On characterizing microscopically the adhesion interphases with humidity aging time for the adhesion between brass-plated steel cords and rubber compounds by Auger Electron Spectroscopy and FE-SEM

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Abstract

The effect of humidity aging time of adhesion samples made up of brass-plated steel cord and rubber compound on the adhesion interphase was studied by the depth profiling of Auger electron spectroscopy and FE-SEM. It was shown that humidity aging time of adhesion samples played major role of formation, growth and deterioration of copper sulfide and zinc oxide at the adhesion interphase with increased humidity aging time of adhesion samples. The adhesion interphase of adhesion sample after cure appeared the spherical shape whereas that after humidity aging treatment appeared the needle-like shape from FE-SEM analyses. The adhesion stability of adhesion samples against humidity aging treatment may be related to the suppression of the excessive growth of copper sulfide and the inhibition of dezincification during humidity aging time. Copyright © 2018 VBRI Press.

Keywords: Adhesion, rubber, brass-plated steel cord, interphase, Auger electron spectroscopy.

Introduction

The passenger and truck/bus tires have been built using various kinds of reinforcing materials such as brass-plated steel cord and fabric cord. Adhesion of rubber compounds to brass-plated steel cord in the tire industry has had significant importance as reinforcing function in tire. For successful use of brass-plated steel cords in radial tires, attainment and maintenance of good rubber compounds to brass-plated steel cords adhesion becomes vital **[1-6]**. The adhesion mechanism is found to be dependent on the chemical composition and the surface structure of the brass plating **[7]**, and the composition of cure system, type and loading of adhesion promoter **[6, 8]** in rubber compounds, and the cure conditions **[9]**. Brass plating on the surface of steel cords reacts with the 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 both copper and zinc **[10]**.Therefore, the adhesion interphase is very complex in terms of components and content, so good adhesion can only be achieved when the adhesion interphase is formed with a suitable thickness and a stable structure. The major components of the adhesion interphase are sulfides, oxides and hydroxides of copper and zinc **[2-8]**. Adhesion becomes weak when copper sulfide is not sufficiently formed in the interphase, but an 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 **[6-8]**. Good adhesion generally requires the use of several groups of adhesion promoters. Several compounds such as cobalt salt **[8]**, resorcinol formaldehyde resin **[11-13]**, and methylene donors **[6]**, 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 in combination in the rubber compounds.

In order to study the effect of humidity aging time in the rubber compound on the adhesion to brass plated steel cord, we prepared rubber compound. The effect of humidity aging time in the adhesion samples on their adhesion to the brass plated steel cords was examined based on the formation, growth, and degradation of the adhesion interphase from the depth profiles of the rubber compounds/brass plated steel cords samples. Since adhesion between two phases implies that some kind of chemical or physical interaction has taken place, much attention was paid to characterize the adhesion interphase formed between the two phases (rubber compound and brass plated steel cord). Samples of adhesion interphases were prepared by inserting a filter paper between the rubber compound and the brass plated steel cord **[6-8]** and they were analyzed by Auger electron spectroscopy (AES) in order to interpret the adhesion properties. In this study, the adhesion interphases between rubber compound and brass plated steel cord were investigated to explain the effect of humidity aging time for the employment of brass plated steel cords on the formation, growth and deterioration of adhesion interphase. In this study, the surface characterization of adhesion interphases which had the intact without the chemical treatment and mechanical force was carried out.

Experimental

A rubber compound was prepared. The formulation of rubber compound was summarized in **Table 1**. All rubber compounds were mixed as described in ASTM D-3184 using 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 150ºC.After the masterbatch had cooled to room temperature, the final mixing components were mixed for 5 min at 30 rpm and discharged at 90ºC. 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 150ºC. The t_{90}time, time required to achieve 90% degree of cure, and maximum torque were determined from the rheograms. Mooney viscosity was also obtained using a Monsanto MV-200 instrument according to ASTM D-1646 at 125ºC. The hardness of vulcanizates was measured using a Shore A durometer according to ASTM D-2240, and tensile properties were measured with a tensile tester (model 6021, Instron, USA) according to ASTM D-412. After vulcanizates were aged thermally for 5 days at 90ºC, mechanical tensile properties were also measured **[1]**.

Based on the procedure described in ASTM D-2229, T-test specimens were cured at 150ºC on a cure press. Curing was continued for 5 min more than t_{90} time. The brass-plated steel cords with 3 × 0.30 construction in which 3 steel wires having the same diameter of 0.30 mm were twisted together, manufactured by Hyosung T&C Co., Korea, were used. For humidity aging, specimens were placed in a humidity chamber at 85ºC under 85% relative humidity for 5, 10, and 15 days. 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. 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 LSWP 142 50, Millipore Co., USA), sandwiched between two uncured pads of rubber compound, and then placed in a pad mold **[6-8]**. 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 Ulvac-PHI Auger spectrometer (model Ulvac-PHI 7000, Ulvac-PHI Ins., U.S.A.). An area of 10 ×10 μm^2 was examined using an electron beam with a potential of 3.0 keV, a current of 10 nA, and an incident angle to the specimen of 60º. 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 2×2mm^2 area for depth profiling. The sputtering rate for the brass film was determined to be 14nm/min. The surfaces of interphases between rubber compound and brass-plated steel cords were observed by scanning electron microscopy (SEM) (JSM-7500F, JEOL, Japan) to investigate changes to the interphases between rubber and steel cord after cure and humidity aging. The surfaces were coated with gold prior to analyses.

Table 1. Formulation of rubber compound.

Material	Brand name	Loading (phr)
Natural rubber	SMR-100	100
Carbon black	N330	45
Processing oil	A#2	2
Activator	ZnO	10
Cobalt salt	Manobond 680C	0.86
Promoter	B-18S	2
Antioxidant	Kumanox-RD	1
Activator	Stearic acid	3
Promoter	Cyrez 964	4
Accelerator	DZ	0.8
Sulfur	Crystex HS OT 20	4
PVI		0.2

Results and discussion

The adhesion properties between rubber compound and brass-plated cord with respect to humidity aging time, were shown in **Table 2**. The pullout force of adhesion sample decreased with increasing humidity aging time. The cohesive failure of adhesion sample was dominant not only after cure but also after humidity treatment.

Table 2. Adhesion property between brass-plated steel cord and rubber compound with respect to humidity aging time.

Pullout force (N)				Rubber coverage (%)			
0[a)]	5	10	15	0	5	10	15
515	356	306	313	90	80	80	90

[a)]Humidity aging time (days)

The adhesion stability of adhesion sample against humidity aging treatment was shown in **Table 2**. The pull-out force and rubber coverage of the adhesion sample after humidity aging of 15 days were both good. With humidity aging, the pull-out forces of adhesion samples decreased. It could be the deformation of adhesion interphase during humidity aging.

The formation, growth and deformation of the adhesion interphase between the rubber compound and the brass plated steel cord can be monitored from the adhesion sample with filter paper placed in the interphase. Since the filter paper adheres neither to rubber nor to brass, the brass plate is easily detached from the rubber compound after cure. The analysis of the surface layer on the brass plate provides information on the formation and disappearance of chemical components in the adhesion interphase during curing process.

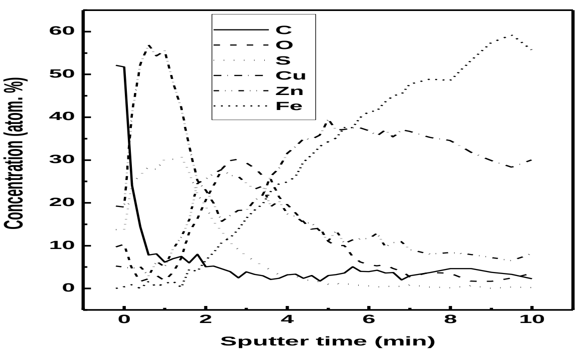

Fig. 1. AES depth profiles of C, O, S, Cu, Zn and Fe for the adhesion interphase of unaged adhesion samples between rubber compound and brass plated steel cord.

Fig. 1 shows AES depth profiles of the unaged adhesion interphase formed between rubber compound and brass-plated steel 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 the increase of 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 **[14]** 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.

Fig. 2 shows the AES depth profiles of the adhesion interphases formed on the brass-plated steel cord by adhering to rubber compound with respect to humidity aging time. Regardless of humidity aging time, the copper and sulfur peaks appeared on the outer surface and their profiles partly coincided with each other, indicating that copper sulfide was formed **[15]**. The thickness of both sulfur and copper increased with humidity aging time in adhesion samples. Because detected depths of copper and sulfur rose with the increase in humidity aging time, the growth of copper sulfide was enhanced on the brass-plated steel cord with humidity aging time. For the adhesion sample without treatment of humidity aging, the thickness of copper and sulfur peaks on the outer surface was narrow and the intensity of those was large on the adhesion interphase, and the zinc and oxygen peaks were observed afterward. Not only copper sulfides, but also zinc oxides were mixed at the adhesion interphase between the brass-plated steel cord and the rubber compound. The thickness of the adhesion interphase of adhesion sample without treatment of humidity aging was narrower than that treatment of humidity aging, because the treatment of humidity aging played the major role in adhesion interphase growth. With increasing humidity aging time, the concentration of oxygen is larger than that of zinc. This has probably existed in another oxide compound. As shown in **Fig. 1**, the zinc oxide on the steel cord with long humidity aging time is affluent. The detection of zinc oxide on steel cord largely depends on the humidity aging time. The ZnO on the steel cord without treatment of humidity aging appeared in the outer depth whereas that with treatment of humidity aging appeared in inner depth. The ZnO in the deep depth do not effectively play on controlling the formation of copper sulfide later. For long humidity aging, excessive growth of copper sulfide may be from the fast copper diffusion to adhesion interphase due to the shortage of zinc oxide layer adjacent to adhesion interphase which play role of diffusion barrier of copper. Therefore, the lower adhesion between the rubber compound and brass-plated steel cord **(Table 2)** could be ascribed to an excessive formation of the adhesion interphase compromising copper sulfide and zinc oxide. The affluence of oxygen over zinc peak in the adhesion interphase appeared in the humidity treated sample. Zinc and oxygen peaks were observed on the inner surface of the brass plated steel cord with increasing humidity aging time. Also, widths of zinc and oxygen peaks increased with humidity aging time, but the intensity of oxygen peak decreased with copper content in brass plating. For adhesion interphase of 15 days of humidity aging time, the severe dezincification appeared, as shown in **Fig. 2(d)**.

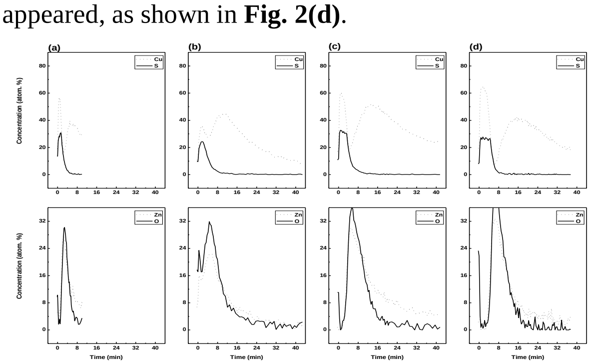

Fig. 2. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of adhesion samples between the rubber compound loaded with 0.86phr of Co salt and brass plated steel cord with respect to humidity aging time: (a) 0 days; (b) 5 days; (c) 10 days; (d) 15 days.

With humidity aging, the adhesion interphase grew compared to that after cure. A copper shoulder peak was observed in the adhesion interphase adhered to the rubber compound with humidity aging and the copper shoulder peak became conspicuous with increasing humidity aging time of adhesion samples. 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. For the cure not humidity aging, the dezincification may be less. Both intensity and width of sulfur peak become large significantly with increasing humidity aging time. Also, both intensity and width of copper shoulder peak become large with increasing humidity aging time of adhesion samples. Compared to the interphase after cure, the width and intensity of sulfur peak for that after humidity aging becomes large and the intensity and width of copper shoulder peak increased.

Zinc and oxygen peaks were observed on the inner surface of the brass plated steel cord rather than copper and sulfur peaks after cure. This phenomenon appeared significantly in the 15 days of humidity aging. It showed that intensities of both zinc and oxygen peaks changed with humidity aging time. And the width of zinc and oxygen peaks increased with humidity aging time. The affluence of ZnO layer in 15 days of humidity aging time of adhesion interphase was resulted in the decline of adhesion durability. The severe dezincification of adhesion interphase was observed in 15 days of humidity aging time.

Humidity aging might have controlled the formation of copper sulfide and zinc oxide layer in the adhesion interphase, resulting in the variation of adhesion property **[16]**.

The excessive formation of copper sulfide, which induces its own cohesive failure leading to deterioration of the adhesion layer, is promoted by the humidity aging time. Dezincification of brass is accelerated in humid conditions since zinc is easily dissolved in the presence of water. The copper atom in brass becomes active due to the loss of the zinc atom, and results in excessive growth of copper sulfide during humidity aging. The adhesion interphase of adhesion sample after cure appeared the spherical shape whereas that after humidity aging treatment appeared the needle-like shape from FE-SEM analyses **(Fig. 3)**. This result supports the mechanical interlocking of adhesion interphase between rubber compound and brass-plated steel cord.

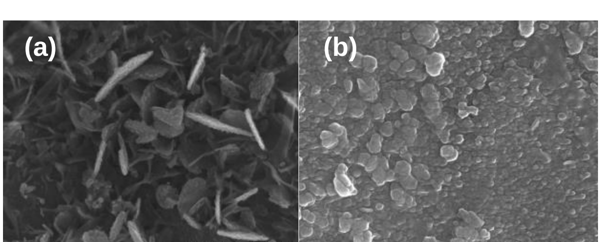

Fig. 3. Micrographs of surface of adhesion interphase of adhesion samples (a) before and (b) after humidity aging of adhesion sample.

Conclusion

The effect of humidity aging time of adhesion samples made up of brass-plated steel cord and rubber compound on the adhesion interphase was studied by the depth profiling of Auger electron spectroscopy and FE-SEM. It was shown that humidity aging time of adhesion samples played major role of formation, growth and deterioration of copper sulfide and zinc oxide at the adhesion interphase with increased humidity aging time of adhesion samples **[6-8]**. The adhesion interphase of adhesion adhesion sample after cure appeared the spherical shape whereas that after humidity aging treatment appeared the needle-like shape from FE-SEM analyses.

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