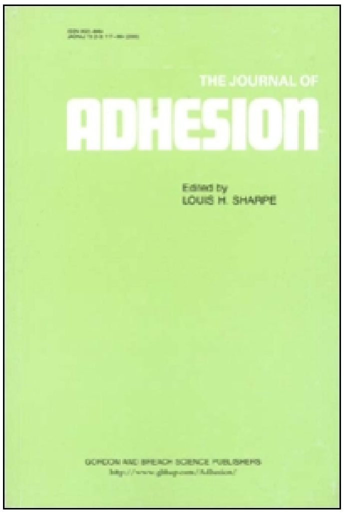

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Adhesion Between Rubber Compounds and Copper-film-coated Steel Plates

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Three copper-film-coated steel plates (abbreviated hereafter as copper-coated plate) with different thicknesses of copper film 30 to 90 nm were prepared and their adhesion properties to rubber compounds were examined. The high adhesion of copper-coated plates to the rubber compound containing resinous bonding additives was obtained at normal and over-cure conditions The copper-coated plate containing an amount of copper coating sufficient to plate the surface with a uniform copper layer showed better adhesion than that having a small amount of copper coating on its surface. The stability against green humidity aging and the cause for the high adhesion of the copper-coated plate were discussed compared with those of the brass plate.

Keywords: Adhesion; rubber compound; copper-coated steel plate; adhesion stability

1. INTRODUCTION

Brass-plated steel cords are used in the belt or carcass of tires to reinforce and enhance the tires' structural support and mechanical stability. In order to absorb the impact appropriately by dissipating stress, and to bear the load of the tire during its service life, good adhesion between the rubber compound and reinforcing material is

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essential. However, steel cord does not adhere to rubber, so brass is plated on the surface of the steel cord for adhesion between them. Copper sulfide is formed at the adhesion interphase as the result of the reaction of the copper in the brass with sulfur in the rubber compound during the curing process [1, 2]. Oxides and hydroxides of copper and zinc are formed simultaneously: thus, the adhesion interphase is complicated concerning its structure and composition.

For a stable and long-service tire, unaged adhesion properties of the steel cord to the rubber compound should be excellent and adhesion degradation after aging treatments ought to be delayed as much as possible to maintain the function of reinforcement. Unfortunately, adhesion degradation is inevitable due to the additional growth of copper sulfide and the loss of metallic zinc in the adhesion interphase, caused by heat generated during tire use, or by contact with moisture in the air [3, 4]. Lowering the amount of brass plating on the steel cord and reducing the copper content in the brass made remarkable improvement in adhesion stability. This was due to the suppression of an additional growth of copper sulfide and the dezincification of the adhesion layer [5, 6]. Additionally, ternary alloy coating by adding cobalt or nickel to brass, and changes in coating order, have been studied in order to improve both unaged and aged adhesion properties [7–9].

Cho *et al.* [10] manufactured thin copper-film-coated steel cords (abbreviated hereafter as copper-coated cords) with copper 30 ~ 90 nm in thickness. Copper was deposited on the uniform surface of a zinc-plated steel filament by the substitution (displacement) plating method. The adhesion properties of the copper-coated cords depended considerably on the amount of copper plating. The copper-coated cord, with a thin copper film of 30 nm on average, exhibited a similar adhesion strength to the rubber compound compared with brass-plated steel cords, which are currently used in tires. Furthermore, the copper-coated cord showed excellent adhesion stability against aging treatments. The suppression of the excessive growth of copper sulfide on the copper-coated cord, due to the limitation of the amount of copper plating, resulted in good stability against aging treatment.

Since the adhesion properties are based on the structure and stability of the adhesion interphase, the investigation of the adhesion interphase between copper-coated cord and the rubber compound is required to understand its high stability. However, it is difficult to obtain a reproducible cord specimen for the investigation of the adhesion interphase from the pullout cord of the adhesion specimen. The copper-film-coated plate is more appropriate than the cord, with respect to surface analysis. The insertion of a filter paper with fine pores between the rubber compound and the copper-coated plate makes it easy to detach the rubber bulk from the metal plate after the curing process [11]. Sulfur and oxygen, which migrate from the rubber compound to the copper film during curing, react with copper and form an adhesion interphase, which remains on the plate after detaching. Since the insertion of filter paper induces a restriction to mass transfer, especially for rubber molecules, the adhesion interphase has some dissimilarities from the real adhesion system. However, it is a very helpful way to prepare reproducible specimens for the study of the adhesion interphase.

We prepared copper-film-coated steel plates (abbreviated hereafter as copper-coated plates), with different thicknesses of copper film, in order to investigate the formation of the adhesion interphase. The adhesion properties between rubber compounds and copper-coated plates and the adhesion interphases remaining on the copper-coated plates were studied to illustrate the potential for the application of copper film as a coating material for the steel cord.

2. EXPERIMENTAL

2.1. The Preparation of Copper-coated Plates

The surface of a steel plate (AISI-SAE 1015) 100 mm long, 32 mm wide and 0.4 mm thick was smoothed with 4000 mesh sandpaper and cleaned by dipping it into acetone to remove grease and other contaminants. The oxide layer of the iron plate was removed by treating it with 5% aqueous sulfuric acid for 60 s. Zinc was electroplated on the iron plate in a zinc sulfate solution of $20\,g \cdot L^{-1}$ for 40 s, forming a zinc layer of 10 nm on average. Copper was then coated on the surface of the zinc-coated plate through substitution plating in a copper sulfate solution of $2.5\,g \cdot L^{-1}$. The formation of an oxide film on the copper-coated plate was suppressed by removing water by dipping it into anhydrous methanol for 30 s. The thickness of the copper film was controlled by changing the contact time of the zinc-coated plate with a copper sulfate solution of constant composition.

The average thickness of the copper film was determined from AES depth profiling. The average thickness could be calculated under the assumption that copper was completely and homogeneously coated on the zinc layer. The thickness of the copper-coated plate was confirmed using XRF (X-ray fluorescence, model 3070, Rigaku Co., Japan). The thicknesses of the copper films were 30, 65 and 90 nm. The copper-coated plate was named Cu( ) plate, with the thickness in nm being the number in parentheses. Brass plates with a composition of Cu/Zn = 66/34 were used for comparison with copper-coated plates.

2.2. Preparation and Evaluation of the Rubber Compound

Two different rubber compounds with and without resinous bonding promoters (RF resin: Resorcinol Formaldehyde Resin, and HMMM: Hexamethoxymethylmelamine) were prepared. The formulations of these compounds are tabulated in Table I. Secondary additives were added into the master batch.

TABLE I Composition of the prepared rubber compounds

Ingredient	*Loading (phr)*	*Manufacturer*
Master batch		
Natural Rubber (SMR-CV60)	100	Lee Rubber Co., Malaysia
Carbon black (N351)	50	Lucky Co., Korea
Aromatic processing oil (A#2)	8	Michang Co., Korea
Zinc oxide	10	Hanil Co., Korea
Antioxidant (Kuma-13)	4	Monsanto Co., USA
Cobalt salt (Manobond 680 C)	2	Rhone Poulenc Co., France
RF resin (B18S)	0[1] or 2.0[2]	Indspec Co., USA
Secondary additive		
Stearic acid	1.5	Pyungwha Co., Korea
Sulfur (80% oil crystex)	5	Akzo Co., The Netherlands
Accelerator (MOR)	0.7	Monsanto Co., USA
Cyrez-964	0[1] or 3.7[2]	Cytec Co., USA

[1] RF resin and HMMM were not loaded on the Rub-00 rubber.

[2] RF resin and HMMM were loaded 2.0 phr and 3.7 phr, respectively on the Rub-BP rubber.

Master batch components were mixed following the procedure described in ASTM D-3184-91, using an internal mixer (Banbury Mixer model 82, Farrel Co., USA). They were mixed for 5 min at a rotor speed of 40 rpm and dumped at 150°C. After the master batch cooled to room temperature, the final mixing components were added and blended for 5 min at 30 rpm and then dumped at 90°C. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co., USA). The rubber compound without bonding promoters was denoted as "Rub-00 rubber" and that with the bonding promoters as "Rub-BP rubber".

Rheocurves were recorded using a Monsanto Rheometer 100 at 150°C and maximum torque was obtained from those rheocurves. Mooney viscosity was also measured on a Monsanto MV-2000 according to ASTM D-1646-91. A tensile sample of the rubber compound was cured at 150°C and 13 MPa. Cure time was determined as 1.1 times the t_{90} time, considering heat transfer of the rubber samples.

Hardness of the vulcanizates was measured using a Shore A durometer according to ASTM D-2240-91, and tensile properties were determined by a tensile tester (model 6021, Instron Co., USA) with a crosshead speed of $500\,\mathrm{mm \cdot min^{-1}}$ as described in ASTM D-412-91. Each value reported was the average derived from six specimens.

2.3. Preparation and Evaluation of the Adhesion Specimens

Adhesion properties were evaluated through a peeling test. The copper-coated plate or brass plate was sandwiched with 2 mm thick rubber pads, and they were cured at 150°C and 13 MPa on a curing press. Curing was maintained for 3 min longer than, the t_{90} time to compensate for heat transfer. For normal cure, Rub-00 rubber was cured for 11 min and Rub-BP rubber was cured for 17 min, 3 min longer than the t_{90} time to compensate for heat transfer. Adhesion specimens of Rub-BP rubber, cured at under-cure and over-cure conditions, were also prepared by curing for 8 min, about 60% of the t_{90} time, and for 45 min, about 350% of the t_{90} time, respectively.

Peeling force was determined as the maximum force exerted by the tensile tester on a peel-test adhesion specimen while peeling at a crosshead speed of $100\,\mathrm{mm \cdot min^{-1}}$. The rubber coverages, which were the relative extent of rubber coverage on the surface of the plate from which the rubber was peeled, were determined by the naked eye. Each value reported was the average derived from five specimens.

In order to evaluate the stability of copper-coated plates exposed to moisture, the plates were placed in a humidity chamber (model 305B, Weiss Technik Co., Germany) for 6 days under conditions of 60°C and 65% relative humidity prior to preparing adhesion specimens. The green humidity aged copper-coated plates and brass plates were sandwiched with Rub-BP rubber pads and cured for 17 min in a curing press as was done for the preparation of the adhesion specimen for the peeling test.

2.4. Analysis of the Adhesion Interphase

Filter paper with a pore size of 5.0 μm (Millipore Co., USA) was placed at the interface between a rubber pad of 2 mm thickness and the copper-coated plate or brass plate. Adhesion specimens of Rub-00 and Rub-BP rubber thus prepared were cured for 11 min and 17 min, respectively. Sulfur from the rubber compound migrated through the pores of the filter paper and reacted with the copper of the copper-coated plate or the brass plate, forming an adhesion interphase. After removing the rubber and filter paper from the metal plate, the adhesion interphase, including copper sulfide and zinc oxide, remained on the metal plate.

The surfaces of copper-coated plates and brass plate were investigated using a SEM (model 840A, JEOL Co., Japan) before and after adhesion on the rubber. The surface composition was analyzed using EDX. The depth profiles from the outer surface to the bulk plate were recorded on a Perkin–Elmer Auger spectrometer (model Phi 670, Perkin–Elmer Co., USA). A surface area of $10 \times 10\,\mu m^2$ was examined using an ion beam with a potential of 5.0 kV, a current of 0.03 μA, and an incident angle of 60° to the specimen, the same conditions described in a previously-published paper [4]. Surface concentrations were determined every 0.5 min from the Auger peaks of detected elements with compensation for their sensitivities. A sputter gun with an argon ion beam rastered on a $2 \times 2\,mm^2$ area for depth profiling. The sputtering rate for the brass film was determined to be $13\,nm \cdot min^{-1}$.

The chemical states of copper and sulfur on the outer surface of the copper-coated plates adhered to the Rub-00 rubber were investigated on an XPS (X-ray Photoelectron Spectroscopy, model 750, Shimadzu Co., Japan) with the Mg source at 8.0 kV and 30 mA. Surface concentrations were determined every 0.2 min for 5 min sputtering with an argon beam at 2.0 kV and 20 mA.

3. RESULTS AND DISCUSSION

3.1. Preparation of the Copper-coated Plates

When copper is coated onto the surface of zinc-coated iron plates using a substitution method, copper is deposited on the plate surface as a metallic surface. The thickness of the copper plating was deduced from AES depth profiles shown in Figure 1. Copper was deposited at the outer surface with oxygen and iron (steel) on the Cu(30) plate, but the amount of copper deposited was too small to form a definite layer on the Cu(30) plate. For the Cu(65) and Cu(90) plates the amount of copper deposited increased, forming a copper-predominant layer, while iron and oxygen were also detected simultaneously. The brass plate showed consistent copper and zinc profiles with a composition of Cu/Zn = 66/34 as wt%. There was a perturbation at the outer surface of the brass plate due to the formation of oxides of zinc and copper.

Zinc was not detected from the AES depth profiles of copper-coated plates. Since copper substituted zinc at the surface of the zinc-coated iron plate, the consumption of zinc was rational. The complete depletion of zinc from all copper-coated plates, however, was not expected. It is not clear whether the zinc was entirely consumed by substitution plating or if some of the zinc was dissolved by the substitution plating solution. However, it is obvious that the coated copper does not make any alloy with zinc. Complete depletion of zinc on the copper-coated plates was confirmed by the EDX results shown in Table II. Detected amounts of zinc were negligible for all three copper-coated plates.

The surface appearances of copper-coated plates varied with the amount of copper coating as shown in Figure 2. The SEM

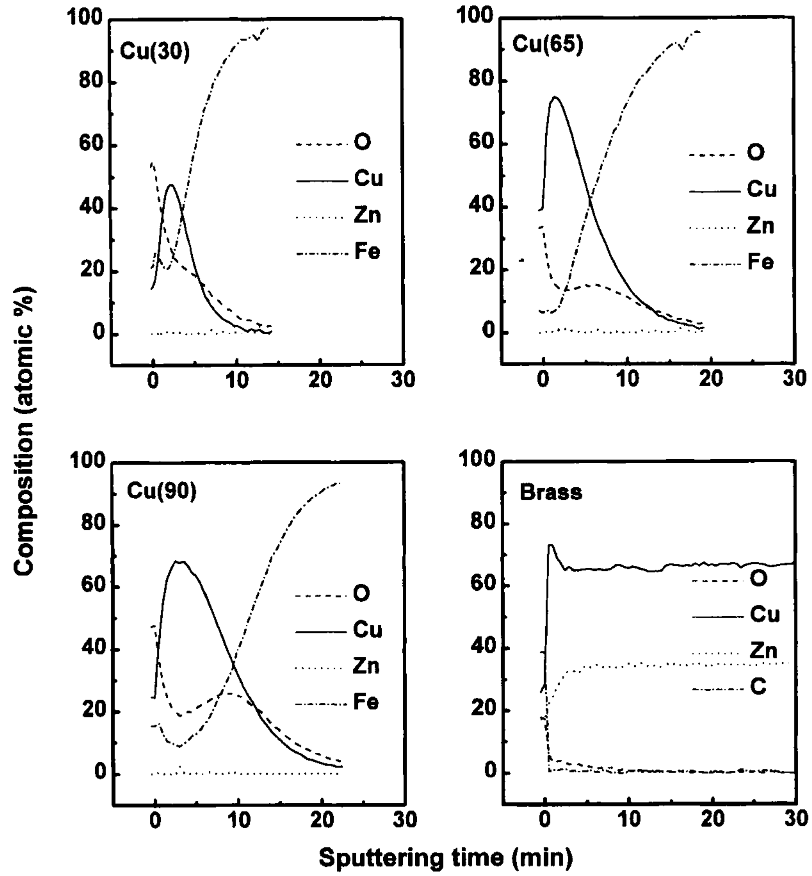


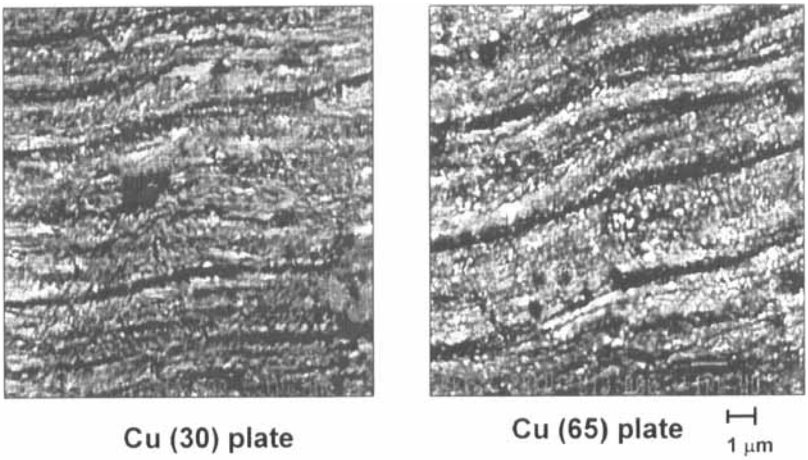
FIGURE 1 AES depth profiles of the copper-coated plates and the brass plate.

TABLE II Relative surface composition[1] of copper, zinc and iron on copper-coated plates

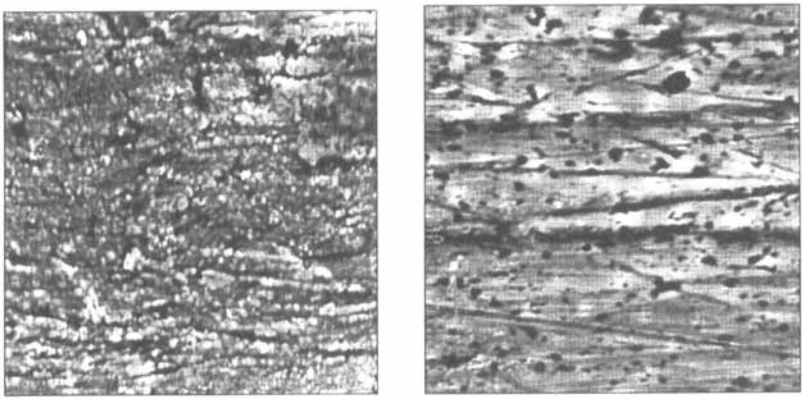
	Composition (atomic %)			
Element\Plate	*Cu*(30)	*Cu*(65)	*Cu*(90)	*Brass*
Cu	3.4 ± 0.2	10.1 ± 1.0	13.6 ± 0.8	66.0 ± 0.6
Zn	0.2 ± 0.1	–	0.2 ± 0.1	34.0 ± 1.2
Fe	89.6 ± 2.0	86.9 ± 2.2	83.3 ± 1.6	–

[1] Measured by EDX.

photographs of the Cu(30) and Cu(65) plates show large troughs formed by the abrasion with sandpaper. The amount of copper coating was small and not enough to form a smooth surface. Fine



Cu (30) plate **Cu (65) plate**



Cu (90) plate **Brass plate**

FIGURE 2 SEM micrographs of the copper-coated plates and the brass plate.

particles of copper were spread on the surface of the Cu(30) plate. The surface of the Cu(65) plate was relatively smooth compared with that of the Cu(30) plate, but large troughs were still observed on it. However, the surface of the Cu(90) plate with its thick copper coating was smooth and traces of abrasion were not observed on it. Iron could possibly be exposed on the surface of the Cu(30) and Cu(65) plates due to the large troughs. The surface of the brass plate was smooth overall except for scratches generated while abrading.

3.2. The Cure Characteristics and Physical Properties of Rubber Compounds

The cure characteristics and physical properties of the rubber compounds varied largely with the presence and absence of resinous bonding promoters. Cure characteristics derived from rheocurve and viscosity measurement on a Mooney viscometer are listed in Table III. The t_{90} time of the Rub-BP rubber containing the bonding promoters was lengthened to almost twice that of the Rub-00 rubber. With the addition of the bonding promoters, torques and the t_5 (representing scorch time) increased slightly. The t_{35} time also increased, indicating the increase in viscosity. The resinous bonding promoters, composed of RF resin and HMMM, reacted with each other and formed a chemical substance of high molecular weight, resulting in the increases in torque and viscosity. Since mass transfer was retarded by the layer of high molecular weight, the cure rate became slow.

Physical properties of the Rub-00 and Rub-BP rubbers unaged and after thermal aging are tabulated in Table IV. Unaged hardness and modulus of the Rub-BP rubber containing the resinous bonding promoters were higher than those of the Rub-00 rubber, but tensile strength and elongation at break were slightly lower. RF resin and HMMM formed an interpenetrating network structure, making the rubber harder and lowering its fatigue properties. Thus, hardness and modulus increased but tensile strength and elongation at break decreased.

The physical properties of both rubber compounds degraded considerably after thermal aging, regardless of the addition of the resinous bonding promoters. After thermal aging of 5 days, tensile strength and elongation at break decreased to a great extent. The Rub-BP rubber showed a slightly lower elongation at break after

TABLE III Cure and viscoelastic characteristics of the rubber compounds

Rubber	*Time (min)*[1]		*Torque (J)*[1]		*Time (min)*[2]	
compound	t_2	t_{90}	*min*	*max*	t_5	t_{35}
Rub-00	2.8	7.7	1.00	4.71	14.8	20.1
Rub-BP	3.0	13.7	1.43	5.49	15.7	23.9

[1] From oscillating disc type rheometer sheared to ± 1° and 1.67 Hz at 150°C.
[2] From Mooney viscometer, sheared to 2 rpm at 125°C.

TABLE IV Physical properties of the rubber compounds unaged and after thermal aging[1]

Rubber compound	*Aging period (day)*	*Shore A Hardness*	*Modulus (MPa)* 50%	*Modulus (MPa)* 100%	*T.S.*[2] *(MPa)*	*E.B.*[3] (%)
Rub-00	0	60	1.3	2.3	25.1	582
	5	79	4.6	–	6.9	76
	10	86	8.8	–	7.8	51
	15	90	–	–	7.7	24
Rub-BP	0	68	1.8	3.2	23.8	488
	5	82	5.3	–	6.1	61
	10	88	–	–	7.4	39
	15	92	–	–	9.0	25

[1] At 95°C for 0, 5, 10 and 15 days.
[2] Tensile strength.
[3] Elongation at break.

thermal aging but, in general, the physical properties of both rubber compounds after thermal aging were not much different.

3.3. The Adhesion Properties of Copper-coated Plate

The adhesion specimens of the Rub-00 rubber were cured at normal cure conditions, whereas those of the Rub-BP rubber were prepared at under, normal, and over-cure conditions in order to investigate the effect of cure time on the adhesion of the copper-coated plate. As shown in Table V, peeling forces of the copper-coated plates and the brass plates adhered to the Rub-00 rubber were not high. The brass plates showed a slightly higher force than the copper-coated plates. SEM micrographs (Fig. 3) of the copper-coated plates peeled from the Rub-00 rubber showed that a little rubber was attached to the Cu(90) plate and the brass plate, whereas no rubber was attached to the Cu(30) and Cu(65) plates. Since the modulus of the Rub-00 rubber was low due to absence of the resinous bonding promoters, the lower peeling forces primarily came from its low modulus, resulting in easy peeling.

The Rub-BP rubber containing the resinous bonding promoters showed high adhesion to the copper-coated plates and brass plates, although this was largely dependent upon the cure conditions. From the adhesion specimens cured with the under-cure condition, the

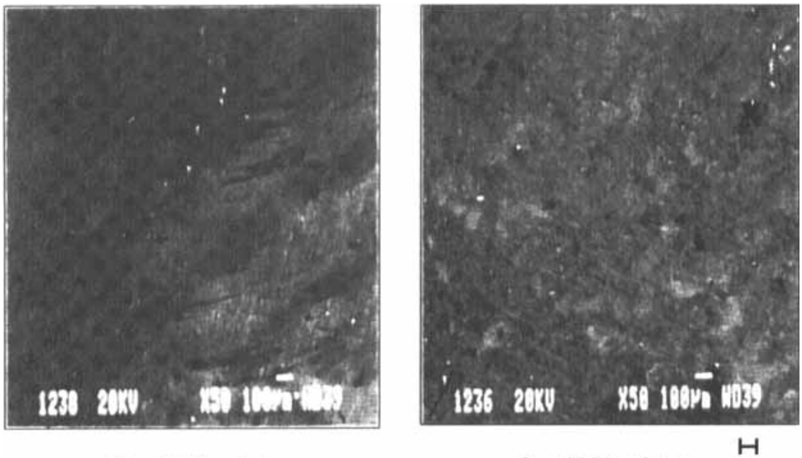
TABLE V Unaged peeling forces for the copper-coated plate adhered to the rubber compounds at various conditions

Rubber compound	*Cure condition*[1] *(min)*	*Copper-coated plate*	*Peeling force (N)*[2]
Rub-00	normal-cure [11 min]	Cu(30)	44
		Cu(65)	46
		Cu(90)	49
		Brass	56
Rub-BP	under-cure [8 min]	Cu(30)	46
		Cu(65)	84
		Cu(90)	78
		Brass	180
Rub-BP	normal-cure [17 min]	Cu(30)	142
		Cu(65)	397
		Cu(90)	447
		Brass	96
Rub-BP	over-cure [45 min]	Cu(30)	59
		Cu(65)	231
		Cu(90)	294
		Brass	98

[1] Cured at 150°C.
[2] Force per plate.

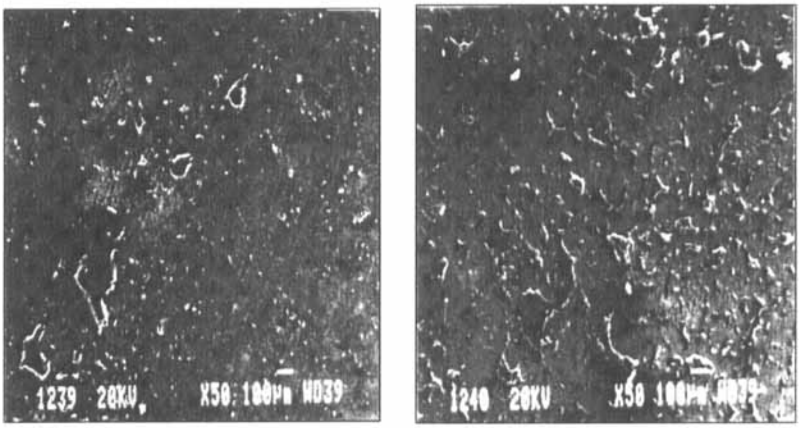
peeling force for the brass plate was higher than those for the copper-coated plates. However, for the adhesion specimens prepared with the normal and over-cure conditions, the peeling forces for the Cu(65) and Cu(90) plates were superior, above 400 N. The adhesion strength for the copper-coated plates was, thus, considerable, even when compared with that of the brass plate. Although the peeling force for the Cu(30) plate from the specimen prepared at the normal-cure condition was three times that for the specimen prepared at the under-cure condition, it was still low compared with those for the Cu(65) and Cu(90) plates. SEM micrographs, shown in Figure 4, also displayed excellent rubber coverages on the surface of the Cu(65) and Cu(90) plates, whereas poor rubber coverages on the brass plates and the Cu(30) plate were found.

Among the copper-coated plates, the Cu(90) plate, which had the largest amount of copper plating, showed superior adhesion properties. Since a sufficient formation of copper sulfide with a large contact area is essential for good adhesion, the copper-coated plate with a large amount of copper coating may prevail, considering only the formation of copper sulfide. On the other hand, the large amount of



Cu (30) plate

Cu (65) plate

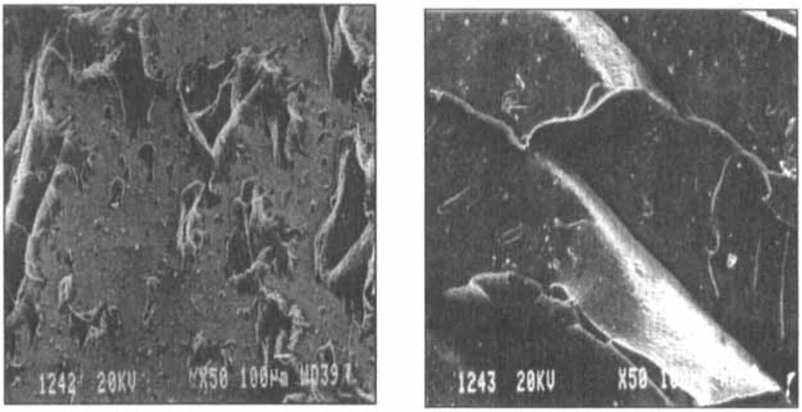


Cu (90) plate

Brass plate

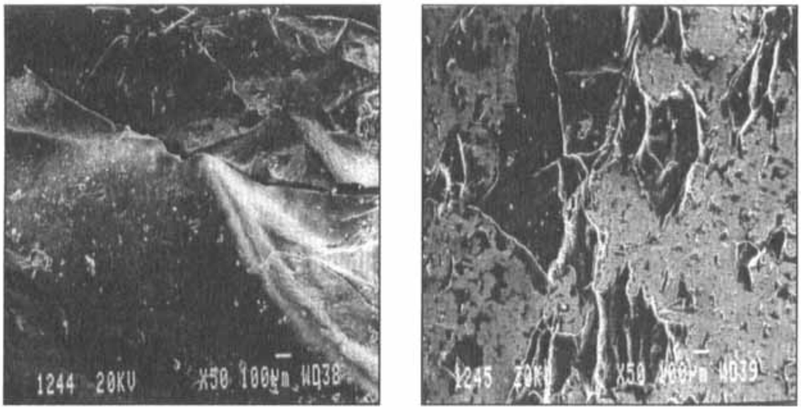
FIGURE 3 SEM micrographs of the surfaces of the copper-coated plates and the brass plate peeled out from the Rub-00 rubber.

copper coating brings about cohesive failure due to excessive growth of copper sulfide. Therefore, the lowest amount of copper which avoids excessive growth of copper sulfide is best for good adhesion, but a certain minimum amount of copper is essential in order to form a sufficiently thick layer of copper sulfide.



Cu (30) plate

Cu (65) plate



Cu (90) plate

Brass plate

FIGURE 4 SEM micrographs of the surfaces of the copper-coated plates and the brass plate peeled out from the Rub-BP rubber.

The surface uniformity of the copper-coated plate is another factor in determining adhesion strength. As shown in Figure 2, deep troughs were observed on the surface of the Cu(30) plate. Iron and oxygen were simultaneously detected together on the outer surface of the Cu(30) plate from the AES depth profiles shown in Figure 1. Partial formation of iron oxide on the outer surface of the Cu(30) plate was inevitable due to its insufficient amount of copper coating. The low homogeneity of the copper layer of the Cu(30) plate lowers its adhesion strength. Theoretically, a small amount of copper loading is recommended to prevent the excessive growth of copper sulfide, but too low loading induces fatal defects on the surface and results in low adhesion. Even though the Cu(90) plate had a relatively large amount of copper coating, uniform coating was a plausible cause of its superior adhesion properties among the copper-coated plates prepared in this study.

Adhesion properties of the copper-coated plates were better when they were adhered to the rubber compound at normal and over-cure conditions, as compared with was under-cure conditions. Conversely, adhesion properties of the brass plate were better when it was cured at under-cure conditions. A definite explanation for this difference between the copper-coated plate and brass plate has not been made, but the difference may be related to the activities of copper and brass in sulfide formation. It may be expected that the high activity of copper for sulfide formation consumes much sulfur, leading to a severe depletion of sulfur and low crosslinking density at the thin rubber layer contacting the plate. Although there is no direct evidence regarding the crosslinking density of interfacial rubber layers, low crosslinking density may be suggested as the cause of poor adhesion to the copper-coated plate at under-cure conditions. The crosslinking density of the thin rubber layer contacting the brass plate was not sufficiently high at under-cure conditions, and the low activity of copper in brass caused a relatively high crosslinking density of the rubber adhered to the brass plate compared with that of the copper-coated plate. The increase in the modulus of the thin rubber layer resists the fatigue between the rubber compound and the plate, resulting in better adhesion.

One of several advantages of the copper-coated cord was the extremely high resistance to moisture [10]. Since the copper-coated plates do not contain zinc, degradation due to dezincification can be excluded. However, copper oxide or copper hydroxide formed on the copper-coated plates by contact with moisture and this may interfere with the formation of the adhesion layer, lowering the adhesion strength. The adhesion degradation of the copper-coated plates and the brass plates with exposure to moisture were evaluated using Rub-BP rubber. As shown in Table VI, the peeling forces of the copper-

TABLE VI Peeling forces between the copper-coated plates and the Rub-BP rubber cured at 150°C for 17 min before and after green humidity aging[1]

	Peeling force $(N)^2$			
Treatment\Plate	*Cu*(30)	*Cu*(65)	*Cu*(90)	*Brass*
Unaged	142	397	447	96
Green-humidity aging	33	119	208	58

[1] Aged at 60°C and 65% relative humidity for 6 days.
[2] Force per plate.

coated plates decreased with green humidity aging. Peeling force for the Cu(90) plate was still high even after green humidity aging, compared with that of the brass plate. The high adhesion of the Cu(90) plate after green humidity aging may be ascribed to the high inertness of copper metal in moisture compared with brass.

3.4. Adhesion Interphase Between Copper-coated Plates and Rubber Compound

Figure 5 shows the AES depth profiles of the adhesion interphases formed on the copper-coated plates and the brass plates by adhering to the Rub-00 rubber. The copper and sulfur peaks appeared on the outer surface and their profiles coincided with each other, indicating that copper sulfide was formed. Since detected amounts of copper and sulfur increased with the increase in copper plating, the growth of copper sulfide was enhanced on the copper-coated plate containing a large amount of copper coating. A large amount of copper sulfide at the adhesion interphase gives a large contact area inducing good adhesion, but its excessive growth brings about a cohesive failure in the sulfide. In contrast to the copper-coated plates, the thicknesses of copper and sulfur on the outer surface was small on the brass plate, and the zinc and oxygen peaks were observed at longer times. Not only copper sulfides but also zinc oxides were mixed at the adhesion interphase between the brass plate and the rubber compound. The thickness of the adhesion interphase of the brass plate was smaller than that of the copper-coated plate, presumably because the activity of copper in brass was low and the migration of reactive species was suppressed by zinc oxide.

Therefore, the lower adhesion between the Rub-00 rubber and copper-coated plates (Tab. V) could not be ascribed to an insufficient

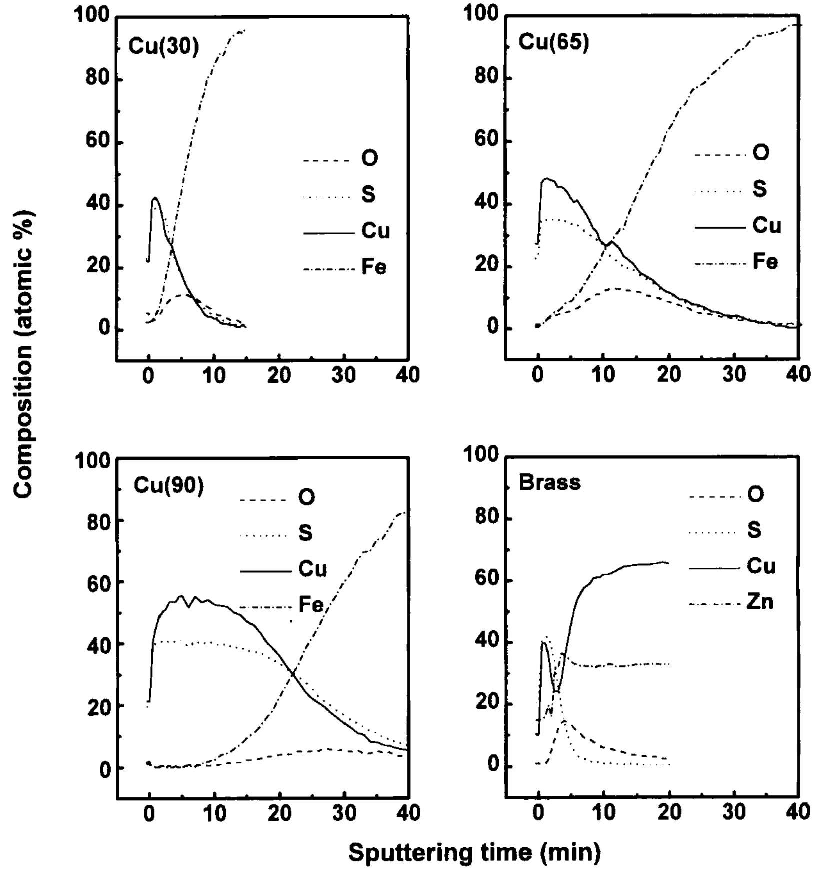


FIGURE 5 AES depth profiles of the adhesion interphases formed on the copper-coated plates and the brass plate. The adhesion specimen, composed of the plate and the Rub-00 rubber with a filter paper at the interface, was prepared using normal curing conditions.

formation of the adhesion interphase. An insufficient crosslinking of the thin rubber layer attached to the plates would be a more plausible reason for low adhesion. Formation of the large copper sulfide layer consumes sulfur, caused a poor modulus or the thin rubber layer. Easy breaking of the rubber layer brought about low peeling forces and the fractured rubber on the plate, as observed in Figure 3. Since the peeling force for this plate was also low, the low modulus of the thin rubber layer was not due to the excessive growth of copper sulfide, but to insufficient time and temperature for optimum cure.

The Rub-BP rubber strongly adhered to the copper-coated plates. Peeling forces for both the Cu(65) and Cu(90) plates were far higher than those for the brass plate. This difference is due to the improvement of the physical properties of the thin rubber layer attached to a metal plate, by incorporation of the resinous bonding promoters. RF resin and HMMM migrated to the interface between the metal plate and rubber [12, 13]. During the curing process, RF resin and HMMM reacted with each other and formed a highly crosslinking network. The modulus of the thin rubber layer attached to the metal plate must be improved considerably, although this improvement cannot be confirmed by conventional tools. The thin rubber layer with a high modulus holds strongly to the copper sulfide layer, resulting in good adhesion of the Cu(65) and Cu(90) plates. A slightly larger growth of copper sulfide may occur for the Rub-BP rubber, which showed the entire surface to be rubber-covered after detachment.

The role of resinous bonding promoters could be inferred from the AES depth profiles of the adhesion interphase between the Rub-BP rubber and copper-coated plates shown in Figure 6. The depth profiles of the Cu(30) and Cu(65) plates with the Rub-BP rubber were almost the same as those with the Rub-00 rubber, whereas the adhesion interphase of the Cu(90) plate with the Rub-BP rubber were remarkably different from that of the Rub-00 rubber. A very thin copper sulfide layer was observed. Since the total amount of copper should remain on either the plates or the rubber, a depletion of copper on the plate implied the migration of a large amount of the copper toward the rubber, and caused the formation of a deep copper sulfide layer to be held to the rubber layer with a high modulus. The superior adhesion properties between the Cu(90) plate and the Rub-BP rubber are attributed to a large formation of copper sulfide with a large contact area, with no accumulation on the metal side to induce cohesive failure.

The chemical states of the copper and sulfur at the adhesion interphase were investigated. Binding energies of carbon, copper, and sulfur were obtained from XPS spectra after sputtering for 5 min (Tab. VII). Binding energies of copper on the copper-coated plates were almost the same as those for the brass, 932.2 ~ 932.3 eV, but sulfur existed in two different chemical states, 161.5 ~ 161.6 eV and 162.8 ~ 162.9 eV. Sulfur with the binding energy of 161.5 ~ 161.6 eV

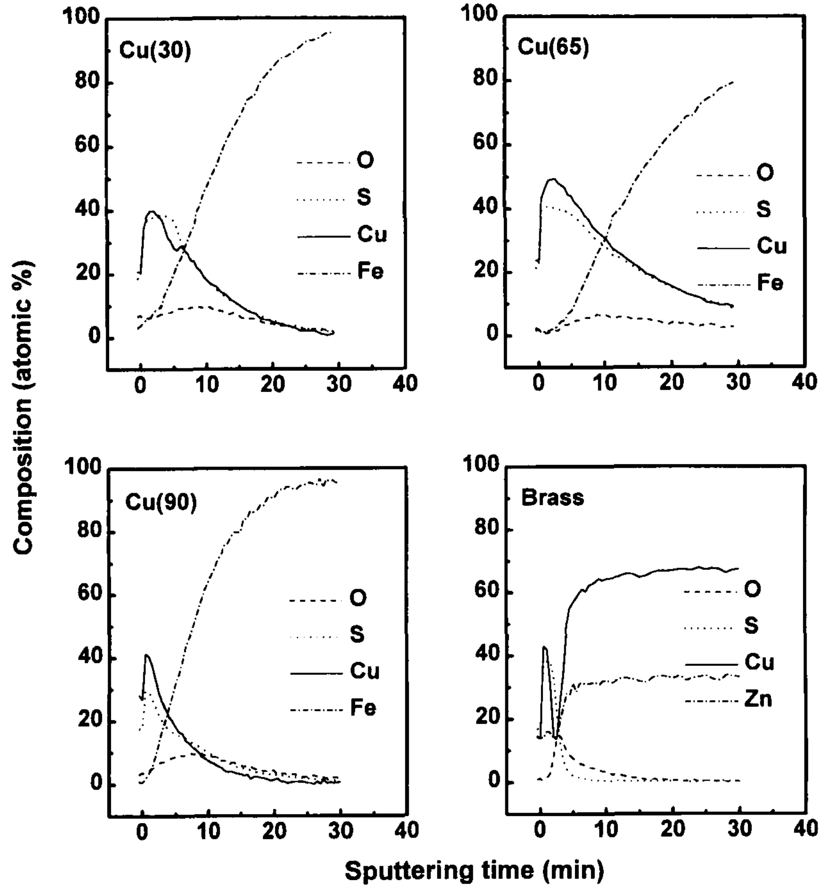


FIGURE 6 AES depth profiles of the adhesion interphases formed on the copper-coated plates and the brass plate. The adhesion specimen, composed of the plate and the Rub-BP rubber with a filter paper at the interface, was prepared using normal curing conditions.

corresponds to the Cu_2S state, and that of 162.8 ~ 162.9 eV to the Cu_xS state [14]. With an increased amount of copper plating, sulfur with the binding energy of 162.8 eV increased slightly. Good adhesion between the brass-plated cord and the rubber compound was attributed to the formation of Cu_xS, the non-stoichiometric compound with high interfacial interaction with other materials [2]; the slight increase of Cu_xS on the Cu(65) and Cu(90) plates and the brass plate might partially contribute to their good adhesion.

TABLE VII Binding energies[1] of C, Cu and S on the surface of the copper-coated plates adhered to the Rub-00 rubber compound determined by XPS

Plate\Element	*Binding energy (eV)* C_{1s}	Cu_{2p}	S_{2p} (%)[2]
Cu(30)	284.8	932.2	161.6(54) 162.9(46)
Cu(65)	284.9	932.3	161.6(50) 162.9(50)
Cu(90)	284.9	932.3	161.5(49) 162.8(51)
Brass	284.8	932.3	161.6(49) 162.8(51)

[1] These values were determined by XPS spectra after sputtering the surfaces of the plates for 5 min. Filter paper was inserted between the copper-coated plate and the rubber compound for easy and reproducible separation after cure.

[2] Relative peak area (%) from a typical run.

4. CONCLUSIONS

A previous study showed that a copper plate did not bond with a rubber compound [14]. However, in the present study copper-coated plate with a thin copper film showed high adhesion with a rubber compound. Although the adhesion properties of the copper-coated plate varied with the composition of the rubber compound and cure conditions, the peeling force for the copper-coated plate with a sufficient amount of copper coating to form a uniform layer was greater than that for the brass plate. Good adhesion to the copper-coated plate was obtained when the rubber compound contained resinous bonding additives, and when either a normal or over-cured condition was employed. The resistance of the copper-coated plate to green humidity aging was better than that of the brass plate. The high adhesion between the copper-coated plate and the rubber compound was ascribed to the sufficient formation of copper sulfide, when the modulus of the rubber layer was high enough to hold strongly to copper sulfide.

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