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Chemical State Analysis of Rubber−Brass Adhesive Interface by Soft and Hard X-ray Photoelectron Spectroscopy

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1 INTRODUCTION

Automotive tires require a mechanical strength while keeping flexibility of rubber. The mechanical reinforcement is achieved by steel cords, which are embedded in the rubber. To realize strong rubber−cord adhesion, brass-plated steel cords are used, since rubber−brass bonding is superior to rubber−steel bonding. Since pioneering works by van Ooij [1], it has been recognized that copper sulfides, which are formed at the rubber−brass interface, act as an adhesive agent. However, details of the agent, especially its chemical composition, have not been clearly understood.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy are powerful tools to investigate chemical composition of solids. However, these electron spectroscopy techniques are sensitive to the surface because of short inelastic mean free paths (IMFPs) of the electrons in solids. If one wants to study a buried interface, the interface must be exposed to the surface for the measurements. However, the chemical state of the adhesive interface may be affected upon interface exposure procedures. Therefore, bulk-sensitive techniques such as X-ray absorption spectroscopy and X-ray emission spectroscopy are more suitable for an *in situ* investigation of the buried interface. XPS utilizing hard X-ray (HAXPES) is another bulk-sensitive technique, since emitted photoelectrons have relatively high kinetic energies so that large IMPFs are expected. In the present study, we have examined the chemical composition of the rubber−brass adhesive interface by XPS utilizing soft X-ray as well as HAXPES to clarify the chemical composition of the adhesive interface as well as the effect of a compositional change on the adhesion strength.

2 EXPERIMENTAL

The HAXPES measurements were carried at BL47XU of SPring-8 using a 7.94-keV hard X-ray for the *in situ* chemical state analysis of a buried rubber−brass interface. The rubber−brass interface was fabricated by heating a brass plate, whose surface was covered with a thin rubber film, at 170°C under pressurization of 8 MPa. The XPS measurements using soft X-rays were done at BL-13B. Interface-exposed samples were prepared by a filter-paper method [2] and were measured to assess the trend of the compositional change upon adhesion degradation.

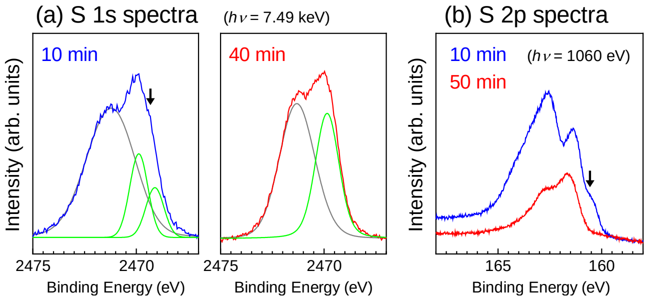

Figure 1 (a) S 1s HAXPES spectra of the rubber-bonded brass samples which were subjected to 10- and 40-min vulcanization. (b) S 2p XPS spectra of the interface exposed samples which were subjected to 10- and 50-min vulcanization. Arrows indicate a characteristic structure which suggests the existence of CuS.

3 RESULTS and DISCUSSION

Fig. 1a shows S 1s spectra of the rubber-bonded brass samples which were subjected to vulcanization for 10 and 40 min. The 10-min vulcanization time is optimum for strong adhesion, whereas adhesion is degraded at longer times. The spectral shape of the 40-min sample is reproduced by two Voigt-shaped peaks, whereas an additional peak is requisite for the 10-min sample to reproduce a characteristic shoulder structure, indicated by an arrow. A similar shoulder structure is also seen in the S 2p spectrum obtained from the interface-exposed surface (Fig. 1b). However, these structures are no more observable on the surfaces subjected to the longer vulcanization times (40 and 50 min). It is known that CuS gives S core-level photoemission peaks, each of which is composed of two components with an intensity ratio of 2-to-1, and that the lower binding-energy component is responsible for the shoulder structure [2]. Thus, the vulcanization time dependence of the spectral feature indicates the variation of the chemical state from a CuS-rich to CuS-deficient state. This change should be responsible for the degradation of rubber−brass adhesion.

References

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