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2 of 800 to 2000 cm^{-1} by using an FT-IR analyzer (FT/IR615; Jasco International Co., Ltd., Tokyo, Japan) at
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4 a resolution of 4.0 cm^{-1} .
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7 The surface elemental contents of the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE,
8 and PMPC grafted CLPE were analyzed using X-ray photoelectron spectroscopy (XPS). The XPS
9 spectra were obtained using an XPS spectrophotometer (AXIS Hsi 165; Kratos Analytical Ltd., Manchester,
10 UK) equipped with an Mg- $K\alpha$ radiation source by applying a voltage of 15 kV at the anode. The take-off
11 angle of the photoelectrons was maintained at 90°. Each measurement was scanned five times; five
12 replicate measurements were performed for each sample, and the average values were considered for the
13 surface elemental contents.
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16 The static water-contact angles of the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE,
17 and PMPC grafted CLPE were measured using an optical bench-type contact angle goniometer (model
18 DM300; Kyowa Interface Science Co., Ltd., Saitama, Japan) by the sessile drop method. Drops of
19 purified water (1 μL) were deposited onto the surface modified CLPE with MPC polymer, and the contact
20 angles were directly measured after 60 s by using a microscope according to the ISO 15989 standard.²⁷
21 Subsequently, fifteen replicate measurements were performed for each sample, and the average values were
22 considered as the contact angles.
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25 **Cross-sectional observation by transmission electron microscopy**

26 A cross-section of the PMB30, PMSi90, and PMPC layers on the CLPE surface was observed using a
27 transmission electron microscope (TEM). The specimens were first embedded in epoxy resin, stained
28 with ruthenium oxide vapor at room temperature, and then sliced into ultra-thin films (approximately
29 100-nm thick) by using a Leica Ultra Cut UC microtome (Leica Microsystems, Ltd., Wetzlar, Germany).
30 A JEM-1010 electron microscope (JEOL, Ltd., Tokyo, Japan) was used for the TEM observation at an
31 acceleration voltage of 100 kV.
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Characterization of protein adsorption by micro bicinchoninic acid method

The amount of protein adsorbed on the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE, and PMPC grafted CLPE surfaces was measured by the micro bicinchoninic acid (BCA) method. Each specimen was immersed in Dulbecco's phosphate-buffered saline (PBS, pH 7.4, ion strength = 0.15 M; Immuno-Biological Laboratories Co., Ltd., Takasaki, Japan) for 1 h to equilibrate the surface modified by the MPC polymer. The specimens were immersed in bovine serum albumin (BSA, $M_w = 6.7 \times 10^4$; Sigma-Aldrich Corp., MO, USA) solution at 37°C for 1 h. The protein solution was prepared in a BSA concentration of 4.5 g/L, i.e., 10% of the concentration of the human plasma levels. Then, the specimens were rinsed five times with fresh PBS and immersed in 1 mass% sodium dodecyl sulfate (SDS) aqueous solution and shaken at room temperature for 1 h to completely detach the adsorbed BSA on the surface modified by the MPC polymer. A protein analysis kit (micro BCA protein assay kit, #23235; Thermo Fisher Scientific Inc., IL, USA) based on the BCA method was used to determine the BSA concentration in the SDS solution, and the amount of BSA adsorbed on the surface modified by the MPC polymer was calculated.

Friction test

A friction test was performed using a ball-on-plate machine (Tribostation 32; Shinto Scientific Co., Ltd., Tokyo, Japan). Each of the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE, and PMPC grafted CLPE surfaces was used to prepare six sample pieces. A Co-Cr-Mo alloy ball with a diameter of 9 mm was prepared. The surface roughness of the ball was $R_a \geq 0.01$, which was comparable to that of femoral ball products. The friction tests were performed at room temperature with various loads in the range of 0.49 to 9.80 N, sliding distance of 25 mm, and frequency of 1 Hz for a maximum of 100 cycles.²⁸ Pure water was used as a lubricant medium. The mean coefficients of dynamic friction were determined by averaging five data points from the 100 (96–100) cycle measurements.

Hip joint simulator wear test

A 12-station hip joint simulator (MTS Systems Corp., MN, USA) with the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE, and PMPC grafted CLPE cups ($n = 2$), both having inner and outer diameters of 26 and 52 mm, respectively, was used for the hip joint simulator wear test. A Co-Cr-Mo alloy femoral ball component with a size of 26 mm (Japan Medical Materials Corp., Osaka, Japan) was used as the femoral component. A mixture of 25 vol% bovine serum, 20 mM/L of ethylene diamine tetraacetic acid (EDTA), and 0.1 mass% sodium azide was used as a lubricant, according to the ISO 14242-1 standard.²⁹ The lubricant was replaced every 0.5×10^6 cycles. Walks that simulated a physiologic loading curve (Paul-type) with double peaks at 1793 and 2744 N loads with a multidirectional (biaxial and orbital) motion of 1 Hz frequency were applied. The wear was determined by weighing the cups at intervals of 0.5×10^6 cycles. Load-soak controls ($n = 2$) were used to compensate the fluid absorption by the specimens.³⁰ The testing was continued until a total of 3.0×10^6 cycles were completed.

Statistical analysis

The results derived from each measurement in the water-contact angle estimation, friction test, and protein adsorption test were expressed as mean values and standard deviation. The statistical significance ($p < 0.05$) was estimated by Student's *t*-test.

RESULTS

Fig. 2 shows the FT-IR/ATR spectra of the untreated CLPE, PMB30 coated CLPE, PMSi90 coated CLPE, and PMPC grafted CLPE. An absorption peak was observed at 1460 cm^{-1} for all test specimens. This peak is mainly attributed to the methylene (CH_2) chain in the CLPE substrate and the MPC polymer chain. However, absorption peaks at 1240, 1080, and 970 cm^{-1} were observed only for the CLPE whose surface was modified by the MPC polymer. These peaks corresponded to the phosphate group (P-O) in the MPC unit. Similarly, an absorption peak at 1720 cm^{-1} observed in the surface modified CLPE

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2 corresponded only to the carbonyl group (C=O) in the MPC unit. The absorption peak intensity of the
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4 P–O group of the PMPC grafted CLPE was the highest in the CLPE whose surface was modified by the
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6 MPC polymer.
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9 Table I summarizes the surface elemental compositions of the untreated CLPE, PMB30 coated CLPE,
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11 PMSi90 coated CLPE, and PMPC grafted CLPE. The nitrogen (N) and phosphorous (P) contents in all
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13 the CLPE specimens whose surface were modified by the MPC polymer were observed. The surface
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15 elemental compositions of both N and P in the surface modified CLPE increased with an increase in the
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17 MPC composition in the polymer for surface modification. In particular, the elemental compositions of N
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19 and P in the PMPC grafted CLPE surface were 5.2 and 5.3 atom%, respectively. The elemental
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21 composition of the PMPC grafted CLPE surface was almost equivalent to the theoretical elemental
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23 composition (N = 5.3, P = 5.3 atom%) of PMPC.
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30 Fig. 3 shows the cross-sectional TEM images of the untreated CLPE, PMB30 coated CLPE, PMSi90
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32 coated CLPE, and PMPC grafted CLPE. For the PMB30 and PMSi90 coatings, and PMPC grafting, a
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34 100 nm-thick MPC polymer layer was clearly observed on the surface of the CLPE substrate. No crack
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36 for poor adhesion and/or delamination was observed at the interface between MPC polymer layer and
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38 CLPE substrate. These results indicate that each surface modification layer on the CLPE substrate is
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40 uniform and cover closely, regardless of the binding conditions: the surface modification layers by the
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42 PMB30 and PMSi90 coatings, and PMPC grafting are combined with the substrate by physical adsorption
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44 and covalent bonds of Si–O–C and C–C, respectively. In the PMB30 coated CLPE, a bilayer structure
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46 attributed to dipping twice was clearly observed on the surface modification layer.
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53 Fig. 4 shows the static water-contact angles of the untreated CLPE, PMB30 coated CLPE, PMSi90
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55 coated CLPE, and PMPC grafted CLPE. The static water-contact angles of the untreated CLPE and
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57 PMB30 coated CLPE were 90° and 100°, respectively, and they decreased markedly to approximately 10°
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59 (i.e., 8°–13°, $p < 0.001$) by the PMSi90 coating and PMPC grafting.
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Fig. 5 shows the amount of BSA adsorbed on the surfaces of the untreated CLPE, PMB30 coated CLPE,

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2 PMSi90 coated CLPE, and PMPC grafted CLPE. The amount of BSA adsorbed on the CLPE surface
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4 modified by the MPC polymer was considerably lesser ($p < 0.001$) than that of the untreated CLPE, i.e.,
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6 0.05–0.10 $\mu\text{g}/\text{cm}^2$. These results imply that the surface modification by the MPC polymer results in good
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8 biocompatibility.
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12 Fig. 6 shows the coefficients of dynamic friction of the untreated CLPE, PMB30 coated CLPE, PMSi90
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14 coated CLPE, and PMPC grafted CLPE. As compared to the untreated specimens, the PMB30 coated
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16 and PMSi90 coated CLPE specimens showed a reduction of approximately 30% (i.e., 25%–30%, not
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18 significant) in their coefficients of dynamic friction. Further, as compared to the untreated CLPE
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20 specimens, the PMPC grafted CLPE specimens showed a reduction of approximately 84% ($p < 0.005$) in
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22 their coefficients of dynamic friction.
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27 Fig. 7 shows the coefficients of dynamic friction of the untreated CLPE, PMB30 coated CLPE, PMSi90
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29 coated CLPE, and PMPC grafted CLPE as a function of the loads in the ball-on-plate friction test. The
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31 untreated CLPE showed the highest coefficient of dynamic friction, i.e., approximately 0.075. This value
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33 was almost constant throughout the experiment. The coefficients of dynamic friction of the PMB30
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35 coated CLPE and PMSi90 coated CLPE were smaller (approximately 0.055) than those of the untreated
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37 CLPE at loads of up to 0.98 N; then, these coefficients increased to the level of the coefficients of the
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39 untreated CLPE at loads above 1.96 N. For both PMB30 coated CLPE and PMSi90 coated CLPE, the
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41 MPC polymer layer coating showed almost the same coefficients of dynamic friction. The PMPC grafted
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43 CLPE showed a remarkably low friction coefficient of approximately 0.026 at a load of 0.49 N; this value
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45 decreased gradually and reached approximately 0.005 at a load of 9.80 N.
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53 Fig. 8 shows the gravimetric wear of the untreated CLPE, PMB30 coated CLPE and PMSi90 coated
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55 CLPE, and PMPC grafted CLPE cups in the hip simulator wear test. It was observed that the wear in the
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57 PMPC grafted CLPE cups was significantly lower than that in the untreated CLPE cups. There was no
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59 significant difference in the wear of the untreated CLPE and PMB30 coated CLPE cups. The PMSi90
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coated CLPE cups showed slightly lower wear than the untreated CLPE cups; however, the weight change

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2 varied for each cup (standard deviation = ± 9.0 mg). The PMPC grafted CLPE cups showed a slight
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4 increase in weight. This was partially attributable to the enhanced fluid absorption in the tested cups as
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6 compared to that in the load-soak controls. While applying the gravimetric method, the weight loss in the
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8 tested cups is corrected by subtracting the weight gain in the load-soak controls; however, this correction
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10 cannot be achieved perfectly because only the tested cups are continuously subjected to motion and load.
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12 Usually, the fluid absorption in the tested cups is generally slightly higher than that in the load-soak controls.
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14 Consequently, the correction of the fluid absorption by using the load-soak data as the correction factor
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16 leads to a slight underestimation of the actual weight loss.^{22,29} In this study, a steady wear rate was
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18 calculated using data from 2.0×10^6 to 3.0×10^6 cycles; in the untreated CLPE, PMB30 coated CLPE, and
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20 PMSi90 coated CLPE cups, these rates were 6.1, 5.9, and 4.5 mg/ 10^6 cycles, respectively. In contrast, the
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22 wear rate of the PMPC grafted CLPE cups was markedly lower, i.e., -1.5 mg/ 10^6 cycles.
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33 DISCUSSION

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35 In this study, we have investigated the surface properties of various surface modification layers formed
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37 on the CLPE surface by the physical and chemical coating of the MPC polymers or photoinduced radical
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39 grafting of MPC. Here, we discuss the durability of the CLPE whose surface is modified by the MPC
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41 polymer in terms of the characteristics of the nanometer-scale layer of the MPC polymer.
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45 The layer whose surface contains the physically coated PMB30 is combined with the substrate by
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47 physical adsorption.^{11,12} The layer whose surface contains the chemically coated PMSi90 is combined
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49 with the substrate by physical adsorption and/or slight Si–O–C covalent bonding ascribed to the 10% MPSi
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51 in the PMSi90 composition; a hydrolyzed silane molecule of PMSi90 has three –OH groups that react with
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53 the –OH groups of the surface oxide layer of the CLPE substrate induced by the O₂ plasma irradiation, and
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55 they form covalently siloxane bonds.²⁷ On the other hand, the surface modification layer obtained by
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57 PMPC grafting is combined with the substrate by strong C–C covalent bonding.^{19–24}
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In Fig. 7, the coefficients of dynamic friction of the PMB30 coated CLPE and PMSi90 coated CLPE

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2 increased to the level of the coefficient of dynamic friction of the untreated CLPE at loads above 1.96 N.
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4 In addition, as shown in Fig. 8, there was no significant difference in the wear of the untreated CLPE and
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6 the MPC polymer coated CLPE cups in the hip joint simulator tests. In contrast, the PMPC grafted CLPE
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8 showed an extremely low and stable coefficient of dynamic friction and volumetric wear as compared to
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10 the untreated CLPE and MPC polymer coated CLPE, as shown in Figs. 7 and 8. These results indicate
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12 that the PMB30 and PMSi90 surface modification layers are removed from the CLPE surface. The
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14 surface modification layers by the PMB30 and PMSi90 coatings are combined with the substrate by
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16 physical adsorption and chemical bonds of Si–O–C, respectively. Therefore, the physical adsorption and
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18 chemical bonds of Si–O–C are ineffective in the case of large and multidirectional loads. The chemical
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20 bonds of Si–O–C are probably insufficient because the MPSi composition in the PMSi90 polymer is 10%.
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22 Therefore, it is thought that a sufficient number of strong bonds between the surface modification layer and
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24 the CLPE surface are essential for the long-term retention of the benefits of the MPC polymer used in
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26 artificial joints under variable and multidirectional loads.
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35 Since MPC is a highly hydrophilic compound, the MPC polymers PMSi90 and PMPC are water-soluble.
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37 The water-wettability of the PMSi90 coated and PMPC grafted CLPE surfaces with a high MPC unit mole
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39 fraction (90% and 100%) was considerably greater than that of the untreated CLPE surface, as shown in
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41 Fig. 4. Kobayashi *et al.* reported that the water molecules adsorbed on the surface of the highly
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43 hydrophilic PMPC act as lubricants and reduce the interaction between the PMPC and the counter-bearing
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45 face.³¹ Therefore, it is thought that the artificial hip joint bearing with the PMSi90 coated and PMPC
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47 grafted surfaces exhibited considerably higher lubricity than that with the untreated CLPE. The amount of
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49 water molecules absorbed on the surface of the CLPE (water thin-film) is expected to play an important
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51 role with regard to the property of low friction.
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58 However, in reality fact as shown in Fig. 6, the PMSi90 coated CLPE specimens exhibited a maximum
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60 reduction of approximately 30% in their coefficients of dynamic friction as compared to the untreated
CLPE specimens. In contrast, the PMPC grafted CLPE specimens exhibited a reduction of

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2 approximately 84%. It was previously reported that the polymer concentration (i.e., viscosity) increased
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4 with the friction coefficient in the mixed lubrication regime.³² Therefore, It is assumed that an ultra-low
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6 friction of PMPC grafted CLPE that occurs during sliding is related to the effective viscosity of the PMPC
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8 in the mixed lubrication of the intermediate hydrated layer. The high-density PMPC graft chains in the
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10 PMPC grafted CLPE are assumed to exhibit a brush-like structure.^{25,33} The viscosity of the PMPC layer
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12 reflects the mobility of the free end groups of the MPC polymer or MPC polymer chains themselves.^{34,35}
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14 In contrast, the mobility of PMSi 90 is limited by the cross-linking and network entanglement of the gel
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16 structure of PMSi90. Hence, we think that the polymer brush-like structure of the PMPC grafted CLPE
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18 with high mobility of polymer chains can function as a considerably better surface hydration lubrication
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20 system of artificial joints than the gel structure of the PMSi90 coated CLPE. These considerations are
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22 based on the previous studies on charged polymers (polyelectrolytes) by Klein, *et al.*^{34,35}
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30 The significant reduction in the coefficient of friction of the grafted PMPC resulted in a substantial
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32 improvement in wear resistance. A previous study reported that the hydrogel cartilage surface was
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34 assumed to have a brush-like structure: a part of the proteoglycan aggregate brush bonds with the collagen
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36 network in the cartilage surface.³⁶ It is thought that the bearing surface with high-density PMPC in
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38 artificial hip joints has a brush-like structure similar to an articular cartilage. We assume that the bearing
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40 surface of the artificial hip joint combined with a 100 nm thick MPC polymer layer results in a fluid film
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42 lubrication (or mixed lubrication) of the intermediate hydrated layer; this suggests that this novel artificial
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44 hip joint mimics the natural joint cartilage.
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50 As shown in Fig. 7, the coefficients of dynamic friction of the untreated CLPE surface were constant for
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52 all load values. In contrast, those of the PMPC grafted CLPE surface decreased with increasing load.
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54 These results show that the PMPC grafted layer does not follow Amonton's law of $F = \mu N$. The
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56 maximum contact stress of approximately 62 MPa at a load of 9.8 N is higher than the yield tensile strength
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58 of the CLPE (approximately 23 MPa). The maximum contact stress is roughly calculated by the Hertzian
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60 theory. The elastic CLPE substrate is deformed slightly by the loads, the low friction coefficient may have

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been shown in order to get much more amount of water thin-film with the larger contact area of concave surface. We also think that these results imply that the lubrication of the PMPC grafted CLPE is dominated by the hydrodynamic lubrication mechanism.

As shown in Fig. 4, the static water-contact angle of the PMB30 coated CLPE was approximately 100°. Sibarani *et al.* reported that the PMB30 coated polymer surfaces showed high advancing (approximately 100°) and low receding (approximately 20°) contact angles.⁵ Moreover, Yamasaki *et al.* reported that the PMB30 coated polymer surfaces required more than 30–300 min to achieve complete equilibrium.³⁷ This indicates that the PMB30 cannot be hydrated easily due to the low MPC unit composition of the copolymer and low mobility of the polymer chain. However, as shown in Fig. 5, the PMB30 coated CLPE surface, which could form a phosphorylcholine enriched surface after equilibrating for 1 h, showed excellent biocompatibility as an anti-adsorption surface for BSA.

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The adsorption of the representative plasma protein, BSA, on the CLPE surface decreased to 9%–18% due to the surface modification by the MPC polymer, as shown in Fig. 5. It is hypothesized that the mechanism of protein adsorption resistivity on the surface modified by the MPC polymer is based on the water structure resulting from the interactions between water molecules and phosphorylcholine groups.^{26,37,38} The large amount of free water around the phosphorylcholine group is considered to detach proteins easily and even prevent conformational changes in the adsorbed proteins.^{26,38} Hence, we expect that the protein adsorption will decrease with increasing MPC unit composition in the MPC copolymer. However, in this study, there was no significant difference in the protein adsorption of the CLPE whose surfaces was modified by the MPC polymer (the MPC unit compositions were 30%, 90%, and 100%). The reduction in protein adsorption is also considered to be caused by the presence of a hydrated layer around the phosphorylcholine group.^{26,39} The latter consideration is consistent with the results of the water contact angle measurement, friction test and cross-sectional TEM observations of the CLPE whose surface is modified CLPE by the MPC polymer (Figs. 3, 4 and 6). The previous studies reported that the protein concentration of lubricants such as bovine serum considerably affected the wear rate of the UHMWPE

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2 cups in the joint simulator test: the protein concentrations in the synovial fluids of both normal and diseased
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4 joints (approximately 20–40 mg/ml), including joints after total arthroplasty, were associated with the
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6 highest wear rates.^{40,41} We think that the anti-protein adsorption surface on the CLPE prepared by the
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8 MPC polymer will prevent the highest adhesive wear rates *in vivo* caused by the protein adsorption.
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10 Moreover, the CLPE whose surface is modified by the MPC polymer is expected to exhibit tissue and
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12 blood compatibility as biocompatibility, because previous studies have reported that the MPC polymer
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14 modified surfaces exhibit *in vivo* biocompatibility.^{3–11}
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CONCLUSION

In this study, we systematically investigated the surface properties of the various surface modification layers formed on the CLPE surface by the MPC polymer by dip coating or photoinduced radical grafting. It is concluded that several important issues are involved in the long-term retention of the benefits of the MPC polymer used in artificial joints under variable and multidirectional loads, for example, strong bonding between the MPC polymer and the CLPE surface and high mobility of the free end groups of the MPC polymer. We should employ the photoinduced radical graft polymerization to create strong covalent bonding between the CLPE substrate and the surface modification layer and also to retain the high mobility of polymer chains of that layer.

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For Peer Review

Figure captions

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- TABLE I Surface elemental composition (atom%) of CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE
- Figure 1. Scheme for the preparation of MPC polymer coated CLPE and PMPC grafted CLPE.
- Figure 2. FT-IR/ATR spectra of untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE.
- Figure 3. Cross-sectional TEM images of untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE. Bar: 200 nm.
- Figure 4. Static-water contact angle of untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE. Bar: Standard deviations. *: Significant difference ($p < 0.001$) as compared to the untreated CLPE, **: significant difference ($p < 0.001$) as compared to the PMB30 coated CLPE.
- Figure 5. Amount of BSA adsorbed on the surfaces of the untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE. Bar: Standard deviations. *: Significant difference ($p < 0.001$) as compared to the untreated CLPE.
- Figure 6. Coefficients of dynamic friction of untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE. Bar: Standard deviations. *: Significant difference ($p < 0.005$) as compared to the untreated CLPE.

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Figure 7. Coefficients of dynamic friction of the untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE as a function of loads in the ball-on-plate friction test. Bar: Standard deviations.

Figure 8. Weight change (volumetric wear) of the untreated CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE in the hip joint simulator wear test. Bar: Standard deviations.

(n = 5)

Sample	C	O	N	P	Si
CLPE (untreated)	99.8 (0.3)**	0.2 (0.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
PMB30 coated CLPE	69.9 (1.0)	25.5 (0.6)	2.1 (0.2)	2.5 (0.3)	0.0 (0.0)
PMSi90 coated CLPE	60.5 (0.7)	30.4 (0.4)	4.1 (0.2)	4.0 (0.2)	1.0 (0.0)
PMPC grafted CLPE	58.0 (0.2)	31.5 (0.2)	5.2 (0.1)	5.3 (0.1)	0.0 (0.0)
PMPC*	57.9	31.6	5.3	5.3	0.0

*Theoretical elemental composition of PMPC.

**The standard deviation is in parentheses.

TABLE I Surface elemental composition (atom%) of CLPE, MPC polymer coated CLPE, and PMPC grafted CLPE
34x15mm (600 x 600 DPI)

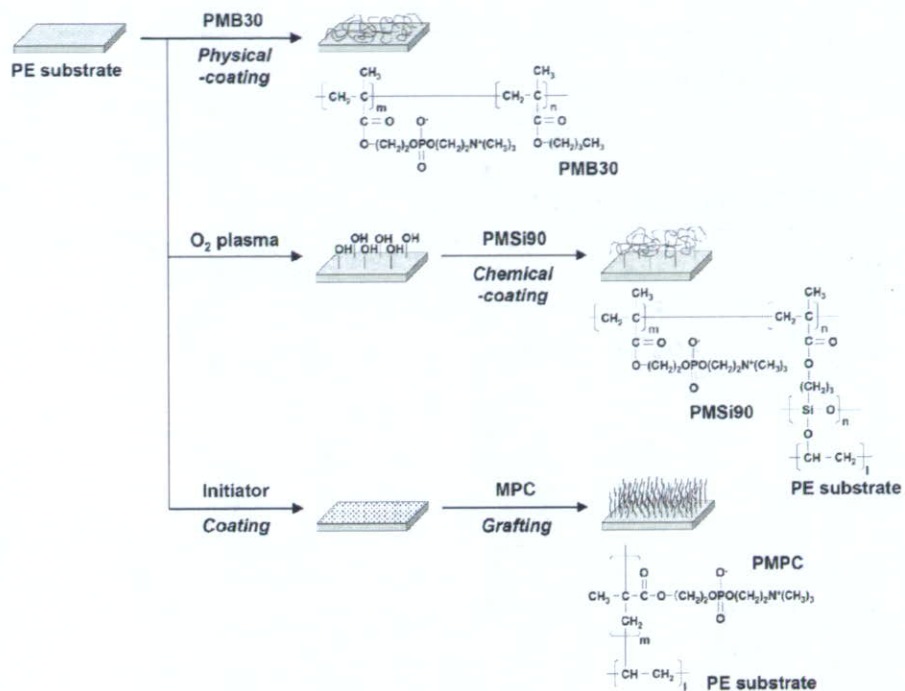


Figure 1. Scheme for the preparation of MPC polymer coated CLPE and PMPC grafted CLPE.

77x60mm (600 x 600 DPI)