



# High-resolution photoelectron spectroscopy analysis of sulfidation of brass at the rubber/brass interface

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## ABSTRACT

High resolution photoelectron spectroscopy is utilized to investigate the chemical composition at the rubber/brass interface to elucidate the origin of strong adhesion as well as the degradation between rubber and brass. Special attention has been given to copper sulfides formed at the interface during the vulcanization reaction at 170 °C. At least five sulfur-containing species are identified in the adhesive interlayer including crystalline CuS and amorphous Cu<sub>x</sub>S ( $x \approx 2$ ). These copper sulfide species are not uniformly distributed within the layer, but there exists the concentration gradation; the concentration of Cu<sub>x</sub>S is high in the region on the rubber side and is diminished in the deeper region, while vice versa for that of CuS. Degradation of the interface adhesive strength by prolonged vulcanization arises from the decrease in the Cu<sub>x</sub>S/CuS ratio accompanying desulfurization of the adhesive layer.

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## 1. Introduction

In automotive tires, steel cords are embedded to give rubber tires a structural strength while maintaining flexibility of rubber. Strong adhesion between rubber and steel cords is crucial for tires to exhibit a good performance for safe controlling of automobiles. The tire manufacturers have employed brass-plated steel cords to realize stiff rubber–cord adhesion. Many studies have been devoted to elucidate the adhesion mechanism between rubber and the steel cords, aging and degradation mechanisms of adhesion, the effect of the compositional change of rubber and the plated brass layer, etc. Good reviews of the studies since 1970s are given in the literatures by van Ooij [1–4].

It has been recognized already in the early 1970s that copper sulfides are formed at the rubber/cord interface and speculated that these species should be responsible for the interface adhesion. The copper sulfides are formed as a result of the interface reaction between sulfur, which is added to rubber, and copper of the plated brass layer during the cure process of tire rubber. van Ooij was first who employed X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition at the rubber/brass interface and confirmed the formation of the copper sulfide, Cu<sub>x</sub>S with

$x = 1.90\text{--}1.97$  [5]. ZnS is also formed at the interface along with Cu<sub>x</sub>S. The author has proposed that the optimum amount of Cu<sub>x</sub>S is important for strong adhesion [5]. A very similar conclusion, i.e. the formation of Cu<sub>x</sub>S and ZnS at the interface, has been drawn from the XPS measurements by Chandra et al. [6] and by Buytaert et al. [7]. Formation of Cu<sub>x</sub>S and ZnS is also confirmed by Auger electron spectroscopy (AES) measurements [7–9]. A commonly accepted view at present is that non-stoichiometric Cu<sub>x</sub>S with  $x = 1.8\text{--}1.97$  is a key adhesive agent to realize a strong rubber-to-brass interface bonding.

On the basis of the thermodynamic consideration of the copper sulfide formation, it is reasonable that Cu<sub>x</sub>S ( $x \approx 2$ ) is more favored than CuS, since the Gibbs value of formation  $\Delta_f G^\circ$  of Cu<sub>2</sub>S (–133 kJ/mol at 170 °C) is larger than that of CuS (–83 kJ/mol) [10,11]. However, Hotaka et al. have identified CuS along with Cu<sub>x</sub>S ( $x \approx 2$ ) at the rubber/brass interface in the XPS measurements [12]. Thus, for understanding the origin of the strong adhesion between rubber and brass, it is crucial to know the formation process of not only Cu<sub>x</sub>S but also CuS and their distribution within the interfacial layer.

The compositional change of the adhesive interlayer should be in close relation with the rubber-to-brass adhesive strength. Therefore, the formation process of the copper sulfides, their distribution within the adhesive interlayer and the influence of the vulcanization time on the chemical composition at the interface should be investigated in more detail. The XPS and AES measurements

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done so far have limited energy resolutions so that a detailed analysis of the chemical composition was impossible. In the present study, therefore, we performed high-energy resolution photoelectron spectroscopy (PES) and investigated the sulfidation process during vulcanization and the chemical composition of the resultant formed adhesive interlayer.

## 2. Experimental

Brass plates (5 mm × 5 mm × 0.5 mm) with a bulk composition of 65 wt% Cu and 35 wt% Zn (Cu<sub>66</sub>Zn<sub>34</sub>; Nilaco Co.) were used as a model sample for a brass-plated steel cord. The surfaces of the brass samples were mechanically polished to mirror finish with alumina paste (0.3 μm). After ultrasonication in acetone, the sample plates were sandwiched by filter papers with thickness of about 0.2 mm [Japanese Industrial Standards (JIS) P 3801 1], embedded into uncured pads of rubber compounds and subjected to vulcanization at 170 °C under the compression of 2 MPa using a home-made thermal-press machine, which consists of heat plates (40 cm × 40 cm) attached to an oil hydraulic press. The brass samples were retrieved from rubber just before the insertion into the ultrahigh vacuum chambers for the PES measurements to avoid oxidation of the brass surfaces. A formulation of the rubber compounds used in the present study is listed in Table 1. Among them, squalene was added to increase fluidity of uncured rubber. Cobalt stearate, N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6PPD) and N,N-dicyclohexyl-2-benzothiazole sulfonamide (DCBS) were, respectively, an adhesion promoter, an antioxidant and a curing accelerator.

One of the difficulties for chemical analysis of the rubber/brass interface by PES is to expose the interface nondestructively. The mechanical cleavage under liquid nitrogen temperature is one of the methods to expose the interface [5]. However, the obtained surfaces are not always the very interface but brittle parts near the interface. Chemical treatments to remove adhered rubber on the brass surface is another option [6]. The drawback of this method is that the chemical agents used to swell and soften rubber could affect the chemical composition of the adhesive interlayer. Therefore, we employed a so-called “filter paper method” [12] as described above. The filter papers block rubber molecules to reach the brass surface so that the direct rubber-to-brass interaction can be avoided. On the other hand, small chemicals such as sulfur and hydrocarbons diffuse through the papers and induce chemical reactions equivalent to the reactions at the rubber/brass interface. Therefore, the surface chemical composition of the brass surface reflects that of the rubber/brass interface even though the brass samples are covered with the filter papers [12].

A possible drawback of the filter paper method is a delay of the onset of the chemical reactions on the brass surface. This is because the reactants from rubber must pass through the paper to reach the brass surface. As we will see below, the vulcanization time less than 2 min is sufficient to convert the brass surface from the ZnO-rich oxidized state to the copper-sulfide-rich sulfidized state. This may suggest a relatively fast transfer of the molecules in the paper so that the delay of the reactions may not be significant. Another

**Table 1**  
Formulation of rubber compounds (phr; parts per hundred rubber).

Natural rubber	100
Carbon black (HAF-LS)	60
Squalene	10
Zinc oxide	10
Sulfur (octasulfur, S <sub>8</sub> )	8
Cobalt stearate	2
N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6PPD)	1
N,N-dicyclohexyl-2-benzothiazole sulfonamide (DCBS)	0.5

drawback one may suppose is that a part of the reaction products on the brass surface is lost by mechanical cleavage by the filter paper so that the obtained results contain some artifacts. However, this possibility could be small because the change in the chemical composition on the brass surface is not random but monotonic with the vulcanization time, as indicated in Section 3. Therefore, the filter paper method is overall an effective way to nondestructively determine the interface chemical states.

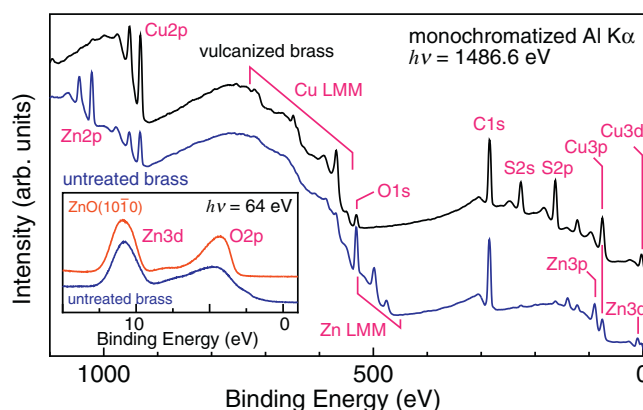
The XPS measurements were performed on PHI 5000 VersaProbe (ULVAC PHI) with monochromatized Al K $\alpha$  radiation (the photon energy  $h\nu = 1486.6$  eV) with a typical energy resolution of 300 meV. The X-ray was incident on the surface from normal direction, and the photoelectrons emitted to 45° were corrected (0° corresponds to the surface normal direction). We also carried out the PES measurements using synchrotron radiation [synchrotron-radiation-excited PES (SR-PES)] at beam lines (BL) 3B and 13A of the Photon Factory, High Energy Accelerator Research organization (KEK). At BL-3B, a VSW HA45 hemispherical electron-energy analyzer was used with the overall energy resolution of 250 meV at 64 eV. At BL-13A, an SES200 (VG Scienta) analyzer was used with the energy resolution of 100–200 meV depending on the photon energy. For both systems, photoelectrons emitted to the surface normal direction were corrected. All XPS and SR-PES measurements were done at room temperature. The photoelectron kinetic energy was calibrated by the Cu LMM Auger peak of the contaminant-free polycrystalline Cu to coincide with the literature value (918.6 eV) [13]. The electron binding energy of the spectra was referenced to the Fermi cut-off in the spectra of Mo sample clips or of Cu sample holders.

We also carried out the X-ray diffraction (XRD) measurements to access the reaction products and their crystallinity on the brass surfaces. For the measurements, an X-ray diffractometer (Bruker D8 Advance) was used with Cu K $\alpha$  radiation.

## 3. Results

### 3.1. Influence of vulcanization

Fig. 1 shows XPS spectra of the brass surface before and after vulcanization. Apart from the C 1s peak from carbon contaminants and the O 1s peak from oxides on the surface, the spectrum of the brass surface before vulcanization gives the peaks from both Cu and Zn. The peak intensities of the Zn-related peaks (Zn 3d, 3p and 2p peaks and LMM Auger peaks) are larger than the Cu-related peaks (Cu 3d, 2p, 2p and LMM) on the untreated brass surface. This indicates that the Zn atoms are accumulated on the surface. From the



**Fig. 1.** XPS spectra of air-oxidized brass (bottom) and the brass sample after vulcanization for 10 min (top). In the inset, valence-band SR-PES spectra of air-oxidized brass (bottom) and single-crystal ZnO (top) are compared.

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