헥사메톡시메틸멜라민이 배합고무와 금속간의 접착에 미치는 영향

전경수
전남도립대학교 소방안전관리과
(gjeon@dorip.ac.kr)

Effect of hexamethoxymethylmelamine in rubber compound on the adhesion between metal and rubber compound

Gyung Soo Jeon
Dept. of Fire-Safety Management, Jeonnam Provincial College
(gjeon@dorip.ac.kr)

INTRODUCTION

Good adhesion of a rubber compound to brass-plated steel cord is very important in radial tires. Brass-plated steel cords inserted in the belt and carcass of tires have long been used as a reinforcing material to provide sufficient mechanical strength and stability to endure cars themselves and their loads [1]. 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 [2]. 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 contents, 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 [3-5]. 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 adequate growth of copper sulfide is essential to form a large contact interface between the rubber and the brass, resulting in good adhesion. Several compounds such as cobalt salt, zinc salt, resinous bonding system composed of 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 together in the rubber compounds. A large content of zinc oxide at the outer surface of the brass induces a cohesive failure, since its mechanical strength is very weak. On the other hand, the coexistence of zinc oxide with zinc in the interphase is helpful to control the mass transfer rate of reacting species in the formation of the adhesion interphase. This contributes to the stability of the adhesion interphase by preventing excessive growth of its components.

The pull-out force and coverage of the rubber compound containing hexamethoxymethylmelamine (HMMM) after pull-out test were compared to those of a HMMM-free rubber compound. The influences of humidity aging as well as loading of HMMM on the adhesion interphase of HMMM-containing rubber compounds were also investigated.

EXPERIMENTAL

Four rubber compounds with different loadings of HMMM were prepared. The loading amounts of HMMM were varied as 0, 2, 4 and 8 phr. All the rubber compounds were mixed as described in ASTM D-3184 using an internal mixer (Banbury Mixer model 82, Farrel Co., USA). Based on the procedure described in ASTM D-2229, T-test specimens were cured at 160 ^{o}C on a 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.

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.

A brass plated steel cord was covered with a filter paper (pore size: 5 m; catalog no LSWP 142 50, Millipore Co., USA), sandwiched between two uncured pads of rubber compound, and then placed in a pad mold. 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 [3-5]. 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. It was difficult, however, to determine the sputter rate precisely for the adhesion interphase because it included various chemical components with variable concentrations. Therefore, the sputter time instead of the absolute depth was used to indicate the depth of the adhesion interphase in this paper.

RESULTS AND DISCUSSION

The decrease in the adhesion properties of the rubber compound to brass-plated steel cord after cure was significant with the incorporation of HMMM into the rubber compared as shown in Table 1. Table 1 shows the pull-out force and rubber coverage of the HMMM-containing rubber compounds both after curing and after humidity aging. There were significant decreases with HMMM loading in the pull-out force in the unaged state. A poor adhesion property was shown with the addition of HMMM. Table 1 shows that the rubber attached to pulled-out cord surface of unaged adhesion samples is significant regardless of HMMM loading. Rubber coverage showed that cohesive failure in rubber layer occurred dominantly regardless of HMMM loading in rubber compounds.

Humidity aging deteriorates adhesion properties, so long aging causes poor adhesion (Table 1). The data after humidity aging for 5, 10 and 15 days are shown in Table 5. After humidity aging for 15 days, the pull-out force decreased, but the extent of decrease in pull-out force was larger for the HMMM-containing rubber compounds. Incorporation of HMMM increased remarkably pull-out forces and extent of decrease in pull-out force compounds compared to HMMM-free rubber compound. Also rubber coverage showed similar behavior to that of the pull-out force. The rubber coverage of the HMMM-containing rubber compounds was similar to that of the HMMM-free rubber compound after humidity aging of 15 days. As shown in Table 1, a small incorporation of HMMM as much as 4 phr into rubber compound significantly enhanced adhesion stability against humidity aging. Table 5 shows that rubber coverage for 8 phr zinc borate addition into the rubber compound is as five times as that of HMMM-free rubber compound after humidity aging of 15 days. From these results, HMMM in rubber compound contributes significantly the adhesion stability against humidity environment, not adhesion property after cure.

The effect of addition of HMMM on the adhesion stability after humidity aging was also studied. As summarized in Table 1, the addition of HMMM enhanced not only pullout force after cure but also the adhesion stability after humidity aging.

The contents of copper and sulfur on the outer surface were studied on the HMMM-containing rubber compounds (Fig. 1). A copper peak shoulder was observed in the adhesion interphase adhered to the rubber compound regardless of HMMM loading but the copper peak shoulder became ambiguous with increasing loading amount of HMMM into rubber compound. It might be from the weak interaction between HMMM in rubber compound and copper in brass-coated steel cord. Also, the sulfur peak of 2 phr HMMM is similar that HMMM-free rubber compound. But both intensity and width of sulfur peak of 4 phr HMMM become small significantly. Also, both intensity and width of copper shoulder peak become small. Compared to the sulfur peak of 4 phr HMMM, the width of sulfur peak of 8 phr HMMM becomes large and the intensity of copper shoulder peak 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 changed with increase in the loading amount of HMMM. Compared to unaged adhesion samples, width of adhesion interphase (copper sulfide and zinc oxide) increased after humidity aging. For the HMMM-free adhesion samples, adhesion interphase of zinc oxide grows significantly and largely deforms as shown in Fig. 2(A) compared to unaged adhesion samples. Moderate sulfur peaks were observed on the outer surface of the brass plated steel cord adhered to the rubber compound with moderate HMMM loading of 4 phr. The width of copper peak decreased significantly with HMMM loading up to 4 phr after humidity aging. Further increase HMMM loading over 4 phr into rubber compounds, the widths of both copper shoulder peaks increased largely under humidity aging treatments. The contents of zinc and oxygen in the adhesion interphase decreased with an increase in the HMMM loading up to 4 phr, indicating that HMMM depressed dezincification during humidity aging. Therefore, good adhesion stability appeared in the moderate loading amount of HMMM under humidity aging. But the growth of copper sulfide was accelerated with the high loading amount 8 phr of HMMM as shown in Fig. 2(D).

CONCLUSIONS

The adhesion between HMMM-containing rubber compounds and brass-plated steel cords was studied to understand the role of HMMM as an adhesion promoter. Adhesion property between rubber compounds and brass-plated steel cords is decreased by incorporation of HMMM after cure. An improvement in adhesion was seen with the loading of 4 phr HMMM for 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 stable depth profile by HMMM incorporation as optimum loading of HMMM of 4 phr, resulting in the enhancement of the adhesion retention. Copper migration in the adhesion interphase was depressed by HMMM incorporation, resulting in only moderate copper sulfide and zinc oxide formation. For the high low loading of HMMM of 8 phr, adhesion interphase grew excessively copper sulfide and zinc oxide layer under humidity aging. Therefore, the loading amount of HMMM into rubber compound should be controlled to expect adhesion retention against hostile aging treatments.

ACKNOWLEDGEMENT

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology(2011-0024214).

REFERENCES

1. F.Wiame, B.Salgin, J.Swiatowska-Mrowiecka, V. Maurice and P. Marcus, *J. Phys. Chem. C Letters*, **112**, 7540 (2008).
2. W. J. Vanooij, P.B. Harakuni and G. Buytaert, *Rubber Chem. Technol.*, **82**, 315 (2009).
3. G.S. Jeon, *J. Adhesion Sci. Technol*, **23,** 913 (2009).
4. G.S. Jeon, *J. Adhesion Sci. Technol*, **22,** 1223 (2008).
5. G.S. Jeon, *J. Adhesion Sci. Technol.*, **19**, 445 (2005).

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

HMMM (phr)	Pullout force (N)				Rubber coverage (%)			
	0[2)]	5	10	15	0	5	10	15
0.5	647	304	235	274	90	60	30	10
1.0	657	421	274	314	90	60	40	30
1.0	480	647	363	353	100	90	30	20
2.0	588	657	421	539	100	90	60	50

[1)] The adhesion samples were humidity aged at 83 ^{o}C and 95% R.H., [2)] Aging period (days).

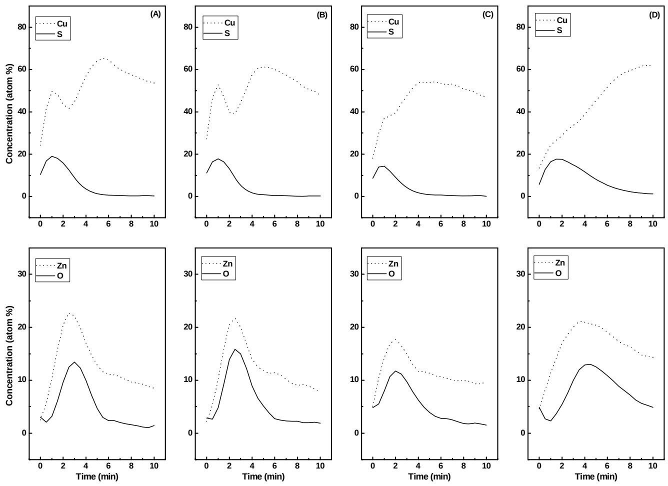

Figure 1. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of unaged adhesion samples between the rubber compound and brass plated steel cord with respect to HMMM loading: (A) 0 phr; (B) 2 phr; (C) 4 phr; (D) 8 phr.

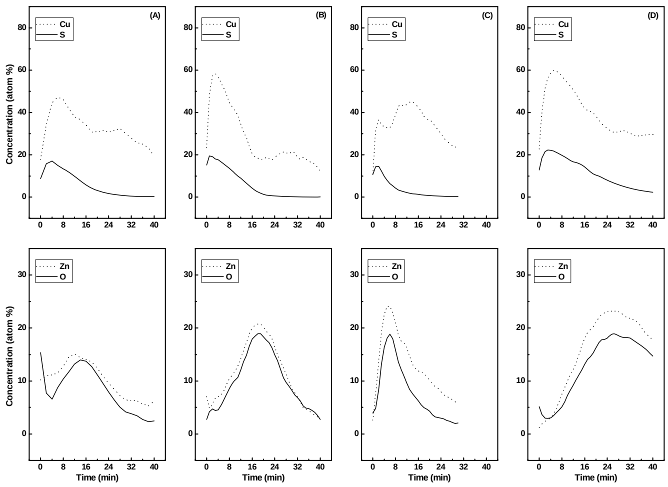

Figure 2. AES depth profiles of Cu, S (top) and Zn, O (bottom) for the adhesion interphases of humidity aged adhesion samples between the rubber compound and brass plated steel cord with respect to HMMM loading: (A) 0 phr; (B) 2 phr; (C) 4 phr; (D) 8 phr. Humidity aging : 15 days, 83 ^{o}C and 95% relative humidity.