

only as a bearing material but also as a structural material in the artificial hip joint system. Generally, increased cross-linking in the CLPE degrades its mechanical properties, producing a trade-off between wear-resistance and mechanical properties [5, 26]. It is desirable to reduce wear while maintaining the mechanical properties necessary for proper *in vivo* function. The advantage of photo-induced radical graft polymerization comes from the fact that the grafted MPC polymer gave a high lubricity only on the surface, and had no effect on the bulk properties of the CLPE substrate.

After 3.0×10^6 cycles in the hip joint simulator test, the wear rate of CLPE-g-MPC cups remained low. The cross-sectional TEM image of the CLPE-g-MPC bearing surface after 3.0×10^6 cycles of the hip simulator test (Fig. 4(c)) showed that most of the bearing surface was covered by the MPC polymer layer even after the hip simulator test. In other words, the CLPE-g-MPC cups showed little wear on inspection, supporting the quite low wear observed in the hip joint simulator test.

On the CLPE-g-MPC surface, the nitrogen and phosphorus attributed to the phosphorylcholine in the MPC units increased with increasing polymerization time. This indicates that the density of the grafted MPC polymer can be controlled by the polymerization time, since the number of polymer chains produced in a radical polymerization is generally proportional to the photo-irradiation time. The elemental composition obtained by XPS (N = 5.1, P = 5.2) of the CLPE-g-MPC surface with a polymerization time of 90 min was almost equivalent to the theoretical elemental composition of MPC polymer. Therefore, the entire surface of the CLPE was assumed to be coated with an MPC polymer layer.

However, the area observed by the X-ray spot (approximately $400 \times 800 \mu\text{m}^2$) in XPS was quite limited. As a supplementary probe to examine the MPC polymer layer, wettability measurement of cups should be performed on many separate areas on the cups. The wettability measurement of a surface is readily performed in the laboratory on well defined, homogeneous, smooth and planar surfaces of prepared specimens. In the case of artificial hip joint cups, for which non-destructive measurements are usually required (and where excision of material samples is usually undesirable), these conditions do not exist and measurement with high precision is a difficult task. Hence, we evaluated wettability of CLPE-g-MPC cup by the spray method, because this method can be used non-destructively on large areas.

Since CLPE-g-MPC reduces the production of wear particles and bone-resorptive responses, periprosthetic osteolysis could be eliminated [12]. Based on the mechanical, tribological and biological advantages, we confidently expect CLPE-g-MPC be used in the next-generation of artificial hip joint systems.

5. Conclusions

In this study, effects of a photo-induced radical graft polymerization technique on physical, mechanical and tribological properties of CLPE-g-MPC were investigated. The crystalline structure, physical and mechanical properties of the CLPE substrate were unchanged after the addition of a layer of MPC polymer by photo-polymerization. However, CLPE-g-MPC cups reduced 88% in the friction coefficient compared with untreated CLPE cups. After 3.0×10^6 cycles in the hip joint simulator test, the wear rate of CLPE-g-MPC cups remained low. We concluded that the advantage of this photo-induced radical graft polymerization technique was that the grafted MPC polymer layer produces high lubricity while only affecting the surface, and has no effect on the properties of the CLPE substrate.

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Figure captions

Figure 1 FT-IR/ATR spectra of CLPE-g-MPC. (a) CLPE (untreated), (b) CLPE-g-MPC. ● : P-O, ▲ : CH₂, ■ : C=O.

Figure 2 XPS spectra of CLPE-g-MPC. (a) CLPE (untreated), (b) CLPE-g-MPC.

Figure 3 Optical microscope images of CLPE-g-MPC cup surface with various photo-polymerization times. (a) 0 min (untreated CLPE), (b) 23 min and (c) 90 min. The water-covered ratio (%) is also shown. The white ring in (c) is due to the reflection of the light used in photography.

Figure 4 Cross-sectional TEM images of CLPE-g-MPC. (a) CLPE (untreated), (b) CLPE-g-MPC before simulator test and (c) CLPE-g-MPC after a 3×10^6 cycle simulator test. Bar; 200 nm.

Table 1 Surface elemental composition (%) of CLPE-g-MPC with various photo-polymerization times

Table 2 Physical properties of CLPE-g-MPC

Table 3 Mechanical properties of CLPE-g-MPC

Table 4 Tribological properties of CLPE-g-MPC

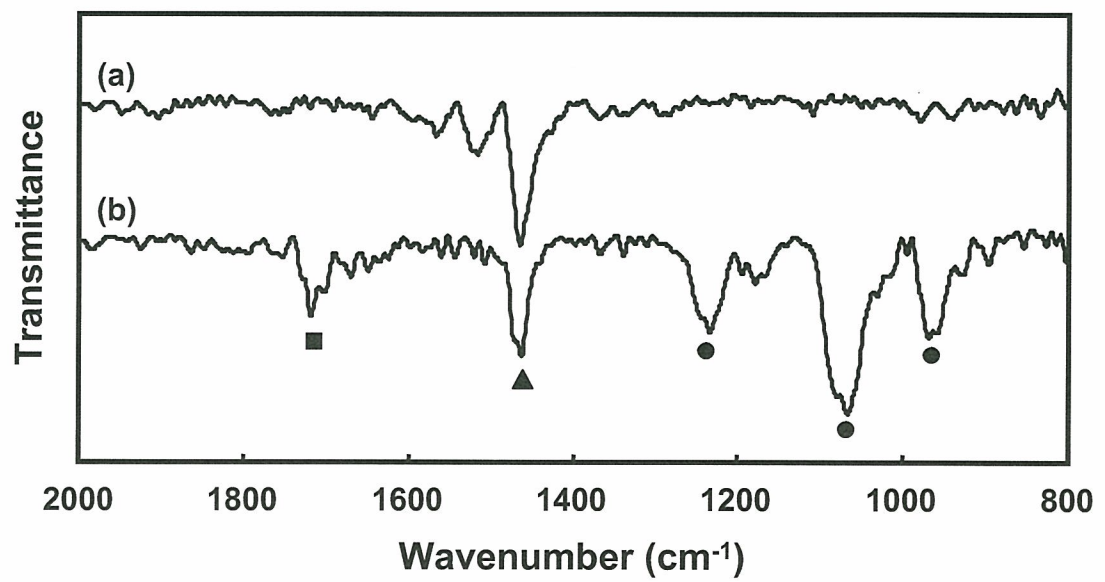


Figure 1

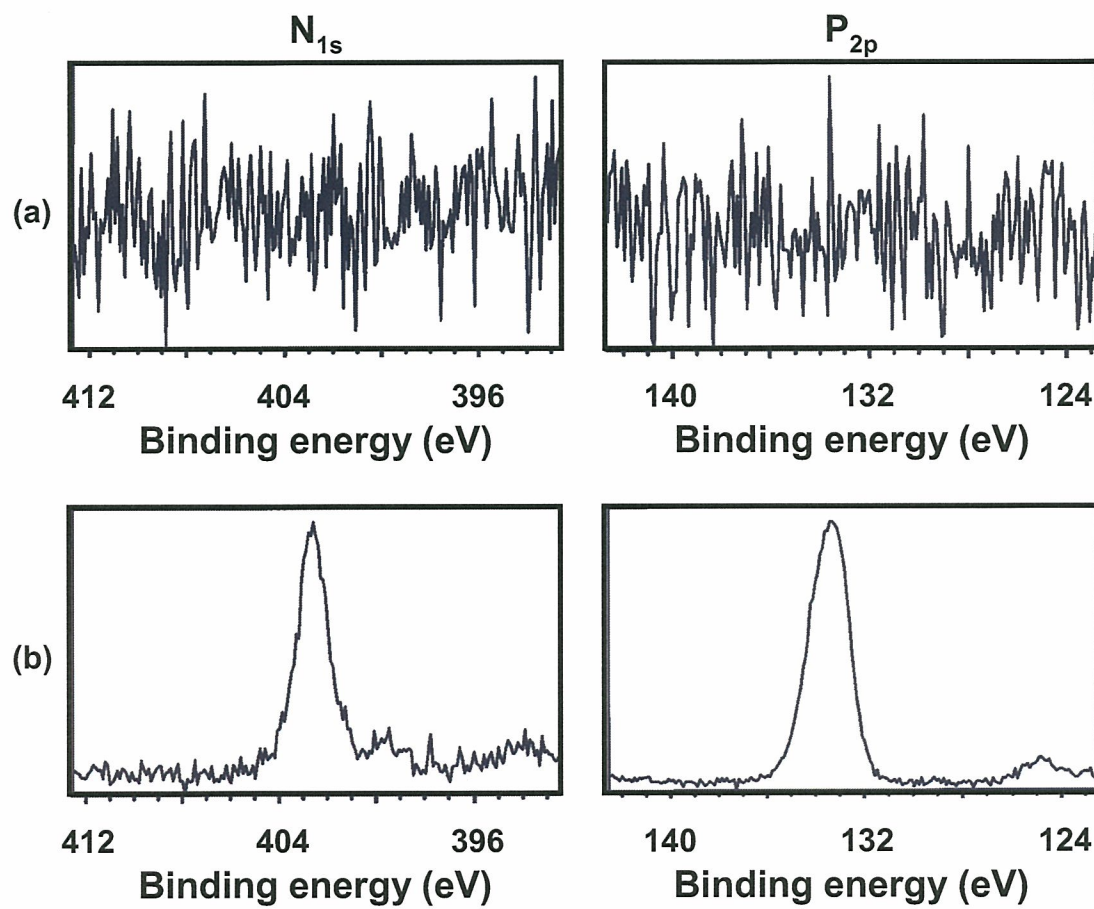


Figure 2

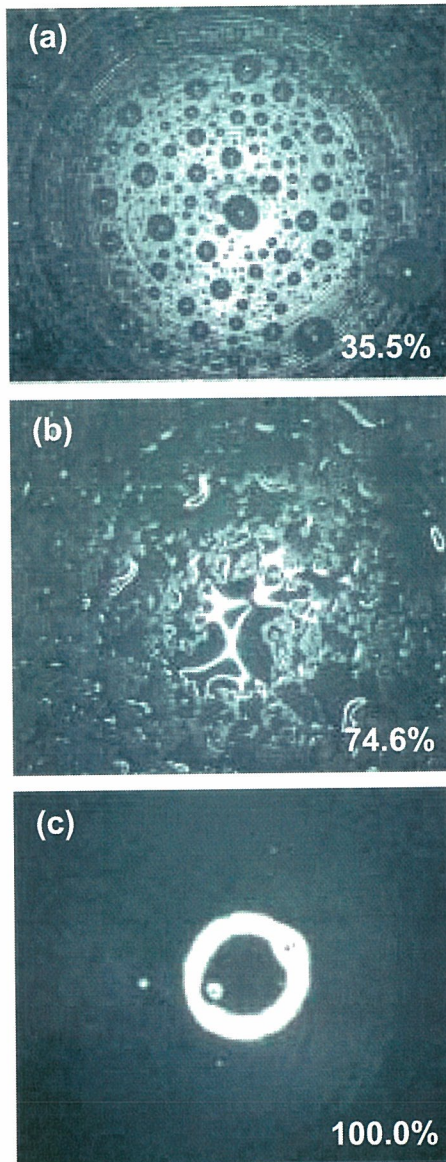


Figure 3

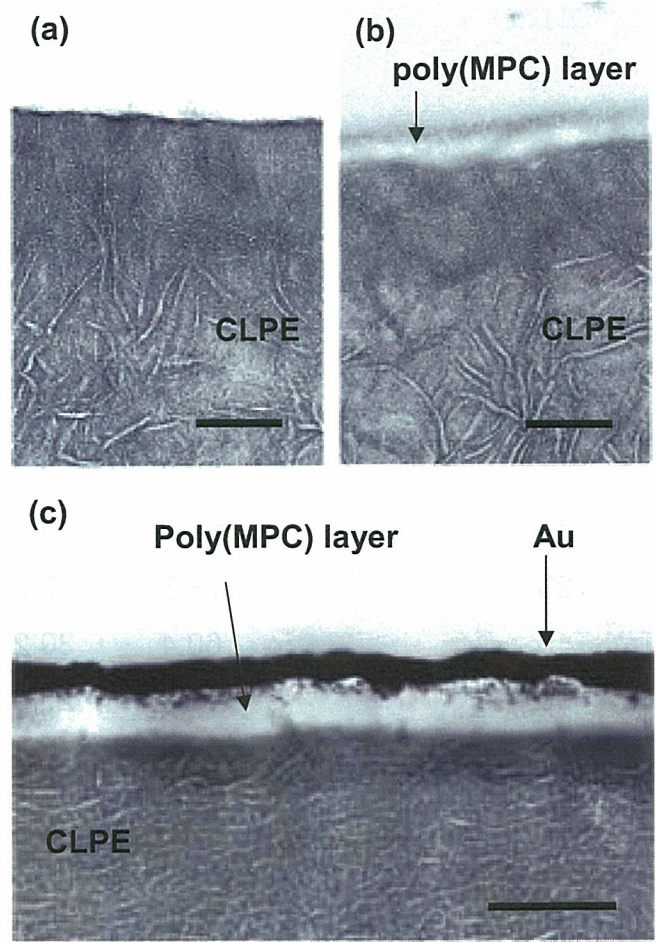


Figure 4

Table 1 Surface elemental composition (%) of CLPE-g-MPC with various photo-polymerization times

Polymerization time (min)	C	O	N	P
0 (untreated CLPE)	99.6	0.4	0.0	0.0
12	96.6	3.4	0.0	0.0
23	78.5	17.0	1.9	2.7
45	60.4	30.2	4.1	5.3
90	61.8	27.9	5.1	5.2
MPC polymer*	57.9	31.6	5.3	5.3

* : Theoretical elemental composition of MPC polymer

Table 2 Physical properties of CLPE-g-MPC

Sample	Density (g/cm ³)	Swelling ratio	Network chain density (x 10 ³ mol/mL)	M.W. between Cross-links (g/mol)	Cross-link density (mol%)
CLPE	0.944 (0.002)	2.99 (0.11)	0.437 (0.043)	2165 (214)	0.65 (0.06)
CLPE-g-MPC	0.943 (0.001)	2.94 (0.10)	0.459 (0.044)	2069 (186)	0.68 (0.07)

The standard deviation is in parentheses.

Table 3 Mechanical properties of CLPE-g-MPC

Sample	Yield strength (MPa)	Impact strength (kJ/m ²)	Creep deformation (%)	Hardness (shore D)
CLPE	23.2 (0.4)	75.0 (1.4)	0.89 (0.17)	68.2 (0.9)
CLPE-g-MPC	23.1 (0.5)	77.0 (1.9)	0.63 (0.40)	68.4 (0.5)

The standard deviation is in parentheses.

Table 4 Tribological properties of CLPE-g-MPC

Sample	Friction coefficient	Wear rate (mg/10 ⁶ cycles)
CLPE	0.0075	3.12
CLPE-g-MPC	0.0009	-1.43

Influences of MPC concentration variability on graft polymerization and its nano-scale modification brings to wear reduction of orthopaedic bearing

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ABSTRACT

We investigated the influences of MPC concentration variability on graft polymerization, which would make it possible to control the grafted poly(MPC) chains, and a nano-scale modification by the graft polymerization on wear reduction of the CLPE-g-MPC orthopaedic bearing. The thickness of grafted poly(MPC) layer increased with an increasing of MPC concentration in feed. The thickness might depend on the molecular weight of grafted poly(MPC), because the poly(MPC) layer had brush like structure. It was confirmed from the hip joint simulator test that the wear rate was much lower in the CLPE-g-MPC cups than in the untreated CLPE cups. Since MPC is a highly hydrophilic compound, the water-wettability of the CLPE-g-MPC surface was greater than that of the untreated CLPE surface because of the poly(MPC) nano-layer. The orthopaedic bearing with an CLPE-g-MPC surface had high lubricity as long as it has a poly(MPC) layer 10 nm thick. Such poly(MPC) layer 10 nm thick is assumed to be responsible for the improved wear resistance. We concluded that the nano-scale modification of poly(MPC) could bring to ultra-longevity for orthopaedic bearings. By changing the MPC concentration in feed, the thickness of poly(MPC) layer could be controlled. And, it was necessary to perform a long irradiation time (polymerization time) to this MPC graft polymerization system which contained a high-concentration monomer before its gelation, to obtain the nano-scale modification of poly(MPC).

Key words: joint replacement; polyethylene; phosphorylcholine; graft polymerization

Running title: Influences of MPC concentration on CLPE-g-MPC

INTRODUCTION

Polymeric biomaterials are widely used in biomedical field for artificial organs, medical devices and disposable clinical apparatus.^{1,2} The number of primary and revised artificial hip and knee joints used are substantially increasing in the world every year.³ This means that the quality of artificial joints as medical devices has been becoming increasingly important. The most popular artificial joint system as medical device is a bearing couple composed of an ultra-high molecular weight polyethylene (UHMWPE) and Co-Cr-Mo alloy. However, osteolysis caused by wear particles of UHMWPE in artificial joint system has emerged as a serious issue.^{4,5} The reduction in the number of UHMWPE wear particles is a method to prevent osteolysis. From this viewpoint, different combinations of bearing surfaces and improvement in the bearing materials have been focused upon.⁶⁻⁹

Surface modification is important for the improvement of the bearing materials. Recently, we have developed a new-concept artificial hip joint with 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer grafted onto the surface of CLPE (CLPE-g-MPC); it has been designed to reduce wear and suppress bone resorption.¹⁰⁻¹³ MPC, a methacrylate monomer with a phospholipid polar group in the side chain, is a novel biomaterial designed and developed by Ishihara et al. that mimics the neutral phospholipids of biomembranes.¹⁴ MPC is one of the most common biocompatible and hydrophilic polymers studied, which has potential application in a variety of fields such as biology, biomedical science and surface chemistry, owing to its unique properties such as well biocompatibility, high lubricity and low friction, anti-protein adsorption, biomembrane-like surface, etc.¹⁵⁻²²

In general, there were two ways to modify the polymer surface. The first one is carried out through surface absorption or reaction with small molecules.²³⁻²⁵ The second one is based on grafting polymeric molecules through covalent bonding to substrate.²⁶ And mostly, the grafting polymerization was conducted via two routes: (1) A surface-initiated graft polymerization is called a “grafting from” system, monomers were polymerized from the initiators or comonomers, and (2) absorption of polymer to substrate as a “grafting to” system (i.e., dipping, cross-linking, and ready-made polymers with reactive end groups reacted with the functional groups on the substrate).^{27, 28} The “grafting from” system has an advantage of preparing high-density polymer brush compared with the “grafting to” system. Our developing novel artificial joint was low-wear bearing with nano-scale modification of MPC polymer; this has been accomplished by using a photo-induced radical polymerization technique as the “grafting from” system. However, photo-induced radical polymerization technique was found that the length and the density of the grafted poly(MPC) are difficult to be controlled, in addition to the complexity of the reaction details.¹⁵ In our previous study, it was confirmed that the density of the grafted poly(MPC) affects wear resistance, and it was controlled with irradiation time (polymerization time).¹²

To solve the one more problem in this study, we investigated that the influences of MPC

concentration variability on graft polymerization, which would make it possible to control the grafted poly(MPC) chains, and its nano-scale modification affects to wear reduction of the CLPE-g-MPC orthopaedic bearing

MATERIALS AND METHODS

Chemicals

Benzophenone and acetone were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). MPC was synthesized industrially using the method reported by Ishihara et al.¹⁴ and was supplied by Ai Bio-Chips Co., Ltd (Tokyo, Japan).

MPC graft polymerization

A compression-molded UHMWPE (GUR1020 resin; Poly-Hi Solidur Inc., IN, USA) bar stock was irradiated with gamma-ray of 50 kGy in N₂ gas and annealed at 120°C for 7.5 h in N₂ gas in order to attain cross-linking. The CLPE specimens were machined from this bar stock after cooling. The specimens were immersed in an acetone solution containing 10 mg/mL benzophenone for 30 s and then dried in the dark at room temperature in order to remove acetone. The amount of benzophenone adsorbed on the surface was reported to be 3.5×10^{-11} mol/cm² by previous studies using ultraviolet spectroscopy.^{15, 16} The MPC was dissolved in degassed pure-water to various concentrations of 0.06 to 1.00 mol/L. The CLPE specimens coated with benzophenone were immersed in the aqueous MPC solution. The photo-induced graft polymerization on the CLPE surface was carried out with an ultraviolet irradiation (UVL-400HA ultra-high pressure mercury lamp, Riko-Kagaku Sangyo Co., Ltd., Funabashi, Japan) of 5 mW/cm² at 60°C for 90 min using a filter (Model D-35; Toshiba Corp., Tokyo, Japan) to pass only ultraviolet light with a wavelength of 350 ± 50 nm. After the polymerization, the CLPE-g-MPC specimens were removed, washed with pure-water and ethanol, and dried at room temperature. The CLPE-g-MPC specimens were gamma-ray-sterilized with a dose of 25 kGy under N₂ gas.

Surface analysis by using X-ray photoelectron spectroscopy, water-contact angle measurement and Fourier-transform infrared spectroscopy

The surface elemental conditions of CLPE-g-MPC polymerized with various polymerization periods or MPC concentrations were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS Hsi 165; Kratos Analytical Ltd., UK) equipped with an Mg-K α radiation source at 15 kV at the anode. The take-off angle of the photoelectrons was kept at 90°. Each measurement was scanned five times, and five replicate measurements were performed on each sample, and the average values were taken as surface elemental conditions.