When this layer is removed from the liner surface, the steady wear rate of the MPC-CLPE liner increases to almost the same (or slight lower) level as that of the untreated CLPE liner (Kyomoto et al., 2011; Moro et al., 2006, 2010). In the present study, MPC-CLPE liners showed weight gains and a significantly lower wear rate during the 15×10^6 cycles. This finding confirmed that the poly(MPC) layer was maintained even after the test.

In the present study, we showed that poly(MPC) grafting onto the CLPE liner surface decreased the production of wear particles by 99% during 15×10^6 cycles of loading in the hip wear simulator. Moreover, poly(MPC) grafting did not affect the size of the wear particles and their distribution. With regard to the relationship between the number of PE particles in the synovial tissue and periprosthetic osteolysis, the critical number was reported to be around 1.0×10^{10} particles/g tissue (Kadoya et al., 1998). Thus, a marked decrease in the number of particles presumably reduces the incidence of osteolysis. Recently, the size of wear products in relation to the complications arising from metal-on-metal articulation has been the topic of concern (Hosman et al., 2010). In this regard, our results suggest that the influences of the wear products of poly(MPC)-grafted liners are similar to those of the CLPE liners.

There are three limitations of this study, with the first being underestimation in the load-soak test (ISO 14242-2) for determining the cause of weight gain in the liner. When using the gravimetric method, the weight loss in the tested liners is corrected for by subtracting the weight gain in the load-soak controls; however, this correction cannot be precisely achieved because only the tested liners are continuously subjected to load and motion. Fluid absorption in the tested liners is generally slightly higher than that in the load-soak controls. Consequently, the correction for fluid absorption through the use of the load-soak control as the correction factor leads to a slight underestimation of the actual weight loss. This underestimation has previously been reported, particularly in several reports on wear-resistant articulating surfaces (Dumbleton et al., 2006; Muratoglu et al., 2001; Oral et al., 2006; Shen et al., 2011). Because of this underestimation, wear could not be quantified by gravimetric analysis; however, weight change in the MPC-CLPE liners suggests the considerable wear-resistance of them. In the present study, we also analyzed the surface of the liner and the amount of wear particles generated from the liner, as well as confirmed that wear resistance of the acetabular liners was considerably improved by poly(MPC) grafting.

The second limitation of this study is the difference between the in vitro study and clinical settings. This difference was a matter of concern in the case of Hylamer (Graeter and Nevins, 1998; Huddleston et al., 2010). We do, however, believe that this issue is relatively insignificant as compared to that with regard to other materials, because poly(MPC)-grafted particles are biologically inert and do not cause the subsequent bone resorptive responses (Moro et al., 2004). Moreover, to the best of our knowledge, there are no reports on the complications of medical devices using MPC polymers.

The third limitation is that we used only Co–Cr alloy heads with a diameter of 26 mm. In clinical settings, there seems to be a tendency to choose large heads and thin acetabular liners in order to reduce the incidence of dislocation. We believe that this drawback is partially offset by the long duration of simulation. At present, we are conducting additional studies using large heads and thin acetabular liners.

In summary, this study shows that poly(MPC) grafting markedly reduces the production of wear particles from CLPE liners, without affecting the size of the particles. These results suggest that poly(MPC) grafting is a promising technique for increasing the longevity of artificial hip joints.

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SYMPOSIUM: ADVANCES IN UHMWPE BIOMATERIALS

Multidirectional Wear and Impact-to-wear Tests of Phospholipid-polymer-grafted and Vitamin E-blended Crosslinked Polyethylene: A Pilot Study

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Abstract

Background Modifying the surface and substrate of a crosslinked polyethylene (CLPE) liner may be beneficial for high wear resistance as well as high oxidative stability and excellent mechanical properties, which would be useful in contributing to the long-term performance of orthopaedic bearings. A grafted poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) layer on a vitamin E-blended crosslinked PE (HD-CLPE[VE]) surface may provide hydrophilicity and lubricity without compromising the oxidative stability or mechanical properties.

Questions/purposes (1) Will the modifications (PMPC grafting and vitamin E blending) affect the lubrication characteristics of the CLPE surface? (2) Will the modifications affect wear resistance? (3) Will the modifications affect fatigue resistance?

Methods We investigated the effects of surface and substrate modifications (PMPC grafting and vitamin E blending) on the wear and fatigue fracture of thin CLPE samples. For each of the untreated and PMPC-grafted CLPE surfaces with and without vitamin E blended (four groups), wettability and lubricity surface analyses were conducted as well as multidirectional wear and impact-to-wear tests using a pin-on-disk testing machine.

Results The water wettability and lubricity (CLPE [mean ± 95% confidence interval]: 23.2° ± 1.8°, 0.005 ± 0.001; HD-CLPE[VE]: 26.0° ± 2.3°, 0.009 ± 0.003) of the PMPC-grafted surfaces were greater ($p < 0.001$) than that (CLPE: 90.3° ± 1.2°, 0.067 ± 0.015; HD-CLPE[VE]: 90.8° ± 2.0°, 0.063 ± 0.008) of the untreated surface regardless of vitamin E additives. It was observed that the PMPC grafting (CLPE: 0.23 ± 0.06 mg; HD-CLPE[VE]: 0.05 ± 0.10 mg) was associated with reduced gravimetric wear (CLPE: 0.53 ± 0.08 mg, $p = 0.004$ HD-CLPE[VE]: 0.23 ± 0.07 mg, $p = 0.038$) in the multidirectional wear test. The PMPC-grafted surface characteristics did not appear to affect the impact fatigue resistance regardless of vitamin E blending.

Conclusions PMPC grafting improved the surface hydrophilicity and lubricity, and it reduced the gravimetric wear in terms of multidirectional sliding. It did not result in differences in terms of the impact-to-unidirectional sliding regardless of vitamin E blending. Further research is needed to evaluate the wear resistance of PMPC-grafted HD-CLPE(VE) in long-term hip simulator tests under normal

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and severe conditions, which may offer useful clues to the possible performance of these materials in vivo.

Clinical Relevance Our preliminary in vitro findings suggest that some improvement in the wear performance of crosslinked polyethylene acetabular liners in total hip arthroplasty could be obtained using PMPC grafting. Further research is needed to evaluate the wear resistance of PMPC-grafted HD-CLPE(VE) in long-term hip simulator tests under normal and severe conditions, which may offer useful clues to the possible performance of these materials in vivo.

Introduction

Wear and oxidative degradation are two important indicators of the clinical performance of polyethylene (PE) acetabular liners. PE wear particles from the acetabular liner are responsible for osteolysis, which may lead to aseptic loosening [10]. Many different strategies or techniques have been introduced to reduce the number of PE wear particles and extend the longevity of THA [5, 16, 25, 26, 29, 34].

To reduce wear and thus suppress bone loss, we recently developed a new articular cartilage-inspired technology for surface modification with synthetic phospholipid polymer grafting using poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) for PE acetabular liners in THAs [18–24, 29, 30, 35, 36]. Modification of the bearing surfaces of an artificial joint with a hydrophilic layer should increase lubrication to levels comparable to that provided by articular cartilage under physiological conditions [17, 20, 21, 23]. 2-Methacryloyloxyethyl phosphorylcholine (MPC) polymers are one of the most common biocompatible and hydrophilic polymers that have been clinically applied [13, 35, 36]. It has been demonstrated that a nanometer-scale layer of PMPC can be formed on a crosslinked PE (CLPE) surface to better reproduce the ideal hydrophilicity and lubricity of the physiological joint surface [18, 20–24].

However, wear is only one of several important indicators of the clinical performance of acetabular liners. Oxidative degradation of some of the first generation of CLPE formulations has been considered a potential limiting factor for the long-term performance of THA [7, 28]. During gamma irradiation (for crosslinking or for sterilization), free radicals formed in the PE molecular structure cause embrittlement through a cascading oxidation reaction [7]. Hence, the incorporation of the antioxidant vitamin E (α-tocopherol) has been proposed to prevent oxidation and has been introduced into clinical use [5, 15, 34]. Vitamin E is a free radical scavenger and is well established as a biological antioxidant.

Moreover, dislocation has been reported to be a major reason for revision in THA [4]. In artificial hips, dislocation is almost always caused by the impingement of the femoral stem neck on the acetabular liner. The impaction between the femoral stem neck and the acetabular cup can be potentially avoided by using a large-diameter femoral head to treat the condition [33]. However, a large-diameter femoral head must be used in conjunction with a thin PE liner owing to the limited volume along the acetabulum, and a thin PE liner poses a risk in terms of wear and fatigue fracture when subjected to severe physiological conditions.

We investigated the effects of surface and substrate modifications (PMPC grafting and vitamin E blending) on the wear and fatigue fracture of thin CLPE samples by conducting a multidirectional wear test and an impact-to-wear test in this pilot study. We sought answers to three questions: (1) Will the modifications (ie, PMPC grafting and vitamin E blending) affect the lubrication characteristics of the CLPE surface? (2) Will the modifications affect wear resistance? (3) Will the modifications affect impact fatigue resistance?

Materials and Methods

Four treatment groups were considered: untreated and PMPC-grafted CLPE with and without vitamin E blending. For each treatment group, 27 sample pieces were prepared for surface lubrication analysis and 12 disks were prepared for specific durability analysis (Fig. 1). To answer the first question regarding the dependent variables of hydration kinetics and stability of the grafted PMPC layer, the hydrophilicity and lubricity of the PMPC layers on the substrates with and without vitamin E were evaluated using the contact angle of a water drop and a ball-on-plate friction test. The dependent variable in our second research question (the wear resistance of the PMPC-grafted substrates with and without vitamin E) was examined using a pin-on-disk (POD) testing machine under a multidirectional sliding condition. Finally, to answer our third question, the fatigue resistance of the PMPC-grafted substrates with and without vitamin E was examined using a POD testing machine under an impact-to-unidirectional sliding condition.

A compression-molded bar stock of 0.1 mass% vitamin E-blended PE (PE[VE]; GUR1020E resin; Orthoplastics Ltd, Lancashire, UK) was gamma-irradiated with a high dose (HD; 100 kGy) in a N_2 gas atmosphere and annealed at 120 °C for 12 hours in N_2 gas to facilitate crosslinking. Hereafter, this PE material is referred to as HD-CLPE(VE). As the control, a compression-molded bar stock of PE without any additives (GUR1020 resin; Orthoplastics Ltd) was gamma-irradiated with a 50-kGy dose in a N_2 gas atmosphere. It was then annealed at 120 °C for 7.5 hours in

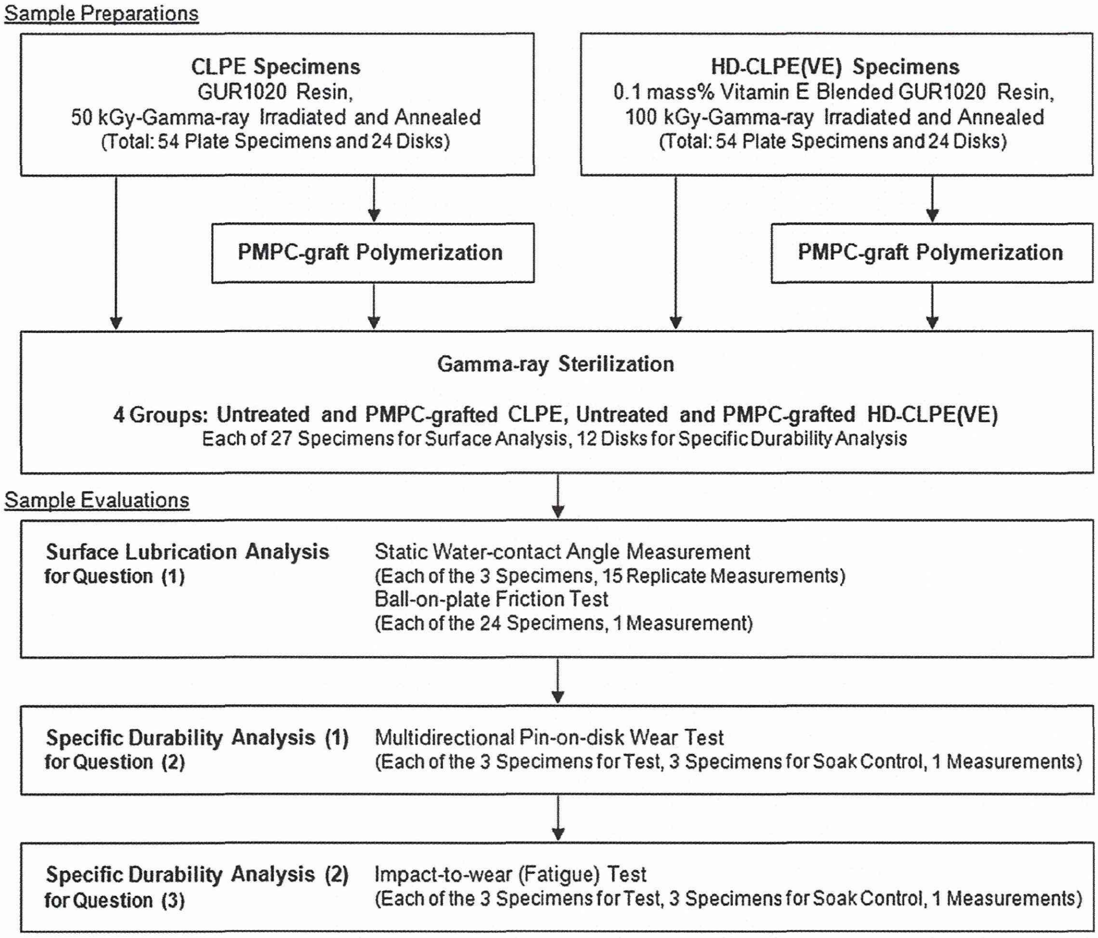

Fig. 1 The flow chart provides an overview of the study.

N_2 gas to facilitate crosslinking. Hereafter, this PE material is referred to as CLPE. Samples of CLPE and HD-CLPE(VE) were machined from the bar stocks and then washed. Surface cleanliness without fouling that involved an antioxidant (radical scavenger) was critical for the polymerization. In particular, the vitamin E surface was fully washed with an aqueous polysorbate-surfactant solution and ethanol to remove vitamin E from the surface. PMPC grafting of the surfaces of the CLPE and HD-CLPE(VE) was performed using a photoinduced polymerization technique as previously reported [17–22, 25, 28, 29]. Photoinduced graft polymerization was carried out on the CLPE and HD-CLPE(VE) surfaces using ultraviolet irradiation with an intensity of 5 mW/cm^2 at 60 °C for 90 minutes and an aqueous 0.5 M MPC (NOF Corp, Tokyo, Japan) solution. The resulting samples were then gamma-radiation-sterilized at 25 kGy under a N_2 gas atmosphere.

The static contact angles of water on PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) were measured with an optical bench-type contact angle goniometer (Model DM300; Kyowa Interface Science Co, Ltd, Saitama, Japan) using the sessile-drop (1 μL) method according to ISO 15989 [11]. Subsequently, 15 measurements were repeated on each of the three samples, and the mean values ± SD were calculated.

The friction test was performed using a ball-on-plate machine (Tribostation 32; Shinto Scientific Co, Ltd, Tokyo, Japan). Six samples of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) were evaluated. A cobalt-chromium-molybdenum (Co-Cr-Mo) alloy ball with a diameter of 9 mm was prepared. The surface roughness (R_a) of the ball was < 0.01 μm, which is comparable to that of femoral head products. The friction test was performed at 37 °C with a load of 0.49 to 9.8 N (the contact pressure roughly calculated using Hertzian theory is approximately 22–62 MPa), sliding distance of 25 mm, frequency of 1 Hz for a maximum of 100 cycles, and pure water as the lubricant. The mean coefficients of dynamic friction were determined by averaging five data points from the 96 to 100 cycle measurements.

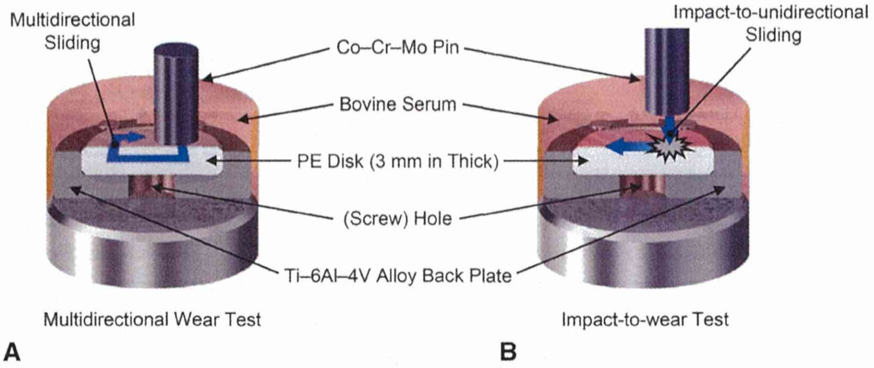

Fig. 2A–B The schematic illustrates the pin-on-disk wear test: (**A**) multidirectional wear test; (**B**) impact-to-wear test.

Multidirectional wear and impact-to-wear tests were conducted using a POD testing machine (Ortho POD; AMTI, Watertown, MA, USA). PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks were used for the wear tests and control soak tests to correct the water absorption increments ($n = 3$). The disks were attached to the POD testing machine with a Ti-6Al-4V alloy fixation component that had an 8-mm-diameter hole to simulate an acetabular shell with a screw hole (Fig. 2). The Co-Cr-Mo alloy pins had a 30-mm surface curvature radius and surface roughness of $R_a < 0.01$. A mixture of 27 vol% fetal bovine serum (Biowest, Nuaillé, France), 20 mM ethylene diamine-N, N, N′, N′-tetraacetic acid, and 0.1 mass% sodium azide was used at 37 °C as the lubricant. The multidirectional wear test was conducted on a rectangular sliding surface. The test conditions were specified to be a static load of 213 N, sliding distance of 30 mm, and frequency of 1 Hz for a maximum of 1.0×10^6 cycles. Impact-to-wear testing was performed on a unidirectional sliding surface with a maximum impact load of 150 N, sliding distance of 10 mm, and frequency of 1 Hz for a maximum of 2.0×10^6 cycles. These sliding conditions were implemented according to ASTM F732 [2]. Gravimetric wear was determined by weighing the disks. Soak controls were used to compensate for fluid absorption by the specimens. Because the gravimetric method was used, the weight loss of each of the tested disks was corrected by subtracting the weight gain resulting from the soak control. After the multidirectional wear and impact-to-wear tests, the volumetric wear of the disks was evaluated using a noncontact optical three-dimensional profiler (Talysurf CCI Lite; Taylor Hobson Ltd, Leicester, UK).

The mean values of the three comparative groups (untreated CLPE versus PMPC-grafted CLPE, untreated HD-CLPE[VE] versus PMPC-grafted HD-CLPE[VE], and PMPC-grafted CLPE versus PMPC-grafted HD-CLPE[VE]) were evaluated using a Student's t-test (statistical significance, $p < 0.05$). The mean values of the coefficient of dynamic friction obtained for each treatment group under four loadings (0.49, 0.98, 4.9, and 9.8 N) in the friction test were compared by one-factor analysis of variance (ANOVA), and the significance of differences was determined by post hoc testing using Bonferroni's method ($p < 0.05$). All statistical analyses were performed using an add-on (Statcel 2; OMS Publishing Inc, Tokorozawa, Japan) to Microsoft Excel® 2003 (Microsoft Corp, Redmond, WA, USA).

Results

The PMPC grafting improved the hydration and friction kinetics of the surfaces, regardless of vitamin E blending. The static water contact angles on the PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) surfaces as well as the coefficients of dynamic friction between water and the surfaces changed as a result of the modification (Fig. 3). The static water contact angles on untreated CLPE and HD-CLPE(VE) were 90.3° (SD = ± 2.3, 95% confidence interval [CI], ± 1.2) and 90.8° (SD = ±3.9, 95% CI, ± 2.0), and they decreased markedly to 23.2° (SD = ± 3.5, 95% CI, ± 1.8, $p < 0.001$) and 26.0° (SD = ± 4.5, 95% CI, ± 2.3, $p < 0.001$), respectively, after PMPC grafting (Fig. 3A). The coefficients of dynamic friction of PMPC-grafted CLPE (mean = 0.005, SD = ± 0.001, 95% CI, ± 0.001) and PMPC-grafted HD-CLPE(VE) (mean = 0.009, SD = ± 0.003, 95% CI, ± 0.002) also decreased markedly with the surfaces exhibiting an approximately 85% to 90% reduction ($p < 0.001$ and $p < 0.001$, respectively) in the coefficient compared with the untreated CLPE (mean = 0.067, SD = ± 0.015, 95% CI, ± 0.008) and untreated HD-CLPE(VE) (mean = 0.063, SD = ± 0.008, 95% CI, ± 0.007) surfaces under 9.8-N loadings (Fig. 3B). Interestingly, the coefficient of dynamic friction of both PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) decreased gradually with an increase in loading.

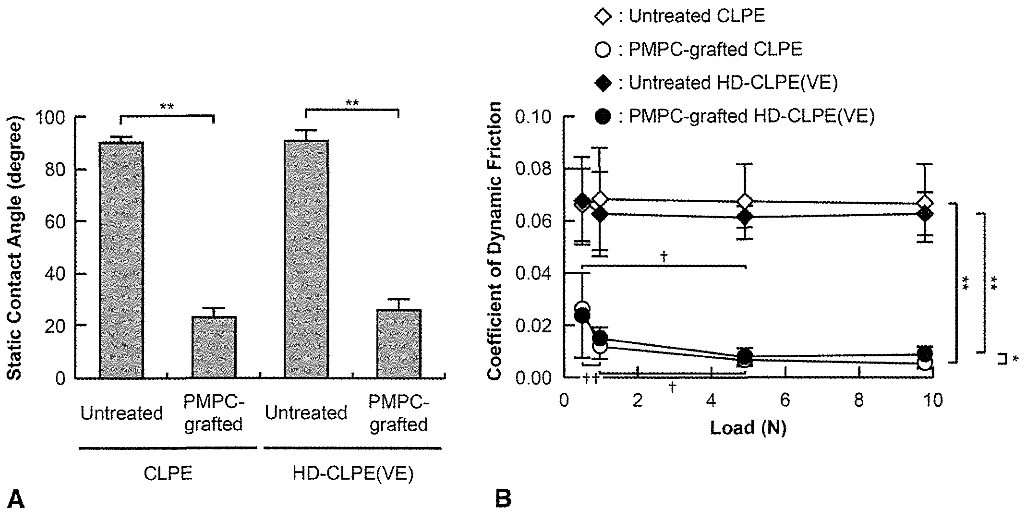

Fig. 3A–B The plots show the results of surface functional analysis of PMPC-grafted CLPE and high-dose CLPE with vitamin E blending (HD-CLPE[VE]). (**A**) The static water contact angles (n = 15) on untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) are shown. The data are expressed as mean values ± SD. As the PMPC grafting proceeded, the CLPE or HD-CLPE(VE) surface became much more wettable, ie, the surface changed from hydrophobic to hydrophilic. The type of material had no discernible effect on the wettability (p = 0.070). (**B**) The coefficient of dynamic friction (n = 6) for untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) is shown. The data are expressed as mean values ± SD. The significance of the results is denoted by: $^{*}p < 0.05$ and $^{**}p < 0.01$ for the t-test; $^{\dagger}p < 0.05$, $^{\dagger\dagger}p < 0.01$ for the one-factor ANOVA and post hoc test. The coefficient of dynamic friction had a tendency to decrease with an increase in the load for the PMPC-grafted materials.

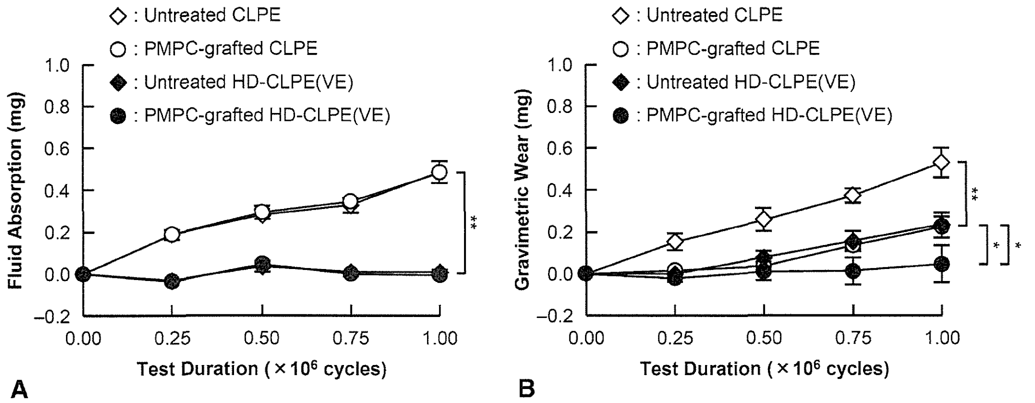

Fig. 4A–B The plots show the time course of (**A**) fluid absorption (n = 3) and (**B**) gravimetric wear (n = 3) of untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) disks during the multidirectional POD wear test. The data are expressed as mean values ± SD. The significance of the results is denoted by: $^{*}p < 0.05$ and $^{**}p < 0.01$. Significant differences (p < 0.001 and p = 0.038 for [**A**] and [**B**], 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.

In the multidirectional wear test, the PMPC-grafted surface characteristics improved wear resistance regardless of vitamin E blending. In the absence of PMPC grafting, fluid (eg, water, proteins, and lipids) absorption in the CLPE soak control disks (untreated: mean = 0.49 mg, SD = ± 0.05, 95% CI, ± 0.06; PMPC grafted: mean = 0.48 mg, SD = ± 0.03, 95% CI, ± 0.03), determined by the weight gain, increased in a cycle-dependent manner (Fig. 4A). In contrast, the fluid absorption in both the untreated and PMPC-grafted HD-CLPE(VE) soak control disks was constant for all test durations (untreated: mean = 0.01 mg, SD = ± 0.01, 95% CI, ± 0.01; PMPC grafted: mean = −0.01 mg, SD = ± 0.01, 95% CI, ± 0.01). During the wear test, the PMPC grafting (CLPE: mean = 0.23 mg, SD = ± 0.05, 95% CI, ± 0.06; HD-CLPE[VE]: mean = 0.05 mg, SD = ± 0.09, 95% CI, ± 0.10) decreased gravimetric wear not only in the CLPE disks (mean = 0.53 mg, SD = ± 0.07, 95% CI, ± 0.08,

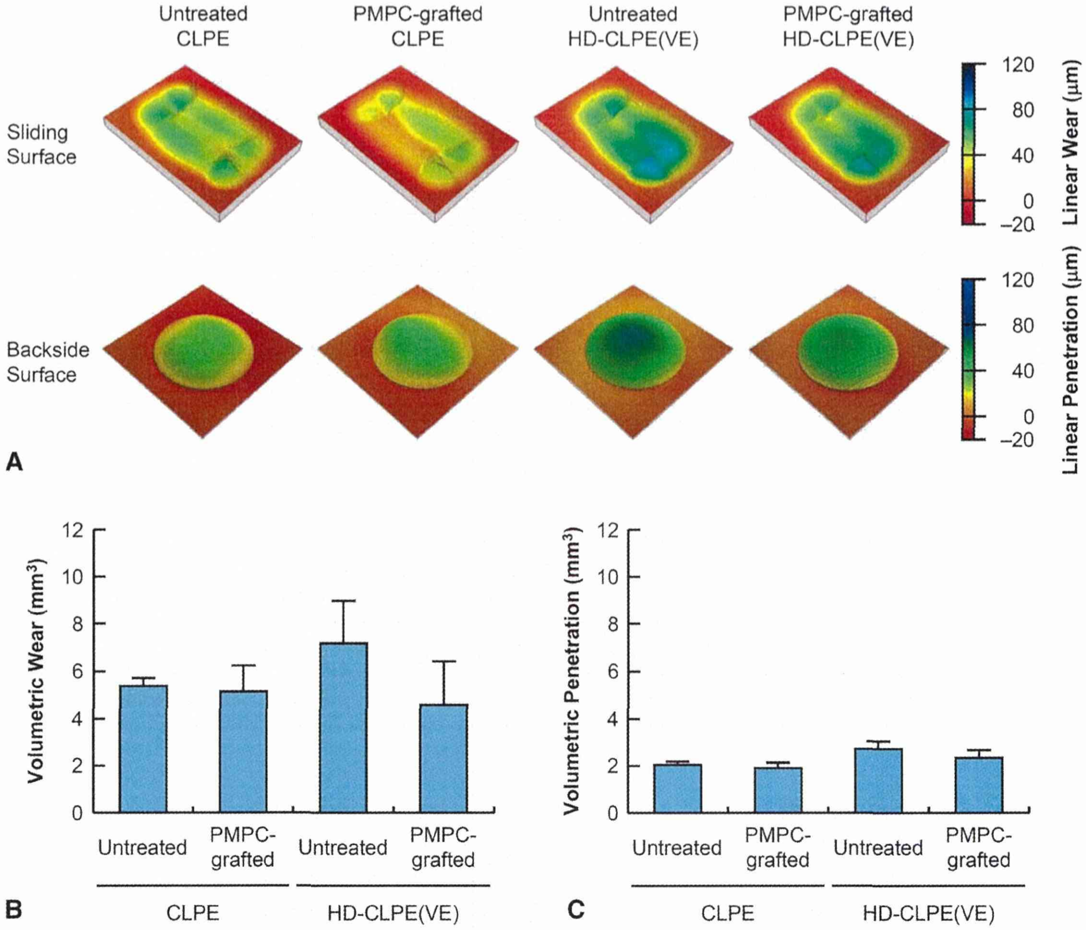

Fig. 5A–C The images and plots summarize the results of volumetric wear analysis of untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) disks after the multidirectional wear test. (**A**) The color maps correspond to three-dimensional profiles of the sliding and backside surfaces of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. The plots show the (**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 were no significant differences in the comparison of volumetric wear or penetration of the three comparative groups (untreated CLPE versus PMPC-grafted CLPE: $p = 0.750$ and $p = 0.523$, respectively; untreated HD-CLPE[VE] versus PMPC-grafted HD-CLPE[VE]: $p = 0.153$ and $p = 0.212$, respectively; PMPC-grafted CLPE versus PMPC-grafted HD-CLPE[VE]: $p = 0.670$ and $p = 0.125$, respectively).

$p = 0.004$), but a similar reduction was also observed in the HD-CLPE(VE) disks (mean = 0.23 mg, SD = ± 0.06, 95% CI, ± 0.07, $p = 0.038$) (Fig. 4B). Three-dimensional profile measurements of sliding surfaces on all disks revealed substantial volumetric wear (Fig. 5A). Penetration and circular scratches that were caused by the edge of the hole were clearly observed on the backside surface of all disks. The type of material had no discernible effect on the backside penetration.

In the impact-to-wear test, the PMPC-grafted surface characteristics did not appear to affect the impact fatigue resistance regardless of vitamin E blending. Also, during the impact-to-wear test, all groups showed an increase in weight. This is partially attributable to greater fluid absorption in the tested disks than in soak controls (Fig. 6). The volumetric wear or penetration of sliding or backside surfaces did not differ among any of the groups examined in this study (Fig. 7). Even after impact loads of 2.0×10^6 cycles, we did not observe either mechanical fracture or delamination in the sliding or backside surfaces of all groups. The type of material had no discernible effect on the impact fatigue resistance, and no differences were observed among the available data.

Discussion

Periprosthetic osteolysis has been recognized as a notable complication affecting the long-term survival of the artificial hip, and wear particles from PE acetabular liners have

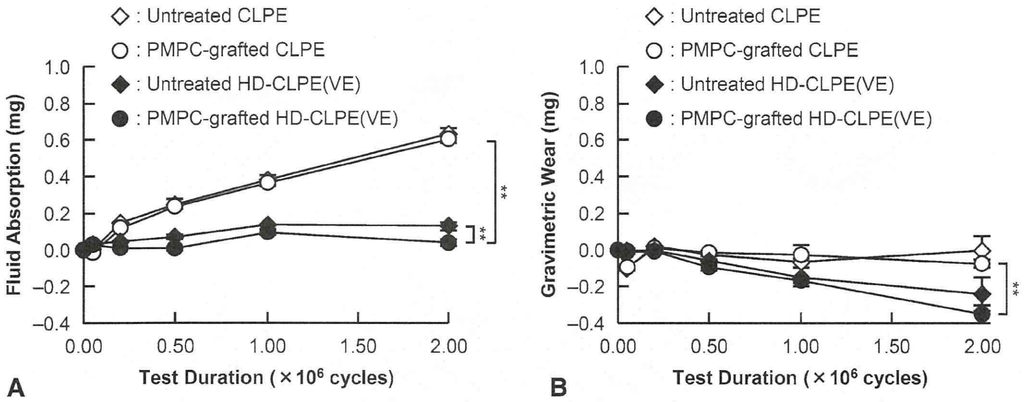

Fig. 6A–B The plots show the time course of (**A**) fluid absorption ($n = 3$) and (**B**) gravimetric wear ($n = 3$) of untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) disks during the POD impact-to-wear test. The data are expressed as mean values ± SD. The significance is denoted by $^{**}p < 0.01$. Significant differences ($p < 0.001$ and $p < 0.001$ for [**A**] and [**B**], 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.

been shown to be responsible for osteolysis. As a result, efforts to improve the lubrication of bearing materials have focused on reducing the number of PE wear particles. The fluid film lubrication provided by the hydrated layer is essential in natural synovial joints, and a phospholipid layer that covers the joint cartilage surface provides hydrophilicity and works as an effective boundary lubricant [9, 14]. Therefore, grafting a phospholipid-like layer onto the surface may realize comparable hydrophilicity and lubricity resembling that of the physiological joint surface. In this study, we asked three questions: (1) Will the modifications (ie, PMPC grafting and vitamin E blending) affect the lubrication characteristics of CLPE surface? (2) Will the modifications affect wear resistance? (3) Will the modifications affect impact fatigue resistance? So far, the experimental results provide preliminary evidence that PMPC grafting positively affects the surface hydrophilicity, lubricity, and wear resistance of the liner regardless of vitamin E blending. In contrast, PMPC grafting or vitamin E blending did not affect impact fatigue resistance, but the resulting modification was essentially equal to untreated CLPE without additives. This suggests the approach may be promising for improving the longevity of THA by using PMPC grafting or even vitamin E-blended CLPE.

Our study was subject to a number of limitations. First, we only tested up to 1.0×10^6 cycles in the multidirectional wear and 2.0×10^6 cycles in the impact-to-wear tests with a POD testing machine for preliminary examination. The tests that we conducted may not have provided a sufficient range of loading and motion conditions relevant to physical walking or during daily routines, although we believe the multidirectional wear and impact-to-wear tests provided some indication of wear and impact fatigue performance [3]. In current tests, we are now running a hip simulator for longer periods using the PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) liners. Thus far, we have confirmed that there was almost no wear on the PMPC-grafted liners after 1×10^7 cycles [27]. Second, the fluid absorption correction using the gravimetric method had shortcomings because only the tested disks were continuously moved and subjected to the load. Fluid absorption in the tested disks was generally slightly higher than that in the soak controls. Consequently, the correction for fluid absorption using the soak data as the correction factor led to a slight underestimation of the actual weight loss. Third, the material properties of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) reported here are only valid for these specific levels of wear and fatigue resistance.

The wettability of the PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) surfaces were imparted by the presence of a PMPC graft layer resulting from the polymerization of the highly hydrophilic MPC monomer. The PMPC hydrated layer clearly affected the friction response; the coefficients of dynamic friction of the PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) surfaces were much lower than those of the untreated CLPE surface. This is attributed to the large increase in hydrophilicity that was evident from the reduction in the static water contact angles of the PMPC-grafted surfaces [20]. Additionally, the improvement in the coefficients of dynamic friction of both PMPC-grafted surfaces with an increase in loading has revealed some very interesting observations—the PMPC grafted layer could not follow Amonton's first law ($F = \mu N$, where F is the frictional force, μ is the friction coefficient, and N is the normal force), which states that the frictional force is proportional to the normal force of two dry solid surfaces sliding against one another; ie, a variable frictional coefficient of both PMPC-grafted surfaces indicates that the bearing surface or interface does not provide

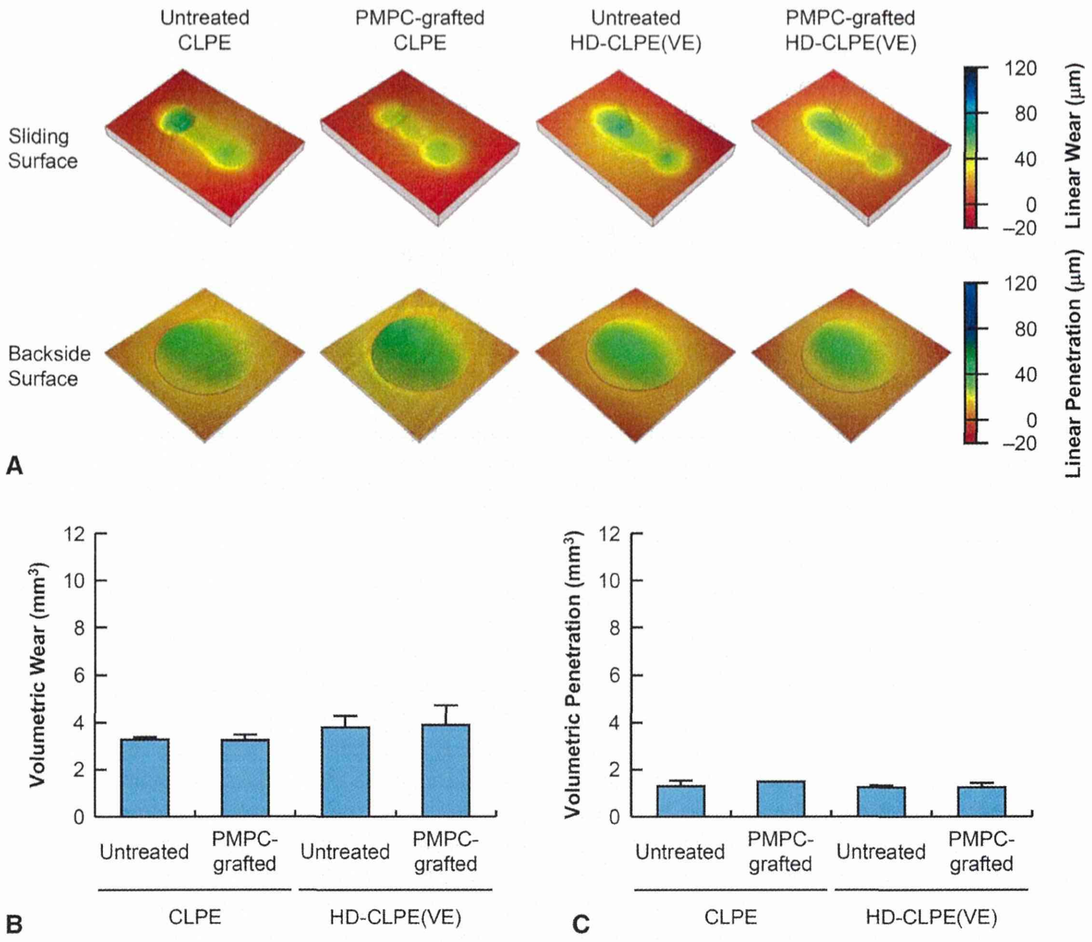

Fig. 7A–C The images and plots summarize the results of volumetric wear analysis of untreated and PMPC-grafted CLPE and untreated and PMPC-grafted HD-CLPE(VE) disks after the impact-to-wear test. (**A**) The color maps correspond to three-dimensional profiles in the sliding and backside surfaces of PMPC-grafted CLPE and PMPC-grafted HD-CLPE(VE) disks. The plots show the (**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 were no significant differences in the comparison of volumetric wear or penetration of the three comparative groups (untreated CLPE versus PMPC-grafted CLPE: $p = 0.803$ and $p = 0.268$, respectively; untreated HD-CLPE[VE] versus PMPC-grafted HD-CLPE[VE]: $p = 0.923$ and $p = 0.986$, respectively; and PMPC-grafted CLPE versus PMPC-grafted HD-CLPE(VE): $p = 0.277$ and $p = 0.092$, respectively).

solid lubrication [8]. Because the viscoelastic CLPE and HD-CLPE(VE) substrates were slightly deformed by the loads, the low frictional coefficient may have been necessary to amass a larger volume of water in the thin film over the larger contact area of the concave surface [21]. We also think that these results imply that the lubrication of the PMPC-grafted surfaces was dominated by the hydration lubrication mechanism [12].

In the multidirectional wear tests, the PMPC-grafted surfaces exhibited high wear resistance regardless of vitamin E blending. We believe that hydration lubrication of the PMPC-grafted surface was provided by the hydrated layer and that it was essential for high wear resistance. Moreover, the PMPC-grafted HD-CLPE(VE) exhibited a higher wear resistance (the gravimetric wear rate was 0.05 mg/10^6 cycles) compared with the PMPC-grafted CLPE (0.22 mg/10^6 cycles) despite similar surface hydrophilicity and lubricity. These values are comparable to the wear rate of 0.9 to 1.7 mg/10^6 cycles that Baykal et al. [3] reviewed for HD-CLPE(VE) (with gamma-ray irradiation doses of 65–150 kGy). In addition, Okubo et al. [31] suggested that a load-dependent frictional improvement of vitamin E-blended PE would be limited to the initial friction only. It has been known that the presence of vitamin E in the PE substrate reduces the crosslinking efficiency because of the establishment of competition between vitamin E and the alkyl or allyl radicals in the reaction with the radicals produced by gamma-ray irradiation [32].