Transactions of the Materials Research Society of Japan 32[2] 579-582 (2007)

Nanoscale Surface Grafting with Phospholipid Polymer to Lubricate Polypropylene Surface

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The purpose of this study is obtaining both biocompatibility and lubricity to biomaterial surfaces. For this purpose, we investigated the effects of a graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) onto polypropylene (PP) surface. The MPC graft nanolayer was prepared using a photo-induced graft polymerization. The poly(MPC)-grafted (PMPC-*g*-PP) surface was characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and static and dynamic water contact angle measurements. As a result, the PMPC grafting clearly increased hydrophilicity and surface mobility. Friction coefficient was measured in air and in water. The friction coefficient of the PMPC surface was 0.019 in water, which was 1/10 compared with air condition. This value is similar to that of the human joints. After the friction test in water, the surface was observed with scanning electron spectroscopy. No flaw was observed on the PMPC surface. It was considered that the PMPC surface showed the behavior of hydrodynamic lubrication in water. Friction test was also performed under biological conditions; in phosphate buffered saline (PBS), PBS containing a bovine serum albumin, and cell culture medium containing fetal bovine serum. The results indicated that the PMPC surface kept highly lubricity under biological conditions.

Key words: phospholipid polymer, photo-induced graft polymerization, friction, hydrodynamic lubrication

1. INTRODUCTION

In recent years there has been increasing interest in surface modification with polymers to give a solid surface necessary surface properties. Among many surface properties, we aimed for giving both biocompatibility and lubricity to biomaterial surface. Lubricity is one of the essential properties for biomaterials such as artificial joints, blood pump bearings, and catheters. As for artificial joints, the loosening caused by wear between the articulating surfaces is the most serious problem limiting their survival and clinical success.

Surface modification is conducted using a variety of methods such as a plasma treatment, physical coating, and surface grafting. In this study we choose a surface-initiated photo-induced graft polymerization method. This polymerization has advantages in simplicity, efficiency and general versatility. The grafting location can be restricted to the surface attached benzophenone used as a photoinitiator. Using this method, we can obtain a polymer-grafted surface with strongly tethering by a covalent bond.

Selection of the grafting polymer is the next parameter. We used 2-methacryloyloxyethyl phosphorylcholine (MPC), which is well known for biocompatible polymer whose side chain is composed of phosphorylcholine resembling phospholipid of cell membrane[1-4]. The polymers with MPC units onto the surface of medical devices have already been shown to suppress biological reactions when they are in contact with living organisms. By using the fundamental research results, the MPC polymers are now clinically used on the surfaces of intravascular stents, guide wires, soft contact lenses, and artificial lung[5-7]. Surface grafting of the MPC polymer is also excellent method to obtain the biocompatibility[8-10]. We expected that the MPC polymer grafting improve not only biocompatibility but also lubricity of a solid surface because there are the same phosphorylcholine groups on the surface of the human articular cartilage. It has been reported that the MPC polymer grafting onto the polyethylene liner of the artificial hip joint clearly reduced wear between the articulating surfaces for long term[11]. But why the MPC polymer grafting increases surface lubricity has not been clear yet. In this study we investigated the mechanism of lubricity of MPC polymer grafted surface. We studied the mechanical and biological effects of the MPC grafting onto the surface of polypropylene (PP).

2. EXPERIMENTS

2.1 Preparation of poly(MPC)-grafted PP (PMPC-*g*-PP) surface

The grafting of MPC on PP surface was carried out by photo-induced graft polymerization[12]. The PP substrates were cut into 2.5cm x 7.5cm x 0.1cm(t) and rinsed sufficiently with acetone and hexane. The substrates were immersed in an acetone solution containing 0.5wt% benzophenone for 1min. The substrates were dried in vacuo under dark condition overnight at room temperature. The 0.5mol/L of MPC aqueous solution was prepared in degassed pure water. The benzophenone coated PP substrates were immersed in the MPC

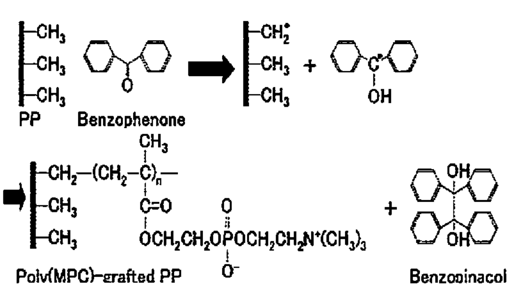

Fig.1 Synthesis route of the PMPC-*g*-PP surface

monomer solution. The photo polymerization on the PP surface was carried out using a 500W ultra-high pressure mercury lamp for 120 min at 60°C. After the reaction, the substrates were successively washed in water and ethanol and dried in vacuo for 24h at room temperature. The scheme of the reaction is shown in Fig.1.

2.2 Surface characterization

XPS: The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS). All samples were completely dried in vacuo before use. Survey scans (0-1100eV) were performed to identify the C, N, O, and P elements. A take off angle of the photoelectrons was 90°. All binding energies were referenced the C_{1s} peak at 285.0eV.

ATR-FTIR: The measurement of the IR spectrum of the surface modified and unmodified PP substrates was carried out with an attenuated total reflection (ATR) apparatus spectrometer under dry conditions. The spectra were recorded from 650 cm^{-1} to 4000 cm^{-1} at a 4cm^{-1} resolution. A single beam reference spectrum of a freshly cleaned ZnSe crystal at an incident angle of 45° was recorded before the measurements and used as the background spectrum.

Water contact angle: The static water contact angles were measured using a goniometer at room temperature. The samples were dried in vacuo for 24h before the measurements. Water droplets of 6μL were contacted onto the substrates and the contact angles at 10s were directly measured by photographic images. The data was collected at 5 positions on each sample. The advancing and receding contact angle were measured using Wilhelmy plate method. The data was averaged through 4 cycles.

2.3 Friction test

The surface kinetic frictional coefficients were measured using a tribo-tester. The schematic illustration of the tribo-tester is shown in Fig.2. The samples were dried in vacuo for 24h before the measurements. The measurements were carried out in air, in water, and under biological conditions; in phosphate buffered saline (PBS), PBS solution containing 0.45g/dL of a bovine serum albumin (albumin-PBS), and cell culture medium containing 10% fetal bovine serum (FBS). The measurements were conducted by sliding the substrates under a 50g load using a stainless-steel ball (10mm in diameter). The sliding speed was 10mm/sec and the sliding scale was 20mm. The sliding repeated 100 cycles.

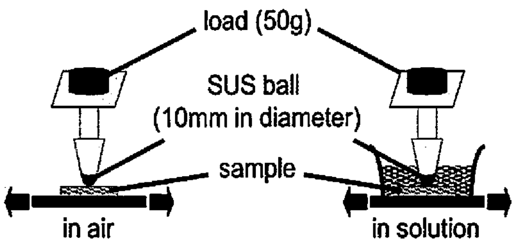

Fig.2 Schematic illustration of the tribo-tester. The left side is the friction test in air, and the right side is in solutions. Load was 50g, the jig was a stainless-steel ball (10mm in diameter), the sliding speed was 10mm/sec, and the sliding sacale was 20mm.

After the friction test in water, the surfaces were observed with Scanning electronic microscopy (SEM).

3. RESULTS AND DISUCUSSIONS

3.1 MPC graft polymerization on PP

Fig.1 illustrates the MPC graft polymerization scheme on the PP surface. The benzophenone absorbed on the substrate exhibits a well-known photochemical reaction. The benzophenone is excited to the triplet state, which extracts a hydrogen atom from the α-methyl group of the substrate to produce polymer radicals capable of initiating graft polymerization of the monomers. The excited benzophenone finally changes to benzopinacol. The location of MPC polymerization was restricted to the surface because radicals as the starting points of the polymerization were only produced on the surface and MPC was not dissolved in PP.

3.2 Surface characterization

The stable grafting of MPC on the PP was confirmed using XPS (Fig.3). The peaks in the carbon atom region (C_{1s}) at 286.5eV and 289eV indicated the ether bond and the ester bond, respectively, and those in the nitrogen atom region (N_{1s}) at 403eV and phosphorus atom region (P_{2p}) at 133eV were specific to the phosphorylcholine group in the MPC unit.

Fig.4 shows the ATR-FTIR spectra of the PP and the PMPC-*g*-PP surface under dry conditions. Among the PMPC-*g*-PP surface, the peak at 1719cm^{-1} corresponded to the ester group in the MPC and a few peaks between 800cm^{-1} and 1300cm^{-1} originated from the phosphorylcholine group in the MPC unit.

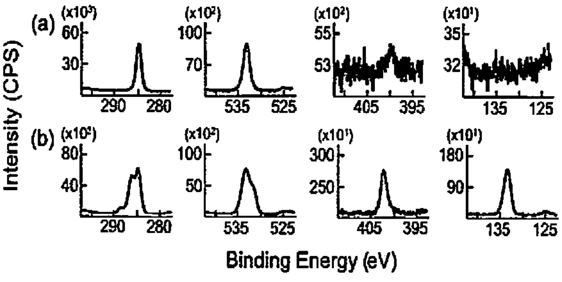

Fig.3 XPS charts of (a) unmodified PP and (b) PMPC-*g*-PP surface

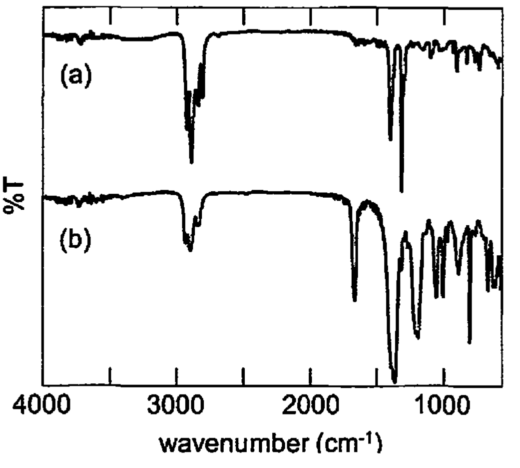

Fig.4 ATR-FTIR spectrum of (a) unmodified PP and (b) PMPC-*g*-PP surface

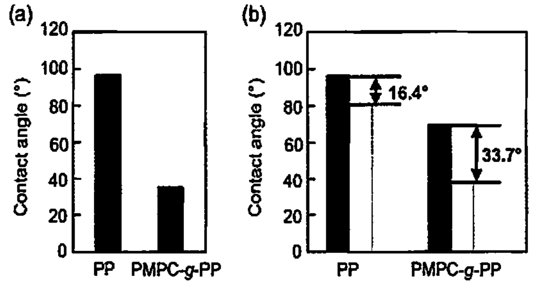

Fig.5 Water contact angle of PP and PMPC-*g*-PP surface. (a) Static contact angle, (b) dynamic contact angle, black bars: advancing contact angle, white bars: receding contact angle

Fig.5 shows the static and dynamic water contact angle of the PP and the PMPC-*g*-PP surface. The static contact angle on the PMPC-*g*-PP surface was 35.6°, which was about 1/3 of those on the unmodified PP surface. This result indicated that the PMPC grafting on PP surface greatly increased hydrophilicity. From the result of hysteresis between the advancing contact angle and the receding contact angle, hysteresis of the PMPC-*g*-PP surface was about two times larger than that of unmodified PP. This result was caused by extending of PMPC graft chains in water because PMPC had high hydrophilicity. It was confirmed that PMPC-g-PP surface had large surface mobility in water.

3.3 Friction properties

Fig.6 shows the kinetic friction coefficients of the PMPC-*g*-PP surface and unmodified PP at every 10 cycle in air and in water. In air, the friction coefficient of the PMPC-g-PP surface was 0.20, which is the same frictional property as that of unmodified PP. However in water, the lubricity of the PMPC-g-PP surface was greatly increased. The average of the friction coefficient of the PMPC-*g*-PP surface in water was 0.019, which reduced 90% compared with air condition and reduced 89% compared with unmodified PP in water. This value is similar to that of the human joints. These results indicated that the presence of water is a necessary condition for lubricating the PP surface by PMPC grafting.

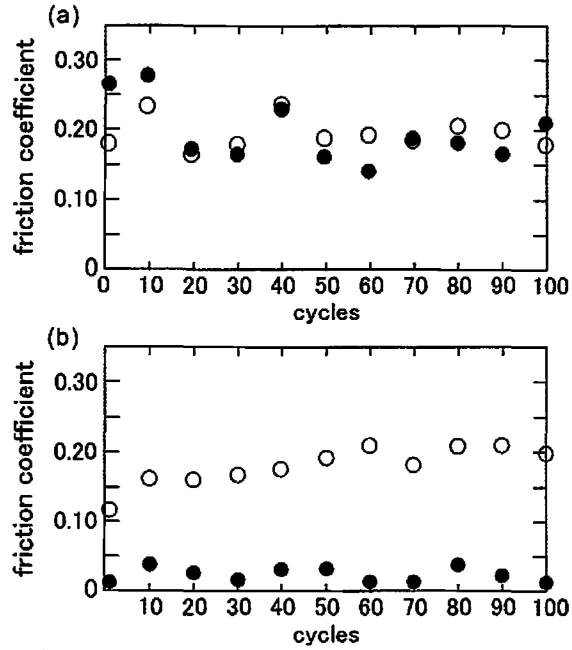

Fig.6 Friction coefficient of PP and PMPC-*g*-PP surface. The measurement was carried out (a) in air and (b) in water, white circle: unmodified PP, black circle: PMPC-*g*-PP surface.

Fig.7 shows the SEM observation of the PP and the PMPC-*g*-PP surface before and after the friction test in water. There was a flaw on the unmodified PP surface made by the friction test, while no flaw was observed on the PMPC-*g*-PP surface. It was considered that the grafted PMPC could keep hydration layer between the frictional surfaces and this hydrated PMPC layer completely kept the frictional surfaces apart during the friction test. The PMPC-*g*-PP surface showed the behavior of hydrodynamic lubrication in water.

Our solution of the lubricity mechanism is as follows. On the condition of hydrodynamic lubrication, surface friction is dependent on the mobility of liquid layer between the friction surfaces. Kitano found that the PMPC had a very small effect on the structure of the hydrogen-bonding network of water molecules[13]. The structure of hydrated layer in the vicinity of the PMPC graft chains are similar to that of bulk water which has high mobility. In short, the reason why the PMPC-*g*-PP surface clearly reduces surface friction in water is that the PMPC graft chains have high mobile hydrated layer between the friction surfaces. In air in which hydrated later could not exist, friction coefficient of PMPC-g-PP had no difference from that of unmodified PP in air in spite of PMPC existed on the surface.

Friction test was also performed under biological conditions. Fig.8 shows the friction coefficients of the PP and the PMPC-*g*-PP surface at every 10 cycle in PBS, in albumin-PBS, and in FBS. The average of the friction coefficient of unmodified PP was 0.30 in albumin-PBS and 0.25 in FBS. These values were clearly higher than those in water and in PBS. We expected that protein adsorption onto the unmodified PP surface caused this

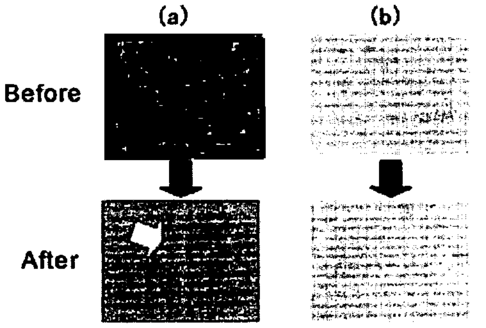

Fig.7 SEM images of (a) unmodified PP and (b) PMPC-*g*-PP surface before and after the friction test in water through 100 cycles.

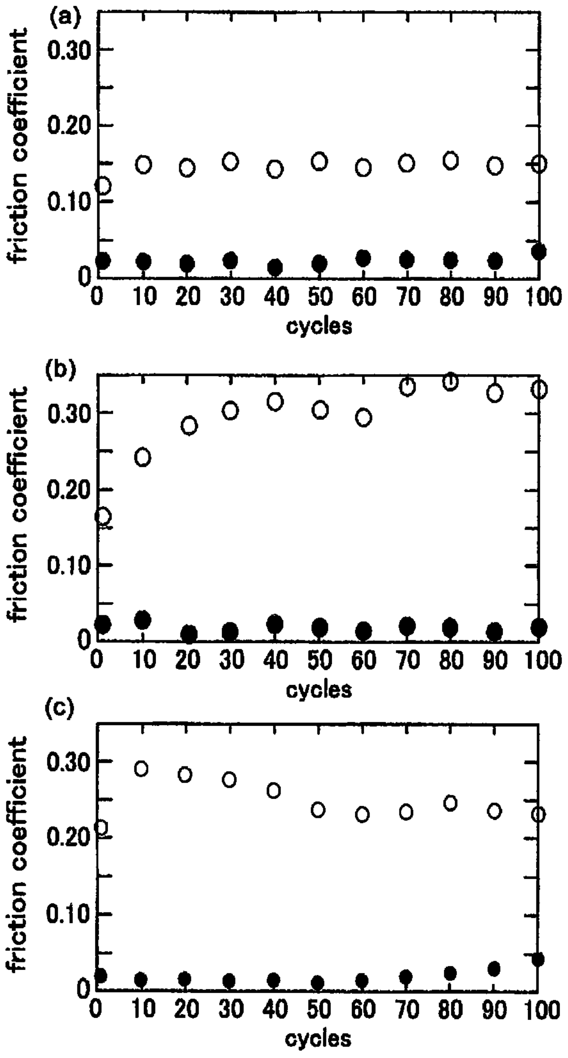

Fig.8 Friction coefficient of PP and PMPC-*g*-PP surface. The measurement was carried out (a) in PBS, (b) in PBS solution containing 0.45g/dL of a bovine serum albumin, (c) in cell culture medium containing 10% of fetal bovine serum, white circle: unmodified PP, black circle: PMPC-*g*-PP surface.

high friction coefficient. On the other hand, the friction coefficients of the PMPC-*g*-PP surface were 0.022 in PBS, 0.017 in albumin-PBS, and 0.017 in FBS. These results were equal to those in water. Lubrication properties of the PMPC-*g*-PP surface were not affected by every ion or protein. In short, the PMPC grafting could give not only high lubricity but also good biocompatibility.

4. CONCLUSIONS

We reported the preparation of a poly(MPC)-grafted PP in order to enhance its surface hydrophilicity, biocompatibility, and lubricity. A convenient polymerization was conducted using the UV-induced free radical "grafting-from" method based on the physically absorbed benzophenone on the PP. Friction test revealed the reduced friction coefficients on the PMPC-g-PP surface in water. The value of the friction coefficients of the PMPC-*g*-PP surface was similar to that of human joints. SEM observation indicated that the hydrated layer around the PMPC graft chains kept the frictional surfaces apart. It was concluded that the presence of this nanoscale hydrated layer, which had high mobility like bulk water, leads to the high lubricity. This high lubricity was maintained under the biological conditions. The PMPC grafting on solid surfaces is available for improving frictional properties of many medical devices.

5. REFERENCES

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(Received December 9, 2006;Accepted March 20, 2007)