Journal of Biomedical
Materials Research
Part B: Applied Biomaterials

Enhanced wear resistance of orthopaedic bearing due to the cross-linking of poly(MPC) graft chains induced by gamma-ray irradiation

Journal:	*Journal of Biomedical Materials Research: Part B - Applied Biomaterials*
Manuscript ID:	draft
Wiley - Manuscript type:	Original Research Report
Date Submitted by the Author:	n/a
Complete List of Authors:	Kyomoto, Masayuki; Japan Medical Materials Corporation, Research Division Moro, Toru; The University of Tokyo, Department of Orthopaedic Surgery, School of Medicine Miyaji, Fumiaki; Japan Medical Materials Corporation, Research Division Konno, Tomohiro; The University of Tokyo, Department of Materials Engineering, School of Engineering and Center for NanoBio Integration Hashimoto, Masami; Japan Fine Ceramics Center, Materials Research and Development Laboratory Kawaguchi, Hiroshi; The University of Tokyo, Department of Orthopaedic Surgery, School of Medicine Takatori, Yoshio; The University of Tokyo, Department of Orthopaedic Surgery, School of Medicine Nakamura, Kozo; The University of Tokyo, Department of Orthopaedic Surgery, School of Medicine Ishihara, Kazuhiko; The University of Tokyo, Department of Materials Engineering, School of Engineering and Center for NanoBio Integration
Keywords:	joint replacement, polyethylene (UHMWPE), sterilization, phosphorylcholine

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]

[1]*Research Division, Japan Medical Materials Corporation, Osaka, Japan*

[2]*Department of Materials Engineering, School of Engineering and Center for NanoBio Integration, The University of Tokyo, Tokyo, Japan*

[3]*Department of Orthopaedic Surgery, School of Medicine, The University of Tokyo, Tokyo, Japan*

[4]*Materials Research and Development Laboratory, Japan Fine Ceramics Center, Nagoya, Japan*

*Corresponding author.

Tel.: +81-6-6350-1014; fax: +81-6-6350-5752

Uemura Nissei Bldg. 9F, 3-3-31 Miyahara, Yodogawa-ku, Osaka 532-0003, JAPAN

E-mail address: kyomotom@jmmc.jp (M. Kyomoto)

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 non-sterilized 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 non-sterilized 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.

Keywords: Joint replacements; Polyethylene; Phosphorylcholine; Sterilization

Running title: Enhanced wear resistance with cross-links of poly(MPC) graft chains

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 CLPE (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 the reduction of protein adsorption and cell adhesion.[9–18] Based on 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, e.g., 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 re-termination 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, Ltd. (Osaka, Japan). MPC was industrially synthesized using the method reported by Ishihara et al.[8] and was supplied by Ai Bio-Chips Corp., Ltd (Tokyo, Japan).

A compression-molded UHMWPE (GUR1020 resin, Poly Hi-Solidur Inc., IN, USA) 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 in order 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 Co., Ltd., Funabashi, Japan) of 5 mW/cm^2 at 60°C for 90 min using a filter (Model D-35; Toshiba Corp., Tokyo, Japan) to pass only ultraviolet light with a wavelength of 350 ± 50 nm. After the polymerization, the CLPE-*g*-MPC specimens were removed, washed with pure water and ethanol, and dried at room temperature. The CLPE 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 non-sterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC surfaces were examined by Fourier-transform infrared (FT-IR) spectroscopy using attenuated total reflection (ATR) equipment. The FT-IR/ATR spectra were obtained in 32 scans over a range of 800 to 2000 cm^{-1} using an FT-IR analyzer (FT/IR-615; JASCO International Co., Ltd., 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 Ltd., 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 Co., Ltd., 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 Co., Ltd., 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 ≥ 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.

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 mm 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 Corp., MN, USA). A Co-Cr-Mo alloy femoral ball component with a size of 26 mm (Japan Medical Materials Corp., Osaka, Japan) was used as an acetabular component. A mixture of 25vol% bovine serum, 20 mM/L of ethylene diamine tetraacetic acid (EDTA), and 0.1mass% sodium azide was used as lubricant, according to the ISO 14242-1 standard.[27] The lubricant was replaced every 0.5×10^6 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]

In order 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 Corp., Tokyo, Japan)

after a simulator test with 5.0×10^6 cycles.

RESULTS

Figure 1 shows the FT-IR/ATR spectra for the non-sterilized 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 FT-IR/ATR spectra did not differ significantly between the non-sterilized and gamma-ray sterilized CLPE-*g*-MPC.

Table I summarizes the elemental compositions of the untreated CLPE and the non-sterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Both the elemental composition of nitrogen and phosphorous in the non-sterilized 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 non-sterilized one.

Figure 2 shows the static water-contact angle of the untreated CLPE and the non-sterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. The static water-contact angle of the untreated CLPE was approximately 90° before and after gamma-ray sterilization, and it drastically decreased (approximately 30°) due to 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 non-sterilized 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 as 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 to 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 non-sterilization.

Figure 5 shows the weight change (gravimetric wear) of the gamma-ray sterilized CLPE cups and non-sterilized 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 subtracting 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 non-sterilized 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 as 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 non-sterilized 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 bearing surfaces of the CLPE cups. After the simulator test, the machining marks on these surfaces disappeared completely. On the contrary, clear machining marks with regular circles were observed on the surface of the non-sterilized 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 exhibited the fluid film lubrication (or mixed lubrication) of the intermediate hydrated layer.[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 re-termination 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 non-sterilized 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 to 50 kGy is clearly responsible for producing more cross-links.

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 non-sterilized 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) as compared with the non-sterilized 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 non-sterilized 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 non-sterilized 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 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.[41, 42] 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, 43] It has also been reported that the oxygen content might be almost zero in the body.[42, 44] Thus, although the oxidation degradation of polyethylene *in vivo* is related to the surrounding oxygen concentration, i.e., 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.[45] Based on 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.[45] 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.[46] 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 non-sterilized 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,[2, 47, 48] and tribological advantages of MPC polymers, CLPE-*g*-MPC is believed to be promising for use in the next-generation artificial hip joint systems.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology (#15390449), and a Health and Welfare Research Grant for Translational Research from the Japanese Ministry of Health, Labour and Welfare. The authors also express special thanks to Dr. Masaru Ueno, Mr. Takatoshi Miyashita, and Mr. Noboru Yamawaki (Japan Medical Materials Corp.) for their excellent technical assistance.

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(7):1487–97.
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(5):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, in press.
8. Ishihara K, Ueda T, Nakabayashi N. Preparation of phospholipid polymers and their properties as polymer hydrogel membranes. Polym J 1990;22(5):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(3):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(30):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, in press.
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(1):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(1):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(3):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(23):4767–4778.
16. Konno T, Hasuda H, Ishihara K, Ito Y. Photo-immobilization of a phospholipid polymer for surface modification. Biomaterials 2005;26(12):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(19):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(23):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 polyethylene in artificial hip joints. J Mater Sci Mater Med, in press.
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(7-9):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(12):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(5):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(7):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, 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(12):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(18):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(2):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(2):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(2):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(7):944–949.
41. 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(3):477–489.
42. 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(4):815–823.
43. 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(1):59–70.
44. Treuhaft PS, McCarty DJ. Synovial fluid pH, lactate, oxygen and carbon dioxide partial pressure in various joint diseases. Arthritis Rheum 1971;14(4):475–84.
45. 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(7):840–849.

46. Greer KW, King RS, Chan FW. The effects of raw material, irradiation dose, and irradiation source on crosslinking of UHMWPE. Kurtz SM, Gsell RA, Martell J, editors. Crosslinked and thermally treated ultra-high molecular weight polyethylene for joint replacements. West Conshohocken: American Society for Testing and Materials; 2003:209–220.
47. 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.
48. 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(11):1397–1407.

Figure captions

Figure 1 FT-IR/ATR spectra for non-sterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC.

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

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

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

Figure 5 Weight change (gravimetric wear) of gamma-ray sterilized CLPE cups and non-sterilized 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 before the hip simulator test, (b) CLPE (gamma-ray sterilized), (c) CLPE-*g*-MPC (non-sterilized) and (d) CLPE-*g*-MPC (gamma-ray sterilized) after the hip simulator test. The bar indicates 500 μm.

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

TABLE I Surface elemental composition (%) of gamma-ray sterilized CLPE and CLPE-*g*-MPC

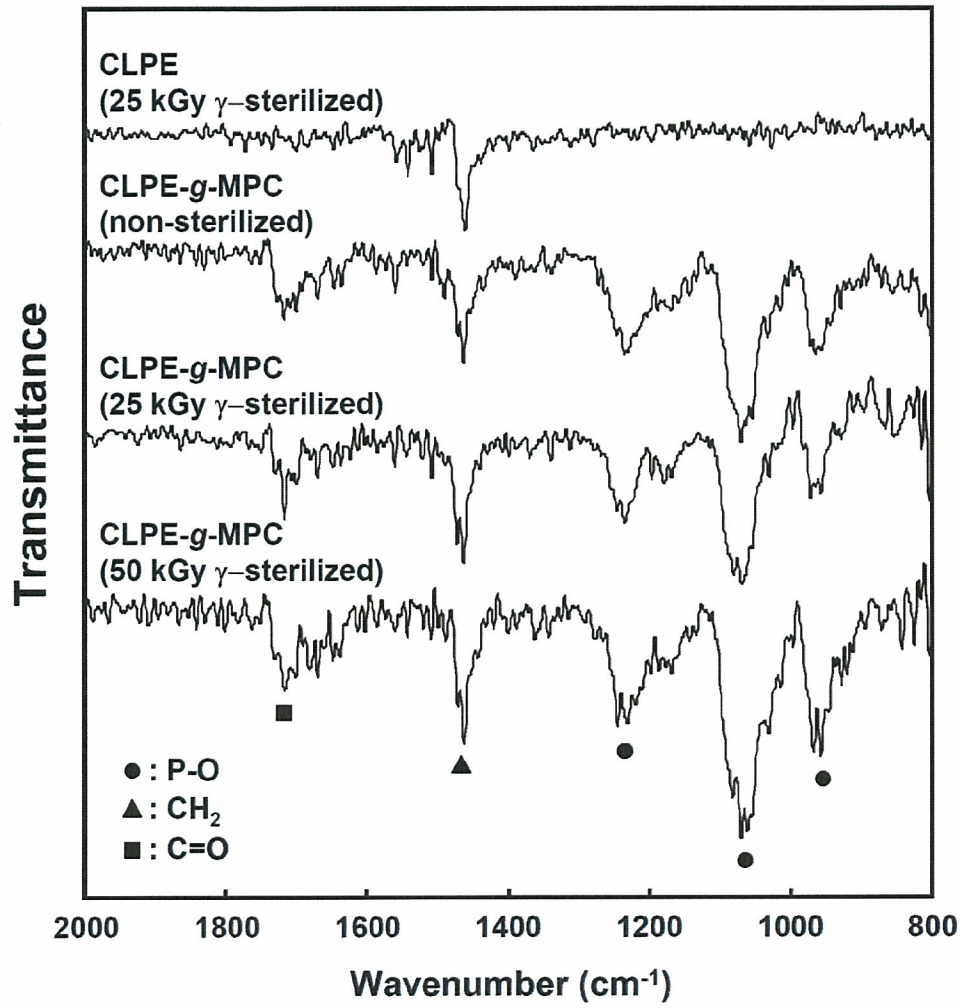

Figure 1. FT-IR/ATR spectra for non-sterilized and gamma-ray sterilized CLPE and CLPE-*g*-MPC.

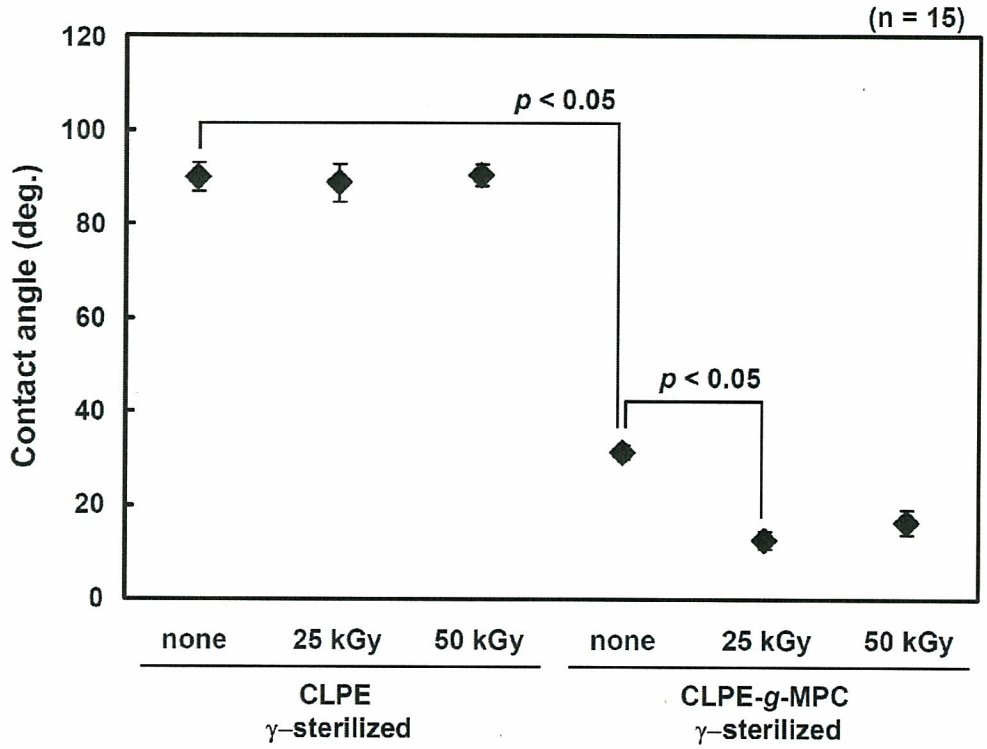

Figure 2. Static water-contact angle of the untreated CLPE and the non-sterilized and thhe gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.

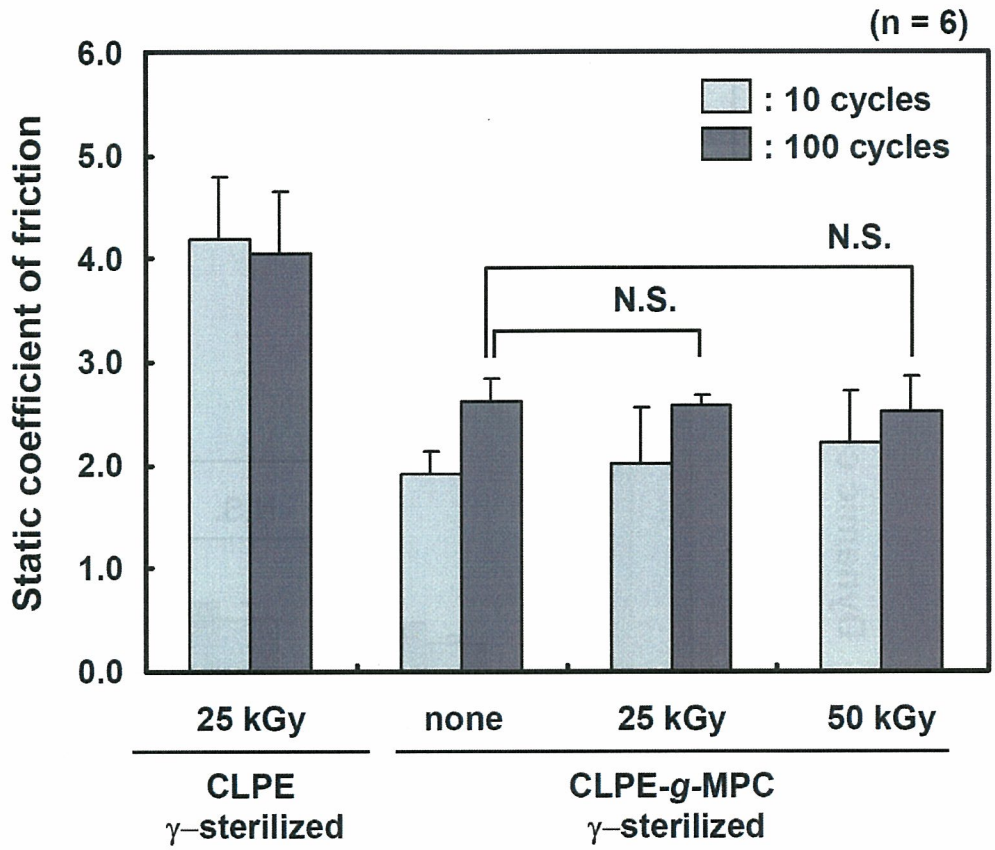

Figure 3. Static coefficients of friction of the gamma-ray sterilized CLPE surfaces and non-sterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.

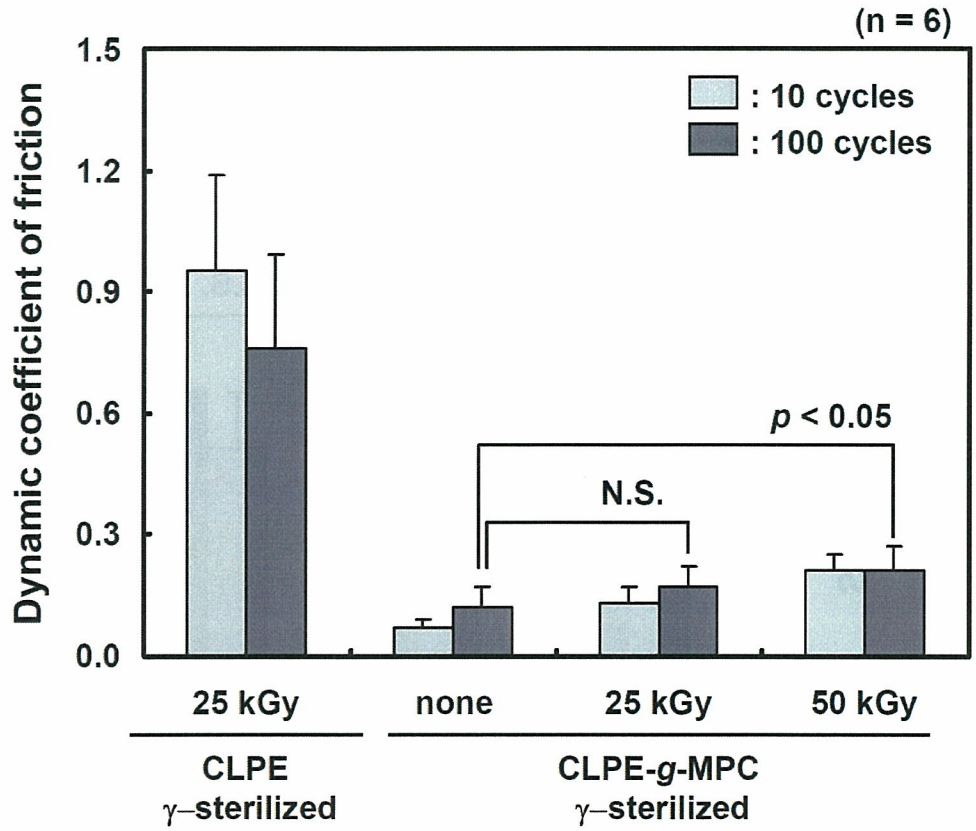

Figure 4. Dynamic coefficients of friction of gamma-ray sterilized CLPE surfaces and non-sterilized and gamma-ray sterilized CLPE-*g*-MPC surfaces. Bar; Standard deviations.