다양한 접착증진제를 함유하는 배합고무와 황동피복 스틸코드간의 접착 Ⅱ. 배합고무에서 가황촉진제 함량의 효과

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

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INTRODUCTION

The production of tires is among the most important automotive applications of adhesion. A steel-belted radial tire contains several reinforcing materials such as brass-plated steel cords and polyester fabric cords. The adhesion of rubber compounds to these cords is of critical importance for the performance and safety of tire[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.

The major components of the adhesion interphase are sulfides, oxides and hydroxides of copper and zinc[2]. Adhesion becomes weak when copper sulfide is not sufficiently grown in the interphase, but an excessive growth of copper sulfide or zinc oxide brings about their own cohesive failures. Failure generally occurs cohesively within the sulfide film or adhesively in an interphase below the sulfide film. 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. Good adhesion generally requires the use of several groups of adhesion promoters. Several compounds such as cobalt salt, zinc borate, 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.

Sulfidation of brass surface is not due to its interaction with elemental sulfur, but it is the result of the interaction between the brass surface and accelerator-sulfur reaction products which can be represented by the general structure, Ac-S_y-Ac and Ac-S_y-H, where Ac is an accelerator-derived moiety. The value of subscript, y, increases with the ratio of the concentration of sulfur to the concentration of accelerator used in the cure system[3]. It is known that high sulfur system in rubber compounds is beneficial to good adhesion to brass plated steel cord. According to recent results reported by Jeon[4], adhesion property of rubber compound to brass plated steel cord was found to be largely dependent on the type of adhesion promoter incorporated in the study of the effect of sulfur loading on the adhesion property.

In this study, the adhesion properties between rubber compounds with different loading amounts of accelerator and brass plated steel cords were investigated to explain the effect of the accelerator in rubber compounds containing cobalt salt, zinc borate and resinous adhesion promoter (methylene donor/methylene acceptor) individually for the employment of brass plated steel cords on the formation, growth and deterioration of adhesion interphase from the depth profiles of AES. Also, the adhesion property was studied to know the effect of loading amount of accelerator in rubber compounds on the adhesion to brass plated steel cords.

EXPERIMENTAL

Six kinds of rubber compounds having different loading amount of accelerator 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 accelerator (0.4 phr) and in the high loading of accelerator (1.6 phr). Other two kinds of rubber compounds containing 1 phr of zinc borate were in the low loading of accelerator (0.4 phr) and in the high loading of accelerator (1.6 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 accelerator (0.4 phr) and in the high loading of accelerator (1.6 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

Adhesion properties of the rubber compounds to brass plated steel cord were found to be significantly dependent on the type of adhesion promoter and the loading amount of accelerator in the rubber compounds as shown in Fig. 1. 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 accelerator in the rubber compounds on adhesion properties varied with the type of adhesion promoter incorporated. With the various adhesion promoters incorporated, zinc borate showed the largest enhancement of adhesion properties after cure.

For the rubber compounds containing zinc borate, pull-out force increased as much as two times with increasing loading amount of accelerator from 0.4 phr to 1.6 phr. But for the rubber compounds containing either resinous adhesion promoter or cobalt salt, pull-out force decreased slightly with increasing loading amount of accelerator. Regardless of the type of adhesion promoter incorporated, cohesive failure in the rubber layer occurred after the pull-out test. The adhesion of rubber compounds containing zinc borate to brass plated steel cords was very sensitive to loading amount of accelerator in the rubber compounds. But the adhesion of rubber compounds containing either resinous adhesion promoter or cobalt salt to brass plated steel cords was not sensitive to loading amount of accelerator in the rubber compounds. The resinous adhesion promoter formed the interpenetrating network closely near the adhesion interphase during vulcanization. Both sulfur crosslink network and interpenetrating network made the accelerator to retard the diffusion from the bulk rubber to the rubber layer closely near the adhesion interphase. The high loading of accelerator in the rubber compounds containing resinous adhesion promoter reduced the weak boundary layer adjacent to the adhesion interphase because of affluence of accelerator in the rubber layer closely adjacent to the adhesion interphase. The cobalt salt in the rubber compounds is known to accelerate adhesion interphase formation during vulcanization. As shown in Fig. 1, increasing the loading amount of accelerator from 0.4 phr to 1.6 phr in the rubber compounds did not increase adhesion properties significantly.

The humidity aging deteriorates the adhesion properties of rubber compounds to brass plated steel cord. After humidity aging for 15 days, the pull-out force decreased compared to that immediately after cure for all rubber compounds, but the extent of decrease in pull-out force varied with the loading amount of accelerator and the type of adhesion promoter incorporated. For the rubber compounds containing resinous adhesion promoter, adhesion retention after humidity aging increased significantly with increasing loading amount of accelerator. For the rubber compounds containing cobalt salt, adhesion retention decreased with increasing loading amount of accelerator. For the rubber compounds containing zinc borate, poor adhesion retention appeared for high loading of accelerator. For cobalt salt incorporated, adhesion failure after humidity aging dominantly occurs in the adhesion interphase whereas adhesion failure partly occurs in the weak boundary layer closely adjacent to the adhesion interphase for both resinous adhesion promoter and zinc borate.

Fig. 2 shows AES depth profiles of the unaged adhesion interphase formed between the brass plated steel cord and the rubber compound containing 0.4 phr of accelerator and resinous adhesion promoter. The intensities and widths of both copper shoulder peak and sulfur peak in the interphase changed with respect to the the amount of accelerator after cure. A copper shoulder peak was observed in the adhesion interphase adhered to the rubber compound containing resinous adhesion promoter regardless of loading amount of accelerator, but the ratio of sulfur peak to copper shoulder peak in the adhesion interphase decreased with increasing the loading amount of accelerator (Fig. 2). For the rubber compounds containing resinous adhesion promoter, sulfidation of copper in the adhesion interphase reduced with increasing the loading amount of accelerator in the rubber compounds. In the adhesion system of resinous adhesion promoter containing low accelerator loading, the resin in the rubber compounds attracted strongly the copper in the adhesion interphase. As a result, zinc mobility in the adhesion interphase increased and the zinc peak became large. The ratio of oxygen peak to zinc peak in the adhesion interphases decreased with increasing the loading amount of accelerator.

CONCLUSIONS

The adhesion property of the rubber compounds to brass plated steel cord was found to be largely dependent on the type of adhesion promoter and the loading amount of accelerator in the rubber compound. The adhesion of rubber compounds containing zinc borate to brass plated steel cords was very sensitive to loading amount of accelerator in the rubber compound. The enhancement in the unaged adhesion properties was significant with high loading of accelerator in the rubber compounds containing zinc borate. For cobalt salt incorporation, interfacial failure between adhesion interphase and rubber compound after humidity aging occurs dominantly whereas cohesive failure significantly occurs in the weak boundary layer closely adjacent to the adhesion interphase for both resinous adhesion promoter and zinc borate. From the analysis of adhesion interphases by AES depth profiling, it was found that the suppression of dezincification occurred in the adhesion interphase of the rubber compound containing high loading of accelerator.

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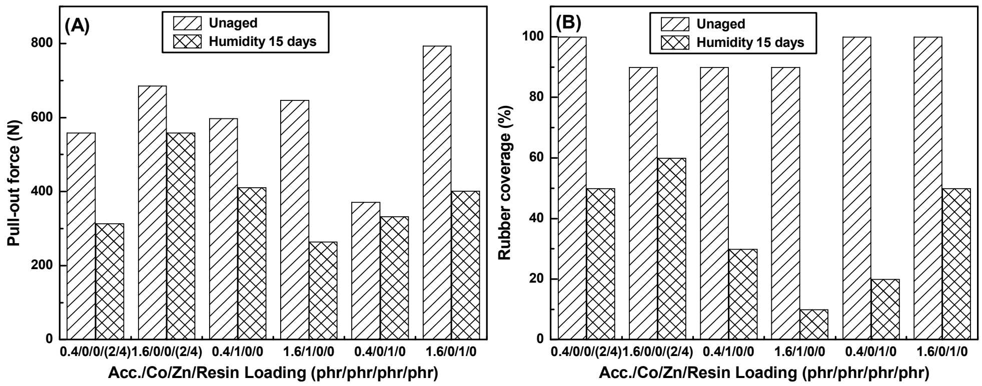

Figure 1. Adhesion properties of rubber compounds with different loading amounts of accelerator and adhesion promoters (cobalt salt/zinc borate/resin) to brass plated steel cord both immediately after cure and after humidity aging at 83 ^{o}C and 95% relative humidity for 15 days ; (A) pull-out force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

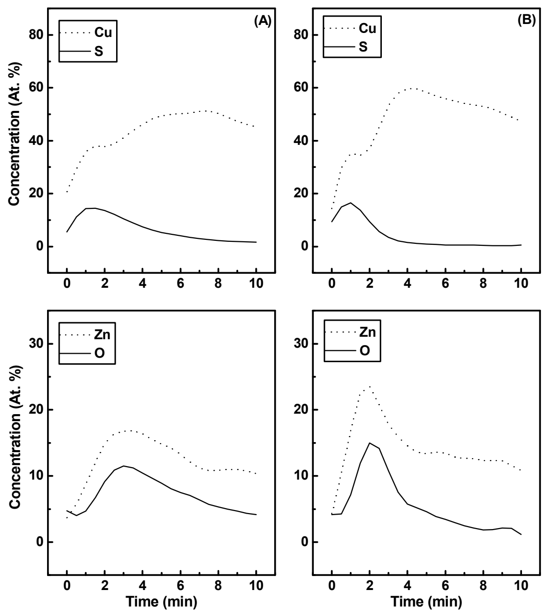

Figure 2. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples between the rubber compounds, loaded with both 2 phr of methylene donor and 4 phr of methylene acceptor, and brass plated steel cord with respect to loading amounts of accelerator: (A) 0.4 phr ; (B) 1.6 phr.