Application of Wood-Utilized Synthesized Copper-Based Particle for the Improvement of Wear Resistance of Epoxy Resin

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Abstract

Improving the wear resistance of polymer-based materials can lead to high energy efficiency of transport machineries owing to the higher strength-to-weight ratio. Oxidized wood-utilized synthesized copper-based particles (OWCu) was incorporated into epoxy resin to investigate its effect on the wear resistance of OWCu-incorporated epoxy with the steel counterpart using a ball-on-plate tribometer. OWCu was mainly composed of CuO with a small amount of graphitic carbon, and the average particle size was approximately 0.5 μm. A higher wear resistance was observed for the OWCu-incorporated epoxy at more than 0.6 mass% compared to the neat epoxy. The mechanism for the improvement of the wear resistance property was discussed, and it was revealed that the surface roughness of the steel counterpart was maintained at a low level for the OWCu-incorporated epoxy, which played a dominant role in reducing the wear of the OWCu-incorporated epoxy. The polishing effect of OWCu could reduce the surface roughness of the steel counterpart in the friction process. In addition, at higher concentrations of more than 5.0 mass%, OWCu adhered to the steel surface, which decreased the wear of the steel surface. OWCu is a promising material to enhance the wear resistance of polymer-based materials, especially with low elongation.

Keywords
copper-based particle, wood-utilized synthesis, friction, wear resistance, epoxy

1 Introduction

Recently, lightweight materials such as fiber-reinforced composites have become the material of choice for transportation systems. The reason is that their usage can significantly enhance the energy efficiency of transportation systems. However, when compared with metal-based materials, composite materials have disadvantage in the wear resistance properties due to the use of resin-based materials as matrix. Therefore, it is important to improve the wear resistance properties of the resin to enhance the applicability of composite materials for mechanical parts.

Various properties such as the mechanical and thermal properties of resin-based materials can be improved by incorporating fillers [1–3]. With regard to the frictional properties, the incorporation of metal-based particles [4–14], polymer-based particles [14–16], and carbon-based particles [17–23] can improve the friction and wear resistance properties. While the mechanism for the improvement of friction and wear resistance of resin-based materials has not been completely clarified, metal particles incorporated in resin function by reacting with the metal counterpart and assisting in the formation of a transfer film of the resin on its metal counterpart, thus reducing the friction and wear of resins [4, 5, 24].

Wood-utilized synthesis of metal particles is a process that utilizes natural wood to synthesize carbon or metal particles [25–29]. The particles are formed in the wood cell microstructure as a growth medium. Since metal particles can be produced on a large scale, cost-effective metal particles are produced using this process. In addition, wood-utilized synthesized metal particles contain unique compositions based on natural wood, including carbon, which possesses low friction and high wear resistance properties of bearing steel as a lubricant additive under boundary lubrication conditions [28]. Therefore, the incorporation of wood-utilized synthesized metal particles in a resin could effectively improve the wear resistance of resin-based materials. In addition, the development of cost-effective fillers could increase the applications of wear-resistant polymer materials. In this study, oxidized wood-utilized synthesized copper-based particles (OWCu) were incorporated into epoxy resin to investigate the improvement of the wear resistance of the composite. Epoxy has been used as a matrix resin for fiber-
reinforced plastic. However, the tribological properties are not favorable [30, 31]. The friction and wear resistance of the composite was evaluated using a ball-on-plate friction test with a metal counterpart under water lubrication conditions and the role of the OWCu was discussed.

2 Experiments

The processes involved in the synthesis of OWCu were described in a previous study [28]. First, wood powders of Japanese cedar were mixed with an aqueous metal-salt solution of copper nitrate and dried to adsorb Cu ions onto the wood powder surface. The treated wood powders were heated under a nitrogen flow of 0.4 L/min at 400°C for 1 h. After oxidation by heating in air at 600°C for 2 h to eliminate the amorphous carbon, powdered-state OWCu was obtained. Figure 1 shows the characterization of OWCu using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The particles consist of copper, oxygen, and carbon, and the average particle size is 0.64 μm, as measured by SEM image shown in Fig. 1(b). The crystalline structure of the OWCu is mainly composed of CuO, as identified by XRD shown in Fig. 1(c). In addition, graphitic carbon was also included.

Bisphenol-A epoxy resin (JER828 with ST11 hardener, Mitsubishi Chemical Corporation) was used as the base material. OWCu was dispersed in epoxy resin at various concentrations (0.6–10 mass%) using mechanical stirring and ultrasonication. After defoaming in vacuum, the epoxy resin was cured at 80°C for 5 h and at 20°C for 24 h with a thickness of 0.1 mm. The surface morphologies of the composite specimens were observed using confocal laser microscopy.

The mechanical properties of the specimens were measured by tensile and nanoindentation tests. For tensile tests, dumbbell-shaped specimens were prepared by mechanically cutting the cured epoxy resin using a mold (length of 35 mm, width of 6 mm, gauge length of 12 mm and width of 2 mm). Tensile tests were conducted at 0–10 mass% to measure the tensile strength, tensile modulus, and elongation averaged by 5 specimens. The indentation hardness and modulus were measured by nanoindentation tests at the maximum indentation load of 100 mN. The measurements were carried out 100 times using the Berkovich tip to evaluate the average indentation hardness and modulus.

The wear resistance of the composite specimens was measured using reciprocating ball-on-plate friction tests under water lubrication conditions. Epoxy plates containing OWCu were tested using a 100Cr6 steel ball with a diameter of 2 mm as the counterpart. A normal load of 1 N was applied by dead weight. A sinusoidal reciprocation at amplitude of 2.5 mm and a frequency of 5 Hz were applied to the plate. Friction forces were measured using a strain gauge installed on the ball side. Wear volumes were evaluated for the cross-sectional area of the wear track using confocal laser microscopy. Specific wear rates were calculated by the wear volume at unit sliding length and load; it was evaluated at 36,000 cycles for the OWCu concentration effect and at 18,000 cycles for the initial steel surface roughness effect. The area surface roughness Sa was measured. The worn surfaces of the composite and steel ball were observed by SEM, and elemental analysis was conducted by energy dispersive X-ray spectroscopy (EDX).

3 Results

3.1 Fabrication of OWCu-incorporated epoxy

Figure 2 shows the optical microscopy images of the OWCu-incorporated epoxy. OWCu is uniformly dispersed in
the epoxy. At a concentration of 5.0 mass%, as shown in Fig. 2(c), partially agglomerated OWCu particles more than 10 μm in diameter were observed. The surface roughness of the composite is shown in Fig. 2(d). Sa ranges from 0.1 to 0.3 μm and tends to be higher than 0.2 μm at more than 5.0 mass% of the OWCu.

Figure 3 shows the tensile test results of the OWCu-incorporated epoxy. For the neat epoxy, a tensile strength of 66 MPa, an elastic modulus of 1421 MPa, and an elongation of 6.8% were measured. With the incorporation of OWCu, no notable changes in the concentration of OWCu were observed for the tensile strength, elastic modulus, and elongation in the concentration of OWCu 0–10 mass%. Figure 4 shows the nanoindentation test results. The increase in the indentation hardness and modulus compared to the neat epoxy was detected by the incorporation of OWCu at the concentration of 1.2 and 5.0 mass%, and it deteriorated at a higher content of 5.0 mass%.

3.2 Tribological properties of OWCu-incorporated epoxy

Figure 5 shows friction coefficients of the OWCu-incorporated epoxy measured by ball-on-plate reciprocation tribometer. Friction coefficient gradually increased with an increase in the number of cycles till 10,000 cycles, and then it became constant. The stable regions of 18,000–36,000 cycles were averaged in Fig. 5(b). More than 5.0 mass% of OWCu resulted in an approximately 25% decrease in the friction coefficient, as shown in Fig. 5(b). Carbon content in OWCu could support friction reduction of the composite.

Figure 6 shows the SEM images of the wear track of the OWCu-incorporated epoxy with concentrations of 0, 1.2, and 5.0 mass% at 36,000 cycles. The sliding is in the perpendicular direction. Abrasive wear surface was observed for 0 mass%, where severe wear tracks were formed parallel to the sliding direction. In contrast, the wear tracks parallel to the sliding direction were not observed for the OWCu-incorporated epoxy. Additionally, relatively smooth wear surface was formed for 1.2 mass% compared to 5.0 mass%, in which irregular hollows were formed, as indicated in Fig. 6(c).

Figure 7 shows the wear-resistance property of the OWCu-incorporated epoxy. The wear volumes for 0, 1.2, and 5.0 mass% were compared.
mass% OWCu-incorporated epoxy increased proportional to the number of cycles. Additionally, OWCu-incorporated epoxy indicated lower wear volume compared to the neat epoxy, which implies that higher wear resistance was indicated with OWCu. Specific wear rates at 36,000 cycles with the OWCu concentrations are shown in Fig. 7(b). It was clear that lower specific wear rates compared to neat epoxy were observed for all tested concentration of 0.6–10 mass%, and the lowest specific wear rate was obtained at 1.2 mass%.

Figure 8 shows wear scars of the steel ball slide with the OWCu-incorporated epoxy at 36,000 cycles observed using optical microscopy and confocal laser microscopy. Clear wear scars were observed at 0, 1.2, and 5.0 mass%. The surface roughness of the steel ball slide with neat epoxy was relatively higher than that with OWCu-incorporated epoxy. The specific wear rates of the steel ball were highly depending on the OWCu concentration. The minimum value of less than 1.0×10^-6 mm^3/Nm was observed at more than 5.0 mass% of OWCu. Figure 9 shows the transition of the surface roughness of the steel ball with the number of cycles. It was clear that the surface roughness gradually increased with the number of cycles for 0, 1.2, and 5.0 mass%, which is approximately proportional to the number of cycles. Therefore, the increase in the surface roughness of the steel ball by friction for neat epoxy was higher than that for OWCu-incorporated epoxy.

Figure 10 shows SEM images of the wear scar on the steel ball for 0, 1.2, and 5.0 mass% at 36,000 cycles. The sliding is in the perpendicular direction. In the magnified images, severe wear tracks parallel to the sliding direction, caused by abrasive wear, were observed for 0 mass% as well as the epoxy surface. Relatively mild abrasive wear tracks were observed for 1.2 mass%, where the highest wear resistance of the composite was obtained. In contrast, continuous abrasive wear tracks parallel...
to the sliding direction were not observed for 5.0 mass%. The EDX results of the wear scars indicated by the boxes in the SEM images are shown in Fig. 10(d). The steel ball before friction test is shown as comparison. The composition for the 1.2 mass% showed almost no change compared with the surface before test. An increase in carbon was observed for 0 and 5.0 mass%, which corresponds to the transfer of the epoxy composite. Moreover, copper and oxygen contents were observed for 5.0 mass%, which corresponds to the OWCu included in the composite. It was noted that almost no OWCu was transferred to the steel surface slide with 1.2 mass% OWCu-incorporated epoxy. The reasons are discussed below.

4 Discussion

The wear resistance of the epoxy was improved by the incorporation of OWCu. A possible effect of the OWCu on the wear resistance of epoxy is due to its mechanical properties. The tensile strength, elastic modulus, and elongation of the epoxy were not changed by the addition of OWCu. In general, the elongation of the polymers highly affects the wear resistance property, where higher elongation results in higher wear resistance [30], although this is not the case in this study. In contrast, the indentation properties of epoxy were improved by the addition of OWCu, especially at a concentration of 1.2 mass%, which helped to improve the wear resistance of the OWCu-incorporated epoxy.

The wear resistance of low-elongation polymers as epoxy is highly affected by the roughness of the harder steel counterpart [30]. Figure 11 shows the effect of the initial surface roughness of the steel ball on the specific wear rate of the neat epoxy, which was evaluated at 18,000 cycles. The specific wear rate was almost proportional to the Sa of the steel ball; that is, the increase in the roughness of the steel ball due to friction results in an increase in the specific wear rate of the epoxy. In fact, it was observed that the surface roughness of the steel ball slide with neat epoxy was higher than that of the OWCu-incorporated epoxy, as shown in Fig. 8. Therefore, it is thought that the lower roughness of steel ball sliding with the OWCu-incorporated epoxy would reduce the wear amount of the composite. The surface roughness of the steel was related to the wear of the steel. It has been reported that 100Cr6 steel, which is harder than epoxy, is worn by sliding with soft polymers because of the formation of large wear debris induced by the tribo-induced chemical reaction of iron [32]. The severe abrasive wear scars of the steel ball slide with neat epoxy, as shown in Fig. 10(a), corresponds to this phenomenon. The wear volume of the steel
ball was revealed to depend on the concentration of the OWCu, where more than 2 mass% of OWCu reduced the wear of the steel ball, as shown in Fig. 8(d). At 5.0 mass% of OWCu, copper was detected on the steel ball surface by EDX. This means that OWCu was adhered to the steel ball surface at a concentration of more than 2.0 mass%. The adhesion of OWCu on the steel ball could reduce the wear of the steel ball because of the restriction of the tribo-induced chemical reaction of the steel and resulted in the reduction of the Sa. The highest wear resistance of the composite, however, was obtained at 1.2 mass%, in which no adhesion of OWCu on the steel ball was observed. This could be due to no existence of large agglomerated particles of OWCu at 1.2 mass% as shown in Fig. 2. Characteristically, the surface roughness of the steel ball was as low as 5.0 mass% despite the higher wear amount of the steel ball for 1.2 mass%, where severe abrasive wear tracks of steel were not observed, as shown in Fig. 10(b). This could be explained by the polishing effect of OWCu. The worn steel surface could be polished by the OWCu while the surface roughness was maintained at a low level. Consequently, the wear of the composite decreased at a concentration of 1.2 mass%. In fact, uniform wear tracks parallel to the sliding direction were observed on the steel surface, as shown in Fig. 10(b). As another characteristic feature for the 1.2 mass% having best wear resistance, no transfer of epoxy on the
steel ball occurred. Compared to the 5.0 mass%, the transfer of the epoxy could cause degradation of the wear resistance property of the OWCu-incorporated epoxy. In addition, OWCu removal from the epoxy matrix would cause the degradation of the wear resistance at 5.0 mass%. OWCu is a promising material to enhance the wear resistance of polymer-based materials, especially having low elongation.

5 Conclusion

The incorporation of OWCu improved the wear resistance of epoxy. At a concentration of 1.2 mass%, OWCu leads to the highest wear resistance. The dominant mechanism for the improvement in the wear resistance of epoxy is explained by the polishing effect of the OWCu on the steel ball, which enables the steel ball to maintain surface roughness, Sa, as low as 0.5 μm. Additionally, the polishing effect of the OWCu on the steel ball prevents the transfer of the epoxy on the steel ball surface, which may cause degradation of the wear resistance of the OWCu-incorporated epoxy. The adhesion of the OWCu on the steel ball occurs at more than 5 mass%, and the wear of the steel drastically decreases. OWCu is a promising material to enhance the wear resistance of low-elongation polymer materials.

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References


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