Surface Modification of Ultra-High-Molecular-Weight Polyethylene. I. Characterization and Sintering Studies

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ABSTRACT: We performed surface modification of ultra-high-molecular-weight polyethylene (UHMWPE) through chromic acid etching with the aim of improving the performance of UHMWPE's composites with poly(ethylene terephthalate) fibers. In part I of this study, we evaluated the effects of chemical modification on the surface properties of UHMWPE with X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and contact angle measurements. The thermal properties, rheology, and sintering behavior of the modified UHMWPE were compared to those of the base material. XPS and FTIR analysis confirmed the presence of carboxyl and hydroxyl groups on the surface of the modified powders. The substitution of polar groups into the backbone of the polymer decreased its contact angles with water and hexadecane and increased its surface energy, as evidenced by contact angle measurements. The modified UHMWPE was more crystalline than the base resin and less prone to thermal degradation. Although the rheological properties were virtually identical, the modified powders sintered more readily, presumably due to their higher surface energy, which suggested enhanced processability by compression molding. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2344–2351, 2006

Key words: polyethylene (PE); rheology; sintering; surfaces; thermal properties

INTRODUCTION

Ultra-high-molecular-weight polyethylene (UHMWPE) is used in artificial joints because of its high wear resistance and low friction coefficient. A major concern arising during long-term clinical performance of artificial joints is the possibility of adverse tissue reactions caused by the generation of UHMWPE debris. The debris is transported to the tissue surrounding the joint and causes chronic inflammatory reactions and bone resorption. It has been suggested that due to the presence of debris, macrophages release various cytokines and growth factors that induce bone loss.[1] UHMWPE homocomposites and UHMWPE/aramide fiber composites have been used to achieve improved wear rates in artificial joints.[2,3]

The addition of poly(ethylene terephthalate) (PET) fibers in UHMWPE has resulted in lower mechanical properties compared to the base material, presumably due to poor adhesion between the two phases.[4] To achieve satisfactory mechanical properties, it is desirable to improve the interfacial shear strength between PET fibers and the UHMWPE matrix.[4,5] This can be achieved through the surface modification of the matrix and/or fibers. Common surface modification treatments in polyolefins include plasma, corona-discharge, flame, and chemical treatments.[6–9]

The chemical etching of UHMWPE with chromic acid is a well-known method of surface modification that alters both the surface chemistry and surface properties such as roughness. The dissolution of hydrocarbon polymers by hexavalent chromium in acid media proceeds through the formation of a tetravalent chromium intermediate, which hydrolyzes to alcohol. Further oxidation causes chain scission, which yields olefins and aldehydes, ketones, or carboxylic acids.[10] Therefore, the modification mechanism involves the abstraction of hydrogen atoms from the polymer backbone and their replacement with polar groups (hydroxyl, carbonyl, carboxylic acid, and sulfonic acid groups) originating from the oxidizing agents. It is conceivable that hydrogen bonds are formed between the polar groups and the fibers,[9,10] which results in improved adhesion.

In addition to the introduction of polar functional groups to the surface of the polymer, chromic acid preferentially etches the amorphous regions of the polymer.[10,11] Depending on surface crystalline mor-

phology, highly complex root-like cavities may form on the etched surface, which results in dramatic improvements in the wettability and bondability.

In this study, we studied the surface characteristics of UHMWPE powder oxidized with chromic acid with X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and contact angle (θ_i) measurements. The thermal properties, rheology, and sintering behavior of surface-modified UHMWPE were investigated and compared with those of the base resin. This information is important for the assessment of the processing behavior and for the selection of the appropriate conditions for the processing of modified UHMWPE/PET fiber composites by compression molding.

EXPERIMENTAL

Materials

UHMWPE powder (product no. 429015) with a bulk density of 0.94 g/cm^3, a particle size of 150–180 μm, an intrinsic viscosity of 25.5, and a viscosity-average molecular weight of 4,538,730 was provided by Sigma-Aldrich (Oakville, ON, Canada).

We prepared a chromic acid solution by mixing potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), and distilled water in a 7:150:12 mass ratio. The UHMWPE powder was immersed in the etching solution at room temperature for different exposure times ranging from 1 to 60 min. After etching, the powder was washed in distilled water and acetone and was subsequently dried in a vacuum oven at room temperature for 12 h and stored in N_2 gas. Powders obtained with this treatment were subjected to surface characterization together with the base UHMWPE resin, as described later.

Surface characterization

IR spectroscopy

FTIR spectra were recorded between 400 and 4000 cm^{-1} with a Nicolet Avatar 360 ESP spectrometer (Madison, WI). The ratios of the peak intensities of the functional groups of interest to the peak intensity of the C—C peak at 1469 cm^{-1} were calculated.[12]

XPS

XPS analysis was carried out with a Kratos Axis Ultra (Chestnut Ridge, NY) with a monochromatized Al Kα X-ray source. The analyzed area was 700×300 μm in size, and the takeoff angle was 90°. The source was operated at 20 mA and 14 kV. For the survey spectra, a pass energy of 160 eV was used, whereas for the high-resolution spectra, the pass energy was 10 eV. The base chamber pressure was 5×10^{-9} Torr (1 Torr = 133.322 Pa). All data were processed with a Casa XPS (Bend, OR) data-reduction program.

θ_i measurements

θ_i's were measured with an AST Products (Billerica, MA) θ_i goniometer (model VCA-Optima). θ_i's were evaluated with the sessile drop method, with deionized water as the polar liquid and hexadecane as the nonpolar liquid. The surfaces were prepared by compression molding of the powders. Each measurement was taken three times in different areas of the surface to obtain an average value for the entire surface.

The harmonic mean method, which is suitable for low-surface-energy surfaces, was used to calculate the surface tension (γ) of the samples. Substitution of the harmonic mean equation in Young's equation gives[10]

$$(1 + \cos \theta_i)\gamma_i = 4\left(\frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p}\right) \quad (1)$$

where γ_i^d and γ_i^p are the dispersion and polar components, respectively, of the surface tension of the testing liquids, which for deionized water are 22.1 and 50.7 dyne/cm, respectively, and for hexadecane are 27.47 and 0, respectively; γ_s^d and γ_s^p are the dispersion and polar components, respectively, of the solid surface tension, which could be obtained by the measurement of the θ_i's of the liquids with the solid surface and solution of eq. (1) simultaneously for the two liquids.[10]

Scanning electron microscopy (SEM)

Gold-coated powders were examined in a Jeol 840 scanning electron microscope (Peabody, MA) under a voltage of 20 kV.

Thermal properties

The melting and crystallization points and the percentage crystallinity were determined with a TA Instruments differential scanning calorimeter (model Q series 100; New Castle, DE) calibrated with an indium standard at a heating rate of 10°C/min under a nitrogen purge. The ultimate degree of crystallinity (X_c) for the samples was calculated from the crystallization exotherm with eq. (2):

$$X_c = \frac{\Delta h}{\Delta h_{100}} \times 100 \quad (2)$$

where Δh is heat of crystallization of the sample and Δh_{100} is the heat of crystallization for 100% crystalline polyethylene, which was taken as 288 J/g.[13]

Thermogravimetric analysis (TGA) was carried out with a TA thermal analyzer instrument (model Q Se-
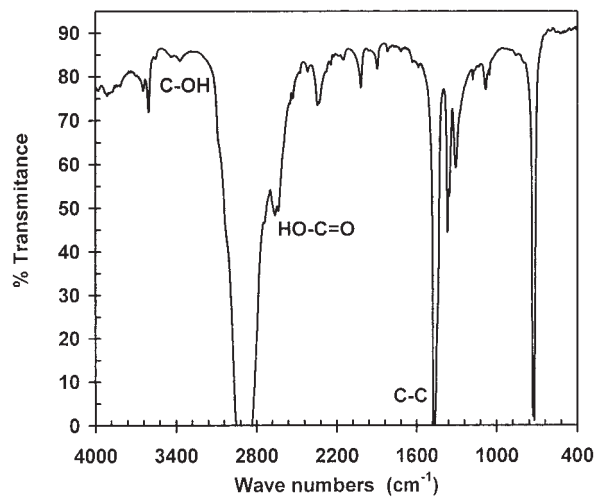
Figure 1 FTIR spectra of modified UHMWPE.

Figure 2 XPS survey spectra for (a) unmodified and (b) modified UHMWPE. (CPS, counts per second.)
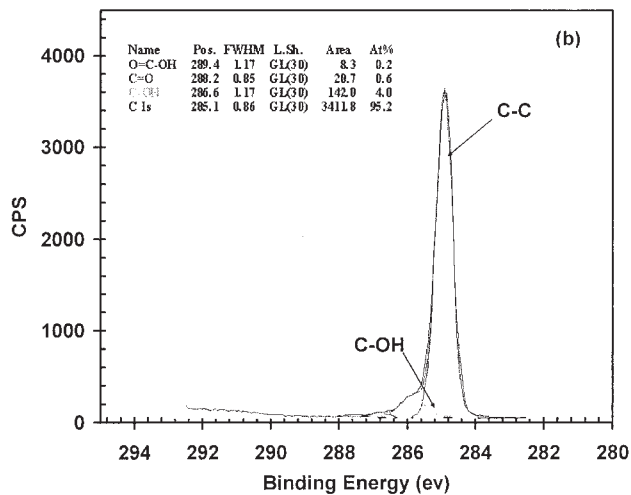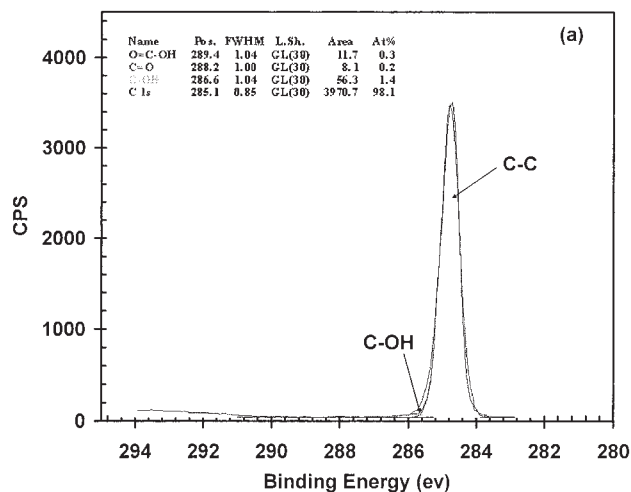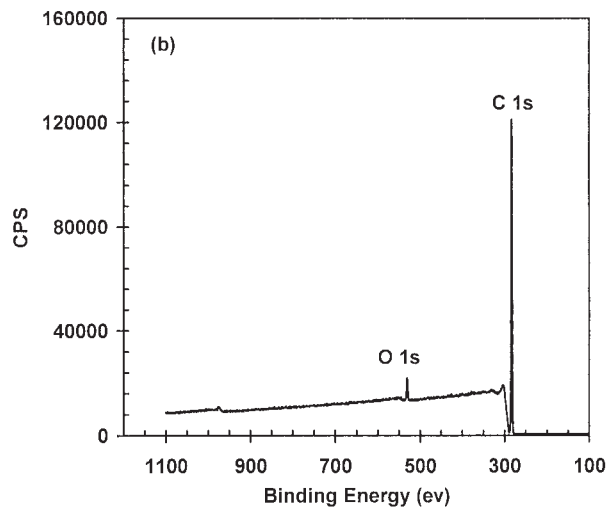

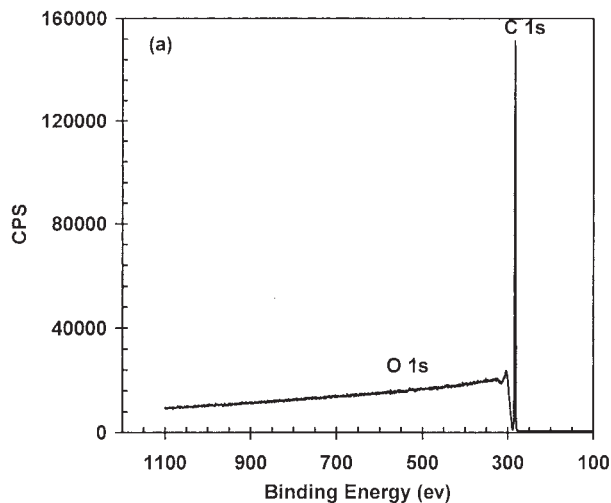
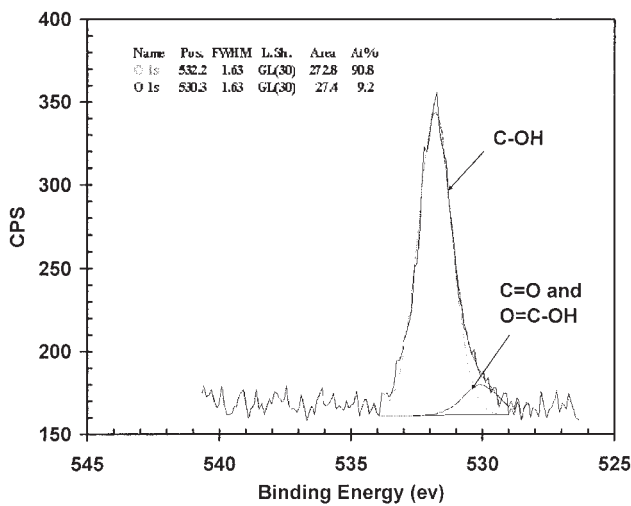**Figure 3** C1s spectra for (a) unmodified and (b) modified UHMWPE.

Figure 4 O1s spectrum from modified UHMWPE.

TABLE I
**Relative Intensities of the Components Representing Functional Groups Present on the Polymer Surface
and Corresponding Values of the O/C Atomic Ratio**

Material	Relative intensity (area) of C1s component (%)				Predicted O/C atomic ratio (%)
	C—C	C—OH	C=O	O=C—OH	
Unmodified UHMWPE	98.1	1.4	0.2	0.3	1.93
Modified UHMWPE	95.2	4	0.6	0.2	5.04

ries 500) to investigate the thermal degradation characteristics of unmodified and modified UHMWPE. A small amount of powder (5–6 mg) was placed in the instrument pan, and measurements were done isothermally at 265°C under nitrogen purge gas.

Rheological properties

An advanced polymer analyzer (Alpha Technologies, model APA 2000 dynamic mechanical rheological tester; Akron, OH) was used to measure the rheological properties as functions of frequency at a temperature range of 200–230°C. A biconical plate fixture was used for the measurements, which were performed under strain control. Strain sweeps were done to establish the region of linear viscoelasticity. Compression-molded disks were equilibrated between the plates at the desired start temperature before the trimming and beginning of the measurements.[14]

Sintering experiments

Sintering experiments were performed with a Linkam (Surray, UK) CSS 450 hot stage controlled by a central processor. The sintering process was recorded with a charge-coupled device camera connected to an SZ-PT 40 Olympus optical stereomicroscope (Melville, NY). Pictures were taken at fixed time intervals and directly saved in electronic format. The particle radius (a) was estimated from the measurements of the projected area of the particles and the diameter of the neck between the particles with the image analysis software Sigma Scan-Pro (Jandel Corp., Chicago, IL; 1993). Each sample consisted of two particles placed on a glass slide. Because the actual compression-molding process includes both isothermal and nonisothermal sintering,[4] sintering experiments were done under nonisothermal and isothermal conditions. Nonisothermal sintering experiments were carried out with a ramped temperature profile, which was programmed to simulate the conditions encountered during the actual compression-molding temperature profile. The neck growth ratio (y/a, where y denotes the length of neck growing between the two particles) was recorded as a function of time.[14,15]

RESULTS AND DISCUSSION

IR spectroscopy

Representative FTIR spectra are presented in Figure 1. Peaks corresponding to the carboxyl groups (2640 cm^{-1}) and hydroxyl groups (3373 cm^{-1}) were detected in both the unmodified and modified UHMWPE. The ratios of the peak heights of the carboxyl groups and hydroxyl groups to the height of the C—C peak occurring at 1469 cm^{-1} were 0.0314 and 0.0023, respectively, for unmodified UHMWPE and 0.0327 and 0.0035, respectively, for modified UHMWPE. This suggested an increase in carboxyl and hydroxyl species in the modified UHMWPE, although no other oxidation products could be identified. There was no detectable difference in the FTIR spectra obtained for different etching times; therefore, in the following sections, only results corresponding to the 30-min exposure time are presented.

It should be noted that FTIR, being a bulk characterization technique, may not have adequate sensitivity for surface characterization. Further analysis was done by XPS spectroscopy, which is much more sensitive due to its shallow penetration (4 nm).

XPS

Figure 2(a,b) compares the XPS survey spectra of UHMWPE powders that were subjected to chromic acid etching for 30 min with those of the base material.

Minor amounts of oxygen were detected in the chromic acid modified UHMWPE powders, although there was no evidence of other elements, such as sulfur or potassium.

TABLE II
**θ and Calculated γ Values for Unmodified
and Modified UHMWPE**

Material	γ at 20°C (dyne/cm)			θ (°) with	
	γ	γ^d	γ^p	Water	Hexadecane
Unmodified UHMWPE	36.0	34.25	1.75	100.8	30.7
Modified UHMWPE	43.3	40.90	2.40	97.0	29.2

Material	X_c (%)	T_m (°C)	$T_{m(\text{onset})}$ (°C)	T_c (°C)	$T_{c(\text{onset})}$ (°C)
Unmodified UHMWPE	46.2	138.3	115.3	118.9	123.0
Modified UHMWPE	53.3	137.5	112.5	115.9	119.8

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

Spectra obtained in the carbon 1s (C1s) and oxygen 1s (O1s) regions are shown in Figures 3 and 4, respectively.

All information on the type and concentration of the surface oxidation products was contained in the tail of the C1s spectrum, which was toward the higher binding energies (Fig. 3). It has been reported that the C1s band shifts by about 1.5 eV for each increase in the oxidation state of carbon.[7] Curve fitting was performed on the basis of the known binding energies of hydroxyl (C—OH; 286.6 eV), carbonyl (C=O; 288.2 eV), and carboxyl (O=C—OH; 289.4 eV) groups. The resulting relative areas of the fitted curves representing surface atomic concentrations are presented in Table I. The modified samples showed a significant increase in C—OH species and a small increase in the higher binding energy component C=O.

The O1s peak was resolved into two peaks (Fig. 4). The major peak was ascribed to C—OH species, and the lower binding energy peak was ascribed to the higher binding energy carbon species, such as C=O and O=C—OH.

θ_i measurements

The γ's of the samples, including the dispersion component (γ^d) and the polar component (γ^p), are presented in Table II. The results show that surface modification of UHMWPE increased its surface energy because of the substitution of polar groups into the backbone of the polymer and, therefore, decreased the θ_i's with the test liquids. Increasing the polarity of the UHMWPE surface should improve its wettability with high-energy fillers, such as PET fibers, and thus improve the physicomechanical properties of their composites.

SEM

There were no detectable differences between the SEM micrographs of the unmodified and surface modified UHMWPE powders, possibly because of the inherently high internal porosity of the UHMWPE particles.

Thermal properties

Figure 5 compares the crystallization endotherms for the unmodified and modified UHMWPE. All of the thermal properties are summarized in Table III. Chromic acid etching preferentially removes the amorphous regions,[10,11] which resulted in a higher ultimate crystallinity for the surface-modified UHMWPE (53.3%) compared to the base polymer (46.2%).
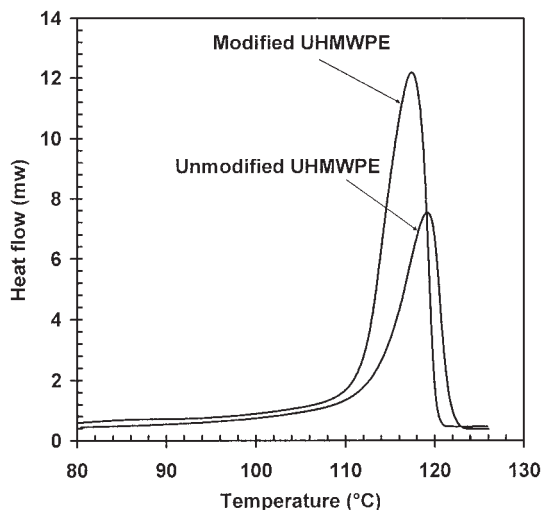
Figure 5 Differential scanning calorimetry endotherms of unmodified and modified UHMWPE versus temperature.
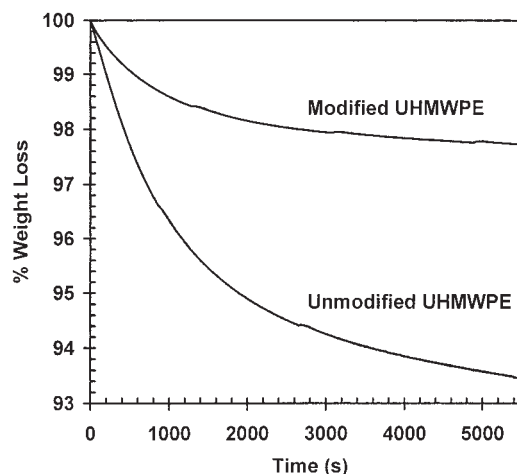
Figure 6 TGA of unmodified and modified UHMWPE (265°C).
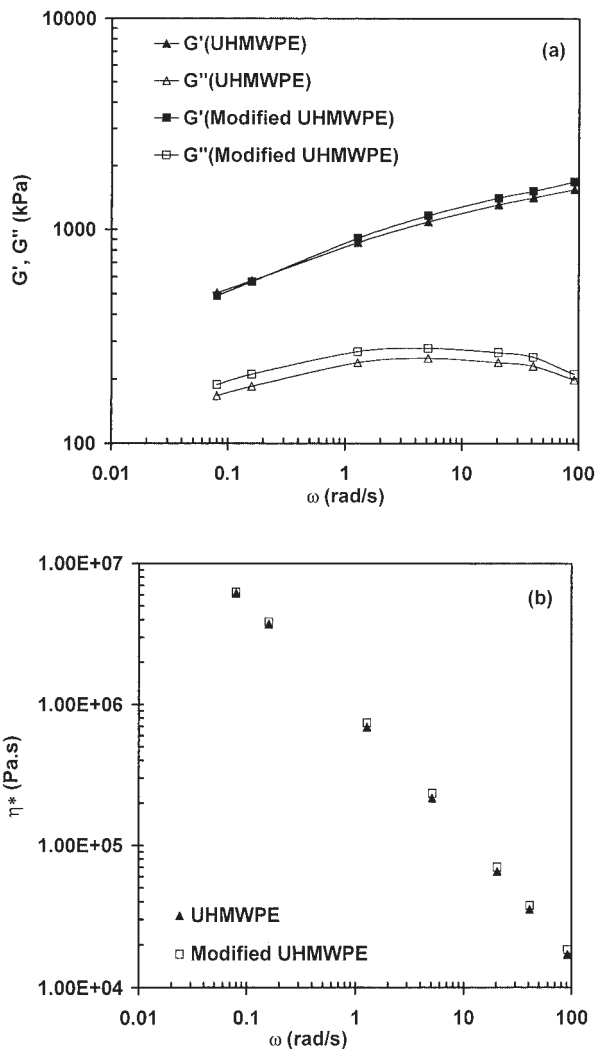
Figure 7 Viscoelastic properties of unmodified and modified UHMWPE as a function of frequency (ω) at a temperature of 230°C: (a) G' and G'' and (b) η^*. In part (a), lines are to guide the eye.

The TGA results shown in Figure 6 reveal that the modified UHMWPE was less prone to thermal degradation than the base resin.

Rheological properties

The dynamic storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) at 230°C, as functions of frequency are shown in Figure 7(a,b). The highly elastic character of these materials was revealed by the higher values of elastic moduli compared to G'', which resulted in tan δ values that were lower than 1 over the whole range of investigated frequencies. The viscoelastic properties of the modified and unmodified resins were virtually identical.

Sintering experiments

The sintering of UHMWPE particles is the controlling mechanism that takes place during compression

molding. Previous work has shown that the sintering of UHMWPE is not governed by viscous flow but rather by the surface properties because of the highly developed internal particle morphology of UHMWPE.[14,16,17] Because of the importance of the surface properties in the process, the effect of surface modification on the sintering behavior of the powders was studied under isothermal and nonisothermal conditions, as reported in the following section.

Nonisothermal sintering

The dimensionless neck growth (y/a) evolution as a function of time and temperature recorded during the nonisothermal experiments is shown in Figure 8(a,b) for the unmodified and modified UHMWPE. The corresponding images of the sintering process, obtained with the optical microscope, are shown in Figure 9.
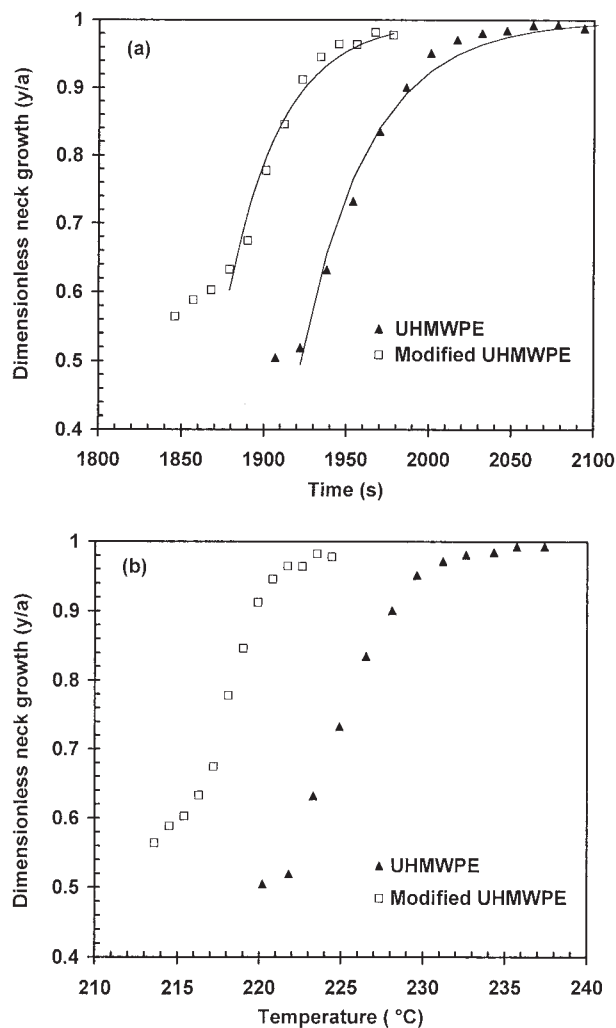
Figure 8 y/a evolution as a function of (a) time and (b) temperature for unmodified and modified UHMWPE under nonisothermal conditions. Symbols represent experimental data, and lines denote fits according to eq. (3).
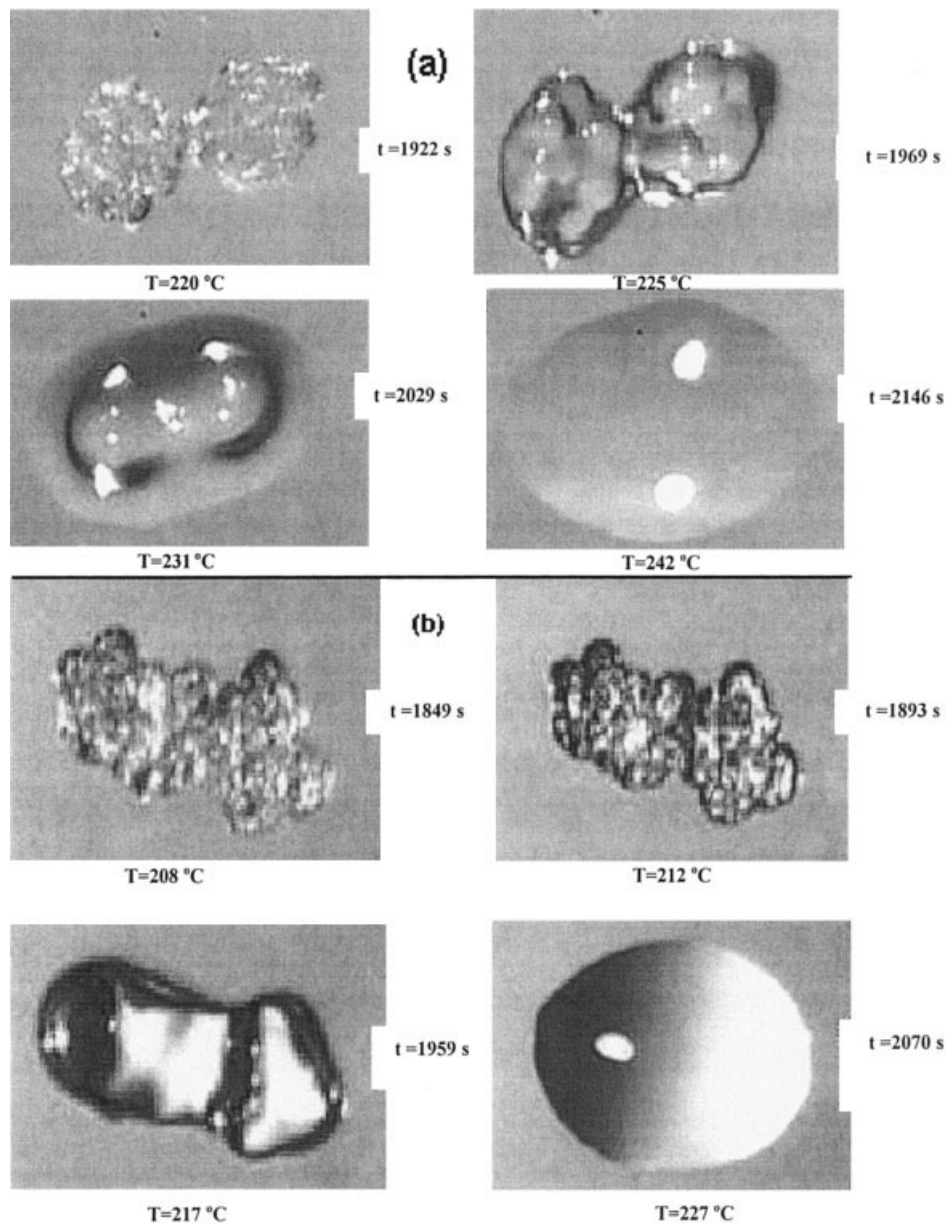
Figure 9 Optical photographs depicting nonisothermal sintering sequences for (a) unmodified and (b) modified UHMWPE under the same conditions as in Figure 8(a).

For comparative purposes, the coalescence curves were described by the performance of curve fitting with the following expression:[14,15]

$$y/a = 1 - Ae^{-(t/t_s)} \qquad (3)$$

where t, t_s, and A are time, characteristic sintering time, and a sintering constant, respectively. The fits are shown in Figure 8(a). To compare the rate of coalescence, the following characteristic parameters were used to describe the coalescence process: the onset time (t_{onset}) and the onset temperature (T_{onset}) at which coalescence began, the time required to reach 99% of complete neck growth, and the initial slope [$d(y/a)/dt$]. These parameters are presented in Table IV.

Although the melting temperatures of the modified and unmodified UHMWPE were very similar (see

TABLE IV
Nonisothermal Sintering Parameters for Unmodified and Modified UHMWPE

Sintering parameter	UHMWPE	Modified UHMWPE
t_{onset} (s)	1922	1849
T_{onset} (°C)	220	214
t_s (s)	41.5	38.14
$d(y/a)/dt$	0.0055	0.0048

Table III), the onset of sintering neck growth occurred significantly earlier in the former, presumably because sintering was facilitated by the increased surface energy of the material.
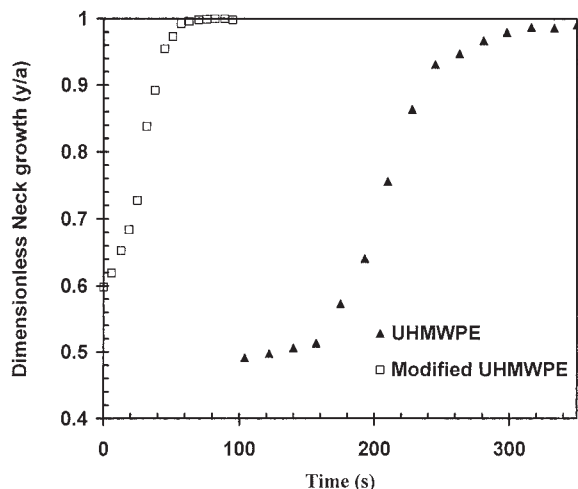
Isothermal sintering

Figure 10 shows the isothermal sintering curves for unmodified and modified UHMWPE at 220°C. t_{onset} and the slopes of the curves obtained at different temperatures are presented in Table V. In agreement with the findings on nonisothermal sintering, lower temperatures were sufficient for the completion of the sintering process in the modified UHMWPE.

CONCLUSIONS

Characterization by XPS and FTIR revealed the presence of carboxyl and hydroxyl oxidation products when UHMWPE powders were oxidized with chromic acid.

The substitution of polar groups into the backbone of the polymer resulted in decreased θ_i's with water and hexadecane and an overall increased surface energy.

Surface modification of UHMWPE removed some amorphous polyethylene and increased the thermal stability and ultimate crystallinity of this polymer.

TABLE V
Isothermal Sintering Parameters for Unmodified and Modified UHMWPE

Temperature (°C)	t_{onset} (s)	$d(y/a)/dt$
Unmodified UHMWPE		
220	157	0.0047
230	70	0.0097
240	42	0.0087
250	8	0.0177
Modified UHMWPE		
195	276	0.0028
200	152	0.0038
210	81	0.0068
220	13	0.0086

Although the rheological properties remained unaltered, the change in surface energy resulted in an enhanced sinterability of the UHMWPE powders.

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Figure 10 Comparison of y/a evolution for unmodified and modified UHMWPE under a constant temperature of 220°C.