Hence, we theorize that the higher wear resistance of the PMPC-grafted HD-CLPE(VE) was caused by the more effective crosslinking with a gamma-ray irradiation dose of 100 kGy compared with the 50-kGy gamma-ray irradiation for the CLPE [32]. Backside damage such as volumetric penetration and circular scratching was observed clearly on the disk surface without PMPC grafting owing to the multidirectional wear and impact-to-wear tests. Using finite element analysis, Chang et al. [6] reported that the internal stress and plastic flow of PE increases with decreasing PE thickness. We speculate that high internal stress occurred in the thin PE disks and that plastic flow was caused by the backside surface rubbing against the edge of the hole in the fixation component. Based on these results, we conclude that backside damage was affected mainly by the PE thickness. Thus, backside damage still needs to be considered even in a PMPC-grafted acetabular liner.

Cyclic impact loading such as heel strike and toe-off as a person walks are motion conditions that can be expected for acetabular liners, particularly in active patients. Unfortunately, the hydrated PMPC layer in our study was not effective despite vitamin E blending, and it could not support the cyclic impact loadings owing to a lack of thickness (approximately 100 nm) of the grafted PMPC layer. As a result, the cyclic impact loadings were supported by the CLPE or HD-CLPE(VE) substrate. The retention of the bulk properties of the substrates is important because the CLPE or HD-CLPE(VE) used as acetabular liners act not only as surface-functional materials, but also as structural materials in vivo. The advantage of PMPC grafting was that the grafted PMPC layer produces high lubricity while only affecting the surface, and it has no effect on the properties of the substrate [18, 27]. Recently, a review of voluntary reports of fractured CLPE liners showed that liners thinner than 7 mm at weight-bearing or liners that are 4.8 mm thick at the rim should be used with caution [1]. Our group focused on the effect of thin PE disks on wear and impact fatigue. In this study, we did not observe either mechanical fracture or delamination in the sliding or backside surfaces of all groups. Therefore, these POD tests thus far suggest that the CLPE and HD-CLPE(VE) substrates may have sufficiently strong mechanical properties and cyclic impact fatigue resistance.

Further research is needed to evaluate the wear resistance of PMPC-grafted HD-CLPE(VE) in long-term hip simulator tests under normal [27] and severe conditions, which may offer useful clues to the possible performance of these materials in vivo. However, in vitro findings do not always translate to clinical success. We conducted clinical trials (80 patients) of PMPC-grafted CLPE liners at multiple medical centers between 2007 and 2009 in Japan [35, 36]. We observed neither osteolysis nor a need for revision surgery during followup periods of up to 7 years for the clinical trials. Further followup is also needed to determine whether PMPC-grafted CLPE liners improve long-term clinical outcomes.

Acknowledgments We thank Dr Fumiaki Miyaji, Mr Kenichi Watanabe, Mr Kenichi Saiga, and Ms Shihori Yamane (KYOCERA Medical Corporation) for their technical assistance.

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Japan College of Rheumatology
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http://informahealthcare.com/mor
ISSN 1439-7595 (print), 1439-7609 (online)

Mod Rheumatol, 2015; 25(2): 286–291

DOI: 10.3109/14397595.2014.941438

informa healthcare

ORIGINAL ARTICLE

Clinical and radiographic outcomes of total hip replacement with poly(2-methacryloyloxyethyl phosphorylcholine)-grafted highly cross-linked polyethylene liners: Three-year results of a prospective consecutive series

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Abstract

Objectives. This study aimed to evaluate the clinical safety and wear-resistance of the novel highly cross-linked polyethylene (HXLPE) acetabular liner with surface grafting of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) at 3 years after total hip replacement (THR).
Methods. Eighty consecutive patients underwent cementless THR using a 26-mm diameter cobalt–chromium–molybdenum alloy femoral head and a PMPC-grafted HXLPE liner for the bearing couplings. We evaluated the clinical and radiographic outcomes of 76 patients at 3 years after the index surgery.
Results. The clinical results at 3 years were equivalent to a Harris hip score of 95.6 points. No adverse events were associated with the implanted PMPC-grafted HXLPE liner, and no periprosthetic osteolysis was detected. The mean femoral head penetration rate was 0.002 mm/year, representing marked reduction compared with other HXLPE liners.
Conclusions. A PMPC-grafted HXLPE liner is a safe option in THR and probably reduces the generation of wear particles.

Keywords

Arthroplasty, Hip prosthesis, Joint replacement, Polyethylene (UHMWPE), Wear

History

Received 26 March 2014
Accepted 18 June 2014
Published online 12 August 2014

Introduction

Total hip replacement (THR) is an established treatment modality for patients with end-stage hip disorders such as osteoarthritis and rheumatoid arthritis. However, periprosthetic osteolysis has been recognized as a notable complication affecting the long-term survival of THR; extensive research has shown that wear particles from the polyethylene (PE) liners are responsible for osteolysis [1]. Hence, many approaches have been adopted for reducing the generation of wear particles thereby improving the survival of THR.

Recent observations of the healthy mammalian articular cartilage surface have disclosed that it is covered with a nanometer-scaled phospholipid layer that protects the articulating surface from mechanical wear and facilitates a smooth motion of joints during daily activities [2,3]. Hence, grafting a polymer with a phospholipid-like layer on the liner surface may mimic the surface conditions of healthy articular cartilage. Based on this hypothesis, we have successfully produced a biocompatible and highly hydrophilic surface via nanometer-scaled grafting of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) onto highly cross-linked polyethylene (HXLPE) [4]. Our hip simulator studies revealed that such grafting remarkably reduced the wear of an HXLPE liner up to 20×10^6 cycles [5–7]. We reported that PMPC-grafted surfaces captured water molecules and reduced the friction between the bearing surfaces via the hydration lubrication mechanism [8]. In addition, we reported that the PMPC-grafted particles were biologically inert and did not cause subsequent bone-resorptive responses [4], indicating that this technology prevents wear particle production and biological reactions to such particles in THR. Since then, PMPC-grafted HXLPE liners have been used in hip replacement surgery to address the concerns of wear and osteolysis.

From the perspective of material engineering, the PMPC-grafted HXLPE liner is a new medical implant prepared from MPC polymer, which has been used on the surface of artificial lungs [9], intravascular stents [10], soft contact lenses [11], and the artificial hearts [12]. Such implants were introduced into clinical practice from 1997, and since then, no adverse reactions to MPC polymer have been reported. The major difference between other devices and the PMPC-grafted HXLPE liner is the method used for its MPC polymer coating, the photo-induced graft polymerization, which is considered appropriate for withstanding weight [4].

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The purpose of this follow-up for a prospective cohort study, in which 80 primary cementless THRs were performed using a PMPC-grafted HXLPE liner [13], was to report the clinical and radiographic outcomes, including femoral head penetration, at 3 years after the index surgery. The outline of this study was disclosed as UMIN000003681.

Methods

Between April 2007 and September 2008, 80 consecutive patients who underwent THR for a Charnley Class A or Class B painful, non-infectious hip disorder were recruited from five participating hospitals [14]. The institutional review board of each participating hospital granted ethical approval, and informed consent was obtained from all participants before the study commenced.

All patients received the K-MAX cementless THR (KYOCERA Medical Corporation, Osaka, Japan) consisting of a collarless femoral stem (K-MAX HS-6) and a low-profile porous-coated acetabular component with four peripheral fins (K-MAX Q5LP). For the bearing coupling, a 26-mm-diameter cobalt–chromium–molybdenum (Co–Cr–Mo) alloy femoral head and a PMPC-grafted HXLPE liner were employed. PMPC grafting of the surfaces of the HXLPE liner was performed using a photoinduced polymerization technique as previously reported [4].

The surgeries were performed by 10 surgeons of 5 institutions, who used the posterior approach. Patients underwent the routine thromboprophylaxis regimen and postoperative rehabilitation program of each institution.

All patients were prospectively followed for 3 years after the index surgery. During the course of the study, all adverse events suspected to correlate with the implanted PMPC-grafted HXLPE liner were recorded. Orthopedic surgeons other than the operators evaluated clinical performance using the evaluation chart of hip joint function authorized by the Japanese Orthopaedic Association (JOA score) [15]. The JOA score consists of four categories: pain (40 points), range of motion (20 points), gait (20 points), and activities of daily living (20 points). Fujisawa et al. reported that there was an excellent correlation between the JOA and Harris hip scores (coefficient of correlation = 0.843) [16]. Therefore, we calculated the equivalent Harris hip score using the following regression formula: Harris hip score = JOA score $\times$ 0.979 + 4.363.

Anteroposterior pelvic radiographs were obtained with the patient in supine, immediately after surgery and at 3 weeks, 3 months, 6 months, 1 year, and 3 years postoperatively. The distance between the X-ray tube and the imaging plate was set to 100 cm, and the center of the X-ray beam was directed at the cranial end of the pubic symphysis. The digitized image data were stored at a resolution of 0.13–0.20 mm/pixel.

We compared the radiographs obtained at 3 weeks with those obtained at up to 3 years for detecting periprosthetic osteolysis and assessing implant stability. Periprosthetic osteolysis was defined as new cystic lucency localized on the endosteal surface of the bone [17]. Migration of the femoral component was defined as a change of 3 mm or above in the position of the implant [18]. To assess the stability of the acetabular component, we modified the method described by Engh et al. [19]. The acetabular component was defined as stable, suboptimally stable (migrated $\leq$2 mm or tilted $\leq$5°), or unstable (migrated $>$2 mm or tilted $>$5°).

In addition, three independent reviewers measured the position of the femoral head on digitized radiographic images obtained at 3 weeks, 6 months, 1 year, and 3 years after implantation, without any clinical information. They employed a 2D computerized method—the PolyWare technique (Draftware Inc., Vevay, IN) [20]. Each reviewer measured the position of the femoral head thrice on a radiograph and recorded the median as the measured value. The authors calculated the average value of the three measured values recorded by the three reviewers and stored it in a database as the observed data. Then, they calculated the change in the femoral head position in each patient as the amount of femoral head penetration using the position at 3 weeks as the original position.

Several authors have reported a biphasic pattern in the progression of femoral head penetration into an HXLPE liner [19,21–25]. In the first phase, the femoral head rapidly moves into the liner; this phenomenon is called "bedding-in" and is largely attributed to permanent plastic deformation of the material and setting of the liner in the metal shell [22]. In the second phase, the femoral head slowly moves into the liner; this phenomenon is largely attributed to true wear—material loss in the form of particles—and is considered the "steady-state wear rate". We used these terms to describe the measurement results.

Statistical methods

The paired t-test was used to compare the JOA scores recorded before surgery and at 3 years after surgery. Pearson's correlation coefficient or the Mann–Whitney *U* test was employed to test the correlations between the measurement of femoral head penetration and patient characteristics, such as body mass index (BMI).

Results

Of the original 80 patients, 1 died of a cause unrelated to the joint replacement and 3 were lost or refused to return for follow-up at 3 years postoperatively. Thus, the study group comprised 76 patients (Table 1).

No adverse events suspected to correlate with the implanted PMPC-grafted HXLPE liner were recorded, and no revision

Table 1. Preoperative demographic data.

Items	Patients (%)
All patients	76
Sex	
Male	14 (18.4)
Female	62 (81.6)
Age (years)	
40–49	5 (6.6)
50–59	30 (39.5)
60–69	22 (28.9)
70–75	19 (25.0)
Diagnosis	
Osteoarthritis	73 (96.1)
Osteonecrosis	3 (3.9)
Charnley Category	
A	40 (52.6)
B	36 (47.4)
Side	
Right	42 (55.3)
Left	34 (44.7)
Body Height (cm)	
$>$140 to $\leqq$150	17 (22.4)
$>$150 to $\leqq$160	40 (52.6)
$>$160 to $\leqq$170	18 (23.7)
$>$170 to $\leqq$180	1 (1.3)
Mean $\pm$ SD	155.5 $\pm$ 6.5
Body Weight (kg)	
$>$30 to $\leqq$40	4 (5.3)
$>$40 to $\leqq$50	17 (22.4)
$>$50 to $\leqq$60	41 (53.9)
$>$60 to $\leqq$70	13 (17.1)
$>$70 to $\leqq$80	1 (1.3)
Mean $\pm$ SD	54.4 $\pm$ 7.4
Body Mass Index	
$>$15 to $\leqq$20	11 (14.5)
$>$20 to $\leqq$25	49 (64.5)
$>$25 to $\leqq$30	16 (21.1)
Mean $\pm$ SD	22.5 $\pm$ 2.5

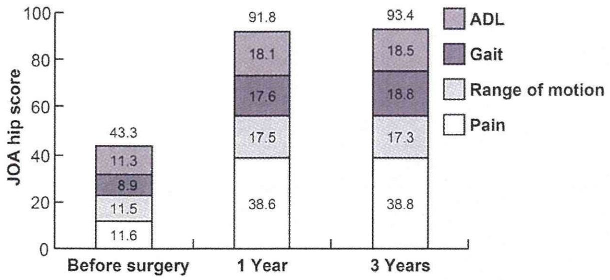

Figure 1. Average Japanese Orthopaedic Association hip score before surgery and at 1 and 3 years after surgery. The change was most apparent in the pain category.

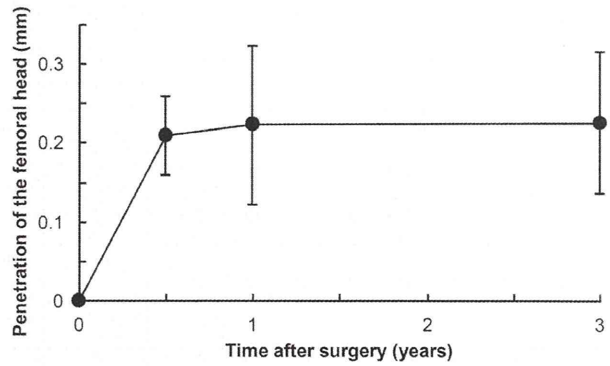

Figure 3. Femoral head penetration at 6 months, 1 year, and 3 years after surgery. The amount of femoral head penetration is calculated using the position at 3 weeks as the original position. Penetration during the first year is larger than that in the subsequent 2 years. Standard deviation bars are displayed.

operations were performed during the follow-up period. Three patients had deep vein thrombosis, which was treated successfully with anticoagulants in each case. Two patients had dislocation, which was treated nonoperatively and no deep infection occurred.

The mean JOA score improved at 3 years postoperatively ($p < 0.01$; Figure 1). According to Fujisawa's regression formula [16], the mean JOA score immediately after THR and at 3 years after THR corresponded with Harris hip scores of 46.7 and 95.6, respectively. Therefore, the clinical outcomes of the present cohort were similar to those of other contemporary cementless THRs [22,24].

On radiographic analysis, neither periprosthetic osteolysis nor femoral component migration was detected in all 76 patients (Figure 2). Seventy-four patients had a stable acetabular component and two had a suboptimally stable component. In the two patients with a suboptimally stable acetabular component, the component had changed its position up to 6 months after the index surgery and was stable afterwards. Similar observations have been reported in other cementless acetabular components and are not compatible with the predictive radiographic findings for the early diagnosis of loosening [19,26]. We attributed this limited migration to insufficient initial seating of the component.

Penetration during the first year was regarded as bedding-in and that after 1 year as steady-state wear [21,25]. Among all patients, 38 (50%) had negative wear between 1 and 3 years. The mean femoral head penetration rate between 1 and 3 years was 0.002 mm/year (Figure 3), representing marked reduction compared with the mean wear rate of other HXLPE liners [19,21–25]. The mean femoral head penetration rate correlated weakly with patient age ($R = 0.331$), but it did not correlate with sex, preoperative diagnosis, body weight, or BMI.

In the present cohort, the mean penetration at 1 year was 0.210 mm, and was slightly greater in male patients than that in female patients ($p = 0.021$). Although men were heavier than women ($p = 0.014$), the mean penetration did not correlate with body weight. We also found no correlation between mean penetration at 1 year and patient age, preoperative diagnosis, and BMI. Mean penetration at 3 years correlated weakly with BMI (Figure 4), but it did not correlate with sex, age, preoperative diagnosis, or body weight.

We compared the data of the 2 patients with a suboptimally stable acetabular component with those of the 74 patients with a stable component (Table 2). In one patient (Case 33), a large amount of penetration was observed at 6 months, and the value decreased up to 3 years after surgery. In the other patient (Case 36), the amount of penetration was relatively small at 1 year and relatively large at 3 years. As a result, this patient showed a high wear rate between 1 and 3 years. The cause of these unusual observations is unclear and continued follow-up is required to determine their relevance to the clinical outcome.

Discussion

To support the continued use of a new implant, updated clinical data should be available on the safety and efficacy. PMPC-grafted HXLPE liners were introduced to address concerns of wear and osteolysis in hip replacement. Regarding the safety of these implants, this study demonstrated that THR using this liner provided good clinical results, and no adverse events associated with the liner occurred during the 3 years after implantation. Therefore, this liner should be considered as a safe option in hip replacement.

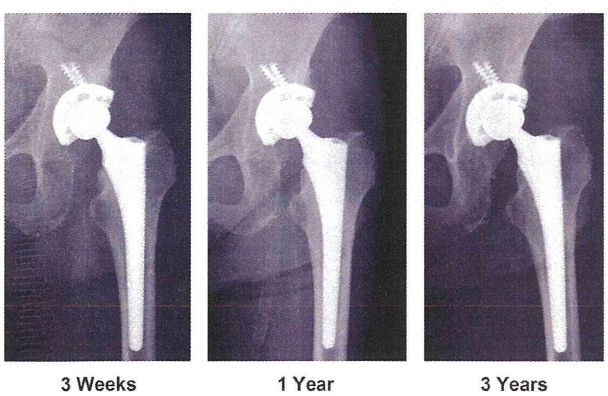

Figure 2. Radiographs of a representative case (Case 66). Radiographs obtained 3 weeks, 1 year, and 3 years after surgery, showing no findings related to implant migration or periprosthetic osteolysis.

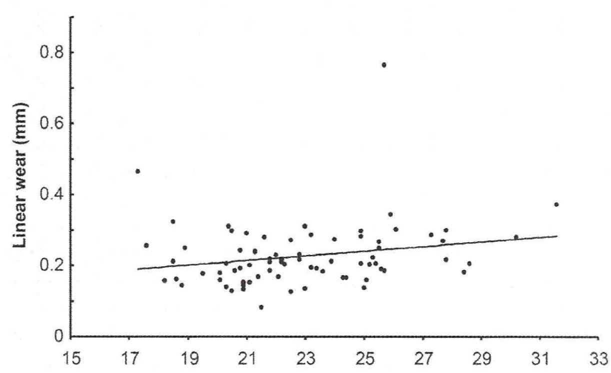

Figure 4. Relationship between amount of femoral head penetration at 3 years after surgery and body mass index. y = 0.0065x + 0.077; $R = 0.215$.

Table 2. Summary of the results of measurement of the penetration of the femoral heads.

	All hips (76 hips)*	Stable (74 hips)*	Suboptimally stable (2 hips)	
			Case 33	Case 36
6 months (mm)	0.210 ± 0.050	0.196 ± 0.050	1.050	0.170
1 year (mm)	0.223 ± 0.100	0.214 ± 0.069	0.863	0.137
3 years (mm)	0.226 ± 0.090	0.218 ± 0.065	0.765	0.302
Wear rate (mm/year)	0.002 ± 0.043	0.002 ± 0.041	− 0.049	0.083

*Values are expressed as mean and standard deviation.

Regarding the efficacy of PMPC-grafting in reducing wear, the mean amount of bedding-in was 0.210 mm and the steady-state wear rate was 0.002 mm/year in the present study. We found no osteolysis on serial radiographs. For comparison, the results of six other prospective studies are summarized in Table 3 [19,21–25]. In these studies, a 26- or 28-mm-diameter Co–Cr–Mo alloy femoral head and HXLPE liner secured in a cementless shell were used for the bearing coupling, and the patients were followed for at least 3 years. Among these studies, three reported detailed data on bedding-in: it occurred from 6 months to 1 year after surgery, and the mean amount of penetration ranged from 0.123 to 0.260 mm. Thus, in the first year, the behavior of the PMPC-grafted HXLPE liner is quite similar to that of other liners. Because PMPC grafting is nanometer-scaled surface modification, this technique does not affect the physical or mechanical properties of the HXLPE substrate [27]. Hence, we attributed the differences in the amount of penetration to the characteristics of the HXLPE liners. They can vary in terms of resin type, radiation technique used for cross-linking, post-irradiation stabilization process, and sterilization modality, any of which can influence the mechanical properties, crystallinity, and pre-aging and post-aging oxidation levels of the components [28]. For instance, Medel et al. reported that annealing preserves the mechanical properties better than remelting with regard to both fatigue and fracture resistance [29]. Meanwhile, all six studies reported steady-state penetration rates: they varied from 0.01 to 0.06 mm/year. Although PE wear is a multifactorial process [18], the results of the present study seem to compare favorably with those of the other six studies in terms of marked reduction. Among patient characteristics, the body weight of the patients was significantly lesser in the present study than in the other studies. Therefore, we believe that PMPC grafting is a promising method for reducing HXLPE wear, and the results of the present study support the continued use of these liners. We plan to conduct a longer follow-up to elucidate the true clinical benefit of PMPC-grafted HXLPE liners in hip replacement surgery.

This study has several limitations. First, it was not a randomized controlled trial. A randomized controlled trial comparing HXLPE liners and PMPC-grafted HXLPE liners would be the best scientific method to evaluate the efficacy of PMPC grafting. However, most candidates reported that they preferred the new liner and did not want to join a clinical trial in which their liner was chosen by a chance mechanism. Therefore, we performed a prospective cohort study to address this issue.

Second, 76 individuals and a 3-year follow-up may not be sufficient to deny the possibility of rare adverse reactions related to these new bearings. Thus, a long-term follow-up study (UMIN000003681) is underway for an extended investigation.

Third, the radiostereometric analysis (RSA) method, which has been reported to be the most accurate tool for in vivo assessment of PE wear [30], was not used in this study because of the need for the placement of marker balls. Many potential candidates believed that these metals provided no benefit. Therefore,

Table 3. Summary of six prospective studies using a 26- or 28-mm cobalt–chromium–molybdenum alloy femoral head with highly cross-linked polyethylene liner.

Authors	HXLPE	Head size (mm)	n	Body weight (kg)	BMI	Follow-up (year)*	Measurement technique	Bedding-in duration (year)	Amount of Bedding-in (mm)†	Steady-state penetration rate (mm/y)‡
Engh et al. (2006) [19]	Marathon®	28	76	84.4 ± 21.3 (51.3–149.4)	28.6 ± 5.5 (19.9–47.3)	5.5 (4.1–7.0)	Hip Analysis Suite	0.75 ≦	0.22 ± 0.31	0.01 ± 0.07
Calvert et al. (2009) [22]	Marathon®	28	59	NA	NA	4	PolyWare Auto	0.5	NA	0.0239 (−0.008–0.0558)
Glyn-Jones et al. (2008) [21]	Longevity®	28	26	79 (49–117)	NA	3	RSA	1	0.26 ± 0.17	0.03 ± 0.06
Lachiewicz et al. (2009) [23]	Longevity®	26	14	NA	29 (18.9–46.4)	5.7 (5–8)	Hip Analysis Suite	NA	NA	0.060 ± 0.042
Lachiewicz et al. (2009) [23]	Longevity®	28	33	NA	29 (18.9–46.4)	5.7 (5–8)	Hip Analysis Suite	NA	NA	0.032 ± 0.019
Whittaker et al. (2010) [24]	Longevity®	28	36	78.9 ± 13.8	29.3 ± 3.9	7.64 (6.60–8.53)	Hip Analysis Suite	NA	NA	0.025 (0.009–0.042)
Whittaker et al. (2010) [24]	XLPE®	28	47	88.7 ± 23.4	31.1 ± 6.3	6.42 (5.0–8.01)	Hip Analysis Suite	NA	NA	0.026 (0.004–0.047)
Capello et al. (2011) [25]	Crossfire®	28	42	79.2 ± 19.6	27.4 ± 4.5	8.6 (7.0–10.3)	Livermore	1	0.123	0.031 ± 0.014
Present study	Poly(MPC)-grafted	26	76	55.1 ± 8.2 (37.0–77.9)	22.9 ± 3.0 (17.3–31.6)	3	PolyWare	1	0.223 ± 0.100	0.002 ± 0.043

HXLPE highly cross-linked polyethylene, *NA* not available

*Values are expressed as the mean, with the range in parentheses.

†Values are expressed as the mean and standard deviation.

‡Values are expressed as the mean and standard deviation, or 95% confidence limit in parentheses.

we employed the PolyWare technique instead. As reported by Stilling et al., mean PE wear measured with PolyWare tends to be greater than that measured using the RSA method [31]. Consequently, the present study possibly overestimated the amount of penetration.

Fourth, among all patients, 38 (50%) had negative wear between 1 and 3 years. Such results are common in short-term studies of HXLPE liners [19,23,24]. Engh et al. reported a negative wear rate in 32% of the patients in their study [19]. As Lachiewicz et al. pointed out, these paradoxical observations should be attributed to the detection limits of the measurement technique [23].

Fifth, we used 26-mm-diameter Co–Cr–Mo alloy heads on the femoral side. However, in the clinical setting, various femoral heads of larger sizes and materials are available. Although we confirmed that improvements due to PMPC grafting surpassed those due to changes in the femoral head sizes or materials in the hip joint simulator studies [32], the outcome of THR using other femoral heads should be evaluated to determine the clinical utility of PMPC-grafted HXLPE liners. A multicenter study (UMIN000008730) is currently underway for the evaluation of other femoral heads, including zirconia-toughened alumina ceramic femoral heads and femoral heads with a larger diameter [33].

In conclusion, this study demonstrated that use of a PMPC-grafted HXLPE liner in THR appears to provide good clinical and radiographic results at 3 years after the index surgery. Further follow-up is needed to determine whether PMPC-grafted HXLPE liners improve long-term clinical outcomes.

Acknowledgments

The authors would like to thank the late Dr. Shuhei Morimoto for his invaluable contribution and participation in the present study since 2006.

Conflict of interest

One or more of the authors or institutions received outside funding or grants from KYOCERA Medical Corporation. One of the authors (K.M.) is employed by KYOCERA Medical Corporation.

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Tribology Online
Japanese Society of Tribologists

Tribology Online, 10, 1 (2015) 1-10.
ISSN 1881-2198
DOI 10.2474/trol.10.1

Article

Investigation on Oxidation of Shelf-Aged Crosslinked Ultra-High Molecular Weight Polyethylene (UHMWPE) and Its Effects on Wear Characteristics

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(Manuscript received 9 May 2014; accepted 15 November 2014; published 15 January 2015)

Oxidation degradation of gamma-irradiated UHMWPE (Ultra-high Molecular Weight Polyethylene) is a well-known problem related to the failure of total joint replacement. The purpose of this study is to investigate the effects of oxidation on the mechanical and wear properties and to identify the main causes of the change of wear mechanisms of crosslinked UHMWPE (50 kGy and 100 kGy) after long-term shelf-ageing. The techniques used were FTIR mapping and micro-indentation test, which were performed on the same cross-section of UHMWPE specimen. Three distinct regions (the surface region, the more oxidized subsurface region, and the less oxidized center region) were prepared to carry out the differential scanning calorimetry (DSC) and multi-directional wear tests. The worn surfaces were checked by optical microscopy and scanning electron microscopy to reveal the wear mechanisms. The experimental results showed that the micro-hardness, elastic modulus and crystallinity increased with the increase of the oxidation index. The wear resistance deteriorated when the oxidation index increased. The slope of specific wear rate against oxidation index of the 100 kGy sample is higher than that of the 50 kGy sample. Our results may indicate that, when the oxidation index is lower than the critical threshold, the wear mechanism is mainly dependent on crosslinking density; when the oxidation index is higher than the critical threshold, the oxidation behavior plays an important role in the change of wear mechanisms.

Keywords: UHMWPE, wear, oxidation, crosslinking, gamma-irradiation, shelf-ageing

1. Introduction

It is now acknowledged that the wear of UHMWPE (Ultra-high Molecular Weight Polyethylene) is a main factor restricting the service life of total joint prosthesis. Thus, numerous studies dealing with microstructure and mechanical properties of UHMWPE to eliminate wear of this polymer were developed [1-4]. Among them, the most popular and successful technique to improve the wear-resistance is to crosslink the UHMWPE by gamma radiation [5-7].

However, free radicals, which are susceptible to oxidation degradation that alters the physical, chemical, and mechanical properties of UHMWPE, are generated along the backbone of the UHMWPE molecule through breaking C-C and C-H bonds within the amorphous and crystalline phases during gamma irradiation [8]. The free radicals are supposed to recombine with each other to form the crosslinks, but not all of the free radicals are mobile enough to recombine with each other. In fact, the free radicals formed in crystalline phases of the UHMWPE are thought to be trapped and react with oxygen to cause oxidation in the long term [8,9]. Thermal treatment on post-irradiated UHMWPE is generally applied to eliminate the residual free radicals and alleviate the oxidation degradation [5,10]. Remelting above the melting point of UHMWPE is capable to eliminate the residual free radicals to undetectable level and is effective in preventing the UHMWPE component from oxidizing, but diminishes fatigue crack propagation resistance. Annealing below the melting point can also reduce the amount of free radicals, delay the oxidation, and results in better wear and fatigue resistance compared to the remelting method. However, some free radicals remain and the long-term oxidative degradation is hardly prevented.

In addition, the generated free radical concentration has been proved to be proportional to the radiation dose

[11,12] and crosslinked UHMWPEs with different dose levels probably differ from each other in the oxidation behavior. O'Neill et al. [13] found that the maximum oxidation occurred close to the surface and its value and position were dose-dependent, however the related mechanical and wear properties were not referred in his paper. Furthermore, the UHMWPE components are usually stored for a period of time due to business needs. Currier et al. [14] and Kyomoto et al. [15] reported that the shelf time before implantation appears to be a significant factor in the success or failure of UHMWPE bearings that are gamma sterilized in air. Fisher et al. [16] and Toohey et al. [17] also reported that crosslinked UHMWPE had a higher wear rate after ageing.

The oxygen concentration, which related to the oxidation, is influenced by the storage condition and *in vivo* condition. During 1990s, most of the UHMWPE components were packaged and stored in an air-permeable condition, which is roughly 8 times the oxygen content *in vivo* [18]. Due to the higher oxygen content compared with *in vivo* condition, the oxidation occurred during the shelf-storage is assumed to be the key factor in the wear resistance of the UHMWPE components [15]. Although the UHMWPE components are packaged in reduced oxygen environment after 1998, all the polymer materials commonly used for packaging are proved to be permeable to oxygen [19]. Thus, a variable amount of oxygen could be available to cause the oxidation. Besides, there are a lot of crosslinked UHMWPE components shelf-stored without barrier packaging in use. Therefore, it is meaningful to know the effect of oxidation on the mechanical and wear properties of shelf-aged crosslinked UHMWPE materials.

Despite valuable studies about the wear behavior of gamma-irradiated UHMWPE derived from earlier researchers, in-depth investigation of the relationship between the oxidation, mechanical properties and wear behavior of shelf-aged crosslinked UHMWPE is scarce. In this study, gamma-irradiated (dose level: 50 kGy, 100 kGy) and annealed UHMWPEs, which were shelf-aged for 7 years, were chosen as the research objects. The main objectives were to evaluate the effects of oxidation on mechanical and wear properties of crosslinked UHMWPE, and to identify the main causes of the change of wear mechanisms.

2. Experimental procedure

2.1. Material selection and preparation

Compression-moulded GUR 1050 UHMWPE rods with a molecular weight of 5.5-6 million-g/mol and a density of 0.93 g/cm^3 were chosen as the testing material in this paper. The UHMWPE rods were irradiated in air at room temperature with gamma rays from cobalt 60 to the total dose of 50 kGy and 100 kGy which are commonly used on the UHMWPE crosslinking and the dose rate is 10 kGy/h. After irradiation, the rods were annealed by heating at 110°C for 8 hours inside a vacuum oven, and then slowly cooled down in the oven to ambient temperature over a period of 24 hours. Any surface oxidation products that occurred during the in-air irradiation were removed prior to machining into the final cylinder shape with a diameter of 6 mm and a length of 15 mm. Finally, all specimens without sterilization were shelf-aged at ambient temperature in an air-containing double PE package for 7 years. The non-crosslinked UHMWPE cylinder with non-shelf-ageing was used as control sample.

2.2. Characterization techniques

The shelf-aged specimens were initially cut in half and microtomed along the radial direction by using the Leica RM 2125 RTS manual microtome at ambient temperature to obtain flat and smooth cross-sections for the following tests. A Fourier transform infrared (FTIR) spectroscope (Nicolet iN10 MX infrared imaging microscope, Thermo Scientific, USA) equipped with x-y motorized micro-positioning stage (precision 1 μm) was used to investigate the oxidation behavior of the cross-sections. All the spectra were run in attenuated total reflection (ATR) mode with a 4 cm^{-1} resolution and reported in absorbance (A). The analysis area was allowed to collect on a 10 μm×10 μm surface but 60 μm×60 μm was used in the present study. The line-scan spectra based on 64 scans were carried out with an interval of 200 μm along the radial direction through the microtomed cross-section of the cylinder. Oxidation levels were quantified as an oxidation index (OI), calculated by normalizing the carbonyl absorbance over 1685-1745 cm^{-1} to the reference absorbance over 1330-1390 cm^{-1} wavenumbers according to the ASTM F2102-06$^{\varepsilon 1}$.

The same specimen prepared for the FTIR analysis has also been used for micro-indentation testing. Micro-indents were performed on a DUH-211 dynamic ultra-micro-hardness tester (Shimadzu Corporation, Japan) with a peak load of 100 mN at a loading rate of 13.3 mN/s. After a holding time of 5 s, the load was released at the same constant rate as in the loading cycle. The indentation testing traversed the whole cross-section by a series of 30 indents separated with an interval of 200 μm. The micro-hardness and modulus were calculated according to the ISO 14577-1 (Annex A) by the instrument.

The crystallinity was determined using additional microtomed thin sections (at least n=3 each). Three distinct regions were tested: the surface region, the more oxidized subsurface region, and the less oxidized center region. The samples (around 8 mg each) were sealed in aluminum pans and tested on a Differential Scanning Calorimetry (DSC, X-DSC 7000, SII Nano Technology Co., Ltd., Japan). The sample pan, along with an empty reference pan, was placed in the DSC chamber, which housed two heaters, one for each pan. The heating runs were performed from 30°C to 185°C at a heating rate of 10°C/min under dry nitrogen atmosphere, then cooled