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High-Resolution Photoelectron Spectroscopy Analysis of Sulfidation of Brass at the Rubber/Brass Interface

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Abstract

High resolution photoelectron spectroscopy is utilized to investigate the chemical composition at the rubber/brass interface to elucidate the origin of strong adhesion as well as the degradation between rubber and brass. Special attention has been given to copper sulfides formed at the interface during the vulcanization reaction at 170°C. At least five sulfur-containing species are identified in the adhesive interlayer including crystalline CuS and amorphous Cu_xS ($x \simeq 2$). These copper sulfide species are not uniformly distributed within the layer, but there exits the concentration gradation; the concentration of Cu_xS is high in the region on the rubber side and is diminished in the deeper region, while vice versa for that of CuS. Degradation of the interface adhesive strength by prolonged vulcanization arises from the decrease in the Cu_xS/CuS ratio accompanying desulfurization of the adhesive layer.

Keywords: Photoelectron spectroscopy, Rubber, Brass, Adhesion, Copper sulfide

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1. Introduction

In automotive tires, steel cords are embedded to give rubber tires a structural strength while maintaining flexibility of rubber. Strong adhesion between rubber and the steel cords is crucial that tires exhibit a good performance for safe controlling of automobiles. The tire manufacturers have employed brass-plated steel cords to realize stiff rubber-cord adhesion. Many studies have been devoted to elucidate the adhesion mechanism between rubber and the steel cords, aging and degradation mechanisms of adhesion, the effect of the compositional change of rubber and the plated brass layer, etc. Good reviews of the studies since 1970's are given in the literatures by van Ooij [1–4].

It has been recognized already in the early 1970's that copper sulfides are formed at the rubber/cord interface and speculated that these species should be responsible for the interface adhesion. The copper sulfides are formed as a result of the interface reaction between sulfur, which is added to rubber, and copper of the plated brass layer during the cure process of tire rubber. Van Ooij was first employed X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition at the rubber/brass interface and confirmed the formation of the copper sulfide, Cu_xS with $x = 1.90 - 1.97$ [5]. ZnS is also formed at the interface along with Cu_xS. The author has proposed that the optimum amount of Cu_xS is important for strong adhesion [5]. A very similar conclusion, i.e. the formation of Cu_xS and ZnS at the interface, has been drawn from the XPS measurements by Chandra et al. [6] and by Buytaert et al. [7] Formation of Cu_xS and ZnS is also confirmed by Auger electron spectroscopy (AES) measurements [7–9]. A commonly accepted view at present is that nonstoichiometric Cu_xS with $x = 1.8 - 1.97$ is a key adhesive agent to realize a strong rubber-to-brass interface bonding.

On the basis of the thermodynamic consideration of the copper sulfide formation, it is reasonable that Cu_xS ($x \simeq 2$) is more favored than CuS, since the Gibbs of formation $\Delta_f G^\circ$ of Cu_2S (-133 kJ/mol at 170°C) is larger than that of CuS (-83 kJ/mol) [10, 11]. However, Hotaka et al. have identified CuS along with Cu_xS ($x \simeq 2$) at the rubber/brass interface in the XPS measurements [12]. Thus, for understanding the origin of the strong adhesion between rubber and brass, it is crucial to know the formation process of not only Cu_xS but also CuS and their distribution within the interfacial layer.

The compositional change of the adhesive interlayer should be in close relation with the rubber-to-brass adhesive strength. Therefore, the formation

process of the copper sulfides, their distribution within the adhesive interlayer and the influence of the vulcanization time on the chemical composition at the interface should be investigated in more detail. The XPS and AES measurements done so far have limited energy resolutions so that a detailed analysis of the chemical composition was impossible. In the present study, therefore, we performed high-energy resolution photoelectron spectroscopy (PES) and investigated the sulfidation process during vulcanization and the chemical composition of the resultantly formed adhesive interlayer.

2. Experimental

Brass plates ($5 \times 5 \times 0.5$ mm^3) with a bulk composition of 65 wt% Cu and 35 wt% Zn ($Cu_{66}Zn_{34}$; Nilaco Co.) were used as a model sample for a brass-plated steel cord. The surfaces of the brass samples were mechanically polished to mirror finish with alumina paste (0.3 μm). After ultrasonication in acetone, the sample plates were sandwiched by filter papers with thickness of about 0.2 mm [Japanese Industrial Standards (JIS) P 3801 1], embedded into uncured pads of rubber compounds and subjected to vulcanization at 170°C under the compression of 2 MPa using a home-made thermal-press machine, which consists of heat plates (40×40 cm^2) attached to an oil hydraulic press. The brass samples were retrieved from rubber just before the insertion into the ultrahigh vacuum chambers for the PES measurements to avoid oxidation of the brass surfaces. A formulation of the rubber compounds used in the present study is listed in Table 1. Among them, squalene was added to increase fluidity of uncured rubber. Cobalt stearate, N-phenyl-N'-(1,3-dimethylbuthyl)-p-phenylenediamine (6PPD) and N,N-dicyclohexyl-2-benzothiazole sulfonamide (DCBS) were, respectively, an adhesion promoter, an antioxidant and a curing accelerator.

One of the difficulty for chemical analysis of the rubber/brass interface by PES is to expose the interface nondestructively. The mechanical cleavage under liquid nitrogen temperature is one of the method to exposed the interface [5]. However, the obtained surfaces are not always the very interface but brittle parts near the interface. Chemical treatments to remove adhered rubber on the brass surface is another option [6]. The drawback of this method is that the chemical agents used to swell and soften rubber could affect the chemical composition of the adhesive interlayer. Therefore, we employed a so-called "filter paper method" [12] as described above. The filter papers block rubber molecules to reach the brass surface so that the direct rubber-

Table 1: Formulation of rubber compounds (phr; parts per hundred rubber).

Natural rubber	100
Carbon black (HAF-LS)	60
Squalene	10
Zinc oxide	10
Sulfur (octasulfur, S_8)	8
Cobalt stearate	2
N-phenyl-N'-(1,3-dimethylbuthyl)-p-phenylenediamine (6PPD)	1
N,N-dicyclohexyl-2-benzothiazole sulfonamide (DCBS)	0.5

to-brass interaction can be avoided. On the other hand, small chemicals such as sulfur and hydrocarbons diffuse through the papers and induce chemical reactions equivalent to the reactions at the rubber/brass interface. Therefore, the surface chemical composition of the brass surface reflects that of the rubber/brass interface even though the brass samples are covered with the filter papers [12].

A possible drawback of the filter paper method is a delay of the onset of the chemical reactions on the brass surface. This is because the reactants from rubber must pass through the paper to reach the brass surface. As we will see below, the vulcanization time less than 2 min is sufficient to convert the brass surface from the ZnO-rich oxidized state to the cupper-sulfide-rich sulfidized state. This may suggest a relatively fast transfer of the molecules in the paper so that the delay of the reactions may not be significant. Another drawback one may suppose is that a part of the reaction products on the brass surface is lost by mechanical cleavage by the filter paper so that the obtained results contain some artifacts. However, this possibility could be small because the change in the chemical composition on the brass surface is not random but monotonic with the vulcanization time, as indicated in Sec. 3. Therefore, the filter paper method is overall an effective way to nondestructively determine the interface chemical states.

The XPS measurements were performed on PHI 5000 VersaProbe (ULVAC PHI) with monochromatized Al Kα radiation (the photon energy $h\nu =$ 1486.6 eV) with a typical energy resolution of 300 meV. The X-ray was incident on the surface from normal direction, and the photoelectrons emitted to 45° were corrected (0° corresponds to the surface normal direction). We also carried out the PES measurements using synchrotron radiation [synchrotron-radiation-excited PES (SR-PES)] at beam lines (BL) 3B and 13A of the

Photon Factory, High Energy Accelerator Research organization (KEK). At BL-3B, a VSW HA45 hemispherical electron-energy analyzer was used with the overall energy resolution of 250 meV at 64 eV. At BL-13A, an SES200 (VG Scienta) analyzer was used with the energy resolution of 100–200 meV depending on the photon energy. For both systems, photoelectrons emitted to the surface normal direction were corrected. All XPS and SR-PES measurements were done at room temperature. The photoelectron kinetic energy was calibrated by the Cu LMM Auger peak of the contaminant-free polycrystalline Cu to coincide with the literature value (918.6 eV) [13]. The electron binding energy of the spectra was referenced to the Fermi cut-off in the spectra of Mo sample clips or of Cu sample holders.

We also carried out the X-ray diffraction (XRD) measurements to access the reaction products and their crystallinity on the brass surfaces. For the measurements, an X-ray diffractometer (Bruker D8 Advance) was used with Cu Kα radiation.

3. Results

3.1. Influence of vulcanization

Fig. 1 shows XPS spectra of the brass surface before and after vulcanization. Apart from the C 1s peak from carbon contaminants and the O 1s peak from oxides on the surface, the spectrum of the brass surface before vulcanization gives the peaks from both Cu and Zn. The peak intensities of the Zn-related peaks (Zn 3d, 3p and 2p peaks and LMM Auger peaks) are larger than the Cu-related peaks (Cu 3d, 2p, 2p and LMM) on the untreated brass surface. This indicates that the Zn atoms are accumulated on the surface. From the Cu 2p/Zn 2p peak intensity ratio, the surface Cu/Zn atomic ratio is estimated to be 0.7, which is far smaller than the value in the bulk ($66/34 \simeq 1.9$). The excess Zn atoms are in the form of ZnO, as evident from the comparison of the spectral lineshape between the brass surface and the single crystal ZnO surface (the inset of Fig. 1).

The surface excess Zn atoms are largely reduced by vulcanization, because the Zn-related peaks are no more observed on the brass surface after vulcanization for 10 min (Figs. 2a and 2b). Missing of the Zn 3d and 3p peak is also confirmed in the XPS spectrum in Fig. 1. Vulcanization also leads to a significant change of the O 1s spectrum. The O 1s spectrum of untreated brass is composed of two peaks (Fig. 2c); one at 532.1 eV and the other at 530.4 eV. The latter falls in the binding-energy region of the O 1s

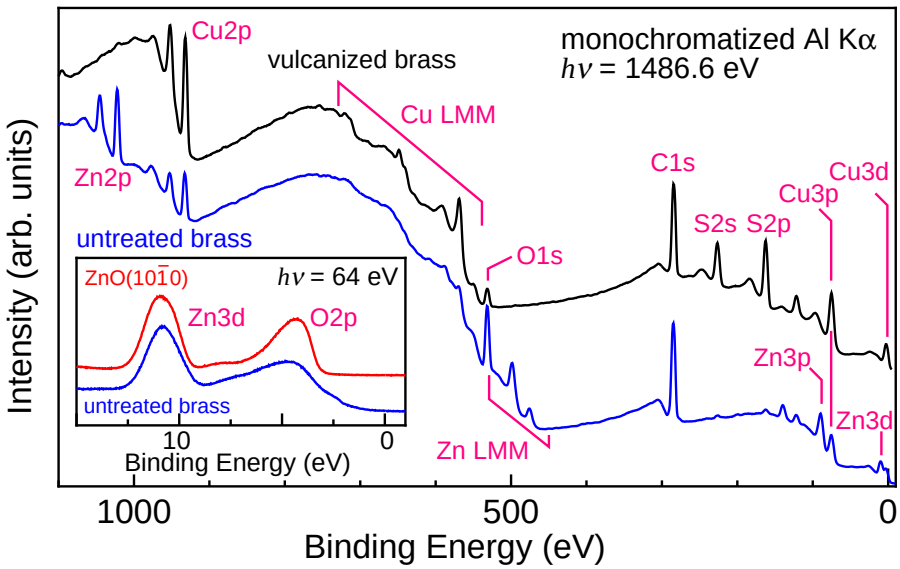


Figure 1: XPS spectra of air-oxidized brass (bottom) and the brass sample after vulcanization for 10 min. In the inset, valence-band SR-PES spectra of air-oxidized brass (bottom) and single-crystal ZnO (top) are compared.

peak from single crystal ZnO (529.7–530.8 eV) [14] and, thus, is associated with ZnO. The former is ascribed to O atoms of surface contaminants [15]. On the vulcanized brass surface, the ZnO-related O atoms are unobserved. Therefore, vulcanization results in the elimination of the ZnO layer on the air-exposed brass surface. Considering the escape depth of the Zn 3d photoelectrons with the kinetic energy of about 1470 eV (excited by the Al Kα line) and the detection angle of the photoelectrons of 45° from the surface normal direction, ZnO is missing in the region from the surface up to the depth of at least 2 nm[1].

On the brass surface after vulcanization, the Cu- and S-related peaks

[1]The photoelectrons from buried ZnO, if exists, are assumed to pass through the adhesive layer composed of Cu_2S, CuS, ZnS as well as the hydrocarbon layer. The inelastic mean free paths (IMFPs) of the photoelectrons in these substances are calculated using a TPP-2M equation (Cu_2S, CuS and ZnS) [16] and an empirical equation (the hydrocarbon layer) [17]. The IMFPs are 2.5 nm (Cu_2S), 2.7 nm (CuS), 2.9 nm (ZnS) and 4 nm (hydrocarbon). By multiplying the averaged value (3 nm) by 0.7 (= $\cos 45°$), we obtain 2 nm. Note that this value only indicates the lower limit of the detection depth.

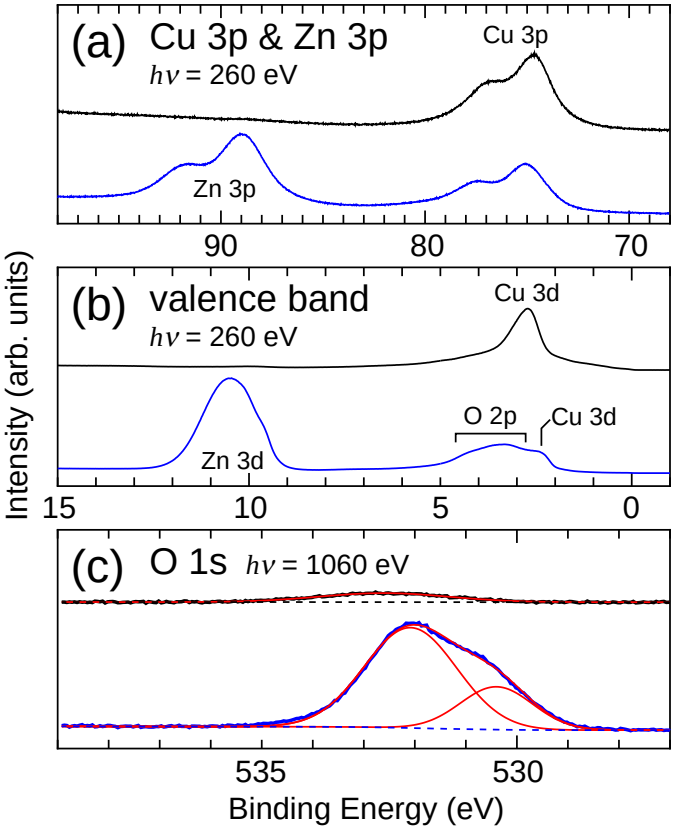


Figure 2: SR-PES spectra of (a) the Cu and Zn 3p core-level region, (b) the valence band region, and (c) the O 1s core-level region. Lower and upper spectra in each panel are obtained from air-oxidized and 10-min vulcanized brass, respectively. Least square fitting using Gaussian functions are carried for each O 1s spectrum, whose Shirley-type background (dashed lines) was subtracted before fitting. Two components are required for the spectrum of air-oxidized brass, while the spectrum of vulcanized brass is reproduced by a single component.

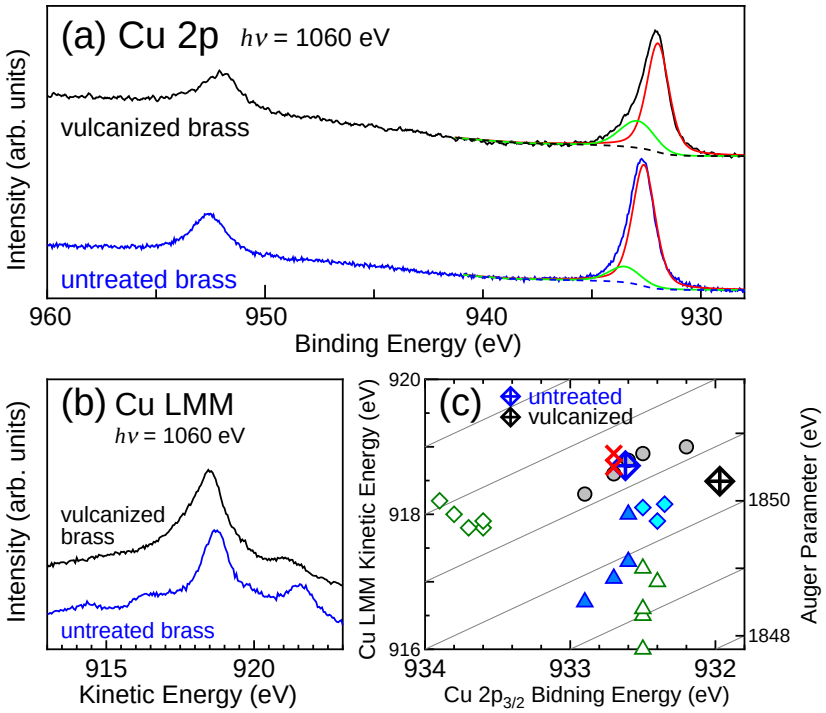


Figure 3: (a) Cu 2p core-level photoemission spectra and (b) Cu LMM Auger electron spectra of air-oxidized brass (bottom) and 10-min vulcanized brass (top). Intensity of the spectra are normalized by the integrated intensities of the observed peaks so as to easily compare the spectral lineshape. The result of peak fitting of the Cu $2p_{3/2}$ core level is also shown. (c) Wagner plot for various copper-containing species; open circles for metallic Cu [13, 18–21], × for brass [13, 22], open triangles and diamonds for Cu_2O and CuO, respectively [13, 18, 20–23], filled triangles for Cu_2S [13, 20, 24, 25], and filled diamonds for CuS [20, 24, 25]. Large diamonds with a cross inside are the data of the present study.

are observed with a sufficient intensity. This is due to the formation of copper sulfides. To access the change in the oxidation state of Cu, the Cu 2p core-level and Cu LMM Auger spectra are compared before and after vulcanization (Figs. 3a and 3b). The untreated brass surface gives the Cu 2p peaks at 932.6 eV (Cu $3p_{3/2}$) and 952.5 eV (Cu $3p_{1/2}$) in the binding energy and the Cu $L_3M_{45}M_{45}$ peak at 918.7 eV in the kinetic energy. The Cu 2p peaks are slightly skewed toward the higher-binding-energy side, and this is due to the existence of a subcomponent at 933.5 eV (Cu $2p_{3/2}$). The energy position of the subcomponent implies that there exist Cu(II) species, possibly in the form of CuO [13, 18, 20–23], although a satellite structure characteristic of the Cu(II) configuration is not apparent. The binding energy of the main Cu $2p_{3/2}$ component (932.6 eV) coincides with that of Cu(0) or Cu(I) species [13, 18–21]. From a Wagner plot shown in Fig. 3c, however, we can conclude that the main Cu species on the untreated brass surface is zerovalent, because the plotted point overlaps those of metallic Cu and brass. Thus, most of the Cu species on the oxidized brass surface are in a metallic state before vulcanization. Although there is no direct evidence to prove in the present study, the copper oxides may form a very thin film on top of the thick ZnO film, as several authors have suggested [5, 7], and the zerovalent Cu species should exist on top of and/or inside the ZnO film in the form of clusters.

The vulcanized brass surface bears the Cu LMM peak at 918.5 eV, which is shifted from 918.7 eV on the untreated surface. This energy shift suggests the oxidation of Cu. However, the Cu 2p peak moves towards the lower-binding-energy side, the direction usually considered for reduction of elements. The Cu $2p_{3/2}$ peak of the vulcanized brass surface is observed at 932.0 eV with a subcomponent at 932.9 eV. This unexpectedly low binding energy of the main Cu 2p peak has been reported by van Ooij [5], who observed the Cu $2p_{3/2}$ peak at 931.6 eV on vulcanized brass. Although the origin of this vulcanization-induced peak shift is not known so far, vulcanization leads to substantial change of the chemical state of Cu. The position of the main component on the Wagner plot (Fig. 3c) do not coincide with any of the materials considered here. However, judging from the Auger parameter (1850.5 eV), the formation of CuS is suggested.

The XRD measurements were made to identify the reaction products with crystallinity on vulcanized brass. Fig. 4 shows the XRD pattern obtained from the brass surface subjected to 10-min vulcanization. Strong peaks of 42.5°, 49.4°, 72.3° and 87.4° are due to reflections from (111), (200), (220)

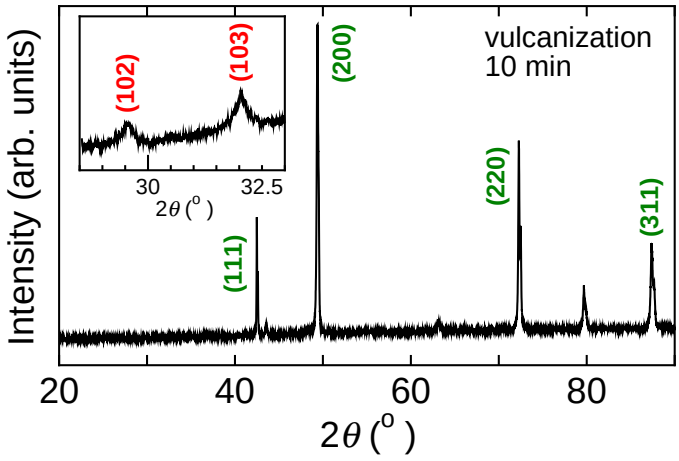


Figure 4: XRD pattern of the brass surface subjected to 10-min vulcanization. Diffraction peaks from covellite (CuS) are observed at 29.6° and 32.0°. Other peaks are from α-brass.

and (311) planes of α-brass, respectively (ICDD-ICSD 04-003-2952). In a 2θ region below 40°, where no diffraction peak from α-brass is present, a detailed measurement reveals weak but distinct peaks at 29.6° and 32.0°, both of which are associated with (102) and (103) reflections from covellite (CuS) (04-008-8150). Thus, the formation of covellite by vulcanization is confirmed. On the other hand, peaks associated with Cu_2S (chalcocite) (01-073-6145), $Cu_{1.8}S$ (00-056-1256) and Cu_7S_4 (00-023-0958) are not detected. This implies that these species are not formed or, if formed, they are in an amorphous phase.

Further information on the chemical composition on the vulcanized brass surface can be obtained from the S 2p core-level spectra. Fig. 5 shows the S 2p core-level spectra measured with two different photon energies ($h\nu$ = 260 and 1060 eV). Considering the IMFP of the emitted photoelectrons excited by $h\nu$ = 260 and 1060 eV (0.4–0.55 nm and 1.5–2.8 nm, respectively, based on the TPP-2M equation [16]), the spectrum measured by 260 eV contains more information on the surface than the spectrum by 1060 eV. The spectral lineshape differs greatly from each other, indicating that there exist several S-containing species on the surface with different depth distribution. We, therefore, carried out the peak fitting analysis to isolate individual spectral components. In the analysis, after the Shirley-type background subtraction, a least-square fitting was performed using six spin-orbit doublets. Each spin-orbit doublet is constructed by two Gaussian functions with a splitting energy

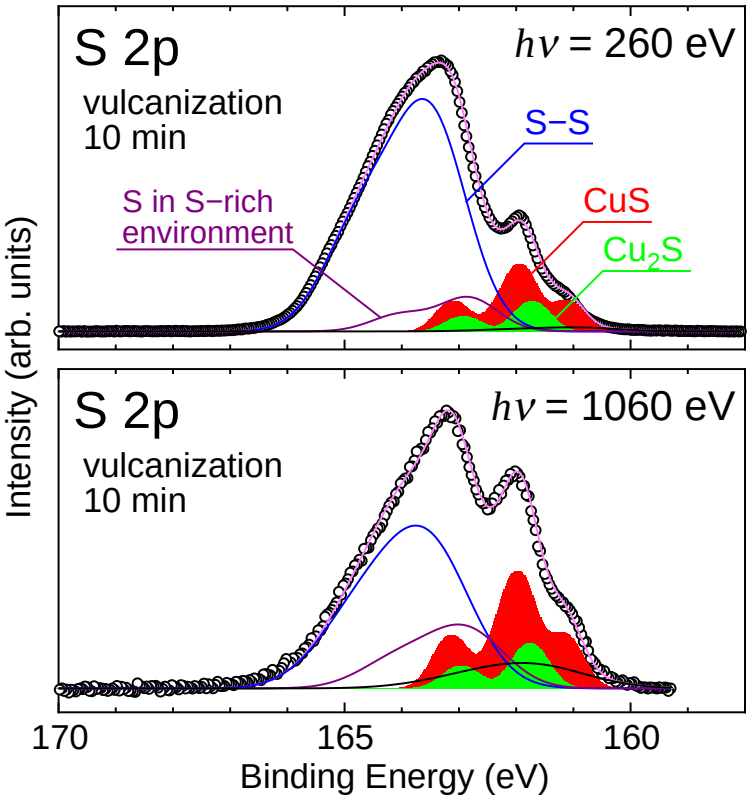


Figure 5: S 2p SR-PES spectra of vulcanized brass (10 min) measured with two different photon energies. The Shirley-type background curves are subtracted. Curves drawn by circles are the measured spectra, and solid lines are results of peak deconvolution. See the text for details of the deconvolution.

of 1.2 eV and the intensity ratio of $2p_{3/2}/2p_{1/2} = 2$ [25]. Two doublets out of six are used to reproduce the characteristic S 2p peaks of covellite (CuS), which contains monosulfide (S) and disulfide (S_2) in the crystal [26]. The S $2p_{3/2}$ binding energies of these species are 161.2 and 161.9 eV, in good agreement with the literature values [25, 26]. Following the study by Kundu et al., one doublet is introduced for Cu_2S in the energy region which overlaps the S 2p peaks of CuS [25]. The S $2p_{3/2}$ peak of Cu_2S is found at 161.7 eV. We should stress that, because the energy difference between Cu_2S and Cu_7S_4 is only 0.1 eV [25], copper sulfides with the Cu/S ratio near 2, i.e., $Cu_{1.8}S$ and Cu_7S_4, could also contribute to the doublet at 161.7 eV.

Two more doublets are required to reproduce the spectra at the higher-binding-energy side; one at 162.6 eV and the other at 163.5 eV. We temporarily assign these components to the S atoms in the S-rich environment (162.6 eV) and the S atoms in the S–S configuration, possibly in the form of polysulfides including octasulfur (163.5 eV) [25]. The concentration of these S-containing species is high on the surface as well as in the near-surface region because the relative peak intensities are higher in the spectrum at $h\nu =$ 260 eV than that at 1060 eV. Contrastingly, S species, which give the sixth doublet at $\sim$ 161.6 eV with a relatively broad feature, should be accumulated in a region far below the surface, because the S 2p peak intensity from this species is larger in the spectrum at $h\nu = 1060$ eV than that at 260 eV. Since the S 2p peak of this species overlaps those of CuS and Cu_2S, a precursor for CuS and Cu_2S is a possible candidate.

The lineshape analysis of the S 2p spectra reveals that there exist at least five S-containing species. Among them, CuS and Cu_xS ($x \simeq 2$) are known to play a role in adhesion between rubber and brass by forming Cu–S–rubber bonding [1, 2]. The Cu_2S/CuS peak-intensity ratio is 0.35 in the spectrum measured with $h\nu = 260$ eV and 0.30 with 1060 eV. Considering a difference in the photoelectron escape depth (0.4–0.55 nm for $h\nu = 260$ eV and 1.5–2.8 nm for 1060 eV), a concentration of Cu_xS ($x \simeq 2$) is higher in the shallow region than in the deeper region, while the trend is opposite for CuS.

It is emphasized that the depth profiling of the S-containing species as presented above is successfully achieved by the PES measurements using different photon energies. The same information cannot be obtained if the ion-sputtering depth profiling is employed because of the destruction of the chemical species upon irradiation of ion beam. Actually, the fine structure of the S 2p peak as shown in Fig. 5 is lost after mild Ar^+ sputtering (1 keV for 10 min with a sample current of 0.7 μA). Thus, the SR-PES technique

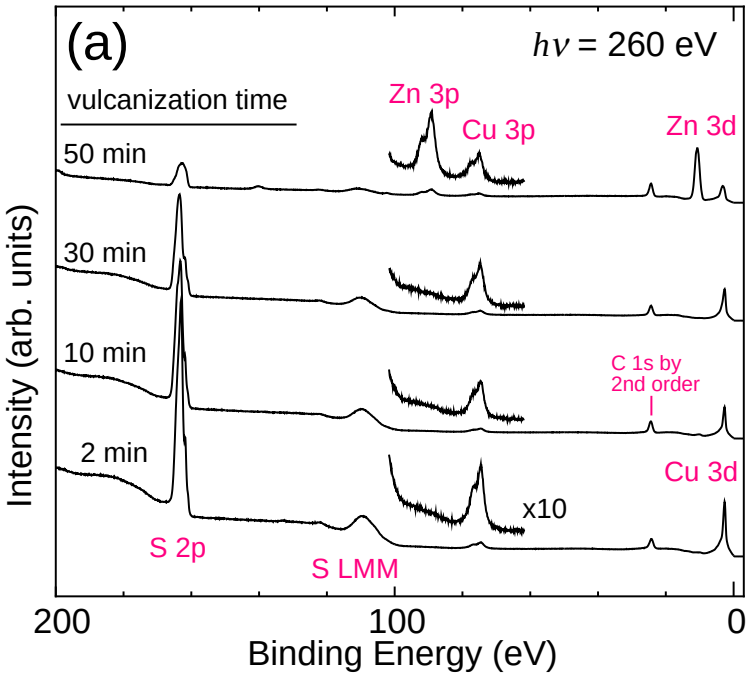


Figure 6: SR-PES spectra obtained from the brass surfaces subjected to vulcanization for 2 to 50 min. The intensity in the Cu and Zn 3p core-level region is multiplied by 10 in order to easily see the change of the Cu and Zn 3p peaks. The peak at $\sim$ 24 eV is the C 1s peak excited by the second-order light ($h\nu = 520$ eV).

should be a prime choice to examine the depth distribution of the reaction products, although an examinable region is limited to a relatively shallow region.

3.2. Vulcanization time dependence

The adhesion layer formed during vulcanization at the rubber/brass interface has a complex composition with at least five S-containing species including CuS and Cu_xS ($x \simeq 2$). In order to elucidate the formation process of the interface layer, the chemical composition of the brass surfaces after vulcanization with different times from 2 to 50 min is examined. The compositional change is expected because the adhesion properties between rubber and brass is known to be greatly affected depending on the vulcanization time, with a weaker rubber-to-brass bonding with a longer reaction time [1, 27]. In the present study, we have also confirmed that the force needed to pull brass-plated steel cords out of rubber is decreased from 566 N to 497

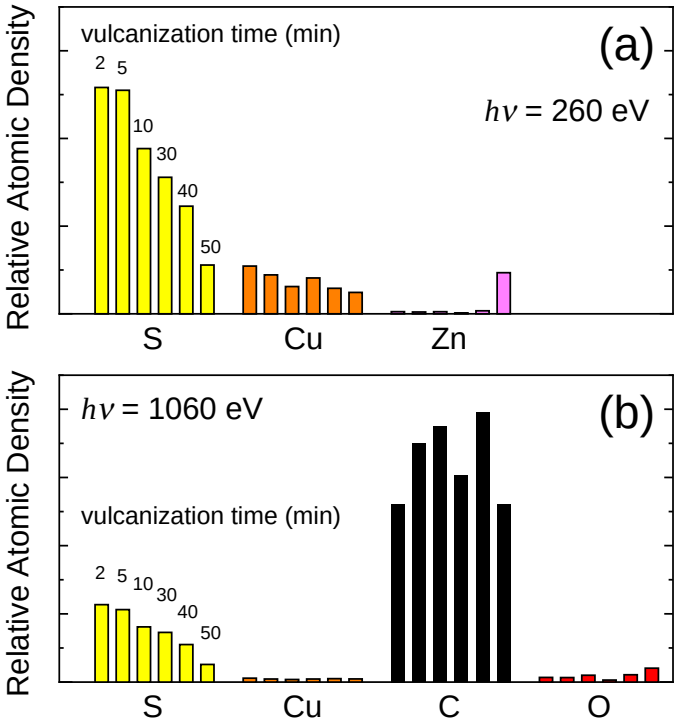


Figure 7: Change in relative densities of major elements (S, Cu, Zn, C and O) on the brass surfaces as a function of the vulcanization time.

N to 451 N at the vulcanization times from 10 min to 30 min to 50 min, respectively, indicating degradation of rubber-to-brass adhesion.[2]

Fig. 6 shows wide-range SR-PES spectra of vulcanized brass surfaces measured with $h\nu = 260$ eV. A strong S 2p peak is gradually attenuated with the vulcanization time. Also diminished are the intensities of the Cu 3d and 3p peaks. On the other hand, the Zn-related peaks appear in the spectrum at 50-min vulcanization, although their peak intensities remain low at the vulcanization times shorter than 50 min.

From the observed spectra measured with $h\nu = 1060$ eV (not shown), the surface atomic densities of S, Cu, C and O are estimated from the integral intensities of the emission peaks from the S 2p (163 eV), Cu 2p (932 and 952 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively), C 1s (284 eV) and O 1s (532 eV) core levels, respectively, and their photoionization cross sections [28]. Similarly, the S 2p (163 eV), Cu 3p (76 eV) and Zn 3p (90 eV) peaks in the spectra measured with $h\nu = 260$ eV (Fig. 6) are used respectively to estimate the S, Cu and Zn atomic densities. Fig. 7 shows the change in the atomic densities of the brass surface as a function of the vulcanization time. The dominant element on the surface is C, which should originate from hydrocarbon molecules including short chain of the rubber molecules (polyisoprene). The density of C does not exhibit a particular vulcanization-time dependence. On the other hand, the S atomic density, which is the second highest, exhibits a sharp decrease with the reaction time, meaning that desulfurization of the adhesive interlayer proceeds during vulcanization. The Cu density also shows a decreasing trend. Thus, desulfurization should accompany the decomposition of copper sulfides. Both Zn and O densities remain low up to 40 min, although they are the main species before vulcanization (Fig. 1). However, 50-min vulcanization results in re-accumulation of Zn and O on the surface.

In order to gain more detailed view of the change in the S densities, the S 2p core-level spectra are examined, and the result of the lineshape analysis is shown in Fig. 8. The relative intensity of the five S-containing species varies with the vulcanization time; those from CuS, Cu_xS ($x \simeq 2$) and S in the S-rich environment are in a decreasing trend with the time, whereas the intensity of the dominant peak from polysulfide is increased up to 10–30 min

[2]In the pull-out test, the brass-plated steel cords with the embedment length of 12.5 mm were pulled out from the cured rubber compounds, following the procedure regulated by American Society for Testing and Materials (ASTM) D2229.

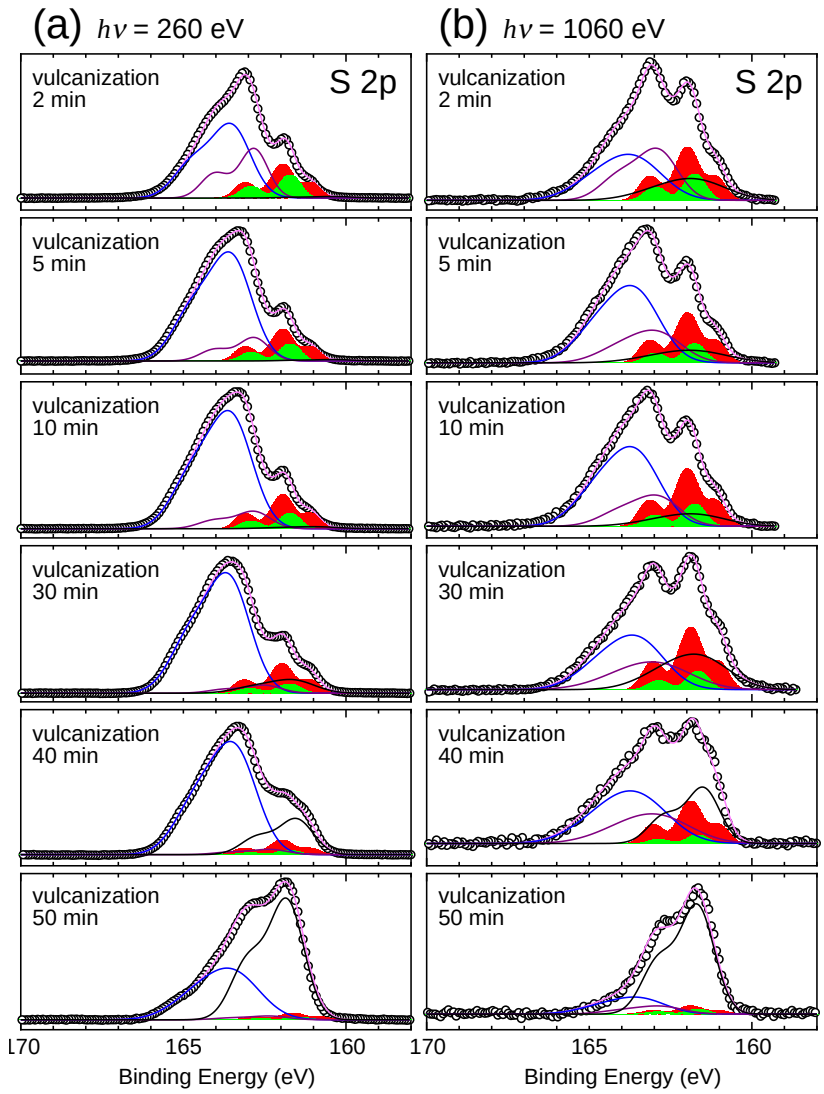


Figure 8: S 2p spectra from the brass surfaces at various vulcanization time. Spectra of 10-min vulcanized sample is the same as those in Fig. 5.

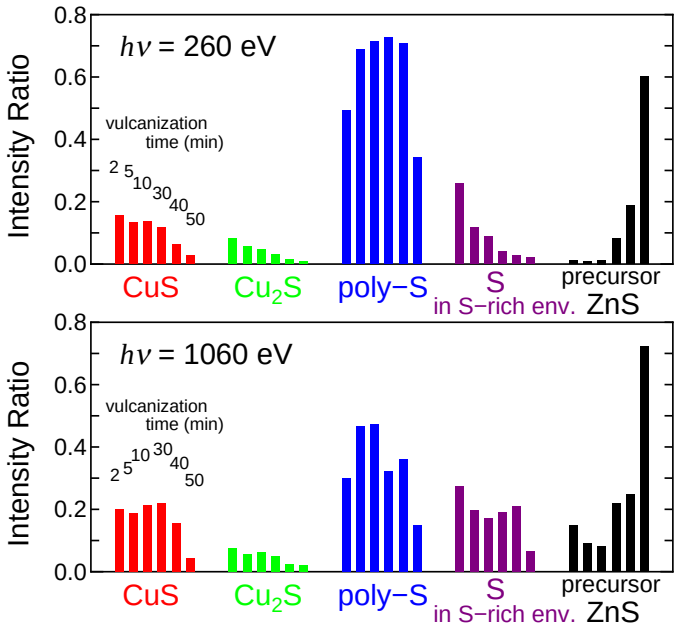


Figure 9: Intensity ratio of the S 2p peaks of S-containing species. The total intensity of the S 2p spectrum from each brass sample is normalized to 1.

and turns to be decreased for longer times. In Fig. 9, change in the relative peak intensity of each S-containing species as a function of the vulcanization time is shown. The intensity of the S 2p peak at 161.8 eV ($2p_{3/2}$) is relatively low with the time shorter than 30 min, but it becomes dominant at 50 min. This is the origin for the drastic change of the spectral lineshape at 50 min. In the previous section, we associate the peak at 161.8 eV with a precursor to CuS and Cu_2S. However, since the Zn atoms are accumulated on the surface after 50-min vulcanization (Fig. 7a), the contribution of ZnS to the this peak should also be taken into account. This interpretation is reinforced by the fact that ZnS gives the S 2p peak at 161.6 eV [13].

4. Discussion

The surface of air-exposed brass with the bulk composition of $Cu_{66}Zn_{34}$ is Zn-enriched with the Cu/Zn atomic ratio of 0.7. The Zn-enriched surface arises from the preferential oxidation of Zn rather than Cu so that the ZnO layer covers the brass surface. However, vulcanization removes ZnO from the surface region. This reaction is so fast that 2 min is enough to eliminate ZnO from the surface up to the depth of at least 2 nm. In the preceding studies, van Ooij et al. have proposed that the thick copper-sulfide layer is formed on top of the ZnO layer and that the ZnO layer is buried in the region about 50 nm deep from the surface [1, 2]. Thus, one of the reason for the absence of ZnO in the surface region is the formation of the thick copper-sulfide layer on top of ZnO. This process should accompany a partial dissolution of ZnO into rubber, because it has been found that the concentration of Zn is high in rubber near the rubber/brass interface [1, 5]. Moreover, we have found in our separate study that ZnO on the brass surface is removed when the brass sample is dipped in isoprene, the monomer of natural rubber, at 0°C for several days [29]. Thus, vulcanization leads to decomposition of ZnO as well as the formation of the copper sulfides on top of the ZnO layer.

In the sulfidation reaction at the rubber/brass interface, polysulfides including S_8 diffused from rubber is important as a source of sulfur. A curing accelerator, DCBS in the case of the present study, is proposed to play a crucial role to transform the polysulfides into an active S species for sulfidation [3]. ZnS is not the main product of sulfidation when the vulcanization time is short (up to 30 min), although the atomic concentration of Zn is high on the brass surface in the form of ZnO before vulcanization. This is reasonable because the reaction between ZnO and S to form ZnS is thermodynamically

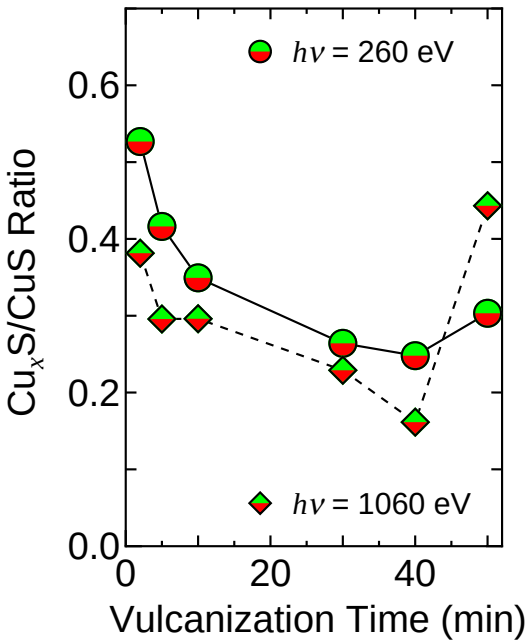


Figure 10: Change in the Cu_xS/CuS ratio (the S 2p peak intensity ratio) as a function of the vulcanization time.

unfavorable ($ZnO + S \rightarrow ZnS + 1/2O_2, \Delta_f G^\circ = 137$ kJ/mol at 170°C [10]). The same consideration is applied to the conversion from CuO to copper sulfides. CuO is formed on the oxidized brass surface, giving the subcomponent in the Cu $2p_{3/2}$ peak at 933.5 eV (Fig. 3a). Chemical reactions to form CuS and Cu_2S from CuO are also thermodynamically unfavorable. Thus, the copper sulfides should be formed by the reaction between polymerized S and the Cu atoms, which migrate from brass through the ZnO layer.

The lineshape analysis of the S 2p spectra (Fig. 5) reveals that there exist CuS and Cu_xS ($x \simeq 2$) in the adhesive interlayer. As shown in Fig. 10, the Cu_xS/CuS ratio is always less than 1 and shows a monotonic decrease up to 40 min. The values at 50 min are increased, but this trend may be artifact because the emission peaks from Cu_xS and CuS is so small (see the bottom panels in Fig. 8) that the uncertainty of the peak intensities is large. Thus, we will consider in the following discussion the data up to 40 min.

The Cu_xS/CuS values smaller than the unity means that CuS should be more favored than Cu_xS. This is opposite to the expected result from the thermodynamic consideration. Since $\Delta_f G^\circ$ of Cu_2S and CuS are -133 and

−83 kJ/mol at 170°C, respectively [10, 11], one expects that Cu_2S is a final product of sulfidation of Cu. Kundu et al. have investigated the sulfidation process of the Cu metal surface by deposition of the S atoms and found that Cu_2S is formed in the initial stage and is converted to CuS for a longer reaction time [25]. This experimental finding implies that the densities of Cu and S in the reaction front should be a more important factor to define the reaction product. At the rubber/brass interface, the Cu atoms from brass react with polymerized S with the help of DCBS from rubber to form Cu_xS ($x \simeq 2$) in the very beginning of vulcanization. Cu_xS is then converted to CuS by an additional supply of S ($Cu_2S+S \rightarrow 2CuS$). This reaction sequence should be completed within 2 min.

Longer vulcanization leads to desulfurization of the interface so that the concentration of S is diminished (Figs. 6 and 7). Desulfurization accompanies decomposition of CuS and Cu_xS ($x \simeq 2$) with a faster decomposition rate of Cu_xS, as inferred from the plot in Fig. 10. Fig. 10 also tells us the fact that the concentration of Cu_xS is higher in the region on the rubber side than that on the brass side, because the Cu_xS/CuS ratio deduced from the spectra at $h\nu = 260$ eV is higher than that at 1060 eV for the vulcanization time shorter than 40 min. Such a compositional gradation is interesting because, within the copper sulfide layer, the Cu atomic density is higher on the rubber side and is lower on the brass side (the Cu densities in Cu_2S and CuS are 44 and 30 atoms/nm^3, respectively, which are calculated from the lattice constants of these crystals [30, 31]). Thus, it is considered that the reaction, $Cu_2S + S \rightarrow 2CuS$, should be operative in the region near the brass surface by incorporation of elemental or anionic S into the copper sulfide layer.

The present study reveals that several S-containing species are present at the interface with polymerized S and the copper sulfides as main species on the vulcanized brass at 10 min, which is the reaction condition to realize a good rubber-to-brass adhesion property. The preceding studies done so far indicate nonstoichiometric Cu_xS with $x = 1.8 - 1.97$ at the rubber/brass interface is responsible for strong rubber-to-brass adhesion. The same conclusion can also be drawn from two observed results deduced from the present measurements. Firstly, the copper sulfide layer is characterized by a higher concentration of Cu_xS ($x \simeq 2$) on the rubber side in comparison with that on the brass side. Secondly, the longer vulcanization time leads to a decrease of the Cu_xS/CuS ratio up to 40 min. Prolonged vulcanization leads to degradation of rubber-to-brass adhesion as a result of the change in the chemical composition at the interface [1]. Moreover, an amorphous-to-crystalline tran-

sition of Cu_xS by prolonged vulcanization also contributes to weakening of adhesion because of brittleness of crystalline Cu_xS [4]. Although the morphological change of Cu_xS is not determined in the present study, the above mentioned two findings lead us to conclude that Cu_xS in direct contact with rubber at the interface should be responsible for a strong rubber/brass adhesive force, and degradation of adhesion at the vulcanization time beyond the optimum time (10–20 min) arises from the small amount of Cu_xS within the copper sulfide layer. Although the surface with a higher Cu_xS concentration is realized at 2 min, rubber subjected to a short vulcanization time has still low elasticity because of a low crosslink density. In such a case, therefore, the adhesive strength cannot be properly assessed.

At 50-min vulcanization, the chemical composition on the brass surface is completely different from that on the optimally vulcanized brass surface. On this surface, the copper sulfide layer is diminished almost to an undetectable level, whereas a substantial amount of the Zn atoms are accumulated in the form of ZnS and ZnO. The formation of ZnS during prolonged vulcanization may proceed along with dissociation of the copper sulfides via the thermodynamically favored reaction; $Cu_xS + Zn(Zn^{2+}) \rightarrow ZnS + xCu(Cu^{\frac{2}{x}+})$, where $x = 1, 2$. Zn in this equation may be supplied in the form of Zn(0) and/or Zn^{2+} from brass and/or ZnO, both of which are buried below the copper sulfide layer. The source of Zn also taken into account is ZnO in the rubber compound. Fulton have proved from secondary ion mass spectroscopy measurements utilizing Zn isotope labeling that a large amount of Zn accumulated at the interface in the form of ZnS originates from ZnO in the rubber compound added as an additive [32]. This indicates that the transport of ZnO from rubber to the interface cannot be negligible in the prolonged vulcanization reaction. Thus, ZnO on the brass surface after long vulcanization should arise partly from this migrated ZnO from the rubber side, while oxidation of Zn supplied from the brass side should be also responsible for the accumulation of ZnO. Since both ZnS and ZnO lack the ability to form strong bonding with the rubber molecules [6, 9], the rubber-to-brass adhesive interaction is quite weak at 50-min vulcanization.

The present study focuses on the chemical composition on the brass surface and successfully specifies Cu_xS ($x \simeq 2$) as a key component for rubber-brass adhesion. Morphology of the Cu_xS layer is important for understanding the strong adhesion force, because dendritic penetration of rubber into the Cu_xS layer and the resultant mechanical interlocking is proposed as a main origin of adhesion [2–4]. Thus, further studies are necessary to establish the

relevance among the chemical composition at the interface, interface morphology and the adhesion strength in order to fully understand the adhesion mechanism.

5. Summary

High-energy-resolution photoelectron spectroscopy is utilized to investigate the chemical composition at the rubber/brass interface after vulcanization at 170°C for 2 min up to 50 min. The brass surface is covered with the ZnO layer before vulcanization. This ZnO layer is, however, removed from the surface region within the detection limit (2 nm) after only 2-min vulcanization, either by a partial dissolution into rubber and by the formation of the thick copper-sulfide layer on top of ZnO. Short vulcanization is also enough to accumulate a large amount of polymerized S at the rubber/brass interface to initiate sulfidation of the Cu atoms to form the copper sulfide layer. The layer is found to be composed of CuS and Cu_xS ($x \simeq 2$) with a larger amount for CuS. These species are not uniformly distributed within the layer; the concentration of Cu_xS is high in the region on the rubber side and is diminished in the deeper region, whereas that of CuS is high in the deep region.

Prolonged vulcanization leads to desulfurization of the interface. Desulfurization accompanies decomposition of CuS and Cu_xS with the faster decomposition rate of Cu_xS. This change in the interface chemical composition should be the key factor for deterioration of adhesive between rubber and brass. Therefore, Cu_xS with $x \simeq 2$ in direct contact with rubber is responsible for the strong rubber-to-brass adhesion.

6. Acknowledgement

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Table caption

Table 1: Formulation of rubber compounds (phr; parts per hundred rubber).

Figure captions

Figure 1: XPS spectra of air-oxidized brass (bottom) and the brass sample after vulcanization for 10 min. In the inset, valence-band SR-PES spectra of air-oxidized brass (bottom) and single-crystal ZnO (top) are compared.

Figure 2: SR-PES spectra of (a) the Cu and Zn 3p core-level region, (b) the valence band region, and (c) the O 1s core-level region. Lower and upper spectra in each panel are obtained from air-oxidized and 10-min vulcanized brass, respectively. Least square fitting using Gaussian functions are carried for each O 1s spectrum, whose Shirley-type background (dashed lines) was subtracted before fitting. Two components are required for the spectrum of air-oxidized brass, while the spectrum of vulcanized brass is reproduced by a single component.

Figure 3: (a) Cu 2p core-level photoemission spectra and (b) Cu LMM Auger electron spectra of air-oxidized brass (bottom) and 10-min vulcanized brass (top). Intensity of the spectra are normalized by the integrated intensities of the observed peaks so as to easily compare the spectral lineshape. The result of peak fitting of the Cu $2p_{3/2}$ core level is also shown. (c) Wagner plot for various copper-containing species; open circles for metallic Cu [13, 18–21], $\times$ for brass [13, 22], open triangles and diamonds for Cu_2O and CuO, respectively [13, 18, 20–23], filled triangles for Cu_2S [13, 20, 24, 25], and filled diamonds for CuS [20, 24, 25]. Large diamonds with a cross inside are the data of the present study.

Figure 4: XRD pattern of the brass surface subjected to 10-min vulcanization. Diffraction peaks from covellite (CuS) are observed at 29.6° and 32.0°. Other peaks are from α-brass.

Figure 5: S 2p SR-PES spectra of vulcanized brass (10 min) measured with two different photon energies. The Shirley-type background curves are subtracted. Curves drawn by circles are the measured spectra, and solid lines are results of peak deconvolution. See the text for details of the deconvolution.

Figure 6: SR-PES spectra obtained from the brass surfaces subjected to vulcanization for 2 to 50 min. The intensity in the Cu and Zn 3p core-level region is multiplied by 10 in order to easily see the change of the Cu and Zn 3p peaks. The peak at $\sim$ 24 eV is the C 1s peak excited by the second-order light ($h\nu = 520$ eV).

Figure 7: Change in relative densities of major elements (S, Cu, Zn, C and O) on the brass surfaces as a function of the vulcanization time.

Figure 8: S 2p spectra from the brass surfaces at various vulcanization time. Spectra of 10-min vulcanized sample is the same as those in Fig. 5.

Figure 9: Intensity ratio of the S 2p peaks of S-containing species. The total intensity of the S 2p spectrum from each brass sample is normalized to 1.

Figure 10: Change in the Cu_xS/CuS ratio (the S 2p peak intensity ratio) as a function of the vulcanization time.