

삼원합금피복 스틸코드와 배합고무와의 접착.

2. 배합고무에서 황과 코발트염 효과

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Adhesion between ternary alloy coated steel cords and rubber compounds.**Part 2. Effect of sulfur and cobalt salt in rubber compounds**

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INTRODUCTION

The passenger and truck/bus tires has been build using various kinds of reinforcing materials such as metal cord, textile cord and filler. Adhesion of rubber compound to brass-plated steel cord in tire industry has been significant importance as reinforcing function. 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. 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 only 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, 2]. Several reagents such as cobalt salts, 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. Cobalt salts have been used as an adhesion promoter in the rubber compound to accelerate the activation of sulfur in the interphase by inducing the formation of an adequate copper sulfide layer, thus making better adhesion possible. Sulfur is the main cross-linking ingredient for the rubber compound and is played in an active state by the accelerator in rubber compound during vulcanization process. It requires 64 Kcal/mol to dissociate the sulfur ring indicating requiring high activation energy of sulfur to react.

Ternary alloy coated steel cord showed slow reaction rate for the formation of adhesion interphase compared to brass-plated steel cord. The high adhesion retention of ternary alloy coated steel cord with 2 wt% cobalt plating after various aging treatments was observed [3]. Therefore, cobalt salts which accelerates adhesion interphase reaction and sulfur which is always needed in the formation of adhesion interphase were varied in the rubber compounds. Samples of adhesion interphases were prepared by inserting a filter paper between the rubber compound and the ternary alloy coated steel cord and they were analyzed by Auger electron spectroscopy (AES) in order to interpret the adhesion properties.

We prepared ternary alloy coated steel cord with 2 wt% cobalt plating and investigated the effect of amount on both cobalt salt and sulfur in rubber compounds on the adhesion to ternary alloy coated steel cord. Also, the effect of cobalt salt and sulfur in rubber compound on the adhesion property to the ternary alloy coated steel cord was examined based on the formation, growth, and degradation of the adhesion interphase from the depth profiles of the rubber compound/ternary alloy coated steel cord samples.

EXPERIMENTAL

Three kinds of rubber compounds having different amount of both cobalt salt and sulfur were prepared as follows. Composition of the masterbatch and final mixed compound are given in Table 1. As shown in Table 1, a rubber compound which had low loading of sulfur (4 phr) without cobalt salt (0.4 phr) was prepared. Another rubber compound which had low loading of sulfur (4 phr) with cobalt salt (0.4 phr) was made. The other rubber compound which had high loading of sulfur (8 phr) with cobalt salt (0.4 phr) was fabricated. The cobalt salt used was Manobond 680C (Cobalt boroacylate, Co 23 wt%, Rhone Poulenc Co., France). The rubber compound was mixed as described in ASTM D-3184 using an internal mixer (Banbury Mixer model 82, Farrel Co., USA).

Ternary alloy coated steel cord with 2 wt% cobalt plating was made with cyanide plating method at 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.

Based on the procedure described in ASTM D-2229, T-test specimens were cured at 160 °C 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 °C under 85% relative humidity for 5, 10, and 15 days. Also, the adhesion samples were aged thermally at 90 °C. 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. 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 compounds, and then placed in a pad mold [4]. Curing and aging conditions for the rubber compound/ternary alloy coated steel cord 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 compounds 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 $10 \times 10 \mu\text{m}^2$ 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 °, the same conditions as described in previously. The sputtering rate was determined to be 7.5 nm/min.

RESULTS AND DISCUSSION

The adhesion properties of the rubber compounds to ternary alloy coated steel cord were significantly dependent on the loading amounts of both cobalt salt and sulfur in rubber compounds as shown in Table 2. It showed the pull-out force and rubber coverage of the ternary alloy coated steels cord to rubber compounds both after only cure and after humidity aging treatment for 15 days. There were remarkable increases with incorporating cobalt salt at constant loading of sulfur (4 phr) in the pull-out force and rubber coverage in the unaged state. As the cobalt salt was incorporated in rubber compound, pull-out force to ternary alloy coated steel cords increased about twice as much as that of cobalt salt-free rubber compound to them. Likely adhesion of rubber compound to brass plated steel cord, incorporating cobalt salt in rubber compound showed the enhancement of adhesion property to ternary alloy coated steel cord. At the constant loading of cobalt salt (0.4 phr), pull-out force to ternary alloy coated steel cord decreased slightly with increasing sulfur loading from 4 phr to 8 phr but rubber coverage kept to the constant to 90% with increasing sulfur loading from 4 phr to 8 phr. From the results mentioned above, incorporating cobalt salt in rubber compounds may contribute the formation of adhesion interphase to ternary alloy coated steel cord. Incorporating cobalt salt as much as 0.4 phr in rubber compounds significantly improved adhesion stability against humidity aging. Incorporating

cobalt salt in rubber compound was very beneficial to increase rubber coverage for pulled-out cord surface from humidity aged adhesion samples. The cobalt salt-free rubber compound and its humidity aged adhesion samples showed both interfacial and cohesive failure but 0.4 phr cobalt salt and its humidity aged adhesion samples dominantly showed cohesive failure in the rubber phase.

The shapes of copper and sulfur on the outer surface changed with respect to the amounts of both cobalt salt and sulfur after cure (Fig. 1). A copper shoulder peak was observed in the adhesion interphase adhered to the rubber compound regardless of amounts of both cobalt salt and sulfur but the ratio of sulfur content to copper shoulder content increased in the outermost surface with incorporating cobalt salt in rubber compounds contained constant sulfur loading. Also the ratio of sulfur content to copper shoulder content increased in the outer surface with increasing sulfur loading from 4 phr to 8 phr in rubber compounds containing constant cobalt salt loading. From the results mentioned above, both incorporating cobalt salt and high sulfur loading in rubber compounds were responsible for the increasing sulfidation of metal in the adhesion interphase. The copper shoulder peak increased with incorporating cobalt salt in rubber compounds supporting the increase of copper mobility during cure. It was well known that the cobalt salt in rubber compounds increased copper mobility in adhesion interphase during cure and various aging treatments. In the rubber compound containing 8 phr of sulfur and 0.4 phr of cobalt salt, copper shoulder peak became small compared to that in the rubber compound containing 4 phr of sulfur and 0.4 phr of cobalt salt. This may be explained that the sufficient copper mobility, which was stemmed from the incorporation of cobalt salt, increased additionally with increasing sulfur loading amount from 4 phr to 8 phr. Therefore, the migration of copper from adhesion interphase to rubber compound adjacent to adhesion interphase occurred and the copper shoulder peak in adhesion interphase decreased. The zinc and oxygen peaks changed with loading amounts of cobalt salt and sulfur in rubber compounds. With incorporating cobalt salt in rubber compounds, the intensities of both zinc and oxygen decreased but the widths of two elements increased. In the rubber compounds loaded constant cobalt salt, the intensities of both zinc and oxygen increased significantly with increasing sulfur loading from 4 phr to 8 phr, but the widths of two elements decreased conspicuously. In the constant cobalt salt loaded rubber compound, the excess sulfur is responsible for the dezincification in the adhesion interphase. This can be explained as follows; some of fully excited copper in adhesion interphase diffused into cobalt salt loaded rubber compound during cure. This phenomenon was accelerated in the high sulfur and cobalt salt loaded rubber compound. As a result, the copper mobility increased and zinc activity increased simultaneously resulting in surface enrichment of zinc in adhesion interphase during cure. In the cobalt salt and low sulfur loaded rubber compound, cobalt may selectively play role of accelerating the formation of copper sulfide in the adhesion interphase and suppressing the dezincification. In the cobalt salt and high sulfur loaded rubber compound, cobalt accelerated dezincification in the adhesion interphase and catalyzed the formation of metal sulfide such as zinc sulfide and cobalt sulfide.

CONCLUSIONS

Adhesion stability between rubber compound and ternary alloy coated steel cord is significantly dependent on the loading amount of both sulfur and cobalt salt in rubber compound. The low sulfur and cobalt salt played role of controlling the copper migration to rubber compound during cure resulting in moderate copper sulfide and zinc sulfide formation resulted in the enhancement of adhesion stability and suppression of dezincification. Especially, a portion of cobalt salt was needed to obtain high adhesion force of rubber compound to ternary alloy coated steel cord. The cobalt salt and low sulfur in rubber compound showed the high adhesion retention after various aging treatments. The cobalt salt in rubber compound acted as an adhesion interphase stabilizer to ternary alloy coated steel cord in various hostile environments.

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REFERENCES

1. P. Y. Patil and W. J. Van Ooij, *J. Adhesion Sci. Technol.*, **18**, 1367 (2004).
2. S. Fulton, G. C. Smith and K. J. Titchener, *Appl. Surface Sci.*, **221**, 69 (2004).
3. G. S. Jeon, *J. Adhesion Sci. Technol.*, accepted.
4. G. S. Jeon and S.W. Jeong, *J. Adhesion Sci. Technol.*, **18**, 925 (2004).

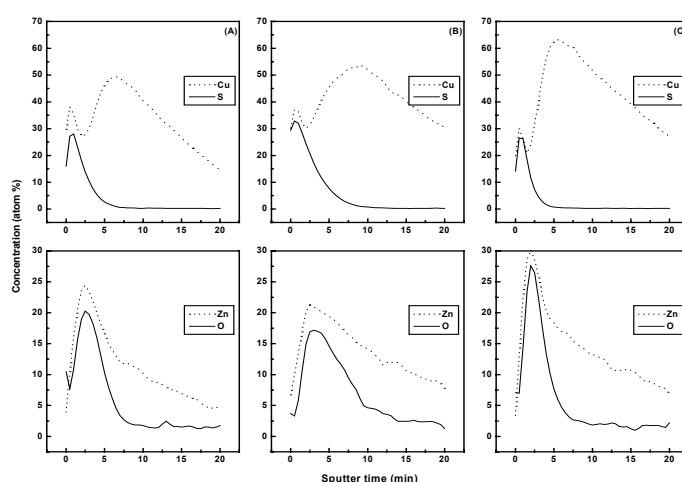
Table 1. Recipe of rubber compounds used.

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
Cobalt salt	Manobond 680C	Rhone Poulenc Co, France	varied
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	varied

Table 2. The adhesion properties of various aged adhesion samples between rubber compounds with different loading amounts of cobalt salt and sulfur and ternary alloy coated steel cord.

Loading (phr)		Pull-out force (N)			Rubber coverage (%)		
Sulfur	Co salt	0 ¹⁾	15(t) ²⁾	15(h) ³⁾	0	15(t)	15(h)
4	0	265	196	284	60	75	75
4	0.4	529	333	480	90	90	90
8	0.4	480	333	451	90	90	90

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

**Figure 1.** AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples between the rubber compounds and ternary alloy coated steel cord with respect to loading amounts of both sulfur and cobalt salt (phr/phr); (A) 4/0; (B) 4/0.4; (C) 8/0.4.