



Evidence for chemical bond formation at rubber–brass interface: Photoelectron spectroscopy study of bonding interaction between copper sulfide and model molecules of natural rubber



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ABSTRACT

Strong adhesion between rubber and brass has been considered to arise mainly from the mechanical interaction, which is characterized by dendritic interlocking at the interface. In order to examine a possible contribution of the chemical interaction, chemical state analysis was carried out for model molecules of natural rubber (2-methyl-2-butene and isoprene) adsorbed on Cu₂S, a key chemical species for adhesion, by means of photoelectron spectroscopy (PES). Absence of a C 1s PES component associated with C=C bonds and the appearance of adsorption-induced components in the S 2p region indicate that the molecules interact with the Cu₂S surface via the C=C bond to form C–S covalent bonds. This proves that the chemical interaction certainly plays a role in rubber–brass adhesion along with the mechanical interaction.

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1. Introduction

Rubber-to-metal bonding is industrially important because rubber–metal composite materials are used in many aspects of our modern life such as anti-vibration mounts, shock absorbers and abrasion-resistant linings. Automotive tires are one of the rubber–metal composites. To give a tire a mechanical strength while keeping flexibility of rubber, brass-plated steel cords are embedded in tire rubber. The steel cords are retained in the rubber compound owing to strong adhesion between the rubber molecules and the plated brass film. The bonding agent is considered to be copper sulfides, which are formed at the interface between rubber and brass during vulcanization of the tire rubber compound [1,2].

Various spectroscopic studies have revealed the formation of the copper sulfides Cu_xS with x ranging from 1 to 2 at the interface [3–7], and photoelectron spectroscopy (PES) studies have indicated that CuS ($x = 1$) and Cu_xS ($x \approx 2$) are the main components with a larger amount of CuS than Cu_xS [8–10]. Among Cu_xS ($1 \leq x \leq 2$), Cu_xS with $x \approx 2$ has been proposed to be a key adhesive agent [1,2]. A

commonly accepted view at present is that non-stoichiometric Cu_xS with $x \approx 1.8$ is crucial to realize strong adhesion [1,2].

Regarding the bonding mechanism between rubber and brass, mechanical and chemical interactions have been taken into account. The mechanical interaction is characterized by dendritic interlocking between rubber and the copper sulfide layer [1]. This interlocking is realized by a dendritic growth of the copper sulfides into the rubber compound, in which the density of crosslinking is still low at early stages of vulcanization. The mechanical interaction has been considered to be a major cause of strong adhesion [5,6]. On the other hand, the chemical interaction originates from covalent bonding between the rubber molecule, i.e. cis-polyisoprene, and the copper sulfides. Although Persoone et al. have suggested the existence of a –C–S– component from the Auger electron spectroscopy (AES) study [11], the origin of this component has not been identified yet.

In the present study, PES utilizing synchrotron radiation has been employed to elucidate the bonding interaction between the rubber molecule and the copper sulfide. For this purpose, we have examined adsorption states of 2-methyl-2-butene and isoprene (2-methyl-1,3-butadiene) on polycrystalline Cu₂S. These molecules are employed as model molecules of natural rubber, i.e. cis-polyisoprene, because isoprene is a monomer of the rubber molecule and the structure of 2-methyl-2-butene resembles a part of polyisoprene (Fig. 1a).

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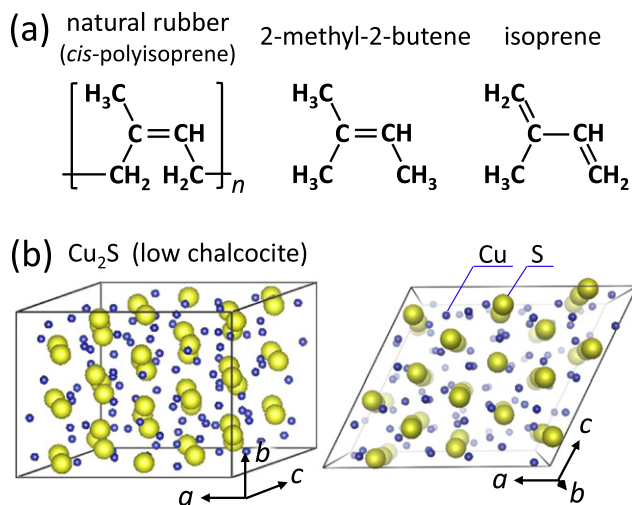


Fig. 1. (a) Structural formulas for *cis*-polyisoprene, 2-methyl-2-butene and isoprene. (b) Crystal structure for monoclinic Cu₂S (low chalcocite) and an atomic arrangement seen from the *b* axis. Large and small circles correspond to S and Cu atoms, respectively. The sizes of the circles reflect the ionic radii of S²⁻ and Cu⁺. The model structures are drawn by VESTA [16].

Core-level PES spectra show that, as the model molecules adsorb on Cu₂S, chemically shifted states emerge in the S 2p region. Lineshape analysis of the C 1s core-level spectra reveals that all components of the C 1s peak is associated with sp³ C atoms and no trace of sp² C is identified. These results indicate that the model molecules are chemically bonded to the surface S atoms to form S–C covalent bonds through the C=C bonds.

2. Experimental

The experiments were performed at beam lines (BLs) 3B [12] and 13B [13] of the Photon Factory, High Energy Accelerator Research Organization (KEK). The PES measurements were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 2 \times 10^{-8}$ Pa at BL-13B. The PES spectra were acquired by a hemispherical electron-energy analyzer (Gamma Data/Scienta SES200) with total energy resolutions of 0.15 eV and 0.6 eV at photon energies of $h\nu = 400$ eV and 1050 eV, respectively. The binding energies (BEs) of the PES spectra were referenced to the Fermi level of a Ta foil.

Cu₂S (99.99%, Sigma-Aldrich) in powder form was pressed into a pellet with 40 kgf/cm². The pellet (ϕ 5 mm \times 0.5 mm) was mounted on a Cu sample holder using Mo clips. Carbon and oxygen were main contaminants of the sample. These impurities were removed by cycles of Ar⁺ sputtering (2–3 kV) and annealing at 620–630 K in the sample preparation chamber that was connected to the measurement chamber. These cleaning parameters were chosen so as to efficiently eliminate C and O while keeping the Cu/S atomic ratio. The surface cleanliness was evaluated by AES measurements at BL-3B and by core-level PES measurements at BL-13B. Although the O atoms were successfully removed, a small amount of C still existed on the surface after extensive sputtering-annealing cycles.

Isoprene and 2-methyl-2-butene are both liquid at room temperature. High purity liquids (>99.0% for isoprene, Tokyo Chemical Industry, and 99+% for 2-methyl-2-butene, Acros Organics) were degassed by several freeze-pump-thaw cycles before use. Adsorption of isoprene and 2-methyl-2-butene on the Cu₂S surface was carried out in the UHV chamber which was connected to the sample preparation chamber. Vapors of the molecules were admitted to the UHV chamber through a variable leak valve, and the Cu₂S surface was

exposed to the vapors at room temperature. The amount of exposure is expressed by Langmuir (L; 1.0 L = 1.33×10^6 Pa sec).

3. Results

3.1. PES spectra of Cu₂S

Stoichiometric Cu₂S (chalcocite) has three different phases depending on the temperature; a monoclinic phase, also called a low chalcocite phase, which is realized at $\leq 103.5^\circ\text{C}$, a hexagonal phase (a high chalcocite phase) in the temperature range between 103.5°C and 436°C, and a cubic phase at $\geq 436^\circ\text{C}$ [14,15]. Since the PES measurements were carried out at room temperature, Cu₂S should be in the monoclinic phase. A left part of Fig. 1b shows a crystal structure of monoclinic Cu₂S [16].

PES spectra of the clean Cu₂S surface are shown in Fig. 2. The Cu 2p_{3/2} peak is observed at 932.2 eV in BE and the Cu L₃M_{4,5}M_{4,5} Auger electron peak is found at 918.2 eV in kinetic energy. The Auger parameter is thus $\alpha = 1850.4$ eV. Although these values are close to literature values for Cu₂S, it is difficult to distinguish Cu₂S from CuS by the Cu-related parameters because both sulfides give similar values [17]. However, as we will see later, Cu₂S is assured by S 2p spectra.

The S 2p spectra show 2p_{3/2} and 2p_{1/2} peaks with spin-orbit splitting of ~ 1.1 eV (Fig. 2c). The spectra have a tail structure at the higher BEs, suggesting a contribution of several S components to the observed spectra. We will discuss the S 2p spectra in more details shortly after.

The valence-band structure is characterized by an intense peak centered at ~ 3 eV with an emission tail up to the Fermi level (Fig. 2d). This spectral feature is in good agreement with that reported earlier by Kashida et al. [18] and with a theoretically examined density of states of monoclinic Cu₂S. [14]. Cu₂S is a p-type semiconductor with a band gap of around 1.2 eV [19]. The p-type character is brought about by Cu deficiency, and the Fermi level moves even below the top of the valence band if the density of the Cu vacancies is high enough [14]. In the present Cu₂S sample, a strong p-type electronic structure is realized because the position of the valence-band maximum coincides with the Fermi level (Fig. 2d). This indicates that there should exist Cu vacancies in the surface and near-surface regions of Cu₂S.

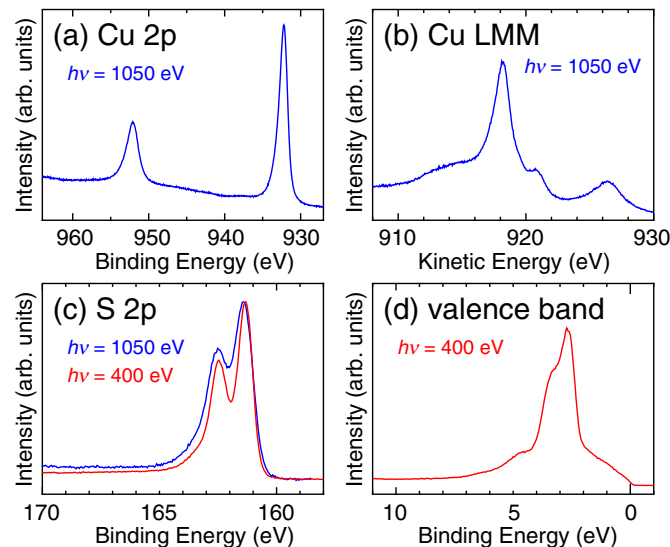


Fig. 2. Core-level spectra of Cu₂S. The photon energy of 1050 eV was used to measure the Cu 2p, Cu LMM and S 2p spectra, and the S 2p and valence band spectra were acquired at $h\nu = 400$ eV.

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