

# Surface Modification of Ultra-High-Molecular-Weight Polyethylene. II. Effect on the Physicomechanical and Tribological Properties of Ultra-High-Molecular-Weight Polyethylene/Poly(ethylene terephthalate) Composites

Mostafa Rezaei,<sup>1</sup> Azadeh Shirzad,<sup>1</sup> Nadereh Golshan Ebrahimi,<sup>1</sup> Marianna Kontopoulou<sup>2</sup>

<sup>1</sup>*Polymer Engineering Group, Chemical Engineering Department, Engineering Faculty, Tarbiat Modarres University, P.O. Box 14115-4838, Tehran, Iran*

<sup>2</sup>*Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada*

Received 19 January 2005; accepted 22 April 2005

DOI 10.1002/app.22688

Published online 12 December 2005 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** We performed surface modification of ultra-high-molecular-weight polyethylene (UHMWPE) through chromic acid etching, with the aim of improving the performance of its composites with poly(ethylene terephthalate) (PET) fibers. In this article, we report on the morphology and physicomechanical and tribological properties of modified UHMWPE/PET composites. Composites containing chemically modified UHMWPE had higher impact properties than those based on unmodified UHMWPE because of improved interfacial bonding between the polymer matrix and the fibers and better dispersion of the fibers within the modified UHM-

WPE matrix. Chemical modification of UHMWPE before the introduction of PET fibers resulted in composites exhibiting improved wear resistance compared to the base material and compared to unmodified UHMWPE/PET composites. On the basis of the morphological studies of worn samples, microploughing and fatigue failure associated with microcracking were identified as the principle wear mechanisms. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2352–2358, 2006

**Key words:** composites; fibers; mechanical properties; polyethylene (PE); surfaces

## INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE) is an engineering plastic used widely in orthopedic prosthesis because of its high strength, excellent toughness, high resistance to chemicals, physical abrasion, and low friction coefficient. Currently, approximately 1 million UHMWPE components are implanted annually, worldwide. Metal-on-UHMWPE total-joint arthroplasty offers effective pain relief and a remarkable restoration of mobility for patients with disabilities.<sup>1</sup>

Despite the success of total-joint arthroplasty, wear is a major obstacle limiting the long-term performance of implanted UHMWPE components. The major concern is adverse tissue reactions caused by the generation of UHMWPE debris particles. The debris is transported to the tissue surrounding the joint and causes a

chronic inflammatory reaction and bone resorption. It has been suggested that because of the presence of debris, macrophages release various cytokines and growth factors that induce bone loss.<sup>2</sup>

Many methods have been used to improve the wear resistance and mechanical properties of UHMWPE. Chemical crosslinking by peroxides and organosiloxanes and plasma and  $\gamma$ -ray radiation crosslinking are widely practiced. The incorporation of fillers or fibers into UHMWPE is another promising approach.<sup>3–8</sup> The quality of filler dispersion and the interfacial adhesion among various components play an important role in the determination of the wear resistance and the mechanical properties of these composites.

Our previous study, in which poly(ethylene terephthalate) (PET) fibers were used to improve the abrasive wear behavior of the UHMWPE matrix, showed that the mechanical properties of the composites were lower than those predicted by the additivity rule.<sup>9</sup> That study highlighted the necessity of the surface modification of the matrix and/or fibers to improve the interfacial shear strength between the two phases. In this article, we report the effects of the chemical modification of UHMWPE powders on the physicomechanical and tribological properties of UHMWPE/PET composites.

Correspondence to: M. Kontopoulou (kontop@chee.queensu.ca).

Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada.

Contract grant sponsor: Ministry of Science Research and Technology of Iran (in the form of a scholarship to M.R.).

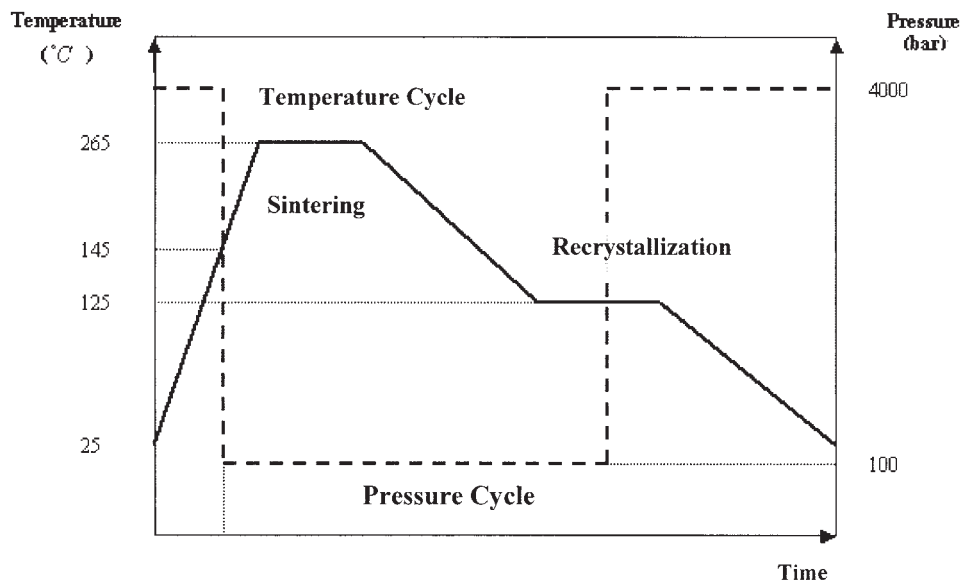


Figure 1 UHMWPE compression-molding cycle.

## EXPERIMENTAL

### Sample preparation

UHMWPE powder (product no. 429015) with a bulk density of  $0.94 \text{ g/cm}^3$ , particle size of  $150\text{--}180 \text{ }\mu\text{m}$ , intrinsic viscosity of  $25.5 \text{ dL/g}$ , and viscosity-average molecular weight of  $4,538,730 \text{ g/mol}$  was provided by Sigma-Aldrich (Oakville, ON, Canada). PET fibers were obtained from Iran Polyacryl Co. (Isfahan, Iran) with a fineness of 150 deniers and a diameter of  $18 \text{ }\mu\text{m}$ . The sizing of the PET fibers was removed by petroleum ether. Composites containing 5 wt % PET were prepared by the mechanical mixing of the UHMWPE powder and chopped PET fibers (ca. 6 mm in length) under an inert atmosphere to create electrical charges by triboelectrification. With this method, the fiber agglomerates were broken, and a nearly homogeneous mixture was achieved. Compression-molded samples were prepared with the temperature and pressure profiles depicted in Figure 1.<sup>9</sup>

### Surface modification of UHMWPE

Etching by chromic acid (CA) was used for surface modification. A CA solution was prepared by the mixture of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and distilled water in a 7:150:12 mass ratio. The UHMWPE powder was submerged in the etching solution at room temperature for 30 min. After etching, the powder was washed in distilled water and acetone, dried in a vacuum oven at room temperature for 12 h, and stored in  $\text{N}_2$  gas. A detailed characterization of the modified samples is presented in part I of this article.<sup>10</sup>

### Differential scanning calorimetry (DSC)

The degree of crystallinity ( $X_c$ ), melting temperature ( $T_m$ ), and crystallization temperature ( $T_c$ ) were determined with a TA Instruments (New Castle, DE) differential scanning calorimeter (model Q series 100) calibrated with indium standard. Samples were heated at a rate of  $10^\circ\text{C/min}$  under a nitrogen purge to  $180^\circ\text{C}$  and kept at this temperature for 10 min to eliminate the influence of their previous thermal history. Subsequently, the samples were cooled to  $25^\circ\text{C}$  at  $5^\circ\text{C/min}$  and reheated to  $180^\circ\text{C}$ .  $X_c$ 's and  $T_m$ 's were obtained from the first and second heating endotherms.

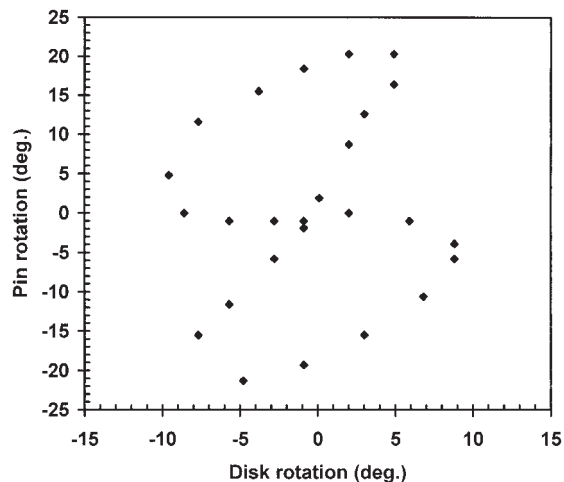


Figure 2 Figure-8 mode used in wear experiments.

**TABLE I**  
**Thermal Properties of UHMWPE and Unmodified and Modified UHMWPE/PET Composites**

Material	$X_c$ (%) <sup>a</sup>	$T_m$ (°C) <sup>a</sup>	$T_{m(\text{onset})}$ (°C) <sup>a</sup>	$T_c$ (°C)	$T_{c(\text{onset})}$ (°C)
UHMWPE	51.6, 46.2	145.9, 138.3	122.8, 115.3	118.9	123.0
Unmodified composite	53.5, 51.5	142.9, 141.4	116.1, 113.2	115.8	121.2
Modified composite	54.7, 53.7	141.4, 141.2	116.4, 113.5	115.2	120.5

$T_{m(\text{onset})}$ , onset temperature of melting;  $T_{c(\text{onset})}$ , onset temperature of crystallization.

<sup>a</sup> The first number corresponds to the first heating, and the second number corresponds to the second heating.

### Scanning electron microscopy (SEM)

The morphologies of the impact fracture surfaces of the samples and the worn surfaces of UHMWPE and the unmodified and modified UHMWPE/PET composites were observed with a Jeol 840 scanning electron microscope (Peabody, MA). All samples were coated with a thin layer of gold before SEM observations.

A SZ-PT 40 Olympus optical stereomicroscope was used to observe the distribution of fibers inside the polymer matrix. The pictures were taken with a charge-coupled device camera connected to microscope and were directly saved in electronic format.

### Tensile tests

Tensile tests were performed on the molded samples with a Zwick material testing machine (type BZ2.51TH1S) (Leominster, UK). Test specimens were stamped from compression-molded sheets with a metal cutting die. The specimens were prepared and tested according to ASTM D 638 (type III) at room temperature. The speed of testing was 1 mm/min, and the gauge length was 15 mm. The stress at break, strain at break, yield stress, and yield strain of the samples were calculated from the stress versus strain data. The average value of three experiments is reported.

### Impact tests

Impact tests were conducted on double-notched specimens prepared with compression molding according to ASTM D 256-93a. An Instron BLI impact tester

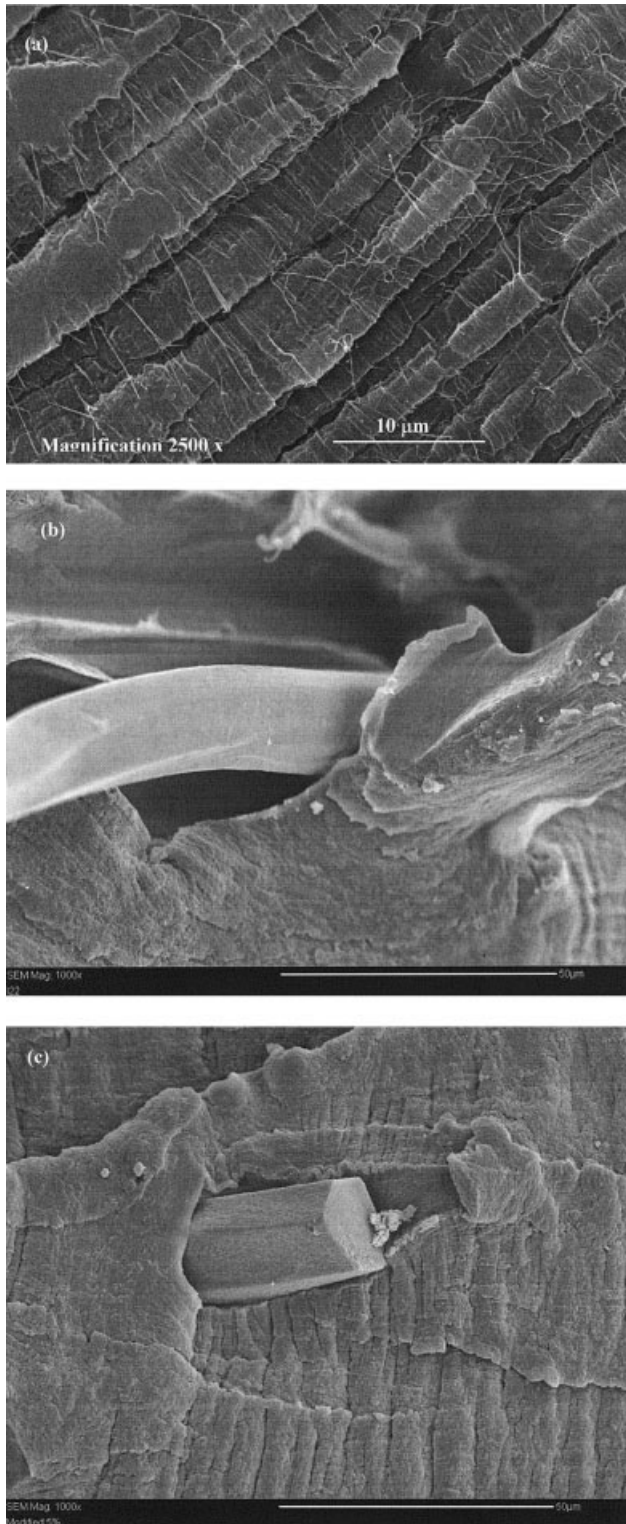
(SATEC model DI-300) (Burlington, ON, Canada) with a 240 cm kg hammer was used at room temperature. The average value of three experiments is reported.

### Wear tests

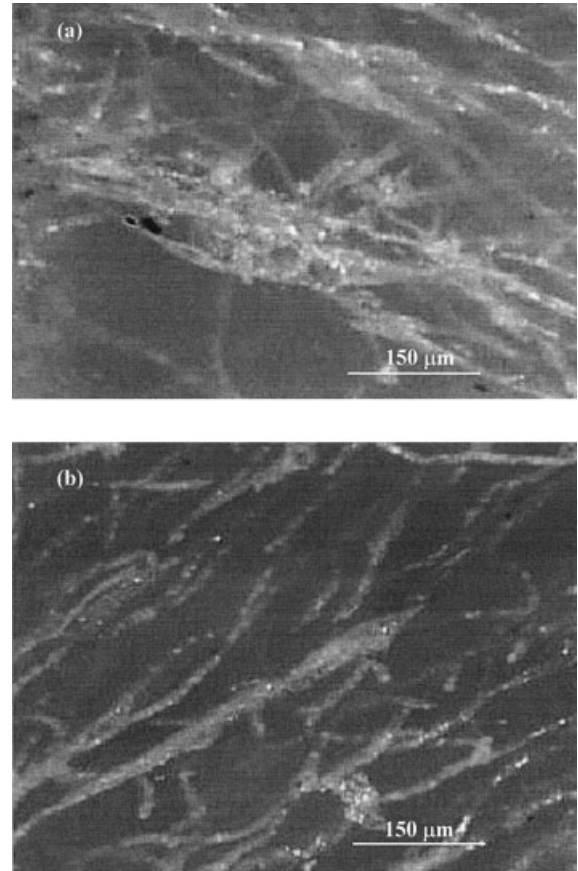
Wear testing of the composites was conducted on a model AMTI Ortho-POD (Watertown, MA) multimotion pin-on-disc wear-testing machine that was capable of testing six specimens concurrently. The wear rates of UHMWPE were dependent on the test conditions. The unidirectional smooth test produced less wear than the multidirectional test. In this study, a figure-8 wear pass, shown in Figure 2, was selected to apply cross shear to the samples. Pin-shaped samples with a length of 30 mm and a diameter of 10 mm were machined out of the compression-molded parts and used for the wear tests. The disc-shaped counterface was made of stainless steel with a surface roughness of 0.1  $\mu\text{m}$ . Wear tests were carried out at a normal load of 225 N, which produced a nominal contact stress of 2.87 MPa at a rotating velocity of 2 Hz and room temperature. Fetal bovine serum (Sigma-Aldrich, product no. F0926) was used as a lubricant. To minimize bacterial degradation, 0.2 wt % sodium azide was added to the fluid medium. Ethylenediaminetetraacetic acid was added to the serum at a concentration of 20 mM to bind calcium in solution and to minimize precipitation of calcium phosphate onto the bearing surfaces. The later event has been shown to strongly affect the friction and wear properties (ASTM F 732-82 and ASTM F 1714-96). After completion of the wear test, the pins were removed and cleaned. We determined the mass loss by weighing the test samples on a digital balance before and after wear testing.

**TABLE II**  
**Mechanical Properties of Plain UHMWPE and Unmodified and Modified 5 wt % UHMWPE/PET Composites**

Material	Yield stress (MPa)	Yield strain (%)	Stress at break (MPa)	Strain at break (%)	Impact strength (J/m <sup>2</sup> )
UHMWPE	19 ± 0.94	13.9 ± 0.51	29.2 ± 2.44	297 ± 15.02	0.075 ± 0.008
Unmodified composite	20.8 ± 1.13	13.9 ± 1.06	26 ± 1.41	211 ± 15.90	0.069 ± 0.005
Modified composite	19.2 ± 0.36	12.7 ± 1.21	23.7 ± 0.95	231 ± 31.79	0.102 ± 0.012



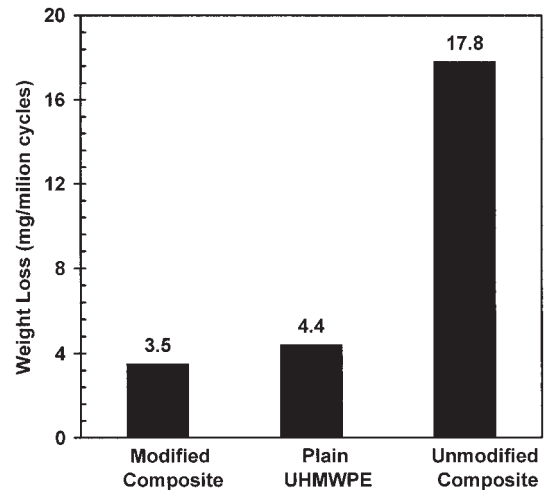
**Figure 3** SEM micrographs of (a) UHMWPE, (b) the UHMWPE/PET composite, and (c) the modified UHMWPE/PET composite (magnification = 1000×).



**Figure 4** Optical photographs of the surfaces of the (a) UHMWPE/PET and (b) modified UHMWPE/PET composites.

The volumetric wear rate ( $\dot{W}_v$ ) was calculated from the expression<sup>7</sup>

$$\dot{W}_v = \frac{\Delta m}{\rho N} \tag{1}$$



**Figure 5** Wear test results for plain UHMWPE and the UHMWPE/PET composites.

**TABLE III**  
Density, Friction Coefficient, and Volume Loss  
Values Obtained from the Wear Tests

Material	Friction coefficient	Density (kg/m <sup>3</sup> )	Volume loss (cm <sup>3</sup> /million cycles)
UHMWPE	0.0361	930	0.0047
Unmodified composite	0.0360	939	0.0189
Modified composite	0.0359	948	0.0037

where  $\Delta m$  is the weight loss,  $\rho$  the density of the material, and  $N$  is the number of rotating cycles. The reciprocal of  $\dot{W}_v$  rate is considered to be the wear resistance of the material.

The density of the samples, needed in eq. (1), was measured with an electronic densimeter (Mirage Trading Co. Ltd., Osaka, Japan) model MD-200S with a den-

sity resolution of 0.001 g/cm<sup>3</sup>). This densimeter used the Archimedes' principle and the determination of the relative density value based on the density of water at 4°C.

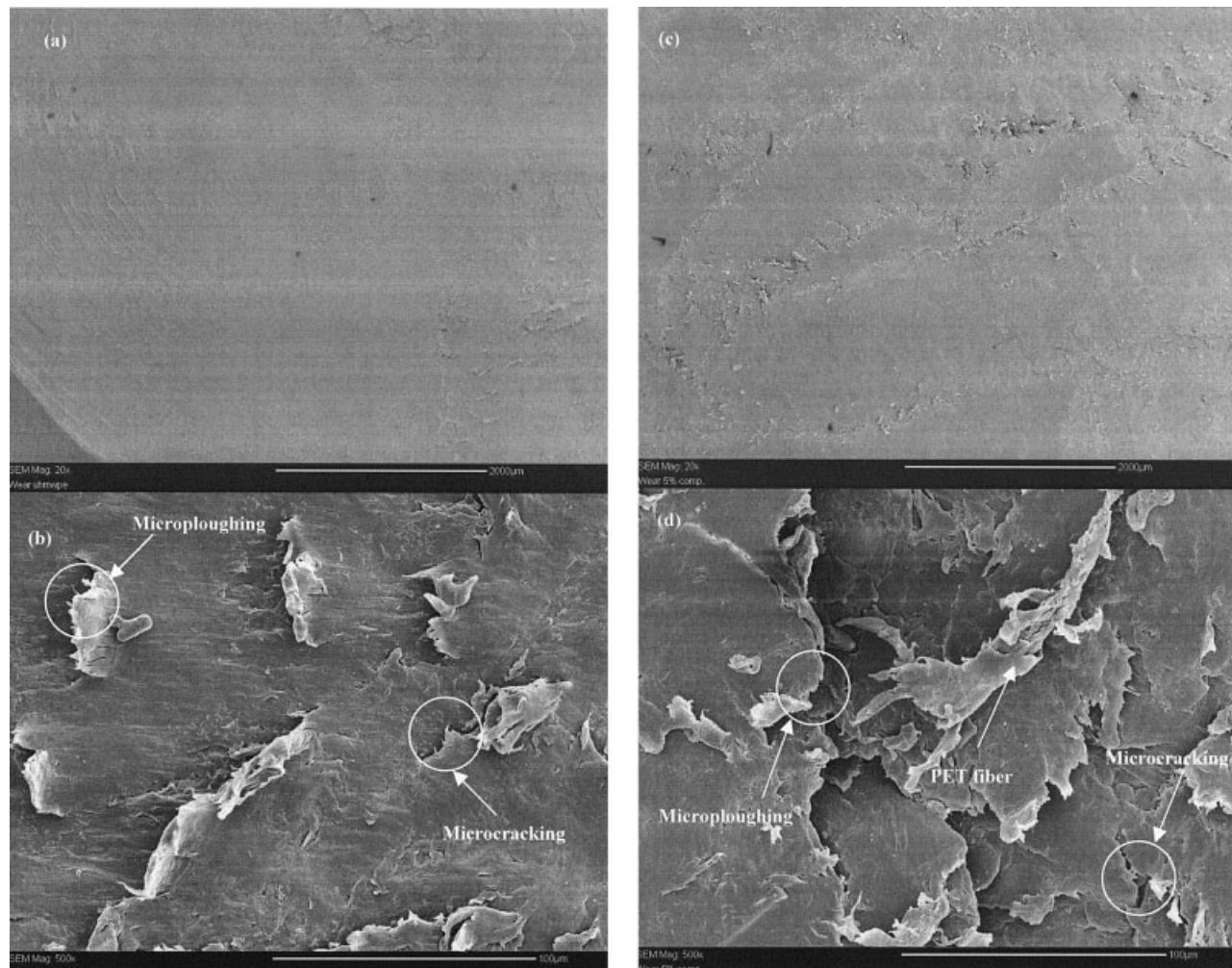
## RESULTS AND DISCUSSION

### Thermal properties

The DSC results are shown in Table I. In accordance with our previous findings,<sup>11</sup> the presence of PET fibers resulted in a higher crystallinity but delayed crystallization slightly, as evidenced by a decrease in  $T_c$ .  $X_c$  of the modified UHMWPE/PET composites was slightly higher than that of the unmodified composites, presumably because of the higher crystallinity of the modified UHMWPE, as discussed in part I.

### Mechanical properties

Overall the tensile properties of UHMWPE remained relatively unaffected by the addition of fibers, as



**Figure 6** SEM micrographs of worn surfaces of (a,b) plain UHMWPE, (c,d) the unmodified UHMWPE/PET composite, and (e,f) the modified UHMWPE/PET composite.

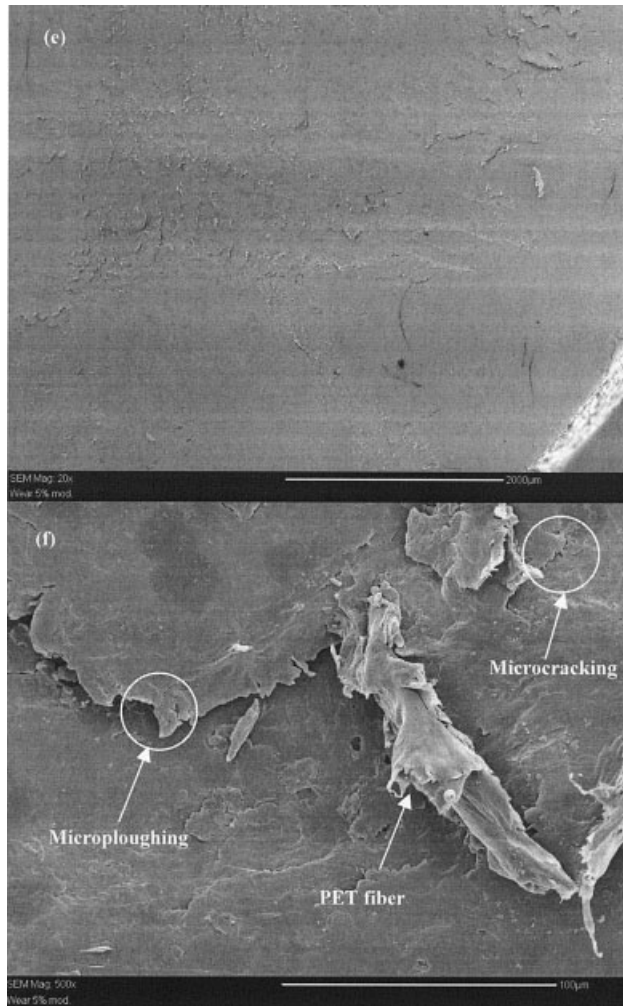


Figure 6 (Continued from the previous page)

shown in Table II. Although no substantial differences could be detected in the tensile properties between the unmodified and modified composites, the impact strength of the modified composite increased by 49 and 36% in comparison with the unmodified composite and plain UHMWPE, respectively.

The observed improvement of the impact properties may have been due to stronger fiber–matrix interactions, which stemmed from the presence of polar functional groups on the surface of modified UHMWPE, as discussed in part I. These groups increased the surface energy and wettability of the polymer and may have acted as sites for chemical or physical interactions with the fibers.<sup>1,2</sup>

This was corroborated by SEM observations of the impact fracture surfaces, shown in Figure 3(a–c). Figure 3(b) shows that the PET fibers pulled out and separated easily from the matrix; this provided evidence of poor interfacial bonding between the two phases. Interfacial adhesion between the two components was improved after the treatment of UHMWPE by CA, as shown in Figure 3(c).

Another possible explanation for the observed improvement in toughness is the enhanced dispersion of fibers in the modified matrix, as evidenced by images of the surface of the unmodified and modified UHMWPE/PET composites obtained by optical microscopy (Fig. 4).

Generally, because of the dry-mixing procedure and compression molding, the composites had a three-dimensional discontinuous fiber orientation. The main mechanism of dispersion of the fibers inside the matrix during dry blending was through triboelectrification, where the PET fibers and UHMWPE powder came in contact with each other and with the glass wall of the mixing apparatus, thus becoming electrically charged. In addition to electrostatic attraction, it has been reported that the oxidation of the powders and the presence of polar groups on the polymer surface, which can form hydrogen bonds with the PET fibers, may improve the state of dispersion of the fibers within the matrix.<sup>12</sup>

### Tribological properties

Figure 5 compares the wear properties of the two composites and the plain UHMWPE in terms of  $\Delta m$  per million cycles. The densities of the samples, friction coefficients, and volumetric loss [calculated from eq. (1)] are presented in Table III. The results show that although there was no significant difference between the friction coefficients of the composites, the volumetric loss of the modified UHMWPE/PET composite was 25% lower than that of the plain UHMWPE and 408% less than that of the unmodified composite.

The mechanism through which wear properties improved in the composites arose from the transfer of the contact load from the matrix to the fiber, which caused the contact pressure experienced by the matrix to be less than the nominal pressure exerted on it. Good fiber–matrix interaction and the homogeneous dispersion of the fibers were necessary conditions to improve the load-bearing capability of the composite. Apparently, this was not the case for the unmodified UHMWPE/PET composites because they experienced very severe  $\Delta m$ . Improved fiber–matrix interaction and more homogeneous dispersion were achieved by the chemical modification of the matrix, which led to substantially improved tribomechanical properties.

In general, wear in polymeric materials is a complex function of strong adhesion, abrasion, fatigue, macro-shearing, thermal and thermooxidative interaction, corrosion, cavitations, and so on.<sup>1,13</sup> The wear mechanism in polymeric materials is so complex that it is difficult to establish a unique model to describe it. It has been reported that adhesion and abrasion wear depend on the bulk properties and on the surface properties of the materials.<sup>1</sup> Improved wear resistance

is frequently associated with better mechanical properties. On the basis of our results, it can be concluded that the surface modification of UHMWPE results in improved toughness and a reduced volume of wear.

Figure 6 shows SEM images of the worn surfaces of UHMWPE and the unmodified and modified UHMWPE/PET composites at different magnifications. Scratch grooves were detectable on the worn surfaces under low magnification [Figs. 6(a,c,e)]. Two distinct wear mechanisms, microcracking and microploughing, were observed under higher magnifications [Figs. 6(b,d,f)]. The disparate thermal expansion properties of the fibers and matrix led to an inevitable buildup of residual stresses during fabrication. Therefore, it is possible that higher stress concentrations existed at the fiber ends, which caused weak areas that were more susceptible to damage during wear testing.<sup>5</sup> More defects were observed on the surface of the unmodified UHMWPE/PET composite because of the nonhomogeneous dispersion of fibers in the matrix, more pronounced fiber agglomeration, and poor adhesion with the matrix.

### CONCLUSIONS

Chemical modification of UHMWPE before the introduction of PET fibers resulted in composites with improved impact properties and wear resistance compared to the base material and to unmodified UHMWPE/PET composites. These improvements were attributed to improved interfacial bonding between the

polymer matrix and the fibers and to better dispersion of the fibers within the modified UHMWPE matrix.

Microploughing and microcracking associated with fatigue failure were observed on worn samples.

The authors would like to thank Leone Ploeg of the Human Mobility Research Center of Queen's University for her help in performing the pin-on-disk experiments.

### References

1. Xie, X. L.; Tang, C. Y.; Chan, K. Y. Y.; Wu, X. C.; Tsui, C. P.; Cheung, C. Y. *Biomaterials* 2003, 24, 1889.
2. Hofste, J. M.; Schut, H. G.; Pennings, A. J. *J Mater Sci Mater Med* 1998, 9, 561.
3. Marrs, H.; Barton, D. C.; Barton, R. A.; Jones, R. A.; Ward, I. M.; Fisher, J. *J Mater Sci Mater Med* 1999, 10, 333.
4. Liu, G.; Xiang, M.; Li, H. *Polym Eng Sci* 2004, 44, 197.
5. Hofste, J. M.; Smit, H. G.; Pennings, A. J. *Polym Bull* 1996, 37, 385.
6. Hofste, J. M.; Voorn, B. V.; Pennings, A. J. *Polym Bull* 1997, 38, 485.
7. Deng, M.; Shalaby, S. W. *Biomaterials* 1997, 18, 645.
8. Mosleh, M. *Alternative Bearing Surfaces in Total Joint Replacement*; ASTM STP 1346; American Society for Testing and Materials: West Conshohocken, PA, 1998; p 256.
9. Rezaei, M. PhD Thesis, Tarbiat Modarres University, Tehran, Iran, 2005.
10. Rezaei, M.; Ebrahimi, N. G.; Kontopoulou, M. *J Appl Polym Sci* 2006, 99, 2344.
11. Rezaei, M.; Ebrahimi, N. G.; Kontopoulou, M. *Polym Eng Sci* 2005, 45, 678.
12. Hofste, J. M.; Kersten, M. J. E.; Turnhout, J. V.; Pennings, A. J. *J Electrostat* 1998, 45, 69.
13. Schmalzried, T. P.; Callaghan, J. J. *J Bone Joint Surg A* 1999, 81, 115.