

Wear resistance of some modified ultra-high molecular weight polyethylenes and its correlation with tensile properties

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Received: 13 January 1999/Revised version: 1 March 1999/Accepted: 16 March 1999

Summary

Ultra-high molecular weight polyethylene (UHMWPE) was modified on purpose to enhance the wear resistance. The modification was done either by crosslinking the amorphous region of the surface using difunctional monomers or by crosslinking the bulk in the melt state using peroxide. The changes in thermal and tensile properties indicated that the modifications were effected. The volumetric wear rate, determined on a pin-on-disk wear tester, was suppressed by the modifications. The correlation between the tensile properties and the wear rates was sought. Any single tensile property or tensile rupture energy did not correlate well with the observed wear rate. Instead, the ratio of maximum contact stress calculated by the Hertz's contact theory to yield stress appeared to correlate well with volumetric wear rate.

Introduction

UHMWPE has been used as a substitute for damaged or diseased cartilage in total joint prosthesis for many years (1,2). Beside its superb wear resistance, the good mechanical property, chemical resistance, and biocompatibility were the factors that ensure the extensive use of UHMWPE. However, cases indicating problems associated with the material have been reported in recent years. The primary problem is the constant generation of submicron-sized wear debris, which overwhelms the body's ability to remove the material, limiting the longevity of total joint prosthesis (3,4). This debris may be responsible for initiating a series of deleterious processes resulting in loosening of the implant, pain to the patients, and eventually revision surgery for some patients.

Many efforts were exercised to enhance the wear resistance of UHMWPE, although few of them appeared to be successful. In an effort of the same sort, UHMWPE was modified with two different methods in the present study. One was introducing semi-interpenetrating network (IPN) structure or crosslinks only in the amorphous region of UHMWPE, maintaining the crystalline region intact. Two aromatic difunctional monomers, divinylbenzene (DVB) and diallyl phthalate (DAP), were used. The other was chemical crosslinking in the melt state, consequently reducing the crystallinity of UHMWPE. Dicumyl peroxide (DCP) and triallyl cyanurate (TAC) were used as a crosslinking agent and a crosslinking promoter, respectively.

Another objective of this study was to seek a relationship between mechanical property

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and wear resistance of polymer, since there has not been a clear explanation on the correlation between wear and mechanical properties. In the course of investigating the structure, mechanical and wear properties of the modified UHMWPE, a possible parameter involving contact stress and tensile property is proposed.

Experimental

Materials and Modifications

Two types of UHMWPE were used; powder for compression molding and bulk for surface modification. The powder UHMWPE was medical grade Hizex 240M supplied by Mitsui Petrochemical Industrial Co. The bulk UHMWPE was supplied in the form of a rod by The Hospital for Special Surgery/Poly Hi Solidur, which was ram-extruded GUR415 resin from Hoechst-Celanese.

The modification by DVB or DAP was performed by first soaking a sample in the liquid monomer containing 5 wt % of α -hydroxy- α,α -dimethyl acetophenone (Darocure 1173) as a photoinitiator at 120 °C for 30 min. Gravimetric analysis indicated that the diffusion of the monomer into a 300- μ m thick film was saturated in 15 min. The samples were then irradiated by UV with a 2-kW high-pressure mercury lamp in N₂ atmosphere at 60 °C for 60 min. The modification with DCP or DCP/TAC was carried out in the melt state. 100 g of UHMWPE powder were mixed with the solution in which 0.5 g of DCP or the same amount of DCP together with 2.0 g of TAC were dissolved in 300 mL of acetone. After removing acetone using a rotary evaporator and subsequently a vacuum drying oven at 40 °C for 24 hours, the mixture was compression molded to film or disk specimen at 180 °C. The crosslinking modification was effected in this stage.

Thermal characterization

Thermal properties were characterized with a Perkin-Elmer DSC-4 differential scanning calorimeter. Samples of ca. 5.0 mg in aluminum cells were heated from room temperature to 180 °C at a rate of 10 °C/min, held for 5 min, and then cooled to room temperature at 10 °C/min. Melting temperature, T_m , and crystallization temperature, T_{mc} , were identified at the peaks of melting endotherm and crystallization exotherm, respectively. Heat of fusion was determined by comparing the area under melting endotherm with that of Indium standard having a known heat of fusion of 28.4 J/g (5). The degree of crystallinity, X_c , was calculated by dividing the measured heat of fusion per gram by the heat of fusion of an ideal polyethylene crystal of 292 J/g (6).

Tensile measurement

The tensile specimen of DVB-or DAP- modified UHMWPE was prepared by first compression molding a 300- μ m thick film with UHMWPE powder, cut to strips of 10 mm width, and modified. DCP- or DCP/TAC-modified UHMWPE powder was compression molded to a film and cut to strips. Using a Lloyd LR-10K universal testing machine, tensile tests were conducted at room temperature with a crosshead speed of 500 mm/min and a gauge length of 50 mm according to ASTM D882-91.

Wear test

The pin-on-disk type wear test machine constructed and used was composed of a

stationary metal pin and a rotating polymer disk. A Co-Cr alloy pin with a diameter of 1 mm and a hemispherical tip with the radius of curvature of 10.42 mm slid on the surface of polymer disk tracking a circle of 36 mm in diameter at a sliding velocity of 107 mm/s. The pin was cut out from the femoral head component of an actual prosthesis, polished with a sand paper and lapped to have a center-line average roughness, r_a , of ca. 0.03 μm . The polymer disk of DVB- or DAP-modified UHMWPE was prepared as follows: A disk was cut out of the rod to have a dimension of 70 mm diameter and 10 mm thickness, lapped to r_a below 0.05 μm , and modified. DCP- or DCP/TAC-modified UHMWPE powder was compression molded to a disk with the same dimension, and polished to the same surface roughness as above.

Wear tests were lubricated with calf serum containing 0.2 vol % sodium azide to inhibit bacterial contamination, and were carried out at room temperature. A constant normal load of 10 N was applied vertically on the pin, and the number of sliding cycles was fixed at 200000 for all the tests. During the tests, friction coefficients were monitored by the equipped load cell. Wear rate or volumetric wear per cycle, R_w , was determined by measuring the cross-sectional area of the wear track after removing the pin, using a Tencor Instruments Alpha-Step profilometer.

Results and discussion

Thermal properties

The thermal properties of the modified UHMWPE measured by DSC were shown in Table 1. At the first heating scan, the crystallinity and the melting temperature of DVB- or DAP-modified UHMWPE were little changed from those of the control sample. This indicated that the monomers penetrated selectively into the amorphous region of UHMWPE, and that the crystalline phase was little influenced by the diffusion and photopolymerization of the monomers. At the second heating scan, however, the modified UHMWPE showed lower T_m and X_c than those obtained at the first scan. The smaller lamellar thickness and lower crystallinity were attributed to the fact that during the cooling process after the first heating scan, the crosslinks formed by the modification in the amorphous region of UHMWPE hindered the chains from crystallizing (7). The decrease in T_{mc} also reflected the hindered crystallization.

For DCP- or DCP/TAC-modified UHMWPE, since the specimens were crosslinked in the melt state and then cooled, X_c , T_m , and T_{mc} determined at the first heating scan and cooling were lower than those of unmodified UHMWPE. Crystallization process appeared to be

Table 1. Thermal properties of modified UHMWPE

Modifier	T_m ($^{\circ}\text{C}$)		X_c (%)		T_{mc} ($^{\circ}\text{C}$)
	1st scan	2nd scan	1st scan	2nd scan	
DVB	131.8	129.5	47.2	34.6	113.6
DAP	133.2	129.7	48.8	37.7	113.5
None (control)	132.0	-	46.9	-	116.0
DCP	126.4	-	41.5	-	114.0
DCP/TAC	118.0	-	35.3	-	106.0

much more hindered in DCP/TAC-modified UHMWPE than in DCP-modified UHMWPE, which was indicated by the much lower values of X_c , T_m , and T_{mc} . It was suggested that crosslinking efficiency be greatly enhanced by the addition of TAC (8).

Tensile properties

The stress-strain curves of the modified UHMWPE were shown in Figure 1, and the tensile properties were summarized in Table 2. The Young's modulus, E , and the yield stress, σ_y , of DVB- or DAP-modified UHMWPE were higher than those of the unmodified UHMWPE. The increases were thought to be due to the structural change and the stiffening in the amorphous region of UHMWPE. Although it is true that both properties are directly influenced by crystallinity (9), the changes in crystallinity were negligible from the control specimen. It was therefore considered that the rigid aromatic monomers, by either forming semi-IPN with UHMWPE chains or crosslinking UHMWPE chains, reinforced the amorphous region of UHMWPE, leaving the crystals alone. The reinforcing effect was larger in the DVB modification due presumably to the fact that DVB was smaller in molecular size and more compatible with UHMWPE than DAP was. The calculated solubility parameter values for UHMWPE, DVB, and DAP were 16.0, 17.4, and 18.1 $\text{MPa}^{1/2}$, respectively (10).

E and σ_y of DCP- or DCP/TAC-modified UHMWPE were lower than those of the unmodified UHMWPE. In these instances, the decreases in crystallinity and lamellar thickness appeared to result in the decrease in these small-strain tensile properties (11,12). When TAC was used with DCP, both properties were further decreased, reflecting the enhanced crosslinking in the melt state and the consequent lower crystallizability.

The tensile behavior of the modified UHMWPE at large deformations was different from the small-deformation tensile behavior discussed above. The elongations at break of the modified UHMWPE were lower than that of the unmodified UHMWPE. The results were also attributed to the structural changes in the amorphous and crystalline regions of the modified UHMWPE.

Unlike other polyethylenes, UHMWPE shows early onset of strain hardening after yield without apparent yield drop, which is a characteristic found in elastomeric materials (13).

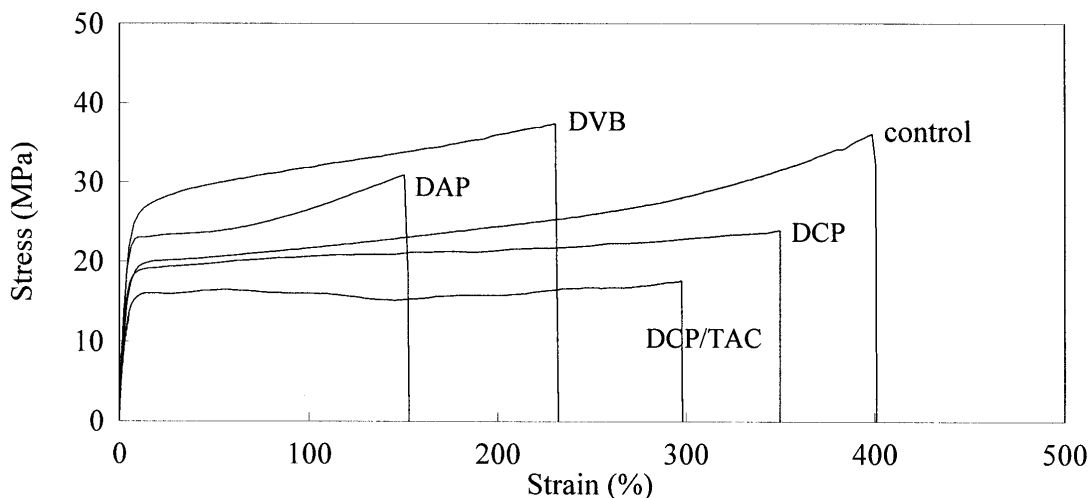


Figure 1. Stress strain curves of the control and the modified UHMWPE.

Table 2. Tensile and wear properties of modified UHMWPE

Modifier	E (MPa)	σ_y (MPa)	σ_u (MPa)	ϵ_u	R_w^*	$\sigma_u \epsilon_u$ (MPa)	σ_{max} (MPa)	σ_{max}/σ_y
DVB	916	27.1	37.4	2.32	4.84	88.2	28.9	1.07
DAP	817	23.1	30.9	1.52	5.58	47.0	26.8	1.16
None (control)	721	19.9	36.1	4.01	10.53	144.0	24.7	1.24
DCP	640	19.0	23.9	3.50	6.73	130.0	22.8	1.20
DCP/TAC	416	16.0	17.6	2.98	4.74	71.5	17.1	1.07

* volumetric wear per cycle ($\times 10^{-6}$ mm³/cycle)

The behavior originates from the unique microstructure of UHMWPE. The microstructure of UHMWPE is not fully spherulitic. Rather it is a composite-like structure in which small crystalline lamellae, connected by tie molecules, are dispersed over the amorphous matrix (14,15). Upon the deformation beyond yield point, entanglements in the amorphous region and lamellar blocks act as physical and chemical crosslinks, hindering molecular chains from slipping and orienting along the direction of applied stress. The role of physical crosslinks in reducing the drawability has been well known in the molecular weight effect. Increase in entanglement density with increasing molecular weight results in the decrease in elongation at break of polyethylene (9).

The elongation at break or ultimate strain, ϵ_u , of DVB- or DAP-modified UHMWPE was lower than the control specimen by a factor of about two. The decrease could be explained by the effect of added physical and chemical crosslinks, which were introduced to the amorphous region by the modification. The semi-IPN and crosslinks further hindered the slippage and orientation of the chains, resulting in the lower drawability of the specimens. The tensile strength or the ultimate stress, σ_u , of the modified specimen was kept high due apparently to the high yield stress and the subsequent strain hardening.

The lower ϵ_u of DCP- or DCP/TAC-modified UHMWPE could also be attributed to the effect of added crosslinks by the modification. The lower σ_u and the less-limited drawability of these specimens, compared with those of DVB- or DAP-modified specimens, were thought to be due to the smaller amount of crystalline lamellae, which acted as the crosslinks and strain-hardened the specimen. In all of the four modified UHMWPE, the product of σ_u and ϵ_u , which is known as tensile rupture energy, were lower than that of the unmodified UHMWPE.

Wear resistance and its correlation to tensile property

The results of profilometry showing the cross-section of the wear tracks were presented in Figure 2, and the wear rates, R_w , of the specimens were listed in Table 2. The wear rates of all four of the modified UHMWPE were lower than the unmodified UHMWPE, indicating the enhanced wear resistance by the modifications. Tensile properties were widely varied in these materials depending on the modification method, as discussed above. None of the properties, however, appeared to directly correlate with the observed wear rate.

In the previous studies, various mechanical properties have been suggested as the governing factor that would determine the wear rate. Modulus, yield stress, and tensile

strength were reported to be inversely proportional to R_w in a study with polyethylene (16). Tensile rupture energy ($\sigma_u \epsilon_u$) has been suggested and widely accepted to correlate well with wear resistance in many polymers (17-19). However, the correlation has failed in many cases, especially when the contacting interface was smooth. Although it is known, in polyethylene, that wear rate decreases with increasing molecular weight (20), tensile rupture energy decreases significantly (9). The wear rate of UHMWPE reinforced with Aramid or Spectra (UHMWPE) fiber was reported to be suppressed, despite the decrease in $\sigma_u \epsilon_u$ (21, 22). Also in the present work, $\sigma_u \epsilon_u$ did not correlate with R_w , as shown in Table 2.

Adhesive, abrasive, and fatigue wear have been identified as the wear mechanisms on retrieved implants (23). When the harder metallic surface is very smooth and the contacting interface is well lubricated as in the present tests, the adhesion component of wear becomes negligible. The monitored friction coefficient was in the range between 0.1 and 0.2, and no transfer film was observed on the pin. Under this condition, the wear of a polymer is generated exclusively by mechanical processes, i.e., abrasion and fatigue, and the wear resistance can be determined by the mechanical properties of polymer and the magnitude of contact stress. We thought, therefore, that it was appropriate to examine the interaction between stress and material property that responds to the stress.

Generation of wear debris can be divided into three successive processes; plastic deformation, crack formation, and tearing of debris from the surface. In the early stage of wear the resistance to plastic deformation, rather than ultimate properties like tensile rupture energy may be more important, especially when the contacting interface is smooth enough to avoid excessive cutting. In this context the yield stress, which is defined as the stress at the start of plastic deformation, may be the mechanical property that governs the early stage wear. Since the number of sliding cycle of 200000 was not very high, it was considered that yield stress might correlate well with the wear result of the present work.

The stress that actually acts on and causes the wear of surface is contact stress rather than

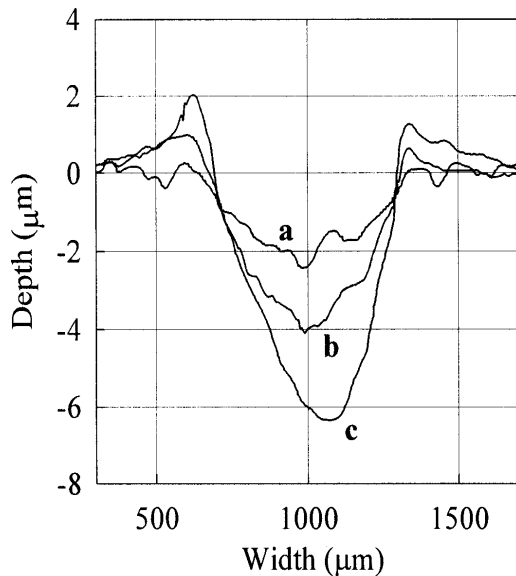


Figure 2. Profiles of the cross section of wear tracks: (a) DVB-modified, (b) DCP-modified, and (c) the control UHMWPE.

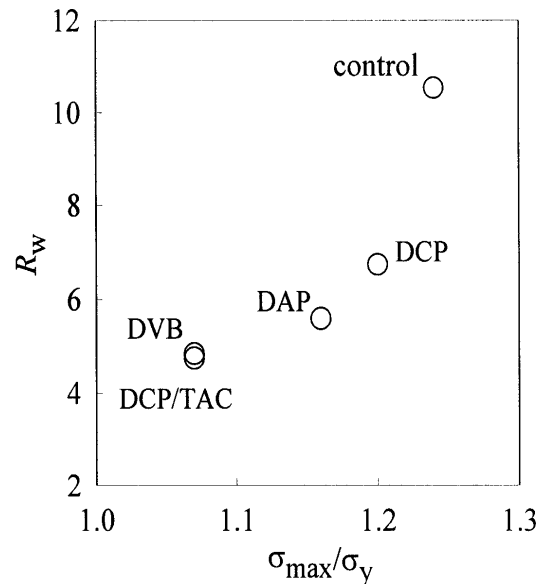


Figure 3. Relation between the wear rate and the ratio of maximum contact stress to yield stress.

mere applied stress. The magnitude of contact stress can be estimated by using Hertz's elastic contact theory (24), which calculates the stress from contact geometry and material parameters. It was thought that the elastic theory could be used for the present purpose, since the apparent contact stress (based on the full contact) of 12 MPa was well below the yield stress of UHMWPE.

For the calculation the reduced radius of curvature, r_{red} , and the reduced Young's modulus, E_{red} , were calculated by the following equations:

$$r_{\text{red}} = \left[\frac{2}{r_p} + \frac{2}{r_d} \right]^{-1} \quad \text{and} \quad E_{\text{red}} = \left[\frac{1}{2} \left(\frac{1 - \nu_p^2}{E_p} + \frac{1 - \nu_d^2}{E_d} \right) \right]^{-1}.$$

The radii of curvature (r) and the Poisson's ratios (ν) of the pin and the disk were $r_p = 10.42$ mm, $r_d = \infty$, $\nu_p = 0.3$, and $\nu_d = 0.46$ (25). The Young's moduli used were 210 GPa (26) for Co-Cr (E_p) and the values determined in the tensile tests for the polymers (E_d). Radius of contact circle, r_c , was given by the equation

$$r_c = \left[\frac{3Lr_{\text{red}}}{E_{\text{red}}} \right]^{1/3},$$

where L was the normal load. Finally, maximum contact stress, σ_{max} , the largest of the stress distribution and at the center of contact circle, could be calculated by the equation

$$\sigma_{\text{max}} = \frac{3L}{2\pi r_c^2}.$$

Using the applied normal load of 10 N, σ_{max} for the specimens were calculated and listed in Table 2.

We propose the ratio of maximum contact stress to yield stress, $\sigma_{\text{max}}/\sigma_y$, as a possible parameter that can predict the wear resistance. Although the ratio is not a material property, it is a physical parameter that compares actual deforming stress with resistance to deformation. As shown in Figure 3, the parameter correlated well with the wear rate for the modified and the unmodified UHMWPE. The correlation appeared to hold for the wear of Aramid fiber reinforced UHMWPE (21), for which $\sigma_u \epsilon_u$ failed to be the factor.

The dominant wear mechanism exerted in the present experiment was considered to be the ploughing, which is one of the abrasive wear mechanisms (27). The cutting mechanism of abrasive wear was thought to be much suppressed, since the surface of the pin was very smooth and the calculated contact stress was not large enough to cause a fast rupture. Fatigue wear was also not considered to be the major wear mechanism, for the number of wear cycle was not large enough.

Conclusions

In UHMWPE modified only in the amorphous region, modulus and yield stress were higher than those of the unmodified UHMWPE, while those of UHMWPE crosslinked in the melt state were lower. Elongations at break and tensile rupture energies of the modified UHMWPE were lower than those of the unmodified UHMWPE. Wear resistances of the modified UHMWPE were higher than that of the unmodified UHMWPE. The wear result did not correlate with any single tensile property. The ratio of

maximum contact stress to yield stress, σ_{\max}/σ_y , appeared to correlate well with the observed wear resistance, and was proposed as a parameter that can predict wear resistance of polymer in the early stage of wear.

Acknowledgment. Financial supports by Korea Institute of Science and Technology (KIST 2000) and Education of Research Foundation of SNU (Engineering Research Fund, 1997) are gratefully acknowledged.

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