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Legends

Fig. 1 Overview of the study.

Fig. 2A-B Schematic illustration of pin-on-disk wear test: (A) Multidirectional wear test; (B) impact-to-wear test.

Fig. 3A-B Surface functional analysis of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC)-grafted cross-linked polyethylene (CLPE) and high-dose CLPE with vitamin E blending (HD-CLPE(VE)). (A) Static water contact angle (n = 15) on untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE). The data are expressed as mean values ± SD. As the PMPC grafting proceeded, the CLPE or HD-CLPE(VE) surface became drastically wettable, i.e., the surface changed from hydrophobic to hydrophilic. The type of material had no discernible effect on the wettability (p = 0.070). (B) Dynamic coefficients of friction (n = 6) for untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE). The data are expressed as mean values ± SD. * indicates $p < 0.05$, ** indicates $p < 0.01$. The dynamic coefficient of friction had a tendency to decrease with an increase in the load.

Fig. 4A-B Time course of (A) fluid absorption (n = 3) and (B) gravimetric wear (n = 3) of untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE) disks during the multidirectional wear test. The data are expressed as mean values ± SD. * indicates $p < 0.05$, ** indicates $p < 0.01$. Significant differences ($p = 6.35 \times 10^{-6}$ and p

= 3.78×10^{-2}, respectively) were observed in the comparison of fluid absorption or gravimetric wear between PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) after the test.

Fig. 5A-C Volumetric wear analysis of untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE) disks after the multidirectional wear test. (A) Three-dimensional profiles in the sliding and backside surfaces of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. (B) Volumetric wear in the sliding surface and (C) volumetric penetration in the backside surface of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. The data are expressed as mean values ± SD. There was no significant differences in the comparison of volumetric wear or penetration of the three comparative groups (untreated CLPE vs. PMPC-grafted CLPE, $p = 0.750$ and $p = 0.523$; untreated HD-CLPE(VE) vs. PMPC-grafted HD-CLPE(VE), $p = 0.153$ and $p = 0.212$; and PMPC-grafted CLPE vs. PMPC-grafted HD-CLPE(VE), $p = 0.670$ and $p = 0.125$).

Fig. 6A-B Time course of (A) fluid absorption ($n = 3$) and (B) gravimetric wear ($n = 3$) of untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE) disks during the impact-to-wear test. The data are expressed as mean values ± SD. ** indicates $p < 0.01$. Significant differences ($p = 3.31 \times 10^{-6}$ and $p = 9.61 \times 10^{-4}$, respectively) were observed in the comparison of fluid absorption or gravimetric wear between PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) after the test.

Fig. 7A-C Volumetric wear analysis of untreated and PMPC-grafted CLPE, and untreated and PMPC-grafted HD-CLPE(VE) disks after the impact-to-wear test. (A) Three-dimensional profiles in the sliding and backside surfaces of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. (B) Volumetric wear in the sliding surface and (C) volumetric penetration in the backside surface of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. The data are expressed as mean values ± SD. There was no significant differences in the comparison of volumetric wear or penetration of the three comparative groups (untreated CLPE vs. PMPC-grafted CLPE, $p = 0.803$ and $p = 0.268$; untreated HD-CLPE(VE) vs. PMPC-grafted HD-CLPE(VE), $p = 0.923$ and $p = 0.986$; and PMPC-grafted CLPE vs. PMPC-grafted HD-CLPE(VE), $p = 0.277$ and $p = 0.092$).

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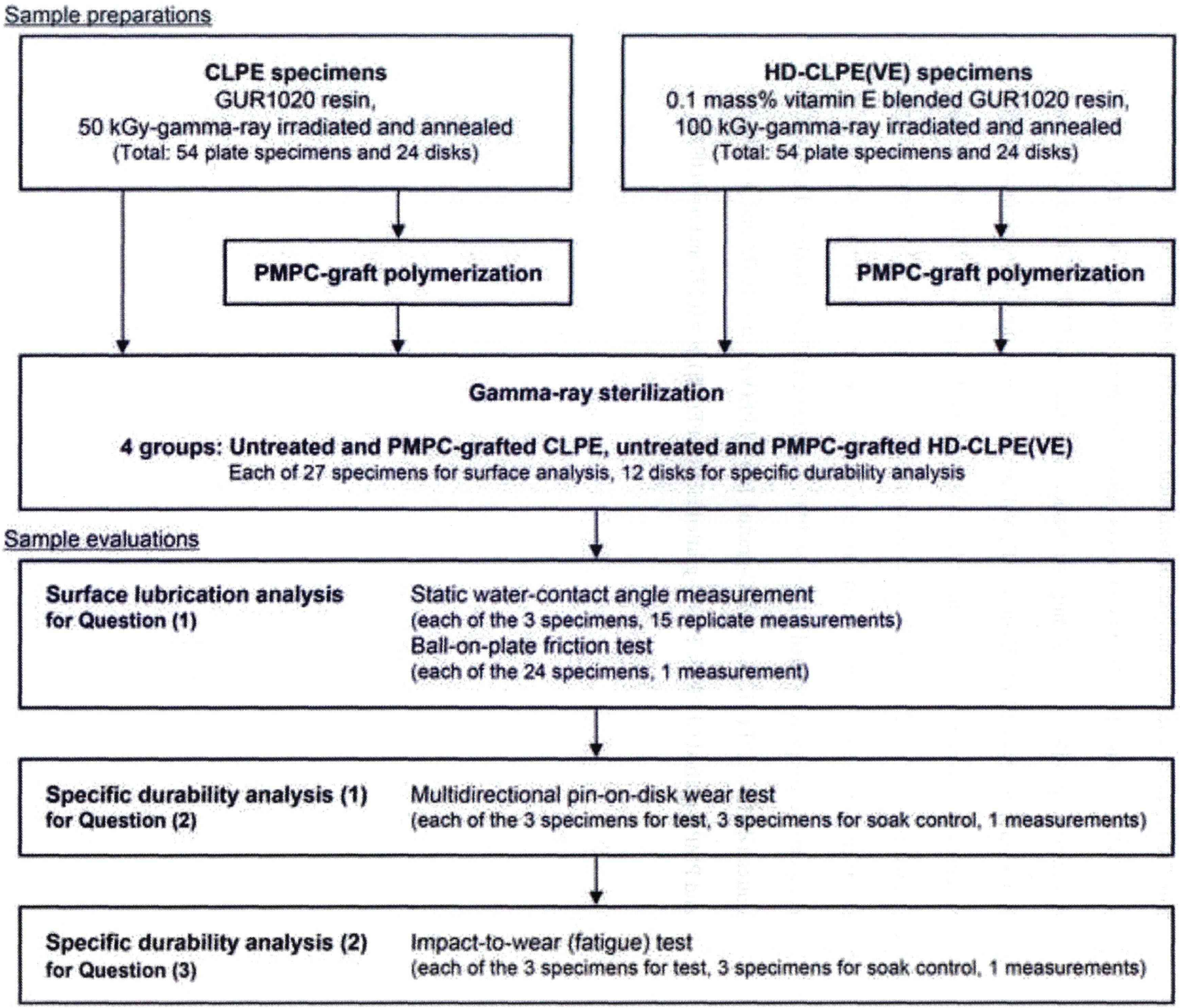

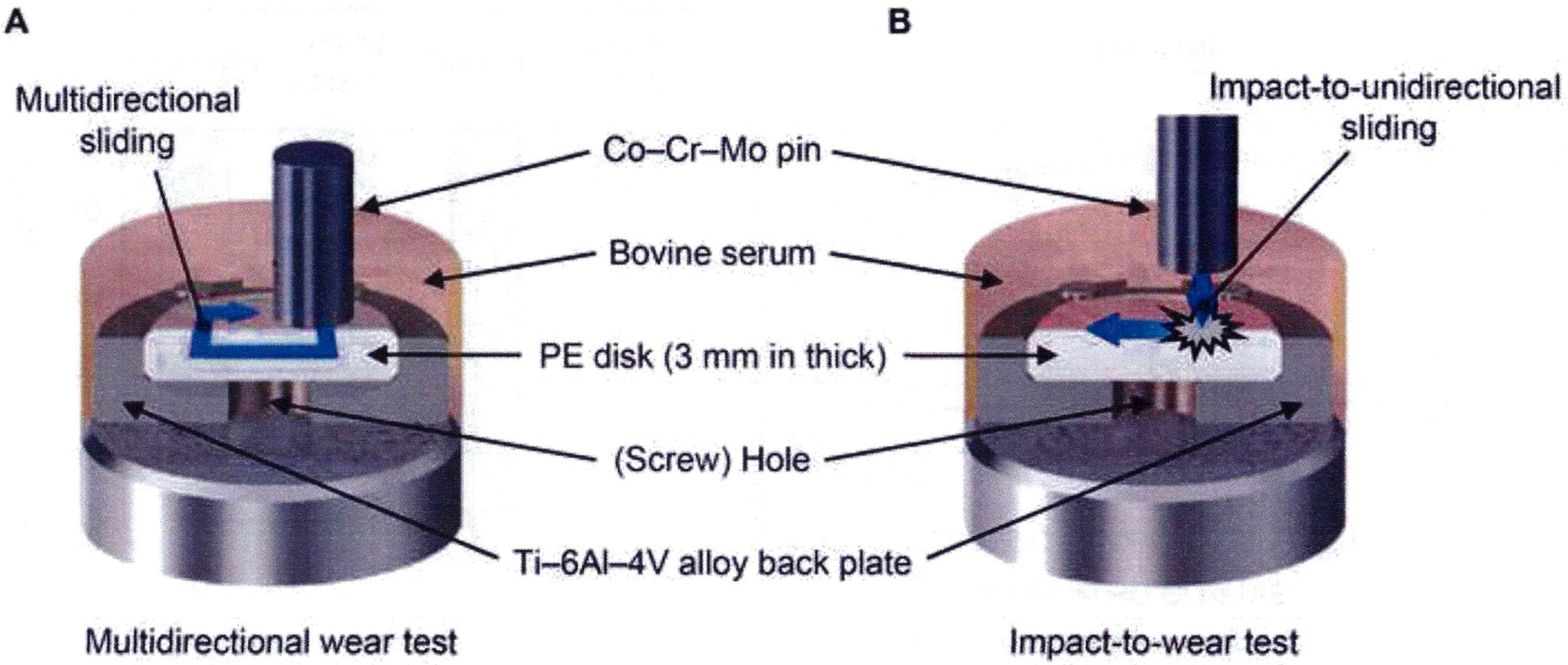
A
B
Multidirectional sliding
Co–Cr–Mo pin
Impact-to-unidirectional sliding
Bovine serum
PE disk (3 mm in thick)
(Screw) Hole
Ti–6Al–4V alloy back plate
Multidirectional wear test
Impact-to-wear test

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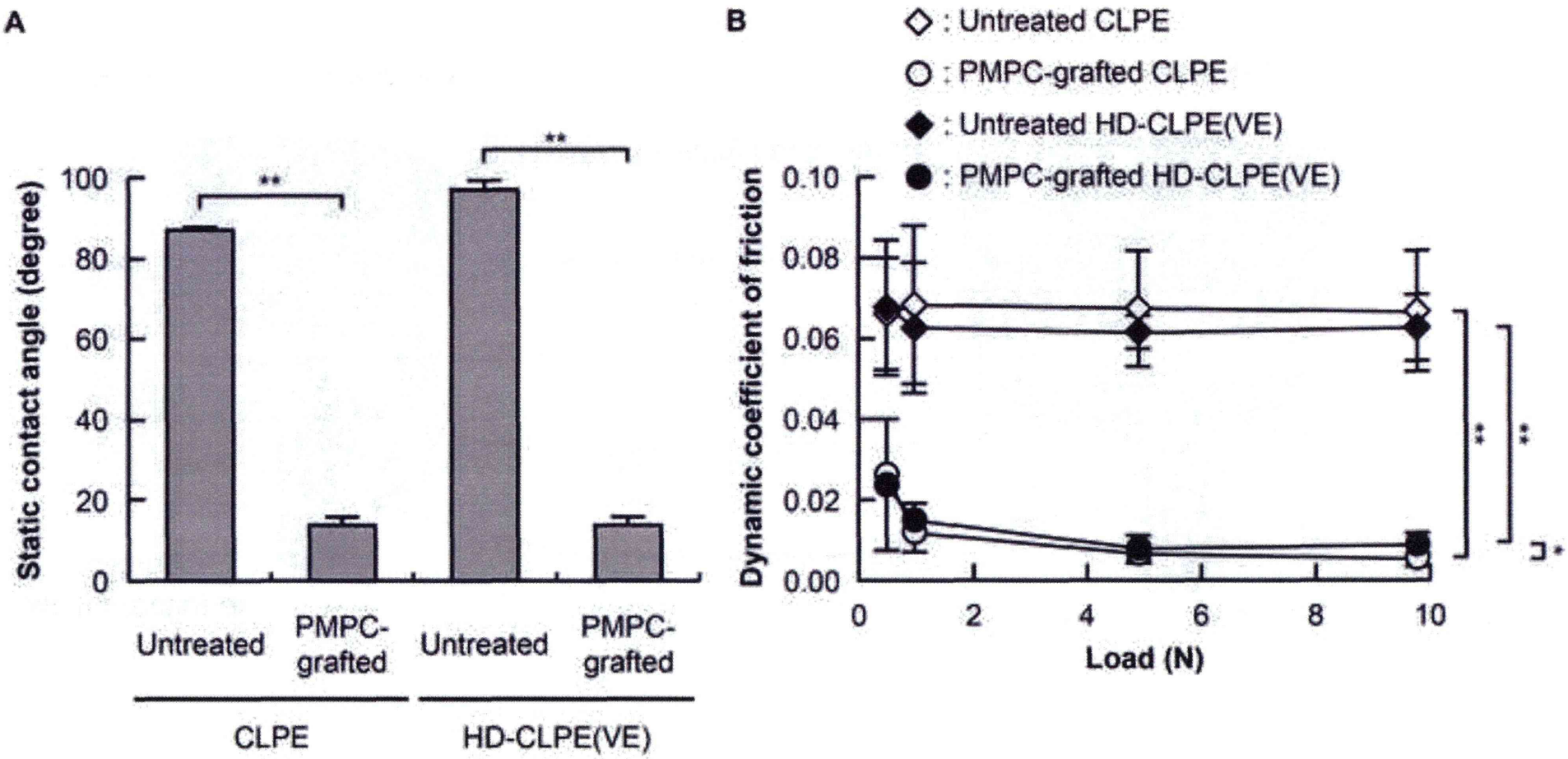

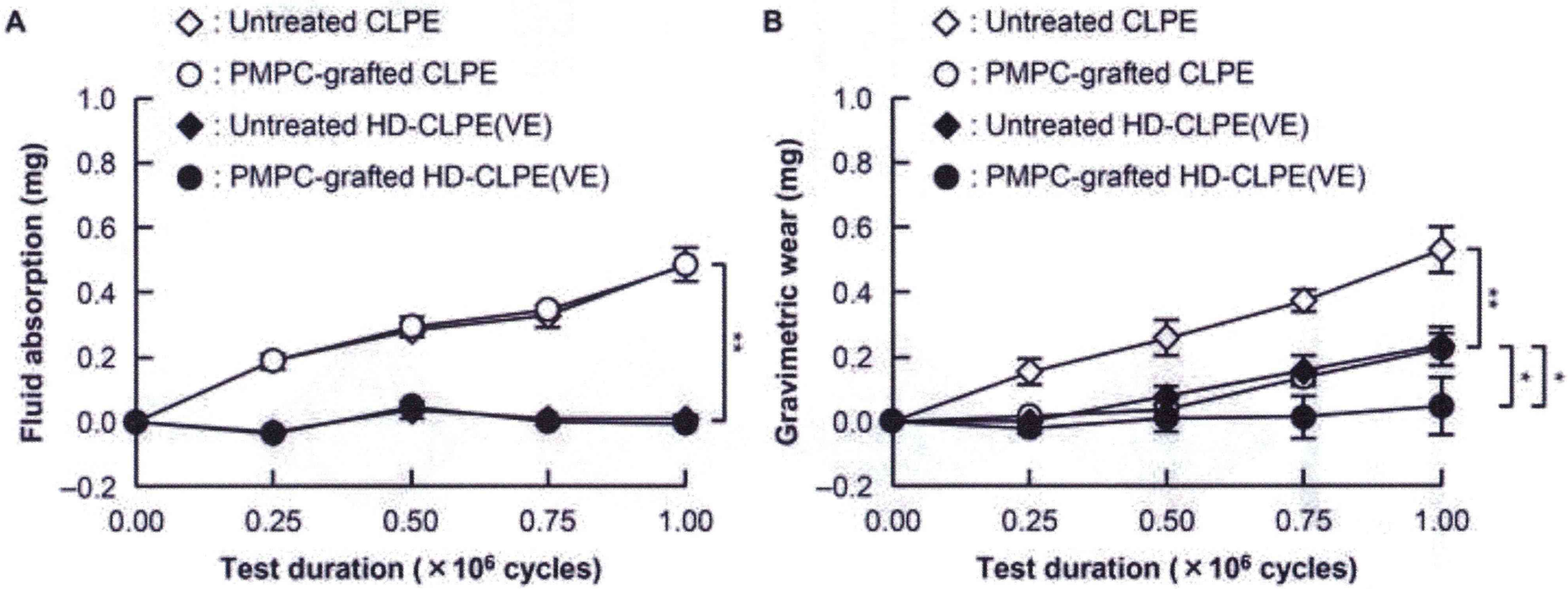
A
◇ : Untreated CLPE
○ : PMPC-grafted CLPE
◆ : Untreated HD-CLPE(VE)
● : PMPC-grafted HD-CLPE(VE)
Fluid absorption (mg)
1.0
0.8
0.6
0.4
0.2
0.0
–0.2
0.00
0.25
0.50
0.75
1.00
Test duration (×10⁶ cycles)
**
B
◇ : Untreated CLPE
○ : PMPC-grafted CLPE
◆ : Untreated HD-CLPE(VE)
● : PMPC-grafted HD-CLPE(VE)
Gravimetric wear (mg)
1.0
0.8
0.6
0.4
0.2
0.0
–0.2
0.00
0.25
0.50
0.75
1.00
Test duration (×10⁶ cycles)
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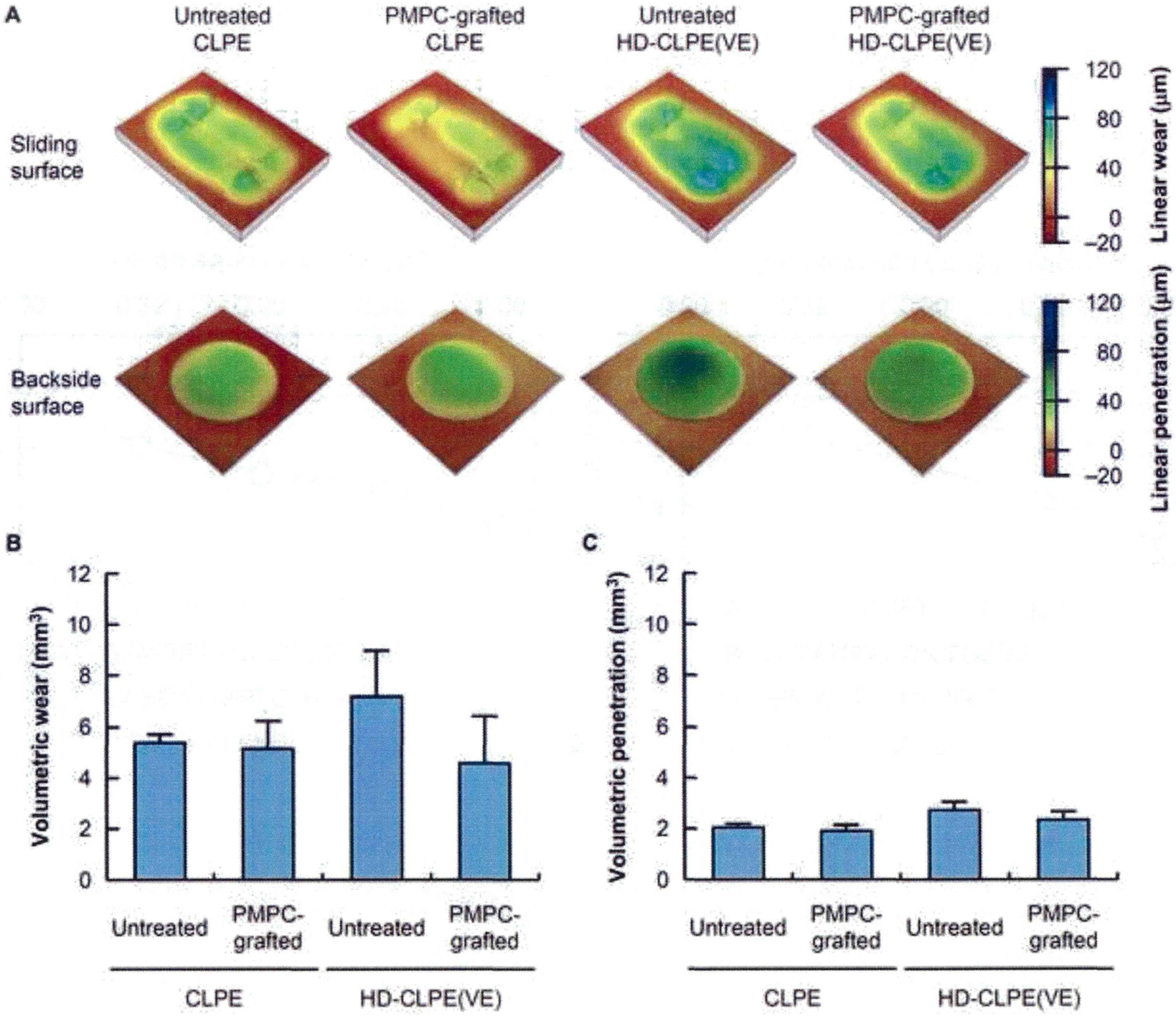

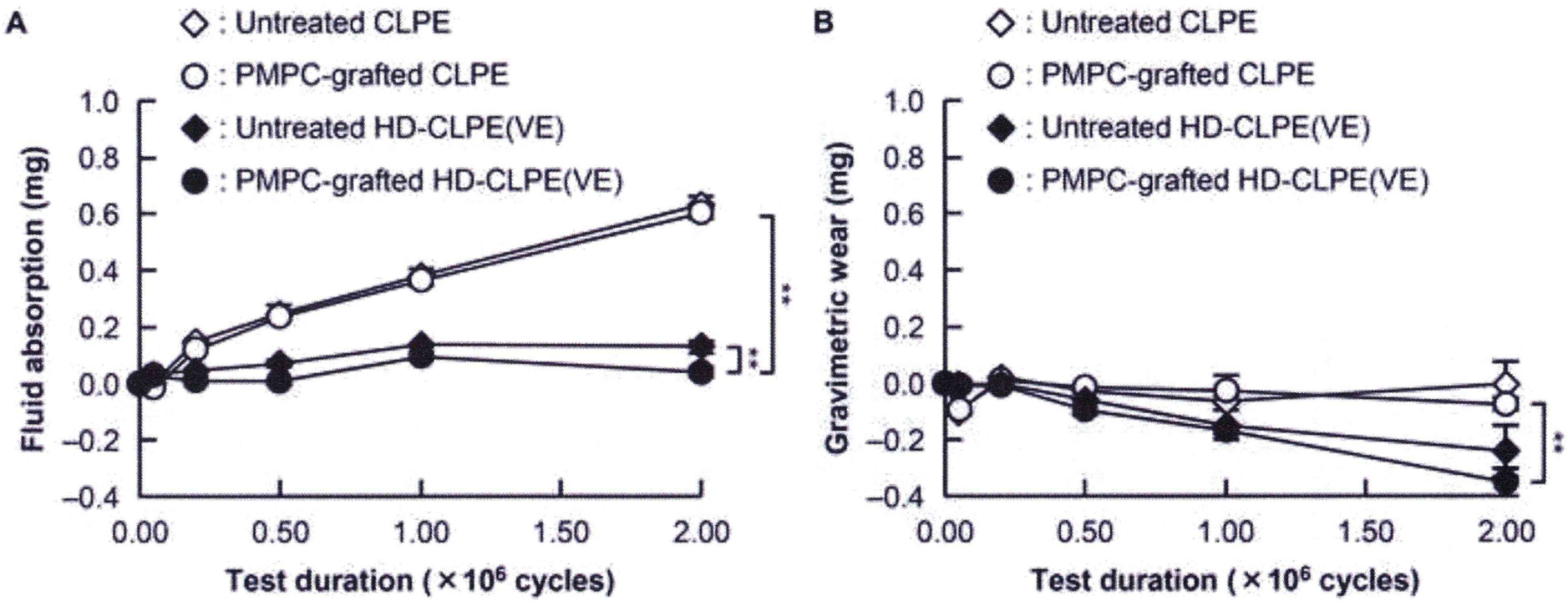
A
◇ : Untreated CLPE
○ : PMPC-grafted CLPE
◆ : Untreated HD-CLPE(VE)
● : PMPC-grafted HD-CLPE(VE)
Fluid absorption (mg)
1.0
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−0.2
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1.00
1.50
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Test duration (×10⁶ cycles)
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B
◇ : Untreated CLPE
○ : PMPC-grafted CLPE
◆ : Untreated HD-CLPE(VE)
● : PMPC-grafted HD-CLPE(VE)
Gravimetric wear (mg)
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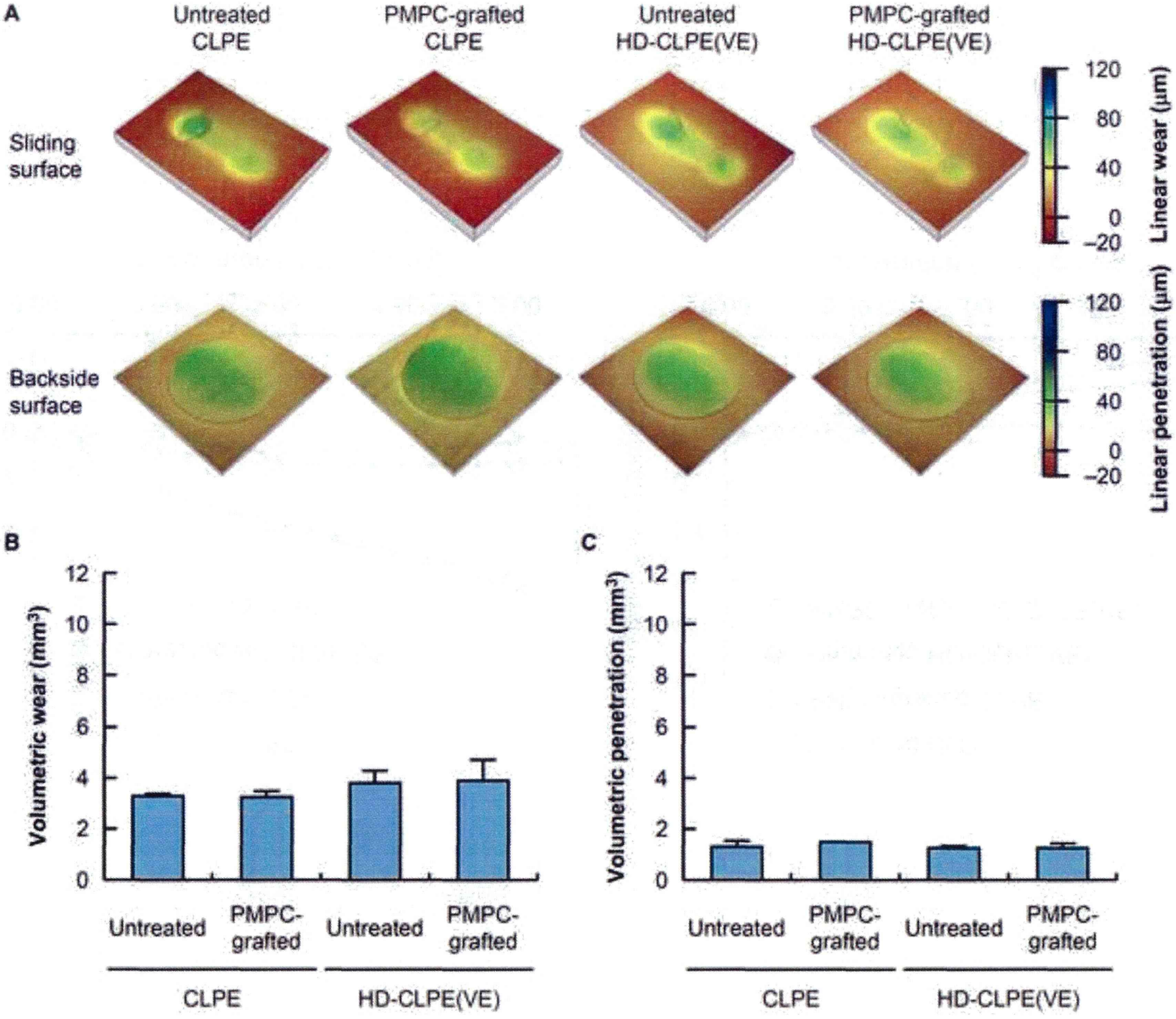

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Title: Poly(2-methacryloyloxyethyl phosphorylcholine) grafting and vitamin E blending for high wear resistance and oxidative stability of life-long orthopedic bearings

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Keywords: joint replacement; polyethylene; phosphorylcholine; antioxidant; wear mechanism; oxidation

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Abstract: The ultimate goal in manipulating the surface and substrate of a cross-linked polyethylene (CLPE) liner is to obtain not only high wear resistance but also high oxidative stability and high-mechanical properties for life-long orthopedic bearings. We have demonstrated the fabrication of highly hydrophilic and lubricious poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) grafting layer onto the antioxidant vitamin E blended CLPE (HD-CLPE(VE)) surface. The PMPC grafting layer with a thickness of 100 nm was successfully fabricated on the vitamin E-blended CLPE surface by using photoinduced-radical graft polymerization. Since PMPC has a highly hydrophilic nature, the water wettability and lubricity of the PMPC-grafted CLPE and HD-CLPE(VE) surfaces were greater than that of the untreated CLPE surface. The PMPC grafting contributed significantly to wear reduction in a hip-joint simulator wear test. Despite high-dose gamma-ray irradiation for cross-linking and further UV irradiation for PMPC grafting, the substrate modified by vitamin E blending maintained high-oxidative stability because vitamin E is an extremely efficient radical scavenger. Furthermore, the mechanical properties of the substrate remained almost unchanged even after PMPC grafting or vitamin E blending, or both PMPC grafting and vitamin E blending. In conclusion, the PMPC-grafted HD-CLPE(VE) provided simultaneously high-wear resistance, oxidative stability, and mechanical properties.

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Effect of UV-irradiation intensity on graft polymerization of 2-methacryloyloxyethyl phosphorylcholine on orthopedic bearing substrate

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Abstract: Photoinduced grafting of 2-methacryloyloxyethyl phosphorylcholine (MPC) onto cross-linked polyethylene (CLPE) was investigated for its ability to reduce the wear of orthopedic bearings. We investigated the effect of UV-irradiation intensity on the extent of poly(MPC) (PMPC) grafting, and found that it increased with increasing intensity up to 7.5 mW/cm^2, and the remained fairly constant. It was found to be extremely important to carefully control the UV intensity, as at higher values, a PMPC gel formed via homopolymerization of the MPC, resulting in the formation of cracks at the interface of the PMPC layer and the CLPE substrate. When the CLPE was exposed to UV-irradiation during the graft polymerization process, some of its physical and mechanical properties were slightly changed due to cross-linking and scission effects in the surface region; however, the results of all of the tests exceed the lower limits of the ASTM standards. Modification of the CLPE surface with the hydrophilic PMPC layer increased lubrication to levels that match articular cartilage. The highly hydrated thin PMPC films mimicked the native cartilage extracellular matrix that covers synovial joint surface, acting as an extremely efficient lubricant, and providing high-wear resistance. © 2013 Wiley Periodicals, Inc. J Biomed Mater Res Part A: 00A:000–000, 2013.

Key Words: joint replacement, polyethylene, phosphorylcholine, graft polymerization, photoirradiation

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INTRODUCTION

Total hip arthroplasty (THA) has consistently been one of the most successful joint surgeries to date. Owing to the aging global population, the number of primary and revised THAs increases significantly year on year.[1] However, the incidence of osteolysis greatly limits the duration and clinical outcome of this type of surgery.[2,3] Osteolysis is triggered by a host inflammatory response to wear particles produced at the bearing interface of the artificial joint. A typical device consists of cross-linked polyethylene (CLPE) acetabular liner and a cobalt–chromium–molybdenum (Co–Cr–Mo) alloy femoral head, particles of which undergo phagocytosis by macrophages and induce the secretion of bone resorptive cytokines.[4,5] Efforts to reduce the number of these particles and increase the longevity of artificial hip joints have focused on a number of bearing alternatives and improvements to the currently used materials.[6–11] The use of a hard-on-hard THA, such as a metal-on-metal bearing, has been proposed to reduce the wear. However, this has raised new concerns regarding adverse local and systemic effects of metal ion release and electrochemical corrosion, which could cause serious problems such as local soft tissue reactions and pseudotumor formation.[12]

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The bearing surfaces of a natural synovial joint are covered with a specialized type of hyaline cartilage, termed articular cartilage, which protects the joint interface from mechanical wear and facilitates a smooth motion of joints during daily activity.[13,14] Articular cartilage consists of chondrocytes surrounded by extracellular matrix macromolecules (e.g., proteoglycans, glycosaminoglycans, and collagens) and surface active phospholipids (e.g., phosphatidylcholine derivatives). Owing to the charge on these molecules, they can trap water to maintain the water–fluid and electrolyte balance within the articular cartilage tissue, making it highly hydrophilic and providing an effective boundary lubricant.[14,15] The fluid thin-film lubrication achieved by the presence of this hydrated layer is essential for the smooth motion of natural synovial joints. Learning from and mimicking nature has been shown to be a highly successful approach to producing artificial tissues and implants. Therefore, the strategy of investigating and then reproducing the natural bearing surfaces in artificial joints in order to mimic the role of cartilage has great potential.

In this study, we produced nanometer-scale hydrophilic layers composed of 2-methacryloyloxyethyl phosphorylcholine (MPC) on the CLPE surface of an artificial hip joint, with the aim of reducing wear and avoiding bone resorption. Modification of the bearing surfaces of an artificial joint with a hydrophilic layer should increase lubrication to levels that match articular cartilage under physiological conditions. MPC is commonly used to synthesize highly hydrophilic and antibiofouling polymer biomaterials.[16–22] Polymers based on this structure have great potential in the fields of biomedical science and bioengineering because they possess beneficial properties such as excellent antibiofouling ability and low friction. Thus, several medical devices, including intravascular stents,[19] soft contact lenses,[20] artificial hearts,[21] and artificial hip joints,[22] have been developed from MPC polymers and subsequently clinically applied. The biomedical efficacy and safety of MPC polymers are therefore well established. In this study, the nanometer-scale surface modification was accomplished using a photoinduced (i.e., ultraviolet (UV) irradiation) radical polymerization technique[23] similar to the "grafting from" method. This approach has an advantage in that it facilitates the synthesis of both semi-dilute and high-density polymer brushes.[24] This is in contrast to photoinitiated cross-linking and scission reactions of polyolefins, which are similarly used.[25,26] When polyolefins are exposed to UV-irradiation under the radical graft polymerization processing, the effect would be a result of complicated combination of different processes.

In the present study, we investigated the effect of different intensities of UV-irradiation on the extent of photopolymerization of MPC to form a poly(MPC) (PMPC) layer on a CLPE substrate. Such investigations are of great importance in the design of life-long artificial joints, and for obtaining better understanding of their lubrication and wear mechanisms. Here, we evaluated whether UV-irradiation intensity would affect the extent of the PMPC grafting and the properties of the CLPE substrate. In addition, we assessed the potential of the PMPC-graft and/or its layer characteristics for improving the durability of artificial hip joints.

MATERIALS AND METHODS

Graft polymerization with different UV-irradiation intensities

A compression-molded polyethylene (PE; GUR1020 resin; Quadrant PHS Deutschland GmbH, Vreden, Germany) bar stock was irradiated with a 50 kGy dose of gamma rays in a N_2 gas atmosphere, and annealed at 120°C for 7.5 h in N_2 gas in order to facilitate cross-linking. The resulting CLPE specimens were then machined from this bar stock after cooling.

The CLPE specimens were immersed in acetone (Wako Pure Chemical Industries, Ltd., Osaka, Japan) containing 10 mg/mL benzophenone (Wako Pure Chemical Industries) for 30 s, and then dried in the dark at room temperature in order to remove the acetone. MPC was industrially synthesized using the method reported by Ishihara et al. and supplied by NOF Corp. (Tokyo, Japan).[16] The MPC was dissolved in degassed pure water to a concentration of 0.5 mol/L. Subsequently, the benzophenone-coated CLPE specimens were immersed in the MPC aqueous solutions. Photoinduced graft polymerization was carried out on the CLPE surface using UV irradiation (UVL-400HA ultra-high pressure mercury lamp; Riko-Kagaku Sangyo, Funabashi, Japan) with an intensity of 1.5–15 mW/cm^2 at 60°C for 90 min; a filter (model D-35; Toshiba, Tokyo, Japan) was used to restrict the passage of UV light to a wavelengths of 350 ± 50 nm. After the polymerization, the PMPC-grafted CLPE specimens were removed, washed with pure water and ethanol, and dried at room temperature.

Surface analyses

The PMPC-grafted CLPE samples obtained using the range of UV-irradiation intensities were stained using an aqueous solution of 200 ppm (mass) rhodamine 6G (Wako Pure Chemical Industries) because it rapidly associates with the MPC polymer, which is structurally highly similar to lipids.[27] The PMPC-grafted CLPE samples were immersed in the rhodamine 6G solution for 30 s and then washed twice with distilled water for 30 s, and dried. All the samples were examined and imaged using fluorescence microscopy (Axioskop 2 Plus; Carl Zeiss AG, Oberkochen, Germany). 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 Co.). Lenses with a ×10 magnification and an appropriate exposure time (~0.1 s) were employed to obtain clear images of the samples.

The surface phosphorus concentration of the PMPC-grafted CLPE samples were analyzed using X-ray photoelectron spectroscopy (XPS) using an AXIS-HSi165 spectrometer (Kratos/Shimadzu Co., Kyoto, Japan) equipped with a 15 kV Mg-Kα radiation source at the anode. The take-off angle of the photoelectrons was maintained at 90°, and the P 2p peak was used for phosphorus quantification. Six specimens of each of the PMPC-grafted CLPE samples were prepared, and each sample was scanned five times.

Cross-sectional observations by transmission electron microscopy

Cross-sections of each of the PMPC-grafted CLPE samples were observed using transmission electron microscopy (TEM). The specimens were embedded in epoxy resin, stained with ruthenium oxide vapor at room temperature, and finally sliced into ultra-thin films (approximately 100 nm thick) using a Leica Ultra Cut UC microtome (Leica Microsystems, Wetzlar, Germany). A JEM-1010 electron microscope (JEOL, Tokyo, Japan) was used for the TEM observations at an acceleration voltage of 100 kV. The thickness of the PMPC layer was determined by averaging 10 points on each cross-sectional TEM image.

Wettability and friction tests

Static-water contact angles were measured on each of the PMPC-grafted CLPE samples by employing the 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 on the PMPC-grafted CLPE surfaces, and the contact angles were directly measured after 60 s using a microscope. Fifteen areas were evaluated for each sample, and average values were calculated.

Unidirectional friction tests were performed using a ball-on-plate machine (Tribostation 32; Shinto Scientific, Tokyo, Japan). Six samples of PMPC-grafted CLPE for each irradiation intensities were evaluated. Each specimen was either left non-sterilized or was sterilized by 25 kGy gamma-rays in N_2 gas. A 9 mm diameter pin made from Co–Cr–Mo alloy was also prepared. The surface roughness (R_a) of the pin was <0.01, which was comparable with that of currently used femoral head products. The friction test was performed for each specimen at room temperature using a load of 0.98 or 9.8 N (contact stress roughly calculated by Hertzian theory was ~29 or 62 MPa, respectively), a sliding distance of 25 mm, and a frequency of 1 Hz. A maximum of 100 cycles were carried out, and pure water was used for lubrication. The mean dynamic coefficients of friction were determined by averaging the values of five data points taken from the 96–100 cycles.

Evaluation of physical properties

The swelling ratio and cross-link density of the PMPC-grafted CLPE substrates obtained with various UV-irradiation intensities were evaluated according to previously reported methods.[28] Each of the PMPC-grafted CLPE specimens (23 × 23 × 1 mm) was divided into three sample pieces. The specimens were weighed (approximately 0.5 g, V_1), allowed to swell for 72 h in *p*-xylene containing 0.5 mass% 2-*t*-butyl-4-methylphenol at 130°C, and then reweighed (V_2). The samples were then immersed in acetone, dried at 60°C under vacuum, and weighed again (V_3). The swelling ratio was determined from the weight gain and densities of the PE and xylene, and the physical properties were calculated as follows:

(a) Swelling ratio (q):

$$q = V_2/V_3 \tag{1}$$

(b) Cross-link density:

$$v^* = In(1 - q^1) + q^1 + \chi q^2/V_1\left(q^{-2/3} - 0.5q^{-1}\right) \tag{2}$$

where v^* is the network chain density, $V_1 = 136$ mL/mol, and $\chi = 0.37$ (for PE)

$$M_c = 1/\overline{M}c = Vv* \tag{3}$$

where M_c is the molecular weight between cross-links, and $V = 1$/specimen density.

$$XLD = M_0/\overline{M}c \tag{4}$$

where XLD is the cross-link density, and $M_0 = 14$ (PE)

Mechanical tests

The mechanical properties of the PMPC-grafted CLPE substrates were evaluated using a series of tests. Tensile testing was performed according to ASTM D638 using type IV tensile bar specimens of 1.0 and 2.0 mm in thickness, and a crosshead speed of 50.8 mm/min. Each of the PMPC-grafted CLPE specimens was divided into ten sample pieces, with each evaluated individually. Shore hardness (D) was measured according to the ASTM D2240 test method, with five samples tested for each UV intensity. A double-notched (notch depth = 4.57 ± 0.08 mm) Izod impact test was performed to ASTM F648 standard, with six samples tested for each UV intensity. A small punch test was performed according to ASTM F2183, using a disk specimen of diameter 6.4 mm and thickness 0.5 mm, and a crosshead speed of 0.5 mm/min. Ten sample pieces were evaluated for each UV intensity.

Hip simulator wear test

A 12-station hip simulator (MTS Systems Corp., Eden Prairie, MN) using untreated CLPE and the PMPC-grafted CLPE liners with an inner and outer diameter of 26 and 52 mm, respectively, was used for the wear test according to ISO 14242-3. PMPC-grafted CLPE liners were obtained using UV-irradiation intensities of 1.5, 5.0, and 15 mW/cm^2 and subsequently subject to hip simulator wear test. Three samples of each of the untreated CLPE and the PMPC-grafted CLPE liners were prepared. A Co–Cr–Mo alloy ball 26 mm in diameter (K-MAX® HH-02; KYOCERA Medical Corp., Osaka, Japan) was used as the femoral head. A mixture of 25 vol % bovine serum, 20 mmol/L ethylene diamine tetraacetic acid (EDTA), and 0.1 mass % sodium azide was used as the lubricant. The lubricant was replaced every 5.0 × 10^5 cycles. Gait cycles were applied to simulate a physiological loading curve (Paul-type) with double peaks at 1793 and 2744 N, and a multidirectional (biaxial and orbital) motion of 1 Hz frequency. Gravimetric wear was determined by weighing the liners at intervals of 5.0 × 10^5 cycles. Load-soak controls ($n = 2$) were used to compensate for