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3 due to the dissemination of wear particles to the other parts of the body have been reported.¹³
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6 In order to reduce such wear particles, improvements in the bearing materials and surface
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8 modifications of the Co-Cr-Mo alloy have been attempted.^{14,15} Surface coating may reduce the
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10 UHMWPE wear without compromising the bulk mechanical properties of the implant materials.
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12 Various “hardening treatments” of metal bearing surfaces, such as diamond-like carbon coating,
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14 titanium nitride coating and ion implantation have also been attempted.^{16,17} Although these surface
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16 modifications may improve THA survivorship, the limited THA longevity imposes restrictions for
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18 its application to younger patients. Consequently, the possibility of replacing the femoral head
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20 alone, whether solid or articular surface replacement, remains an attractive feature of such implants
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22 during revision surgeries of THA. However, the Co-Cr-Mo alloy or the hardening-treated
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24 Co-Cr-Mo alloy may induce damage to cartilaginous tissue.
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37 On the other hand, the previous study reported that highly lubricious hydrogel polymer used as an
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39 artificial cartilage did not damage cartilaginous tissue.¹⁸ We have recently developed a highly
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41 lubricious artificial hip joint system by a “mild treatment” with soft materials. In this treatment,
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43 poly(2-methacryloyloxyethyl phosphorylcholine (MPC)) was grafted onto the surface of CLPE
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45 (CLPE-*g*-MPC).¹⁹⁻²¹ MPC is a methacrylate with a phospholipid polar group in a side chain, and it
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47 has both good solubility in polar solvents including water and polymerization ability by
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49 conventional radical polymerization.²² Many MPC polymers have been widely investigated as
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51 biomaterials.²³⁻²⁷ As a result, various medical devices have already been developed using MPC
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53 polymers and they are being used clinically. The efficacy of MPC polymers as biomaterials has
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been well verified.²⁸⁻³⁰

In general, there are two methods for modifying the polymer surface. The first method involves surface absorption or reaction with small molecules^{31,32} and the second, grafting polymeric molecules onto the substrate through covalent bonding.³³ Most frequently, grafting polymerization is performed using either of the following methods: (1) surface-initiated graft polymerization, termed as the “grafting from” method, in which monomers are polymerized from initiators or comonomers; and (2) adsorption of the polymer to the substrate, termed as the “grafting to” method (i.e., dipping, cross-linking, and ready-made polymers with reactive end groups reacting with the functional groups of the substrate).^{34,35} The “grafting from” method has an advantage over the “grafting to” method in that it synthesizes a high-density polymer brush. The novel artificial joint developed in this study is super-lubricious surface with nanometer-scale poly(MPC) modification. This surface modification was accomplished by using a photo-induced radical polymerization technique that was similar to the one used in the “grafting from” method.

To ensure *in vivo* long-term retention of this poly(MPC) graft on the Co-Cr-Mo alloy, it is necessary to create strong covalent bonding between the Co-Cr-Mo alloy substrate and the poly(MPC) graft chain. Organosilanes have already been known as surface coupling agents to enhance bonding between a metal or a metal oxide surface and an organic resin such as dental resin, and they can strongly bind metals to resins in dental implants.³⁶ Organic silanes or silane coupling agents comprise at least a hydrolyzable alkoxyethyl or chlorosilyl group and an organofunctional group.³⁷ The agents are effective to introduce organofunctional groups into the siloxane network

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polymer. The organofunctional group in the silane could be useful to improve bonding with the organic overlayer. 3-Methacryloxypropyl trimethoxysilane (MPSi) is a simple surface coupling agent consisting of three methoxy groups, a propyl chain, and a functional methacrylate, and the structure of its main chain is equivalent to that of MPC.

In this study, based on the advantages of biocompatibility and hydrophilicity of poly(MPC), the “grafting from” method and the polymer strongly bound to the metal of silanization, a super-lubricious metal bearing material in which the poly(MPC) was grafted onto the surface of the Co-Cr-Mo alloy (Co-Cr-Mo-g-MPC) has been introduced for developing a novel artificial hip joint system, i.e., artificial femoral head and metal-on-metal (Co-Cr-Mo/Co-Cr-Mo) type for THA. The surface structure and tribological properties of Co-Cr-Mo-g-MPC were also investigated.

MATERIALS AND METHODS

Chemicals

MPC was synthesized industrially by using the method developed by Ishihara et al.²² and it was supplied by AI Bio-Chips Co., Ltd. (Tokyo, Japan). MPSi was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Succinic acid and ethanol were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). 2-Hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-propanone (DAROCUR[®] 2959; D2959) was purchased from Ciba Specialty Chemicals Holding Inc. (Basel, Switzerland). D2959 is a highly efficient radical photoinitiator for ultraviolet (UV) curing of the systems containing unsaturated monomers and prepolymers, and it is particularly well known as a

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cytocompatible UV photoinitiator with UV intensities of $<6 \text{ mW/cm}^2$ that can perform polymerization for up to 10 min with a UV light of 365 nm.³⁸

Co-Cr-Mo alloy substrate and pretreatments

The Co-Cr-Mo alloy was supplied by Yoneda Advanced Casting Co., Ltd (Takaoka, Japan). The chemical composition of the Co-Cr-Mo alloy used in this study is described in Table 1. This alloy was manufactured according to the ASTM F75 standard specification for Co-28Cr-6Mo alloy.³⁹ The Co-Cr-Mo samples were polished so that the average surface roughness ranged between 0.01–0.02 μm .

The polished Co-Cr-Mo samples were washed with acetone, and then immersed in 35 vol% nitric acid at room temperature for 35 min according to the ASTM F86-04 standard.^{40,41} This treatment results in passivation by surface oxidation and it could lead to the dissolution of certain foreign materials that may remain from the previous procedure. Moreover, a previous study reported that the surface of as-polished Co-Cr-Mo alloy might lack the Cr content that the bulk possesses, and that surface etching by nitric acid treatment would have produced a Cr-rich surface layer.⁴¹ We therefore treated the surface with nitric acid with the aim of increasing the Cr concentration by “re-surfacing.”

After the nitric acid treatment, the Co-Cr-Mo samples were irradiated with O₂ plasma at a 500-W high-frequency output and 150-mL/min O₂ gas flow for 5 min by using an O₂ plasma etcher (PR500, Yamato Scientific Co., Ltd., Tokyo, Japan). The O₂ plasma treatment increased the thickness of the

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2 surface oxide layer.⁴²
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8 9 **MPSi silanization and MPC graft polymerization**

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11 The synthesis of Co-Cr-Mo-g-MPC is schematically illustrated in Fig. 1. The pretreated
12 Co-Cr-Mo samples were immersed in an ethanol solution containing 5 mass% MPSi, 1 mass%
13 succinic acid, and 0.1 mass% D2959 at room temperature for 12 h for silanization of the
14 trimethoxysilane group. They were then annealed at 70°C for 3 h in air for dehydration. The
15 MPC was dissolved in degassed pure water to attain concentrations ranging from 0.25 to 1.00 mol/L.
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17 Subsequently, the MPSi (containing D2959)-coated Co-Cr-Mo samples were immersed in aqueous
18 MPC solutions. Photoinduced graft polymerization on the Co-Cr-Mo surface was performed using
19 ultraviolet irradiation (UVL-400HA ultra-high pressure mercury lamp; Riko-Kagaku Sangyo Co.,
20 Ltd., Funabashi, Japan) with an intensity of 5 mW/cm² at 60°C for 23 to 180 min; a filter (Model
21 D-35; Toshiba Corp., Tokyo, Japan) was used restrict the passage of ultraviolet light to wavelengths
22 of 350 ± 50 nm. After the polymerization, the Co-Cr-Mo-g-MPC samples were removed from the
23 solution, washed with pure water and ethanol, and dried at room temperature. For purification,
24 washing with pure water and ethanol enables the removal of the free poly(MPC) and/or
25 poly(MPC-co-MPSi) adsorbed on the Co-Cr-Mo surface.⁴³
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MPC graft polymerization on cross-linked polyethylene

Compression-molded UHMWPE (GUR1020 resin, Poly Hi Solidur Inc., IN, USA) bar stock was

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3 gamma-ray irradiated at 50 kGy in N₂ gas and annealed at 120°C in N₂ gas for crosslinking. After
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6 cooling, the cross-linked polyethylene (CLPE) specimens were machined from this bar stock.

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8 MPC grafting onto the CLPE surface was performed as described in previous studies.^{43–45} The
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12 CLPE specimens were immersed in an acetone solution containing 10 mg/mL benzophenone for 30
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15 s and then dried in the dark at room temperature to remove the acetone. MPC was dissolved in
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18 degassed pure water to a concentration of 0.5 mol/L. The benzophenone-coated CLPE samples
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21 were immersed in the aqueous MPC solution. Photoinduced graft polymerization on the CLPE
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24 surface was carried out using UV irradiation with an intensity of 5 mW/cm² at 60°C for 90 min.
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27 After the polymerization, the CLPE-g-MPC samples were removed from the solution, washed with
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30 pure water and ethanol, and dried.
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37 **Articular cartilage from porcine ankle joint**

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40 Using a surgical hand corer or surgical saw, articular cartilage specimens were harvested from the
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43 flat part of the ankle joint of the fresh frozen porcine tibia (ages 6–9 months). Pin-type articular
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46 cartilage specimens were shaped as cylinders with a height of 5 mm and diameter of 9 mm, and they
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49 had approximately 1 mm of cartilage layer and subcondral bone used for mounting. Throughout
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52 the procedure, the articular cartilage surface was hydrated regularly with Dulbecco's
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55 phosphate-buffered saline (PBS, pH 7.4, ion strength = 0.15 M; Immuno-Biological Laboratories
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58 Co., Ltd., Takasaki, Japan). All the articular cartilage specimens were then stored in Dulbecco's
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61 PBS and frozen at -80°C.⁴⁶

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6 **Surface analysis by Fourier-transform infrared spectroscopy, X-ray photoelectron**
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8 **spectroscopy, and water-contact angle measurement**
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11 The functional group vibrations of the Co-Cr-Mo alloy surfaces before and after the MPC grafting
12 were examined by Fourier-transform infrared (FT-IR) spectroscopy with attenuated total reflection
13 (ATR) equipment. The FT-IR/ATR spectra were obtained using an FT-IR analyzer (FT/IR615,
14 JASCO Co. Ltd., Tokyo, Japan) for 32 scans (1.2 s/scan) over the range of 800 to 2000 cm^{-1} at a
15 resolution of 4.0 cm^{-1} .
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19 The surface elemental conditions of the Co-Cr-Mo alloy before and after the MPC grafting were
20 analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an
21 XPS spectrophotometer (AXIS-HSi165, Kratos Analytical Ltd., Manchester, UK) equipped with a
22 15-kV Mg- $K\alpha$ radiation source at the anode. The take-off angle of the photoelectrons was
23 maintained at 90°. Five scans (approximately 260 to 425 s/scan depending on the atomic signal
24 strength) were taken for each sample.
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28 The static-water contact angles on the Co-Cr-Mo surfaces that were subjected to different types of
29 pretreatments before and after the MPC grafting were measured by the sessile drop method using an
30 optical bench-type contact angle goniometer (Model DM300, Kyowa Interface Science Co., Ltd.,
31 Saitama, Japan). Drops of purified water (1 μL) were deposited on the Co-Cr-Mo-g-MPC surface,
32 and the contact angles were directly measured with a microscope after 60 s of dropping, according to
33 the ISO 15989 standard.⁴⁷ Measurements were repeated six times for each sample, and the average
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2 values were considered as the contact angles.
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8 **Cross-sectional observation by transmission electron microscopy**

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11 A cross-section of the poly(MPC) layer on the Co-Cr-Mo surface was observed using a
12 transmission electron microscope (TEM) and by energy dispersive X-ray (EDX) spectroscopy.
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14 The specimens were pre-coated with an aluminum film using a focused ion beam (FIB) system to
15 prevent charging. After pre-coating, a thin film of the samples was prepared by the FIB technique
16 using an FB-2000A (Hitachi High-Technologies Co., Tokyo, Japan) FIB system. The samples
17 were thinned to electron transparency by a low gallium ion beam current. The thin film thus
18 prepared was positioned onto a copper TEM mesh grid. TEM observations were then recorded
19 using an HF-2000 electron microscope (Hitachi High-Technologies Co.) at an acceleration voltage
20 of 200 kV. EDX spectra were analyzed on a cross-section of the untreated Co-Cr-Mo sample and
21 the Co-Cr-Mo-g-MPC sample obtained with 0.50 mol/L MPC concentrations and a 90-min
22 photoirradiation time using a Sigma EDX attachment (Kevex Instruments, Inc., Valencia, CA, USA)
23 at an acceleration voltage of 200 kV. The probe size of the electron beam was maintained at 1 nm.
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53 **Friction test**

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55 The coefficients of dynamic friction between the pins fabricated from various materials and the
56 untreated Co-Cr-Mo or Co-Cr-Mo-g-MPC (obtained with 0.50 mol/L MPC concentrations and a
57 90-min photoirradiation time) plates were measured using a pin-on-plate machine (Tribostation 32;
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2 Shinto Scientific Co., Ltd., Tokyo, Japan). Each pin was a cylinder measuring 5 mm in height and
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6 9 mm in diameter and used to prepare six sample pieces. The friction tests were performed at room
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9 temperature with a load of 0.98 N, sliding distance of 25 mm, and frequency of 1 Hz for a maximum
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11 of 100 cycles.⁴⁸ Pure water was used as a lubricant. The mean coefficients of dynamic friction
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15 were determined by averaging five data points from the 100 (96–100) cycle measurements.
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21 RESULTS

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24 Fig. 2 shows the FT-IR/ATR spectra of the Co-Cr-Mo sample and that of photoirradiated grafting
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26 of MPC under 0.50-mol/L MPC concentration and 90-min photoirradiation time. Absorption
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28 peaks were not observed for the Co-Cr-Mo sample before the MPC graft polymerization in the
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30 wavenumber range of 800 to 2000 cm^{-1} . In contrast, absorption peaks were newly observed only
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32 for the Co-Cr-Mo-g-MPC samples. The peaks at 1720, 1550, and 1460 cm^{-1} are attributed to C=O
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34 and -CH₂- in the MPSi and poly(MPC) graft chains. The peaks at 1180, 1040, 700, and 630 cm^{-1}
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36 are attributed to the trimethoxysilane group in the MPSi unit.⁴⁹ The peaks at 1240, 1080 and 970
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38 cm^{-1} are attributed to the -N⁺(CH₃)₃ and phosphate groups in the MPC unit.⁴⁴
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50 In the XPS spectra of the binding energy region of the silicon (Si_{2p}), nitrogen (N_{1s}), and
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52 phosphorous (P_{2p}) electrons, peaks appeared in the case of Co-Cr-Mo-g-MPC; however, they were not
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54 observed in the case of Co-Cr-Mo (data not shown). The peak at 103 eV was attributed to the Si₂O₃
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56 or SiO₂ in the trimethoxysilane group in the MPSi unit. The peaks at 403 and 134 eV were attributed
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58 to the -N⁺(CH₃)₃ and phosphate groups, respectively. These peaks reflect the phosphorylcholine
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2 present in the MPC units. Fig. 3 shows the Si, N, and P concentrations of the Co-Cr-Mo-g-MPC
3 surface as a function of the photoirradiation time during polymerization for various MPC
4 concentrations in feeds. Both the N and P concentrations in the Co-Cr-Mo-g-MPC surface increased
5 with the photoirradiation time. In the case of higher MPC concentrations, when the photoirradiation
6 time was greater than 90 min, the N and P concentrations became almost constant above 5.0 atom%.
7 These values were almost equivalent to the theoretical elemental composition (N = 5.3 atom%, P = 5.3
8 atom%) of poly(MPC). As a trade-off, the Si concentration at the Co-Cr-Mo-g-MPC surface
9 decreased with an increase in the photoirradiation time.
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28 Fig. 4 shows the static-water contact angle on the Co-Cr-Mo-g-MPC surface as a function of the
29 photoirradiation time during polymerization with various MPC concentrations in feeds. The
30 static-water contact angle on the untreated Co-Cr-Mo surface before the MPC grafting was
31 approximately 80°. The static-water contact angle on the Co-Cr-Mo-g-MPC surface decreased
32 markedly with an increase in the photoirradiation time and the MPC concentration. When the
33 photoirradiation time and MPC concentration were greater than 90 min and 0.50 mol/L, respectively,
34 the static-water contact angle became constant at a low value of 20°.
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50 Fig. 5 shows the cross-sectional TEM images of Co-Cr-Mo-g-MPC obtained with various MPC
51 concentrations and a 90-min photoirradiation time. In the Co-Cr-Mo-g-MPC, a 10–360 nm-thick
52 poly(MPC) layer was clearly observed on the surface of the Co-Cr-Mo substrate. The thickness of
53 the poly(MPC) layer increased with the MPC concentration during polymerization. At an MPC
54 concentration of 0.50 mol/L, the thickness of the poly(MPC) layer was greatest, i.e., 200 nm.
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These results indicate that the length of the poly(MPC) chain (thickness of the poly(MPC) layer) can be controlled by adjusting the MPC concentration during polymerization. This is explained by the fact that the length of the polymer chains produced in a radical polymerization reaction generally correlates with the MPC concentration.

Fig. 6 shows the EDX spectra of the untreated Co-Cr-Mo and Co-Cr-Mo-g-MPC obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time. In spectra (P1) and (P3) of the substrate of the untreated Co-Cr-Mo and Co-Cr-Mo-g-MPC, strong peaks were observed at 0.8, 2.3, 5.4, 6.0, 6.9, and 7.7 keV. These peaks are attributed to the Co, Cr, and Mo atoms in the Co-Cr-Mo substrate. In spectrum (P2) of the surface of the untreated Co-Cr-Mo, a peak was observed at 0.5 keV. This peak is attributed to the O atom in the metal oxide layer of the Co-Cr-Mo. In spectrum (P4) of the intermediate layer of the Co-Cr-Mo-g-MPC, peaks were observed at 0.5 and 1.7 keV. These peaks are attributed to the O and Si atoms in the intermediate layer between the silane of the MPSi and the metal oxide of the Co-Cr-Mo. In spectra (P4) and (P5) of the intermediate layer and the poly(MPC) layer of the Co-Cr-Mo-g-MPC, a significant peak attributed to the P atom was observed at 2.0 keV. This peak is mainly attributed to the MPC units. Several spectra exhibited peaks at 1.5, 8.0, and 8.9 keV. In these cases, the peaks are attributed to the Al and Cu atoms of the Aluminum coating for the preparation of the TEM observation specimen and/or the copper TEM mesh grid.

Fig. 7 shows the coefficients of dynamic friction of the sliding couples, namely, untreated Co-Cr-Mo, CLPE, CLPE-g-MPC, and articular cartilage pins sliding against the untreated

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3 Co-Cr-Mo and Co-Cr-Mo-g-MPC plates. The Co-Cr-Mo/Co-Cr-Mo and CLPE/Co-Cr-Mo
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6 couples showed a high friction coefficient of approximately 0.19 and 0.14 in the initial 10 cycles;
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9 especially, the value of the Co-Cr-Mo/Co-Cr-Mo couple increased and reached approximately 0.41
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12 in the 100 cycles. After the friction test, some scratches parallel to the sliding direction were
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15 clearly observed in the Co-Cr-Mo/Co-Cr-Mo bearing area. The CLPE-g-MPC/Co-Cr-Mo couples
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18 showed a low friction coefficient of about 0.05 for both 10 and 100 cycles. This corresponds to an
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21 approximately 70% reduction when compared to the coefficients of untreated CLPE/Co-Cr-Mo
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24 couples. The coefficients of dynamic friction of all types of pins sliding against the
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27 Co-Cr-Mo-g-MPC couples decreased drastically as compared with those of untreated Co-Cr-Mo
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30 couples. The degree of reduction in the coefficient was approximately 90% (80 to 99%) for both
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33 10 and 100 cycles. In particular, in the CLPE-g-MPC/Co-Cr-Mo-g-MPC couple, the poly(MPC)
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36 layer sliding against the poly(MPC) layer showed the lowest friction coefficient of approximately
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39 0.005, and this value was almost steady during the experiment. The friction coefficient of the
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42 cartilage/Co-Cr-Mo couple increased gradually and reached approximately 0.09 in the 100 cycles.
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45 The friction coefficient of the cartilage/Co-Cr-Mo-g-MPC couple was approximately 0.006 in the
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48 100 cycles and it remained almost steady. This was much lower than the friction coefficient of the
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51 cartilage/Co-Cr-Mo couple.
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DISCUSSION

In this study, with the aim of reducing wear, a super-lubricious Co-Cr-Mo alloy surface by

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3 poly(MPC) grafting was prepared for its application to artificial joints. Several important issues are
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5 involved in the long-term retention of the benefits of poly(MPC) used in artificial joints under
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7 variable and multidirectional loads: strong bonding between the poly(MPC) and the Co-Cr-Mo
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9 surface, high mobility of the free end groups of the poly(MPC) layer, and a high density of the
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11 introduced poly(MPC). Taking these issues into consideration, the MPSi intermediate layer and
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13 the photoinduced radical graft polymerization technique were used to obtain covalent bonding
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15 between the Co-Cr-Mo substrate and the poly(MPC) chain via the MPSi layer.
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24 MPSi binds to the Co-Cr-Mo substrate by a condensation reaction in two steps (Fig. 1). In the first
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26 step, the MPSi is hydrolyzed (activated) and in the second step, the hydrolyzed silane molecule binds
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28 to the surface by an Si–O–metal (M) bond, forming branched hydrophobic siloxane bonds,
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30 Si–O–Si.^{37,49} The hydrolyzed silane molecule has three –OH groups that can react with the –OH
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32 groups of the surface metallic oxide layer to form siloxane bonds covalently. The peaks at 1180 and
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34 1040 cm⁻¹ in the FT-IR/ATR spectrum of the Co-Cr-Mo-g-MPC surface were attributed to Si–O–Si
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36 and Si–O–M, respectively (Fig. 2), and these were observed after the MPC grafting. This suggests
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38 that the trimethoxysilane group of MPSi binds to the metallic oxides with a stable covalent binding
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40 even when the polymerization of MPC was carried out. This MPSi (and/or poly(MPC-co-MPSi))
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42 layer(s) and the Co-Cr-Mo substrate might contribute to the stable polymer/metal interface.⁵⁰
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54 Fig. 3 shows the Si, N, and P concentrations of the Co-Cr-Mo-g-MPC surface obtained with a
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56 0.5-mol/L MPC concentration and a 90-min photoirradiation time. The concentrations became
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58 almost constant at high values of 5.3 and 5.1 atom%, respectively. These values were almost
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3 equivalent to the theoretical elemental composition of poly(MPC). In addition, the static-water
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6 contact angle of the Co-Cr-Mo-g-MPC surface became constant at a low value of 20°, showing a
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9 highly hydrophilic nature. The peak attributed to Si atoms was observed in the intermediate layer
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12 between the poly(MPC) layer and Co-Cr-Mo substrate only, as shown in Fig. 6. Therefore, it was
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15 assumed that the poly(MPC) chain was grafted and that it extended from the methacrylate on the
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18 MPSi. The hydrophilic layer was formed with the poly(MPC) chain, which attained high mobility,
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21 and the poly(MPSi) chain existed as the immobilized end-group of the poly(MPC) graft chains.
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25 In Fig. 3, both the N and P concentrations in the Co-Cr-Mo-g-MPC surface attributed to
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28 poly(MPC) increased with the MPC concentration during polymerization. In addition, in the TEM
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31 images shown in Fig. 5, the thickness of the poly(MPC) layer increased with the MPC concentration.
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34 When the poly(MPC) layer has a brush-like structure, the layer thickness may correlate with the
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37 molecular weight of the grafted poly(MPC). The high-density poly(MPC) graft chains in the
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40 Co-Cr-Mo-g-MPC are assumed to exhibit a brush-like structure.^{24,51} It is generally well known that
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43 the reaction rate of radical polymerization is extremely high.⁵² In this study, the length (molecular
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46 weight) of the poly(MPC) graft chains was assumed to be successfully controlled by the MPC
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49 concentration used for polymerization as a feed solution. This indicates that the length of the
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52 poly(MPC) chain grafted on the Co-Cr-Mo surface increased with the MPC concentration in feed.⁴⁵
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57 The previous study by the authors reported that the density of the poly(MPC) chains on the
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60 surface of the CLPE prepared by photoinduced radical polymerization gradually increased with the
irradiation time. The study also showed that the entire surface of the CLPE was coated using

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3 polymerization times longer than 45 min with almost the same thickness as that of the poly(MPC)
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5 layer for longer irradiation times (100 to 200 nm).⁴⁴ In this study, both the N and P concentrations
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7 in the Co-Cr-Mo-g-MPC surface attributed to poly(MPC) increased with the photoirradiation time.
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9 When the MPC concentration was greater than 0.5 mol/L, the N and P concentrations of the
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11 Co-Cr-Mo-g-MPC surface increased to approximately 5.3 atom%, which was almost equivalent to
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13 the theoretical elemental composition of poly(MPC). In addition, the Co-Cr-Mo-g-MPC surface
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15 obtained with a 0.5-mol/L MPC concentration and a 90-min photoirradiation time retained the
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17 uniform poly(MPC) layer with a thickness of 200 nm, as reported in the previous study. These
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19 observations indicate that irradiation time control is essential to obtain a high-density poly(MPC)
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21 layer.⁴⁴
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34 The coefficients of dynamic friction of various bearing couples obtained in previous studies are
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36 summarized in Table 2. In Fig. 7, the Co-Cr-Mo/Co-Cr-Mo couple shows a friction coefficient of
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38 approximately 0.19, which is as high as that described in previous studies.^{41,53} The
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40 CLPE/Co-Cr-Mo couple also shows a friction coefficient of approximately 0.14, as high as that
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42 described in previous studies.^{41,54,55} In contrast, the Co-Cr-Mo-g-MPC surface with respect to each
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44 material shows an extremely low friction coefficient as compared to that of the untreated Co-Cr-Mo
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46 surface. Since MPC is highly hydrophilic and poly(MPC) is water soluble, the water contact angle
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48 of the Co-Cr-Mo-g-MPC surface was lower than that of the untreated Co-Cr-Mo surface, as shown
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50 in Fig. 4. Consequently, the grafted poly(MPC) layer successfully provided high lubricity in the
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52 form of “surface gel hydration lubrication” to the Co-Cr-Mo surface (Fig. 7).⁵⁶
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Various factors such as the type of bearing material, surface roughness, homogeneity of the surface, and chemical composition affect the lubricity of artificial joints.⁵⁷ In the case of Co-Cr-Mo-g-MPC, the lubricity changes depending on the ambient *in vitro* and *in vivo* conditions. The previous study reported that the hydrogel cartilage surface is assumed to have a brush-like structure: a part of the proteoglycan aggregate brush is bonded with the collagen network on the cartilage surface.⁵⁶ The bearing surface with poly(MPC) in artificial hip joints is assumed to have a brush-like structure similar to that of articular cartilage. CLPE-g-MPC/Co-Cr-Mo-g-MPC or cartilage/Co-Cr-Mo-g-MPC bearing couples can therefore be regarded to mimic the natural joint cartilage *in vivo*. The friction coefficient of cartilage/stainless steel (SUS) pin-on-plate ranges from 0.01 to 0.05,⁵⁸ and that of cartilage/cartilage pin-on-plate is 0.02,⁵⁹ as shown in Table 2. In this study, it was found that CLPE-g-MPC/Co-Cr-Mo-g-MPC or cartilage/Co-Cr-Mo-g-MPC bearing couples mimic a natural joint, showed low friction (friction coefficient was approximately 0.01), as low as that of cartilage/SUS or cartilage/cartilage. Hence, it was considered that the Co-Cr-Mo-g-MPC surface is excellent for the femoral head articulating cartilage, because the cartilage/Co-Cr-Mo-g-MPC bearing couples showed a constant low friction coefficient of 0.006. We expect that the hemi-arthroplasty with the Co-Cr-Mo-g-MPC femoral head bearing will be promising to preserve acetabular cartilage and extend the duration before THA in young patients.

On the other hand, in the previous study, the CLPE-g-MPC/Co-Cr-Mo-g-MPC prepared by the adsorption of the polymer to the substrate, termed as the “grafting to” method bearing couples showed high friction (friction coefficient was 0.12).⁴¹ The poly(MPC) on Co-Cr-Mo used in this

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3 study might have a high density because the polymerization method used was surface-initiated graft
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6 polymerization, termed as the “grafting from” method, in which the monomers are polymerized
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9 from initiators or comonomers, whereas the poly(MPC) on Co-Cr-Mo prepared by the “grafting to”
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12 method might have a low density.^{34,35} Fig. 8 shows the images of high-density grafted
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15 poly(MPC)/low-density grafted poly(MPC) and high-density grafted poly(MPC)/high-density
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18 grafted poly(MPC) bearing interfaces. The high-density grafted poly(MPC)/high-density grafted
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21 poly(MPC) bearing interface shows a remarkably lower friction than the high-density grafted
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24 poly(MPC)/low-density grafted poly(MPC) bearing interface.⁶⁰ Fukuda et al. reported that the
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27 friction of the bearing couple was higher in low-density polymer brushes than in high-density ones.⁶¹
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30 Therefore, it is assumed that a bearing couple with low-density poly(MPC) brushes may cause high
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33 friction by stick-slip motion with interpenetration, as shown in Fig. 8(a).^{60,62} In contrast,
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36 high-density poly(MPC) fabricated by the “grafting from” method may attain low friction, such as
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39 that in the case of “super-lubricity,” owing to resistance to interpenetration by volume effects
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42 resulting from chain mobility. The reduction in friction may contribute to the improvement in
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45 anti-wear properties.¹⁹⁻²¹ Although a hip joint simulator test is necessary to examine tribological
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48 advantages in human body environments, a super-lubricious metal-bearing material would enable
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51 the development of a novel biocompatible artificial hip joint system—artificial femoral head for
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54 partial hemi-arthroplasty and metal-on-polymer/metal type for THA.
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CONCLUSION

We prepared a super-lubricious metal-bearing material for application as a novel artificial hip joint system: poly(MPC) was grafted onto the surface of a Co-Cr-Mo alloy by employing an MPSi intermediate layer and by using the photoinduced radical graft polymerization technique. The thickness and density of the grafted poly(MPC) layer increased with the MPC concentration and photoirradiation time, respectively. In conclusion, the grafted poly(MPC) layer successfully provided super-lubricity to the Co-Cr-Mo surface, and the CLPE-g-MPC/Co-Cr-Mo-g-MPC or cartilage/Co-Cr-Mo-g-MPC bearing interface, which mimicked a natural joint, showed an extremely low friction coefficient of 0.01, a value that is as low as that of a natural cartilage interface.

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