유기탄성체와 금속과의 접착에서 접착계면에 관한 연구

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Adhesion Interphase for the Adhesion between Elastomer and Metal

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INTRODUCTION

The adhesion between rubber and metal has widely applied to various industries. A typical example of the adhesion is that between rubber compound and brass-plated steel cord in tire production, providing a sufficient mechanical strength and stability to endure cars themselves and their loads. Sulfides and oxides of copper and zinc formed through the reaction between the brass and the rubber compose an adhesion interphase of composites [1, 2]. Since the formation rate of these composites of the adhesion interphase largely varies with the cure temperature and time, cure level of composites is an important for their adhesion properties. Under-cure composites cured at low temperature or for short time induce an insufficient formation of the adhesion interphase as well as low cross-linking density of rubber, resulting in poor adhesion. On the contrary, long time cure at high temperature brings about over-cure. Excessive growth of the adhesion interphase also results in poor adhesion because of cohesive failure in sulfides and oxides layers. The poor physical property of over-cured rubber contributes simultaneously to lowering adhesion strength. Therefore, a number of studies for the optimization of the cure conditions as well as rubber compositions has been carried out to strengthen the adhered rubber to the brass surface and to form a stable adhesion interphase. The enhancement of the production efficiency of tire by shortening cure time with rising cure temperature also drives the study on the effect of cure condition on the adhesion.

Although the composition and structure of the adhesion interphase widely vary with cure temperature and time, experimental observation on the interphase is not easy. Since an extremely thin adhesion interphase is located between the cured rubber and the brass, the isolation of the adhesion interphase must accompany some damages of its structure and composition. Thin brass films deposited on glass are useful to analyze the structure of the adhesion interphase, but they do not provide any adhesion property strongly related to the adhesion properties of real brass-plated steel cord [3]. Insertion of a filter paper between rubber compound and brass-plated steel cord is effective to prepare adhesion samples for the interphase without any mechanical shock [4]. Since chemicals except large rubber molecules can migrate through the holes of filter papers, the change on the brass surface after cure provides some information about the reactions occurred during adhesion formation. A partial loss of sulfides and oxides at the adhesion interphase is, however, inevitable at the adhesion system inserting filter paper, because cured rubber is essential to hold the interphase. Therefore, this method is not suitable to obtain samples for quantitative analysis of the adhesion interphase, but is useful to investigate a qualitative inspection of the adhesion interphase. High simplicity and reproducibility of the samples provide valuable information on the variation of the adhesion interphase in terms of components and contents with cure level of composites.

The present study concerns the effect of cure condition, especially cure levels such as under-cure, optimum-cure, and over-cure, on the adhesion between rubber compound and brass-plated steel cord. Cure temperature and time were adjusted to obtain various cure levels of composites. Adhesion property of embedded cords in rubber compound was discussed relating to the deduced adhesion interphase from AES analysis on filter-paper-inserted adhesion samples.

EXPERIMENTAL

Preparation of Rubber Compound

A rubber compound with the basic formulation written below was prepared.
Masterbatch components are as follows:

- natural rubber (Lee Rubber Co., SMR 20, Malaysia) 100 phr,
- carbon black N351 (Lucky Co., South Korea) 55 phr,
- aromatic processing oil (Michang Co., A#2, South Korea) 5 phr,
- zinc oxide (Hanil Co., South Korea) 10 phr,
- antioxidant (Monsanto Co., Kumanox-13, N-(1,3-dimethylbutyl), N-phenyl-p-phenylenediamine, USA) 1 phr,
- Co salt (Taekwang Chem. Co., Co-stearate, 10wt% Co, South Korea) 1 phr
- resorcinol formaldehyde resin (Indspec Co., Penacolite B-18-S, USA) 3 phr

Final mixing components are as follows:.

- masterbatched rubber compound
- stearic acid (Pyungwha Co., South Korea) 1 phr,
- methylene donor (Cytec Co., Cyrez, hexamethoxymethylmelamine, USA) 3 phr
- accelerator (Monsanto Co., Santocure MOR, 2-(morpholinothio) benzothiazole sulfenamide, USA) 0.6 phr.
- insoluble sulfur (Akzo Co., Crystex HS OT 20, The Netherlands) 5.0 phr, .

The rubber compound was mixed following the procedures described in ASTM D3184-80. Mixing was carried out in two stages using an internal mixer (Farrel Co., Banbury Mixer model 82) with the capacity of 1.2 kg batch weight. All the masterbatch components were mixed for 10 min at a rotor speed of 40 rpm and discharged at 150 ^{o}C. After the masterbatched compound was cooled to room temperature, the final mixing components were added. Then the final mixing compound were mixed for 5 min at a rotor speed of 30 rpm and dumped at 90 ^{o}C. The final mixed rubber compound was rolled into a sheet on a two roll open mill (Farrel Co., model MKIII).

Measurement of Cure Rate and Physical Properties

Rheocurves of the prepared rubber compound were recorded using a Monsanto Rheometer (model Rheo-100) in the range of temperature from 130 ^{o}C to 170 ^{o}C with an interval of 20 ^{o}C following the procedure described in ASTM D-2084. A Shore A durometer was employed to measure hardness of vulcanizates described in ASTM D-2240. Tensile properties of vulcanizates were determined from stress-strain curves recorded according to ASTM D-412 using a tensile tester (Instron model 6021).

Adhesion Test and Adhesion-Interphase Analysis

Five T-test adhesion samples, with different cure levels composed of brass-plated steel cord (3 x 0.30) and the rubber compound, were prepared by changing temperature and time for the cure of these composites. The plating weight of brass on the brass-plated steel cord manufactured by the Kiswire Co. Korea, was 3.6 g/kg and the copper content of the brass was 63.6%. According to the procedure described in ASTM D-2229, the adhesion samples were cured using a cure press (Osaka Jack Co. Ltd) under the pressure of 2.4 MPa. Under-cure adhesion samples were cured at 130 ^{o}C for 20 min and at 150 ^{o}C for 5 min. Optimum-cure adhesion samples were obtained with curing at 150 ^{o}C for 20 min. In addition, cure conditions such as 150 ^{o}C and 80 min and 170 ^{o}C and 20 min were employed for the preparation of over-cure adhesion samples. Cure times were selected based on t_{90} time at 150 ^{o}C: 20% of t_{90} time for under-cure, 100% for the optimum-cure, and 400% for the over-cure. In order to investigate the effect of humidity aging on the adhesion, the cured samples were placed in a humid chamber adjusted at 85 ^{o}C and 85% relative humidity for 15 days.

Pullout force was determined as the maximum force exerted by the tensile tester on a T-test sample during the pullout test with 10 mm/min crosshead speed. Rubber coverage defined as a percentage of the surface covered by rubber, were also measured with an interval of 5% by naked eyes. Each value reported was an average of six samples.

Cord samples for the investigation of the adhesion interphase were prepared by inserting a filter paper (pore size 5 μm, catalog No. 142 50, Millipore Co., USA) between the rubber compound and the brass-plated steel cords described in our previous paper [4]. Cure and humidity aging conditions of the samples for the adhesion interphase were the same with those in the preparation of the T-test adhesion samples for the pullout test. By only removing the rubber block adhered on filter paper from the cord, the cured samples reacted with rubber compounds were obtained.

The depth profiles from the adhesion interphase to bulk brass were recorded on a Perkin-Elmer Auger spectrometer (Phi 670). A 10 x 10 μm^2 area of the surface was examined with 5.0 keV of *Ep*, 0.03 μA of *Ip*, and an incident angle of 30^o to the specimen. Compositions of exposed surface were measured at every 0.5 min. Data were collected in dE N(E)/dE mode using a lock-in amplifier with a 20 ms time constant and an analyzer modulation of 6 eV peak-to-peak. For the depth profiling, a sputter gun with an argon ion beam rastered at 2 x 2 mm^2 was used. The sputtering rate for the brass film was determined to be 25 nm/min. The determination of the sputtering rate for the adhesion interphase, however, was difficult because it included various chemical components with variable concentrations. Therefore, sputtering time instead of absolute depth was used in this paper for indicating the depth of the adhesion interphase.

RESULTS AND DISCUSSION

Variation of adhesion with cure level

The adhesion samples with different cure levels showed different adhesion properties as shown in Table 1. Pullout forces of the optimum-cured adhesion samples, either unaged or humidity aged, are higher than those of under-cured and over-cured adhesion samples. The rubber coverages of unaged, under-cured adhesion samples are lower at 55% and 60%, but those of over-cured adhesion samples are higher at 90%. Both pullout force and rubber coverage for under-cured adhesion samples increase with humidity aging. On the other hand, rubber coverages of over-cured adhesion samples keep constant, while pullout forces of them decrease with humidity aging. The cure temperature and time for the optimum cure of the rubber-steel cord composite was set to achieve 90% cure of the rubber compound. This condition considers only the cross-linking density of the rubber compound not the state of adhesion interphase. The fact that the adhesion properties of the composites was obtained from the optimum-cured adhesion sample, showed the importance of physical property of rubber compound for the adhesion property of composites. Since weak rubber easily departs from the adhesion interphase at pullout test, under-cured adhesion samples with low modulus exhibited low coverage as well as low pullout force. Over-cured adhesion samples also showed lower adhesion properties than the optimum-cured adhesion sample did. Deterioration of rubber properties caused by the the reversion of cured rubber due to higher temperature or long-time cure made a significant decrease in the adhesion properties.

Characterization of Adhesion Interphase

Adhesion interphase between rubber compound and brass-plated steel cord is generally composed of sulfides and oxides of copper and zinc. The depth profiles of copper, zinc, sulfur, oxygen, carbon, and iron obtained from the samples which were prepared using a filter paper for analysis of adhesion interphase were measured. Depth profiles were calculated from AES spectra recorded with sputtering from the brass surface to the steel core. The coincidence in profiles of different species suggests the formation of such compounds. Since the inserted filter paper prevents a direct contact of rubber with the brass surface, obtained depth profiles reveals only the reactions between migrating chemicals from the rubber compound and the brass surface. The loss of the components of the adhesion interphase is also inevitable because of rubber exclusion.

The outer surface of the brass was contaminated with carbon, but carbon peak was rapidly diminished with sputtering. Copper sulfides and zinc oxides - main components of the adhesion interphase - located beneath carbon layer. Copper and zinc were still remained after 5 min sputtering even though sulfur and oxygen were negligible, indicating the presence of non-reacted brass. Iron content gradually increases from the brass surface, supposing of an unevenness of steel cord surface.

Although the adhesion interphase formed between rubber compound and brass-plated steel cord show similar depth profiles of sulfides, oxides and non-reacted brass, their distribution pattern and content at the interphase are considerably different according to cure condition. Tthe depth profiles of copper, sulfur, zinc, and oxygen at the brass surface of adhesion samples which were prepared by inserting filter papers and cured at different temperatures were measured. The large difference in the contents of copper and sulfur indicates that only a small part of copper forms copper sulfide. On the contrary, a small difference in the contents of zinc and oxygen supposes that the most of zinc converts to zinc oxide or zinc hydroxide.

The cure temperature altered depth profiles of four elements. Although the formation of copper sulfide and zinc oxide were coincident regardless of cure temperature, the depth profiles were complex just not to be able to explain by the further formation of sulfide and oxide with rising temperature. At 130 ^oC cure, the structure of adhesion interphase was very simple composing of small amounts of copper sulfide and zinc oxide. Non-reacted brass was remained beneath these materials. On the other hand, oxygen content exceeds zinc content from the depth profiles of adhesion samples cured at 150 °C, indicating a formation of copper oxide. The disappearance of the first peak of copper at the outer surface and the shift of the maximum position of zinc to the surface indicate the loss of weak layer formed at the interphase. However, the depth profiles obtained from the adhesion sample cured at 170 °C are considerably different. A large, broad sulfur peak at the outer surface and disagreement in the zinc and oxygen profiles suggests the formation of zinc sulfide. Rapid formation of zinc sulfide at elevated temperature suppresses the formation of copper sulfide and zinc oxide [3].

The variation of depth profiles with cure temperature can be summarized like below: 1) the formation of the adhesion interphase is not sufficient at low cure temperature, 2) at moderate cure temperature copper sulfide and oxide are simultaneously formed and some of them are removed at departing step, and 3) the formation of zinc sulfide as well as copper sulfide is clear at 170 °C.

Cure time also affects on the formation of the adhesion interphase. The depth profiles at the adhesion interphase of adhesion samples cured at 150 °C for different cure times were also measured. Formation of copper sulfide was not evident for 4 min cure, while that of zinc oxide was clear at the outer surface. Too short cure time brought about insufficient formation adhesion interphase. As mentioned before, the depth profiles for the optimum-cure were explained in terms of the formation of sulfide and oxide of copper and their partial loss. The further increase in cure time continues the formation reaction of sulfides and oxides of copper and zinc and oxide at the interphase. Since mechanical strength of these materials are weak, especially oxides of zinc and copper, resulting in a partial loss of them at the surface and remaining a small amount of them at the interphase.

CONCLUSION

Cure condition has a large effect on the adhesion between rubber compound and brass-plated steel cords because it affects both the physical property of the rubber compound and the conditions of the adhesion interphase. The adhesion properties of the adhesion samples could be interpreted by the changes in the physical property of rubber compound and the adhesion interphase. The adhesion samples have a stable adhesion interphase formed by curing at 130-170 °C.

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Table 1. Unaged and humidity aged[1)] adhesion properties of adhesion samples varied with cure condition

Classification	Cure condition		Pullout force(N)		Rubber coverage (%)	
	Temp	Time	unaged	humidity-aged[1)]	unaged	humidity-aged
under-cure	130 °C	20 min	215	302	55	90
	150 °C	5 min	246	296	60	90
optimum-cure	150 °C	20 min	470	427	90	90
over-cure	150 °C	80 min	425	389	90	90
	170 °C	20 min	347	350	90	90

[1)] Humidity aging for 15 days at 85 °C and 85% relative humidity.