삼원합금피복 스틸코드와 배합고무와의 접착. 1. 삼원합금피복 스틸코드에서 코발트 피복량의 효과

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Adhesion between ternary-alloy-coated steel cords and rubber compounds. Part 1. Effect of cobalt plating amount in the ternary-alloy-coated steel cords

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INTRODUCTION

Adhesion of rubber compound to brass-plated steel cord has been of paramount importance in tires. Brass-plated steel cords inserted in the belt and carcass of tires has long been used as a reinforcing material to provide a sufficient mechanical strength and stability to endure cars themselves and their loads depending on the tires' performance and durability. Therefore, it is essential not only to have high adhesion force between rubber compound and brass-plated steel cord but also to maintain stable adhesion retention under various hostile aging environments.

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 [1].

The major components of the adhesion interphase are sulfides, oxides and hydroxides of copper and zinc. 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 optimum growth of copper sulfide is essential to form a large contact interface between the rubber and the brass, resulting in good adhesion [2].

Therefore, the rate control of sulfidation of copper in vulcanization is needed to achieve good adhesion. Cobalt is one of noble metals and its reactivity to sulfur is relatively lower than copper. It is well known that the reactivity of cobalt to sulfur controls the reaction rate of brass to sulfur. Above mentioned, it is appeared that cobalt salt in rubber compound showed an adverse influence resulting in the oxidation of rubber. To avoid the adverse effect of cobalt salt, we prepared ternary alloy coated steel cords in which the cobalt was plated to brass plated steel cord in stead of incorporating cobalt salt in rubber compound.

We prepared ternary alloy coated steel cords in order to investigate the effect of cobalt plating amount in ternary alloy coated steel cord on the adhesion of rubber compound to them. The effect of cobalt plating in ternary alloy coated steel cord on the adhesion property between the rubber compound and ternary alloy coated steel cord was examined based on the formation and degradation of the adhesion interphase between rubber compound and ternary alloy coated steel cords from the AES depth profiles.

The adhesion properties between rubber compounds and ternary alloy coated steel cords having different cobalt plating amount were studied to illustrate the potential for the application of ternary alloy coated steel cord as an alternative reinforcement material of brass-plated steel cord in tire and to know the effect of cobalt plating amount on the adhesion of rubber compound to ternary alloy coated steel cord.

EXPERIMENTAL

A compound was prepared. Composition of the masterbatch and final mixed compound are given in Table 1. Bonding systems in rubber compound were excluded in order to observe the effect of cobalt plating amount in ternary alloy coated steel cord on the structure and composition of the adhesion interphase more clearly. The rubber compound was 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 ^oC. After the masterbatch had cooled to room temperature, the final mixing components were mixed for 5 min at 30 rpm and discharged at 90 ^oC. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co. USA).

Ternary alloy coated steel cords with having two kind of cobalt plating amount on brass plated steel cords were made with cyanide plating method in Kiswire Co., Korea. The construction structure of 3 x 0.30 in which 3 steel filaments having the same diameter of 0.30 mm were twisted together was used. The plating element compositions of ternary alloy coated steel cords determined by atomic absorption spectrometer (AA-6800F, Shimadzu Co, Japan) and plating weight determined by weighing of its dissolution with hydrochloric solution, were measured. For the comparison, the brass-plated steel cords with same construction structure of ternary alloy coated steel cords, manufactured by Kiswire Co., Korea, was used.

Based on the procedure described in ASTM D-2229, T-test specimens were cured at 160 ^oC on a cure press. Curing was continued for 5 min more than t_{90} time. For humidity aging, specimens were placed in a humidity chamber at 85 ^oC under 85% relative humidity for 5, 10, and 15 days. Also, the adhesion samples were aged thermally at 90 ^oC. Pullout force was determined as the maximum force exerted by the tensile tester on the T-test adhesion sample during the pullout test, at a crosshead speed of 10 mm/min. Rubber coverage was also noted. Each value reported is an average of six specimens tested. The morphology of the pulled-out steel cord surface after measuring pullout force was studied using a scanning electron microscope (JEOL JSM 7400, Japan).

Ternary alloy coated steel cords were covered with a filter paper (pore size: 5 µm; catalog no 142 50, Millipore Co., USA), sandwiched between two uncured pads of rubber compound, and then placed in a pad mold [3]. 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 plating elements of the ternary alloy coated steel cord, forming an adhesion interphase. After removing the rubber and filter paper from the ternary alloy coated steel cord, the adhesion interphase, including copper sulfide and zinc oxide, remained on the ternary alloy coated steel cord.

The depth profiles from the interphase in contact with the rubber compound to the bulk of the ternary alloy coated steel cord were recorded on a Perkin-Elmer Auger spectrometer (model Phi 670, Perkin-Elmer Co., U.S.A.). An area of 10 ×10 μm^2 was examined using an ion beam with a potential of 5.0 kV, a current of 0.03 µA, and an incident angle to the specimen of 60 ^{o}, the same conditions as described in previously published papers. The sputtering rate was determined to be 7.5 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.

RESULTS AND DISCUSSION

The adhesion properties of the rubber compound to ternary alloy coated steel cord were significantly enhanced with the cobalt plating up to 2 wt% on ternary alloy coated steel cord compared to that of brass plated steel cord as shown in Table 2 . There were significant increases with cobalt plating up to 2 wt% in the pullout force and rubber coverage in the unaged state. Further increase of cobalt plating amount showed the poor adhesion property compound compared to brass plated steel cord. Rubber coverage showed the same trend as the pullout force. The rubber coverage is very significant in the cobalt plating of 2 wt% on ternary alloy coated steel cord. Humidity aging deteriorates adhesion properties, so long aging causes poor adhesion (Table 2). After humidity aging for 15 days, the pullout force decreased, but the extent of decrease lessened with increasing cobalt plating. After humidity aging for 15 days, the highest adhesion property of ternary alloy coated steel cords to rubber compound showed in the 2 wt% cobalt plating which is the same trend of unaged adhesion property. Further increase of cobalt plating amount decreased pullout forces of the rubber compounds. Also rubber coverage showed similar behavior to that of the pullout force. The rubber coverage of the ternary alloy coated steel cords up to 2 wt% cobalt plating was higher than that of the brass plated steel cord after humidity aging of 15 days. As shown in Table 2, a small plating of cobalt plating as many as 2 wt% into ternary alloy coated steel cord significantly improves adhesion stability against humidity aging. The optimum cobalt plating in ternary alloy coated steel cord is very beneficial to increase rubber coverage for pulled-out cord surface of humidity aged adhesion samples.

It is impossible to separate the AES peak of cobalt and iron respectively due to the superposition of AES peak of cobalt and iron. The shapes of copper and sulfur on the outer surface did not change significantly with respect to the cobalt plating after cure (Fig. 1). A copper peak shoulder was observed in the adhesion interphase adhered to the rubber compound regardless of cobalt plating amount but the ratio of sulfur content to copper shoulder content increased on the outer surface with increasing cobalt plating amount. Also copper peak shoulder decreased with cobalt plating up to 2 wt%. Further increase of cobalt plating amount enlarged the copper peak shoulder. The zinc and oxygen peaks decreased with cobalt plating amount up to 2 wt%. Further increase of cobalt plating increased the oxygen peak and the oxygen peak was larger than zinc peak. This indicates that excessive cobalt plating induces a oxide compound in the adhesion interphase and the suppression of dezincification in the low cobalt plating which is important for good adhesion stability. As shown in Fig. 1(C), the S peak is larger than that of shoulder copper peak in the adhesion interphase for 4 wt% cobalt plating. This result may be the formation of cobalt sulfide, cobalt oxide and/or zinc sulfide layer in the adhesion interphase which suppresses the growth of adhesion interphase, especially copper sulfide layer. In the low cobalt plating, cobalt may selectively play role of controlling the formation of copper sulfide in the adhesion interphase and the cobalt plated may not easily convert to cobalt oxide and/or cobalt sulfide, which are supported from the decrease of both sulfur and oxygen peaks in the adhesion interphases. In the high copper plating, cobalt may convert to cobalt oxide and/or cobalt sulfide during cure which are supported to the increase of both sulfur and oxygen peaks in the adhesion interphase. Also, the severe dezincification in the higher cobalt plating may occur.

The zinc profile was similar to the oxygen profile on the outer surface, regardless of cobalt plating amount, suggesting the formation of zinc oxide. However, the detected depth and the amount of zinc oxide formed varied with cobalt plating amount. With plating of cobalt up to 2 wt%, the detected depth of zinc shifted to the outer surface and the content of zinc oxide in the adhesion interphase decreased. The partly formation of ZnS instead of ZnO in the adhesion interphase is accelerated by cobalt plating as corrosion inhibitor and prevents excessive growth of copper sulfide, resulting in the lowering of dezincification in the adhesion interphase. But the high cobalt plating, the formation of cobalt sulfide and cobalt oxide may dominantly occur compared to that of the zinc sulfide.

CONCLUSIONS

Adhesion stability between rubber compounds and ternary alloy coated steel cord is considerably enhanced by plating cobalt. Copper migration to the rubber bulk was accelerated by cobalt plating, resulting in moderate copper sulfide and zinc sulfide formation and the enhancement of adhesion stability. The optimum cobalt plating suppressed dezincification significantly after humidity aging. The optimum cobalt plating acts as an adhesion stabilizer in various hostile environments.

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Table 1. Recipe of rubber compound used

Component	Chemical or Trade name	Manufacturer	Content (phr)
natural rubber	SMR-20	Lee Rubber Co., Malaysia	100
carbon black	N330	Lucky Co., Korea	43
processing oil	A#2	Michang Co., Korea	1
activator	ZnO	Hanil Co., Korea	5
activator	Stearic acid	Pyungwha Co., Korea	0.5
accelerator	Santocure MOR[1)]	Monsanto Co., USA	0.6
sulfur	Crystex HS OT 20	Akzo Co., The Netherlands	8

Table 2. The adhesion properties of various aged adhesion samples between rubber compound and ternary alloy coated steel cords.

Co amount (wt%)	Pullout force (N)			Rubber coverage (%)		
	0[1]	15(t)[2]	15(h)[3]	0	15(t)	15(h)
0	353	303	284	70	70	75
2	402	353	372	85	80	85
4	265	284	255	65	60	70

[1] Aging period (days). [2] Thermal aging. [3] Humidity aging.

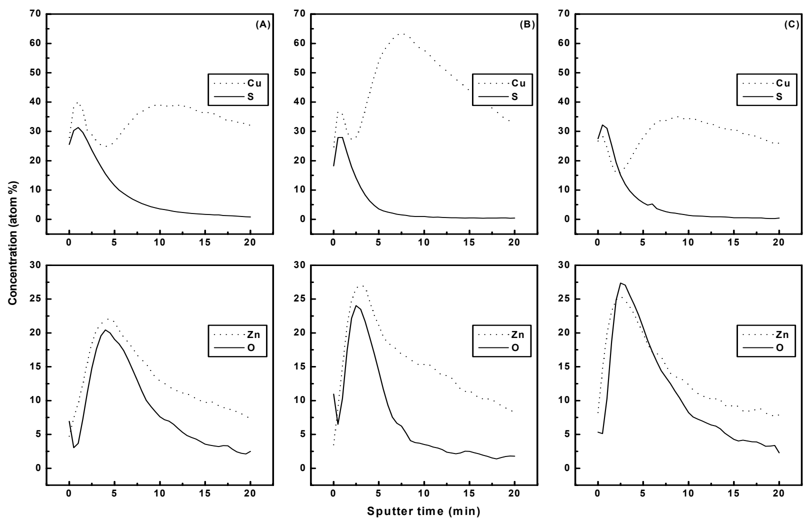

Figure 1. AES depth profiles of adhesion interphases between rubber compound and ternary alloy coated steel cords with having different cobalt plating. (A) 0 wt%, (B) 2 wt% and (C) 4 wt%.