나노구리 박판의 제조와 AES 깊이별 조성분포 분석을 통한 배합고무와의 접착특성

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Preparation of nano-copper-coated steel plates and characterization of adhesion to rubber compounds by analysis of AES depth profile

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INTRODUCTION

For a stable and long-service tire, unaged adhesion properties of the steel cord to the rubber compound should be excellent and adhesion degradation after aging treatments ought to be delayed as much as possible to maintain the function of reinforcement.   Unfortunately, adhesion degradation is inevitable due to the additional growth of copper sulfide and the loss of metallic zinc in the adhesion interphase, caused by heat generated during tire use, or by contact with moisture in the air[1]. Lowering the amount of brass plating on the steel cord and reducing the copper content in the brass made remarkable improvement in adhesion stability.   This was due to the suppression of an additional growth of copper sulfide and the dezincification of the adhesion layer.

Seo *et al.* [2] manufactured thin Cu/Zn film-coated steel cords (not brass-coated steel cords) as new material and plates with 30-90 nm of copper thickness.   Copper was deposited on the uniform surface of a zinc-plated steel filament or plate by the substitution plating method.   The adhesion properties of the Cu/Zn film-coated steel cords and its plates were depended considerably on the amount of both copper and zinc plating.   The Cu/Zn film-coated steel cord, with a thin copper film of 30 nm on average, exhibited similar adhesion strength to the rubber compound compared to brass-plated steel cords, which are currently used in tires[3].   Furthermore, the Cu/Zn film-coated steel cords showed excellent adhesion stability against aging treatments.   The suppression of the excessive growth of copper sulfide on the Cu/Zn film-coated steel cords, due to the limitation of the amount of copper plating, resulted in a good stability against aging treatment.

The uniform surface of iron is absolute prerequisite of coating of copper on it. In general, iron surface is very rough. Therefore, the process is needed to smooth the iron surface. In this Cu/Zn film-coated steel cord, zinc as soft metal plays a role of smoothing iron with rough surface. But the zinc plating in Cu/Zn film-coated steel cord has the several problems on the application of reinforcing materials to rubber compounds. Among the problems, the exposed zinc on thin Cu/Zn film-coated steel cord is very easy to oxidize as zinc oxide which is very harmful to adhesion retention under hostile aging conditions.

The plate is more appropriate than the cord, concerning the analysis of surface and adhesion interphase. Therefore, our group has developed nano-copper-coated steel plate prior to application of nano-copper-plated steel cord. In this study, we manufactured three kind of nano-copper-coated steel plates with copper thickness from 29 nm to 56 nm by RF sputtering technique. Also, brass plate was used to compare the adhesion property to rubber compound with that of nano-copper-coated steel plates. We prepared the copper nano-copper-coated steel plates with different thicknesses of copper in order to investigate adhesion property to rubber compound and the structure   of the adhesion interphase. The adhesion properties between rubber compounds and nano-copper-coated steel plates and structure of the adhesion interphases remaining on the nano-copper-coated steel plates were studied to illustrate the potential for the application of nano-copper-film as a coating material of the steel plate with respect to the extent of cure.

EXPERIMENTAL

The surface of an iron plate (purity : 99.9%) with 100 mm long, 70 mm wide and 0.4 mm thick (Jungdo Testing Co., Korea) was smoothed with 4000 mesh sandpaper and cleaned by dipping it into acetone to remove grease and other contaminants.   The oxide layer of the iron plate was removed by treating it with 5% sulfuric acid for 60 s. The nano-copper-film was sputtered onto iron plate treated above mentioned using CVD reactor in the sputter system (PECVD & Sputter Sys., Sam-Han Vacuum Development Co., Korea) for constant time at 10^{-4} - 10^{-5} Torr under argon plasma.   The CVD power was controlled to 50 W. After the iron plate had been put into the CVD rector, the vacuum pretreatment of it was done for 5 min at the 5×10^{-5} Torr in order to remove the surface contaminants on iron plate.   After the vacuum pretreatment of it had been done, the argon plasma was generated under the argon flow of 25 cm^3/min and at the power of 50 W.   The thickness of the nano-copper-film on iron plate was controlled by changing the sputter time for 5, 8 and 10 min respectively.   The average thickness of the nano-copper-film on iron plate was determined by Ar$^+$ sputtering of Auger electron spectroscopy. The thicknesses of the nano-copper-film were 29, 41 and 56 nm respectively. The nano-copper-coated plate was named Cu( ) plate, with the thickness in nm being the number in parentheses.   Brass plate (Ohio Gasket & Shim Co., U.S.A.) with a composition of 70 wt% of Cu was used for comparison with nano-copper-coated steel plates.

A rubber compound was prepared.   The formulation of the rubber compound is tabulated in Table 1. Adhesion properties were evaluated through a peel-out test.   The nano-copper-coated steel plates or brass plate was sandwiched with 2 mm thick rubber pads, and they were cured at 160 ^{o}C and 13 MPa on a cure press.   Curing was maintained for 3 min longer than t_{90} time to compensate for heat transfer. For optimum cure, adhesion samples were cured for 15 min, which is 3 min longer than t_{90} time to compensate for heat transfer. For over cure, adhesion specimens were also prepared by curing for 51 min, which is 3 min longer than four times of t_{90} time to compensate for heat transfer.

Peel-out force was determined as the maximum force exerted by the tensile tester on a peel-test adhesion specimen with 20 mm length and 100 mm length while peeling out at 50 mm · min^{-1} of crosshead speed.   The rubber coverages, which were the relative extent of rubber covered on the surface of the plate peeled out, were determined by the naked eye.   Each value reported was the average derived from five specimens. The surface morphology of peeled nano-copper-coated steel plate after measuring adhesion force was investigated using image analyzer (Matrox Co., U.S.A.).

Filter paper with a pore of 5.0 μm (Millipore Co., U.S.A.) was placed at the interface between a rubber pad of 2 mm and the nano-copper-coated steel plates or brass plate.   Adhesion specimens were cured at 160 ^{o}C for 15 min (optimum cure) and 51 min (over cure), respectively.   Sulfur from the rubber compound migrated through the pores of the filter paper and reacted with the copper of the nano-copper-coated steel plates or the brass plate, forming an adhesion interphase.   After removing the rubber and filter paper from the metal plate, the adhesion interphase, mainly copper sulfide, remained on the metal plate.   The depth profiles from the outer surface to the bulk plate were recorded on a Perkin-Elmer Auger spectrometer (model Phi 670, Perkin-Elmer Co., U.S.A.).   A surface of 10 $\times$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 of 60 ^{o} to the specimen, the same conditions described in a previously published paper.   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 on a 2 $\times$2 mm^2 area for depth profiling.   The sputtering rate was determined to be 4.5 nm·min^{-1} using tantalum pentoxide plate as reference material.

RESULTS AND DISCUSSION

When copper is coated onto the surface of iron plates using RF sputtering method, copper is deposited on the plate surface as a metallic surface.   The thicknesses of the copper plating with RF coating time were deduced from AES depth profiles.   Copper was deposited at the outer surface with oxygen and carbon on the Cu(29) plate, and the deposited amount of copper formed a definite layer of copper on the Cu(29) plate. This supports the homogeneous plating of copper in spite of very thin

plating of copper using RF sputtering. At the Cu(41) and Cu(56) plates, the amount of copper deposited increased, forming a copper predominant layer, while carbon and oxygen were also detected simultaneously at the outer surface. The outer oxygen on nano-copper-coated steel plate may be resulted from the oxidation of copper plating. As the oxygen detected from outer surface to sputter time of 2 min, copper oxide formed with 9 nm on copper metal in nano-copper-coated steel plate. However, it is obvious that the copper coating does not make any alloy with iron. With increasing sputter time, carbon concentration decreased exponentially and detected a small concentration of trace level from 2 min of sputter time. Detected carbon at outer surface may be resulted from the surface contamination on nano-copper-coated steel plate. Oxygen concentration also decreased exponentially with sputter time from outer surface. But oxygen peak detected at boundary between surface of beginning plated copper and surface of iron substrate. This may be explained by insufficient grinding of iron oxide layer on iron plate prior to the plating of copper on iron substrate. Regardless of thickness of copper plating, the shape and size of oxygen peak at boundary between copper and iron did not show a significant difference.

The adhesion specimens of nano-copper-coated steel plate to rubber compound were cured at optimum cure and over cure conditions in order to investigate the effect of cure time on the adhesion of the nano-copper-coated steel plates.   As shown in Table 2, peel-out forces of the nano-copper-coated steel plates to rubber compound were significantly different with respect to the thickness of copper plating and cure condition.   For both optimum and over cure, brass plates showed lower peel-out force than the nano-copper-coated steel plates. For the optimum cure, peel-out force increased with increasing the thickness of copper plating, especially in Cu(56) plate. SEM micrographs of the nano-copper-coated steel plates peeled out from the rubber showed that a little rubber was attached to the (29) plate and the brass plate, whereas significant rubber attached to the Cu(56) plate.

Unlikely the case of optimum cure, peel-out force for over cure decreased with increasing the thickness of copper plating. The peeling force of nano-copper-coated steel plates to rubber compound increased with increasing cure time. For further increase of increasing cure time over optimum, peel-out force of nano-copper-coated steel plates to rubber compound increased especially in Cu(29) plate compared to that in optimum cure. The peel-out force of brass plate in over cure decreased to a half of that in optimum cure. This forecasts the excellent adhesion endurance of nano-copper-coated steel plate over brass plate.

Among the nano-copper-coated steel plates, the Cu(29) plate which had the smallest amount of copper plating showed superior adhesion properties.   Since a sufficient formation of copper sulfide with a large contact area is essential for good adhesion, the nano-copper-coated steel plates with a small amount of copper coating as many as 29 nm of Cu thickness may prevail.   On the other hand, the large amount of copper coating brings about cohesive failure due to excessive growth of copper sulfide.   Therefore, the lowest amount of copper coating is recommended for good adhesion preventing excessive growth of copper sulfide, but minimum loading is essential in order to form a sufficient thickness of the copper sulfide layer.

For over cure, the thin Cu plating in nano-copper-coated steel plate showed good adhesion. The adhesion interphses formed at over cure are very different from those at optimum cure. The sufficient copper sulfide at adhesion interphase appeared in the Cu(29) plate at over cure. With increasing the thickness of Cu plating in nano-copper-coated steel plates at over cure, the excess copper sulfide formed. This led to poor adhesion property. This phenomenon is explained that copper sulfide formation at adhesion interphase formation is dominant at over cure.

CONCLUSIONS

The adhesion property of nano-copper-coated steel plates to the rubber compound largely depended on the cure condition and the thickness of Cu plating. At optimum cure, the nano-copper-coated steel plate with thick copper coating (56 nm) showed better adhesion to rubber compound than that having thin copper coating.   But the nano-copper-coated steel plate with thin copper coating (29 nm) showed better adhesion to rubber compound than that having thick copper coating at over cure.

These phenomena may be explained as the reaction rates of copper sulfide formation and surface migration of iron over copper at adhesion interphase under the cure of rubber compound to nano-copper-coated steel plate. At optimum cure, surface migration of iron over copper at adhesion interphase is dominant whereas copper sulfide formation at adhesion interphase formation is dominant at over cure. This fact was confirmed by the depth profile of adhesion interphases using Ar^+ sputtering of Auger electron spectroscopy.

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Table 1.
Composition of rubber compounds prepared

Material	Trade name	Manufacturer	Content (phr)
Masterbatch			
natural rubber	SMR-20	Lee Rubber Co., Malaysia	100
carbon black	N330	Lucky Co., Korea	60
processing oil	A#2	Michang Co., Korea	3.5
activator	ZnO	Hanil Co., Korea	8
antioxidant	Kumanox-13	Monsanto Co., U.S.A.	1
adhesion promoter	B-18S	Indspec Co., U.S.A.	2
adhesion promoter	Manobond-680C	Rhone Poulenc Co., France	0.5
Final Mixing			
activator	Stearic acid	Pyungwha Co., Korea	1.5
accelerator	DCBS	Monsanto Co., U.S.A.	0.7
sulfur	Crystex HS 20	Akzo Co., The Netherlands	5
adhesion promoter	Cyrez-964	Cytec Co., U.S.A.	3

Table 2.
The adhesion properties of adhesion samples for both optimum and over cured with respect to the thickness of Cu plating in nano-copper-coated steel plates to rubber compound

Cu plate	Peel-out force (N)	
	Optimum cure	Over cure
Cu(29) plate	128	339
Cu(41) plate	130	237
Cu(56) plate	188	217
brass plate	112	65