Chemistry

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Surface Chemical Composition of Polycrystalline Brass (Cu-35wt%Zn) in Vulcanized Rubber: Effect of Cobalt Additive

Kenichi OZAWA*, [1], Takashi KAKUBO[2], Naoya AMINO[2], Kazuhiko MASE[3]
[1]Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan
[2]The Yokohama Rubber Co., Ltd., Hiratsuka, Kanagawa 254-8601, Japan
[3]Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-08-1, Japan

Introduction

Automotive tires are fabricated by the rubber within which steel cords are embedded to reinforce the structural strength and to elongate their lifetime. Stiff adhesion between the steel cords and the rubber is essential. Using the brass-plated steel cords, enhanced adhesion is achieved by the chemical bonds between the rubber molecules and the S atoms of copper sulfide formed at the rubber-brass interface. However, the adhesion strength is decreased after the long usage of the tire. Although the overgrowth of the copper-sulfide layer is proposed to be one of the reasons for this deterioration, details on the mechanism has not been fully understood. In the present study, we examined the surface chemical composition of polycrystalline brass embedded in the vulcanized rubber by photoelectron spectroscopy (PES) and examined the effect of organic acid cobalt on the brass surface.

Experimental

The PES measurements were carried out at beam line 13A of the Photon Factory. Polycrystalline brass plates with bulk composition of $Cu_{66}Zn_{34}$ (Cu-35wt%Zn) was purchased from Nilaco Corp. The brass plates were wrapped by filter papers and embedded in the rubber, which was subjected to vulcanization at 170°C for 10 min. The rubbers with different contents of organic acid cobalt [0, 2, 20, and 40 parts per hundred rubber (phr)] were used. The filter paper only blocks the polymerized rubber, while short-length rubber fragments, sulphur (octasulfer S_8), organic acid cobalt, carbon and other additives can pass through the paper to reach the brass surface and induce surface chemical reactions. Thus, the model system should reproduce the chemical reactions at the true rubber-brass interface. After vulcanization, the brass plates were retrieved from the rubber and inserted in the UHV chamber to examine the surface electronic structure.

Results and Discussion

Photoemission measurements reveal that the major element on the brass surface is C, which is associated with the rubber molecule and/or carbon additive. The second major element is S. Cu and Zn, constituents of the brass substrate, are only minor species. Fig. 1a shows that the amounts of the surface elements depend on the amount of organic acid cobalt added in the rubber. Cobalt ions is known to acts as a promoter for the vulcanization reaction so that isolated S, probably in the form of S_8, is diminished in the rubber at the high Co contents. Thus, the smaller amount of S at high Co than at low Co results from the less transferred S from the rubber to the brass surface and should suppress sulfurization of Cu on the brass surface. This is why both S and Cu concentrations are decreased with the Co contents.

Fig. 1b shows the S 2p spectra. Each spectrum is composed of four components; polymerized S (S_n), isolated S, and copper sulfides of Cu_2S and CuS. The amount of CuS surpasses that of Cu_2S in the subsurface, while Cu_2S is dominant over CuS in the surface region. The copper sulfide layer is, thus, a double-layer system with Cu_2S in direct contact with the rubber molecules.

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

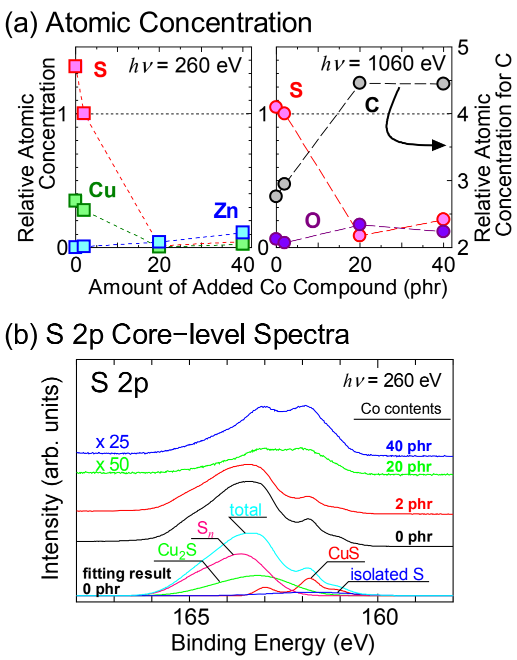

Fig. 1 (a) Change in surface atomic concentration as a function of the Co content. The S concentration at 2-phr Co is taken as a reference point. (b) S 2p spectra at four Co concentrations. The least-square fitting result for the 0-phr spectrum is shown at the bottom.