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Enhancement of adhesion between polyphenylene sulfide and copper by surface treatments

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ABSTRACT

In this paper, we introduce methods which can effectively enhance the adhesion between polyphenylene sulfide (PPS) and bulk Cu. One of the methods involved the thermal evaporation of PPS to form a buffer layer on Cu and the other involved plasma treatment with reactive gases such as O_2, H_2, and N_2 on the PPS buffer layer. The adhesion strength of samples prepared by PPS thin film coating (~26 MPa) was largely enhanced when compared to that of samples obtained by only etching (~15 MPa). Among the samples obtained by plasma treatment using various reactive gases, the samples treated using H_2 plasma showed the best adhesion strength (of ~32 MPa) in comparison to the other samples owing to the adhesion between hydrophobic surfaces.

1. Introduction

Plastic resins are widely used in aerospace, automotive, medical, and electronic applications [1]. Engineering polymers have specifically drawn much attention recently with the rapid developments in the fabrication of secondary Li-ion batteries for application in hybrid and electric vehicles. In the context of application to Li-ion batteries, the polymers are mainly used to produce hermetic packages for the battery cells [2]. In order to keep the cells hermetically sealed, it is necessary that the engineering polymers are attached perfectly with the metals used as negative/positive battery terminals. However, the strengths of adhesion between engineering polymers and metals achieved to date are below par and insufficient for application in batteries [3–5]. Among metals, aluminum metal is well known as both positive current collector and battery terminal material. Copper (Cu) metal is also mainly used as both negative current collector and battery terminal material. Among many engineering polymers, polyphenylene sulfide (PPS) is a high-temperature thermoplastic having a thermosetting/thermoplastic character with a glass transition temperature of 90 °C and a melting temperature of 280 °C, which shows exceptional chemical and oxidation resistance as well as dimensional stability, minimum water absorption, good isolation behavior, and low flow gas density [6,7]. Roman et al. evaluated the suitability of adhesion of PPS and Cu based on the density functional theory [8,9]. According to the studies, PPS is quite promising engineering polymer for seal adhesive of battery cell.

Many studies have attempted to promote the polymer–metal interfacial bonding by surface treatments such as morphology modification [10–12], plasma treatment [3,4,13–15], and chemical modification of polar groups [16–18]. The results of these previous studies demonstrate that it is possible to improve the adhesive bonding between PPS and metal. However, PPS–Cu adhesion strengths showing less than 25 MPa reported so far are insufficient, especially to cater to the special requirements for their application in batteries [19,20].

In this study, we fabricated PPS-coated Cu plates and subsequently plasma-treated the samples to improve the adhesion strength of Cu with bulk PPS. In addition, chemically etched metallic Cu was also used as the substrate for coating PPS films. The surface energy (SE) and chemical bonding states of PPS deposited on etched metallic Cu and samples that were plasma-treated were assessed. Further, the bonding strengths of the samples were also measured. We expect that the methods suggested by us in this report may prove as valuable techniques for enhancing the bonding strength between PPS and Cu.

2. Experimental procedure

Cu samples, 10 × 20 mm^2 in area and 1 mm in thickness, were prepared. The specimens were mechanically polished and rinsed

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with distilled water prior to degreasing ultrasonically with acetone. First, Cu plates were cleaned with HNO_3 (15%) prior to being exposed to a solution of acetic acid (99%), H_3PO_4 (85%), and HNO_3 (70%). Subsequently, the samples were treated with a solution of NaOH and $K_2S_2O_8$ at 70 °C for several minutes after which the samples were thermally oxidized at 250 °C in the air for 1 min.

For the deposition of a thin layer of PPS, the etched Cu and granular PPS were placed on the top and bottom of a crucible, respectively. Then, PPS was evaporated at 240 °C for 10 min and a film with a thickness of about 40 nm was deposited. Plasma treatment at atmospheric pressure was carried out on the PPS samples deposited on etched Cu using various reactive gases such as H_2, N_2, and O_2 to generate functional groups on the surface of the PPS layer. The distance between the plasma head and the sample was fixed at 15 mm and gas flow rates of argon and reactive gases were maintained at 4 lpm (liter per minute) and 50 sccm (standard cubic centimeters per minute), respectively. The plasma treatment was performed at a radio frequency power of 120 W for 2 min.

The surface morphology and SEs were evaluated by field emission scanning electron microscopy (FESEM, Hitachi, S-4700, with the microscope operated at an acceleration voltage of 15 KV) and by contact angle (CA) measurements (Dataphysics, OCA10), respectively. The chemical bonding states on the film surface was investigated by X-ray photoelectron spectroscopy (XPS, VG Scientific, ESCALAB250). The adhesive bond strength was calculated as the measured load when two Cu plates were separated by a compressive load for a given bonding area. The lap-shear tensile strength of metal-to-metal joints was determined in accordance with the modified ASTM Method D-1002. Before overlapping the metal plates, 2 mm in length and 10 mm in width, the $2 \times 10\ mm^2$ lap area was coated with solution-based PPS adhesive. The thickness of the overlapped PPS film was approximately 100 μm. The bond strength of the lap shear specimens is the maximum load at failure divided by the total bonding area. A schematic representation of the sample is shown in Fig. 1. The cylindrical type PPS shots, 1 mm in diameter and 2 mm in length, were spread on a Cu plate and temperature was elevated to about 50 °C, which is onset temperature of melting endothermic reaction [7], and then the shots were pressed by another Cu plate using a pressure of 50 g/cm^2. The various samples dealt with in this study have been labeled as AE (etched Cu without polymer), AEP (PPS layer on an etched Cu substrate), AEPH, AEPN, and AEPO (plasma-treated AEP samples with H_2, N_2, and O_2 gases, respectively).

3. Results and discussion

Fig. 2 shows the SEM images of the Cu substrate surface prepared at different conditions. The surface of AE exhibited leaf shaped morphology and the surface roughness of the Cu substrate dramatically increased (Fig. 2(b)) when compared to that of the substrate before etching. After PPS deposition, the leaf shaped morphology of the samples (Fig. 2(c)) was not changed. After plasma treatment, there were also hardly any changes in the surface morphologies of the samples (Fig. 2(d)–(f)) when compared to that of AEP.

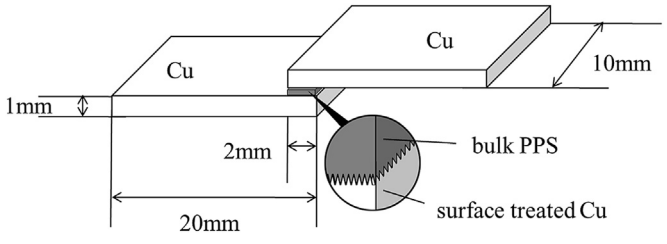

Fig. 1. Schematic of the specimen used for the shear lap test.

The wettabilities of AE, AEP, and plasma-treated AEP samples were measured and the results are shown in Table 1. For the AE sample, the CAs of water, ethylene glycol (EG), and *n*-octane were 7.5°, 3.8°, and 2.4°, respectively. The CAs of water on AEP was larger than that on the AE by about 95.6°. Hence, the hydrophobic nature of the PPS layer deposited on the surface of AE could be confirmed. After plasma treatment, the nature of AEPO and AEPN sample surfaces became hydrophilic, while the AEPH sample became slightly more hydrophobic when compared to the AEP samples. The SEs of the samples were calculated from the CAs by employing the OWRK method [21]. The total SE was composed of dispersive, polar, and H–H components.

The increase in the total SEs is considered to result from the increase in the polar component of the SE as a consequence of the binding of hydrophilic groups to the surfaces of AE, AEPN, and AEPO samples. These results seem to suggest that low SEs and high CAs may enhance the adhesion between bulk PPS and PPS-coated Cu plate because of the presence of an identical hydrophobic PPS.

Fig. 3 shows the results of the high-resolution XPS analysis and presents the Cu 2p, C 1s, and O 1s peaks acquired from pure-Cu and plasma-treated AEP samples. However, the peak corresponding to S 1s was absent in the spectra because of the insignificant amount of S atoms in the deposited PPS thin layer and hence, the peak is not displayed here.

In the case of the Cu 2p peaks, peaks associated with binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core levels were observed at 932.7 and 953.0 eV, respectively (Fig. 3(a)). The peaks obtained from AEPN and AEPO samples became broad and other less intense satellite peaks also appeared. The main broad Cu $2p_{3/2}$ peak of AEPO could be deconvoluted into two peaks, which are marked as A and B in Fig. 3(b). The peaks A and B can be related to Cu_2O or Cu and CuO, respectively [22]. The Cu and Cu_2O peaks are indistinguishable by the fitting procedure used in this study because of the proximity in the binding energies of the two species that differ by only within 0.1 eV [23]. The presence of Cu–O binding groups on the surfaces of APEN and APEO samples obtained by N_2 and O_2 plasma treatment, respectively, may be inferred from these results. This behavior may be attributed to the decomposition of the polymer in part by the reaction with the reactive N_2 or O_2 plasmas. The C 1s peaks (Fig. 3(c)) were similar for all the samples, except for pure-Cu and AE samples on which PPS thin layer was not deposited.

In the case of O 1s peaks (Fig. 3(d)), four peaks associated with –OH, C–O, Cu–O–Cu and Cu–O were deconvoluted [22,24,25]. In the pure-Cu sample, the oxygen bonding groups associated with Cu were observed. The most part of them was Cu_2O which is naturally oxidized in the ambient air. On the other hand, the increased signal of hydroxyl group (–OH) was detected in the AE sample, which might be induced by chemical etching. In case of the AEPH sample, hydrogen radicals could cleave the –OH bonded with surficial carbon and then ether group (–COC–) would be formed owing to reaction between atmospheric oxygen molecules and carbon [26]. It is assumed by increasing the intensity of –CO group and decreasing the intensity of –OH group, which led the increase of hydrophobicity of the deposited PPS layer [27]. However, In the AEPO and AEPN samples, the area from the hydroxyl groups was increased by 24% than that of AEP sample. This behavior may be due to the binding of oxygen-containing radicals such as –O and –OH to the surface of the samples.

Compared to the pure-Cu and AE samples, the intensities of the peaks corresponding to Cu–O–Cu obtained from AEP and AEPH could be not changed due to the contribution of the relatively small amount of oxygen only in air. Meanwhile, the intensities of the peaks corresponding to Cu–O obtained from AEPN and AEPO could be increased owing to the exposure of the etched-Cu with rough surface by reaction of the polymer and N_2 or O_2 plasma in part.