Table 2 Disease management activities

	Total		Pre OA		Primary		Progressive		End		*P*-Value[a]	
	n	%	*n*	%	*n*	%	*n*	%	*n*	%		
	330	100	56	100	49	100	68	100	157	100		
I try not to remain standing for long periods of time	282	85%	37	66%	41	84%	61	90%	143	91%	<.001	***
I do not choose shoes with high heels or hard soles	281	85%	33	59%	42	86%	60	88%	146	93%	<.001	***
I am careful about the walking distance and speed in daily life	259	78%	37	66%	40	82%	57	84%	125	80%	0.10	
I use a cane or hold a handrail when necessary	257	78%	20	36%	35	71%	55	81%	147	94%	<.001	***
I try not to lift heavy objects	251	76%	26	46%	35	71%	49	72%	141	90%	<.001	***
I do muscle training	241	73%	35	63%	30	61%	52	76%	124	79%	0.00	**
I am careful with my diet to avoid weight gain	241	73%	35	63%	30	61%	52	76%	124	79%	0.00	**
I do stretching	148	45%	26	46%	23	47%	36	53%	63	40%	0.33	
I do exercise to prevent weight gain	146	44%	22	39%	28	57%	30	44%	66	42%	0.70	

[a] Mantel-Haenszel's chi-square test *P*-value $^{*}P < 0.05$, $^{**}P < 0.01$, and $^{***}P < 0.001$.

Table 3 Differences between uni-lateral hip OA and bi-lateral hip OA of disease management activities

	Uni-lateral		Bi-lateral		*t*-Score	*P*-Value[a]
	n = 127		*n* = 203			
	Mean	SD	Mean	SD		
I try not to remain standing for long periods of time	0.8	(0.4)	0.8	(0.4)	−0.49	0.63
I do not choose shoes with high heels or hard soles	0.8	(0.4)	0.9	(0.3)	0.91	0.36
I am careful about the walking distance and speed in daily life	0.9	(0.3)	0.8	(0.4)	0.36	0.72
I use a cane or hold a handrail when necessary	0.8	(0.4)	0.7	(0.4)	1.94	0.05
I try not to lift heavy objects	0.7	(0.5)	0.7	(0.4)	0.64	0.53
I do muscle training	0.4	(0.5)	0.4	(0.5)	−0.92	0.36
I am careful with my diet to avoid weight gain	0.8	(0.4)	0.7	(0.4)	−0.44	0.66
I do stretching	0.3	(0.5)	0.4	(0.5)	−1.13	0.26
I do exercise to prevent weight gain	0.4	(0.5)	0.5	(0.5)	0.18	0.85

[a] *t*-Test *P*-value $^{*}P < 0.05$, $^{**}P < 0.01$, and $^{***}P < 0.001$.

range of 0.63–0.69, indicating that the internal consistency remained at the acceptable level. Then we summed up the figures of each domain to obtain the personal management activity score of the domain.

Table 6 shows the correlation between the disease management activity score of domain 3 and each related factor. No factor was found significantly relevant in a statistical sense for ⟨Muscle training and weight management activities⟩. ⟨Activities to prevent load on hip⟩ had a statistically significant relevance to higher age ($r = 0.38$, $P < 0.001$), more advanced disease stage ($r = 0.51$, $P < 0.001$), larger BMI ($r = 0.13$, $P = 0.02$), lower total JOA score ($r = -0.33$, $P < 0.001$), lower score in each subscale of JOA score ($r = -0.32 - 0.49$, $P < 0.001$), more difficulty in finding medical specialists nearby ($r = 0.25$, $P < 0.001$), more difficulty in weight management ($r = 0.18$, $P = 0.00$), more difficulty in controlling pain ($r = 0.25$, $P < 0.001$), more difficulty in moving joints ($r = 0.41$, $P < 0.001$), more difficulty in choosing a therapy course ($r = 0.20$, $P = 0.00$), stronger feeling of placing burden on family or friends ($r = 0.30$, $P < 0.001$), and more difficulty in sleeping due to pain ($r = 0.16$, $P = 0.00$).

⟨Activities to aid careful walking⟩ had a statistically significant relevance to higher age ($r = 0.17$, $P = 0.00$), more advanced disease stage ($r = 0.18$, $P = 0.00$), lower JOA pain score ($r = -0.14$, $P = 0.01$), lower JOA ability to walk score ($r = -0.22$, $P < 0.001$), lower JOA ADL score ($r = -0.24$, $P < 0.001$), more difficulty in finding medical specialists nearby ($r = 0.14$, $P = 0.01$), more difficulty in weight management ($r = 0.12$, $P = 0.03$), more difficulty in moving joints ($r = 0.22$, $P < 0.001$), more difficulty in choosing a therapy course ($r = 0.11$, $P = 0.05$), stronger feeling of placing burden on family or friends ($r = 0.20$, $P = 0.00$).

Discussion

The present study clarified the current status of the disease management activities of the patients who were in conservative treatment courses, the relevant factors, and the reasons why they performed the activities.

Current status of disease management activities

Seventy-three percent of all the patients, and more than 60% of those in each disease stage, answered yes to the statement "I do muscle training." This percentage was higher among the patients who were at the more advanced stage than the pre OA of OA with few symptoms. Muscle training is the foundation of the conservative therapies and is sometimes difficult for patients to continue; however, the present study showed that many patients actually did the muscle training. It is important to strengthen the gluteus medius muscle to enhance the bearing ability of the hip joint, and muscle training was proved by a large RCT to be effective (Messier et al., 2004). A previous study indicated that, since the difference in instructional methods had no difference in their effects (Ravaud et al., 2004), making appropriate efforts for the individual patient, such as personal guidance, group exercise, or home exercise, was necessary for continuing muscle training. In particular, since only a limited number of exercises can prevent putting a burden on joints, information to individual patients about suitable exercise should be received from specialists.

Only less than half of the patients were performing "stretching" or "exercise to prevent weight gain". This may indicate that the ease of the

Table 4 Reason for the disease management activities

	Total		Pre OA		Primary		Progressive		End		P-Value[a]	
	N	%	n	%	n	%	n	%	n	%		
	330	100	56	100	49	100	68	100	157	100		
I do not want to let OA progress	245	74%	42	75%	37	76%	56	82%	110	70%	0.38	
I want to control pain	224	68%	29	52%	36	73%	46	68%	113	72%	0.03	*
I do not want to have surgery	173	52%	24	43%	26	53%	39	57%	84	54%	0.25	
I cannot walk	135	41%	13	23%	14	29%	23	34%	85	54%	<.001	***
I cannot move joint	129	39%	12	21%	12	24%	18	26%	87	55%	<.001	***
I was told by doctors to do so	75	23%	11	20%	18	37%	15	22%	31	20%	0.36	
I am anxious about the way of walking	61	18%	2	4%	11	22%	13	19%	35	22%	0.01	*
Because it is the condition that it can't operate at present	36	11%	4	7%	6	12%	12	18%	14	9%	1.00	

As for the reasons of the disease control behavior, it asked in several answers.
[a] Mantel-Haenszel's chi-square test *P*-value $^{*}P < 0.05$, $^{**}P < 0.01$, and $^{***}P < 0.001$.

activities made a difference in actual performance. According to the guideline, exercises including stretching and muscle training are expected to have the effect of suppressing the progress of OA. Future progression of OA could be slowed by performing and continuing the disease management activities in the primary stage of the disease. It may be necessary to develop a program to improve the management activities that are not easy for patients to perform.

There were no significant differences between one-side hip OA and two-side hip OA of disease management activities. It may be because there were more than half of patients who performed disease management activities.

Reasons for disease management activities

The top reason for performing the management activities was "I do not want to let OA progress", to which 74% of the patients answered yes. Sixty-eight percent chose the reason "I want to control pain" and about half of the patients selected the reason "I do not want to have surgery". The reason "I was told by the doctor to do so" was chosen by only 23% of the patients. The patients performed the management activities to prevent progression of OA, and the information provision and suggestion from doctors did not largely enhance their motivation. Doctor's advice of performing the management activities did not always lead to actual performance of the activities. Personal guidance in accordance with individual understanding or interest may also be necessary.

Relevant factors in disease management activities

We found that higher age, more advanced disease stage, and lower score in each subscale of the JOA score were relevant to ⟨Activities to prevent load on hip⟩ and ⟨Activities to aid careful walking⟩. Patients at a higher age tended to be in a more advanced disease stage and present a lower JOA score, and hence the patients at a higher age had severe symptoms in the advanced stage and had to decide whether to perform the management activities. Also, a statistically significant relevance was found in difficulty in finding medical specialists nearby, difficulty in weight management, difficulty in controlling pain, difficulty in moving joints, difficulty in choosing a therapy course, feeling of placing a burden on family or friends, and difficulty in sleeping due to pain. In consideration of the result that the difficulty in their daily lives was

Table 5 The results of factor analysis of the disease management activities: factor loadings after Promax rotation and Cronbach's alpha coefficients ($N = 330$)

	Factor 1	Factor 2	Factor 3
Muscle training and weight management activities $\alpha = 0.69$			
I do muscle training	*0.70*	−0.01	0.01
I do stretching	*0.67*	0.02	−0.06
I do exercise to prevent weight gain	*0.63*	−0.05	0.03
I am careful with my diet to avoid weight gain	*0.31*	0.25	0.07
Activities to prevent load on hip $\alpha = 0.63$			
I use a cane or hold a handrail when necessary	−0.04	*0.59*	0.01
I do not choose shoes with high heels or hard soles	−0.04	*0.55*	−0.03
I try not to lift heavy objects	0.07	*0.48*	0.18
Activities to aid careful walking $\alpha = 0.66$			
I am careful about the walking distance and speed in daily life	0.00	0.09	*0.53*
I try not to remain standing for long periods of time	−0.03	0.18	*0.54*
Total contribution 38%			

Table 6 Related factors of the disease management activities

$N = 330$	Muscle training and weight management activities		Activities to prevent load on hip			Activities to aid careful walking		
	r[a]	*P*-Value	r[a]	*P*-Value		r[a]	*P*-Value	
Age	0.07	0.22	0.38	<.001	***	0.17	0.00	***
Duration of osteoarthritis	−0.02	0.78	0.00	0.98		−0.04	0.46	
Disease stage	0.02	0.76	0.51	<.001	***	0.18	0.00	***
BMI	−0.05	0.34	0.13	0.02	*	0.07	0.22	
JOA score								
Range of motion	0.08	0.15	−0.33	<.001	***	−0.09	0.11	
Pain	0.03	0.60	−0.32	<.001	***	−0.14	0.01	**
Walk	−0.04	0.45	−0.46	<.001	***	−0.22	<.001	***
ADL	0.04	0.48	−0.49	<.001	***	−0.24	<.001	***
Difficulty in their daily life[b]								
There are no local medical specialists for disease management	0.03	0.60	0.25	<.001	***	0.14	0.01	**
I find it difficult to maintain my body weight appropriately	−0.07	0.18	0.18	0.00	***	0.12	0.03	*
I have a hard time controlling pain in daily life	0.01	0.91	0.25	<.001	***	0.08	0.16	
I am reluctant to use a walking stick	−0.07	0.18	0.02	0.76		0.08	0.13	
I have a hard time moving joints as I wish	−0.02	0.68	0.41	<.001	***	0.22	<.001	***
It difficulty to choose a treatment method	−0.01	0.85	0.20	0.00	***	0.11	0.05	*
I feel that I am putting burdens on my family or friends	0.04	0.47	0.30	<.001	***	0.20	0.00	***
I have a hard the sleeping well due to pain	0.03	0.64	0.16	0.00	***	0.07	0.19	

[a] r are expressed as Spearman's coefficients. *P*-value $^{*}P < 0.05$, $^{**}P < 0.01$, and $^{***}P < 0.001$.

[b] Difficulty in their daily life using answers graded from 1 to 5 which ranged from "I feel exactly the same" to "I do not feel any at all".

statistically significant, it is likely that the patients performed the management activities out of necessity because they had problems caused by OA symptoms.

Since weight loss and muscle training can relieve the pain of OA and improve the range of motion (van Baar et al., 1998) and exercises including stretching and muscle training are expected to slow the progression of OA (Hochberg et al., 1995; Anon., 2000), we consider it necessary to advise patients at an earlier stage of the disease to perform the management activities and to develop a program to link the advice to actual performance of the activities.

In terms of muscle training and weight management activities, a small number of patients performed half of its items. Also, stages of the disease did not affect motivation of patients' training performance. These two facts are considered to be the reasons why there were no related factors.

Caution is required when generalizing this result since the present study focused on the patients of an orthopaedic outpatient service specializing in hip joints at one university hospital. Also, we used the answers from the patients to determine whether they performed the disease management activities, and did not verify whether they actually did or did not. Since it is important to continue the management activities, we consider it necessary to study temporal change of the result in addition to the present cross-sectional survey at a specific point in time.

Conclusions

The present study clarified the status of the disease management activities of the patients who were having conservative treatment. We consider it necessary to advise patients at an earlier stage of the disease to perform the management activities and to develop a program to link the advice to actual performance of the activities.

References

Anon, 2000. Recommendations for the medical management of osteoarthritis of the hip and knee. American College of Rheumatology Subcommittee on Osteoarthritis Guidelines. Arthritis and Rheumatism 43(9), 1905–1915.

Arokoski, J.P.A., 2005. Physical therapy and rehabilitation programs in the management of hip osteoarthritis. Europa Medicophysica 41 (2), 155–161.

Creamer, P., Flores, R., Hochberg, M.C., 1998. Management of osteoarthritis in older adults. Clinics in Geriatric Medicine 14 (3), 435–454.

Davy, D.T., Kotzar, G.M., Brown, R.H., Heiple, K.G., Goldberg, V.M., Heiple Jr., K.G., et al., 1988. Telemetric force measurements across the hip after total arthroplasty. Journal of Bone and Joint Surgery 70 (1), 45–50.

Dolin, S.J., Williams, A.C., Ashford, N., George, J., Pereira, L., Perello, A., 2003. Factors affecting medical decision-making in patients with osteoarthritis of the hip: allocation of surgical priority. Disability and Rehabilitation 25 (14), 771–777.

Hochberg, M.C., Altman, R.D., Brandt, K.D., Clark, B.M., Dieppe, P.A., Griffin, M.R., et al., 1995. Guidelines for the medical management of osteoarthritis. Part I. Osteoarthritis of the hip.American College of Rheumatology. Arthritis and Rheumatism 38 (11), 1535–1540.

Honda, M., Kitagawa, Y., Shishido, H., Namiki, S., Shiraishi, H., 1999. Our surgical indication for conservative surgery of the hip joint with coxarthosis. Hip Joint 25, 73–77 (in Japanese).

Manek, N.J., Lane, N.E., 2000. Osteoarthritis: current concepts in diagnosis and management. American Family Physician 61 (6), 1795–1804.

Messier, S.P., Loeser, R.F., Miller, G.D., Morgan, T.M., Rejeski, W.J., Sevick, M.A., et al., 2004. Exercise and dietary weight loss in overweight and obese older adults with knee osteoarthritis: the arthritis, diet, and activity promotion trial. Arthritis and Rheumatism 50 (5), 1501–1510.

Ravaud, P., Giraudeau, B., Logeart, I., Larguier, J.S., Rolland, D., Treves, R., et al., 2004. Management of osteoarthritis (OA) with an unsupervised home based exercise programme and/or patient administered assessment tools. A cluster randomised controlled trial with a 2×2 factorial design. Annals of the Rheumatic Diseases 63 (6), 703–708.

van Baar, M.E., Dekker, J., Oostendorp, R.A., Bijl, D., Voorn, T.B., Lemmens, J.A., et al., 1998. The effectiveness of exercise therapy in patients with osteoarthritis of the hip or knee: a randomized clinical trial. Journal of Rheumatology 25 (12), 2432–2439.

Erratum

Enhanced Wear Resistance of Orthopaedic Bearing Due to the Cross-Linking of Poly(MPC) Graft Chains Induced by Gamma-Ray Irradiation

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The authors have requested the following revisions for the article listed above, published in J Biomed Mater Res B Appl Biomater 2008; 84B: 320–327. The updated Figures 3 and 4 appear below. The authors regret any confusion caused by these errors.

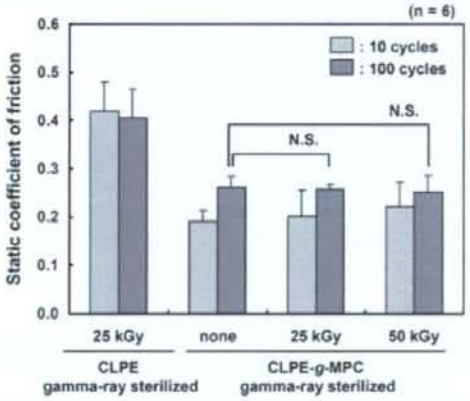

Figure 3. Static coefficients of friction of the gamma-ray sterilized CLPE surfaces and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar, Standard deviations.

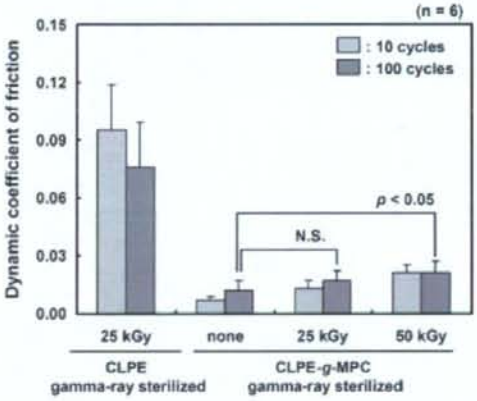

Figure 4. Dynamic coefficients of friction of gamma-ray sterilized CLPE surfaces and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar, Standard deviations.

Enhanced Wear Resistance of Orthopaedic Bearing Due to the Cross-Linking of Poly(MPC) Graft Chains Induced by Gamma-Ray Irradiation

Masayuki Kyomoto,[1,2] Toru Moro,[3] Fumiaki Miyaji,[1] Tomohiro Konno,[2] Masami Hashimoto,[4] Hiroshi Kawaguchi,[3] Yoshio Takatori,[3] Kozo Nakamura,[3] Kazuhiko Ishihara[2]

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Abstract: We assumed that the extra energy supplied by gamma-ray irradiation produced cross-links in 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer grafted cross-linked polyethylene (CLPE-*g*-MPC) and investigated its effects on the tribological properties of CLPE-*g*-MPC. In this study, we found that the gamma-ray irradiation produced cross-links in three kinds of regions of CLPE-*g*-MPC: poly(MPC) layer, CLPE-MPC interface, and CLPE substrate. The dynamic coefficient of friction of CLPE-*g*-MPC slightly increased with increasing irradiation doses. After the simulator test, both the nonsterilized and gamma-ray sterilized CLPE-g-MPC cups exhibited lower wear than the untreated CLPE ones. In particular, the gamma-ray sterilized CLPE-g-MPC cups showed extremely low and stable wear. As for the nonsterilized CLPE-*g*-MPC cups, the weight change varied with each cup. When the CLPE surface is modified by poly(MPC) grafting, the MPC graft polymer leads to a significant reduction in the sliding friction between the surfaces that are grafted because water thin films formed can behave as extremely efficient lubricants. Such a cross-link of poly(MPC) slightly increases the friction of CLPE by gamma-ray irradiation but provides a stable wear resistant layer on the friction surface. The cross-links formed by gamma-ray irradiation would give further longevity to the CLPE-*g*-MPC cups. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 84B: 320–327, 2008

Keywords: joint replacements; polyethylene; phosphorylcholine; sterilization

INTRODUCTION

The number of primary and revised artificial hip and knee joints used are substantially increasing in the world every year.[1] This means that the quality of artificial joints has been becoming increasingly important. Most of the patients who receive an artificial joint experience a dramatic pain relief and enjoy a rapid improvement in the quality of life. The most popular artificial joint system 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 has emerged as a serious issue.[2–4] 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.

We have recently developed a novel artificial joint system with 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer grafted onto the surface of cross-linked polyethylene (CLPE-*g*-MPC),[5–7] aiming to reduce wear and avoid bone resorption. MPC is a methacrylate monomer that has a phospholipid polar group in a side chain and is used to make novel biomaterials as designed by Ishihara et al., who were inspired by the natural phospholipids of biomembranes.[8] MPC can be a good polymer biomaterial owing to

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the reduction of protein adsorption and cell adhesion.[9–18] On the basis of the biocompatibility and hydrophilicity of MPC polymers, we have been developing new artificial joints with highly lubricated bearing surfaces that are produced by photo-induced radical graft polymerization.[19] This technique grafts MPC directly onto CLPE, forming C—C covalent bonds between the CLPE substrate and the MPC polymer.

Medical devices, including artificial joints, are normally sterilized by using several methods, for example, gamma-ray sterilization, ethylene oxide gas sterilization, and gas plasma sterilization. In particular, gamma-ray irradiation is the sterilization method typically used for the UHMWPE components of artificial joints. However, gamma-ray sterilization probably influences the properties of medical devices. Generally, when a high energy beam generated by gamma-ray sterilization is irradiated on to a polymer, free radicals are formed by the scission of the molecular chains. This is followed by the retermination and cross-linking of the molecules. The irradiation of high-dose gamma-rays onto UHMWPE severs the C—C or C—H bonds, and it then produces cross-linking and subsequent chemical bonding involving C=O and C—C.[20] It has been reported that gamma-ray sterilized UHMWPE sometimes exhibits improved wear resistance due to the formation of many cross-links. Several investigators have reported that wear resistance is better in gamma-ray sterilized UHMWPE than that in ethylene oxide sterilized UHMWPE.[21–24]

The purpose of this study is to investigate the dependence of gamma-ray irradiation on the tribological (friction and *in vitro* wear) properties of CLPE-*g*-MPC and to examine the possibility of controlling the longevity of artificial joints by using this material. This is based on the hypothesis that the extra energy supplied by gamma-ray irradiation could produce cross-links in CLPE-*g*-MPC.

MATERIALS AND METHODS

Chemicals and MPC Graft Polymerization

Benzophenone and acetone were purchased from Wako Pure Chemical Industries (Osaka, Japan). MPC was industrially synthesized using the method reported by Ishihara et al.[8] and was supplied by Ai Bio-Chips (Tokyo, Japan).

A compression-molded UHMWPE (GUR1020 resin, Poly Hi-Solidur, IN) bar stock was treated with a dose of 50 kGy gamma irradiation in N_2 gas and annealed at 120°C for 7.5 h in N_2 gas in order to attain cross-linking. The CLPE specimens were machined from this bar stock after cooling. They were immersed in an acetone solution containing 10 mg/mL benzophenone for 30 s and then dried in the dark at room temperature to remove acetone. The amount of benzophenone adsorbed on the surface was 3.5×10^{-11} mol/cm^2.[25] The MPC monomer was dissolved in pure degassed water up to a concentration of 0.5 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, Funabashi, Japan) of 5 mW/cm^2 at 60°C for 90 min using a filter (Model D-35; Toshiba, 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 and CLPE-*g*-MPC specimens were sterilized by gamma-ray irradiation of 25 or 50 kGy in N_2 gas.

Surface Analysis by Fourier-Transform Infrared and X-ray Photoelectron Spectroscopies and Water-Contact Angle Measurement

The functional group vibrations of both the nonsterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC surfaces were examined by Fourier-transform infrared (FTIR) spectroscopy using attenuated total reflection (ATR) equipment. The FTIR/ATR spectra were obtained in 32 scans over a range of 800–2000 cm^{-1} using an FTIR analyzer (FT/IR-615; JASCO International, Tokyo, Japan) at a resolution of 4.0 cm^{-1}.

The surface elemental conditions of CLPE before and after MPC grafting were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS Hsi 165; Kratos Analytical, UK) equipped with an Mg-Kα radiation source at 15 kV at the anode. The take-off angle of the photoelectrons was kept at 90°. Each sample was scanned five times.

The static water-contact angles of CLPE-*g*-MPC with various photo-polymerization periods were measured by a sessile drop method using an optical bench-type contact angle goniometer (Model DM300; Kyowa Interface Science, Saitama, Japan). Drops of purified water (1 μL) were deposited onto the surface of CLPE-*g*-MPC, and the contact angles were directly measured by using a microscope after 60 s according to the ISO 15989 standard.[26] Fifteen replicate measurements were performed on each sample, and the average values were taken as contact angles.

Friction Test

The friction test was performed using a ball-on-plate machine (Tribostation 32; Shinto Scientific, Tokyo, Japan). Six sample pieces were prepared using each of the sterilization methods. The Co-Cr-Mo alloy ball was 9 mm in diameter and its surface roughness was Ra $\geq$ 0.01—as smooth as a femoral ball. The friction tests were carried out with a load of 0.98 N and a sliding distance of 25 mm with a frequency of 1 Hz at room temperature. The measurements were performed using pure water as lubricant. The friction tests were performed up to a maximum of 100 cycles. The mean static (μ_s) and dynamic (μ_d) coefficients of friction were determined by averaging five data points in 10 (8–12) and 100 (96–100) cycle measurements.

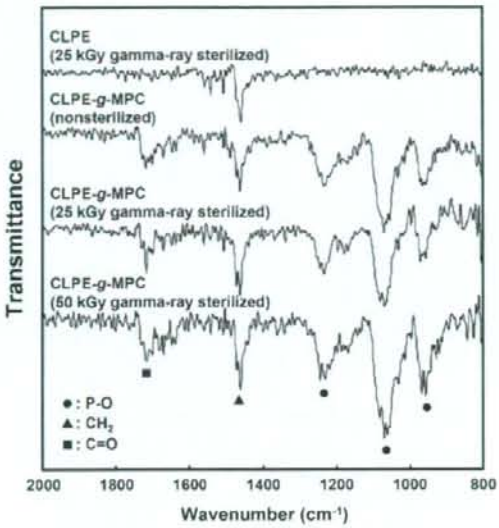

Figure 1. FTIR/ATR spectra for nonsterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC.

Statistical Analysis

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

Hip Joint Simulator Test

The inner and outer diameters of the CLPE and CLPE-*g*-MPC cups used in the hip joint simulator were 26 and 52 mm, respectively. Four pieces for each condition was prepared. The wear test was performed using a 12-station hip joint simulator (MTS Systems, MN). A Co-Cr-Mo alloy femoral ball component with a size of 26 mm (Japan Medical Materials, Osaka, Japan) was used as *a 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 lubricant, according to the ISO 14242-1 standard.[27] The lubricant was replaced every 0.5 $\times 10^6$ cycles. Loads simulating a physiologic loading curve with double peaks of 1793 and 2744 N loads were applied with a frequency of 1 Hz. The wear was determined by weighing the polyethylene cups. Load-soak controls ($n = 2$) were used to compensate the fluid absorption of specimens. The weights of the cups were measured every 0.5×10^6 cycles. Then, the testing was continued until a total of 5.0×10^6 cycles were completed.[28]

To evaluate the wear conditions, the surface features of the bearing surfaces of the cups were observed with a confocal laser scanning microscope (OLS1200; Olympus, Tokyo, Japan) after a simulator test with 5.0×10^6 cycles.

RESULTS

Figure 1 shows the FTIR/ATR spectra for the nonsterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC. An absorption peak was observed at 1460 cm^{-1} for both CLPE and CLPE-*g*-MPC. This peak is attributed mainly to the methylene chain in the CLPE substrate and MPC graft polymer. However, the transmission absorptions at 1240, 1080, and 970 cm^{-1} were observed only for the CLPE-*g*-MPC. These peaks are due to the phosphate group in the MPC unit. Similarly, an absorption peak at 1720 cm^{-1} observed for CLPE-*g*-MPC only corresponds to the carbonyl group in the MPC unit. The FTIR/ATR spectra did not differ significantly between the nonsterilized and gamma-ray sterilized CLPE-*g*-MPC.

Table I summarizes the elemental compositions of the untreated CLPE and the nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Both the elemental composition of nitrogen and phosphorous in the nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surface were approximately 5.2. It should be noted that the contents of nitrogen and phosphorous in the CLPE-*g*-MPC surface remained unchanged after gamma-ray sterilization. The elemental composition of the CLPE-*g*-MPC surface was almost equivalent to the theoretical elemental composition (N = 5.3, P = 5.3) of poly(MPC). On the other hand, the carbon content in the gamma-ray sterilized CLPE-*g*-MPC slightly increased as compared with that of the nonsterilized one.

Figure 2 shows the static water-contact angle of the untreated CLPE and the nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. The static water-contact angle

TABLE I. Surface Elemental Composition (%) of Gamma-Ray Sterilized CLPE and CLPE-*g*-MPC

Sample (Sterilization Method)	Surface Elemental Composition (%) (n = 5)			
	C	O	N	P
CLPE (nonsterilized)	99.8 (0.3)[a]	0.2 (0.3)	0.0 (0.0)	0.0 (0.0)
CLPE (25 kGy γ-sterilized)	99.5 (0.2)	0.6 (0.2)	0.0 (0.0)	0.0 (0.0)
CLPE (50 kGy γ-sterilized)	99.1 (0.2)	0.9 (0.2)	0.0 (0.0)	0.0 (0.0)
CLPE-*g*-MPC (nonsterilized)	58.0 (0.2)	31.5 (0.2)	5.2 (0.1)	5.3 (0.1)
CLPE-*g*-MPC (25 kGy γ-sterilized)	63.7 (2.3)	26.0 (2.3)	5.2 (0.1)	5.1 (0.2)
CLPE-*g*-MPC (50 kGy γ-sterilized)	65.0 (0.6)	24.6 (0.5)	5.2 (0.1)	5.2 (0.1)
MPC polymer[b]	57.9	31.6	5.3	5.3

[a] The standard deviation is in parentheses.
[b] Theoretical elemental composition of MPC polymer.

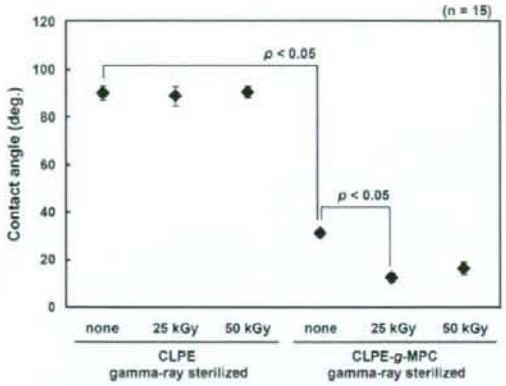

Figure 2. Static water-contact angle of the untreated CLPE and the nonsterilized and the gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.

of the untreated CLPE was approximately 90° before and after gamma-ray sterilization, and it drastically decreased (approximately 30°) because of MPC grafting. Furthermore, the static water-contact angles of CLPE-*g*-MPC decreased to 15° after gamma-ray sterilization.

The static and dynamic coefficients of friction of gamma-ray sterilized CLPE and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC are shown in Figures 3 and 4. Both the static and dynamic coefficients of friction of CLPE-*g*-MPC decreased drastically when compared with those of untreated CLPE. The degree of reduction in the coefficient was larger in the latter as compared to the former. Considering the gamma-ray sterilized CLPE-*g*-MPC, regardless of the dose of the gamma-ray sterilization and the cycles, approximately 50% reduction (i.e., 46–65%) was observed in the static coefficients of friction for both the 10 and 100 cycles when compared with those of untreated CLPE. On the other hand, the dose of gamma-ray sterilization affected the dynamic coefficient of friction of CLPE-*g*-MPC. That is, it slightly increased from 0.007 (none) to 0.021 (50 kGy) with an increase in the gamma-ray sterilization dose for 10 cycles. The dynamic coefficient of friction of CLPE-*g*-MPC with gamma-ray sterilization of 50 kGy was 75% greater ($p < 0.05$) than that of CLPE-*g*-MPC with nonsterilization.

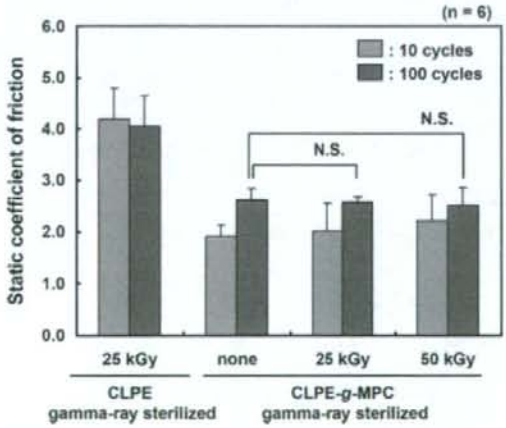

Figure 3. Static coefficients of friction of the gamma-ray sterilized CLPE surfaces and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.

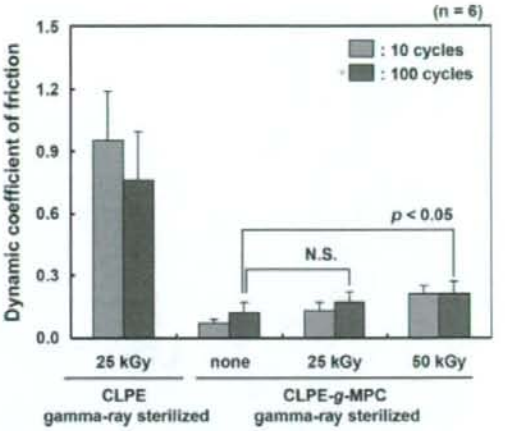

Figure 4. Dynamic coefficients of friction of gamma-ray sterilized CLPE surfaces and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.

Figure 5 shows the weight change (gravimetric wear) of the gamma-ray sterilized CLPE cups and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC cups in the hip joint simulation test. When the gravimetric method is used, the weight loss was corrected for the fluid absorption by sub-

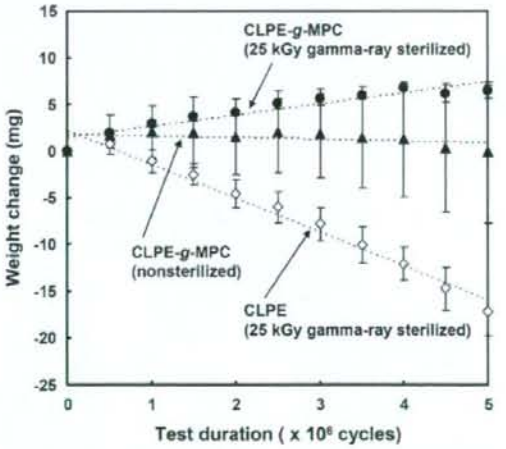

Figure 5. Weight change (gravimetric wear) of gamma-ray sterilized CLPE cups and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC cups in the hip joint simulation test. Bar; Standard deviations.

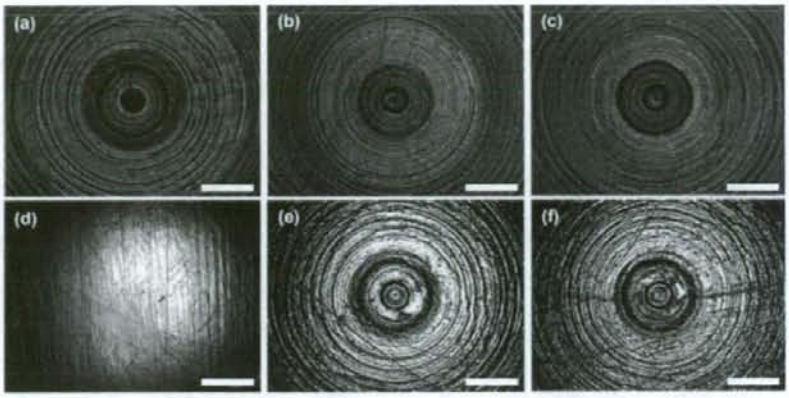

Figure 6. Confocal laser scanning microscope images of the CLPE and CLPE-*g*-MPC bearing surfaces before and after the hip simulator test. (a) CLPE (gamma-ray sterilized), (b) CLPE-*g*-MPC (nonsterilized), (c) CLPE-*g*-MPC (gamma-ray sterilized) before the hip simulator test, (d) CLPE (gamma-ray sterilized), (e) CLPE-*g*-MPC (nonsterilized), and (f) CLPE-*g*-MPC (gamma-ray sterilized) after the hip simulator test. The bar indicates 500 μm.

tracting the weight gain that occurred in the load-soak controls. Since the tested cups are subjected to a motion and load, such a "load-soak" correction is not necessarily satisfactory. Therefore, the tested cups absorb slightly more fluid than their load-soak controls. Consequently, the correction for using the load-soak control data may result in a slight underestimation of the actual weight loss. After 5.0 $\times$ 10^6 cycles of the simulator test, both the CLPE-*g*-MPC cups were found to undergo lesser wear than the untreated CLPE cups. In particular, the gamma-ray sterilized CLPE-*g*-MPC cups showed extremely low and stable wear. As for the nonsterilized CLPE-*g*-MPC cups, the weight change varied for each cup (standard deviation = 7.6 mg, n = 4). Figure 5 indicates that certain gamma-ray sterilized CLPE-*g*-MPC cups exhibit a slight increase in weight because of slightly enhanced fluid absorption when compared with that in the load-soak controls.

Figure 6 shows the confocal laser scanning microscope images of the bearing surfaces of the untreated gamma-ray sterilized CLPE cups and nonsterilized and gamma-ray sterilized CLPE-*g*-MPC cups before and after the simulator test. Before the simulator test, regular circular machining marks were seen on the all the bearing surfaces of the CLPE and CLPE-*g*-MPC cups. After the simulator test, the machining marks on these surfaces of the CLPE cups disappeared completely. On the contrary, clear machining marks with regular circles were observed on the surface of the nonsterilized and gamma-ray sterilized CLPE-*g*-MPC cups, indicating almost no wear on the surface.

DISCUSSION

We have developed an artificial hip joint using CLPE-*g*-MPC on the bearing surface with an objective of reducing wear and avoiding bone resorption. The static and dynamic coefficients of friction of CLPE-*g*-MPC reduced by >50% and >90%, respectively, as compared to those of the untreated CLPE, as shown in Figures 3 and 4. These friction coefficients were much lower than those usually found for the measurable shear interactions between UHMWPE and the Co-Cr-Mo alloy.[29,30] The significant reduction in the coefficients of friction of the grafted MPC polymer resulted in a substantial improvement in wear resistance, as shown in Figure 5. We assumed that the bearing surface of the artificial hip joint combined with the MPC polymer layer 100–200 nm thick exhibited the fluid film lubrication (or mixed lubrication) of the intermediate hydrated layer.[5,7,19]

These sterilizations may affect the properties of medical devices. Generally, when a high energy beam by gamma-ray sterilization is irradiated on a polymer, free radicals are formed by the scission of molecular chains.[20] This is followed by the retermination and cross-linking of the molecules. In this study, we therefore assumed that the extra energy supplied by gamma-ray irradiation produced cross-links in three kinds of regions of the CLPE-*g*-MPC: poly (MPC) layer, CLPE-MPC interface, and CLPE substrate, as shown in Figure 7.

As shown in Table I, the contents of nitrogen and phosphorous in the CLPE-*g*-MPC surface were hardly different between the nonsterilized CLPE-*g*-MPC and the gamma-ray sterilized CLPE-*g*-MPC. On the other hand, the contents of carbon and oxygen of CLPE-*g*-MPC slightly increased and decreased (as a trade-off), respectively, with an increase in the gamma-ray irradiation dose. It was assumed that the energy by gamma-ray irradiation would be used in the scission of C=O in the MPC structure by the degassing of O_2 and subsequently produce cross-links of poly(MPC) with chemical bonding involving C—C.[31,32] The extra energy supplied by gamma-ray sterilization of 25–50 kGy is clearly responsible for producing more cross-links.

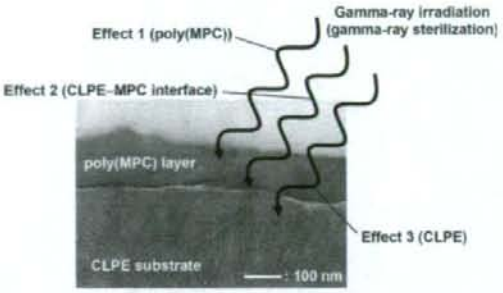

Figure 7. Schematic diagram of the effects of gamma-ray irradiation on CLPE-*g*-MPC.

The dose of gamma-ray sterilization influences the friction response since the dynamic coefficient of friction of CLPE-*g*-MPC slightly increased from 0.007 to 0.021 within the low friction region with an increase in the gamma-ray sterilization dose. It was previously reported that as the polymer concentration (viscosity) increases with the increase in the friction coefficient in the mixed lubrication regime.[33] It was therefore assumed that an ultra-low friction of CLPE-*g*-MPC that appeared during sliding is related to the effective viscosity of poly(MPC) in the mixed lubrication of the intermediate hydrated layer. The viscosity of poly(MPC) reflects the mobility of the free end groups of the MPC polymer or MPC polymer chains themselves; this mobility was limited by the cross-linking of poly(MPC) layer.[34,35] These results seem to suggest that the cross-link corresponds to the viscosity of the poly(MPC) in the bearing interface, the viscosity of the poly(MPC) increases by gamma-ray irradiation, and the poly(MPC) would act as a boundary lubricant in mixed lubrication. These effects are represented as "Effect 1" in Figure 7.

After 5.0×10^6 cycles of the simulator test, the gamma-ray sterilized CLPE-*g*-MPC cups showed low and stable wear (Figure 5). On the contrary, with the nonsterilized CLPE-*g*-MPC cups, the weight change varied in each cup. In the previous study, when a high energy beam was irradiated onto a polymer with a grafted layer, strong bindings were formed between the grafted layer and polymer substrate.[36] Lewis et al. reported that the force required to remove the coating with cross-linking was greater than that without cross-linking.[37] In addition, much more cross-linking and perhaps adhesion to the substrate was induced by the gamma-ray irradiation (gamma-ray sterilization) when compared with the nonsterilized CLPE-*g*-MPC. It is therefore assumed that the higher energy radiation in gamma-ray sterilization induced cross-links not only within the grafting MPC polymer but also between the grafting MPC polymer and CLPE substrate. Then, a much stronger and stable MPC polymer grafted layer was produced on the bearing surface ("Effect 2" in Figure 7).

McKellop et al. reported on the wear performance of UHMWPE in a contemporary hip simulator following gamma-ray irradiation in air as well as in an inert gas and ethylene oxide gas sterilization or gas plasma sterilization.[21] Between 2 and 5×10^6 cycles, the wear rate of the gamma-ray sterilized UHMWPE was significantly lower than that of the UHMWPE sterilized either by gas plasma or ethylene oxide. A similar trend has been reported by Wang et al. who observed more than 50% drop in the hip simulator wear rate after single 25 kGy doses of gamma-ray sterilization.[22] These studies have reported that the wear resistance is better in gamma-ray sterilized UHMWPE than in ethylene oxide sterilized UHMWPE.[21–24] It is therefore assumed that gamma-ray irradiation improved the wear resistance of the CLPE substrate ("Effect 3" in Figure 7).

In the cross-link process of this study, the UHMWPE bar stock was irradiated with a dose of 50 kGy, and then CLPE and CLPE-*g*-MPC were gamma-ray sterilized with a nominal dose of 25 kGy. Thus, the total dosage for the gamma-ray sterilized CLPE and CLPE-*g*-MPC was 75 kGy. The nonsterilized CLPE-*g*-MPC received a total dose of 50 kGy only; this would be a disadvantage for the anti-wear property.[38–40] However, as shown in Figure 6, clear machining marks with regular circles remained on the surfaces of the nonsterilized as well as gamma-ray sterilized CLPE-*g*-MPC cups even after the simulator test. The observed CLPE-*g*-MPC cups were virtually unworn, which is consistent with the relatively low wear in the hip joint simulator tests, as shown in Figure 5. In contrast, the machining marks disappeared from the surface of the gamma-ray sterilized CLPE cups [Figure 6(b)]. In other words, the presence of poly(MPC) on the CLPE surface by MPC grafting would have a greater effect on the wear resistance than the additional cross-links of the CLPE substrate by the gamma-ray irradiation of 25 kGy. The CLPE surface with the poly(MPC) exhibited considerably higher lubricity than that without the poly(MPC) (Figures 2–4). The significant reduction in the coefficient of friction of the grafted poly(MPC) resulted in a substantial improvement in wear resistance. The bearing surface of the artificial hip joint combined with poly(MPC) might exhibit the fluid film lubrication (or mixed lubrication) of the intermediate hydrated layer. This means that artificial hip joints utilizing CLPE-*g*-MPC mimic the natural joint cartilage.[41,42]

The concern about the degradation of polyethylene during shelf aging prompted several orthopedic manufacturers to adopt the sterilization method using gas plasma or ethylene oxide gas for conventional UHMWPE.[43,44] These sterilization methods admittedly generate no free radicals that could be subsequently oxidized during shelf storage. However, UHMWPE sterilized using these methods did not receive the tribological benefit associated with radiation-induced cross-linking. Moreover, the oxidation index of the degraded polyethylene was lower *in vivo* than *in vitro*.[21,45] It has also been reported that the oxygen content might be almost zero in the body.[44,46] Thus, although the oxidation

degradation of polyethylene *in vivo* is related to the surrounding oxygen concentration, that is, that of the body fluid, it is not a main factor of the degradation as a whole. However, recent studies reported that conventional or cross-linked gamma-ray sterilized polyethylene liners undergo *in vivo* oxidation, especially in unworn bearing surface regions and the rim. In contrast, the oxidation of a worn bearing surface was not observed.[47] On the basis of these studies, we assumed that when oxygen is excluded from the package during sterilization, further cross-linking, and additional improvement in the wear performance are attained. However, we must pay attention to the rim fracture in CLPE-*g*-MPC cup by the possible impingements based on the abovementioned studies.[47] In the previous study, for gamma-ray irradiation, the lower molecular weight cross-linked GUR1020 materials had higher mechanical properties (tensile and impact properties) for all doses as compared to the higher molecular weight cross-linked GUR1050 materials.[48] Therefore, we selected a GUR1020 compression-molded bar stock as the CLPE substrate. Nevertheless, the cross-linked GUR1020 materials showed the same wear rate as the cross-linked GUR1050 materials.

Gamma-ray sterilization has had a long history and it has been one of the most popular sterilization methods for various medical products to date. A barrier package has been widely adopted to satisfactorily address the historical problem of the oxidation of gamma-ray sterilized products during shelf storage. In this study, we confirmed that the extra energy supplied by gamma-ray irradiation produced cross-linking in the three regions of the CLPE-*g*-MPC: poly(MPC) layer, CLPE-MPC interface, and CLPE substrate. When the CLPE surface is modified by poly(MPC) grafting, the MPC graft polymer leads to a significant reduction in the sliding friction between the surfaces which are grafted because water thin films formed can act as extremely efficient lubricants. Gamma-ray sterilized CLPE-*g*-MPC showed a slightly higher friction than the nonsterilized one. However, the wear resistance is more stable in the former than in the latter. The cross-links formed by gamma-ray irradiation would give further longevity to CLPE-*g*-MPC cups. Based on the mechanical,[19] biological,[5,49,50] and tribological advantages of MPC polymers, CLPE-*g*-MPC is believed to be promising for use in the next-generation artificial hip joint systems.

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REFERENCES

1. Kurtz S, Mowat F, Ong K, Chan N, Lau E, Halpern M. Prevalence of primary and revision total hip and knee arthroplasty in the United States from 1990 through 2002. J Bone Joint Surg Am 2005;87:1487–1497.
2. Harris WH. The problem is osteolysis. Clin Orthop 1995;311:46–53.
3. Kobayashi A, Freeman MA, Bonfield W, Kadoya Y, Yamac T, Al-Saffar N, Scott G, Revell PA. Number of polyethylene particles and osteolysis in total joint replacements. A quantitative study using a tissue-digestion method. J Bone Joint Surg Br 1997;79:844–848.
4. Sochart DH. Relationship of acetabular wear to osteolysis and loosening in total hip arthroplasty. Clin Orthop 1999;363:135–150.
5. Moro T, Takatori Y, Ishihara K, Konno T, Takigawa Y, Matsushita T, Chung UI, Nakamura K, Kawaguchi H. Surface grafting of artificial joints with a biocompatible polymer for preventing periprosthetic osteolysis. Nature Mater 2004;3:829–837.
6. Moro T, Takatori Y, Ishihara K, Nakamura K, Kawaguchi H. Grafting of biocompatible polymer for longevity of artificial hip joints. Clin Orthop Relat Res 2006;453:58–63.
7. Kyomoto M, Moro T, Konno T, Takadama H, Yamawaki N, Kawaguchi H, Takatori Y, Nakamura K, Ishihara K. Enhanced wear resistance of modified cross-linked polyethylene by grafting with poly(2-methacryloyloxyethyl phosphorylcholine). J Biomed Mater Res A 2007;82:10–17.
8. Ishihara K, Ueda T, Nakabayashi N. Preparation of phospholipid polymers and their properties as polymer hydrogel membranes. Polym J 1990;22:355–360.
9. Sawada S, Iwasaki Y, Nakabayashi N, Ishihara K. Stress response of adherent cells on a polymer blend surface composed of a segmented polyurethane and MPC copolymers. J Biomed Mater Res A 2006;79:476–484.
10. Goda T, Konno T, Takai M, Moro T, Ishihara K. Biomimetic phosphorylcholine polymer grafting from polydimethylsiloxane surface using photo-induced polymerization. Biomaterials 2006;27:5151–5160.
11. Sibarani J, Takai M, Ishihara K. Surface modification on microfluidic devices with 2-methacryloyloxyethyl phosphorylcholine polymers for reducing unfavorable protein adsorption. Colloids Surf B Biointerfaces 2007;54:88–93.
12. Ueda H, Watanabe J, Konno T, Takai M, Saito A, Ishihara K. Asymmetrically functional surface properties on biocompatible phospholipid polymer membrane for bioartificial kidney. J Biomed Mater Res A 2006;77:19–27.
13. Bakhai A, Booth J, Delahunty N, Nugara F, Clayton T, McNeill J, Davies SW, Cumberland DC, Stables RH, SV Stent Investigators. The SV stent study: A prospective, multicentre, angiographic evaluation of the BiodivYsio phosphorylcholine coated small vessel stent in small coronary vessels. Int J Cardiol 2005;102:95–102.
14. Watanabe J, Ishihara K. Cell engineering biointerface focusing on cytocompatibility using phospholipid polymer with an isomeric oligo(lactic acid) segment. Biomacromolecules 2005;6:1797–1802.
15. Abraham S, Brahim S, Ishihara K, Guiseppi-Elie A. Molecularly engineered p(HEMA)-based hydrogels for implant biochip biocompatibility. Biomaterials 2005;26:4767–4778.
16. Konno T, Hasuda H, Ishihara K, Ito Y. Photo-immobilization of a phospholipid polymer for surface modification. Biomaterials 2005;26:1381–1388.
17. Palmer RR, Lewis AL, Kirkwood LC, Rose SF, Lloyd AW, Vick TA, Stratford PW. Biological evaluation and drug delivery application of cationically modified phospholipid polymers. Biomaterials 2004;25:4785–4796.
18. Long SF, Clarke S, Davies MC, Lewis AL, Hanlon GW, Lloyd AW. Controlled biological response on blends of a phosphorylcholine-based copolymer with poly(butyl methacrylate). Biomaterials 2003;24:4115–4121.
19. Kyomoto M, Moro T, Konno T, Takadama H, Kawaguchi H, Takatori Y, Nakamura K, Yamawaki N, Ishihara K. Effects of photo-induced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine on physical properties of cross-linked poly-

ethylene in artificial hip joints. J Mater Sci Mater Med, Forthcoming.
20. Costa L, Luda MP, Trossarelli L, Brach del Prever EM, Crova M, Gallinaro P. Oxidation in orthopaedic UHMWPE sterilized by gamma-ray radiation and ethylene oxide. Biomaterials 1998;19:659–668.
21. McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Effect of sterilization method and other modifications on the wear resistance of acetabular cups made of ultra-high molecular weight polyethylene. A hip-simulator study. J Bone Joint Surg Am 2000;82:1708–1725.
22. Wang A, Sun DC, Yau SS, Edwards B, Sokol M, Essner A, Polineni VK, Stark C, Dumbleton JH. Orientation softening in the deformation and wear of ultra-high molecular weight polyethylene. Wear 1997;203–204:230–241.
23. Digas G, Thanner J, Nivbrant B, Rohrl S, Strom H, Karrholm J. Increase in early polyethylene wear after sterilization with ethylene oxide: Radiostereometric analyses of 201 total hips. Acta Orthop Scand 2003;74:531–541.
24. Manning DW, Chiang PP, Martell JM, Galante JO, Harris WH. In vivo comparative wear study of traditional and highly cross-linked polyethylene in total hip arthroplasty. J Arthroplasty 2005;20:880–886.
25. Ishihara K, Iwasaki Y, Ebihara S, Shindo Y, Nakabayashi N. Photoinduced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine on polyethylene membrane surface for obtaining blood cell adhesion resistance. Colloids Surf B 2000;18:325–335.
26. International Organization for Standardization 15989. Plastics–Film and sheeting–Measurement of water-contact angle of corona-treated films, Geneva, 2004.
27. International Organization for Standardization 14242–1. Implants for surgery–Wear of total hip-joint prostheses–Part 1: Loading and displacement parameters for wear-testing machines and corresponding environmental conditions for test, 2002.
28. International Organization for Standardization 14242–2. Implants for surgery–Wear of total hip-joint prostheses–Part 2: Methods of measurement, 2000.
29. Saikko V. Wear and friction properties of prosthetic joint materials evaluated on a reciprocating pin-on-flat apparatus. Wear 1993;166:169–178.
30. Yao JQ, Laurent MP, Johnson TS, Blanchard CR, Crowninshield RD. The influences of lubricant and material on polymer/CoCr sliding friction. Wear 2003;255:780–784.
31. Bracco P, Brunella V, Luda MP, Brach del Prever EM, Zanetti M, Costa L. Oxidation behaviour in prosthetic UHMWPE components sterilised with high energy radiation in a low-oxygen environment. Polym Degrad Stab 2006;91:3057–3064.
32. Premnath V, Harris WH, Jasty M, Merrill EW. Gamma sterilization of UHMWPE articular implants: An analysis of the oxidation problem. Ultra high molecular weight poly ethylene. Biomaterials 1996;17:1741–1753.
33. de Vicente J, Stokes JR, Spikes HA. Soft lubrication of model hydrocolloids. Food Hydrocolloids 2006;20:483–491.
34. Raviv U, Frey J, Sak R, Laurat P, Tadmor R, Klein J. Properties and interactions of physigrafted end-functionalized poly (ethylene glycol) layers. Langmuir 2002;18:7482–7495.
35. Raviv U, Glasson S, Kampf N, Gohy JF, Jérôme R, Klein J. Lubrication by charged polymers. Nature 2003;425:163–165.
36. Salleh NG, Glasel HJ, Mehnert R. Development of hard materials by radiation curing technology. Radiat Phys Chem 2002;63:475–479.
37. Lewis AL, Cumming ZL, Goreish HH, Kirkwood LC, Tolhurst LA, Stratford PW. Crosslinkable coatings from phosphorylcholine-based polymers. Biomaterials 2001;22:99–111.
38. McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. J Orthop Res 1999;17:157–167.
39. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH. A novel method of crosslinking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties. Recipient of the 1999 HAP Paul Award. J Arthroplasty 2001;16:149–160.
40. Oonishi H, Kim SC, Takao Y, Kyomoto M, Iwamoto M, Ueno M. Wear of highly cross-linked polyethylene acetabular cup in Japan. J Arthroplasty 2006;21:944–949.
41. Dowson D, Jin ZM. Micro-elastohydrodynamic lubrication of synovial joints. Eng Med 1986;15:63–65.
42. Williams PF III, Powell GL, LaBerge M. Sliding friction analysis of phosphatidylcholine as a boundary lubricant for articular cartilage. Proc Inst Mech Eng [H] 1993;207:59–66.
43. Willie BM, Ashrafi S, Alajbegovic S, Burnett T, Bloebaum RD. Quantifying the effect of resin type and sterilization method on the degradation of ultrahigh molecular weight polyethylene after 4 years of real-time shelf aging. J Biomed Mater Res A 2004;69:477–489.
44. Kurtz SM, Rimnac CM, Hozack WJ, Turner J, Marcolongo M, Goldberg VM, Kraay MJ, Edidin AA. In vivo degradation of polyethylene liners after gamma-ray sterilization in air. J Bone Joint Surg Am 2005;87:815–823.
45. Kyomoto M, Ueno M, Kim SC, Oonishi H, Oonishi H. Wear of "100 Mrad" cross-linked polyethylene: Effects of packaging after 30 years real-time shelf-aging. J Biomed Sci Polym Edn 2007;18:59–70.
46. Treuhaft PS, McCarty DJ. Synovial fluid pH, lactate, oxygen and carbon dioxide partial pressure in various joint diseases. Arthritis Rheum 1971;14:475–484.
47. Kurtz SM, Hozack W, Turner J, Purtill J, MacDonald D, Sharkey P, Parvizi J, Manley M, Rothman R. Mechanical properties of retrieved highly cross-linked crossfire liners after short-term implantation. J Arthroplasty 2005;20:840–849.
48. Greer KW, King RS, Chan FW. The effects of raw material, irradiation dose, and irradiation source on crosslinking of UHMWPE. In: Kurtz SM, Gsell RA, Martell J, editors. Cross-linked and thermally treated ultra-high molecular weight polyethylene for joint replacements. West Conshohocken: American Society for Testing and Materials; 2003. pp 209–220.
49. Ishihara K, Aragaki R, Ueda T, Watanabe A, Nakabayashi N. Reduced thrombogenicity of polymers having phospholipid polar groups. J Biomed Mater Res 1990;24:1069–1077.
50. Ishihara K, Ziats NP, Tierney BP, Nakabayashi N, Anderson JM. Protein adsorption from human plasma is reduced on phospholipids polymers. J Biomed Mater Res 1991;25:1397–1407.

Effect of 2-methacryloyloxyethyl phosphorylcholine concentration on photo-induced graft polymerization of polyethylene in reducing the wear of orthopaedic bearing surface

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Abstract: Photo-induced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) on cross-linked polyethylene (CLPE) has been developed as a novel technology for reducing wear of orthopaedic bearings. In this study, the effect of MPC concentration on graft polymerization and the resultant properties of the grafted poly (MPC) layer have been investigated. The grafted poly (MPC) layer thickness increased with the MPC concentration in feed. The hip simulator wear test confirmed that CLPE-*g*-MPC cups exhibited minimal wear compared with untreated CLPE cups. Since MPC is a highly hydrophilic methacrylate, the water-wettability of CLPE-*g*-MPC was greater than that of untreated CLPE due to the formation of a poly(MPC) nanometer-scale layer. The CLPE-*g*-MPC orthopaedic bearing surface exhibited high lubricity, because of the present of the poly(MPC) layer even at a thickness of 10 nm. This layer is considered responsible for the improved wear resistance. Nanometer-scale modification of CLPE with poly(MPC) is expected to significantly increase the durability of the orthopaedic bearings. Poly (MPC) layer thickness can be controlled by changing the MPC concentration in feed. In order to achieve nanometer-scale modification of poly(MPC) in this manner, it is necessary to use a long photo-irradiation time for the MPC graft polymerization system, which contains a high-concentration monomer without its gelation. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res 86A: 439–447, 2008

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

INTRODUCTION

Polymeric biomaterials are widely used in the biomedical field for manufacturing artificial organs, medical devices, and disposable clinical apparatus.[1,2] The number of artificial hip and knee joints used for primary and revised hip and knee replacement are substantially increasing in the worldwide every year.[3] This indicates that the quality of medical devices such as artificial joints has become increasingly important. The most popular artificial joint system used as a medical device is a bearing couple composed of ultra-high molecular weight polyethylene (UHMWPE) and cobalt–chromium–molybdenum (Co-Cr-Mo) alloy. However, osteolysis caused by the wear particles of UHMWPE in the artificial joint system has emerged as a serious issue.[4,5] Different combinations of bearing surfaces and improvements in bearing materials have been studied with the aim of reducing the number of UHMWPE wear particles inducing osteolysis.[6–9]

Surface modification is important for the improvement of bearing materials. Recently, we developed an artificial hip joint based on a new concept by using 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer grafted onto the surface of cross-linked polyethylene (CLPE; CLPE-*g*-MPC); this device was designed to reduce wear and suppress bone resorp-

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tion.[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., and it mimics the neutral phospholipids of cell membranes.[14] MPC polymers are one of the most common biocompatible and hydrophilic polymers studied thus far, which have potential application in a variety of fields such as biology, biomedical science, and surface chemistry because they possess the unique properties of good biocompatibility, high lubricity and low friction, anti-protein adsorption, and cell membrane-like surface.[15–22]

In general, there are two methods for modifying the polymer surface. The first method involves surface absorption or reaction with small molecules[23–25] and the second, grafting polymeric molecules onto the substrate through covalent bonding.[26] 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 the monomers are polymerized from initiators or comonomers; and (2) adsorption of the polymer to the substrate termed as the "grafting to" methods (i.e., dipping, cross-linking, and ready-made polymers with reactive end groups reacting with the functional groups of the substrate).[27,28] 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 low-wear bearing with nanometer-scale poly(MPC) surface modification. This surface modification was accomplished by using a photo-induced radical polymerization technique that was similar to that used in the "grafting from" method. However, in this technique, controlling the length and density of the grafted poly(MPC) was difficult.[15] Our previous study confirmed that the density of the grafted poly(MPC) affects wear resistance and that it was controlled by the photo-irradiation time.[12]

In an attempt to resolve another issue in this study, we investigated the effect of MPC concentration variability on photo-induced graft polymerization. The results revealed that it was possible to control the grafted poly(MPC) chains with nanometer scale modification in order to reduce wear of the CLPE-*g*-MPC orthopaedic bearing surface.

MATERIALS AND METHODS

Chemicals

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

MPC graft polymerization

A compression-molded UHMWPE (GUR1020 resin; Poly Hi Solidur, IN, USA) bar stock was irradiated with gamma-ray of 50 kGy in N_2 gas and annealed at 120°C for 7.5 h in N_2 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 to remove acetone. Using ultraviolet spectroscopy, the amount of benzophenone adsorbed on the surface was reported to be 3.5×10^{-11} mol/cm^2 in previous studies.[15,16] The MPC was dissolved in degassed pure water to attain concentrations ranging from 0.06 to 1.00 mol/L. Subsequently, the CLPE specimens coated with benzophenone were immersed in the aqueous MPC solutions. Photo-induced graft polymerization on the CLPE surface was performed using ultraviolet irradiation (UVL-400HA ultra-high pressure mercury lamp; Riko-Kagaku Sangyo, Funabashi, Japan) with an intensity of 5 mW/cm^2 at 60°C for 12–90 min; a filter (Model D-35; Toshiba, Tokyo, Japan) was used restrict the passage of ultraviolet light to wavelengths of 350 ± 50 nm. After polymerization, the CLPE-*g*-MPC specimens were removed, washed with pure water and ethanol, and dried at room temperature. These specimens were then sterilized by 25 kGy gamma-ray under N_2 gas.

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

The surface elemental contents of CLPE-*g*-MPC obtained with various photo-irradiation times or MPC concentrations were analyzed using X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS Hsi 165; Kratos Analytical, UK) equipped with an Mg-Kα radiation source by applying a voltage of 15 kV at the anode. The take-off angle of the photoelectrons was maintained at 90°. Each measurement was scanned five times, and five replicate measurements were performed on each sample, and the average values were considered for the surface elemental contents.

The static water-contact angles of CLPE-*g*-MPC obtained at various MPC concentrations were measured with an optical bench-type contact angle goniometer (Model DM300; Kyowa Interface Science, Saitama, Japan) using a sessile drop method. Drops of purified water (1 μL) were deposited on the CLPE-*g*-MPC surfaces, and the contact angles were directly measured after 60 s by using a microscope according to the ISO standard 15989.[29] Subsequently, 15 replicate measurements were performed on each sample, and the average values were taken as the contact angles.

The functional group vibrations of the CLPE-*g*-MPC surface that was polymerized with various MPC concentrations were examined using attenuated total reflection (ATR) by Fourier-transform infrared (FTIR) spectroscopy. FTIR/ATR spectra were obtained in 32 scans over a range of 800–2000 cm^{-1} by using an FTIR analyzer (FT/IR615; Jasco International, Tokyo, Japan) at a resolution of 4.0 cm^{-1}.

Cross-sectional observation of CLPE-g-MPC by transmission electron microscopy

A cross-section of the poly(MPC) layer on the CLPE-g-MPC surface produced at various MPC concentrations was observed using a transmission electron microscope (TEM). The specimens were first embedded in epoxy resin, stained with ruthenium oxide vapor at room temperature, and then sliced into ultra-thin films (approximately 100-nm thick) by using a Leica Ultra Cut UC microtome (Leica Microsystems, Wetzlar, Germany). A JEM-1010 electron microscope (JEOL, Tokyo, Japan) was used for the TEM observation at an acceleration voltage of 100 kV.

Surface coated-area observation by Fluorescence Microscopy (FM)

We used rhodamine 6G (Wako Pure Chemical Industries) because it can be easily and rapidly applied to a polymer coating and imaged using fluorescence microscopy (FM) (Axioskop 2 Plus; Carl Zeiss AG, Oberkochen, Germany). Wang et al. observed that rhodamine 6G effectively stains the MPC polymer, which shares very high structural similarity to lipids.[30]

An aqueous solution of 200 mass ppm rhodamine 6G was used for all the staining experiments. All the samples were stained using a two-step procedure. (1) The samples were immersed in the rhodamine 6G solution for 30 s and then removed. (2) Subsequently, they were washed twice consecutively in distilled water for 30 s and dried.

All the samples were examined and imaged using FM. Pseudo-color images were obtained using a charge-coupled-device (CCD) camera (VB-7010; Keyence, Osaka, Japan) and imaging software (VH analyzer 2.51; Keyence). Lenses with a 10× magnification and an appropriate exposure time (approximately 1/10 s) were employed to obtain clear images of the samples.

Friction test

The friction test was performed using a ball-on-plate machine (Tribostation 32; Shinto Scientific, Tokyo, Japan). Each of the CLPE-g-MPC surfaces with various MPC concentrations were used to prepare six sample pieces. A Co-Cr-Mo alloy ball with 9 mm in diameter was prepared. The surface roughness of the ball was Ra = 0.01, which was comparable with that of femoral ball products. The friction tests were performed at room temperature with a load of 0.98 N, sliding distance of 25 mm, and frequency of 1 Hz for a maximum of 100 cycles.[31] Pure water was used as a lubricant. The mean static (μ_s) and dynamic (μ_d) coefficients of friction were determined by averaging five data points from the 100 (96–100) cycle measurements.

Hip simulator wear test

A 12-station hip joint simulator (MTS Systems, MN, USA) with CLPE and CLPE-g-MPC cups both having an inner and outer diameter of 26 and 52 mm, respectively, was used for the hip simulator wear test. For each MPC concentration [0 (untreated), 0.25, and 0.50 mol/L], two sample pieces were prepared. A Co-Cr-Mo alloy femoral ball component with a size of 26 mm (Japan Medical Materials, 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 0.1mass % sodium azide was used as a lubricant, according to the ISO standard 14242-1.[32] The lubricant was replaced every 0.5×10^6 cycles. Walks, which 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. 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.[33] The testing was continued until a total of 5.0×10^6 cycles were completed.

RESULTS

Figure 1 shows the phosphorous (P) concentration of the CLPE-g-MPC surface as a function of the photo-irradiation time during polymerization. The P concentration increased proportionally with the photo-irradiation time. When the photo-irradiation time was greater than 45 min, the P concentration of the CLPE-g-MPC surface with 0.17, 0.25, and 0.50 mol/L MPC concentration became almost constant at high values of 2.9, 3.8, and 4.6 atom %, respectively.

Figure 2 shows the nitrogen (N) and P content in the CLPE-g-MPC surface polymerized with various MPC concentrations and a 90-min photo-irradiation time. Both the N and P content in the CLPE-g-MPC surface increased to 5.2 up to an MPC concentration of 0.50 mol/L; it then gradually decreased with an

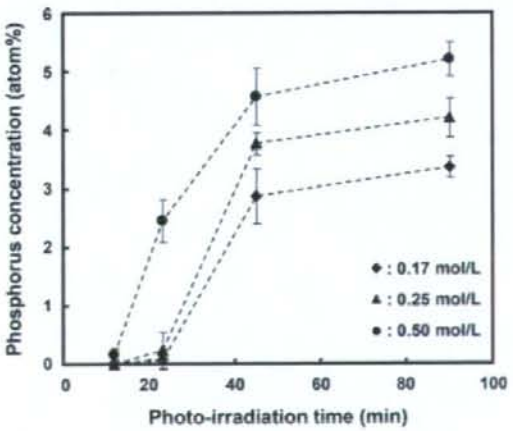

Figure 1. Phosphorus concentration in the CLPE-g-MPC surface as a function of the photo-irradiation time.

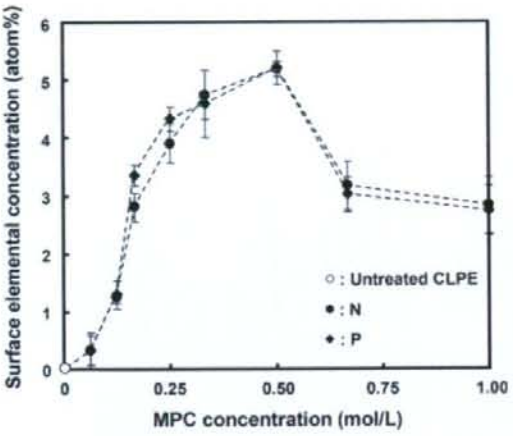

Figure 2. Surface elemental concentration of CLPE-*g*-MPC as a function of the MPC concentration with a 90-min photo-irradiation time.

increase in the MPC concentration. The N and P content at 0.50 mol/L MPC concentration was almost equivalent to the theoretical elemental composition (N = 5.3, P = 5.3) of poly(MPC).

Figure 3 shows the static water-contact angle of CLPE-*g*-MPC as a function of the MPC concentration used for polymerization (90-min photo-irradiation time). The static water-contact angle of untreated CLPE was 90° and decreased markedly with an increase in the MPC concentration during polymerization. When the MPC concentration was between 0.25 and 0.50 mol/L, the static water-contact angle was constant; the lowest value was recorded at 15°.

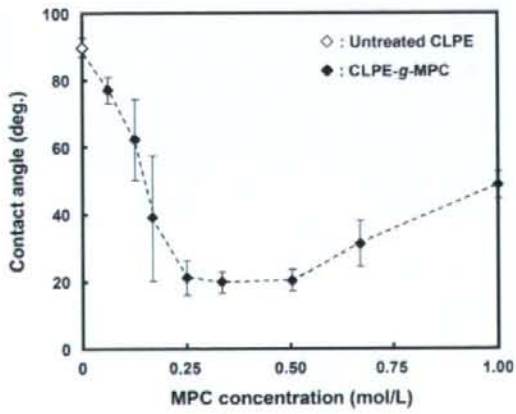

Figure 3. Static water-contact angle of CLPE-*g*-MPC as a function of the MPC concentration with a 90-min photo-irradiation time.

Figure 4 shows the FTIR/ATR spectra of untreated CLPE and CLPE-*g*-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time. An absorption peak was observed at 1460 cm^{-1} for both CLPE and CLPE-*g*-MPC. This peak is chiefly attributed to the methylene (CH_2) chain in the CLPE substrate and the poly(MPC) chain. However, transmission absorption peaks at 1240, 1080, and 970 cm^{-1} were observed only for CLPE-*g*-MPC. These peaks corresponded to the phosphate group (P—O) in the MPC unit. Similarly, an absorption peak at 1720 cm^{-1} observed in CLPE-*g*-MPC corresponded only to the carbonyl group (C=O) in the MPC unit. The absorption peak intensity of the P—O group increased with the MPC concentration used for polymerization and reached its maximum at a concentration of 0.5 mol/L.

Figure 5 shows the cross-sectional TEM images of CLPE-*g*-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time. At MPC concentrations greater than 0.25 mol/L, a 10–250-nm thick grafted poly(MPC) layer was clearly observed on the surface of the CLPE substrate. At an MPC concentration of 1.00 mol/L, the MPC-covered region coexisted with the uncovered regions, although the thickness of the poly(MPC) layer was greatest in the cover region, that is, 200–250 nm. At MPC concentrations below 0.06 mol/L, no poly(MPC) layer was observed on the CLPE surface (data not shown). These results indicate that the length of the grafted

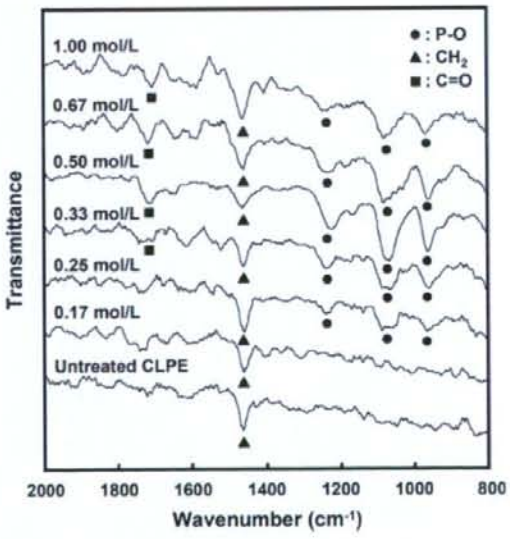

Figure 4. FT-IR/ATR spectra of CLPE-*g*-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time.

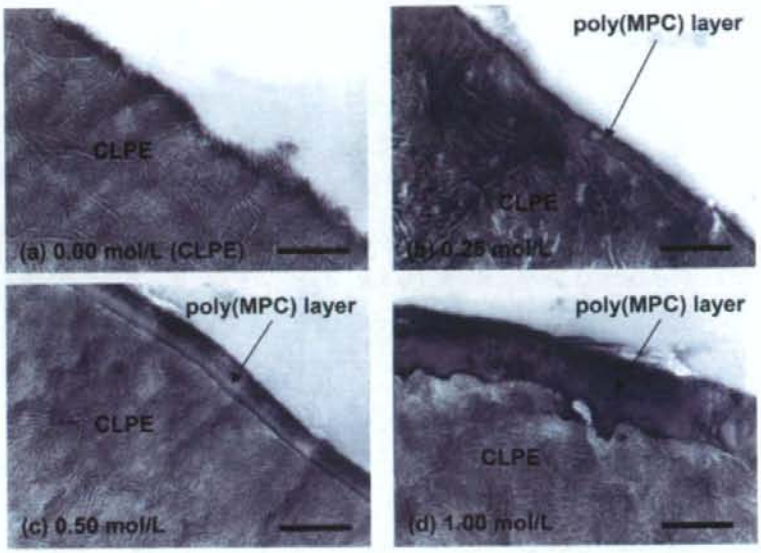

Figure 5. Cross-sectional TEM images of CLPE-g-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time. Bar; 200 nm.

poly(MPC) chain (thickness of the poly(MPC) layer) can be controlled by adjusting the MPC concentration during polymerization. This is attributable to the fact that the length of the polymer chains produced in a radical polymerization reaction generally correlates with the MPC concentration.

Figure 6 shows the FM images of the CLPE-g-MPC surface with 0.50 and 1.00 mol/L MPC concentrations and a 90-min photo-irradiation time. The multiple lines observed on the FM images are machining marks. On the CLPE-g-MPC surface with an MPC concentration of 0.50 mol/L, the poly(MPC) layer stained with rhodamine 6G was clearly visible and showed uniform staining. On the CLPE-g-MPC surface with an MPC concentration of 1.00 mol/L, an ungrafted (unstained) region was observed, indicating nonuniform grafting of the poly(MPC) layer on the CLPE surface.

Figure 7 shows the static and dynamic coefficients of friction of CLPE-g-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time. For CLPE-g-MPC, These coefficients of friction decreased markedly with an increase in MPC concentration and were the lowest at 0.5 and 0.25–0.5 mol/L, respectively; however, they increased at MPC concentrations above 0.67 mol/L. The CLPE-g-MPC specimens obtained with MPC concentrations of 0.25 and 0.50 mol/L exhibited ~80% reduction (i.e., 75–80%) in their dynamic coefficients of friction when compared with the untreated CLPE specimens.

Figure 8 shows the relationship between the dynamic coefficient of friction and the contact angle.

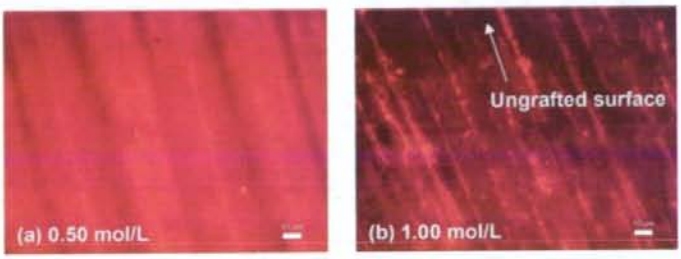

Figure 6. FM images of CLPE-g-MPC obtained with various MPC concentrations and a 90-min photo-irradiation time. Bar; 10 μm.

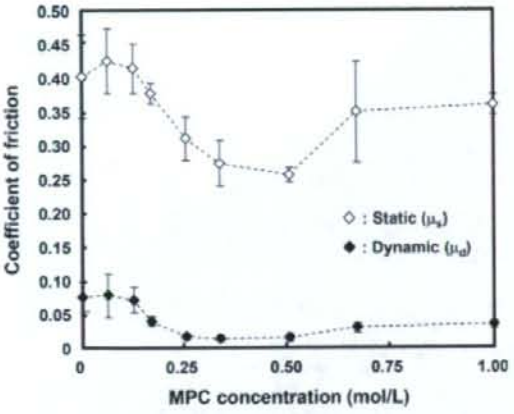

Figure 7. Coefficients of friction of the CLPE-*g*-MPC surface as a function of MPC concentration with a 90-min photo-irradiation time.

The dynamic coefficient of friction tended to increase with the contact angle. This increase was linear to a degree of accuracy, and the correlation coefficient was 0.920.

Figure 9 shows the gravimetric wear of the untreated CLPE and CLPE-*g*-MPC cups in the hip simulator wear test obtained with 0.25 and 0.50 mol/L MPC concentrations and a 90-min photo-irradiation time. It was observed that wear was significantly lower in the CLPE-*g*-MPC cups than in the untreated CLPE cups. There was no significant difference in wear of the CLPE-*g*-MPC cups obtained with 0.25 and 0.50 mol/L MPC concentrations. The CLPE-*g*-MPC

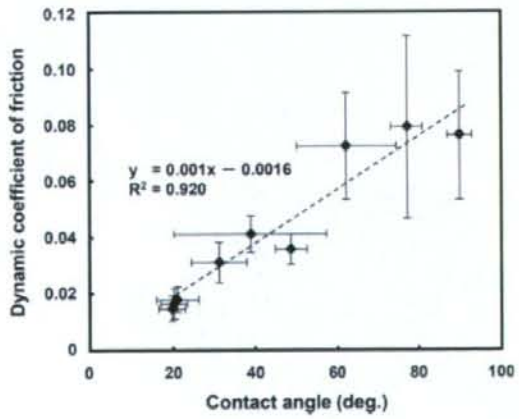

Figure 8. Relationship between dynamic coefficient of friction and contact angle in the CLPE-*g*-MPC surface. Bar; Standard deviations.

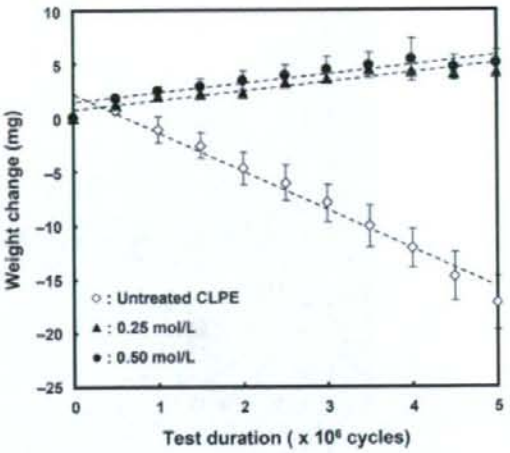

Figure 9. Weight change of the CLPE-*g*-MPC cups obtained with various MPC concentrations and a 90-min photo-irradiation in the hip joint simulator wear test. Bar; Standard deviations.

cups exhibited a slight increase in weight. This was partially attributable to enhanced fluid absorption in the tested cups than in the load-soak controls. When using the gravimetric method, the weight loss in the tested cups is corrected by subtracting the weight gain in the load-soak controls; however, this correction can not be perfectly achieved because only the tested cups are continuously subjected to motion and load. Fluid absorption in the tested cups is generally slightly higher than that in the load-soak controls. Consequently, the correction for fluid absorption by using the load-soak data as the correction factor leads to a slight underestimation of the actual weight loss.[12,33] In this study, a steady wear rate was calculated using data from 4.0×10^6 to 5.0×10^6 cycles; this value was 5.11 mg/10^6 cycles in the untreated CLPE cups. In contrast, the wear rates of the CLPE-*g*-MPC cups with 0.25 and 0.50 mol/L MPC concentrations were markedly lower, that is, 0.12 and 0.32 mg/10^6 cycles, respectively.

DISCUSSION

In this study, we investigated the properties of the poly(MPC) layer formed on the CLPE surface with various MPC concentrations by using photo-induced radical graft polymerization. The wear resistant properties of CLPE-*g*-MPC in terms of the characteristics of the nanometer-scale layer of poly(MPC) will be discussed hereafter.

In Figure 2, both the N and P content in the CLPE-*g*-MPC surface attributed to poly(MPC) increased to