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SiO_2-reinforced Poly (methyl methacrylate): Tribology Performance as Service Life Sensor

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Poly (methyl methacrylate) (PMMA), which is suitable for use in the human body owing to its biocompatibility, is commonly used in medical applications such as bone nails, bone cement, and dentures. However, owing to its hard and brittle nature, PMMA can cause damage when it is subjected to excessive stress and can also cause severe wear. In this study, three different sizes of silica particles were used as reinforcing additives to enhance the wear resistance of PMMA composites. A pin-on-disk wear test was conducted to record the coefficient of friction and wear volume, and the wear volume was measured using a 3D laser scanning microscope. In the wear test, the transfer film of micron and submicron particles produced a plowing effect, resulting in wide grooved wear scars and a higher wear rate than the raw material. The nanoparticle transfer film reduced direct material wear, the wear scars were fine and flat, and the wear rate was decreased, reducing the wear of SiO_2-reinforced PMMA composites by 40%. The experimental results revealed that the wear volume is proportional to the wear time. In addition, the observed area of the transfer film on the wear counterpart can be used as a service life sensor of the coating material.

1. Introduction

Developments in medical sciences are becoming increasingly important with the advent of the aging society.(1) All organs and joints in the human body are subject to wear and tear over time. Degeneration of the hip and knee joints is a common disease in middle-aged and elderly people, which may lead to deformity, joint pain, and even motor dysfunction in severe cases.(2,3)

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As a result, joint replacement surgery has been developed to improve the quality of life. According to multiple studies, over 450000 joint replacements are performed annually in the United States (population: 300 million), and 15000 replacements are performed in Taiwan (population: 23 million).(4,5) The goal of a joint replacement is to remove the diseased area, which is the mainstay treatment for severe arthritis, providing pain relief and restoring joint function and range of motion.(2)

Joint replacement surgery is common, but the life span of artificial joints, i.e., implants, is limited. Common implant materials include stainless steel, cobalt-chrome, zirconia, titanium, tantalum, ceramics, and polymers, with metal being the bulk material. As such, implant materials must be considered for corrosion, biocompatibility, friction, and joint surface wear. Usually, these materials degrade after 10–15 years of use; thus, patients must undergo revision surgery after a specific period.(6) Many factors result in the need for joint revision surgery, such as aseptic loosening, subluxation, osteolysis, fracture, infection, rupture and wear, and pain.(7)

The surface of biomaterials is modified to improve the implant surface's biological, chemical, and mechanical properties to enhance corrosion resistance, wear resistance, antibacterial properties, and tissue compatibility. Surface modification techniques include surface texturing, surface grafting, and surface coating, which are applied to reduce the friction and wear of implants.(8) Among the surface coating methods, sol-gel deposition offers advantages such as high uniformity, low sintering temperature, and complex-shaped coatings.

Coatings are often used in industrial applications, especially to provide protective properties such as anti-wear and lubrication.(9,10) During the friction process of polymer materials, the materials wear and generate debris, which is not immediately removed from the system and adheres to the surface of the wear-resistant part during the friction cycle, forming a transfer film, a third body, which reduces the direct friction between materials, thus improving the friction performance. Fibers and particles added while preparing polymer composite materials are released and rolled into the interface to reduce friction during the friction process. The broken polymer and released particles accumulate on the surface of the wear-resistant part to form a composite film.(11)

Godet(12) proposed the third-body concept to explain the change in wear patterns during friction. The third body is defined as the medium between two contact surfaces, which may be composed of artificially injected lubricant or abrasive particles separated from the friction surface. Under dry friction, the third body usually comprises particles separated from the friction surface. Berthier *et al.*(13) proposed the velocity regulation mode, in which five interfaces and four regulation modes exist to accommodate the velocity difference between the two first bodies in the three-body concept. Descartes and Berthier(14) introduced the concepts of rheology and third-body flow to establish a tribological circuit for friction cycles. In the friction process, the material is broken to produce separated particles, and the particles are broken, accumulated, and discharged in the system to form a third-body flow. The wear and friction coefficient (COF) change with increasing duration. Therefore, the third body can be used as a sensor for predicting the lifetime of materials.(15,16) In this study, it was assumed that a SiO_2-reinforced additive could enhance the wear resistance of Poly (methyl methacrylate) (PMMA). In addition, because of the additive, the wear of the SiO_2/PMMA composite material can be more easily observed.

Therefore, the tribological properties of a SiO_2/PMMA protective coating on the surface of human implants should change linearly over time and can be used as a service life sensor.(16)

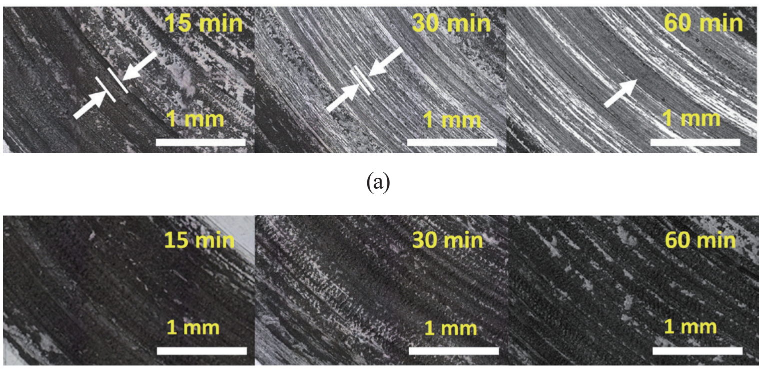
2. Materials and Methods

Commercially available PMMA is produced using the in situ polymerization method and is mainly used in photo frames and display stands. The manufacturing process of lab-made PMMA/SiO_2 composites can be found in the literature.(17) In this study, SiO_2 particles with different particle sizes and concentrations were used as additives to form the composite material. The particle sizes were 22, 234, and 1202 nm and the concentrations were 0.05, 0.1, 0.2, and 0.3 vol.%. The wear property of the composite material was measured using a pin-on-disk rotary wear tester (POD-FM406-10NT, Fu Li Fong Precision Machine, Kaohsiung, Taiwan). The material was a 25-mm-diameter circular specimen, and the wear-resistant part was 5 mm in diameter, 10 mm in length, and made of an SUJ2 bearing steel pin. The test conditions were a pressure of 1.2 MPa, a rotation speed of 300 rpm, and wear times of 15, 30, and 60 min. The wear test was performed at 25 °C and RH 70%. After completing the wear test, the wear scar area was measured with a 3D laser profile microscope (VK-9500, Keyence, Japan) to calculate the wear volume. In this experiment, the transfer film on the pin was photographed using the 3D laser profile microscope, and the ratio of the transfer film area was calculated using Image J.

3. Results and Discussion

3.1 Observation of PMMA/SiO_2 wear scars

Figure 1 shows the wear scars of commercially available acrylic and lab-made PMMA samples. After 15 min, the broken PMMA had formed wear debris and entered the friction cycle; the coarser abrasive grains produced a plowing phenomenon, causing wide grooved wear scars. After 30 min, the wear debris had been pulverized and refined through multiple cycles, reducing the width of the fine lines in the wear scars. Finally, after 60 min, a PMMA transfer film had



(b)

Fig. 1. (Color online) Wear scars of (a) commercially available PMMA and (b) lab-made PMMA.

appeared on the wear-resistant part, and the groove-like fine lines had mixed with the flat wear scars appearing in the wear scars. The formation mechanism of the transfer layer is the accumulation of wear debris.[18]

Figure 2 shows the wear scars of the nanocomposite material. After 15 min, the samples showed wide grooved wear scars. After 30 min, the width of the fine lines of wear scars had decreased, and several flat wear scars had appeared. Figure 3 shows the wear scars of the submicron composite material. After 15 min, grooved wear scars had appeared in all samples. After 30 min, the widths of the fine lines of the 0.05 and 0.1% samples had decreased, whereas the 0.2 and 0.3% samples still showed wide grooved wear scars. After 60 min, the width of the fine lines in the wear scars had decreased, but there are more wide fine lines than those for the nanocomposite material.

Figure 4 shows the wear scars of the micron composite material. After 15 min, all samples showed grooved wear scars. After 30 min, the fine lines of the 0.05 and 0.1% samples had reduced in width, whereas the 0.2% sample still showed wide grooved wear scars and the 0.3% sample showed jumping and discontinuous wear scars. After 60 min, the 0.2% sample showed wide grooved wear scars mixed with flat ones, while the 0.3% sample still showed many discontinuous wear scars.

These wear scars suggest that the transfer films of micron and submicron particles cause plowing during the wear process, resulting in many grooved wear scars. In contrast, the transfer film of nanoparticles reduces the plowing phenomenon and leads to many flat wear scars.

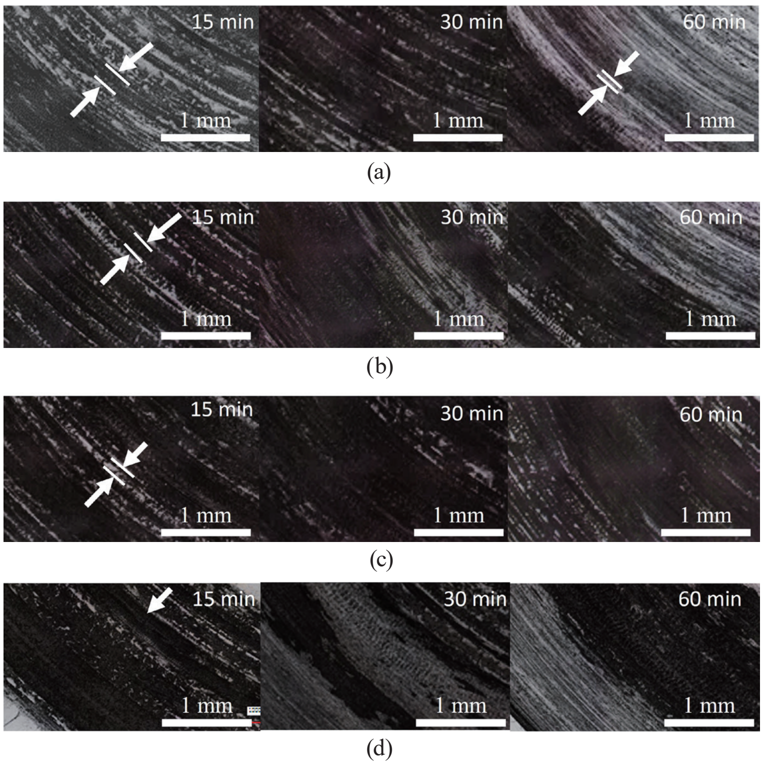


Fig. 2. Wear scars of nanocomposite material for concentrations of (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.3%.

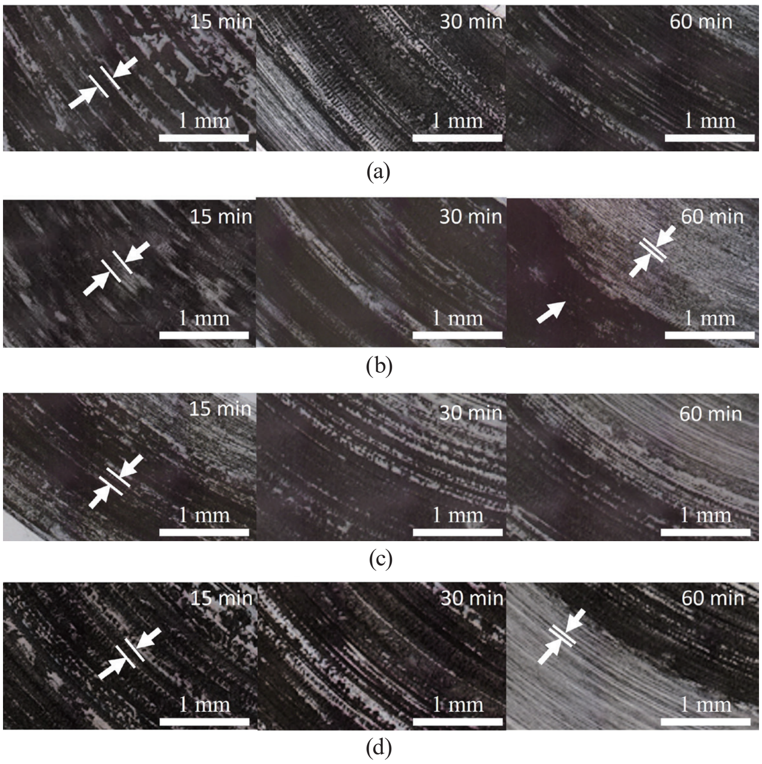


Fig. 3. Wear scars of submicron composite material for concentrations of (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.3%.

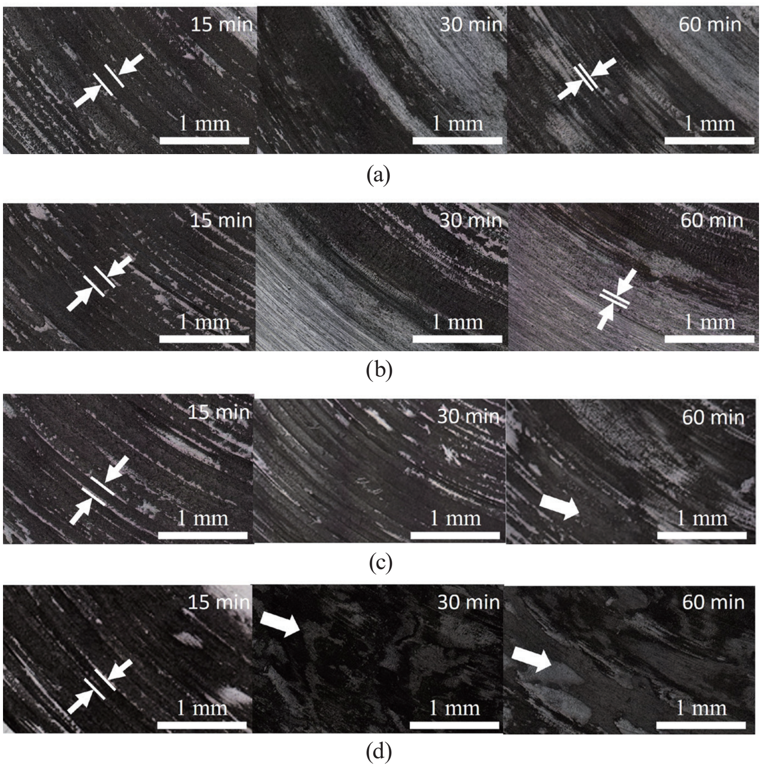
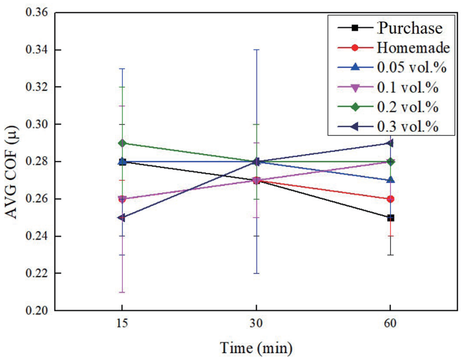


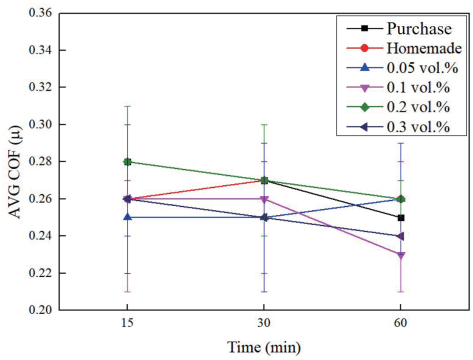
Fig. 4. Wear scars of micron composite material for concentrations of (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.3%.

3.2 Comparison of COF and wear rate of PMMA/SiO_2

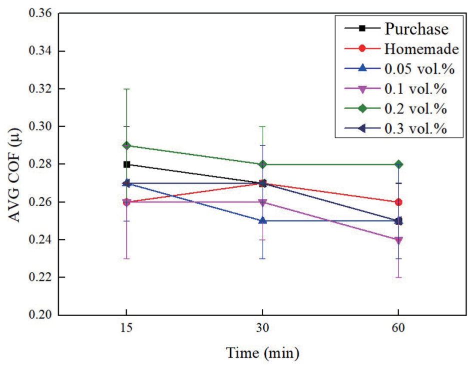
Figure 5 shows the variation in the COF of the composite materials. The COFs of the composite material and PMMA are both in the range of 0.27 ± 0.02, and the COF decreases slightly with increasing wear time. As the variation between the groups is insignificant, the variation in the COF cannot be used to judge the service life. Figure 6 shows the area of the transfer film of the wear-resistant part, which is approximately 20% at 15 min and increases with time to approximately 50% at 60 min. Thus, the service life of the transfer film can be evaluated from its area after long use periods. Figure 7 shows the relationship between the wear volume and dissipation energy of the composite materials. As the load applied in this experiment was fixed, this figure can be considered to indicate the relationship between the wear volume of the composite material and the wear rate. Two main points can be observed from Fig. 7. One is that the composite material with added SiO_2 has excellent wear resistance (superior to that of commercially available products) and that the effectiveness of using SiO_2 nanoparticles as the reinforcing factor is greatest. The second is that the coating of the composite material increases linearly with the time of use. Debris is produced during the wear of the composite material, which is brought into the wear cycle to produce a plowing effect. After 15 min, all samples showed wide and deep grooved wear scars. Over time, the debris was broken in the system cycle, the filler in the debris was released, and a transfer film was formed on the surface of the wear-



(a)



(b)



(c)

Fig. 5. (Color online) COF of PMMA composites with additives of (a) nanoparticles, (b) submicron particles, and (c) micron particles.

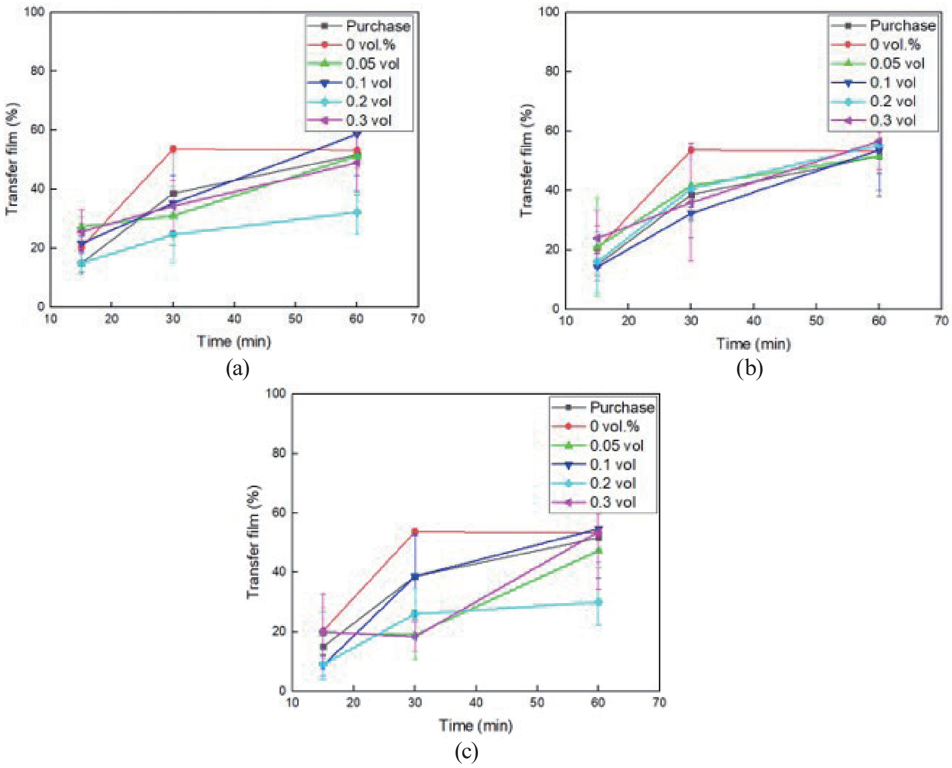


Fig. 6. (Color online) Area of transfer film of PMMA composites with additives of (a) nanoparticles, (b) submicron particles, and (c) micron particles.

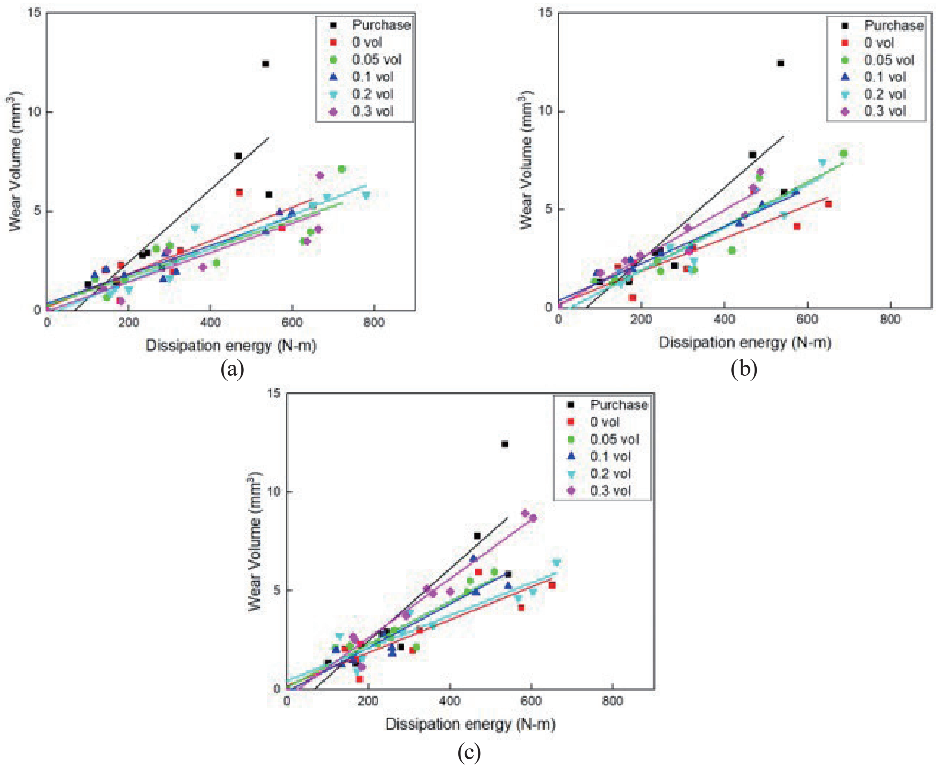


Fig. 7. (Color online) Tribology performance of PMMA composites with additives of (a) nanoparticles, (b) submicron particles, and (c) micron particles.

resistant part. After 30 min, the transfer film of the nanoparticles had formed flat wear scars and had a lower wear rate. In contrast, the transfer films of the submicron and micron particles produced a plowing effect, resulting in wider fine lines and a higher wear rate. After increasing the concentration of added micron particles to 0.3%, the friction between the transfer film and the accumulated particles generated vibration and discontinuous wear scars. Overall, the area of the transfer film can be used as the basis for the service life of the coating and as a sensor for evaluating the service life of the coating.

4. Conclusions

Nano-SiO_2 additives effectively improve the wear resistance of PMMA composites by 40%, which makes wear scars easier to observe, promotes the production of the transfer film, and improves the wear resistance of the composites. In the wear process, a transfer film appears and increases with time. The nanoparticle transfer film reduces the plowing effect and wear rate, while the transfer films with submicron and micron particles plow the substrate and cause wider and deeper grooved wear scars, increasing the wear rate. Because the wear properties of the SiO_2/PMMA composite material change linearly with time, it can be used as a service life sensor of protective coatings on the surface of human implants.

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