

# ON CHARACTERIZING MICROSCOPICALLY THE ADHESION INTERPHASE FOR THE ADHESION BETWEEN BRASS-PLATED STEEL CORD WITH LOW BRASS PLATING AND RUBBER COMPOUND WITH ADHESION PROMOTER OF COBALT SALT BY AUGER ELECTRON SPECTROSCOPY

Gyung Soo Jeon<sup>1</sup>

<sup>1</sup>Department of Fire-Safety Management, Jeonnam Provincial College,  
152 Juknokwonro Damyanggeup Damyanggun Jeonnam 57337, South Korea  
Email: gjeon@dorip.ac.kr, Web Page: <http://www.dorip.ac.kr>

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## Abstract

The effect of the Co salt loading in rubber compound on the adhesion interphase to brass-plated steel cord with low brass plating was studied to elucidate the adhesion retention after hostile aging. Adhesion properties improved with the increase in the cobalt salt in rubber compound. The high adhesion of brass-plated steel cord with low brass plating to the rubber was obtained after cure and after hostile aging treatments. The stability against humidity aging and the cause for the high adhesion of the brass-plated steel cord with low brass plating were discussed in conjunction with the formation and growth of adhesion interphase determined by AES depth profile. The good adhesion property of brass-plated cord with low brass plating can be explained by the proper formation of the adhesion interphase due to the low brass plating in brass-plated steel cord and Co salt in rubber compound.

## 1. Introduction

Adhesion between rubber compound and metal has been widely used in many industrial fields. Brass-plated steel cords inserted in the belt and carcass of tires have long been used as a reinforcing material to provide sufficient mechanical strength and stability to endure cars themselves and their loads [1]. Good adhesion of a rubber compound to brass-plated steel cord is very important in radial tires. The adhesion between the rubber compound and the brass-plated steel cord is obtained by the reaction of copper in the brass and sulfur in the rubber compound during vulcanization, forming copper sulfide in the adhesion interphase [2-5]. Therefore, the adhesion interphase is very complex in terms of components and contents, so good adhesion can only be achieved when the adhesion interphase is formed with a sufficient thickness and a stable structure. Thus the adequate growth of copper sulfide is essential to form a large contact interface between the rubber and the brass, resulting in good adhesion [4-8]. Brass plating on the surface of steel cords reacts with sulfur in the rubber compound during the curing process of tire manufacturing, forming an adhesion interphase between the rubber compound and the steel cord [4-5, 8]. Copper and zinc also react with oxygen and water in the rubber, forming oxides and hydroxides of copper and zinc. Therefore, the adhesion interphase is very complex in terms of components and contents, so good adhesion can only be achieved when the adhesion interphase is formed with a sufficient thickness and a stable structure [9-12].

The excessive growths of sulfides and oxides result in cohesive rupture of the adhesion interphase, so a continuous search has been made for substitutes which maintain adhesion interphase integrity under severe service conditions for a long period. The superior adhesion stability can be expected if copper

content is low enough not to induce cohesive failure in the copper sulfide layer. Low brass plating as a plating material has significant advantages because there is a controlled adhesion interphase. The advantages of brass-plated steel cord with low brass plating is adhesion stability arisen from the controlled thickness of adhesion interphase. The major components of the adhesion interphase are sulfides, oxides and hydroxides of copper and zinc [3-5, 7-8, 13]. Adhesion becomes weak when copper sulfide is not sufficiently grown in the interphase, but the excessive growth of copper sulfide or zinc oxide brings about their own cohesive failures. Thus the adequate growth of copper sulfide is essential to form a large contact interface between the rubber and the brass, resulting in good adhesion. Several compounds such as cobalt salt [13], zinc salt, resinous bonding system [5, 12] composed of resorcinol-formaldehyde resin, and methylene donors are commercially used as adhesion promoters to enhance the migration of copper, forming the necessary amount of copper sulfide in the adhesion interphase. They are used either individually or together in the rubber compounds.

Thus the adequate growth of copper sulfide is essential to form a large contact interface between the rubber and the brass, resulting in good adhesion. A large content of zinc oxide at the outer surface of the brass induces a cohesive failure, since its mechanical strength is very weak. On the other hand, the coexistence of zinc oxide with zinc in the interphase is helpful to control the mass transfer rate of reacting species in the formation of the adhesion interphase. This contributes to the stability of the adhesion interphase by preventing excessive growth of its components. The transformation of zinc oxide with zinc metal at surface to zinc sulfide during vulcanization is very beneficial to keep from growing and transforming the adhesion interphase under hostile atmospheres.

Therefore, the interphase analysis such as depth profile of Auger electron spectroscopy is needed to elucidate the effect of brass-plating amount on the adhesion property. The microscopic analysis of adhesion interphase between rubber compound and brass-plated steel cord has been carried by Auger electron spectroscopy. Recently the role of brass-plating amount on brass-plated steel cord was elucidated by depth profile of Auger electron spectroscopy of adhesion interphase to rubber compound [4].

In this research, the effect of the Co salt loading in rubber compound on the adhesion interphase to brass-plated steel cord with low brass plating was studied to elucidate the adhesion retention after hostile aging. The adhesion properties between the rubber compound and the brass-plated cord were investigated, and adhesion stability was also studied under thermal and humidity aging treatments.

## 2. Experimental

Three kinds of rubber compounds were prepared. Three rubber compounds with different loadings of Co salt were prepared. The loading amounts of Co salt were varied as 0, 0.43 and 0.86 phr. Masterbatch components were as follows; natural rubber (Lee Rubber Co., Malaysia, SMR-100), 100 phr; carbon black N330 (Lucky Co., Korea), 45 phr; aromatic processing oil (Michang Co., Korea, A#2), 4 phr; zinc oxide (Hanil Co., Korea), 10 phr; antioxidant (Monsanto Co., USA Kumanox-RD, 2,2,4-trimethyl-1,2-dihydroquinone), 1 phr; and cobalt salt (Rhône-Poulenc Co., France, Manobond 680C), varied; adhesion promoter (Indspec Co., USA, B-18S), 2 phr. Final rubber compound components were as follows: masticated rubber masterbatch, 100 phr; stearic acid (Pyungwha Co., Korea), 3 phr; accelerator (Monsanto Co., USA, Santocure DZ, N-Dicyclohexylbenzothiazole-2-sulfenamide), 0.8 phr; and insoluble sulfur (Akzo Co., The Netherlands, Crystex HS OT 20), 4 phr; adhesion promoter (Cytec Co., USA, Cyrez-964), 4 phr; PVI (Monsanto Co., USA, N-Cyclohexylthiophthalimide), 0.2 phr. All the rubber compounds were mixed as described in ASTM D-3184 using an internal mixer (Banbury Mixer model 82, Farrel Co., USA). Ingredients for the masterbatch were mixed for 10 min at a rotor speed of 40 rpm and discharged at 150 °C. After the masterbatch had cooled to room temperature, the final mixing components were mixed for 5 min at 30 rpm and discharged at 90 °C. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co. USA). Rheocurves were recorded using a Monsanto Rheometer 100 at 160 °C.

The brass-plated steel cords with 3 x 0.35 construction in which 3 steel wires having the same diameter of 0.35 mm and the brass plating weight of 2.62g/kg, were twisted together, manufactured by Hyosung T&C Co., Korea, were used. Pull-out force was determined as the maximum force exerted

by the tensile tester on the T-test adhesion sample during the pull-out test, at a crosshead speed of 10 mm/min. Rubber coverage, defined as the percentage of rubber-adhered area on cord surface, was also noted. Each value reported is an average of six specimens tested.

A brass plated steel cord was covered with a filter paper (pore size: 5  $\mu\text{m}$ ; catalog no LSWP 142 50, Millipore Co., USA), sandwiched between two uncured pads of rubber compound, and then placed in a pad mold. Curing and aging conditions for the rubber compound/brass plate samples were the same as in the preparation of the T-test specimens. After the various treatments, samples for the surface analysis of the adhesion interphase were obtained by peeling away the filter paper. Sulfur from the rubber compound migrated through the pores of the filter paper and reacted with the copper and zinc of the brass-plated steel cord, forming an adhesion interphase. After removing the rubber and filter paper from the brass-plated steel cord, the adhesion interphase, including copper sulfide and zinc oxide, remained on the brass-plated steel cord.

The depth profiles from the interphase in contact with the rubber compound to the bulk of the brass were recorded on Ulvac-PHI Auger spectrometer. An area of  $10 \times 10 \mu\text{m}^2$  was examined using an ion beam with a potential of 5.0 kV, a current of 0.03  $\mu\text{A}$ , and an incident angle to the specimen of  $60^\circ$ : the same conditions as described in previously published papers [4-5]. 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 a  $2 \times 2 \text{mm}^2$  area for depth profiling. The sputtering rate for the brass film was determined to be 14 nm/min. It was difficult, however, to determine the sputter rate precisely for the adhesion interphase because it included various chemical components with variable concentrations. Therefore, the sputter time instead of the absolute depth was used to indicate the depth of the adhesion interphase in this paper.

### 3. Results and Discussion

The cure characteristics and Mooney viscosity of rubber compounds were summarized in Table 1. As the Co salt was loaded in rubber compound, cure time of rubber compound decreased with increasing the loading amount of Co salt. This may be explained as the accelerating role of Co salt in vulcanization of rubber compound. Also, the maximum torque of rubber compound increased with increase of Co salt in rubber compound. The Co salt played role of enhancing the crosslinking density of rubber networks. The Mooney viscosity of rubber compound decreased with increase of Co salt. This result may be explained that the anion of Co salt played role of lubricant of rubber network.

**Table 1.** Results from oscillating disc type rheometer<sup>1)</sup> and Mooney viscometer test<sup>2)</sup> for rubber compounds

Co salt (phr)	Time (min)			CRI <sup>6)</sup> (min <sup>-1</sup> )	Torque (J)		Viscosity <sup>7)</sup> (J)
	$t_2$ <sup>3)</sup>	$t_{40}$ <sup>4)</sup>	$t_{90}$ <sup>5)</sup>		min	max	
0	3.1	12.0	27.2	4.1	1.99	5.38	5.67
0.43	3.4	10.3	22.6	5.2	2.09	5.93	5.57
0.86	3.4	12.1	21.4	5.6	2.10	6.03	5.39

<sup>1)</sup> The rubber compounds were sheared to  $\pm 1^\circ$  and 1.67 Hz at 160°C.

<sup>2)</sup> The rubber compounds were sheared to 2 rpm at 100°C.

<sup>3)</sup> Time required to attain 2% degree of cure. <sup>4)</sup> Time required to attain 40% degree of cure.

<sup>5)</sup> Time required to attain 90% degree of cure. <sup>6)</sup> CRI (Cure Rate Index) =  $100/(t_{90} - t_2)$ .

<sup>7)</sup> Represented as torque,  $\text{ML}_{1+4, 100^\circ\text{C}}$ .

The physical property of vulcanizates was summarized in Table 2. With increasing the amount of Co salt in rubber compound, the modulus of vulcanizates increased but both the tensile strength and elongation decreased.

**Table 2.** Physical properties of vulcanizates

Treatment	Co salt (phr)	Hardness (Shore A)	Modulus (MPa)			T.S. <sup>1)</sup> (MPa)	E.B. <sup>2)</sup> (%)
			50%	100%	300%		
Cured <sup>3)</sup>	0	63	1.39	2.62	11.9	21.0	469
	0.43	64	1.55	2.92	12.7	18.5	407
	0.86	66	1.55	2.95	12.8	18.2	400
Cured and aged <sup>4)</sup>	0	66	1.72	3.52	-	7.7	189
	0.43	67	2.09	4.20	-	7.2	156
	0.86	68	2.11	4.23	-	6.8	153

<sup>1)</sup> Tensile Strength. <sup>2)</sup> Elongation-at-Break. <sup>3)</sup> The green compound was vulcanized for 25 min at 150 °C. <sup>4)</sup> The vulcanizate was thermally aged for 5 days at 90 °C.

The adhesion properties between rubber compound with different loading of Co salt and brass-plated steel cord having low brass-plating amount were shown in Table 3. With increasing Co salt on rubber compound, the pullout force after unaged increased. The rubber coverage after pullout test increased with increase of Co salt. The significant adhesion failure occurred in Co salt-free rubber compound but the cohesive failure occurred in Co salt-loaded rubber compound. The Co salt in rubber compound appeared to enhance the adhesion property. After humidity aging, the pullout force decreased compared to unaged regardless of the loading amount of Co salt. After humidity treatment of adhesion samples, the pullout force increased with increasing of the loading amount of Co salt. Regardless of the loading amount of Co salt, the cohesive failure occurred in rubber layer.

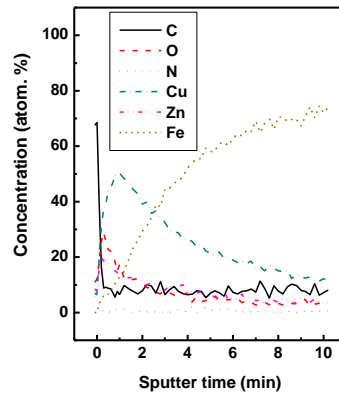
**Table 3.** Adhesion test results for hostile-aged adhesion samples between rubber compounds with loading of Co salt and brass-plated steel cord having low brass plating

Aging Type	Co salt (phr)	Pullout force(N)				Rubber coverage (%)			
		0 <sup>1)</sup>	5	10	15	0	5	10	15
HA <sup>2)</sup>	0	480	367	379	338	70	90	90	95
	0.43	557	423	352	380	95	80	90	90
	0.86	594	406	401	411	95	100	95	95
TA <sup>3)</sup>	0	480	347	277	218	70	90	90	50
	0.43	557	379	300	282	95	85	90	95
	0.86	594	381	271	274	95	90	100	85

<sup>1)</sup> Aging period (days). <sup>2)</sup> The adhesion samples were humidity aged at 85 °C and 85% relative humidity. <sup>3)</sup> The adhesion samples were thermally aged at 90 °C.

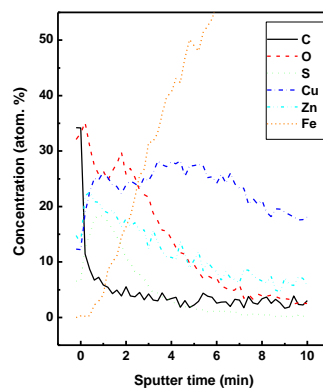
The surface composition for raw brass-plated steel cords having low brass plating was examined by depth profiling of AES (Fig. 1). For the brass-plated steel cord, the carbon peak of steel cord decreased abruptly with increasing sputter time. At the 1 min of sputter time, the carbon concentration is nearly trace level. The concentration of copper and zinc is linearly increased with sputter time up to 2 min. Further increase of sputter time of 2 min, the ratio of copper to zinc is nearly constant indicating the

existence of brass. The iron detected after the sputter time of 1 min and its concentration was linearly increasing with sputter time. The nitrogen detected in the outermost surface of brass-plated steel cord. This is may be resulted from the residual lubricant on steel cord which may be arisen from the manufacturing process of drawing of filament.



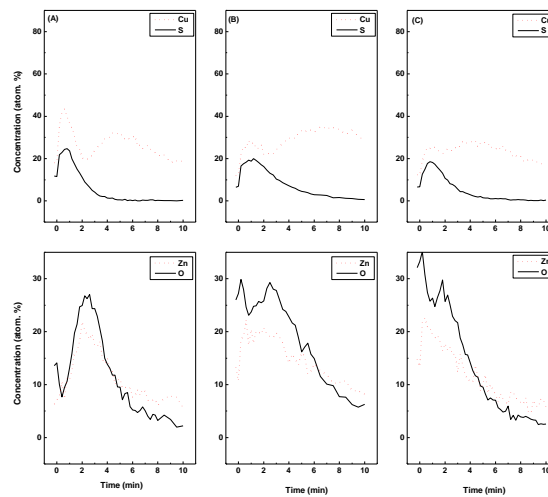
**Figure 1.** AES depth profiles of raw brass-plated steel cord with low brass plating

Fig. 2 shows AES depth profiles of the unaged adhesion interphase formed between rubber compound and brass-plated cord. At the outer surface of the brass plated steel cord adhered to the rubber compound, carbon, copper and sulfur were detected. Beneath these elements, zinc, oxygen and iron were detected. The affluence of carbon at outermost interphase is due to surface contamination. With increasing sputter time, carbon concentration decreased exponentially. Iron detected significantly from 1 min of sputtering and increased linearly up to 10 min of sputtering. After 4 min of sputtering, the ratio of copper to zinc was constant with depth, indicating non-reacted brass. This depth profile shows that copper sulfide is formed on the outer surface of the brass plated steel cord and zinc oxide on the inner side, although the oxidation states of these elements are not clearly identified.



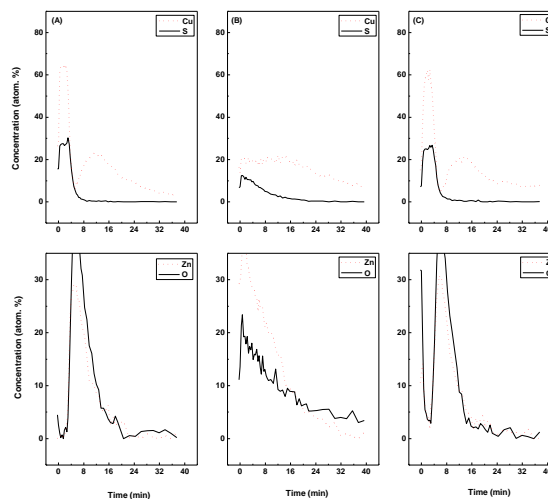
**Figure 2.** AES depth profiles of C, O, S, Cu, Zn and Fe for the adhesion interphase of unaged adhesion samples between rubber compound and brass plated steel cord with low brass plating

Figure 3 shows the AES depth profiles of the adhesion interphases formed on the brass-plated steel cord by adhering to rubber compound after cure. The copper and sulfur peaks appeared on the outer surface and their profiles partly coincided with each other, indicating that copper sulfide was formed. The ratio of sulfur to copper in the adhesion interphase increased with increasing Co salt in rubber compound. The thickness of both sulfur and copper increased with increasing Co salt in rubber compound.



**Figure 3.** AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples varying Co salt loading (phr) : (A) 0 (B) 0.43, (C) 0.86

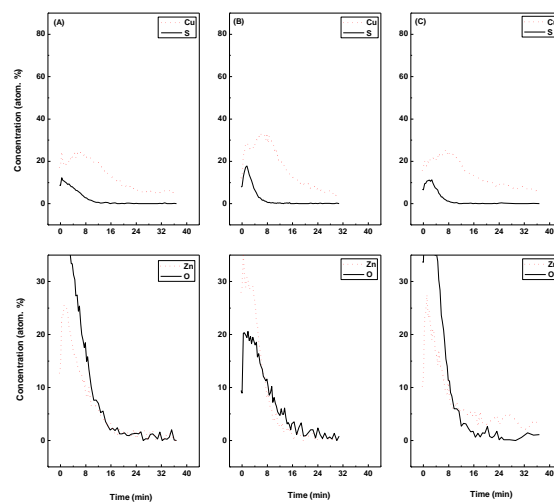
Figure 4 shows the depth profiles of the humidity-aged adhesion interphases formed on the brass side adhered to the rubber compound. With humidity aging, the adhesion interphase grew compared to that after cure [14-15]. It may be due to dezincification of the unreacted Cu-Zn layer under humidity aging which increased the relative concentration of Cu at the subsurface after the sulfide layer and appeared as copper shoulder peak. The width of sulfur peak of adhesion interphase become significantly large with increasing with increasing Co salt in rubber compound. Zinc and oxygen peaks were observed on the inner surface of the brass plated steel cord rather than copper and sulfur peaks after cure. For the adhesion interphase of high loading of Co salt in rubber compound, the ZnO is affluent in the adhesion interphase.



**Figure 4.** AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of humidity-aged adhesion samples varying Co salt loading (phr) : (A) 0 (B) 0.43, (C) 0.86

Figure 5 shows the depth profiles of the thermal-aged adhesion interphases formed on the brass side adhered to the rubber compound. With thermal aging, the adhesion interphase did not grow conspicuously compared to that after cure. The affluence of oxygen to zinc in the adhesion interphase explained that the oxidation of adhesion interphase occurred during thermal aging regardless of the loading amount of Co salt in rubber compound. The severe growth of adhesion interphase after thermal aging did not appear.

The adhesion properties of the brass-plated steel cord with low brass plating cord was good after humidity or thermal aging. The adhesion properties of brass-plated steel cord with low brass plating are strongly related to the structure and stability of the adhesion interphase, and the specificity of brass-plated steel cord. The excessive formation of copper sulfide, which induces its own cohesive failure leading to deterioration of the adhesion layer [16-17], is limited by the low brass plating on brass-plated steel cord. The control of copper sulfide growth on the brass-plated steel cord with low brass-plating also contributes to the excellent adhesion stability during hostile aging treatments.



**Figure 5.** AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of thermal-aged adhesion samples varying Co salt loading (phr) : (A) 0 (B) 0.43, (C) 0.86

#### 4. Conclusions

The incorporation of the Co salt in rubber compound on the adhesion interphase to brass-plated steel cord with low brass plating enhanced significantly adhesion property not only after cure but also after hostile aging treatment. The brass-plated steel cord with low brass plating suffered the deficiency of the brass to form adhesion interphase to rubber compound. The loading of Co salt in rubber compound accelerated the formation of adhesion interphase to brass-plated steel cord with low brass plating. The loading of Co salt in rubber compound may play role of activating of brass on brass-plated steel cord during cure to rubber compound. Especially, the affluence of ZnO at the adhesion interphase appeared in the high loading of Co salt in rubber compound. The Co salt in rubber compound activated zinc on brass-plated steel cord with low brass plating and subsequently the increased the mobility of copper on the brass-plated steel cord during both cure and hostile aging treatment. This result suggested to overcome the low reactivity of brass on brass-plated steel cord with low brass plating to addition of the appropriate amount of Co salt in rubber compound. The good adhesion property of brass-plated cord with low brass plating can be explained by the proper formation of adhesion interphase due to the low brass plating in brass-plated steel cord and Co salt in rubber compound.

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