



## High-resolution photoelectron spectroscopy study of degradation of rubber-to-brass adhesion by thermal aging

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### ABSTRACT

High resolution photoelectron spectroscopy is utilized to investigate degradation of rubber-to-brass adhesion by thermal aging. Special attention is given to the role of water in the environment surrounding brass-embedded rubber so that three aging processes are employed; hydrothermal aging, moist-heat aging and dry-heat aging. All aging processes lead to the decrease in the amount of S at the rubber/brass interface. This desulfurization accompanies the decrease in the ratio of  $\text{Cu}_x\text{S}$  ( $x \approx 2$ ) to CuS, i.e.,  $\text{Cu}_x\text{S}/\text{CuS}$ , and the increase in the amount of ZnO,  $\text{Zn}(\text{OH})_2$  and ZnS, all of which are key factors for degradation of adhesion. The changes in the chemical composition are enhanced by water in the surrounding environment during the aging treatments, indicating that the water molecules accelerate degradation of rubber-to-brass adhesion.

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### 1. Introduction

Steel-cord-reinforced rubber tires are nowadays a standard type of automotive tires. Strong adhesion between rubber and steel cords is requisite for good performance of tires as well as a prolonged lifetime. To realize strong rubber-to-cord adhesion, the brass-plated steel cords are employed. It has long been recognized that a copper-sulfide layer is formed at the rubber/brass interface, and this interface layer is crucial to realize strong rubber-to-brass adhesion [1–4]. Adhesive properties can be controlled by the vulcanization temperature and time, with a typical condition of 150–180 °C for ~10 min to obtain good adhesion [5,6]. The copper-sulfide layer is mainly composed of CuS and  $\text{Cu}_x\text{S}$  with  $x \approx 2$  [7,8], and Ozawa et al. have revealed in a recent high-resolution photoelectron spectroscopy (PES) study [8] that there is a concentration gradation of both  $\text{Cu}_x\text{S}$  ( $x \approx 2$ ) and CuS; although CuS is more favored than  $\text{Cu}_x\text{S}$  throughout the entire layer, the concentration of  $\text{Cu}_x\text{S}$  is higher at the rubber side than at the brass side. Since there is a correlation between the concentration of  $\text{Cu}_x\text{S}$  ( $x \approx 2$ ) and the

adhesion strength,  $\text{Cu}_x\text{S}$  rather than CuS is crucial to realize strong interaction between rubber and brass [1,8].

Long-term usage of the automotive tires induces the loss of the rubber-to-cord adhesion strength. This has been confirmed by accelerated aging tests such as thermal aging and steam aging [2,5,6,9]. One of the proposed degradation mechanisms is the overgrowth of the copper-sulfide layer beyond the optimum thickness [2,9]. The overgrowth may accompany the transformation of amorphous  $\text{Cu}_x\text{S}$  ( $x \approx 2$ ) to crystalline one [4], which is brittle and can be easily cleaved, so that the mechanical strength of the adhesive interlayer should be lowered. Accumulation of Zn in the form of ZnO,  $\text{Zn}(\text{OH})_2$  and ZnS at the rubber/brass interface is another factor of degradation, because these species bear poor bonding with rubber compounds [1,3,9]. The role of iron, which is migrated from steel beneath the brass coating, is also suggested by Patil and van Ooij [10]. Despite the extensive studies, it is still not clear how the chemical composition at the rubber/brass interface is altered during tire aging. The knowledge of the compositional change is important for the development of long-lived tires.

In the present study, we have performed chemical-state analysis of the rubber/brass interface by high-resolution PES to examine the change in the chemical composition induced by three different thermal aging processes, i.e., dry-heat aging, moist-heat aging and hydrothermal aging. It is found that thermal aging induces the loss

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of the copper-sulfide species, especially  $\text{Cu}_x\text{S}$  ( $x \approx 2$ ) and the accumulation of  $\text{ZnO}/\text{Zn}(\text{OH})_2$  and  $\text{ZnS}$  at the interface. Water in the surrounding environment during aging promotes these changes in the chemical composition and thus adhesive degradation.

## 2. Experimental

Brass plates ( $5 \times 5 \times 0.5 \text{ mm}^3$ ) with a bulk composition of 65 wt% Cu and 35 wt% Zn ( $\text{Cu}_{66}\text{Zn}_{34}$ ; Nilaco Co.) were used as a model sample for a brass-plated steel cord. The sample preparation was the same as that employed in our previous study [8]. Briefly, the brass plates were sandwiched by filter papers and embedded into uncured pads of rubber compounds. Brass-embedded rubber was subjected to vulcanization at  $170^\circ\text{C}$  for 10 min under the pressure of 2 MPa. The advantage of the so-called “filter paper method” employed in this study is that chemical reactions equivalent to those at the rubber/brass interface take place on the brass surface while avoiding strong rubber-to-brass adhesion [7,8]. We also discussed possible drawbacks of this method in our previous paper [8]. The formulation of rubber compounds was as follows; natural rubber (100 phr; parts per hundred rubber), carbon black (60 phr), squalene (10 phr), zinc oxide (10 phr), sulfur (8 phr), cobalt stearate (2 phr), an antioxidant (1 phr) and a curing accelerator (0.5 phr). For details, see Ref. [8].

After vulcanization, thermal aging was conducted at  $70^\circ\text{C}$  in three different environmental conditions; one in dry air (dry-heat aging), one in moist air with relative humidity of 96% (moist-heat aging), and one in hot water (hydrothermal aging). The duration of aging was 1 week and 2 weeks. We also prepared unaged samples for comparison.

After the aging treatments, the brass plates were taken out from rubber, placed on sample holders and inserted into the ultrahigh vacuum chambers for the PES measurements. Both synchrotron radiation and laboratory X-ray source were used for the measurements. The synchrotron-radiation PES (SR-PES) measurements were conducted at beam lines (BL) 13A of the Photon Factory, High Energy Accelerator Research Organization (KEK) [11] and BL27SU of SPring-8 [12]. A Gamma Data/Scienta SES200 electron-energy analyzer was used for acquisition of the SR-PES spectra at BL-13A. Typical overall energy resolution was 140 and 250 meV at the photon energies ( $h\nu$ ) of 260 and 1060 eV, respectively. At BL27SU, the SPECS PHOIBOS 150 analyzer was used. The energy resolution was 300 and 350 meV at  $h\nu=260$  and 1250 eV, respectively. For both systems, the samples were placed so that the sample normal direction was parallel to the lens axes of the analyzers. For the x-ray PES (XPS) measurements, monochromatized Al  $K\alpha$  radiation ( $h\nu=1486.6 \text{ eV}$ ) was used. A PHI 5000 VersaProbe (ULVAC PHI) analyzer was utilized with an energy resolution of 300 meV. The angle between the lens axis and the sample normal direction was  $45^\circ$ . The electron binding energy of the PES spectra was referenced to the Fermi cut-off in the spectra of the metal plates (Au, Cu or Mo), which were electrically in contact with the brass samples.

In order to evaluate the influence of thermal aging on the rubber-to-brass adhesion strength, forces required to pull brass-plated steel cords out of the rubber compounds were measured. The cords were constructed by seven filaments ( $\phi 0.25 \text{ mm}$ ) which were helically stranded (a  $1 \times 6$  structure). The composition of the plated brass film was 63.5 wt% Cu and 36.5 wt% Zn with a mean film thickness of  $0.23 \mu\text{m}$ . The pull-out test was carried out following the standard test method for adhesion between steel tire cords and rubber (ASTM D2229). The steel cords with the embedment length of 12.5 mm were pulled out from rubber, which was cured at  $170^\circ\text{C}$  for 10 min and was subjected to two-week-long thermal aging with the same conditions described above.

**Table 1**

Influence of thermal aging on the force (N) required to pull the brass-plated steel cords out of cured rubber and on the rubber coverage (%) on the cords. The period of aging was 2 weeks.

	Pull-out force (N)	Coverage (%)
Unaged	652	100
Dry-heat aging	566	100
Moist-heat aging	471	75
Hydrothermal aging	350	68

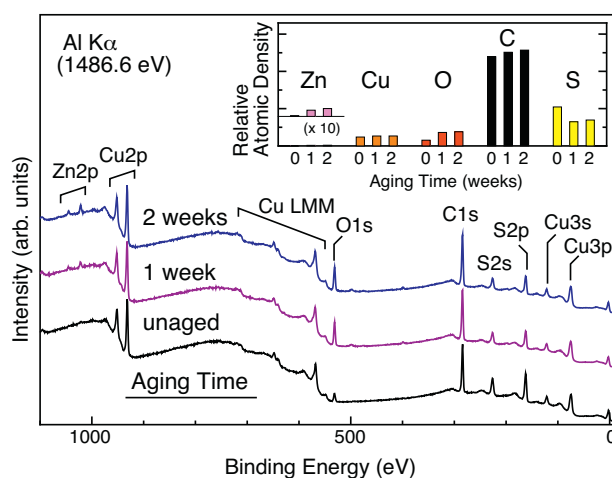
## 3. Results

### 3.1. Pull-out test

Thermal aging is known to reduce the rubber-to-brass adhesion strength. This aging-induced degradation is determined by the pull-out test, in which the forces needed to pull the brass-plated steel cords out of the cured rubber compounds are estimated. The result is shown in Table 1. The pull-out force of the unaged sample is 652 N, and it is reduced to 566, 471 and 350 N after dry-heat, moist-heat and hydrothermal aging for 2 weeks, respectively. The force is diminished as the content of water in the surrounding environment during thermal aging is increased. In Table 1 the coverage of rubber, which remains on the cord surfaces after pulled out, are also shown. The decrease in the coverage with the water content is another indication of degradation of adhesion. The negative influence of humidity on the adhesion strength has already been pointed out by Van Ooij [2], Jeon and Seo [5,6] and Buytaert et al [9]. The result of the pull-out test clearly demonstrates that the water molecules in the surrounding environment accelerate adhesion degradation during thermal aging. On the basis of the PES measurements, we show in the following sections that there is a good correlation between water-stimulated degradation and the chemical composition at the rubber/brass interface.

### 3.2. Hydrothermal aging

Fig. 1 shows XPS spectra of the vulcanized brass surfaces subjected to hydrothermal aging for 0 (unaged), 1 and 2 weeks. Peaks associated with Cu (Cu  $2p_{3/2}$  and  $2p_{1/2}$  at 932 and 952 eV, respectively, Cu LMM at 568 eV, and Cu 3p at 75 eV), C (C 1s at 284 eV), S (S 2s at 226 eV and S 2p at 162 eV) are observed as major peaks on



**Fig. 1.** XPS spectra of the vulcanized brass samples subjected to hydrothermal aging for 0 (unaged), 1 and 2 weeks. The inset shows relative atomic densities of the major elements on the surfaces. The densities are obtained from the integrated intensities of the core-level peaks (Zn 2p, Cu 2p, O 1s, C 1s and S 2p) and their photoionization cross sections [13].

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