다양한 접착증진제를 함유하는 배합고무와 황동피복 스틸코드간의 접착. Ⅰ. 배합고무에서 황 함량의 효과

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Adhesion between Rubber Compounds Containing Various Adhesion Promoters and Brass Plated Steel Cords. I. Effect of Sulfur Loading in Rubber Compounds

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INTRODUCTION

Brass-plated steel cords employed in the belt and carcass of radial tires have been used as a reinforcing material for providing stiffness and strength to tires. 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]. The adhesion mechanism is found to be dependent on the chemical composition and the surface structure of the brass plating and the composition of cure system (sulfur and accelerator), type and loading of adhesion promoter in rubber compounds and cure conditions (cure temperature and time). 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 both copper and zinc.

Cobalt salt has been used as an adhesion promoter in the rubber compound to accelerate the activation of sulfur in the interphase by inducing formation of an adequate copper sulfide layer, thus making better adhesion possible[2]. 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. Zinc borate has been also used as adhesion promoter in rubber compounds to maintain stable adhesion retention by the playing role of inhibiting corrosion of boron[3]. Resorcinol formaldehyde resin has been employed in rubber compounds to enhance adhesion retention under hostile environments by suppressing the growth of copper sulfide at the adhesion interphase. Methylene acceptor has been used together methylene donor such as resorcinol formaldehyde resin and was capable of capturing amine generated, which is the principal cause of corrosion at the adhesion interphase, during vulcanization of rubber compounds[4]. Also, it reacted with methylene donor and subsequently formed interpenetrating network near the adhesion interphase during vulcanization. The formed interpenetrating network structure is responsible for the reinforcement of weak boundary layer adjacent to adhesion interphase.

In order to study the effect of sulfur loading in the rubber compound containing various adhesion promoters on the adhesion to brass plated steel cord, we prepared rubber compounds containing cobalt salt, zinc borate and resinous adhesion promoters (methylene donor/methylene acceptor) individually and with variable of sulfur loading. Also, the effect of loading amount of sulfur in the rubber compounds 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.

In this study, the adhesion properties between rubber compounds with different amounts of sulfur and brass plated steel cords were investigated to explain the effect of sulfur in rubber compounds containing adhesion promoters for the employment of brass plated steel cords on the formation, growth and deterioration of adhesion interphase and to know the effect of loading amount of sulfur in rubber compounds on the adhesion to brass plated steel cords.

EXPERIMENTAL

Six kinds of rubber compounds having different loading amount of sulfur and type of adhesion promoters were prepared as follows. Two kinds of rubber compounds containing 1 phr of cobalt salt were prepared in the low loading of sulfur (4 phr) and in the high loading of sulfur (8 phr). Other two kinds of rubber compounds containing 1 phr of zinc borate were prepared in the low loading of sulfur (4 phr) and in the high loading of sulfur (8 phr). The other two kinds of rubber compounds containing 2 phr of methylene donor/4 phr of methylene acceptor were prepared in the low loading of sulfur (4 phr) and in the high loading of sulfur (8 phr). The cobalt salt used was Manobond 680C (Cobalt boroacylate, Co 23 wt%, Rhone Poulenc Co., France). The zinc borate incorporated was zinc borate hydrate (Borax Co., USA). The methylene acceptor loaded was B-18S (resorcinol formaldehyde resin, Indspec Co., USA) and methylene acceptor was Cyrez-964 (Hexamethoxymethylmelamine with 35wt% silica, Cytec Co., USA). Based on the procedure described in ASTM D-2229, T-test specimens with 12.7 mm cord embedment in the rubber block were cured at 160 ^{o}C on a cure press. A construction structure of 3 x 0.35 in which 3 steel filaments having the same diameter of 0.35 mm were twisted together was used. The copper composition in brass plating was 63.7 wt%. Curing was continued for 5 min longer than the t_{90} time. For humidity aging, specimens were placed in a humidity chamber at 83 ^{o}C / 95% 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.

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[5]. Curing and aging conditions for the adhesion interphase sample of rubber compound/brass plated steel cord were the same as in the preparation of the T-test specimens. After the various treatments such as vulcanization and/or aging, samples for analysis of the adhesion interphase were obtained by peeling away the filter paper placed rubber compound. Sulfur from the rubber compound migrated through the pores of the filter paper and reacted with brass plating of brass plated steel cord, forming an adhesion interphase. After removing the rubber and filter paper from the brass plated steel cord, the adhesion interphase, which contains 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 plated steel cord were recorded on a Perkin-Elmer Auger spectrometer (model Phi 670, Perkin-Elmer Co., U.S.A.). A 10×10 μm^2 area 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}. Surface concentrations were determined every 0.5 min from the Auger peaks of detected elements with compensation for their sensitivity factors. A sputter gun with an argon ion beam rastered a 2×2 mm^2 area for depth profiling. The sputter rate was determined to be 4.4 nm/min using tantalum pentoxide.

RESULTS AND DISCUSSION

Fig.1 shows the pull-out force and rubber coverage of the brass plated steel cord to rubber compounds both immediately after cure and after humidity aging treatment for 15 days.

The effect of the loading amount of sulfur in the rubber compounds on adhesion properties varied with the type of adhesion promoter incorporated. For the rubber compounds containing resinous adhesion promoters, pull-out force increased considerably with increasing loading amount of sulfur. But for the rubber compounds containing cobalt salt or zinc borate, pull-out force decreased slightly with increasing loading amount of sulfur. Regardless of type of adhesion promoters incorporated, cohesive failure in rubber layer occurred after the pull-out test supporting from the 100% rubber coverage as shown in Fig. 1. In the various adhesion promoters incorporated, cobalt salt showed the largest enhancement of adhesion properties after cure.

For the rubber compounds containing resinous adhesion promoters, adhesion retention after humidity aging decreased sharply with increasing loading amount of sulfur. Because excess sulfur in rubber compound is affluent in high loading of sulfur, the adhesion interphase is easily grown under humidity aging. Therefore, adhesive failure at rubber layer closely adjacent to adhesion interphase is dominant in the high loading of sulfur. For the rubber compounds containing cobalt salt, adhesion retention increased with increasing loading amount of sulfur. It may be suggested that adhesion interphase sufficiently grew for the low loading of sulfur in rubber compounds after cure. For the rubber compounds containing zinc borate, excellent adhesion retention appeared in low loading of sulfur. It is well known that boron plays the role of the inhibition of corrosion under hostile environments. For the rubber compounds containing low loading of sulfur, excellent adhesion retention may be arisen from the controlled growth of adhesion interphase. For cobalt salt incorporated, adhesive failure after humidity aging may partly occur in adhesion interphase whereas cohesive failure may partly occur in weak boundary layer closely adjacent to adhesion interphase for resinous adhesion promoters or zinc borate.

As shown in Fig. 1, incorporating low loading of sulfur and zinc borate as much as 1 phr in rubber compounds significantly improves adhesion stability against humidity aging. The incorporation of zinc borate in the rubber compound containing low loading of sulfur is very beneficial to increase the rubber coverage for pulled-out cord surface from humidity aged adhesion samples. This summary suggests that maintaining adhesion durability against various hostile aging environments depended on the loading amount of sulfur incorporated into rubber compounds.

For the rubber compounds containing resinous adhesion promoters, sulfidation of copper at the adhesion interphase accelerated with increasing the loading amounts of sulfur in rubber compounds (Fig. 2). In the adhesion system of resinous adhesion promoters containing high sulfur loading, resin in rubber compounds attracted strongly the copper at the adhesion interphase. As a result, zinc mobility at the adhesion interphase increased and the zinc peak became large. The ratio of oxygen peak to zinc peak at the adhesion interphases increased with increasing the loading amount of sulfur incorporated.

For the rubber compound containing cobalt salt, adhesion interphase is very different from that of containing resinous adhesion promoters. The copper shoulder peak increased with incorporating cobalt salt in rubber compounds supporting the increase of copper mobility during cure. In the adhesion system of cobalt salt containing low loading of sulfur, the widths of copper sulfide and zinc oxide at the adhesion interphase became largely. With increasing loading amount of sulfur in rubber compounds, both copper shoulder peak and sulfur peak decreased significantly. Both zinc peak and oxygen peak at the adhesion interphases became narrow but their intensities kept to constant with increasing sulfur loading. In the adhesion system of cobalt salt containing low loading of sulfur, cobalt salt in rubber compounds increased with the copper mobility at the adhesion interphase.

For the rubber compounds containing zinc borate, copper shoulder peaks at the adhesion interphase did not show clearly irrespective of the loading amount of sulfur. Compared to shapes of copper shoulder peak and sulfur peak for the rubber compounds containing the other adhesion promoters, those containing zinc borate are very small.

CONCLUSIONS

The effects of loading amount of sulfur in rubber compounds on their adhesion properties to brass plated steel cord can be summarized as: 1) The enhancement in the unaged adhesion properties was significant with incorporating low loading of sulfur in rubber compounds containing cobalt salt. 2) Under humidity aging treatment, the change of adhesion retention with respect to the loading amount of sulfur after humidity aging depended largely on the type of adhesion promoters incorporated. 3) For cobalt salt incorporated, adhesive failure after humidity aging may partly occur in adhesion interphase whereas cohesive failure may partly occur in weak boundary layer closely adjacent to adhesion interphase for resinous adhesion promoters or zinc borate. 4) Under thermal aging, adhesion retention increased with loading amount of sulfur in the rubber compounds irrespective of type of adhesion promoters incorporated. 5) Regardless of type of adhesion promoters incorporated, cohesive failure of thermally aged adhesion samples is dominant after pulled out test. The interphases between the rubber compounds and the brass plated steel cords using AES were interpreted in conjunction with adhesion property.

REFERENCES

1. P. Y. Patil and W. J. van Ooij, *Rubber Chem. Technol.,* **79**, 82 (2006).
2. S. Fulton, *Rubber Chem. Technol.*, **78**, 426 (2005).
3. Y. Ishikawa and T. Hotaka, *Wire J. Intl.*, **35**, 69 (2002).
4. A. K. Chandra, A. S. Deuri, R. Mukhopadhyay and A. K. Bhowmick, *Kautsch Gummi Kunstst.*, **50**, 106 (1997).
5. G.. S. Jeon, *J. Adhesion Sci. Technol.*, **19**, 445 (2005).

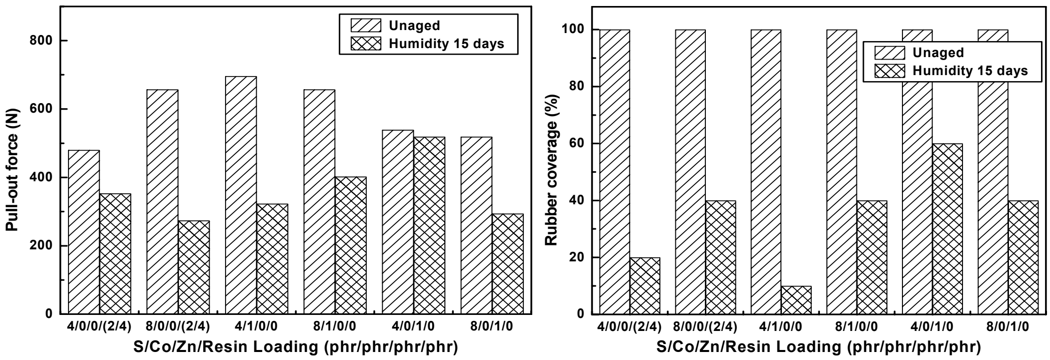

Figure 1. Adhesion properties of rubber compounds with different loading amounts of sulfur and adhesion promoters (cobalt salt/zinc borate/resin) to brass plated steel cord both immediately after cure and after humidity aging at 83 ^{o}C and 95% relative humidity for 15 days ; (A) pull-out force and (B) rubber coverage.

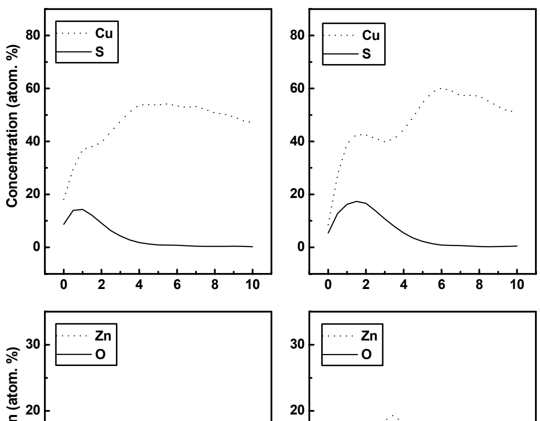

Figure 2. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples between the rubber compounds, loaded with both methylene acceptor of 2 phr and methylene acceptor of 4 phr, and brass plated steel cord with respect to loading amounts of sulfur; (A) 4 phr ; (B) 8 phr.