Interaction Between Cu$_2$S and 2-methyl-2-butene

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Introduction

A sulphur-added rubber compound is known to be strongly bonded to metal copper and copper alloys such as brass (a Cu-Zn alloy). Strong adhesion is realized by the copper sulfide layer, which is formed at the interface and acts as an adhesive agent between rubber and metal. Several preceding studies have suggested that Cu$_2$S and/or nonstoichiometric Cu$_x$S ($n = 1.8—1.97$) are more important than CuS for adhesion [1]. This is because Cu$_x$S ($x = 1.8—2$) is formed at the forefront of the adhesion interface and is in direct contact with the rubber compound.

One of the proposed mechanisms for adhesion between rubber and Cu$_2$S is that rubber penetrates into the dendritically structured Cu$_2$S layer during the vulcanization process to form a firm interlocked rubber/Cu$_2$S interface [2]. The adhesion interaction by this mechanical interlocking is further reinforced by van der Waals interaction and chemical bonding. Although the contribution of chemical bonding is considered to be minor [3], the chemical interaction between rubber and Cu$_x$S has not been directly verified.

In the present study, photoelectron spectroscopy (PES) is utilized to investigate how the rubber molecule chemically interacts with Cu$_2$S and to clarify the chemical contribution to the overall adhesion strength between rubber and Cu$_2$S. Here, 2-methyl-2-butene (2M2B) is used as a model molecule instead of the rubber molecule, i.e., cis-polyisoprene, because a part of the rubber molecule is structurally analogous to 2M2B (Fig. 1a). Thus, the interaction manner between rubber and Cu$_2$S can be accessed by examining the 2M2B-Cu$_2$S interaction.

Experimental

The PES measurements were carried out at BL-13B. A disk-shaped pellet ($8 \times 1$ mm$^3$) of the high purity Cu$_2$S powder (99.99%) was used as a sample. The sample surface was cleaned in an ultrahigh vacuum chamber by cycles of Ar$^+$ sputtering (2 kV, $1 \times 10^4$ Pa Ar) and annealing at 180—200$^\circ$C until the C 1s PES peak was largely eliminated. As indicated in Fig. 1b, however, the C contaminants was not completely removed. 2M2B, in a liquid phase at room temperature (RT), was purified by freeze-thaw-pomp cycles, and the vapour of 2M2B was introduced into the chamber through a variable leak valve for adsorption. The sample was kept at RT during 2M2B adsorption and the PES measurements.

Results and Discussion

Fig. 1b—e shows C 1s, S 2p and Cu 3p core-level spectra of 2M2B-free and 2M2B-adsorbed Cu$_2$S. Adsorption of 2M2B on Cu$_2$S reaches saturation at 11000 L (1 L = $1.3 \times 10^{-7}$ Pa s). 2M2B adsorption induces a decrease in the emission intensity of the Cu 3p spectrum without changing the peak profile, whereas a significant change of the lineshape is induced in the S 2p spectrum. A shoulder structure in the S 2p spectrum formed upon 2M2B adsorption is associated with chemical-shift components. These observations indicate that 2M2B is exclusively bonded to the surface S atoms through its C=C bond as revealed by lineshape analysis of the C 1s peak.

Although the role of the chemical bonding interaction is considered less important than the mechanical interlocking [3], the rubber molecules should be anchored to Cu$_2$S by the C–S covalent bonds. Thus, the chemical interaction certainly contributes to the overall adhesive strength.

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References


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