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Cellulose/Collagen Hybrid Lubricant in Artificial Knee Joint as a Potential Service Life Sensor

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The combination of ultrahigh-molecular-weight polyethylene (UHMWPE) pads and zirconia joints has been used extensively in all artificial knee joints. The wear of UHMWPE is the leading cause of artificial joint failure. However, it is unlikely to detect UHMWPE damage until the patient feels pain. Therefore, developing a sensor to detect the wear of UHMWPE outside the human body is crucial. In this study, the surface of UHMWPE and zirconia was treated with low-temperature atmospheric plasma to increase the surface energy so that the lubricating fluid can be effectively adsorbed on the surface of the material. Furthermore, adding the appropriate proportion of hydroxypropyl methylcellulose with collagen produces good self-assembly behavior, which can reduce the UHMWPE wear and coefficient of friction (COF) by 50%. Therefore, the wear consumption of UHMWPE can be observed simply by sensing the changes in COF, which can be used as a life sensor for joint damage. At a distance of 9500 m continuous use, the COF increases by 17%, which means that the use of UHMWPE can be predicted by detecting the changes in COF. Finally, we proposed that the artificial knee joint's service life can be detected by monitoring the variation in COF.

1. Introduction

According to the Agency for Healthcare Research and Quality, more than 600000 arthroplasties are performed each year in the United States. In general, knee arthroplasty lasts approximately 10 to 15 years. One of the causes of knee implant failure is the wear and tear of ultrahigh-molecular-weight polyethylene (UHMWPE) components in total knee arthroplasties. UHMWPE is made up of extremely long chains of polyethylene. It is a very tough thermoplastic material with superior impact strength. Its coefficient of friction (COF) is comparable to that of polytetrafluoroethylene (PTFE), but UHMWPE has a higher abrasion resistance than PTFE. It also has low moisture absorption, high chemical stability, high thermal conductivity, low dielectric constant, and UV resistance. Owing to its biocompatibility, UHMWPE is used in biomedical applications such as hip arthroplasty, total knee arthroplasty, and cervical artificial disc replacement. However, as the UHMWPE implant wears out, UHMWPE's wear particles

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can lead to osteolysis, which can accelerate loosening.[1] Kurtz *et al.* investigated the processing, manufacturing, and sterilization of UHMWPE in total joint arthroplasty and the degradation of UHMWPE liners after long-term implantation, as well as the fatigue behavior of oxidized UHMWPE.[2] Bao *et al.* conducted an in-depth study of the tribology of natural and artificial joints and investigated the important factors in designing an artificial disc.[3] Moreover, by compiling various papers, the incidence of osteolysis in total hip arthroplasty affected by wear rate was investigated. UHMWPE was studied for molecular chain modification, and highly cross-linked UHMWPE was developed to improve the traditional wear and tear conditions.

Moreover, the performance characteristics and effects of ceramic-on-ceramic, metal-on-metal, and ceramic-on-cross-linked UHMWPE total hip arthroplasties were investigated to determine the biological effects of metal ion release on the potential for acquired hypersensitivity, mutagenicity, and carcinogenicity.[4] Minoda and colleagues conducted several studies on the properties of polyethylene wear particles generated in arthroplasty and introduced a method of avoiding allogeneic blood transfusion after total knee arthroplasty.[5–7] In addition, they compared the ranges of motion of a standard posterior cruciate-retaining total knee prosthesis with those of a high-flexion posterior cruciate-retaining total knee prosthesis, and investigated the difference in bone mineral density between total knee arthroplasty components made from different materials. Wang *et al.* developed a simulation model to study the wear mechanisms of UHMWPE in total joint arthroplasty.[8] The model shows the interactions between the molecular structure of the UHMWPE and the multi-directional stress field experienced on the articular surfaces of artificial joints. Moreover, the fatigue, wear, deformation, and lubrication of the material were further investigated in the model.

Furthermore, the morphology of UHMWPE wear debris produced by a hip joint simulator was observed under lubricated conditions. Heuberger *et al.* studied the lubrication of artificial hip joints.[9] Synovial fluid is the lubricant of the natural joint; it contains a substantial concentration of albumin. Therefore, the hydrophilicity of the polymer surface has a significant effect on protein adsorption. Moreover, it indicates the different boundary lubrication properties of protein adsorbed on hydrophobic and hydrophilic surfaces.

The wear and tear of UHMWPE is the leading cause of the failure of arthroplasty. Therefore, we aimed to investigate the surface treatment and the improvement of lubricant performance to effectively reduce the wear rate and friction coefficient of the UHMWPE liner in total knee prosthesis without changing the structure of UHMWPE. From the above literature, protein adsorption is a crucial factor in determining the wear rate of UHMWPE. Therefore, in our study, we focus on two topics. First, we modify the surface energy of the artificial joint by low-temperature atmospheric-pressure plasma treatment that is environmentally friendly, nontoxic, and economical. Second, we determine the effect of surface energy change on protein adsorption, and discuss the wear behavior of UHMWPE.

Hydroxypropyl methylcellulose (HPMC) is a nonionic cellulose ether with good water solubility and biocompatibility. It is widely used as a film-forming, anticorrosion coating material and lubricant.[10–13] Ding *et al.* investigated the effect of HPMC on collagen fibril formation.[14] In this study, we show that higher tribology performance was obtained by adding the right amount of HPMC. This study helps us to understand the effect of the wear mechanism of UHMWPE when we integrate low-temperature atmospheric-pressure plasma treatment with collagen/HPMC composites to enhance the wear resistance of UHMWPE. Studies that utilized tribology behavior as an indicator of device lifetime have also received increasing attention in recent years, especially in locations that are not easy to detect, such as in bearings[(15)] and space robots.[(16)] By monitoring tribology behavior, an early indication of wear and impending failure can provide an idea of the health of a machine.[(17)] This study serves two purposes. The first is to reduce the wear and COF of UHMWPE by understanding the wear mechanism of UHMWPE. The second is to observe the changes in the tribology properties of UHMWPE under long-term operation. After more detailed data are established in the future, it is possible to propose a model that predicts lifespan.

2. Materials and Methods

2.1 Preparation of collagen and collagen/HPMC solution

Collagen solution was prepared by adding 5–10 g of food-grade collagen (Nutrarex Biotech, Taichung, Taiwan) into 100 mL of deionized water, followed by ultrasonication for 20 min. HPMC solution was prepared by mixing 5 g of HPMC powder (Pharmacoat 606, Shin Etsu, Japan) with 100 mL of hot water (80 °C), followed by stirring for 60 min. The collagen/HPMC hybrid lubricant was prepared by mixing 100 mL of collagen solution with 25 mL (1:0.25) and 12.5 mL (1:0.125) of HPMC solution.

2.2 Low-temperature atmospheric-pressure plasma treatment

The atmospheric micro-plasma system consisted of a customized high-voltage AC power supply with a tenfold high-voltage amplifier (Taiwan Plasma Corp., Kaohsiung, Taiwan). The front nozzle comprised a quartz tube with an inner diameter of 2.8 mm. A sharply pointed copper tungsten rod of 1.6 mm diameter was used as the internal electrode. A stable plasma flame was generated by applying an 8 kHz/7000 VAC voltage to a parallel argon flow at a flow rate of 4 L/min.

2.3 Surface analysis

The water contact angle was measured using a Contact Angle System (FTA-1000B, First ten angstroms, Portsmouth, UK). Before and after modification, the chemical composition and structure of UHMWPE and ZrO_2 were characterized using a Fourier-transform infrared spectrometer (FTIR, Thermo Nicolet NEXUS 470, Golden Valley, MN, USA). In addition, the lubricant adsorption on UHMWPE was measured with an ultraprecision electronic balance (Precisa XS 225A-SC, Precisa Gravimetrics AG, Dietikon, Switzerland).

2.4 Tribology behavior of UHMWPE

The tribological performance of the hybrid lubricant was measured with the help of the ball-disk friction and wear tester (POD-FM406-10NT, Fu Li Fong Precision Machine, Kaohsiung, Taiwan). The upper counter ball was ZrO_2 (SABO-5406013, SCiKET, Taiwan), and the lower counter disk was UHMWPE (HiShiRon Industries Co., Ltd., Taiwan). The load was 5 N, the rotation radius was 6 mm, the sliding speed was 0.15 m/s, and the friction distance was 3800 m. The wear pair was installed in a metal container to add the lubricant. All tribological experiments are carried out in a well-controlled environment, where the temperature was approximately 25 °C and the relative humidity was 50%. The COF was monitored and recorded by sensors in real time, and the weight loss of UHMWPE was used to calculate the wear volume. The results obtained were derived from the average of three parallel experiments. In the long-distance wear experiment, the wear distance ranged from 1 to 9500 m. Therefore, the COF was recorded in each 1900 m.

3. Results and Discussion

3.1 Effect of plasma treatment on surface hydrophilicity

The effect of low-temperature atmospheric-pressure plasma treatment on the surface energy of UHMWPE and ZrO_2 is shown in Fig. 1. The water contact angle decreases when the plasma treatment duration increases. For example, the water contact angles of UHMWPE and ZrO_2 decreased by 74 and 84% after 360 s of treatment, respectively. This phenomenon indicates that the plasma treatment positively affects the hydrophilic behavior of these two materials.

The water contact angle decreased after the plasma treatment, chemical changes occurred on the surface of UHMWPE, and hydrophilic groups were formed, making the surface more hydrophilic. As shown in Fig. 2(a), FTIR was used to observe the changes in functional groups generated on the surface of materials. At 1725 cm^{-1}, the stretching vibration from C=O (1646

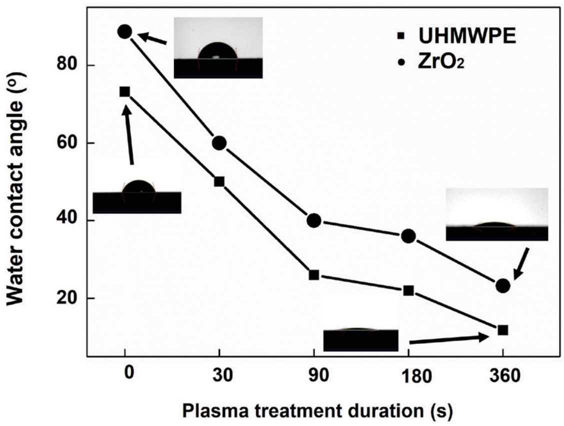


Fig. 1. Changes in water contact angles of UHMWPE and ZrO_2 surfaces after AP treatment.

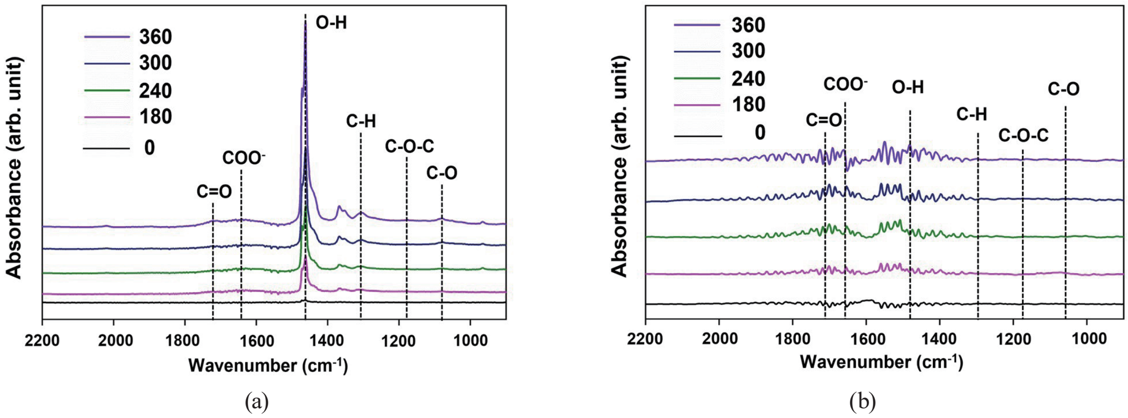


Fig. 2. (Color online) FTIR spectra after AP treatment of (a) UHMWPE and (b) ZrO_2.

cm^{-1}) corresponds to COO-asymmetric stretching. The stretching vibration of the hydroxyl group characterizes the characteristic peak at 1440 cm^{-1}, the 1300 cm^{-1} broadband corresponds to C–H stretching vibration, 1180 cm^{-1} corresponds to C–O–C bonding vibration, and 1075 cm^{-1} corresponds to C–O symmetric stretching. As shown in Fig. 2(b), the characteristic peaks show the mechanism of hydrophilicity enhancement of the UHMWPE surface after AP treatment.

3.2 Tribology behavior

To observe the tribological behavior of UHMWPE and ZrO_2 after the plasma treatment, we carried out an abrasion test by adding five different lubricants separately to the specimens. The results of the wear volume were recorded and are shown in Fig. 3. The experimental results showed that the wear of UHMWPE and ZrO_2 decreased significantly after plasma treatment, indicating the formation of hydrophilic groups on the surface, which positively contributes to the adsorption of lubricants. Plasma-treated UHMWPE specimens have a higher wear volume than ZrO_2 specimens because the surface of UHMWPE experienced an embrittlement phenomenon after long-term plasma treatment. The results of this experiment are consistent with those of Kurtz *et al.*(2) A comparison between 5 and 10% collagen showed that the 10% collagen has a higher anti-wear effect. This shows that the more lubricating substances are present at the interface of specimens, the higher the anti-wear effect. Therefore, HPMC plays an essential role to enhance the structure of lubricating substances. The anti-wear effect of the pure HPMC solution is similar to that of collagen. However, after mixing collagen with HPMC, the anti-wear effect becomes apparent, especially when the mixture ratio of collagen to HPMC is 4:1(C+H:1:0.25), where the anti-wear effect is highest. According to previous studies, mixing HPMC with collagen demonstrates good assembly behavior. In addition, mixing the HPMC solution with collagen: HPMC < 1:0.25 can make the collagen fibers smaller in diameter and densely packed, increasing the density of the lubricating boundary layer and reducing the wear volume.(18) We inferred that the reason for the improved anti-wear properties is that the micelle is more effectively absorbed at the interface, providing more lubrication.

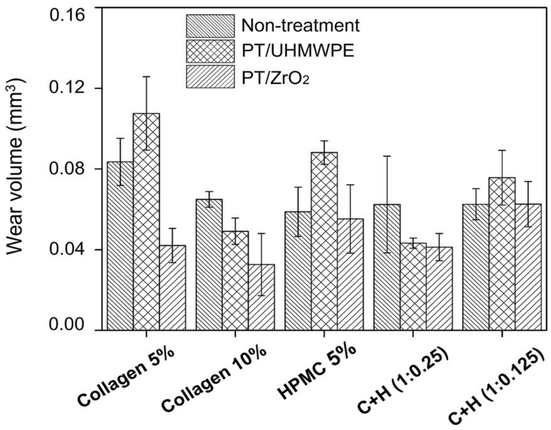


Fig. 3. Wear volumes of UHMWPE in different lubricants.

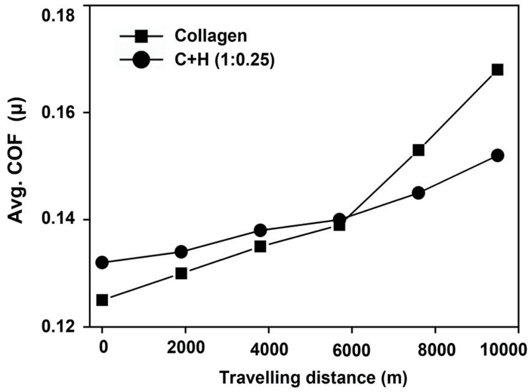


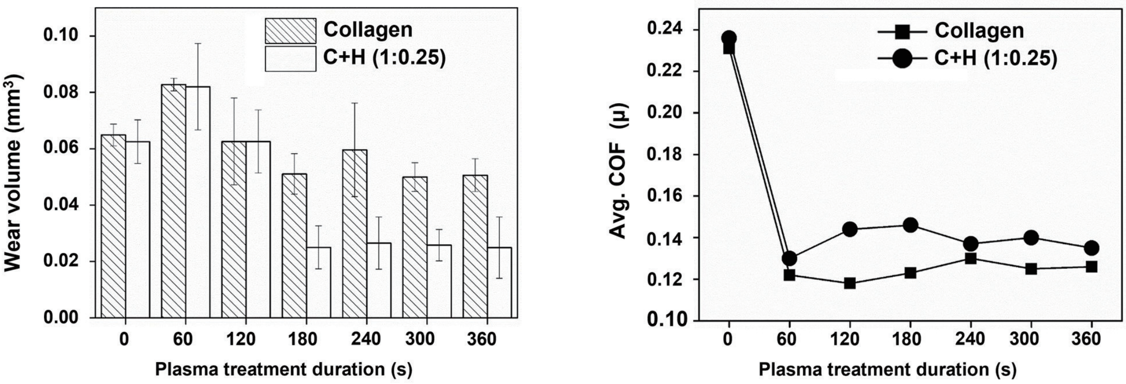
Fig. 4. Adsorption characteristics of the lubricant.

3.3 Lubricant absorption of PT/ZrO_2 in collagen/HPMC solution

It was not easy to observe the nanoscale fibers produced after mixing the food-grade collagen with HPMC. Therefore, the amount of hybrid lubricant adsorbed on the surface of UHMWPE was measured in this experiment as direct evidence. The results are shown in Fig. 4. The longer the duration of plasma treatment, the more hydrophilic groups are formed on the surface, allowing a higher amount of lubricant to be adsorbed. Moreover, the collagen/HPMC hybrid solution also produces a small-diameter fiber, which occupies a smaller surface and allows more molecules to be adsorbed on the surface. However, whether it is because of the increase in the number of hydrophilic groups formed or the miniaturization of fibers, which improves the wear mechanism, the main reason for the improved lubrication effect still needs to be further investigated. The difficulties we have to overcome are quantifying the formation of hydrophilic groups and observing the nanoscale fibers.

3.4 Potential service life sensor

Figure 5 shows that mixing the appropriate proportion of collagen with HPMC provides better grinding properties and reduces the COF of UHMWPE (plasma treatment of 240 s) by larger than 50%. The same results can be seen in Fig. 5(b), which can reduce the COF by 50% after plasma treatment. The COF and the grinding distance in the long-distance wear test are shown in Fig. 6. The average COF has a slow upward trend as the grinding distance increases, which means that the lubricant will deteriorate after a long period of operation. In a practical environment, it is difficult to measure the wear of UHMWPE as a replacement joint. Therefore, by monitoring COF changes, the surface condition of UHMWPE can be determined. In addition, the acoustic wave changes due to COF changes, as measured using an external acoustic sensor, can be used as a basis for determining the service life of UHMWPE.



(a) (b)

Fig. 5. (a) Wear volume and (b) average COF of UHMWPE with various plasma treatment times (wear conditions: 5 N, 3800 m).

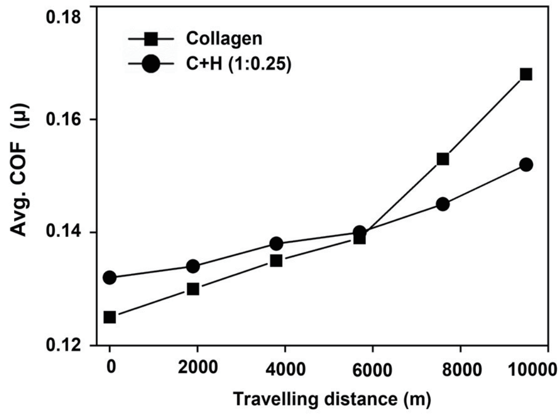


Fig. 6. Average COF for long-distance operation (wear conditions: 5 N, 1–9500 m).

4. Conclusions

Low-temperature atmospheric plasma treatment helps form hydrophilic groups on the UHMWPE and ZrO_2 surfaces, which is beneficial to the adsorption of subsequent lubricants and results in improved anti-wear properties. The collagen/HPMC hybrid lubricant has the highest anti-wear performance because the composite material produces tiny micelles, which help the hybrid lubricant adsorb on the UHMWPE and ZrO_2 surfaces. To effectively reduce the wear of UHMWPE in the UHMWPE-ZrO_2 artificial joint, the amount of lubricant adsorbed on the surface should be considered. When such an amount is high, the wear can be effectively suppressed. The surface tribology behavior of UHMWPE varies with the usage distance, mainly observed in COF. By adding a sound sensor, it can be known whether the implant surface produces wear. Therefore, it can be used as a reference for the service life of UHMWPE. However, the main reason for the trend observed in this study, that is, the COF increases with the service life, remains unknown. Whether the COF increases owing to the deterioration of lubricants caused by temperature or by the wear surface of UHMWPE, more analyses are needed to clarify the primary reason.

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