

# A novel ultra high molecular weight polyethylene–hyaluronan microcomposite for use in total joint replacements. II. Mechanical and tribological property evaluation

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**Abstract:** The mechanical and tribological properties of a new biomaterial, an ultra high molecular weight polyethylene–hyaluronan (UHMWPE–HA) microcomposite, were investigated in this article, which is Part II of a two-part study. Part I presented the synthesis and physical/chemical characterization of the novel microcomposites. The microcomposite was developed for bearing surfaces of total joint replacements and was designed to enhance lubrication and improve wear resistance compared to non-crosslinked UHMWPE. Pin-on-flat wear tests with cross-path motion demonstrated significant decreases for both the wear and wear rate of UHMWPE with the presence of hyaluronan (HA) within and on the microcomposite. Compared to noncrosslinked UHMWPE, a maximum decrease

of 56% in wear and a maximum decrease of 31% in wear rate were observed at 1.0 million cycles. Inferior tensile properties were observed for the microcomposites when compared to noncrosslinked UHMWPE, which resulted from poor intermolecular entanglement of the UHMWPE caused by low remolding temperature throughout microcomposite manufacturing. Similar results were observed for the sham control, which was processed in the same way as the microcomposite, except for the addition of HA. © 2007 Wiley Periodicals, Inc. *J Biomed Mater Res* 82A: 18–26, 2007

**Key words:** UHMWPE; hyaluronan; microcomposites; wear; tensile test

## INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been used as a load-bearing material in total joint replacements (TJRs) for over 30 years. However, wear debris generated from UHMWPE components remains a major cause of implant loosening and failure, limiting the longevity of current TJRs.<sup>1,2</sup> Because of the long molecular chains and their excessive entanglements, UHMWPE exhibits exceptional mechanical and wear-resistance properties,<sup>3</sup> but its extreme hydrophobicity and surface chemistry are very differ-

ent from those of natural cartilage. Thus, current joint replacements, based on UHMWPE, do not enjoy the low friction and wear of natural joints, and operate in the mixed or boundary lubrication regimes.<sup>4,5</sup> The continuous rubbing between the two articular surfaces results in wear of the softer material (i.e., UHMWPE) in TJRs.<sup>4,5</sup> Lubrication involving the human body's natural lubricants has not been a feature of artificial joint design to date.

Hyaluronan (HA) is a well-known natural lubricant present in synovial fluid<sup>6</sup> and on most human tissue surfaces.<sup>7,8</sup> HA exhibits viscoelastic properties in aqueous solution: acting more viscous under slow loading rates and more elastic under high loading rates.<sup>9</sup> The goal of this two-part study was to develop a novel UHMWPE–HA microcomposite to modify the surface of UHMWPE, to better mimic the function of natural cartilage and to enhance the lubrication and improve the wear resistance of UHMWPE. Part I of this study detailed the manufacture of the microcomposites, which were fabricated from UHMWPE pre-

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forms with interconnected micropores and a HA derivative developed in our lab.<sup>10</sup> As presented in Part I, a uniform layer of HA film was achieved on the surface of the UHMWPE microcomposites, which was hydrophilic, completely hydrated, and stable in the enzymatic environment.<sup>11</sup> The theoretical advantage of this fabrication method is that it should provide better mechanical integrity between the microcomposite HA surface and the UHMWPE bulk material than simply grafting HA to the UHMWPE surface because of the entanglement between HA and UHMWPE in the microcomposite.

The current study, Part II, investigated how the presence of HA in the microcomposite changed the mechanical properties and wear resistance of UHMWPE. Prior investigations demonstrated that the presence of hydrophilic poly-L-lysine at the surface layer of UHMWPE significantly decreased the Young's modulus, strength, and creep resistance of UHMWPE, while significantly increasing its elongation to failure. Although the poly-L-lysine caused a decrease in the mechanical properties, the properties remained within the range specified for UHMWPE in ASTM F-648.<sup>12,13</sup> Tensile tests were performed in the current study to determine if HA had the same plasticizing effect on UHMWPE.

The hydrated HA film on the UHMWPE surface is expected to form a lubricious layer to isolate articular surfaces and cushion load in TJRs, therefore increasing the lubricity of UHMWPE and reducing its long-term wear. The tribological properties of the microcomposite were investigated using pin-on-disk experiments with

cross-path motion. The crossing path motion is very important to determine the wear behavior of UHMWPE.<sup>14</sup>

## MATERIALS AND METHODS

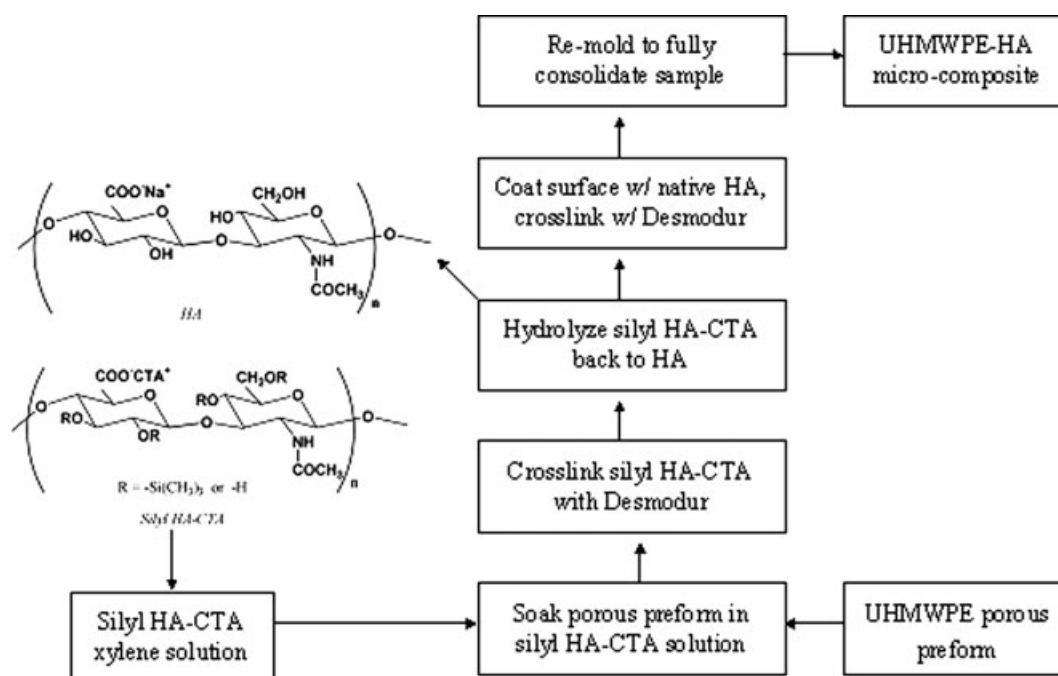
### Materials

UHMWPE porous disk preforms (diameter 3.8 or 10.2 cm) with different porosities (20 and 40%) were made from a GUR 1020 resin, provided by DePuy Orthopaedics (Warsaw, Indiana). The pores of the preforms were interconnected with a size of 1–20  $\mu\text{m}$ . The details of the porous preform fabrication, porosity measurement, and control are described elsewhere.<sup>15</sup>

Sodium hyaluronate (HyluMed<sup>®</sup>, medical grade, MW:  $1.36 \times 10^6$  Da) from Genzyme (Cambridge, MA) was complexed with quaternary ammonium cations (cetyltrimethylammonium cations, CTA<sup>+</sup>), followed by silylation using a method described elsewhere<sup>10</sup> to produce silyl HA-CTA. Desmodur N3200 (1,6-hexamethylene diisocyanate-based polyisocyanate, Bayer, Pittsburgh, PA) was used to crosslink the silyl HA-CTA.

### UHMWPE-HA microcomposite fabrication

The microcomposite samples were made from noncrosslinked UHMWPE preforms. The treatment details of UHMWPE preforms with silyl HA-CTA are described in Part I,<sup>11</sup> and briefly summarized here. The general procedure for HA-UHMWPE microcomposite formation is shown in Figure 1. Initially, a solution of the silyl HA-CTA diffused into the interconnected pores of the UHMWPE preforms for several minutes. Afterwards, the silyl HA-



**Figure 1.** Formation of UHMWPE-HA microcomposite (see Tables I and II for specific samples treatment parameters).

**TABLE I**  
**Treatment Conditions of Microcomposites**

Treatment	Concentration of Silyl HA-CTA (mg/mL)	Concentration of Desmodur (%)	Soaking and Crosslinking	Concentration of Native HA (%)
Method 1	I - 25 II - 50 III - 75	5	I → Desm. → II → Desm. → III → Desm.	1
Method 2	I - 50	2	I → Desm.	1

CTA was crosslinked *in situ* with Desmodur N3200 and then returned to its unmodified state (e.g., native HA) via hydrolysis. The treated porous preforms were finally coated with native HA solution and then crosslinked with Desmodur N3200, followed by remolding to consolidate the UHMWPE. The consolidation was performed at DePuy Orthopaedics under ~15 MPa at 155–160°C within a vacuum chamber (>710 mmHg). To prevent HA from degrading, all specimens, including the control, were remolded at 155–160°C [melting point of UHMWPE: (135.6 ± 4)°C<sup>16</sup>], rather than at 205°C, which is often used to mold UHMWPE powder.

Two different methods of treatment (details summarized in Table I) were used to determine the effect of different process parameters. In Method 1, the preforms were first soaked in a 25 mg/mL silyl HA-CTA solution and then crosslinked with a 5% Desmodur solution. The soaking and crosslinking operations were then repeated in 50 and 75 mg/mL silyl HA-CTA solutions. After hydrolysis, but before remolding, all samples were coated with an aqueous 1% HA solution once and crosslinked with Desmodur solution (5%). The hydrolysis was performed at 45°C for 24 h in a 0.2M NaCl solution of water and ethanol (v/v 1:1).

In Method 2, the preforms were soaked in a 50 mg/mL silyl HA-CTA solution and then crosslinked with a 2% Desmodur solution. Hydrolysis was carried out in a 0.2M NaCl solution of water and ethanol (v/v 1:1) for 40 h, and the solution was changed every 10 h. An ultrasonic water bath was employed to assist hydrolysis, but the total time was not greater than 2 h. The hydrolyzed samples were coated with an aqueous 1% HA solution twice and then crosslinked with a 2% Desmodur solution.

Table II indicates which treatment methods were used on the tensile and wear test samples, the porosity of the original preform, and the approximate HA content within the composite layer and in the surface layer. Furthermore, some of the tensile samples and all of the wear samples were made with a preform layer on top of solid UHMWPE so that only a portion of the sample would be microcomposite and the other portion would be plain UHMWPE. In some of the tensile samples, 50 or 25% of the cross-section was microcomposite with the balance UHMWPE and in the wear samples, only the top 3 mm of the articulating surface (i.e., to a depth of 3 mm below the articulating surface) of the cylindrical wear pin was microcomposite. The solid portions of those tensile and wear test specimens

**TABLE II**  
**Sample Parameters of Microcomposites**

Microcomposites	Treatment Method	Porosity (%)	Consolidated Thickness (mm)		HA Content (%) <sup>a</sup>	
			Original Solid Layer	Porous Layer	Within Composite	Within Surface
<b>Tensile test</b>						
Control		40	0	3.0		
T1-20	1	20	0	3.0	1.46	0.18
T2-40	2	40	0	3.0	0.83	0.97
T2-40-H	2	40	1.5	1.5	0.81	2.58
T2-40-Q	2	40	2.25	0.75	1.63	3.40
<b>Wear test</b>						
Control		40	19.0	3.0		
W1'-20	1	20	19.0	3.0	2.27	3.13
W1'-40	1	40	19.0	3.0	6.35	3.4
W2-40-1	2	40	19.0	3.0	1.10	2.21
W2-40-2	2	40	19.0	3.0	1.12	1.39

Nomenclature: T, tensile (disk diameter 10.2 cm); W, wear (disk diameter 3.8 cm); H, half microcomposite; Q, quarter microcomposite; T2-40-H represents that the microcomposite was treated with Method 2, the porosity of its UHMWPE preform was 40%, and the consolidated thickness of porous layer was half of the total thickness; W1'-20 represents that the microcomposite was fabricated with Method 1, but retreated with HA solution after consolidation, and the porosity of its UHMWPE preform was 20%.

<sup>a</sup>% HA content based on weight gain of sample.

were consolidated in a separate 205°C molding cycle and then the porous preforms were molded onto them before treatment with the HA derivatives.

## Characterization

### Tensile tests

Standard tensile samples were punched from the 10.2-cm-diameter disks (control, T1-20, T2-40, T2-40-H, T2-40-Q) molded at DePuy Orthopaedics according to ASTM Standard D638-99 sample type V. The control was manufactured following the same process as for the microcomposites but without the addition of HA (i.e., sham control). The treatment conditions for all the microcomposites are shown in Table I. Five samples were punched from each disk. Two specimens were used to determine the Young's modulus, while the remaining three were used to measure the yield strength, tensile strength, and elongation to failure. The tests were performed according to ASTM Standard D638-99 on a servohydraulic biaxial mechanical testing system (Bionix, model 809, MTS Corporation, Eden Prairie, MN) with a low force uniaxial load cell (Model 661.19E-01, 4448 N). All the samples were conditioned with distilled water for 24 h before testing.

Two different tests were carried out to determine Young's modulus and strength/elongation-to-failure data, respectively. The modulus could not be accurately determined in a pull-to-failure test because the extensometer used to measure elongation could not accommodate the high elongation to failure of UHMWPE. In the modulus test, an extensometer (model 632.31F-24) with a gage length of 10 mm was used to measure accurately the deformation of specimens up to 0.4 mm. The crosshead speed was 1.27 cm/min with data acquisition at a rate of 10 Hz. The Young's modulus was determined from the slope of a linear regression on the first 1% strain of the stress–strain curve. This method of calculating modulus was similar to that used by Rentfrow<sup>12</sup> and Bennett<sup>17</sup> for the Hospital for Special Surgery (HSS) reference UHMWPE.

In the elongation-to-failure test, specimen deformation was recorded by a video camera. The extensometer used in the modulus test had a much better resolution than the video system used for elongation to failure and thus the two different tests were used. The initial gage length of ~1.0 cm was marked on each sample with black permanent marker and was measured with a caliper. The video resolution and mark size resulted in an approximate resolution of 0.6 mm. The crosshead speed was the same as that used in the modulus test (1.27 cm/min), but the data acquisition rate was decreased to 5 Hz. The distance change between the two marks during testing was recorded with the video camera, and the digitized video was then analyzed using Peak Motus 32 software (Englewood, CO). A 40 mm × 40 mm standard square was used to calibrate the digitized video frames. The yield strength was calculated from the first maximum stress in the engineering stress–strain curve, and the tensile strength was calculated from the absolute maximum stress before sample failure. Thus, if the engineering stress did not increase after yield, the yield and tensile strengths

were equal. The elongation-to-failure was determined by capturing the data of the last frame just before failure.

After the elongation-to-failure test, the fractured specimens were microtomed and the sections were observed under a light microscope to determine whether the samples were consolidated during final molding. Two reference UHMWPE (HSS) tensile samples were also tested to ensure the accuracy of the test methods and procedure.

All tensile data were analyzed using the Data Analysis Tool in MS Excel. A one-tailed student *t* test was used for single comparisons and a one-way ANOVA for multiple comparisons.

### Wear tests

Wear testing was performed at Zimmer (Warsaw, Indiana). Four pins (9.0-mm-diameter and 9.5-mm-long) were machined from each 3.8-cm-diameter disk listed in Table II (control, W1'-20, W1'-40, W2-40-1, and W2-40-2). The control (i.e., sham control) was a sample put through the same processes as the microcomposites but without the addition of HA. The treatment conditions for the four microcomposite samples are shown in Table I. W1'-20 and W1'-40 were actually fabricated with Method 1, but coated a second time with 1% HA solution and crosslinked with Desmodur after consolidation.

Three of these pins were used for wear testing, while the fourth was used as a load soak control. Both non-crosslinked and highly crosslinked UHMWPE pins machined from extruded GUR 1050 bar stock were used as UHMWPE material controls. The noncrosslinked polyethylene ("ConvPE") and the microcomposites were not sterilized. The crosslinked polyethylene ("XLPE") was irradiated for crosslinking to  $100 \pm 5$  kGy with an electron beam, with no subsequent heat treatment. Before testing, the surface profiles for all the pins were analyzed with a 3D Imaging Surface Structure Analyzer (NewView 200, ZYGO Corporation, Middlefield, CT). The pin-on-flat (POF) wear test machine used was Zimmer's custom-built 12-station device, which is capable of crossing motion paths with static load during testing (i.e., it was not capable of a typical gait cycle of fluctuating load). All pins were conditioned in distilled water for 8 h before testing. The wear test was performed at room temperature at 1.0 Hz for 1.0 million cycles. The lubricant was undiluted bovine calf serum (8.2 g/L total protein content, albumin/globulin ratio: 1.0) with sodium azide (3 g/L) as an antibacterial agent. EDTA (8 g/L) was used to bind the calcium in the lubricant, preventing the formation of calcium phosphate on the tested sample surfaces. Superfinished [surface roughness ( $R_a$ ):  $1.3 \pm 0.5$  nm] CoCrMo alloy disks were employed as the wear counterface. A constant load of 445 N was applied to each UHMWPE pin. The wear path was a square (15 mm × 15 mm) with a total length of 60 mm. The square path resulted in UHMWPE cross-shear. The test conditions are also summarized in Table III. Wear (weight loss) were determined gravimetrically for each sample after every quarter million cycles and were the average of three pin samples. Wear rate values reported here were the change of weight loss values normalized with the number of cycles. Prior to weighing,

**TABLE III**  
**Pin-on-Flat Wear Test Conditions**

Parameters	Conditions
Machine	Zimmer's custom-built pin-on-disk machine
Counterface	CoCrMo alloy 2A-74 ( $R_a = 1.3 \pm 0.5$ nm)
Wear path	Square waveform with each side 15 mm
Motion	Hydraulic control
Frequency	1.0 Hz
Load	Constant and pneumatic control, 445 N/pin
Nominal stress	6.9 MPa
Path length	60 mm
Temperature	Room temperature
Lubricant	Undiluted bovine calf serum + 8 g/L EDTA and 3 g/L sodium azide
Number of cycles	1 million
Sliding distance	60 km
Sliding speed	6 cm/s

all pins were cleaned in an ultrasonic bath of deionized water and rinsed with isopropyl alcohol to extract absorbed water. The load soak control was used to check the weight increase of wear pins caused by fluid uptake. The loading conditions for the soak control samples were the same as those used for wear samples (i.e., 445 N), but no motion was applied to them. The height changes of these load soak control samples with time were also monitored during testing, and a creep curve was obtained.

All data were analyzed using Data Analysis Tool of MS Excel. A one-tailed student *t* test was used for single comparisons and a one-way ANOVA for multiple comparisons.

## RESULTS

### Tensile properties

The tensile test results for the sham control and the microcomposites are summarized in Table IV, wherein they are compared to the reference UHMWPE and the ASTM standard specifications. The modulus and yield strength values for the control and microcomposites were within the range of values specified by the ASTM standard, but the ultimate strength and elon-

gation to failure values were much lower than the ASTM specifications and reference materials.

Compared with the control, Young's modulus of microcomposites did not change much ( $p = 0.81$ ). Even for the T1-20 specimen with the lowest modulus, the decrease in modulus compared with the control was less than 8% ( $p = 0.71$ ). Thus, the introduction of HA did not markedly change the modulus of UHMWPE.

The T1-20 specimen had the lowest ultimate tensile strength, which was even lower than that of the T2-40 sample ( $p = 0.02$ ). The three 40% porosity microcomposites did not show much difference from the control and from each other ( $p = 0.67$ ) in the ultimate tensile strength. However, the effects of HA and the preform layer thickness were observable: the presence of HA reduced the ultimate tensile strength of UHMWPE and the strength decreased with increasing the thickness of the preform layer.

The yield strengths of the control, T1-20, and T2-40 specimens were equal to their ultimate tensile strengths, so no comparisons were made for yield strength. However, the T2-40-H and T2-40-Q samples had an ultimate tensile strength higher than the yield strength with the presence of a premolded solid layer.

Elongation-to-failure results showed that the T1-20 specimens were inferior to all other samples. The elongation-to-failure for all the 40% porosity specimens was greatly higher than that of the control, and it increased with increasing thickness of the preform layer. This is the inverse of the strength results.

Observations under a light microscope of the sections microtomed from the fractured sham control and microcomposite specimens showed pronounced particle boundaries, indicating poor fusion of UHMWPE particles and incomplete consolidation of the samples during final molding. The specimens molded from UHMWPE powder at 205°C did not show unfused particles.

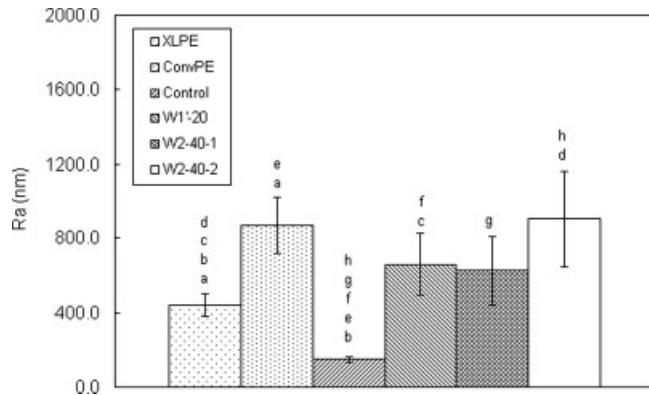
### Tribological properties

All wear specimens exhibited good appearance except some discoloration spots found on specimen

**TABLE IV**  
**Mechanical Properties of the UHMWPE Control and Microcomposites**

Sample	Modulus (MPa)	Yield Strength (MPa)	Ultimate Strength (MPa)	Elongation-to-Failure (%)
Control	786.6 ± 118.9	21.9 ± 0.3	21.9 ± 0.3	68.7 ± 8.8
T1-20	725.4 ± 166.4	15.9 ± 0.9	15.9 ± 0.9	50.0 ± 14.5
T2-40	824.1 ± 59.5	19.6 ± 3.2	19.6 ± 3.2	279.0 ± 73.6
T2-40-H	736.1 ± 19.4	20.3 ± 0.3	21.1 ± 4.9	82.9 ± 5.5
T2-40-Q	797.8 ± 6.9	18.9 ± 1.3	21.5 ± 2.4	70.3 ± 58.5
Reference UHMWPE <sup>a</sup>	944.7	23.3	48.6	384.0
ASTM F648-98 requirements	N/A	19	27	250

<sup>a</sup>Data from the paper by Bennett et al.<sup>16</sup>



**Figure 2.** Surface roughness for all the wear test samples (all pairs marked with the same letter are significantly different,  $p < 0.05$ ).

W1'-20. Figure 2 shows the average surface roughness ( $R_a$ ) of both UHMWPE controls and microcomposites. The surface roughness of the remolded sham control was approximately six-fold lower than ConvPE. For all the microcomposite specimens, their surface roughness did not differ from each other markedly ( $p = 0.15$ ).

Data for load soaked controls are listed in Table V. The weight increases of all samples due to liquid absorption during wear testing were very small compared to the magnitude of weight loss from wear, and thus were considered negligible. Figure 3 shows the creep curves for all load soaks (this data was from the load soak tests, which were somewhat similar to creep tests). The creep of all microcomposite samples was comparable to that of the noncrosslinked polyethylene.

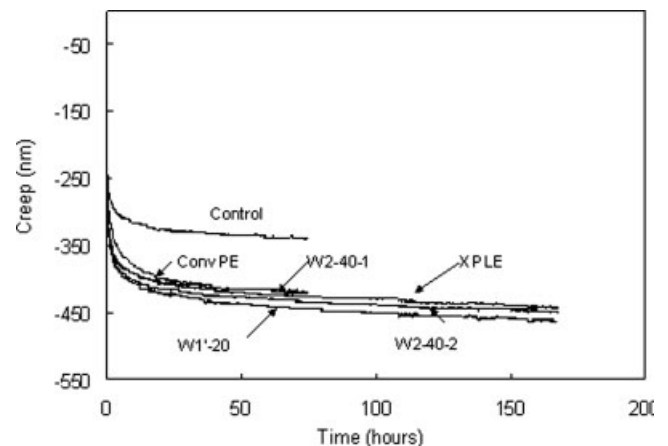
Wear results for both UHMWPE controls and microcomposites are summarized in Figures 4 and 5. The results of sample W1'-40 are not included because all the pins from this material fractured at the interface between the microcomposite layer and bulk UHMWPE.

The wear and wear rates of highly crosslinked UHMWPE (i.e., XLPE) were more than 10-fold lower than that for all of the other materials. The remolded UHMWPE preform sham control (i.e., control) had both higher wear and wear rate than the noncrosslinked UHMWPE control (i.e., ConvPE), but the differences between them decreased with increasing the

test cycles from 25% ( $p = 0.047$ ) at 0.25 million cycles to 9% ( $p = 0.19$ ) at 1.0 million cycles for wear, and from 25% ( $p = 0.048$ ) at 0.25 million cycles to less than 5% ( $p = 0.38$ ) at 1.0 million cycles for wear rate.

As shown in Figure 4, the wear for all microcomposites was lower than that of both remolded sham control and noncrosslinked polyethylene control, and the differences decreased with the wear cycles. Specimen W2-40-1 had the lowest wear at cycles higher than 0.5 million. Moreover, all the differences in wear between W2-40-1 and both controls were statistically significant. The wear values for W2-40-1 were 102% ( $p = 0.019$ ) and 56% ( $p = 0.014$ ) lower than ConvPE, and 153% ( $p = 0.002$ ) and 70% ( $p = 0.03$ ) lower than the sham control at 0.25 and 1.0 million cycles, respectively. The wear values for W2-40-2 were 24% ( $p = 0.06$ ) and 35% ( $p = 0.09$ ) lower than ConvPE and the sham control at 1.0 million cycles, respectively. For specimen W1'-20, at 0.25 million cycles, the wear was three- and four-fold lower than ConvPE and the sham control, respectively, but at 1.0 million cycles, these wear differences were very small [almost zero for ConvPE and 11% ( $p = 0.20$ ) for the sham control].

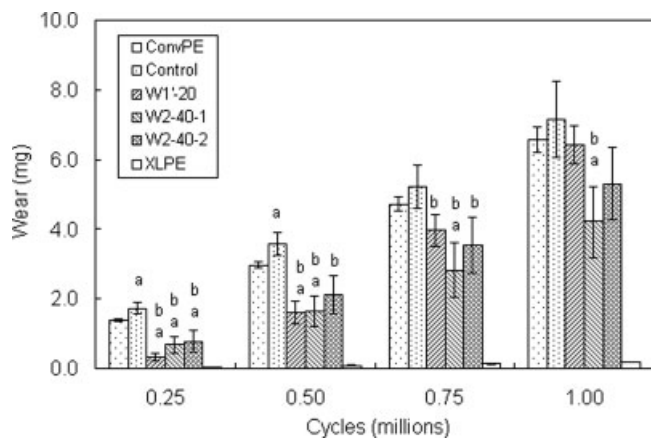
Wear rates are shown in Figure 5. The wear rates for specimens W2-40-1 and W2-40-2 were lower than both controls at all cycles, and the differences decreased as the test cycles increased. Specimen W2-40-1 also had the lowest values beyond 0.5 million cycles, which were 31% ( $p = 0.029$ ) and 37% ( $p = 0.13$ ) lower than ConvPE and the sham control at 1.0 million cycles, respectively. Although, at 0.25 million cycles, the wear rates for specimen W2-40-2 were significantly lower ( $p = 0.04$  for convPE and  $p = 0.007$  for sham control) than both controls, almost no differences ( $p = 0.37$  for both controls) were found at 1.0 million cycles. The wear rate of specimen W1'-20 was the lowest at 0.25 million cycles, three- to four-fold lower than that for both controls. However, after 0.5 million cycles, the wear rates of W1'-20 increased sharply and were about 35% higher than both Con-



**Figure 3.** Creep curves for the load soak controls.

**TABLE V**  
Weight Changes ( $\mu\text{g}$ ) of the Load Soaks

Sample	At 72 h	At 110 h
XLPE	40	N/A
ConvPE	-20	20
Control	-50	-55
W1'-20	680	N/A
W2-40-1	30	100
W2-40-2	10	N/A



**Figure 4.** Wear results for UHMWPE controls and micro-composites (a:  $p < 0.05$  compared to ConvPE; b:  $p < 0.05$  compared to control).

vPE ( $p = 0.03$ ) and sham controls ( $t$  test,  $p = 0.13$ ). In summary, specimen W2-40-1 was the most wear resistant, followed by W2-40-2. Specimen W1'-20 had a good wear resistance before 0.5 million cycles, but had a poorer one after that.

It was also found that the wear rates for both sham and noncrosslinked polyethylene controls were nearly constant. However, for the microcomposites, wear rates increased with the number of cycles.

## DISCUSSION

### Tensile properties

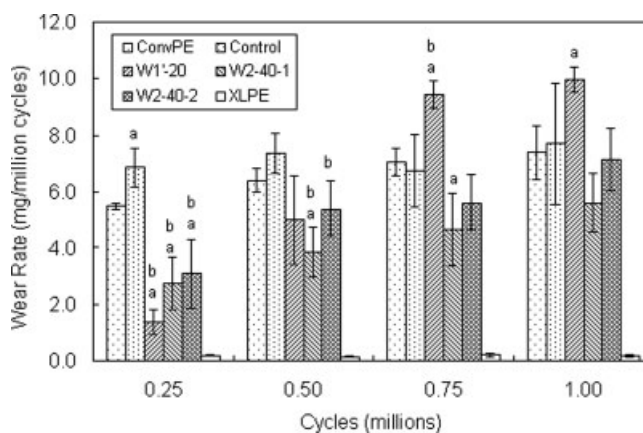
The samples molded from the porous preforms (both control and microcomposites) were so brittle that they could not be strengthened through stretching and alignment of molecular chains, and thus could not produce an ultimate strength higher than the yield strength. However, this is clearly not the result of HA introduction, because the sham control from the remolded 40% porous preforms (without HA treatment) also exhibited a significant decrease of elongation-to-failure. Also the tested properties for the two HSS reference UHMWPE fell within the normal range as previously reported,<sup>12</sup> indicating that the observed embrittlement was not caused by the test method either.

The high elongation-to-failure (i.e., ductility) of high molecular weight, semicrystalline, thermoplastic polymers like UHMWPE is due to entanglement of their long, highly coiled molecular chains in the amorphous regions including the tie chains extending from the crystalline regions into the amorphous regions. It is unentangling and subsequent stretching of these tie chains under tensile stress that results in large plastic deformation before the polymer fails.<sup>18</sup> The factors that prevent the entanglement of tie chains will also reduce the elongation-to-failure of the polymer. The

low molding temperature and large sample size (10.2-cm-diameter) might have reduced the heat energy and heat transfer during remolding, resulting in insufficient UHMWPE flow and particle fusion. In the poorly consolidated UHMWPE, the molecules within two adjacent particles could not entangle and interact with each other sufficiently, forming bridges to transfer the stress through the material, so the specimens may break before their tie chains have a chance to extend, resulting in a brittle behavior.

The solid portions of T2-40-H and T2-40-Q specimens, which were well consolidated in a separate 205°C molding cycle before the preform was molded onto the solid portion, showed an elongation similar to that of HSS UHMWPE (i.e., the video system allowed quantification of elongation-to-failure for each portion of the sample cross section separately as the preform layer broke much earlier than the solid layer). Furthermore, the T2-40 samples with good consolidation quality have the best elongation-to-failure values, even exceeding the ASTM specification. It is important to note that ASTM F-648 is only a standard and does not necessarily represent the minimum values of mechanical properties that would be required for safe and effective clinical performance. All these indicated that incomplete consolidation of the UHMWPE powder particles might be the major cause of the observed specimen embrittlement.

Although the properties of these specimens are not desirable due to the inappropriate remolding conditions, the effect of HA on microcomposite properties can be seen from the analysis of these properties. The presence of HA did not greatly change the Young's modulus of UHMWPE. According to the rule of mixtures for composites,<sup>18</sup> the contribution of HA to the modulus of microcomposite is proportional to its volume fraction. The maximum weight fraction of HA within microcomposites was 1.63% (Table II) in the T2-40-Q specimens, so the volume fraction of



**Figure 5.** Wear rate for UHMWPE controls and micro-composites (a:  $p < 0.05$  compared to ConvPE; b:  $p < 0.05$  compared to control).

HA was small, and thus its contribution to the microcomposite bulk modulus was negligible. However, the small number of samples used in the modulus test ( $n = 2$ ) and the relatively large standard deviations also contribute to the lack of observed statistical significance.

The T1-20 specimen had the lowest tensile strength. This was unexpected, but might be explained by the fact that the HA content within T1-20 was 1.46%, higher than that within T2-40 (0.83%) (Table II). Another possible reason might be the pore-forming-agent (i.e., porogen) residue, which could not be completely removed from the preform due to the low porosity. The pore-forming-agent residue might also contribute to the lowest elongation-to-failure for the T1-20 specimen.

The effects of the HA on the tensile properties of microcomposite were limited, but still observable: the presence of HA in the microcomposites slightly, but significantly, decreases the strength and increases the elongation-to-failure of UHMWPE. This phenomenon is similar to that observed in poly-L-lysine-modified UHMWPE.<sup>12</sup> Interestingly, the T2-40 microcomposite had a much higher elongation than all other samples due to its comparatively good consolidation quality and perhaps a plasticization effect of HA.

The tensile properties of both the sham control and microcomposites were inferior to the reference UHMWPE and ASTM specifications due to incomplete consolidation during the final molding. The molding conditions must be improved to solve the problem. Thermal gravimetric analysis indicated that cross-linked silyl HA-CTA had a degradation temperature above 250°C.<sup>11</sup> With removal of all easily decomposed modification groups [—CTA and —Si(CH<sub>3</sub>)<sub>3</sub>] during hydrolysis, the crosslinked HA within the UHMWPE preforms should be even more heat resistant. Thus, remolding temperatures higher than 160°C should be attempted with longer duration time to make UHMWPE particles fully fuse and achieve extensive entanglement between UHMWPE molecules.

As discussed above, the presence of HA within the microcomposites might not be the cause of the inferior mechanical properties in this study, but the poor bonding between hydrophobic UHMWPE and hydrophilic HA might be a concern for composite properties and should be further investigated.

One shortcoming of this study is the relatively small sample size used in the tensile tests. Larger samples sizes should be used in the future to achieve higher power and confirm the null hypothesis.

### Tribological properties

Although the surface of the remolded UHMWPE preform sham control (i.e., control) was markedly smoother than that of the machined, noncrosslinked

UHMWPE control (ConvPE), its wear and wear rate were higher than ConvPE. This demonstrated that material properties are more important than surface roughness in determining the wear resistance. Two possible reasons for the higher wear and wear rate of the sham control were its lower molecular weight and inferior mechanical properties. The sham control was made from GUR 1020 with an average molecular weight of  $3.5 \times 10^6$  g/mol<sup>19</sup> and remolded at a temperature that could not produce complete consolidation of UHMWPE particles (as discussed in Tensile Properties section above), causing inferior mechanical properties. ConvPE came from extruded GUR 1050 bar stock with an average molecular weight of  $5.5\text{--}6.0 \times 10^6$  g/mol<sup>19</sup> and good consolidation. Kurtz et al.<sup>19</sup> investigated the effects of molecular weight on the wear and mechanical behavior of UHMWPE and found that wear resistance increased with the average molecular weight.

All the microcomposite specimens did not show significant differences from each other in surface roughness. Thus, the large differences in their wear properties are likely due to differences in amount of HA and the film quality. Specimen W2-40-1 had a higher HA content in the composite surface layer than W2-40-2 (Table II), indicating greater amounts of HA molecules were present on the surface, so more HA molecules were involved in the lubrication, and the HA cushion swollen with water was thicker and more effective in separating the two articulating surfaces. For specimen W1'-20, the very low wear and wear rates before 0.5 million cycles are attributed to large amounts of HA on its surface. The extra HA film coated on the surface after consolidation may not be tightly adherent to the sample surface making it more easily rubbed away, leading to an abrupt increase in the wear rate after 0.5 million cycles. Compared with 40% porosity, the use of 20% porosity UHMWPE preforms was expected to reduce the silyl HA-CTA content within the microcomposite, thus increasing the amount of HA on the surface. However, the consequences were not desirable. The low porosity and the solid UHMWPE bulk at the specimen bottom obstructed water from diffusing into the treated preforms, leading to incomplete hydrolysis of silyl HA-CTA, while the degradation of the silyl HA-CTA residue during the final remolding caused local discoloration spots.

The increase in wear rate of microcomposites with the number of wear cycles may have been due to the exposure of some UHMWPE regions at the articulating surface with the removal of HA film. Of course, determining whether the wear of microcomposites occurred only within the HA layer or within both HA and UHMWPE requires further study on the wear surface and the wear debris collected from the lubricant. To avoid the wear of HA itself and further



increase the wear resistance, crosslinking should be optimized and controlled to form a more robust and durable HA surface layer. However, preliminary work has demonstrated that a favorable balance between HA crosslinking density and surface lubricity is required. If the crosslinking is too dense, it will consume too many polar groups, reducing boundary lubrication.

Incomplete preform consolidation due to low-temperature remolding may also adversely affect the wear properties for all microcomposites, as it did to the sham control. Wear resistance of microcomposites is expected to increase with improved treatment and molding processes.

The presence of HA significantly reduced the wear and wear rate of noncrosslinked UHMWPE, but the wear of HA-UHMWPE microcomposites is still significantly higher than that of crosslinked polyethylene (XLPE). Whether the HA treatment can similarly improve the wear resistance of crosslinked UHMWPE is the topic of an ongoing study.

To avoid the fracture at the interface between the microcomposite layer and bulk UHMWPE as happened in W1'-40, future work will also be performed on characterizing the strength of this interface and creating a gradient in composition from the bulk material to the surface layer to avoid sharp, stress rising, interfaces.

## CONCLUSIONS

As expected, the novel microcomposite between HA and UHMWPE was capable of enhancing lubrication of the UHMWPE surface and improving its wear resistance. It is a promising material for TJRs and other lubricated load-bearing surfaces. Although the tensile properties of the new microcomposites are not satisfactory, it does not appear that the HA caused this problem. The poor consolidation of the preform layers is likely the major cause. The remolding processes, especially the final molding temperature, of the treated UHMWPE preforms should be optimized to obtain a completely consolidated microcomposite with a uniform layer of HA film on its surface.

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