

## Origin of Strong Adhesion Between Rubber and Brass

K. Ozawa<sup>1,\*</sup>, T. Kakubo<sup>2</sup>, K. Shimizu<sup>2</sup>, N. Amino<sup>2</sup>, K. Mase<sup>3</sup>, and T. Komatsu<sup>1</sup>

<sup>1</sup>Tokyo Institute of Technology, Tokyo 152-8551, Japan

<sup>2</sup>The Yokohama Rubber Co., Ltd., Hiratsuka 254-8601, Japan

<sup>3</sup>Institute of Materials Structure Science, Tsukuba 305-0801, Japan

### 1 Introduction

Steel-cord reinforced rubber products are used as automotive tires, conveyor belts, etc. In these products, steel cords are embedded to give rubber a structural strength while maintaining flexibility. Strong adhesion between rubber and the steel cords is crucial for a good performance of these rubber products. In automotive tires, brass-plated steel cords are exclusively used to realize stiff rubber-cord adhesion. It has already been recognized in the early 1970's that copper sulfides are formed at the rubber-brass interface and speculated that these sulfides should be responsible for the interface adhesion [1,2]. However, details of chemical composition of copper sulfides and its formation process have not been understood yet. One of the reason is that, because of strong adhesion between rubber and brass, it is difficult to expose the interface nondestructively for chemical analysis by means of electron spectroscopy. In the present study, high-resolution photoelectron spectroscopy (PES) is utilized to investigate the chemical composition at the rubber-brass interface to elucidate the origin of strong adhesion and the degradation between rubber and brass.

### 2 Experiment

The PES measurements were done at beamlines 3B and 13A. As a model sample of brass-plated steel cords, we employed brass plates ( $5 \times 5 \times 0.5 \text{ mm}^3$ ,  $\text{Cu}_{66}\text{Zn}_{34}$ ), which were sandwiched by filtered papers, embedded in uncured pads of rubber compounds. The sample-containing rubber was vulcanized at  $170^\circ\text{C}$ . The sample plates were retrieved from rubber and subjected to the PES measurements.

### 3 Results and Discussion

In the present study, special attention has been given to copper sulfides formed on the brass surface. Fig. 1 shows the S 2p spectra of the brass samples subjected to different vulcanization time from 2 to 50 min. The photon energy of 260 eV was used so that the sampling depth was at least 0.4-to-0.55 nm. By analyzing the S 2p core-level spectra, at least five sulfur-containing species are resolved at the interface. Among them, crystalline CuS and amorphous  $\text{Cu}_2\text{S}$  are identified as copper sulfide species. These species are not uniformly distributed within the layer, but there exists the concentration gradation; the concentration of  $\text{Cu}_2\text{S}$  is high in the shallow region from the surface and is diminished in the deeper region, while vice versa for that of CuS.

The relative intensities of  $\text{Cu}_2\text{S}$  and CuS to the total S 2p peak intensity are monotonically decreased from 2 min to 50 min. This indicates that a large amount of copper sulfides is formed within 2 min, and that prolonged vulcanization leads to decomposition of these species. The decomposition rate is faster for  $\text{Cu}_2\text{S}$  than CuS so that the  $\text{Cu}_2\text{S}/\text{CuS}$  ratio of 0.52 at 2 min is diminished to 0.25 at 40 min (Fig. 2).

It is empirically known that a longer vulcanization time results in degradation of rubber-brass adhesion. Therefore, the present results imply that  $\text{Cu}_2\text{S}$  is more crucial than CuS to realize strong rubber-to-brass interaction.

### References

- [1] W.J. Ooij, Rubber Chem. Technol. **52** (1979) 605.  
[2] W.J. Ooij, Rubber Chem. Technol. **57** (1984) 421.

\* ozawa.k.ab@m.titech.ac.jp

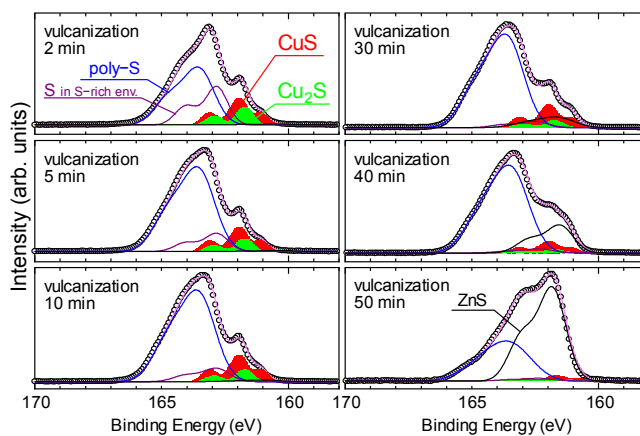


Fig. 1 S 2p spectra from the brass surfaces at various vulcanization time.

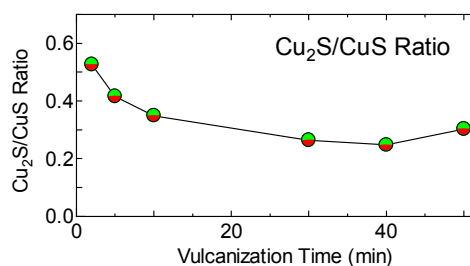


Fig. 2 Change in the  $\text{Cu}_2\text{S}/\text{CuS}$  ratio (the S 2p peak intensity ratio) as a function of the vulcanization time.