HAXPES for a better tire performance: Chemical state analysis of adhesive interface between rubber and steel cords

Most of us routinely use vehicles for transportation, either by driving a car or by taking taxis and buses, and all of us rely on merchandise distribution services, where vehicles play an essential role. Nowadays, there are more than 1.2 billion registered vehicles (passenger cars and commercial vehicles) worldwide from remote regions to urban areas, and around 100 million vehicles are manufactured every year [1]. It is no exaggeration to state that our modern society is supported by vehicles. One of the key components of vehicles is rubber tires. The tires literally support the vehicle, and the tire performance affects the steering control, noise and vibration characteristics, fuel consumption, and other factors.

The present *de facto* standard of vehicular tires is the radial tire, in which twisted steel cords are embedded in a steel belt (Fig. 1(a)). The most important role of the steel belt is to suppress shape deformation of the tire in order for the tire to keep a tight grip on the road surface and to produce efficient transmission of the traction force from the vehicle to the road. However, if the rubber compound surrounding the steel cords fails to hold the cords, the tire will be deformed, making proper steering of the vehicle difficult. Therefore, it is vital to develop strong and durable adhesion between rubber and the steel cords.

To realize strong rubber-to-steel adhesion, brass-plated cords have been commercially used. This is because rubber-to-brass bonding is superior to rubber-to-steel bonding. Electron spectroscopy, such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), has been utilized to elucidate the adhesion mechanism between rubber and brass since the late 1970s [2]. It was soon recognized that copper sulfide is a key chemical species to cause strong adhesion. However, details of the morphology and chemical composition of the adhesive interface still remain unclear.

XPS and AES are powerful tools for the chemical state analysis of solids. However, because of the short inelastic mean free paths of electrons in solid materials, the adhesive interface must be exposed to the surface when these techniques are used. Among several methods to expose a rubber/brass interface, the so-called “filter paper method” [3] is a novel method to obtain a sulfurized brass surface that imitates the rubber/brass adhesive interface without the rubber molecules. Figure 2 shows S 2*p* core-level spectra of two samples whose interface has been “exposed” by the filter paper method [4]: One was prepared under optimum reaction conditions (heating at 170°C for 10 min, which result in strong adhesion), and the other was obtained under overcuring conditions (170°C for 40 min). Lineshape analysis of the spectra enabled us to identify CuS and Cu_xS ($x \approx 2$) on the optimum sample. As the reaction time is prolonged and the adhesion strength is weakened, the amounts of both CuS and Cu_xS decreased while ZnS is increasingly formed. These observations support the already known fact that copper sulfide acts as an adhesive agent at the interface. The new finding is that, although Cu_xS is a minor species, there is a strong correlation between the adhesion strength and the amount of Cu_xS. This implies that Cu_xS ($x \approx 2$) is a more important adhesive agent than CuS.

Despite the fact that the XPS study in combination with the filter paper method has provided useful information on the chemical state at the adhesive interface, the “exposed” interfaces are not guaranteed to reflect the real chemical state of the buried interface. Therefore, bulk-sensitive hard X-ray photoelectron spectroscopy (HAXPES) was employed to directly

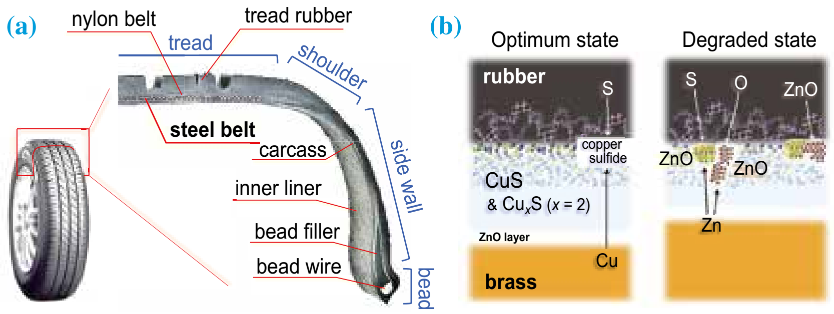

Fig. 1. **(a)** Cross-sectional view of a radial tire. **(b)** Schematic illustrations of the chemical compositions at rubber/brass interfaces proposed by the outcomes of the present study. In the optimum state (left), where strong adhesion is realized, the adhesive interface is mainly composed of copper sulfide. Degradation of the adhesion is characterized by the decomposition of copper sulfide and the accumulation of Zn-containing species (right).

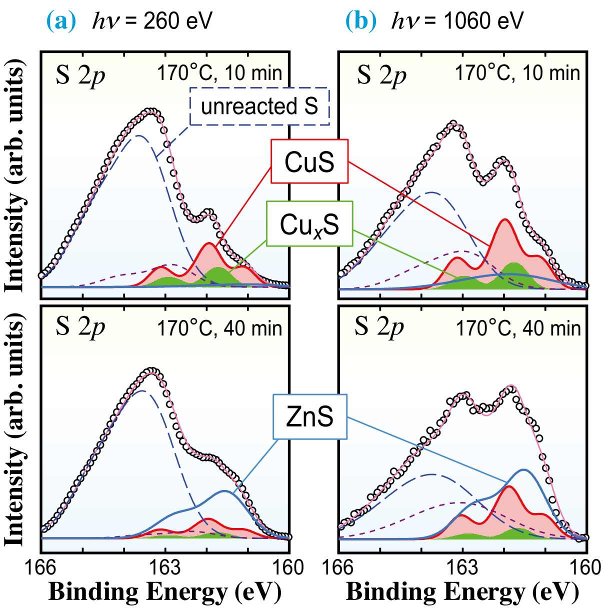

Fig. 2. S $2p$ XPS spectra of the exposed interfaces prepared under the optimum conditions (170°C, 10 min) and the overcuring conditions (170°C, 40 min). The photon energies used were **(a)** 260 eV and **(b)** 1060 eV.

investigate the rubber/brass adhesive interface buried beneath a 100-nm-thick rubber film [5]. The HAXPES measurements were carried out at SPring-8 **BL47XU**, and typical spectra are shown in Fig. 3(a). Here, angle-resolved measurements were concluded to distinguish between the species in the rubber compound and those at the adhesive interface. The S 1*s* spectrum is composed of at least two components: On the basis of the relative intensity variation as a function of the angle, the lower binding-energy (BE) component is assigned to the S species at the interface region, while the higher BE component is related to those in the rubber compound. The lower BE component of the sample prepared under the overcuring conditions is reproduced by a single-peak, whereas a double-peak structure is necessary for the optimum sample (Fig. 3(b)). The double-peak structure is characteristic of CuS. The transformation from the double-peak structure to the single-peak structure as the reaction time is prolonged reflects the decomposition of CuS and the formation of ZnS. Although the identification of Cu_xS ($x \approx 2$) was not possible in the present study, it was demonstrated that HAXPES is capable of following chemical changes at a buried rubber/brass adhesive interface.

On the basis of the results obtained from the present XPS and HAXPES studies, a more accurate view of the chemical composition of the adhesive interface between rubber and brass was obtained (Fig. 1(b)). With this newly proposed model, a technical solution can be found to realize stronger and more degradation-resistant adhesion, enabling the development of new tires with a better performance.

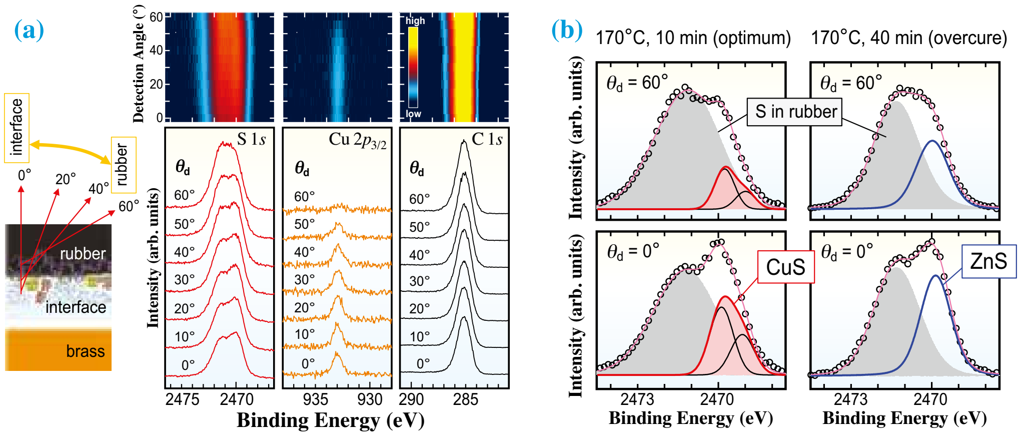

Fig. 3. **(a)** Angle-resolved HAXPES spectra of S 1*s*, Cu $2p_{3/2}$, and C 1*s* core levels of the rubber-bonded brass sample subjected to heating at 170°C for 40 min. The photon energy was 7.94 keV. Upper panels show intensity plots of the spectra, and energy distribution curves are shown in the lower panels. **(b)** S 1*s* spectra of two differently prepared samples measured at detection angles (θ_d) of 0° and 60°. The interface component (the lower BE component) in the spectrum of the optimum sample consists of two subcomponents with a 1:2 intensity ratio, which is characteristic of CuS.

Kenichi Ozawa[a,*], Takashi Kakubo[b] and Naoya Amino[b]

[a] Department of Chemistry, Tokyo Institute of Technology
[b] The Yokohama Rubber Co., Ltd.

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

References

[1] https://www.statista.com/statistics/281134/number-of-vehicles-in-use-worldwide/
[2] W. J. van Ooij: Surf. Sci. **68** (1977) 1.
[3] T. Hotaka *et al*.: Rubber Chem. Technol. **80** (2007) 61.
[4] K. Ozawa *et al*.: Appl. Surf. Sci. **264** (2013) 297.
[5] *K. Ozawa, T. Kakubo, N. Amino, K. Mase, E. Ikenaga, T. Nakamura: Langmuir **33** (2017) 9582.*