oil (Michang Co., South Korea, A#2) 5 phr,
- zinc oxide (Hanil Co., South Korea) 10 phr,
- antioxidant (Monsanto Co., USA, Kumanox-13, N-(1,3-dimethylbutyl), N-phenyl-p-phenylenediamine) 1 phr,
- Co salt (Taekwang Chem. Co., South Korea, Co-stearate, 10 wt% Co) 1 phr
- resorcinol formaldehyde resin (Indspec Co., USA, Penacolite B-18-S) 3 phr

Final mixing components were as follows:

- masterbatched rubber compound
- stearic acid (Pyungwha Co., South Korea) 1 phr,
- methylene donor (Angus Chem. Co., USA, NMP-PLUS, 2-nitro-2-methyl-1-propanol) 3 phr
- accelerator (Monsanto Co., USA, Santocure MOR, 2-(morpholinothio) benzothiazole sulfenamide) 0.5 phr.
- insoluble sulfur (Akzo Co., The Netherlands, Crystex HS OT 20) 4.0 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 the 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 masterbatched 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 over the temperature range from 130°C to 190°C, at intervals of 15°C, the $t_{90}$ time of the rubber compound at each corresponding temperature was measured based on the rheocurve. A Monsanto Rheometer (model Rheo-100) was used to obtain the 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 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 the corresponding temperature for $t_{90}$ plus 5 min 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 at 85°C under 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 sputterer for 70 sec at $2 \times 10^{-6}$ Torr [10, 11]. 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 $2 \times 2\,\text{mm}^2$ 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 for indicating the depth of the adhesion interphase in this paper.

In order to investigate adhesion characteristics on the cure temperature, 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 Adhesion Interphase by Force Modulation 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 the mechanical properties of the sample. An AFM (Auto Probe M5 model, PSI Co., South Korea) tip was designed to scan in contact with the sample for 20 μm, and a z feedback loop maintained a constant cantilever. A signal was applied periodically to the tip and the amplitude of the cantilever modulation that resulted from the 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 length, width 4 μm, and 0.5 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 in the bulk rubber, 2 mm away from the adhesion interphase.

## 3. RESULTS AND DISCUSSION

### 3.1. Cure Characteristics and Physical Properties

The cure characteristics of a rubber compound were investigated over a temperature range of 130°C to 190°C, at 15°C intervals, using an OD rheometer. The higher the cure temperature, the faster the cure rate and the reversion rate. Table I shows the cure characteristics determined from rheocurves. The $t_2$ and $t_{90}$ times decreased remarkably with the rise in cure temperature, and the cure rate at 190°C was 25 times (more) that at 130°C when comparing the cure rate index (CRI). Minimum and maximum torques were not changed together in the same direction by a change in cure temperature. Because of the improved fluidity, minimum torques became slightly lower when the cure temperature increased from 130°C to 145°C. Beyond this temperature,

TABLE I Results of oscillating disc type rheometer⁽¹⁾ with respect to the cure temperature of rubber compounds

| *Cure temp.* | *Time (min)* | | | *CRI* ⁽²⁾ | *Torque (J)* | |
|---|---|---|---|---|---|---|
| (°*C*) | $t_2$ | $t_{40}$ | $t_{90}$ | (*min*$^{-1}$) | *min* | *max* |
| 130 | 14.2 | 20.6 | 40.5 | 3.8 | 1.62 | 5.24 |
| 145 | 5.1 | 8.0 | 17.5 | 8.1 | 1.40 | 5.37 |
| 160 | 2.3 | 3.7 | 7.1 | 20.8 | 1.42 | 5.45 |
| 175 | 1.0 | 1.7 | 3.0 | 50.0 | 1.34 | 5.40 |
| 190 | 0.5 | 0.9 | 1.6 | 90.9 | 1.36 | 5.25 |

⁽¹⁾ The rubber compounds were sheared to ± 1° and 1.67 Hz at 160°C.

⁽²⁾ Cure rate index (CRI) = 100 ÷ ($t_{90} - t_2$).

no significant differences were found. However, maximum torque had its highest value at 160°C. This is because sufficient vulcanization can not be attained at low temperatures due to the slow cure rate, while fast reversion results in a reduced torque at an extremely high temperature. Nevertheless, since the difference in torque is not more than 5% for the cure temperatures tested and the cure time can be adjusted appropriately over this range of temperatures, a similar extent of vulcanization seemed to be achievable even at different cure temperatures.

For the objective of this study, to investigate the effects of the cure temperature on the adhesion properties between brass-plated steel cord and rubber compound, cure time was set at $t_{90}$ plus 5 min to ensure a similar degree of vulcanization regardless of the cure temperature. The addition of 5 min *en bloc* was to compensate for the retarded heat transfer due to sample thickness. Though the same degree of vulcanization should theoretically have been obtained, the physical properties of the rubber compound varied slightly, as shown in Table II, because the $t_{90}$ time was determined from maximum torque and, thus, the rate of cure and reversion became different in accordance with the cure temperature. A maximum value of modulus was obtained for the rubber cured at 145°C, whereas tensile strength and elongation decreased with increasing cure temperature. This fact can be explained by the severe reversion which occurs at elevated temperature. In the temperature range of 130–170°C, discrepancies between physical properties were no more than about 10%.

On the contrary, physical properties for the rubber compounds cured at an elevated temperature of 190°C were significantly lower compared with the other compounds cured at different (lower)

TABLE II Physical properties of vulcanizates with respect to the cure temperature

| *Cure temp.* | *Hardness* | *Modulus (MPa)* | | | *T.S.*(1) | *E.B.*(2) |
|---|---|---|---|---|---|---|
| (°*C*) | (*Shore A*) | 100% | 200% | 300% | (*MPa*) | (%) |
| 130 | 67 | 3.20 | 7.83 | 13.4 | 24.7 | 514 |
| 145 | 67 | 3.67 | 8.74 | 14.3 | 24.6 | 490 |
| 160 | 66 | 3.23 | 8.06 | 13.8 | 24.5 | 488 |
| 175 | 65 | 3.19 | 8.06 | 13.9 | 24.0 | 473 |
| 190 | 64 | 2.76 | 6.99 | 12.4 | 19.9 | 437 |

(1) Tensile strength.
(2) Elongation-at-break.

temperatures. This can be attributed to the reduced homogeneity of rubber due to the accelerated cure rate and to the abundant formation of monosulfidic crosslinking, readily formed at high temperatures, which is a weak bonding force. Furthermore, highly-developed reversion as a result of the relatively large contribution of 5 min added *en bloc* to compensate for the delayed heat transfer due to the rubber thickness, may also account for the diminished physical properties because a $t_{90}$ time of 1.6 min at 190°C is exceedingly short.

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 samples before aging, tensile strength and elongation decreased; however, the tendency of decreasing with the increase in cure temperature is similar to that before aging. The mechanical properties of the rubber vulcanizate cured a 190°C were relatively low, but the difference was small as compared with 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. Although the cure time has been adjusted according to the cure temperature, the adhesion can vary with a small difference in the physical properties of the rubber compound caused by different temperatures. The variation in the structure of the adhesion interphase

TABLE III Physical properties of vulcanizates after thermal aging⁽¹⁾ with respect to the cure temperature

| *Cure temp.* | *Hardness* | *Modulus (MPa)* | | | *T.S.*⁽²⁾ | *E.B.*⁽³⁾ |
|---|---|---|---|---|---|---|
| (°*C*) | (*Shore A*) | 100% | 200% | 300% | (*MPa*) | (%) |
| 130 | 72 | 5.20 | 12.3 | 18.9 | 19.3 | 311 |
| 145 | 75 | 5.98 | 13.6 | – | 18.6 | 270 |
| 160 | 74 | 6.22 | 14.5 | – | 16.6 | 236 |
| 175 | 73 | 6.38 | 14.8 | – | 16.5 | 221 |
| 190 | 72 | 5.51 | 13.5 | – | 14.3 | 218 |

(1) The tensile-test samples were thermally aged for 5 days at 90°C.
(2) Tensile strength.
(3) Elongation-at-break.

can also alter the adhesion. Pull-out force of unaged adhesion samples decreased with the increase in cure temperatures as shown in Figure 1. After thermal aging, a similar trend of pull-out force with cure temperature is observed, and the pull-out force decreased with the rise in the cure temperature. Rubber coverages are generally high except for the rubber compound cured at 190°C. As shown in Figure 2, the attached rubber on the surface of the pulled-out cord is significant with a cure temperature of 130 – 160°C. But the almost bare interphase of pulled-out cord is apparent with a cure temperature of 175 – 190°C. After thermal aging, rubber coverage becomes low only for the

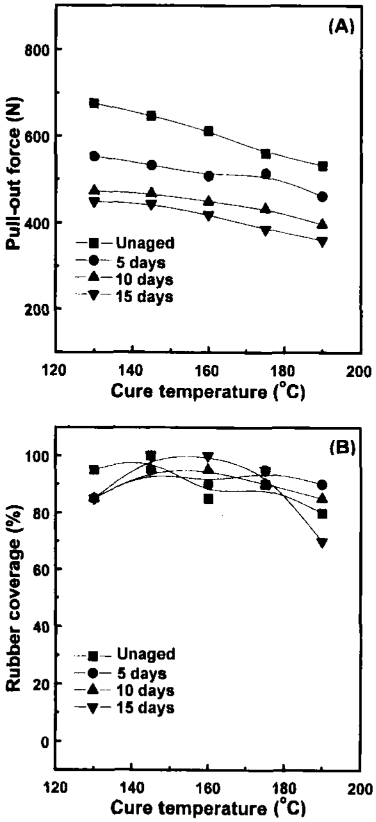

FIGURE 1 Pull-out force (A) of thermally-aged adhesion samples and rubber coverage (B) on the surface of pulled-out steel cord as a function of the cure temperature of rubber compounds.

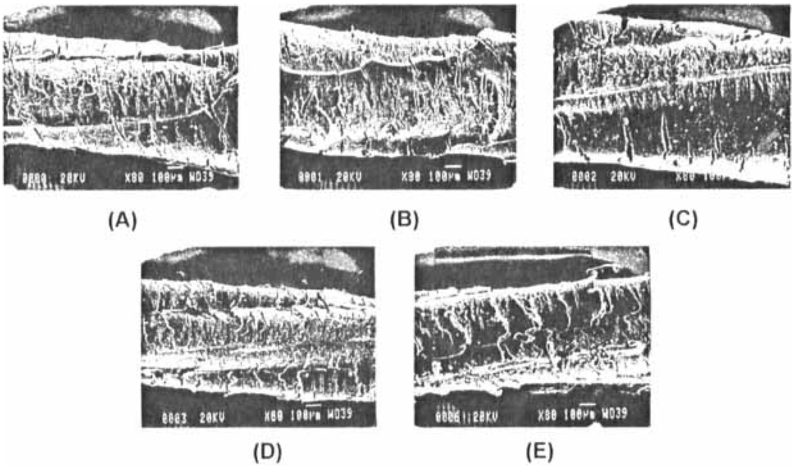

FIGURE 2 SEM micrographs of pulled-out cord surface of unaged adhesion samples with respect to the cure temperature: (A) 130°C; (B) 145°C; (C) 160°C; (D) 175°C; (E) 190°C.

specimens prepared at high temperature and aged for a prolonged time, as shown in Figure 1 and Figure 3.

When the rubber coverage is high, failure proceeds mainly at the rubber interphase rather than at the adhesion interphase. Higher rubber coverage before or after thermal aging suggests that a relationship should be present between the pull-out force and tensile strength, where the tensile strength indicates the resistance against rubber fracture. Figure 4 exhibits the relationship between pull-out force and tensile strength obtained from the unaged samples and after 5 days of thermal aging. Regardless of the cure temperature, a positive relationship exists between tensile strength and pull-out force, indicating that the difference in the physical properties of the rubber compound with cure temperature appears to be a cause for the variation in pull-out force.

Adhesion properties after humidity aging showed a different behavior from that of thermally-aged adhesion samples. As shown in Figure 5, in spite of a little decrement with increasing aging time, values for the pull-out force of specimens cured at 130–175°C lie in a similar range regardless of the cure temperature. However, pull-out force for the specimen vulcanized at 190°C is markedly low. Rubber coverage after humidity aging shows a three times wider scattering

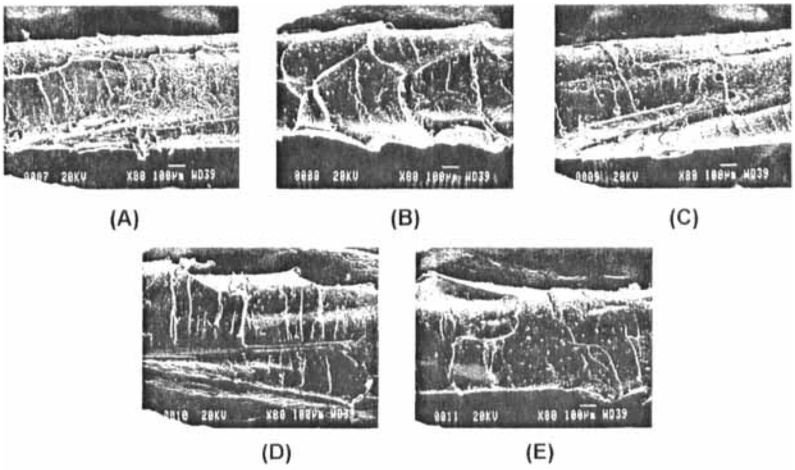

FIGURE 3 SEM micrographs of pulled-out cord surface of adhesion samples thermally aged for 15 days with respect to the cure temperature: (A) 130°C; (B) 145°C; (C) 160°C; (D) 175°C; (E) 190°C.

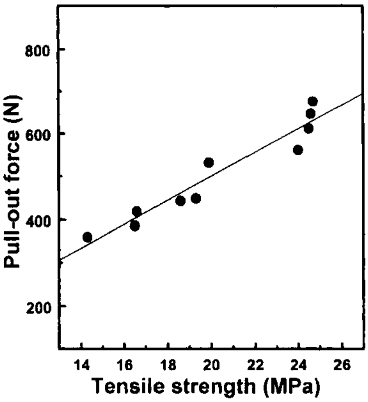

FIGURE 4 Effect of tensile strength of vulcanizates on the pull-out force of adhesion samples.

than pull-out force, while the values for unaged adhesion samples at 130–175°C are similar, as they scattered from 60 to 90%. On the contrary, the sample cured at 190°C shows a fairly low coverage. Figure 6 shows the pulled out cord surface of adhesion samples humidity aged for 15 days. At the cure temperature of 190°C, the

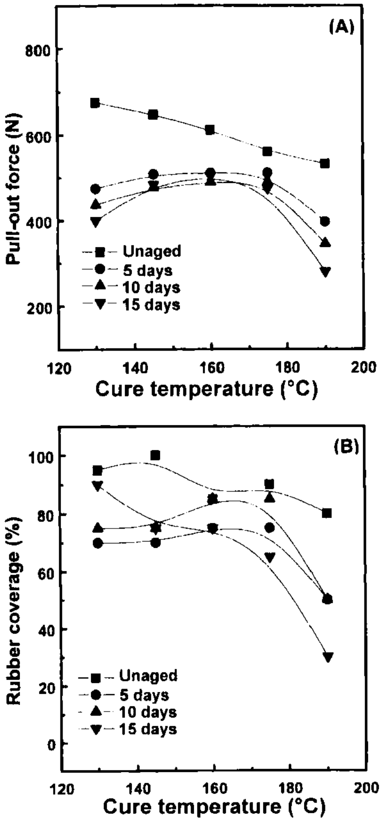

FIGURE 5 Pull-out force (A) of humidity-aged adhesion samples and rubber coverage (B) on the surface of pulled-out steel cord as a function of cure temperature of rubber compounds.

amount of attached rubber on the cord surface is very small, indicating the dominating failure of the adhesion interphase.

In contrast to the thermal aging, adhesion properties after humidity aging for the specimens prepared by vulcanization at 130–175°C showed almost no difference regardless of the cure temperature, whereas those for the samples cured at 190°C were very low. 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 [18], the difference in the adhesion with cure temperature after humidity aging

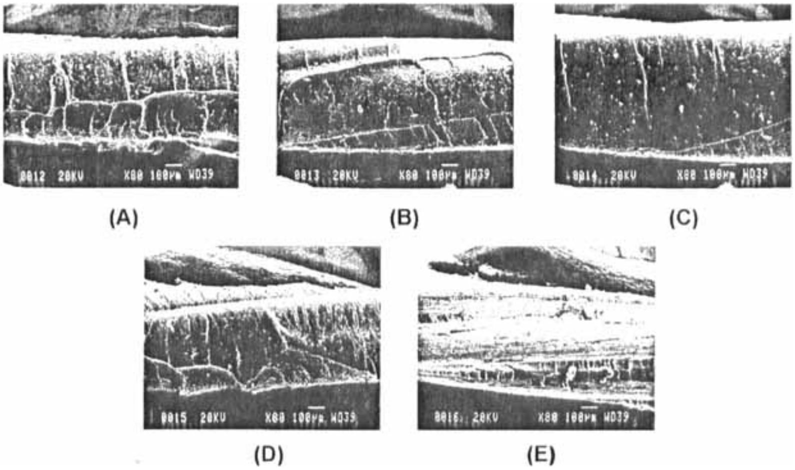

FIGURE 6 SEM micrographs of pulled-out cord surface of adhesion samples humidity aged for 15 days with respect to the cure temperature: (A) 130°C; (B) 145°C; (C) 160°C; (D) 175°C; (E) 190°C.

is due to the change in the adhesion interphase. A divergent structure of the adhesion interphase by highly elevated cure temperatures is probably responsible for the poor rubber coverage or pull-out force after humidity aging, especially for the specimens cured at 190°C.

### 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, distribution of copper, zinc, sulfur and oxygen at the adhesion interphase was obtained through sputtering from the brass surface to rubber using an AES. As elaborated in a monograph by Seo [10] and Jeon *et al.* [11], 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 the adhesion interphases for different cure temperatures, Figure 7 shows the depth

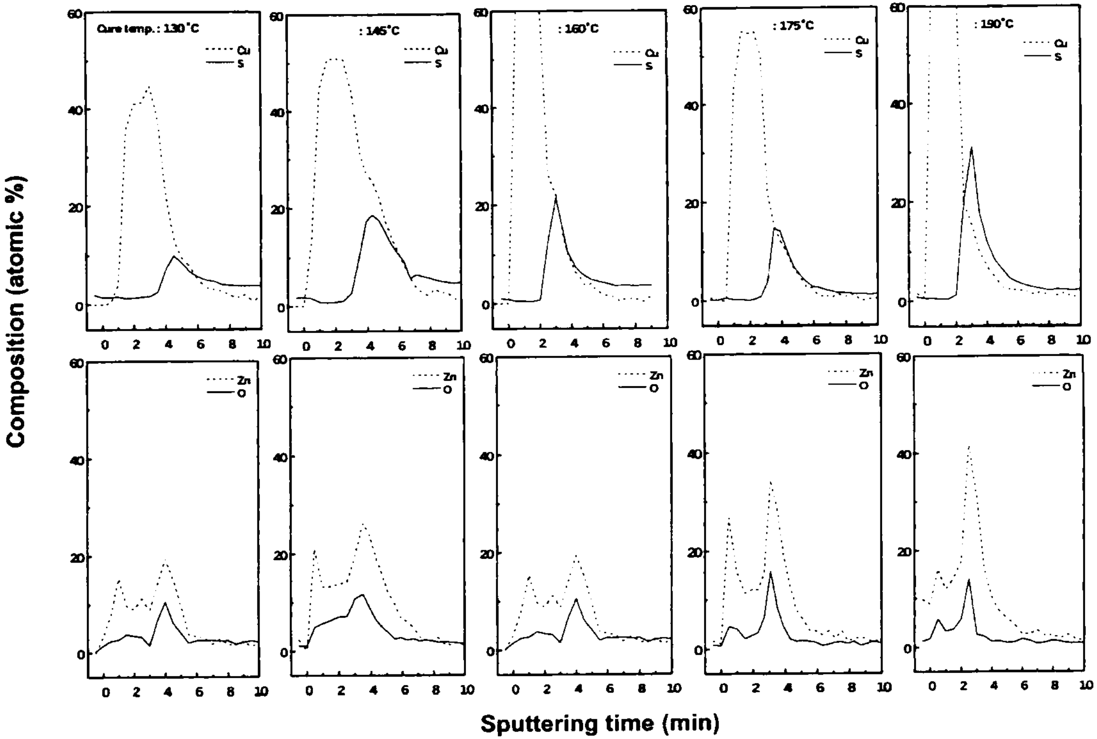

FIGURE 7 AES depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) for the brass-on-glass adhesion samples before aging with respect to the cure temperature.

profiles of sulfur and copper (upper) and that of zinc and (oxygen) (lower) as a function of sputtering time. For the samples cured at 130°C, a shoulder peak appears at the end of the copper peak, where sulfur is detected simultaneously, suggesting the formation of copper sulfide. However, the copper content seems too low for copper sulfide to 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 the 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 outer most 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 elevated temperatures of 145°C and 160°C. However, when the cure temperature increased up to 175°C and 190°C, depth profiles of sulfur and copper were not coincident, suggesting an increase in sulfur having structures other than copper sulfide. For the adhesion samples vulcanized at 190°C, 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 temperature, zinc sulfide forms in abundance rather than copper sulfide [17]. Copper sulfide, zinc sulfide and zinc oxide are mainly generated in the adhesion interphase between the thin deposited brass film and rubber compound cured at low temperatures. However, when the cure temperature rises, the formation of zinc sulfide increases while copper sulfide decreases. Reactivity against sulfur is higher for copper than zinc [5]; however, sulfidation of zinc becomes relatively faster with the rise in temperature and the amount of zinc sulfide formed increases. When the cure temperature is as high as 190°C, formation of zinc sulfide increases.

The adhesion interphase is changed significantly by humidity aging of adhesion samples as shown in Figure 8. At lower cure temperature, severe dezincification and significant growing of the adhesion interphase, especially copper sulfide, occurred. Above a cure temperature of 160°C, the adhesion interphase was unchanged in spite of humidity aging, due to the role of ZnS, a diffusion barrier for moisture.

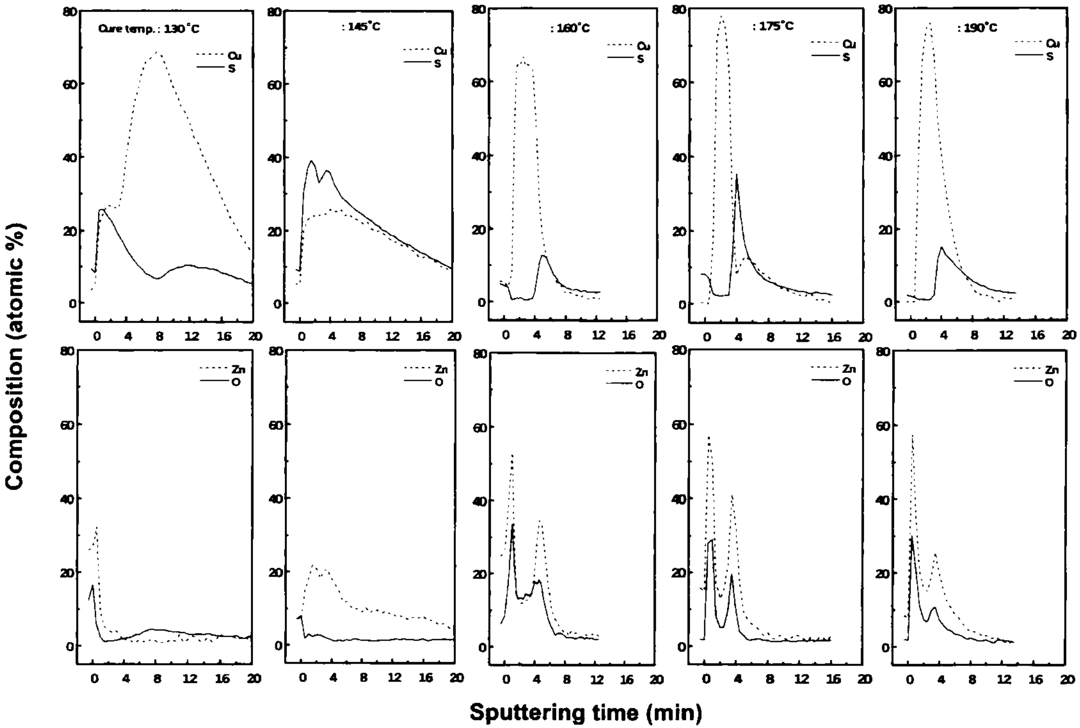

FIGURE 8 AES depth profiles of copper and sulfur (top), and zinc and oxygen (bottom) for the brass-on-glass adhesion samples humidity-aged for 15 days with respect to the cure temperature.

The difference in the extent of cure for the rubber between two sites is summarized in Table IV. In the cure temperature range of 130°C – 160°C, the extent of cure of rubber compound adjacent to the adhesion interphase increased with increasing cure temperature. Above the cure temperature of 160°C, however, significant decline of extent of cure was shown for the rubber near the adhesion interphase compared with that of bulk rubber. At the cure temperature of 190°C, the extent of cure near the adhesion interphase was only a third of that in the bulk rubber. With increasing cure temperature above 160°C, a significant deficiency of sulfur at the adhesion interphase occurred. It is well known that the formation of the adhesion interphase is far faster than rubber cure. At higher cure temperatures, a large portion of sulfur near the adhesion interphase was consumed for the formation of the interphase and, consequently, crosslinking in the bulk rubber occurred very rapidly. Therefore, a concentration gradient of sulfur through the region from near the adhesion interphase to the rubber bulk could be generated, which resulted in a weak boundary layer adjacent to the adhesion interphase. 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 at the high temperature cure.

Therefore, the higher temperature cure caused mass transfer of sulfur which generally results in the poor physical properties of the rubber near the adhesion interphase, one of the major reasons for lower adhesion.

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

| *Cure temp.* | *Average Peak Height* (*V*), $10^{-2}$ | | *Ratio*(3) |
|---|---|---|---|
| (°*C*) | *Away from interphase*(1) | *Adjacent to interphase*(2) | (%) |
| 130 | 3.61 | 1.87 | 52 |
| 145 | 3.69 | 2.40 | 65 |
| 160 | 3.64 | 2.62 | 72 |
| 175 | 3.09 | 2.13 | 69 |
| 190 | 3.54 | 1.17 | 33 |

(1) The analyzed area in 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.
(3) The ratio of average peak height for material away from interphase to that for material adjacent to interphase.

### 3.4. Effect of Cure Temperature on Adhesion Properties

The influence of cure temperature on the adhesion properties of brass-plated steel cords embedded in the rubber compound is very large, because it affects the mechanical properties of both the rubber stock and the adhesion interphase between the brass and rubber compound. With an increase in cure temperature, the cure rate increases. However, the pull-out force decreases with increasing the temperature since the tensile strength of the rubber compound is lowered by the simultaneously increasing reversion rate. Thermal aging brings about deterioration in the adhesion property, 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 remarkably to 30% after 15 days humidity aging of adhesion samples cured at 190°C, and this large drop in rubber coverage can not be fully explained by assuming that the mechanical strength of the rubber vulcanizate is lowered by humidity aging. It can be attributed to the formation of an adhesion interphases which is easily disrupted by humidity aging at elevated temperatures because extremely low rubber coverage indicates that rupture occurs in the adhesion interphase. That is, a large drop in rubber coverage can also result from the effect that the composition or components of the adhesion interphase vary with the cure temperature.

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 film. The formation of zinc sulfide can also be inferred by comparing the composition profiles. The formation of these components varies with the cure temperature. Elevated cure temperature accelerates the formation of zinc sulfide and, for the adhesion samples cured at 190°C, a significant amount of zinc sulfide was formed to the extent that the depth profile curves of sulfur and copper were not coincident with each other. Systematic study on the contribution of cure temperature 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 the nonstoichiometric copper sulfide contributes to the rubber adhesion [18, 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 metal zinc layer is destroyed by humidity aging [17]. 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, and especially the rubber coverage, because the metal support layer disappears due to dezincification by moisture.

It is rather difficult to pinpoint simply the effects of cure temperature since it affects various items 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 at temperatures as high as 190°C, adhesion is lowered because of the decrease in the rubber strength with increasing reversion rate. In addition, adhesion, and particularly the rubber coverage, lowers significantly after humidity aging since the stability of the adhesion interphase is lowered by the excessive formation of zinc sulfide at the adhesion interphase and severe formation of a weak boundary layer in the rubber.

## 4. CONCLUSION

Cure temperature has a large effect on the adhesion between 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 by curing at 130–175°C. On the contrary, when the cure temperature was as high as 190°C, rubber coverage became markedly lower because, in addition to the lowered rubber strength, the adhesion interphase is easily ruptured by humidity aging in which excessive zinc sulfide could be formed at the adhesion interphase, followed by dezincification.

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