Surface degradation features and microstructural properties of ultra-high molecular weight polyethylene (UHMWPe)

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Surface degradation of UHMWPe is recognized as a leading clinical concern, limiting the long-term performance in total knee replacements. Eight retrieved tibial plateaux and six wear screening test samples were evaluated for surface degradation features and microstructural features. The surface degradation features were assessed using stereomicroscopy and scanning electron microscopy. Microstructural features were evaluated using optical microscopy of thin cross-sections and a permanganate etching technique. The pitting mechanism of wear was observed on all eight retrieved TKR and covered an average of 12.6% of the surface area. The size of the pits were similar to the size of grains observed in the microstructural evaluation – approximately 100 to 200 μm. The presented observations of pitting in retrieved knee implants have shown that the post-processing microstructure may influence this mechanism of surface degradation and hence the wear products.

1. Introduction

The surface degradation of ultra-high molecular weight polyethylene (UHMWPe) bearing surfaces in orthopaedic implants is of leading clinical concern [1]. Total joint replacements typically involve the articulation of a metal or ceramic component and a polymeric component. The metal alloy is most commonly fabricated from a cobalt chromium alloy while the polymeric component is almost exclusively UHMWPe. Wear has several detrimental effects including the deterioration of articular performance. Also polymeric debris has been linked to an adverse biological reaction which can lead to loosening of the artificial joint, requiring revision surgery [2, 3]. Studies have demonstrated the relationship between wear properties and various characteristics of polyethylene including surface roughness [4], molecular weight [5] and starting resin [6]. Wrona *et al.* [7] have recently demonstrated an increase in surface degradation with increased incidence of defects in the consolidated UHMWPe of retrieved total knee replacements (TKR) and total hip replacements (THR). However, very little work has examined the role played by the arrangement of molecules within the polymer, or microstructure, on the overall wear properties of UHMWPe.

The role of a material's microstructure in determining its mechanical properties is recognized in most advanced materials. Manufacturing process control is imperative in order to achieve the desired microstructure; this is particularly true of polymeric materials [8]. In the orthopaedic industry, microstructure and grain size specifications exist for all metal alloys and ceramics used in total joint replacements. ASTM standards identify microstructural requirements for Co–Cr alloy (in standards F562 and F563-88); for stainless steel (in standards F55-82 and F138-86); for titanium alloy (in standards F136-84 and F620-87); and for Al_2O_3 ceramic (in standard F603-83). In contrast ASTM standard F648, the specification for UHMWPe, does not specify grain size or microstructural features in the consolidated polymeric component although it does include examination for contamination particles and unpolymerized defects. UHMWPe is a semicrystalline polymer and due to its very high molecular weight, processing is difficult. The most common method of processing UHMWPe is through the consolidation of fine powder via compression moulding or ram extrusion [9]. It has been recently demonstrated that the crystalline phase of a semi-crystalline polymer has a morphology which can be linked to its manufacturing history [10]. Further, it has been demonstrated that the polymer morphology may be altered by post-processing heat treatments and mechanical deformation processes [11–13].

From reports of retrieved knee and hip implants, there are noted differences in the surface degradation mechanisms observed on UHMWPe components. In TKR, there are seven commonly reported mechanisms, including delamination, pitting, abrasion, scratching, burnishing, deformation and embedded debris. Pitting and delamination are considered to be the most worrisome in TKR since they are believed to release the greatest volume of wear particles into the joint [14]. These two mechanisms are thought to propagate via a fatigue-related mechanism [15, 16]. It is not yet known whether these two mechanisms of degradation originate from surface or subsurface flaws but the microstructure of the polymeric component could influence the propagation of cracks once initiated.

The objectives of this work were to: (i) describe the observed microstructure features of retrieved knee implants and wear test samples; and (ii) illustrate the relationship between microstructure and the pitting mechanism of wear in UHMWPe.

2. Materials and methods

2.1. UHMWPe material

Microstructural analysis of UHMWPe was performed on as-received material, on six samples of the same material after wear-screening tests and on eight retrieved total knee replacements. The UHMWPe used in all the wear tests was *Chirulen*™ from Hoechst-Celanese, machined from $1000 \times 500 \times 62$ mm compression moulded plate stock; the starting resin was GUR® 412. The plate had been annealed for a minimum of 15 h at 80 °C and its properties were in accordance with DIN 58836. *In vitro* wear testing and observed features from these tests have been reported elsewhere [17, 18] but the cross-sectional analysis of the polymeric microstructure has not yet been reported. For the UHMWPe from retrieved TKR tibial plateaux, the specific processing details and starting powder were not generally known (one exception is the laboratory of the Hospital for Special Surgery where the components are produced in-house [19, 20]); however it is possible to determine whether the tibial plateaux were machined or subjected to a post-processing 'heat-pressed' treatment.

2.2. Surface evaluation

Surface degradation features were evaluated using stereomicroscopy and scanning electron microscopy. For the retrieved knee implants, a quantitative mapping technique was employed to assess the coverage of the various degradation mechanisms using digital image processing [21]. For the wear test samples, the dominant mechanisms of wear were noted in the wear track. The wear tests deviate from the normally reported ASTM standard wear screening test [22] in that the polymer is the flat component and the metal is the pin for the reciprocating test. The main implication of this 'reversed' configuration is that the relative position of contact on the polymer surface is continually changing with the reciprocating motion which is a closer simulation of the motion and stress environment in TKR than the standard test [18, 23].

2.3. Cross-sections and optical microscopy

Samples from retrieved components and the *Chirulen*™ plate stock were cut into rectangular shapes approximately 150 mm^2 in area. Oddly shaped retrieved samples were embedded in epoxy resin to provide a cutting support and facilitate holding the samples. Thin cross-sections of the UHMWPe samples were obtained using a microtome (American Optics, "Cryo-Cut" Model 840) with a stainless steel blade at temperatures between -10 °C and -20 °C. The cold temperatures were found to produce better cuts with fewer artifacts in the direction of blade travel. Section thicknesses of 20–40 μm were found to be optimal with respect to examination of microstructural features. Moreover, while all sections had a tendency to curl, those which were less than 20 μm thick were very fragile and difficult to unravel while those greater than 40 μm were difficult to produce with uniform thickness and tended to have more surface artifacts from the cutting blade.

Cross-sections were taken from random locations of the bulk UHMWPe plate as well as the machined UHMWPe wear samples. The thin sections were mounted onto standard glass microscope slides with cover slips. Immersion oil was occasionally used to facilitate interpretation of the internal structure since the matching refractive index of the oil and polymer allowed microstructural features within the polymer to refract light under cross-polarizing filters [24].

Various filters were used to reveal different features of the structure of sectioned UHMWPe with transmitted light microscopy. Cross-polarized light was useful for enhancing "grain" features in certain samples and was especially useful for retrieved tibial plateaux and wear test samples. It also allowed the sub-surface damage to be observed because regions of residual strain exhibited coloured fringes due to a birefringent effect [25]. Nomarski interference contrast was used to enhance surface topographical features using both transmitted and reflected light microscopy.

2.4. Permanganate etching

UHMWPe is a semi-crystalline polymer in which the crystalline phase is commonly arranged in lamellae or radiating structures. In the present samples, the degree of crystallinity was determined to be 49.9% by X-ray diffraction measurement. The premise behind the etching technique is to reveal the crystalline phase morphology by preferentially removing the amorphous regions of the polymer. The basic etching technique was developed by Bassett [10] in which approximately 1 μm of material is removed in the etching process, which is less than typical lamellar widths. The etchant was a 0.7% weight/volume solution of potassium permanganate in concentrated sulphuric acid. Samples were immersed in the stagnant etchant at room temperature for times ranging from 15 min to 2 h. Etching was arrested by rinsing the sample in a mixture of hydrogen peroxide and aqueous sulphuric acid, followed by rinsing in acetone and drying in a fume hood.

It should be noted, however, that the interpretation of polymeric morphology was confounded by the inconsistency of the etching technique and the production of artifacts. Naylor and Philips [26] conducted an extensive study on artifacts using the etching technique in various polyethylenes and provided insight for the interpretation of etching results.

3. Results

3.1. Surface degradation evaluation

A summary of the clinical information for the eight retrieved knee implants is included in Table I along with detail about the UHMWPe components. All the femoral components were fabricated of cobalt chromium alloy. The average service lifetime of the implants was 7.2 years, ranging from 0.8 years to 14.4 years. The pitting mechanism of surface degradation was observed on all eight surfaces (Fig. 1a); the average projected area of pitting relative to the area of the bearing surface was 12.6% coverage with a range from 3.4% to 24.1%. There were two typical morphologies of pitting (Fig. 1b): a tufted appearance with small particulate debris evident in the pit and characteristically shaped polygonal pits.

In the wear screening device, six pin-on-flat pairs were exposed to identical loading conditions and should, therefore, provide very similar results. In the present tests, however, one sample of the six was measured to have a higher wear rate than the other five. In this sample, the microstructure was readily visible in the wear track (Fig. 2a) whereas it could not be discerned in the other samples. The direction of reciprocating motion is indicated with arrows in Fig. 2a; the original machining marks are oriented vertically in the photo. Scratching is also evident at the top and bottom of the wear track. Nomarski interference contrast was used to enhance the topography of the polygonal features (Fig. 2b). It was determined that the boundaries of the polygonal 'grains' were in fact valleys.

3.2. Cross-sectional microscopy evaluation

The relationship between microstructural features and surface degradation mechanisms in a retrieved tibial plateau is illustrated in Fig. 3a and 3b with a 'heat-pressed' surface treatment. This sample has been sectioned parallel to the direction of articulation (the antero-posterior direction) and Fig. 3a illustrates both

TABLE I Summary of patient and retrieved knee implant characteristics.

Case number	Side	Age[a]	Gender	Weight (kg)	Duration (years)	Thickness (mm)	UHMWPe	Metal-backed?	Pitting (%)	Revision reason
1	L	78	M	64.9	2.9	8	M[b]	Y	3.4	Loosening, radiographic evidence
2	R	71	M	90.5	6.8	8.5	M	Y	23.5	Patella problems
3	L	74	M	80.1	2.0	7	HP[c]	Y	17.3	Pain, radiographic evidence
4	L	68	F	74.8	6.6	10	HP	Y	9.6	Pain, "unstable"
5	R	61	M	85.2	0.8	9	HP	Y	6.4	Loosening
6	L	76	M	86.1	2.0	7	HP	Y	9.0	Radiographic evidence
7	R	68	F	104.0	7.6	11	HP	Y	7.9	Loosening; instability
8	L	77	F	62.5	14.4	7	M	N	24.1	Loosening; discomfort
									12.6	

[a] at revision
[b] M = machined
[c] HP = "heat-pressed"

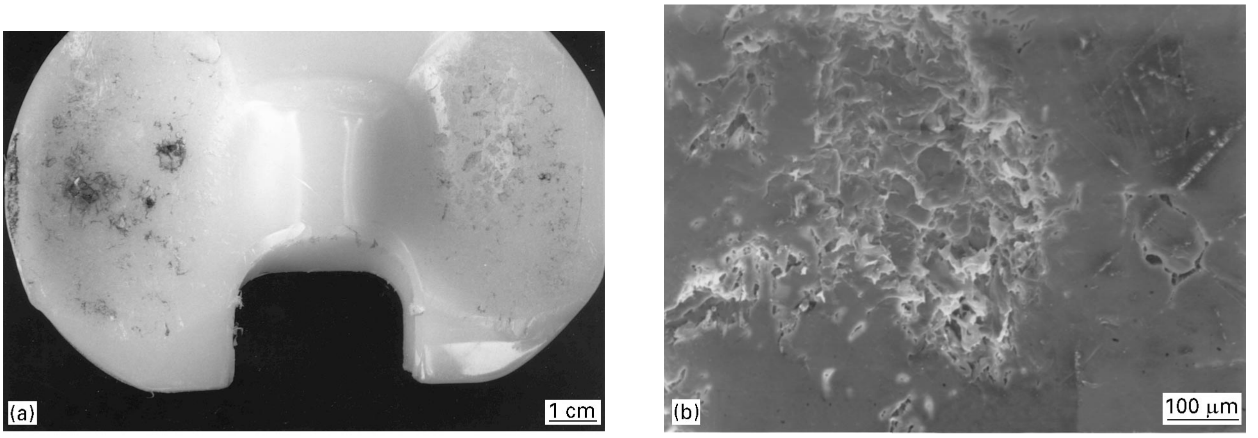

Figure 1. (a) Retrieved tibial plateau from case 2 showing surface pitting. (b) A surface pit observed on a retrieved tibial plateau. Note the polygonal shape of the defect to the right of the surface pit and the cracks surrounding this defect.

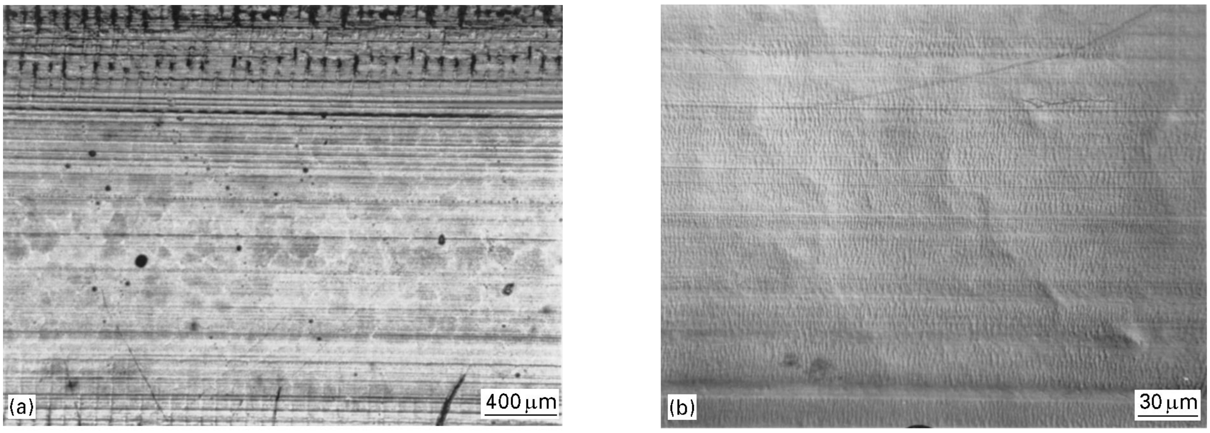

Figure 2. (a) UHMWPe microstructure visible in a wear track produced by *in vitro* wear testing. Direction of tester motion is indicated by the arrows. (b) Higher magnification of same sample using Nomarski filter. Grain boundaries appear as depressions in the surface.

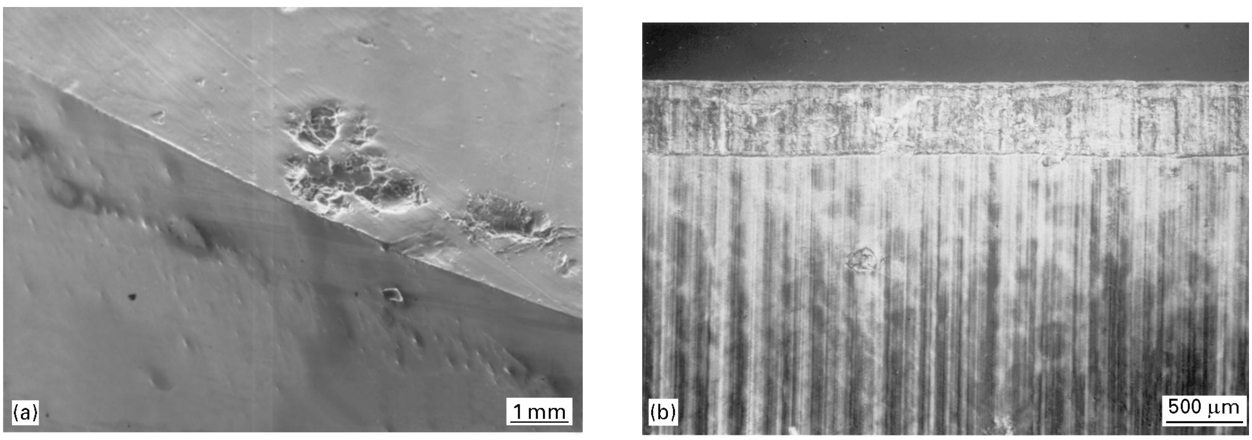

Figure 3. (a) A combined analysis of articular surface (AS) degradation features in the upper right and subsurface features (SS) in the lower left from the tibial plateau of retrieved TKR case 3. (b) Cross-sectional analysis of heat-pressed UHMWPe surface from retrieved TKR shown in Fig. 3a. The band of material affected by post processing appears distinct from the lower bulk region. Also note the polygonal-shaped fusion defect identified with an arrow.

the pitting of the articular surface (AS) and the subsurface features (SS). The line observed in the subsurface region, about 1 mm beneath the surface, demarks the interface between the heat-treated surface layer and the unaffected interior in this UHMWPe [27, 28]. A white band and the microstructure beneath the altered surface layer is evident in the transmitted light cross-section (Fig. 3b). Early failures of UHMWPe tibial plateaux with a heat-pressed surface have been reported by several authors [28, 29], however, it emphasizes the profound effect of post-manufacturing treatment on the material structure and performance.

In the wear test samples, transmitted polarized light through cross-sections revealed residual strain fringes similar to those reported by Cooper *et al.* [25]. A distinct ridge was evident at the demarcation between the wear track (WT) and the adjacent unworn material (Fig. 4). Birefringence, indicative of large residual strains, was observed below the wear track. Also noticeable in Fig. 4 is a faint polygonal network in the subsurface material. This subtle structure was evident in most sections of the *Chirulen*™ UHMWPe. The transmitted polarized light cross-section (Fig. 5) is an example of a more pronounced array of polygonal shapes that were present in many samples of retrieved total knee replacements and some regions of the *Chirulen*™ UHMWPe wear screening test samples. Also present in this sample (Fig. 5) are two obvious voids indicated with arrows. The polygonal shapes were not uniformly present in all samples.

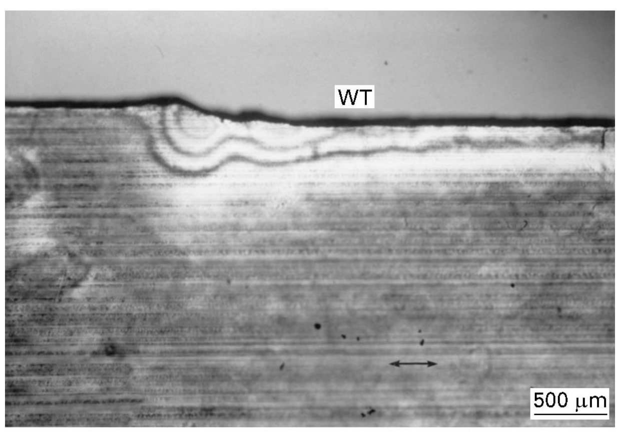

Figure 4. Transmitted light optical micrograph with cross-polarizing filter of wear track cross-section illustrating residual strains in material and faint network of polygonal structure in *Chirulen*™ UHMWPe.

3.3. Permanganate etching

Scanning electron microscopy (SEM) of the etched surface of as-received UHMWPe stock revealed the crystalline morphology and the boundaries between the original UHMWPe powder (Fig. 6a). Starting powder particles contain numerous smaller subparticles or 'crystallites' [3, 30]. The network of voids, which appear as black lines intersecting at triple points, represents the original particle boundaries and is presented schematically in Fig. 6b.

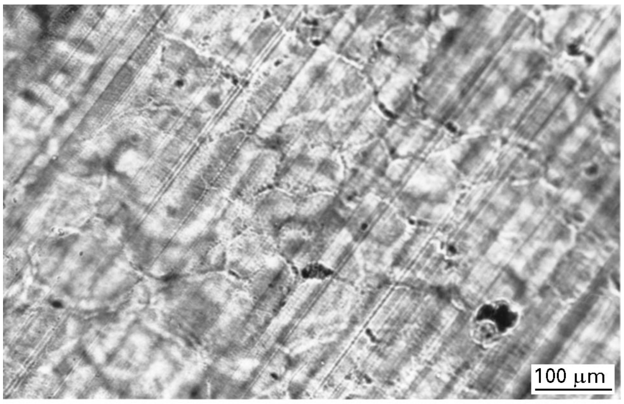

Figure 5. Transmitted light optical micrograph with cross-polarizing filter illustrating a region with pronounced network of polygonal structure. The polygonal shapes have an approximate size of 100 μm. Two voids are indicated with the arrows.

4. Discussion

Pitting is considered to be one of the more serious wear mechanisms in TKR since it is suspected of releasing the most polymeric debris into the knee joint. Pitting is also suspected to result from a fatigue type mechanism [15, 16]; however, it has not been determined whether pits initiate at surface or subsurface flaws. The pits in the SEM micrograph (Fig. 1b) illustrate two types of pit morphology: on the left is a large (approximately 500 μm) pit which has significantly more roughening than the flaw on the right. The damage observed in this pit is typical of an abrasive-type degradation mechanism and likely resulted from third-body damage. The flaw on the right has a shape typical of polygonal grains observed in cross-sectional analysis of retrieved implants and the *Chirulen*™ wear test UHMWPe samples. The obvious cracks surrounding the 100 μm particle are consistent with the polygonal pit in previously reported morphologies [21]. A model for pit formation has been proposed [16] in which fluid entrained in surface cracks become pressurized during articulation. In this model, stress intensities at the crack tip are found to be

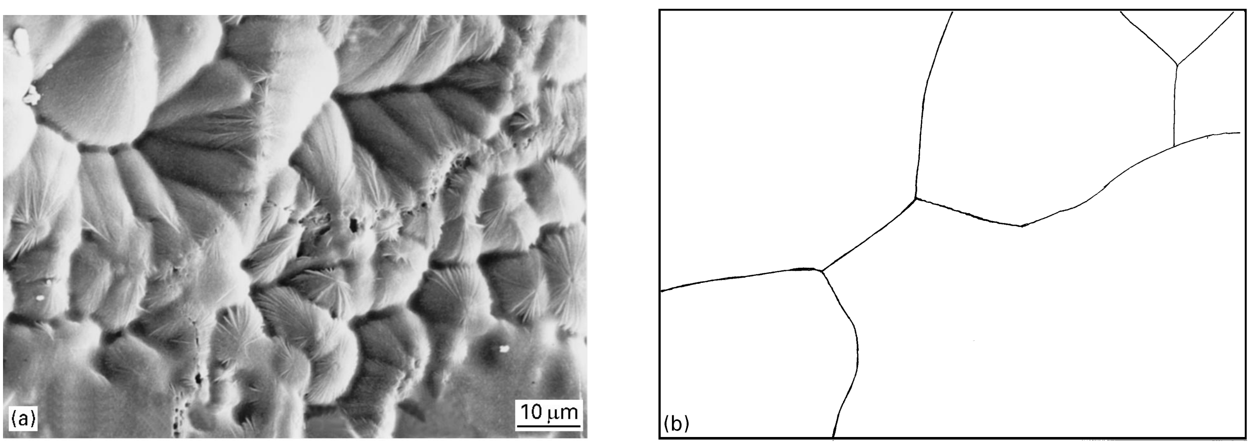

Figure 6. (a) Etched sample showing the crystalline morphology within UHMWPe particles, after removal of amorphous regions. (b) Schematic illustration of the networks of black lines visible, representing particle boundaries prior to etching.

TABLE II Summary of microstructural features of UHMWPe reported in the literature

Author [reference]	Feature description	Microstructure grain size (μm)
Gibbons *et al.* [31]	*Microstructure*: voids, fracture along particle interfaces	< 100
Gibbons [32]	Intermittent small string of voids	? (no scale)
Weightman and Light [6]	*Microstructure*: non-spherulitic, some unfused particles	20–80
Landy and Walker [33]	Intergranular cracking and fusion defects	80–120
Rose and Radin [34]	Fusion defect from processing	40
Blunn *et al.* [35]	Fusion defects and intergranular failure	> 100
Tulp [27]	UHMWPe granules underneath hot-presses layer	50–200
Cooper *et al.* [25]	Residual strain fringes	40–100
Marcus and Allen [36]	*Microstructure*: spherulitic, some unfused particles	50 to 150
Wrona *et al.* [7]	Fusion defects and "grain boundaries"	? (no scale)
Li and Burstein [19]	"Asperities" (implying fusion defects)	? (no scale)

three times higher than those in which there is no fluid. The surface cracks observed in Fig. 1b are examples of defects which could propagate with the proposed model. Microstructural features both at the surface and beneath the surface could affect the resistance to crack propagation.

There are numerous studies of cross sections of UHMWPe in the recent orthopaedic literature (Table II). The main focus of these studies is to illustrate processing flaws, unpolymerized regions or service damage. In most of the figures presented in these articles a regular network of polygonal shapes can be distinguished. Although the authors may have been describing other features, it is suspected that these polygonal shapes represent grain boundaries of the original UHMWPe powder and these observations support the hypothesis that the microstructure will affect the wear performance. The wear test sample described in the present study had a higher wear rate than the other five samples. It was suspected that the amorphous boundaries between grains were worn preferentially since the boundaries were valleys (Fig. 2b); the boundaries between particles often are of lower molecular weight [11]. Rose *et al.* [5] demonstrated the effect of molecular weight on the wear performance of UHMWPe.

Bassett [10] illustrated the importance of considering polymer microstructure, particularly the arrangement of lamellae in semi-crystalline polymers after various heat-treatments. For metals, the microstructure is an important control variable in the manufacturing process which affects the overall material properties. The same attention should be focused on the microstructural characteristics resulting from the manufacturing of UHMWPe for orthopaedic implants. McKellop *et al.* [3] established a qualitative link between wear particle size and the shape with the morphology of the starting powder. It has also been shown that UHMWPe powder is composed of smaller sub-particles or crystallites [3, 30, 37] prior to processing into bulk material. The size of these crystallites is very close to the morphology illustrated in the etched samples (Fig. 6a). The grain boundaries illustrated in the thin sections have also been illustrated in the etched samples. Other investigators have used the etching techniques to examine the effect of mechanical deformation on the microstructure of polyethylene [11, 13].

The similarity in size and shape between specific surface degradation features and the UHMWPe grain structure indicates the importance of understanding the nature of this morphology. The observations of pitting in retrieved knee implants and surface damage in wear test samples have shown that the post-processing microstructure may influence this mechanism of surface degradation and hence the wear properties of UHMWPe.

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