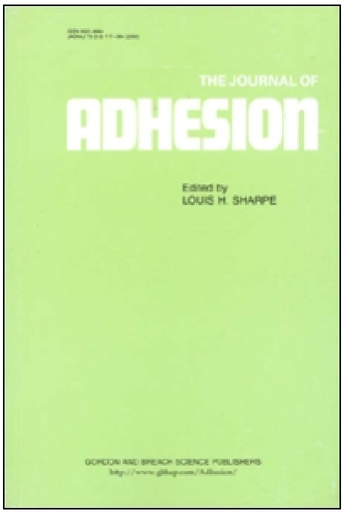

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Effect of cure rate of rubber compound on the adhesion to copper-plated steel cord

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EFFECT OF CURE RATE OF RUBBER COMPOUND ON THE ADHESION TO COPPER-PLATED STEEL CORD

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Copper-plated steel cord was prepared and its adhesion properties to rubber compounds, which have different loading amounts of both sulfur and accelerator, were examined in comparison with brass-plated steel cord. The lower pullout force of copper-plated steel cord to the rubber compounds was shown compared with brass-plated steel cord. The copper-plated steel cord showed higher adhesion retention to rubber compounds than brass-plated steel cord against various hostile environments. The stability against both humidity aging and thermal aging, and the cause for the high adhesion retention of the copper-plated steel cord to rubber compounds, were discussed compared with those of the brass-plated steel cord. The pullout force of copper-plated steel cord to rubber compound is inversely correlated with cure rate after various aging treatments.

Keywords: Adhesion; Rubber compound; Cure rate; Sulfur; Accelerator; Copper-plated steel cord; Brass-plated steel cord; Adhesion retention; Tire

INTRODUCTION

The majority of car and commercial vehicle tires have been constructed using various forms of reinforcement such as fabric cord and brass-plated steel cord. 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

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reinforcing material is essential. However, steel cord does not adhere to rubber, so brass is plated on the surface of the steel cord for adhesion between them. It is during vulcanization that adhesion between rubber compound and brass-plated steel cord occurs. Copper sulfide is formed at the adhesion interphase as the result of the reaction of the copper with the brass and sulfur in the rubber compound during the vulcanization 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 should be delayed as much as possible to maintain the function of reinforcement. Unfortunately, an adhesion degradation for brass-plated steel cord is inevitable due to the additional growth of copper sulfide at the adhesion interphase and the loss (dezincification) of metallic zinc at 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 remarkably improved adhesion stability. This was due to the suppression of an additional growth of copper sulfide at the adhesion interphase and the dezincification of the adhesion layer [5, 6]. Additionally, ZnNi/ZnCo alloy cord [7, 8] and ternary alloy coating by adding either cobalt or nickel to brass have been studied in order to improve both unaged and aged adhesion properties [9]. Recently, an attempt to employ the zinc alloy-coated steel cord, which is not plated with copper, was reported by Yan *et al.* to overcome the disadvantage of brass-plated steel cord [10].

Cho *et al.* [11] manufactured thin copper-plated steel cords with 30∼90 nm of copper thickness. Copper was deposited on the uniform surface of a zinc-plated steel filament by the substitution plating method. The adhesion properties of the copper-plated steel cord depended considerably on the amount of copper plating. The copper-plated steel cord, with a thin copper layer of 30 nm on average, exhibited similar adhesion strength to the rubber compound compared with brass-plated steel cords, which are currently used in tires. Furthermore, the copper-plated steel cord showed excellent adhesion stability against hostile aging treatments [12]. The suppression of the excessive growth of copper sulfide on the copper-plated steel cord, due to the limitation of the amount of copper plating, resulted in good stability against hostile aging treatment.

Sulfur is the main crosslinking ingredient for the rubber compound, and it is placed in an active state by the accelerator in the rubber compound during the vulcanization process. Generally, sulfur does not react with the rubber compound at ambient temperature; it has eight-membered ring in its elemental form with relatively high stability. It requires 64 Kcal/mol to dissociate the sulfur ring, indicating the requirement of a high activation energy of sulfur to react [13]. To make sulfur active, a considerable amount of activation energy must be consumed to split the sulfur ring. The sulfur ring can be split into two segments by the assistance of an accelerator. The active sulfur will react with copper plating on steel filament to form copper sulfide, resulting in the adhesion between the rubber compound and copper-plated steel cord. Therefore, the formation of copper sulfide is the primary adhesion mechanism between rubber compound and copper-plated steel cord [11, 14].

It is well known that the reactivity of copper to sulfur is faster than that of brass to sulfur. Also, the reaction rate of adhesion-interphase formation for adhesion samples is far faster than that of vulcanization of rubber compound. Therefore, most of the adhesion interphase between copper-plated steel cord and rubber compound is formed before the scorch time of rubber compound. Therefore, the cure rate in copper-plated steel cord is more important than that in brass-plated steel cord. The large difference of reaction rate between adhesion-interphase formation and vulcanization is responsible for the formation of a weak boundary layer in the thin rubber layer closely adjacent to the adhesion interphase [15, 16]. During the vulcanization of adhesion samples, the lack of sulfur in the thin rubber layer closely adjacent to the adhesion interphase occurred due to the large consumption of sulfur in the formation of the adhesion interphase instead of in vulcanization. Therefore, the sulfur concentration gradient formed in the thin rubber layer closely adjacent to adhesion interphase, which suffered a lack of sulfur. Unfortunately, the diffusion of sulfur from rubber bulk to thin rubber layer closely adjacent to adhesion interphase may be effectively hindered by the sulfur crosslinking network formed in rubber at the initial vulcanization time. As cure of adhesion samples proceeds, the bulk rubber is completely cured, whereas the thin rubber layer adjacent to adhesion interphase does not cure sufficiently. The thin rubber layer adjacent to the adhesion interphase of copper-plated steel cord may have a low sulfur crosslinking density compared with bulk rubber. Therefore, the cure rate in copper-plated steel cord is more important than that in brass-plated steel cord.

We prepared copper-plated steel cord in order to investigate the effect of cure rate on the adhesion of rubber compound to copper-plated steel cord. The adhesion properties between rubber compounds having different sulfur and accelerator loading amounts and copper-plated steel cord were studied to illustrate the potential for the application of copper-plated steel cord as an alternative reinforcement material for brass-plated steel cord in tires and to know the effect of cure rate on the adhesion of rubber compound to copper-plated steel cord.

EXPERIMENTAL

The Preparation of Copper-Plated Steel Cord

After removing grease and other contaminants from the steel filament by washing it with a 5% NaOH solution and rinsing it with clean water, copper was plated onto it by a cyanide plating method using an aqueous copper cyanide solution of $17{\sim}20\,\mathrm{g{\cdot}L^{-1}}$ at 20°C. The copper-plated filament was washed at 85°C and dried in hot air at 90°C. Copper-plated filaments were twisted together to make the copper-plated steel cord of 3×0.30 construction in which 3 steel filaments with a diameter of 0.30 mm were twisted together. The average thickness of the copper film was determined from AES depth profiling (Figure 1). Copper plating of copper-plated steel cord was 1.1 g/kg. The surfaces of copper-plated steel cord and brass-plated steel cord were investigated using a scanning electron microscope (SEM) (model 840 A, JEOL Co., Tokyo, Japan) before adhesion on the rubber (Figure 2).

A brass-plated steel cord of 3×0.30 construction was used for comparison; its plating weight and composition were 3.5 g/kg (Cu/Zn thickness : 150 nm) and Cu/Zn = 64/36 (wt%), respectively. Copper-plated steel cord and brass-plated steel cord used in this research were manufactured by Kiswire Co., (Pohang, Korea).

Preparation and Evaluation of the Rubber Compound

Nine different rubber compounds with different loading amounts of both accelerator and sulfur were prepared. The formulations of these compounds are tabulated in Table 1. Secondary additives were added into the master batch.

Master batch components were mixed following the procedure described in ASTM D-3184-91, using an internal mixer (Banbury Mixer model 82, Farrel Co., Ansonia, Connecticut, USA). They were mixed for 5 min at a rotor speed of 40 rpm and dumped at 150°C. After the master batch had cooled to room temperature, the final mixing

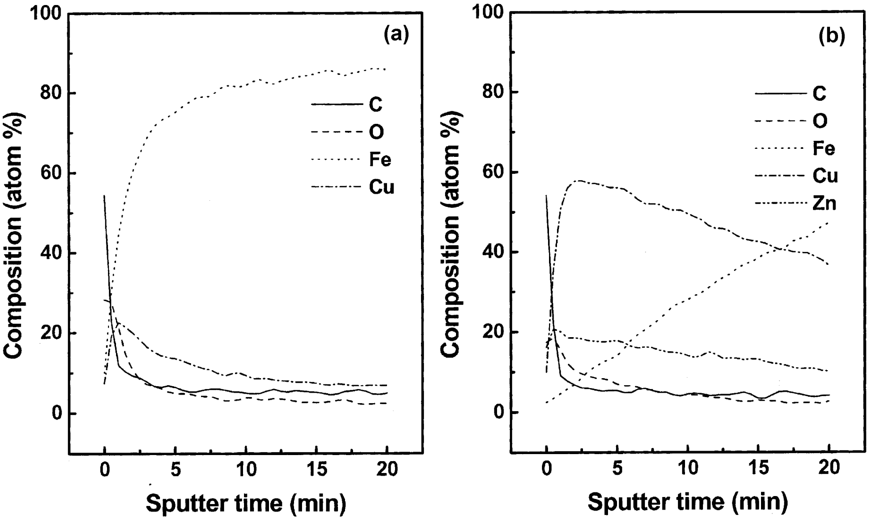

FIGURE 1 AES depth profiles of (a) the copper-plated steel cord and (b) the brass-plated steel cord.

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., Ansonia, Connecticut, USA).

Rheocurves were recorded using a Monsanto Rheometer 100 (Akron, Ohio, USA) at 160°C, and cure rate index (CRI) $= 100/(t_{90} - t_2)$ calculated from t_2 (time required for 2% crosslinking) and t_{90} time (time required for 90% crosslinking) in those rheocurves and torques were obtained from those rheocurves. The CRI is regarded as the cure rate. A tensile sample of the rubber compound was cured at 160°C and 13 MPa. Cure time was determined as 1.1 times 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., Canton, Massachusetts, 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.

Preparation and Evaluation of the Adhesion Specimens

By the procedure described in ASTM D-2229-91, T-test specimens (Figure 3) were cured at 160°C on the cure press. The embedded

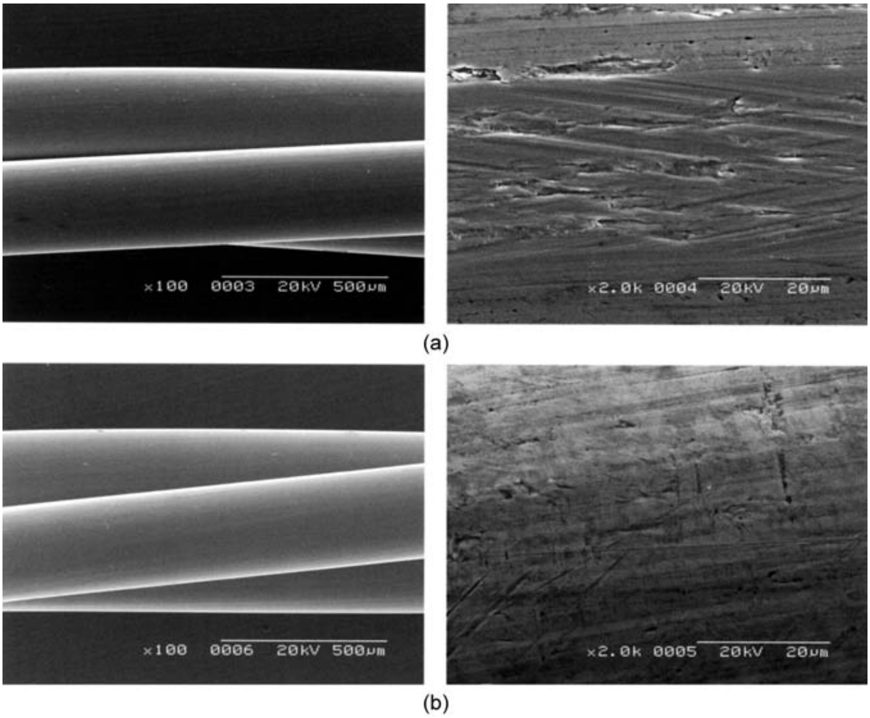

FIGURE 2 SEM micrographs of (a) the copper-plated steel cord and (b) the brass-plated steel cord.

length of steel cord to rubber compound was 12.7 mm. Curing was maintained for 5 min longer than t_{90} time to compensate for the heat transfer of the rubber block. For humidity aging, adhesion samples were placed in a humidity chamber (Weiss Technik, model 305B, Buckinghamshire, UK) for 15 days under conditions of 85°C and 85% relative humidity. Thermal aging was performed under air atmosphere at 95°C for 15 days, and salt solution aging, in which the bottom of the adhesion samples were immersed completely in a 15 wt% NaCl solution, was performed at ambient temperature, for 5 days.

Pullout force was determined as the maximum force exerted by the tensile tester (Instron model 6021) on a T-test adhesion sample during pullout test at 100 mm·min^{-1} of crosshead speed at 25°C after aged adhesion samples had been allowed to rest for 24 h at 25°C. Rubber coverage, defined as the percentage of rubber-adhered area on cord surface, was also noted. The relative extent of rubber coverage on the pulled-out cord estimated by the naked eye was based on the

TABLE 1 Composition of Rubber Compounds Prepared

Material	Trade name	Manufacturer	Content (phr)
Masterbatch			
natural rubber	SMR-20	Lee Rubber Co., Malaysia	100
carbon black	N330	Lucky Co., Korea	60
processing oil	A#2	Michang Co., Korea	3.5
activator	ZnO	Hanil Co., Korea	8
antioxidant	Kumanox-13[1]	Monsanto Co., USA	1
adhesion promoter	B-18S[2]	Indspec Co., USA	2
adhesion promoter	Manobond-680C[3]	Rhone Poulenc Co., France	0.5
Final Mixing			
activator	Stearic acid	Pyungwha Co., Korea	1.5
accelerator	DCBS[4]	Monsanto Co., USA	varied
sulfur	Crystex HS OT 20[5]	Akzo Co., The Netherlands	varied
adhesion promoter	Cyrez-964[6]	Cytec Co., USA	3

[1] N-(1,3-dimethyl-butyl), N-phenyl-p-phenylenediamine.
[2] Resorcinol formaldehyde resin.
[3] Cobalt boroacylate (Co 23 wt%).
[4] N-Dicyclohexylbenzothiazole-2-sulfenamide.
[5] Insoluble sulfur.
[6] 65% Hexamethoxymethylmelamine with 35% silica.

determination of rubber coverage; bare steel cord as 0% to fully covered with rubber as 100%. Both pullout force and rubber coverage reported were the averages derived from six specimens, and those lie within 5% standard deviation.

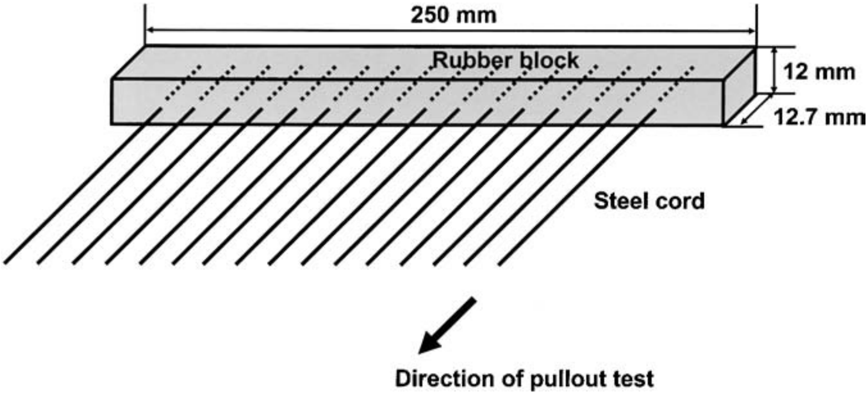

FIGURE 3 Schematic geometry of a T-test specimen.

Surface Characterization of Copper-Plated Steel Cord

The surfaces of the cords were investigated with a SEM (JEOL Co., model 840A, Tokyo, Japan). The depth profiles from the outer cord surface to the inner cord were recorded on a Perkin-Elmer Auger spectrometer (Phi 670, Boston, Massachusetts, USA). A surface area of $10 \times 10\ \mu m^2$ was examined at a potential of 5.0 keV, a current of 0.03 μA, and an incident angle of 60° to the specimen, as in previously published papers [11, 15, 17]. A representative site of copper-plated steel cord was analyzed by means of SEM observation during Auger spectrometer analysis. Surface concentrations were determined at 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 was used for the depth profiling. The sputtering rate for the brass film was determined to be $10\,nm \cdot min^{-1}$.

RESULTS AND DISCUSSION

Characterization of the Copper-Plated Steel Cord

When copper is plated on the surface of steel filament using a substitution method, copper is deposited on the steel-filament surface in the metallic state. 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 on the copper-plated steel cord, forming a copper-predominant layer, while iron and oxygen were also detected simultaneously. Copper oxide may form on the outermost surface of copper-plated steel cord. The average copper thickness of copper-plated steel cord was 50 nm. The brass-plated steel cord showed consistent copper and zinc profiles with a composition of Cu/Zn = 66/34 as wt%. The average brass thickness of brass-plated steel cord was 150 nm. The surface of copper-plated steel cord, while relatively smooth, exhibited a lot of scratches as shown in Figure 2. These scratches presumably were generated during drawing of the steel cord.

The Cure Characteristics of Rubber Compounds

The cure characteristics and physical properties of the rubber compounds were varied by varying the concentrations of both accelerator and sulfur in the rubber compounds. Cure characteristics derived from those rheocurves are listed in Table 2.

TABLE 2 The Cure Characteristics Determined by Oscillating Disc Type Rheometer[1] for Various Rubber Compounds with Respect to the Loading of Sulfur and Accelerator

Accelerator (phr)	Sulfur (phr)	Time (min)			CRI[2] (min^{-1})	Torque (J)	
		t_2	t_{40}	t_{90}		min	max
0.35	1.75	2.3	7.1	13.7	8.7	1.88	4.27
	3.50	2.5	5.9	12.2	10.4	1.82	5.07
	7.00	2.7	5.0	17.4	6.8	1.71	6.27
0.70	1.75	2.6	6.3	10.9	12.0	1.86	4.62
	3.50	2.4	5.3	10.1	13.0	1.77	5.49
	7.00	2.7	4.5	11.2	14.9	1.68	6.73
1.40	1.75	2.6	5.6	9.2	15.0	1.83	5.05
	3.50	2.5	4.8	8.5	16.7	1.74	6.08
	7.00	2.5	4.1	8.8	16.0	1.66	7.20

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

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

The cure rate of the rubber compounds containing a low amount of accelerator (0.35 phr) increased with increasing sulfur loading up to 3.5 phr. Further increase of sulfur loading above 3.5 phr caused delayed cure behavior of the rubber compounds. The cure rate of the rubber compounds containing a medium amount of accelerator (0.7 phr) increased with increasing sulfur loading. The cure rate of the rubber compounds containing a high amount of accelerator (1.40 phr) increased with increasing sulfur loading up to 3.5 phr. Further increase of sulfur loading above 3.5 phr showed slightly delayed cure behaviors of the rubber compounds. As shown in Table 2, the cure rate of rubber compounds was dependent on the relative loading amounts of both accelerator and sulfur.

Regardless of accelerator loading, the minimum torque of the rubber compounds decreased with increasing sulfur loading whereas the maximum torque of the rubber compound increased. Therefore, the mechanical crosslinking density of vulcanizate, which has been traditionally expressed in the rubber industry as the difference between maximum torque and minimum torque in its rheocurve, increased with increasing sulfur loading. As shown in Table 2, the loading amount of sulfur controls the mechanical crosslinking density more than that of the accelerator.

Physical Properties of Vulcanizates

Physical properties of the unaged vulcanizates were tabulated in Table 3. The hardness and modulus of the unaged vulcanizates

TABLE 3 The Tensile Physical Properties of Vulcanizates with Respect to the Loading of Sulfur and Accelerator

Accelerator (phr)	Sulfur (phr)	Hardness (Shore A)	Modulus (MPa) 100%	Modulus (MPa) 200%	Modulus (MPa) 300%	T.S. (MPa)	E.B. (%)
0.35	1.75	68	2.8	7.8	13.8	17.5	364
	3.50	71	3.7	9.9	16.6	21.3	380
	7.00	75	5.3	12.8	20.2	20.6	304
0.70	1.75	68	3.4	9.6	16.3	21.2	381
	3.50	71	4.2	11.0	18.0	23.4	391
	7.00	75	5.5	13.7	21.7	25.3	358
1.40	1.75	69	3.9	10.7	17.8	25.0	418
	3.50	74	5.1	12.9	20.4	25.6	382
	7.00	77	7.0	16.1	23.2	24.0	303

containing a low loading of accelerator increased with increasing sulfur content. The tensile strength and elongation at break of vulcanizates increased with increasing sulfur content up to 3.5 phr of sulfur. Further increase of sulfur content above 3.5 phr decreased both tensile strength and elongation at break of the vulcanizates.

For a medium amount of accelerator loading (0.70 phr), the tensile properties of vulcanizates, except elongation at break, increased with increasing sulfur content. The elongation at break of vulcanizates did not change significantly with increasing sulfur content up to 3.5 phr. Further increase of sulfur loading decreased the elongation at break of the vulcanizates.

For a high amount of accelerator loading (1.40 phr), both hardness and modulus increased with increasing sulfur content. Both tensile strength and elongation at break of the vulcanizates decreased with increasing sulfur loading.

As shown in Table 3, sulfur content is more controlling of the modulus than is the accelerator whereas the loading amount of accelerator dominates the tensile strength more than does sulfur.

The physical properties of rubber compounds degraded considerably after thermal aging, regardless of the loading amounts of both sulfur and accelerator (Table 4). After thermal aging of 5 days, tensile strength and elongation at break of the vulcanizates decreased to a great extent compared with those of unaged vulcanizates. The hardness of the vulcanizates showed a significant increase after thermal aging. As mentioned in torques of rheocurves, the loading amount of accelerator is more influential on tensile strength than sulfur,

TABLE 4 The Tensile Physical Properties of Vulcanizates Treated with Thermal Aging[1] with Respect to the Loading of Accelerator and Sulfur

Accelerator (phr)	Sulfur (phr)	Hardness (Shore A)	Modulus (MPa) 100%	Modulus (MPa) 200%	Modulus (MPa) 300%	T.S. (MPa)	E.B. (%)
0.35	1.75	74	4.6	—	—	9.9	187
	3.50	77	5.9	—	—	7.4	123
	7.00	84	—	—	—	6.8	67
0.70	1.75	75	5.6	—	—	12.6	196
	3.50	79	7.1	—	—	8.5	120
	7.00	83	—	—	—	7.1	71
1.40	1.75	77	6.4	15.0	—	16.6	229
	3.50	82	9.3	—	—	11.4	119
	7.00	86	—	—	—	7.7	62

[1] The tensile test samples were thermally aged for 5 days at 95°C.

whereas the sulfur content is more dominating on modulus than that of the accelerator.

The Adhesion Properties of Copper-Plated Steel Cord

The adhesion properties of copper-plated steel cords were different from those of the brass-plated cord before and after aging treatments, as shown in Table 5. The unaged adhesion properties of copper-plated

TABLE 5 The Adhesion Properties of Thermal Aged[1] Adhesion Samples for Various Rubber Compounds with Respect to the Loading of Accelerator and Sulfur

		Pullout force (N)				Rubber coverage (%)			
		Brass		Copper		Brass		Copper	
Accelerator (phr)	Sulfur (phr)	0[2]	15	0	15	0	15	0	15
0.35	1.75	480	274	225	235	80	80	40	70
	3.50	559	265	294	206	85	95	50	80
	7.00	578	353	235	206	90	95	50	55
0.70	1.75	490	333	196	216	80	90	45	80
	3.50	559	363	216	196	85	95	50	80
	7.00	568	382	265	196	90	95	40	70
1.40	1.75	461	451	167	186	75	85	20	40
	3.50	568	441	196	186	90	90	40	60
	7.00	608	304	235	176	85	90	40	50

[1] The adhesion samples were thermally aged at 95°C.

[2] Aging period (days).

cords were inferior to those of the brass-plated cord. The unaged pullout force and rubber coverage of copper-plated steel cords were low compared with those of brass-plated steel cord. The adhesion characteristics of copper-plated steel cord are as follows.

For the low loading of accelerator (0.35 phr), pullout force of adhesion samples increased with increasing sulfur-loading amount up to 3.5 phr. Further increase of sulfur content above 3.5 phr decreased pullout force. The rubber coverage of pulled-out cord in unaged adhesion samples is nearly constant irrespective of sulfur loading but that in thermally aged adhesion samples increased with sulfur loading up to 3.5 phr. Further increase of sulfur loading above 3.5 phr decreased rubber coverage significantly.

For the medium loading amount of accelerator (0.70 phr), the pullout force of adhesion samples increased with increasing sulfur loading. The rubber coverage is nearly constant from 40% to 50%.

For the high loading amount of accelerator (1.40 phr), pullout force of adhesion samples increased with increasing sulfur content. The rubber coverage increased with increasing sulfur loading.

For the low loading amount of sulfur (1.75 phr), pullout force of adhesion samples decreased significantly with increasing accelerator content. The rubber coverage decreased with increasing accelerator loading. Especially, the rubber coverage of samples with a high loading of accelerator is very poor.

For the medium loading amount of sulfur (3.50 phr), the pullout force of adhesion samples decreased with increasing accelerator loading but rubber coverage was nearly constant regardless of accelerator content up to 0.7 phr. Above 0.7 phr of accelerator loading, rubber coverage decreased slightly for both unaged and thermal by aged adhesion samples.

For a high loading of sulfur (7.00 phr), pullout force after thermal aging decreased with increasing accelerator loading. In thermally aged adhesion samples, rubber coverage increased with accelerator loading up to 0.7 phr. Further increase of accelerator loading above 0.70 phr decreased rubber coverage.

It is well known that the reactivity of copper to sulfur is faster than that of brass to sulfur [18]. Also, the reaction rate of adhesion-interphase formation is far faster than that of vulcanization of rubber compound. Therefore, most of the adhesion-interphase formation on copper-plated steel cord may be completed before the scorch time of the rubber compound. The cure rate in copper-plated steel cord is more important than that in brass-plated steel cord. The large difference of reaction rate between adhesion-interphase formation and vulcanization is responsible for the formation of a weak boundary layer in a thin rubber layer closely adjacent to the adhesion interphase. During the cure of adhesion samples, the lack of sulfur in the thin rubber layer adjacent to the adhesion interphase occurred due to the large consumption of sulfur in adhesion-interphase formation instead of vulcanization. Therefore, a sulfur concentration gradient formed in the thin rubber layer closely adjacent to the adhesion interphase, which suffered a lack of sulfur. Unfortunately, the diffusion of sulfur from rubber bulk to thin rubber layer closely adjacent to adhesion interphase may be effectively hindered by the sulfur crosslinking network formed in the rubber during the initial vulcanization period. As cure of adhesion samples proceeds, the bulk rubber is completely cured, whereas the rubber adjacent to the interphase is not. Due to the mechanism mentioned above, a thin rubber layer adjacent to adhesion interphase has a low sulfur crosslinking density compared with the bulk rubber.

The high adhesion between the copper-plated steel cord and the rubber compound resulted in the sufficient formation of copper sulfide when the modulus of the thin rubber layer adjacent to adhesion interphase was high enough to retain the copper sulfide.

The adhesion properties are degraded by thermal aging as shown in Table 5. But the degradation rate of adhesion properties of copper-plated steel cord is significantly different from that of brass-plated steel cord. For adhesion samples using brass-plated steel cord, adhesion properties after thermal aging worsen. But the adhesion retention of thermally aged adhesion samples using copper-plated steel cord is very high, resulting in an adhesion force equivalent to that of unaged samples.

For a constant loading of accelerator, adhesion retention of copper-plated steel cord, expressed as the ratio of adhesion force after aging treatment to unaged adhesion force, decreased with increasing sulfur loading (Figure 4). Especially, the adhesion retention of copper-plated steel cord decreased significantly for the high loading of accelerator (1.4 phr).

For the constant loading amount of sulfur, adhesion retention of copper-plated steel cord varied with the loading amount of accelerator. For the low and medium loading amounts of sulfur, adhesion retention of copper-plated steel cord increased with increasing accelerator loading. For the high loading of sulfur, adhesion retention decreased with increasing accelerator content.

The adhesion stability of copper-plated steel cords against thermal aging was quite high compared with that of the brass-plated steel cords. Although the unaged adhesion properties of copper-plated cords were inferior to the brass-plated cord, the degradation rate was

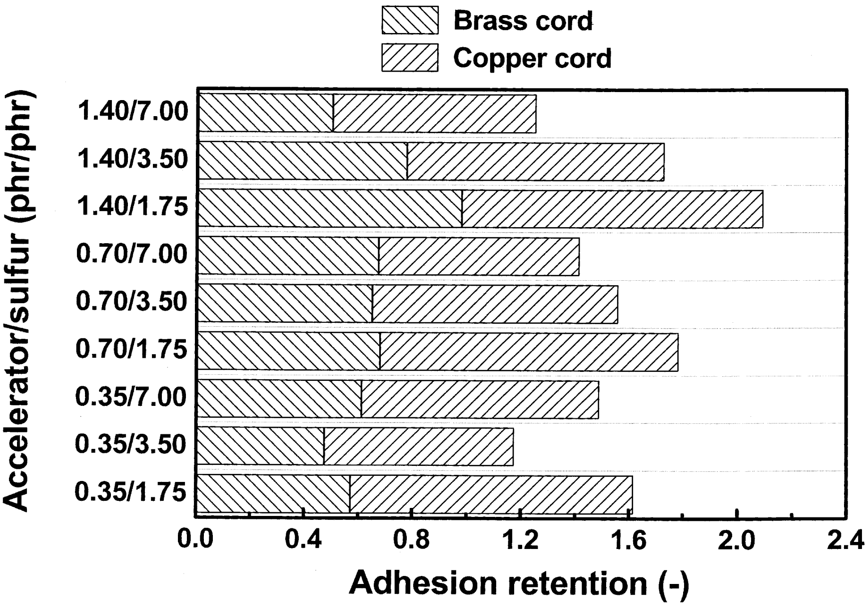

FIGURE 4 Adhesion retention of adhesion samples thermally aged for 15 days with varied accelerator/sulfur contents.

considerably lower for copper-plated cord than for brass-plated steel cord. It is worth noting that, in the unaged state, the pullout force of the copper-plated cord to rubber compound (S/Acc. = 1.75/0.35) was just one-half of the brass-plated cord, but that after thermal aging of 15 days it was almost the same as that of the brass-plated cord. The rubber coverage of the brass-plated cord was almost constant with thermal aging, while that of the copper-plated steel cord significantly improved.

The adhesion stability of copper-plated steel cords was more exceptional than the brass-plated steel cord against humidity aging, as shown in Table 6. With humidity aging, the pullout forces of brass-plated steel cords decreased but those of copper-plated steel cord did not change remarkably. The rubber coverage of the brass-plated steel cord was slightly increased with humidity aging, while that of copper-plated steel cord was significantly improved. This result shows the exceptional adhesion stability of copper-plated steel cord compared with the adhesion degradation of brass-plated steel cord.

For the constant loading amount of accelerator, adhesion retention of copper-plated steel cord varied with sulfur loading (Figure 5).

TABLE 6 The Adhesion Properties of Humid-Aged[1] Adhesion Samples for Various Rubber Compounds with Respect to the Loading of Accelerator and Sulfur

Accelerator (phr)	Sulfur (phr)	Pullout force (N)				Rubber coverage (%)			
		Brass		Copper		Brass		Copper	
		0[2]	15	0	15	0	15	0	15
0.35	1.75	480	304	225	245	80	90	40	85
	3.50	559	402	294	245	85	90	50	85
	7.00	578	421	235	333	90	95	50	75
0.70	1.75	490	421	196	216	80	85	45	75
	3.50	559	461	216	225	85	95	50	85
	7.00	568	470	265	235	90	95	40	75
1.40	1.75	461	470	167	157	75	85	20	30
	3.50	568	490	196	186	90	95	40	70
	7.00	608	480	235	186	85	95	40	70

[1] The adhesion samples were humidly aged at 85°C and 85% relative humidity.
[2] Aging period (days).

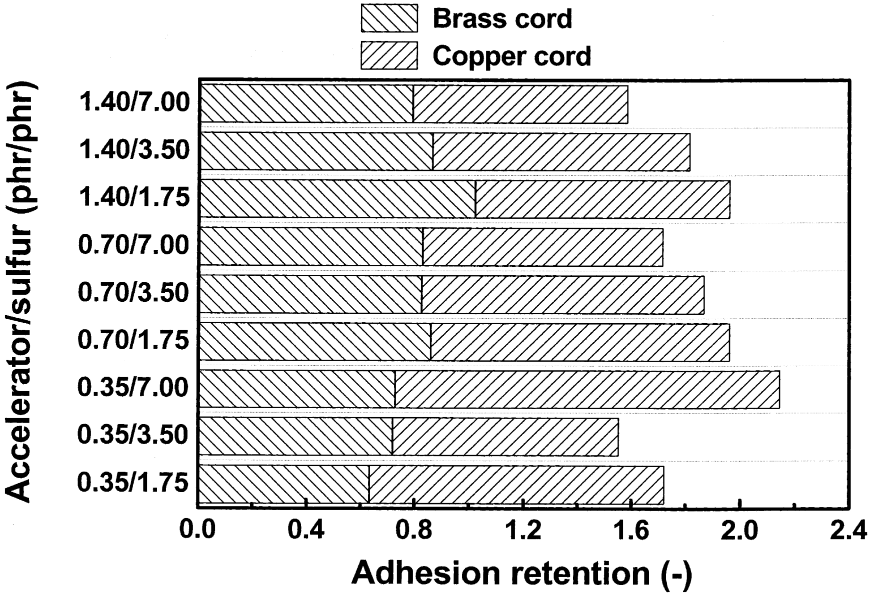

FIGURE 5 Adhesion retention of adhesion samples humidity aged for 15 days with varied accelerator/sulfur contents.

For the low loading amount of accelerator, adhesion retention of copper-plated steel cord increased with increasing sulfur loading. For the medium and high loading amount of accelerator, adhesion retention decreased with increasing loading amount of sulfur.

For a constant loading of sulfur, adhesion retention of copper-plated steel cord did not show any trend with accelerator content.

The adhesion properties between the rubber compound and copper-plated steel cord were also stable during salt solution aging. The adhesion properties after salt solution aging for 5 days are listed in Table 7. Longer aging was impossible due to tremendous corrosion.

As mentioned above, adhesion properties of copper-plated steel cord depended largely on the cure rate. Because of the large difference of reaction rate between adhesion-interphase formation and vulcanization, the weak boundary layer inevitably formed on the thin rubber layer closely adjacent to the adhesion interphase. Therefore, the pullout force with various aging treatments was plotted versus the cure rate of rubber (Figure 6). A clear correlation of pullout force with cure rate is not shown in the unaged case (Figure 6a). Unlike the unaged adhesion properties, the pullout forces after aging treatment show a negative linear correlation with the cure rate of rubber compound. For the brass-plated steel cord, pullout force was positively correlated with cure rate after various aging treatments.

TABLE 7 The Adhesion Properties of Salt-Aged[1] Adhesion Samples for Various Rubber Compounds with Respect to the Loading of Accelerator and Sulfur

		Pullout force (N)				Rubber coverage (%)			
		Brass		Copper		Brass		Copper	
Accelerator (phr)	Sulfur (phr)	0[2]	5	0	5	0	5	0	5
0.35	1.75	480	167	225	108	80	50	40	30
	3.50	559	500	294	196	85	90	50	70
	7.00	578	20	235	235	90	0	50	70
0.70	1.75	490	255	196	127	80	50	45	30
	3.50	559	98	216	225	85	85	50	60
	7.00	568	157	265	225	90	85	40	70
1.40	1.75	461	69	167	78	75	0	20	10
	3.50	568	49	196	176	90	0	40	40
	7.00	608	235	235	167	85	40	40	50

[1] The adhesion samples were aged in 15% NaCl aqueous solution.

[2] Aging time (days).

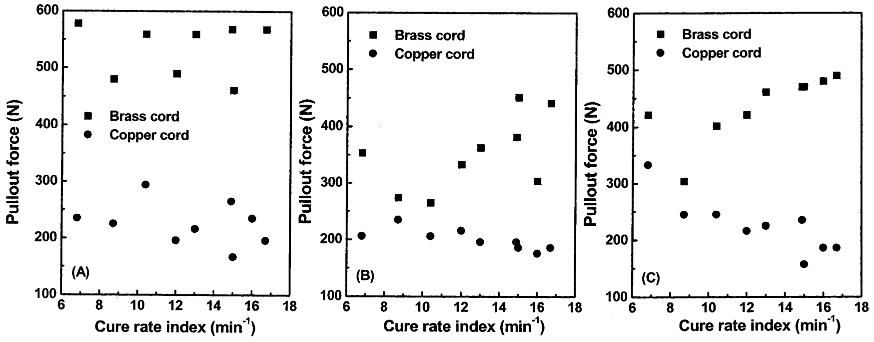

FIGURE 6 Pullout force of adhesion samples with various aging treatments *versus* cure rate of rubber compounds; (a) unaged; (b) thermally aged for 15 days; (c) humidity aged for 15 days.

Adhesion properties of the copper-plated steel cord were better when they were adhered to the rubber compound at slow-cure conditions, as compared with fast-cure conditions. Conversely, adhesion properties of the brass-plated steel cord were better when it was cured under fast-cure conditions (cure rate index ranging from six to eighteen), especially in the aging treatment. A definite explanation for this difference between the copper-plated and brass-plated steel cord 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 the sulfide formation consumes much sulfur, leading to the severe depletion of sulfur at the thin rubber layer closely adjacent to the adhesion interphase and low sulfur crosslinking density at the very thin rubber layer contacting the copper-plated steel cord. Although there is no direct evidence for the crosslinking density of the interfacial rubber layers, the low sulfur crosslinking density may be suggested as the cause of poor adhesion to the copper-plated steel cord at fast-cure conditions. The crosslinking density of the thin rubber layer contacting the brass-plated steel cord was considerable at normal cure conditions, and the low activity of copper in brass caused a relatively high crosslinking density of the rubber adhered to the brass-plated steel cord compared with that of the copper-plated steel cord. The increase in the modulus of the thin rubber layer closely adjacent to the adhesion interphase resists the fatigue between the rubber compound and the cord, resulting in better adhesion.

Another possible explanation of excellent adhesion retention of adhesion samples with slow cure rate is that chemical surface states of copper on copper-plated steel cord changed the metallic form to oxide forms such as CuO and Cu_2O during drawing and the initial vulcanization period. Naturally, oxide forms on the metals once the bare surface of metal contacts the environment [19]. The properties of these oxide films may play a major part in the formation of adhesion during the vulcanization process. The ionic state of copper could be either Cu^+ or Cu^{2+}. It is therefore proposed that copper sulfide is formed by the reaction between the active state of sulfur and the ionic state of copper. These oxides formed on the metallic copper surface during initial vulcanization. The slower the cure rate, the more contact time in vulcanization. Therefore, longer vulcanization time resulted in a higher chance of transforming metallic copper into copper oxide for the copper-plated steel cord. Su and Shemenski [14] reported the surface key ingredient for better adhesion between copper wire and rubber was Cu^{2+}, not copper metal.

One of several advantages of the copper-plated steel cord was the extremely high resistance to moisture [11]. Since the copper-plated steel cord does not contain zinc, degradation due to dezincification can be excluded. However, copper oxide or copper hydroxide forms on the copper-plated steel cord by contact with moisture, and this may correlate with the formation of the adhesion layer.

CONCLUSIONS

Although the adhesion properties of copper-plated steel cord varied with the cure rate of the rubber compound, the pullout force of the copper-plated steel cord was inferior to that of the brass-plated steel cord. High adhesion retention to the copper-plated steel cord was obtained after exposure to a hostile environment compared with brass-plated steel cord. The resistance of the copper-plated steel cord against hostile aging was better than that of the brass-plated steel cord. Pullout force of copper-plated steel cord to rubber compound after various aging treatments is inversely correlated with cure rate. The high adhesion between the copper-plated steel cord 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 copper sulfide.

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