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Figure captions

Table 1 Chemical composition (%) of the Co-Cr-Mo alloy

Table 2 Surface elemental composition (%) of the pretreated Co-Cr-Mo alloy before MPC graft polymerization

Table 3 Surface elemental composition (%) of the Co-Cr-Mo-g-MPC samples that were subjected to different types of pretreatments

Table 4 Friction coefficients of various bearing couples in the previous studies

Fig. 1 Scheme for the synthesis of Co-Cr-Mo-g-MPC.

Fig. 2 FT-IR/ATR spectra of the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo sample (a) before and (b) after MPC grafting.

Fig. 3 XPS spectra of the binding energy region of the Co_{2p}, Cr_{2p}, and Mo_{3d} electrons from the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo samples (a) before and (b) after the 4-META coating.

Fig. 4 XPS spectra (N_{1s} and P_{2p}) of the (a) untreated Co-Cr-Mo and (b) nitric acid- and O_2 plasma-pretreated Co-Cr-Mo-g-MPC samples.

Fig. 5 Static water contact angle on the Co-Cr-Mo surfaces that were subjected to different types of pretreatments before and after the MPC grafting. Open marks, before MPC grafting; closed marks, after MPC grafting.

Fig. 6 FM images of (a), (c) the untreated Co-Cr-Mo and (b), (d) the nitric acid- and O_2 plasma-pretreated Co-Cr-Mo-g-MPC samples. (a), (b) = FM images; (c), (d) = color images from fluorescence intensity of the FM images (a) and (b). Bar = 200 μm . Color scale bar indicates fluorescence intensity (red brightness) for (c) and (d).

Fig. 7 Friction coefficients as a function of the test duration for the various types of pins sliding against the Co-Cr-Mo-g-MPC ($n = 3$) and untreated Co-Cr-Mo ($n = 2$) plates. * $n = 1$. Bars = Standard Deviations.

Fig. 8 Images of grafted non-grafted poly(MPC) /grafted poly(MPC) and poly(MPC)/grafted poly(MPC) bearing interfaces.

Table 1 Chemical composition (%) of the o-Cr-Mo alloy

Cr	Mo	C	Ni	Fe	Si	Mn	Al	Co
28.61	5.96	0.03	0.02	0.03	0.54	0.40	0.02	Bal.

Table 2 Surface elemental composition (%) of the pretreated Co-Cr-Mo alloy before MPC graft polymerization (n = 5)

Pre-treatment	C _{1s}	O _{1s}	N _{1s}	P _{2p}	Co _{2p}	Cr _{2p}	Mo _{3d}
untreated	44.2 (5.1)	39.3 (2.8)	0.6 (0.2)	0.0 (0.0)	10.5 (2.5)	4.5 (0.5)	1.0 (0.2)
Nitric acid	29.6 (3.8)	37.3 (1.6)	0.4 (0.8)	0.0 (0.0)	9.4 (0.7)	21.3 (2.1)	2.1 (0.2)
O ₂ plasma	13.9 (0.5)	53.5 (0.9)	0.0 (0.0)	0.0 (0.0)	30.5 (1.2)	1.8 (0.5)	0.3 (0.1)
Nitric acid+ O ₂ plasma	14.6 (1.3)	52.9 (2.7)	0.0 (0.0)	0.0 (0.0)	26.7 (1.5)	5.4 (0.2)	0.4 (0.0)

The standard deviations are shown in parentheses.

Table 3 Surface elemental composition (%) of the Co-Cr-Mo-g-MPC samples that were subjected to different types of pretreatments (n = 5)

Pre-treatment	MPC treatment	C _{1s}	O _{1s}	N _{1s}	P _{2p}	Co _{2p}	Cr _{2p}	Mo _{3d}
Nitric acid+ O ₂ plasma	Untreated	14.6 (1.3)	52.9 (2.7)	0.0 (0.0)	0.0 (0.0)	26.7 (1.5)	5.4 (0.2)	0.4 (0.0)
Untreated		52.3 (1.3)	35.3 (0.4)	0.3 (0.2)	0.9 (0.1)	4.8 (0.8)	5.6 (1.1)	0.8 (0.1)
Nitric acid	MPC	52.1 (1.1)	36.2 (0.7)	0.4 (0.2)	1.6 (0.2)	3.4 (0.4)	5.7 (0.7)	0.7 (0.2)
O ₂ plasma	treatment	42.1 (1.1)	45.6 (1.1)	0.2 (0.2)	1.0 (0.1)	10.5 (0.7)	0.4 (0.5)	0.2 (0.1)
Nitric acid+ O ₂ plasma		63.3 (0.6)	30.8 (0.7)	3.0 (0.2)	2.9 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
MPC polymer*		57.9	31.6	5.3	5.3	—	—	—

*: Theoretical elemental composition of MPC polymer. The standard deviations are shown in parentheses.

Table 4 Friction coefficients of various bearing couples in the previous studies

Bearing couple		Friction coefficient	Reference
Pin	Disc or plate		
Co-Cr-Mo	Co-Cr-Mo	0.19 – 0.27	[51]
UHMWPE	Co-Cr-Mo	0.05 – 0.09	[52]
UHMWPE	Co-Cr-Mo	0.08 – 0.13	[53]
Cartilage	Stainless steel	0.01 – 0.05	[55]
Cartilage	Cartilage	0.02	[56]

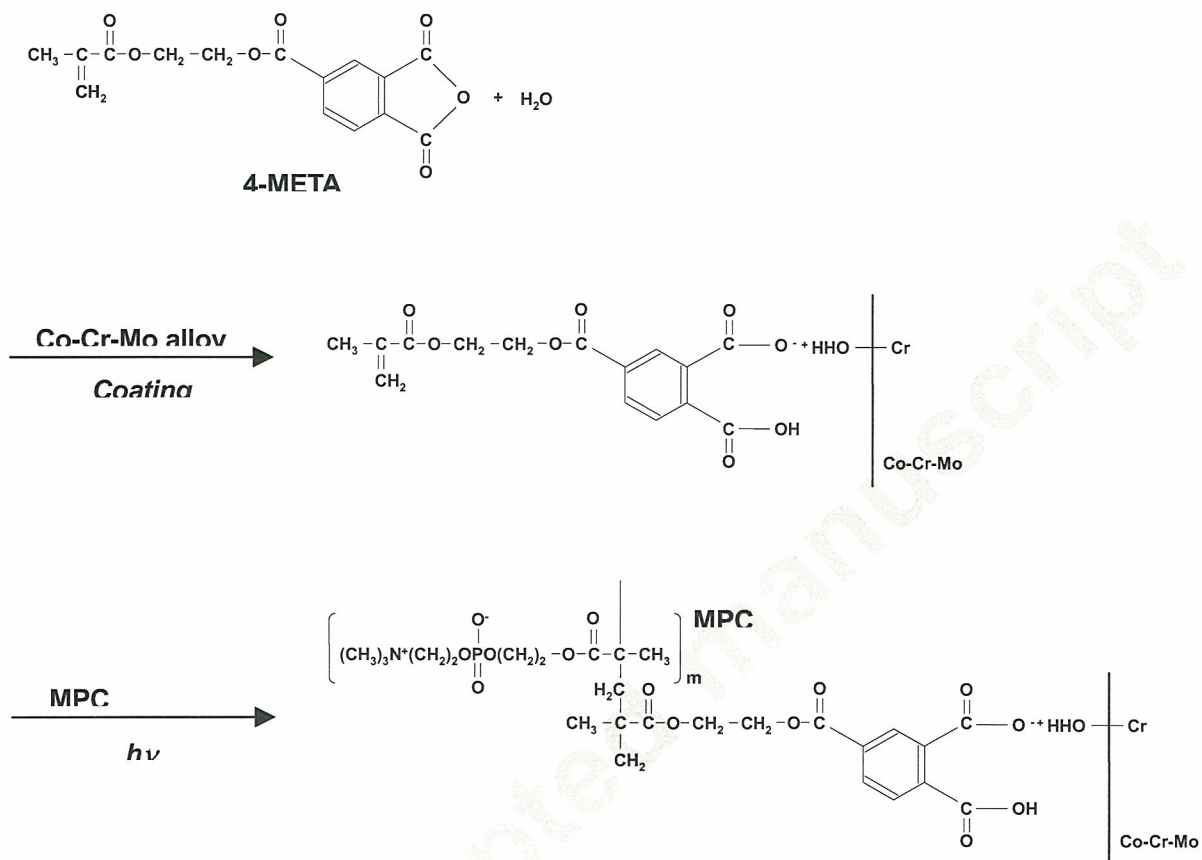


Fig. 1

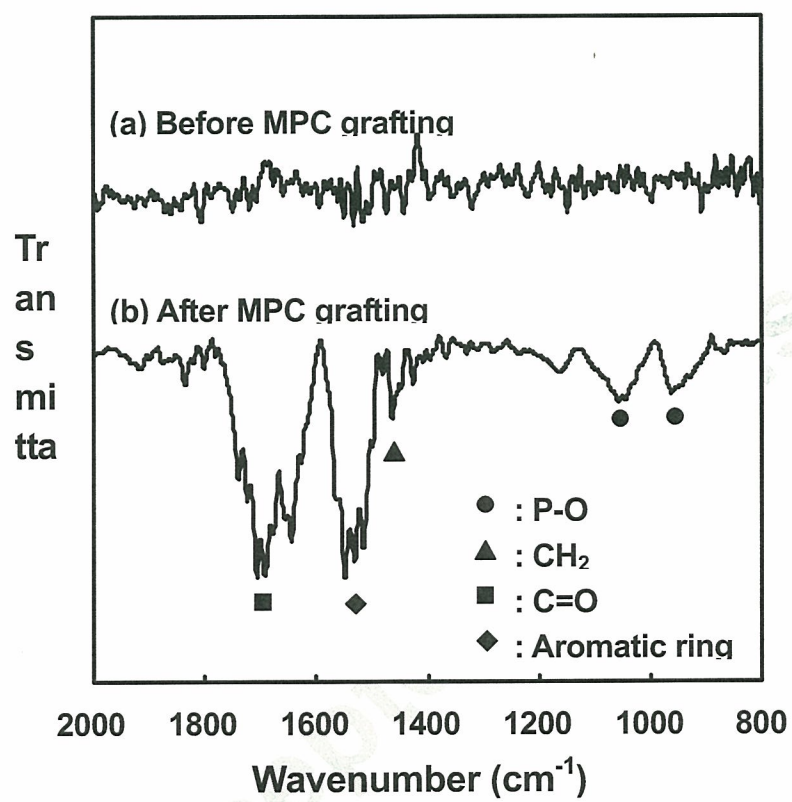


Fig. 2

(b) After 4-META coating

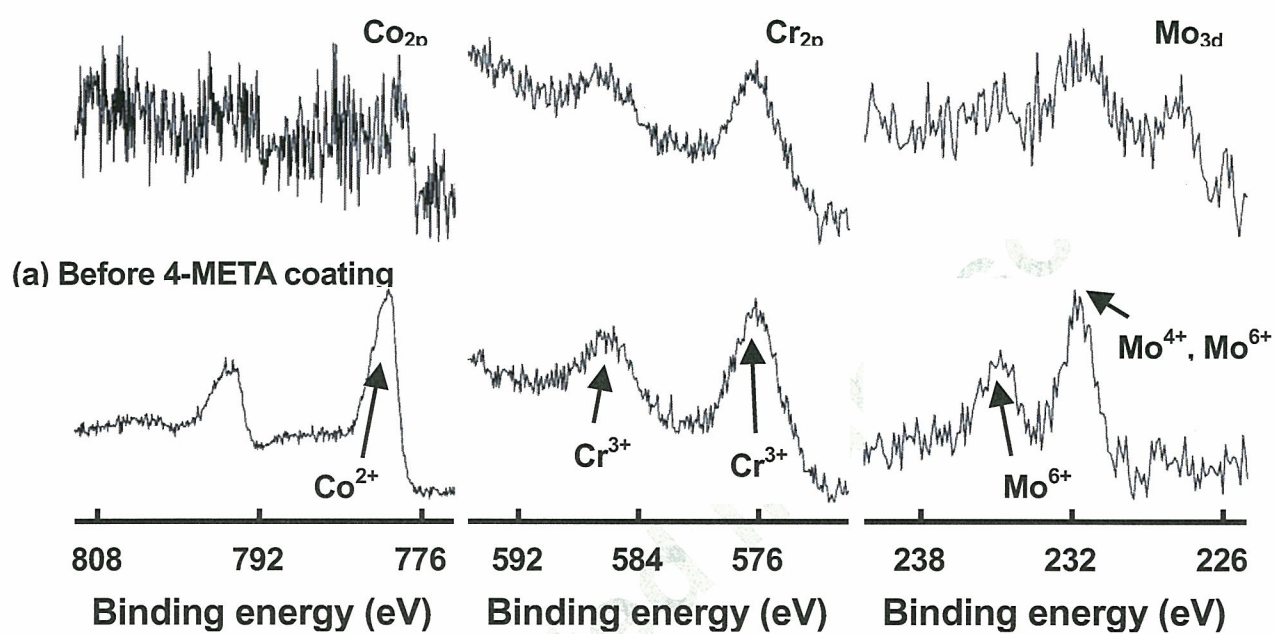


Fig. 3

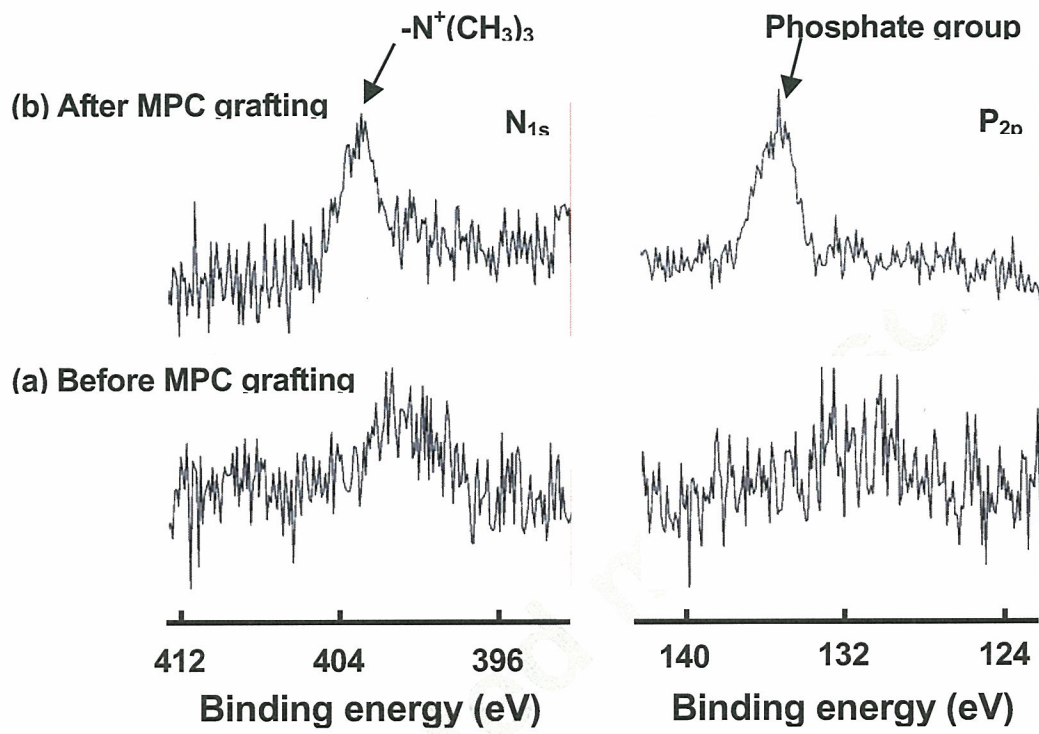


Fig. 4

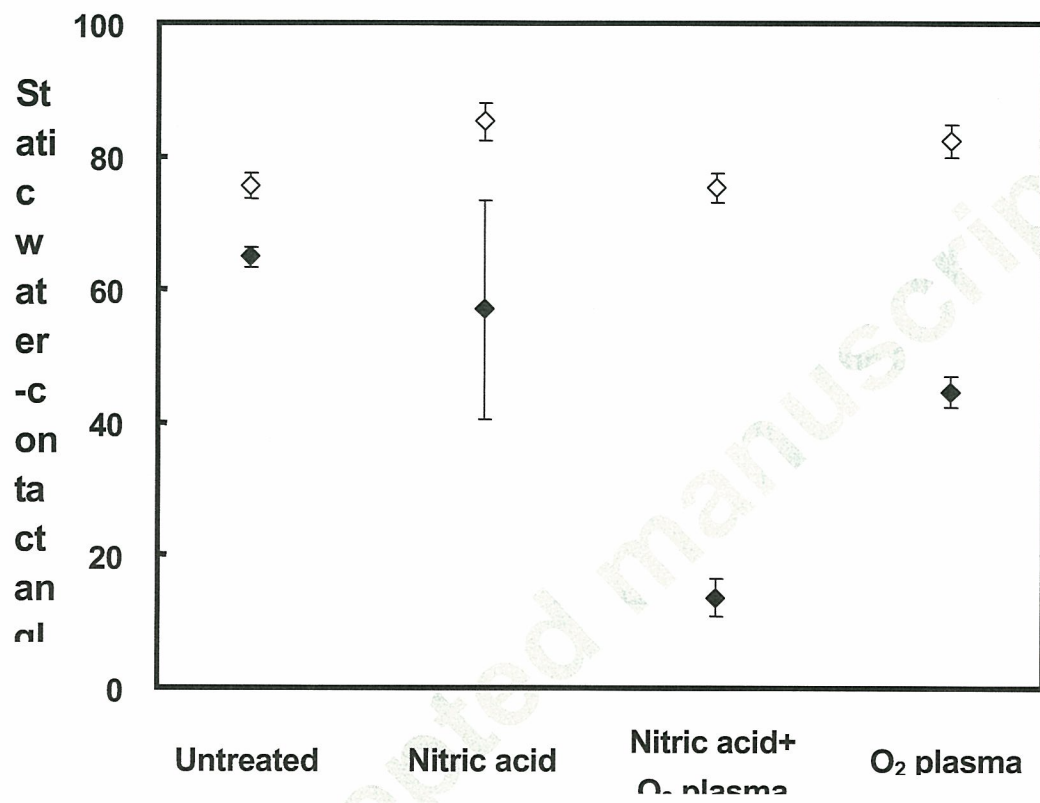


Fig. 5

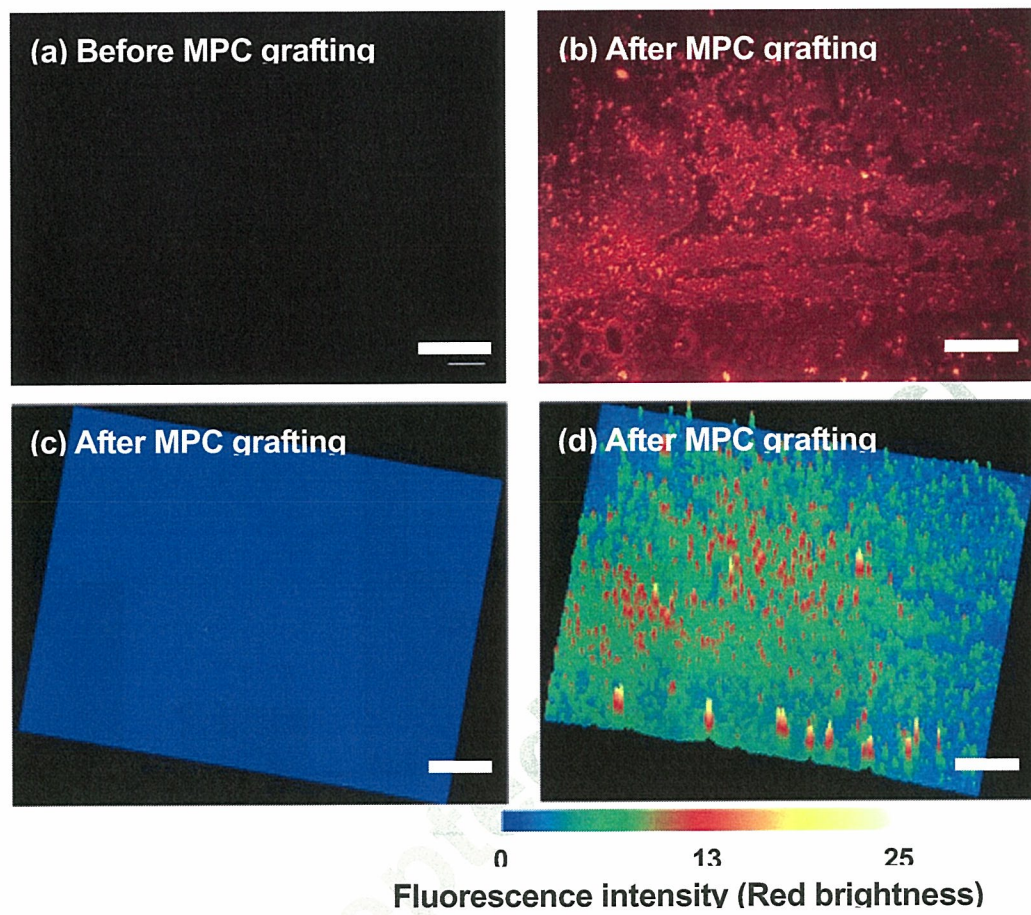


Fig. 6

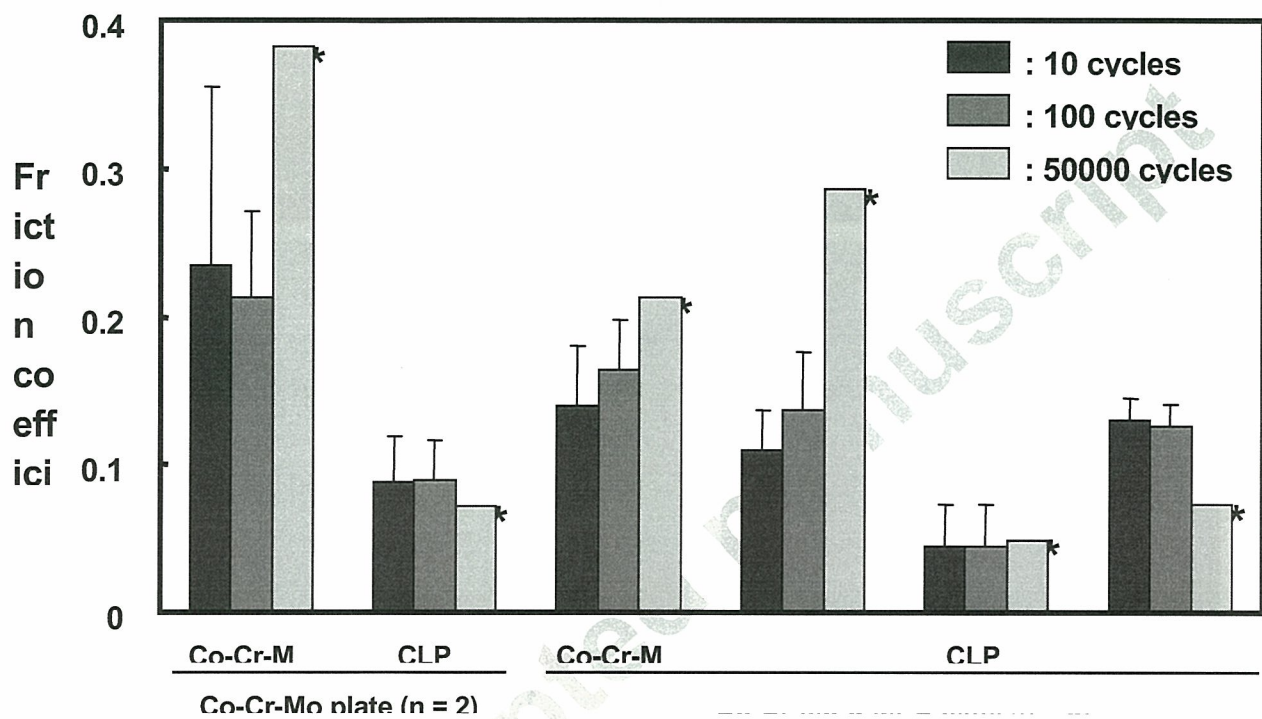


Fig. 7

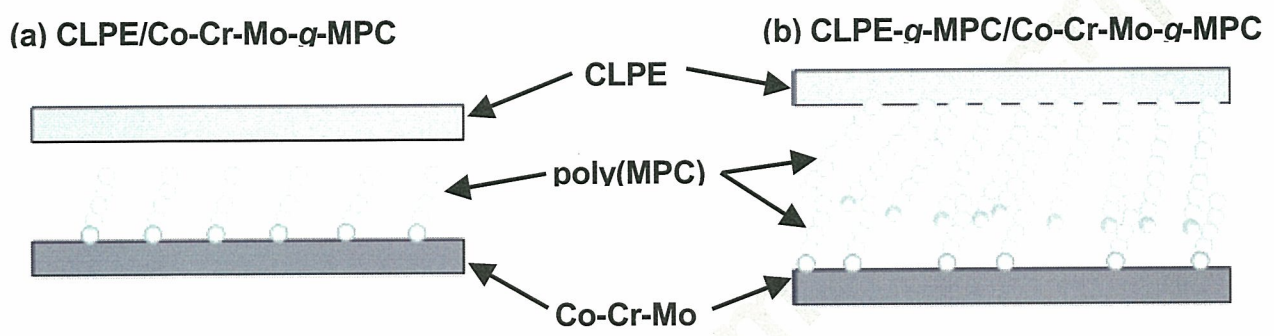


Fig. 8



**Enhanced wear resistance of modified cross-linked polyethylene by
grafting with poly(2-methacryloyloxyethyl phosphorylcholine)**

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Keywords:	Joint replacements, Polyethylene, Phospholipid, phosphorylcholine, Wear mechanisms



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6 **Enhanced wear resistance of modified cross-linked polyethylene by**
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8 **grafting with poly(2-methacryloyloxyethyl phosphorylcholine)**
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ABSTRACT

We developed a cross-linked polyethylene (CLPE) modified with a phospholipid polymer in order to address the serious problem of osteolysis caused by wear particles derived from the polyethylene components of artificial hip joints. Our goal of preventing aseptic loosening could be achieved by avoiding any formation of CLPE wear particles or suppressing the activation of cell systems by the wear particles. We investigated the surface and wear resistance properties of 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer grafted onto the surface of CLPE (CLPE-*g*-MPC). The relative density of MPC polymer chains was determined by the P–O group index. Generally, polymerization times correspond to the number of polymer chains in radical polymerization. After 3.0×10^6 cycles in a hip joint simulator test, the steady wear rates of the untreated CLPE and CLPE-*g*-MPC cups with a low P–O group index were as high as $4 \text{ mg}/10^6$ cycles; those of the CLPE-*g*-MPC cups with high P–O group indexes, i.e., 0.46 and 0.48, markedly decreased to -1.12 and $0.16 \text{ mg}/10^6$ cycles, respectively. Therefore, the grafting of an MPC polymer with high density would be essential in order to maintain the long-term wear resistance of CLPE-*g*-MPC as an orthopedic bearing material.

KEY WORDS: Joint replacements; Polyethylene; Phospholipid; Phosphorylcholine; Wear mechanisms

Running title: Influence of P–O densities on CLPE-*g*-MPC wear

INTRODUCTION

As the number of aged persons in the world increases year by year, the increase in patients with poorly functioning joints due to external injury or disease is becoming a serious social problem. This means that the quality of artificial joints is becoming increasingly important. Most patients who receive an artificial joint experience a dramatic relief of pain and enjoy a rapid improvement in the quality of life. The most widely used bearing couple for artificial joint systems is the combination of an ultra-high molecular weight polyethylene (UHMWPE) acetabular component and a metal (generally Co-Cr-Mo alloy) femoral component. However, osteolysis caused by wear particles of the UHMWPE is a serious problem with artificial hip joints.¹⁻³ Reducing wear particle production from UHMWPE is one way of preventing osteolysis. Efforts to decrease these particles have focused on using combinations other than metal-on-UHMWPE and improving the bearing materials themselves.

Several highly cross-linked polyethylenes (CLPE), irradiated with 50 to 105 kGy, have been launched since 1998 and used extensively.^{4,5} Gamma and electron beam irradiation at various doses are used to produce CLPE, and numerous *in vitro* studies have been performed using it. In published studies, CLPE subjected to 50–105 kGy exhibited an 80% to 90% reduction in wear rate compared with conventional polyethylene.^{6,7} Furthermore, clinical results have confirmed CLPE's effective wear-resistance. However, while the efficacy of the CLPE is evidenced by these reports, *in vivo* the reduction of wear is reported to be only 40% to 60%.⁸⁻¹² Therefore, further improvement of CLPE is desirable.

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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.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 Various polymers containing MPC units are already widely used as biomaterials.^{15, 16} The biomembrane-like surface is readily obtained by treating the substrate materials with MPC polymer. The artificial biomembrane surface thus formed exhibits excellent biocompatibility; it is hydrophilic and forms a thin film of free water under physiological conditions.¹⁷ Several medical devices have already been developed utilizing MPC polymer. These devices have been subjected to clinical use with the approval of the Food and Drug Administration of the USA; therefore, the efficacy and safety of the MPC polymer as a biomaterial are well established.¹⁸⁻²⁰

We have been developing novel artificial joints with very-low-friction bearing surfaces by combining the biocompatible and hydrophilic MPC polymer with CLPE; this has been accomplished by using a photo-induced radical polymerization technique. This technique facilitates direct grafting of MPC to CLPE, thereby forming C-C covalent bonding between the MPC polymer and CLPE substrate. The advantage of this technique is that the MPC polymer graft occurs only on the CLPE surface and has no effect on the bulk properties of the CLPE substrate. The present study investigated the structure and properties of the MPC polymer layer formed on the CLPE surface by photo-induced radical graft polymerization. The wear-resistant properties of the