배합고무와 금속간의 접착계면 구조제어를 통한 접착내구성 향상

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Enhancing the adhesion endurance by controlling the structure of the adhesion interphase between rubber compound and metal

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INTRODUCTION

Adhesion of rubber to brass-plated steel cord is of paramount importance in steel belted 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. 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. 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 content, so good adhesion can be achieved when the adhesion interphase is formed with a sufficient thickness and a stable structure.

The major components of the adhesion interphase are sulfides, oxides and hydroxides of copper and zinc [1]. 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]. Several compounds such as cobalt salt, 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 simultaneously in the rubber compounds. Cobalt salt has been used as an adhesion promoter in the rubber compounds to accelerate the activation of sulfur in the interphase by inducing formation of an adequate copper sulfide layer, thus making better adhesion possible [3]. However, an adverse effect is observed for rubber compounds with high levels of cobalt salt, or after humidity aging, due to the formation of an excessive copper sulfide layer which is prone to cohesive failure. Recently zinc borate as an adhesion promoter has been used to overcome the adverse effect of cobalt salt in tire industry.

The pull-out force and coverage of the rubber compound incorporating zinc borate were measured. The influences of humidity aging as well as zinc borate concentration on the adhesion property of zinc borate -containing rubber compounds were also investigated.

EXPERIMENTAL

Four kinds of rubber compounds having different loading amount of zinc borate were prepared as follows. The zinc borate incorporated was zinc borate hydrate (Borax Co., USA). The loading amounts of zinc borate were varied as 0.5, 1.0, and 2.0 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 ^{o}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 ^{o}C. After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill (model MKIII, Farrel Co. USA).

Based on the procedure described in ASTM D-2229, T-test specimens were cured at 160 ^{o}C on a

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cure press.   Curing was continued for 5 min more than t_{90} time.   The brass-plated steel cords with 3 x 0.35 construction in which 3 steel wires having the same diameter of 0.35 mm were twisted together, manufactured by Hyosung T&C Co., Korea, were used.   The plating weight of the brass was 3.6 g/kg and the copper content 63.6%.   For humidity aging, specimens were placed in a humidity chamber at 83 ^{o}C under 95% relative humidity for 5, 10, and 15 days. Also, the adhesion samples were aged thermally at 100 ^{o}C for 5, 10, and 15 days under air atmospheres. 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 was also noted.   Each value reported is an average of six specimens tested. The morphology of the pulled-out steel cord surface after measuring pull-out force was studied using an image analyzer.

A brass plated steel cord was 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 [4].   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 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.   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 ×2 mm^2 area for depth profiling.   The sputtering rate for the brass film was determined to be 4.4 nm/min.

RESULTS AND DISCUSSION

The decrease in the adhesion properties of the rubber compound to brass-plated steel cord was significant with the incorporation of zinc borate into the rubber compared as shown in Table 1.   Table 1 shows the pull-out force and rubber coverage of the zinc borate -containing rubber compounds both after curing and after humidity aging. There were significant decreases with zinc borate loading as much as 2.0 phr in the pull-out force and rubber coverage in the unaged state.

Humidity aging deteriorates adhesion properties, so long aging causes poor adhesion (Table 1). After humidity aging for 15 days, the pull-out force decreased, but the decrease was small for the zinc borate-containing rubber compounds.   Incorporation of zinc borate increased remarkably pull-out forces of the rubber compounds.   Also rubber coverage showed similar behavior to that of the pull-out force. As shown in Table 1, a small incorporation of zinc borate as much as 1.0 phr into rubber compound significantly enhanced adhesion stability against humidity aging. Zinc borate addition into the rubber compound decreased rubber coverage for pulled-out cord surface of humidity aged adhesion samples.

The formation, growth and deformation of an adhesion interphase between the zinc borate-containing rubber and the brass plated steel cord can be monitored from the adhesion sample with filter paper placed at the interphase. The contents of copper and sulfur on the outer surface increased on the zinc borate-containing rubber compounds (Fig. 1).   A copper peak shoulder was observed in the adhesion interphase adhered to the rubber compound regardless of zinc borate loading.   Also width of copper peak shoulder increased with increasing zinc borate loading of 1 phr.   Width of sulfur peak increased significantly with increasing zinc borate loading of 1 phr.   Zinc and oxygen peaks were observed on the inner surface of the brass plated steel cord rather than copper and sulfur peaks after cure.   Intensities of both zinc peak increased with increasing zinc borate loading. For the

zinc borate loading of 1.0 phr as shown in Fig. 1(B), severe dezincification at the adhesion interphase occurred. This result suggests the controlled incorporation amount of zinc borate is very important in the stability of adhesion interphase such as both copper sulfide layer and zinc oxide layer. The detected depth and the amount of zinc oxide formed varied with zinc borate incorporation.   With an increase in the loading amount of zinc borate, the content of zinc oxide in the adhesion interphase decreased.

Fig. 2 shows the depth profiles of the humidity-aged adhesion interphases formed on the brass side adhered to the rubber compound. The width and shape of copper and sulfur peaks at the outer surface were changed with an increase in the loading amount of zinc borate.   Compared to unaged adhesion samples, width of adhesion interphase increased after humidity aging. Moderate sulfur peaks were observed on the outer surface of the brass plated steel cord adhered to the rubber compound with low zinc borate loading of 1.0 phr. With increasing zinc borate loading into rubber compounds, the widths of both copper shoulder peak and sulfur peak increased largely under humidity aging treatments.

CONCLUSIONS

The adhesion between zinc borate incorporated rubber compounds and brass-plated steel cords was studied to understand the role of zinc borate as an adhesion promoter. Adhesion stability between rubber compounds and brass-plated steel cords is considerably enhanced by incorporation of zinc borate. An improvement in adhesion was not shown with the loading of zinc borate, while decline of adhesion stability was significantly observed with high loading at 2 phr and a long aging time of 15 days under humidity aging.   The adhesion interphase between the brass plated steel cord and the rubber compound studied using AES showed stabilized depth profile by zinc borate incorporation as low loading of zinc borate of 1 phr, resulting in the enhancement of the adhesion retention. For the high low loading of zinc borate, adhesion interphase grew excessively especially ZnO layer under humidity aging. Therefore the loading amount of zinc borate into rubber compound should be controlled to expect adhesion stability against hostile aging treatments.

ACKNOWLEDGEMENT

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Table 1. The result of adhesion test of humidity-aged[1] samples for the rubber compounds with respect to the loading of zinc borate.

Zinc borate (phr)	Pullout force (N)				Rubber coverage (%)			
	0[2]	5	10	15	0	5	10	15
0.5	627	637	510	518	100	80	70	70
1.0[3]	598	637	588	568	100	100	90	80
1.0[4]	598	627	559	568	100	100	90	80
2.0	519	588	480	549	90	90	60	60

[1] The adhesion samples were humidity aged at 83 °C and 95% relative humidity.
[2] Aging period (days).
[3] 2 phr of resorcinol formaldehyde resin and 4 phr of HMMM were added.
[4] 1 phr of cobalt salt, 2 phr of resorcinol formaldehyde resin, and 4 phr of HMMM were added.

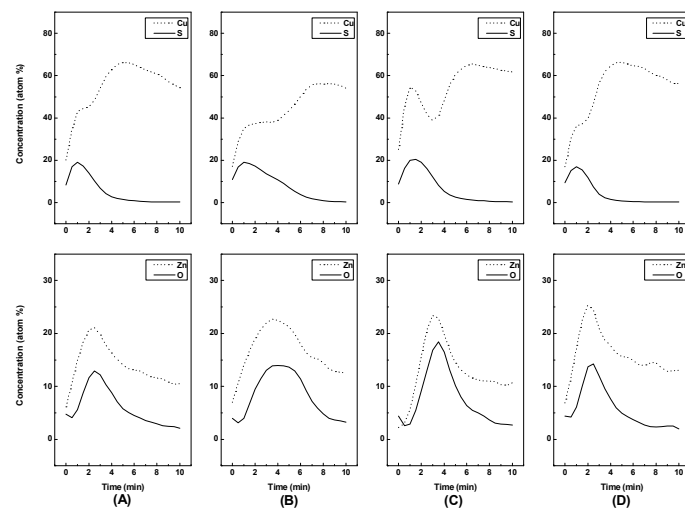*Theories and Applications of Chem. Eng., 2009, Vol. 15, No. 1*

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Figure 1. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples between the rubber compound and brass plated steel cord with respect to zinc borate loading: (A) 0.5 phr; (B) 1.0 phr; (C) 1.0 phr; (D) 2.0 phr.
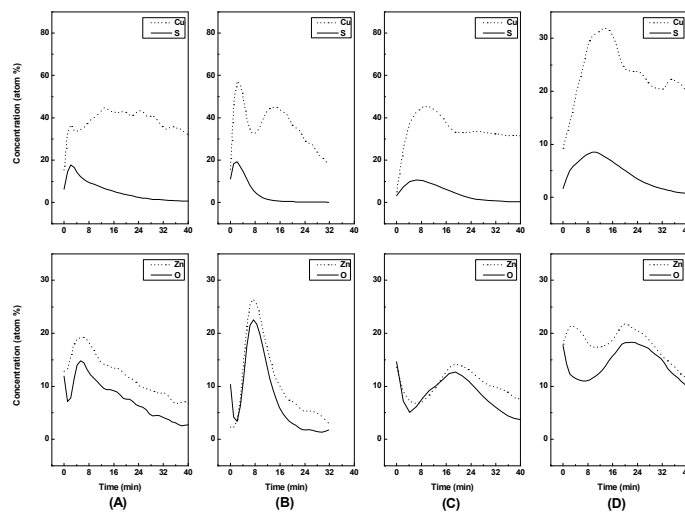

Figure 2. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of humidity aged adhesion samples between the rubber compound and brass plated steel cord with respect to zinc borate loading: (A) 0.5 phr; (B) 1.0 phr; (C) 1.0 phr; (D) 2.0 phr. Humidity aging : 15 days, 83 ^{o}C and 95% relative humidity.