ARTICLE IN PRESS



Available online at www.sciencedirect.com



Biomaterials

Biomaterials ■ (■■■) ■■■-■■■

www.elsevier.com/locate/biomaterials

Review

Deformation, yielding, fracture and fatigue behavior of conventional and highly cross-linked ultra high molecular weight polyethylene

Lisa A. Pruitt*

Department of Mechanical Engineering and Bioengineering, University of California, 5134 Etcheverry Hall, Berkeley, CA 94720, USA

Received 1 March 2004; accepted 24 March 2004

Abstract

Medical grade ultra high molecular weight polyethylene (UHMWPE) has been used as the bearing surface of total joint replacements for over four decades. These polymeric devices are susceptible to accumulated cyclic damage in vivo. Wear debris formation that ultimately leads to a need for revision surgery is linked to the plasticity, fatigue and fracture mechanisms of UHMWPE. This paper examines the deformation, yielding, fracture and fatigue behavior of conventional and highly cross-linked medical grade UHMWPE. Such properties play an important role in determining the long-term success of orthopedic devices. The mechanical properties discussed include the deformation behavior of UHMWPE, the yielding associated with quasi-static tension and compression, fracture toughness, cyclic loading, and fatigue resistance.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: UHMWPE; Deformation; Yield; Fracture; Fatigue

Contents

1.	Introduction	000
2.	Deformation behavior of UHMWPE	000
3.	Plastic flow and yielding behavior of conventional and cross-linked UHMWPE	000
4.	Fracture behavior of conventional and cross-linked UHMWPE	000
5.	Fatigue of conventional and cross-linked UHMWPE	000
6.	Summary and clinical perspective	000
Ref	ferences	000

1. Introduction

Medical grade ultra high molecular weight polyethylene (UHMWPE) remains the material of choice for the bearing surface in total joint replacement components. This polymer offers unique mechanical properties as

E-mail address: lpruitt@maxwell.berkeley.edu (L.A. Pruitt).

well as biocompatibility. In its conventional form, UHMWPE has exceptional mechanical integrity owing to its chain entanglements, high tie molecule density, moderate crystallinity and very high molecular weight [1]. A summary of the physical properties of conventional UHMWPE is provided in Table 1. Over time, however, accumulated damage in vivo coupled with articulation and cyclic contact stresses of UHMWPE components results in wear debris formation. Polyethylene debris leads to inflammation, foreign body

^{*}Corresponding author. Tel.: +1-510-642-2595; fax: +1-510-643-5599

Table 1 Physical properties of conventional (unirradiated) GUR 1050

Physical property	GUR 1050	
Molecular weight	3–6 million g/mol	
Crystallinity	45–50%	
Density	0.93-0.935	
Ultimate tensile strength (21°C)	42–44 MPa	
Ultimate tensile strength (37°C)	36 MPa	
Yield strength (21°C)	20–23 MPa	
Yield strength (37°C)	21 MPa	
Elastic modulus (21°C)	1.0-1.39 GPa	
Elastic modulus (37°C)	0.67 GPa	
Elongation at break (21°C)	330%	
Elongation at break (37°C)	375%	
Shore D hardness (21°C)	60–65	

Mechanical properties are taken from engineering stress-strain plots. Adapted from [1].

response, and the need for revision surgery. This cyclic damage associated with the yielding, fracture, and fatigue processes of UHWMPE remains the limiting factor for the longevity of total joint replacements.

Mechanical degradation of UHMWPE is drastically accelerated if the polymeric device is exposed to an ionizing radiation source in the presence of oxygen. Ionizing radiation, which had been commonly used for sterilization purposes in the past, results in a timedependent process known as shelf aging that is accompanied by chain scission, loss of molecular weight, increased crystallinity, oxidation, and a concomitant decrease in mechanical properties [2]. Many retrieved devices that had been sterilized by gamma radiation in an air environment have shown evidence of pitting, delamination, subsurface oxidation and fatigue cracking. Kurtz et al. [3] provides an excellent review of the history of the processing, sterilization, and mechanical behavior of medical grade UHMWPE for total joint arthroplasty. Gamma radiation in air is no longer employed as a sterilization scheme for medical grade UHMWPE, however there exists a plethora of information related to its mechanical properties and associated clinical performance, and therefore it provides a good baseline comparison for any proposed material improvements to this polymer. The term "conventional" UHMWPE typically refers to UHMWPE sterilized by non-ionizing treatments such as EtO or plasma, but it can also refer to UHMWPE sterilized via low doses of gamma radiation. In general, "conventional" polyethylene refers to UHMWPE in the non-cross-linked form.

Recent developments in improving the performance of this polymer have focused on the utilization of cross-linking methods to improve the wear resistance of UHMWPE in total joint replacements [3–6]. Cross-linking is obtained by exposing the polymer to high doses of gamma radiation or e-beam radiation along with a thermal treatment that can be done below or

above the melt temperature. Commercially cross-linked UHMWPE resins range in doses from 40 kGy through 100 kGy, and these treatments can be followed by heating the material above its melt temperature (135°C) or annealing the polymer below its melt temperature. The thermal processing annihilates free radicals and completes the cross-linking step to prevent time-dependent oxidation of the polymer. The coupled effects of cross-linking and thermal treatments can have considerably different effects on the polymer microstructure and mechanical properties of UHMWPE [7,8].

Cross-linking of the molecular chains in UHMWPE has been shown to dramatically reduce the abrasive and adhesive wear in several in vitro joint simulator studies [4–6]. It has been speculated that cross-linking the polymer enhances the resistance to plastic flow and lamellae alignment at the articulating surface resulting in better resistance to wear [9.10]. Muratoglu et al. [4] and McKellop et al. [5] have shown that wear rates decrease dramatically with radiation dose and begin to saturate at a radiation dose of about 150 kGy. Fig. 1 shows the dramatic reduction in wear rate obtained with elevated radiation doses. However, cross-linking procedures inherently alter the polymer structure and the mechanical properties of UHMWPE. Recent studies [11–21] have shown that high degrees of cross-linking in UHMWPE result in a reduction of several important mechanical properties including strength, ductility, elastic modulus, fracture toughness, and crack propagation resistance. The long-term clinical implications for such changes in mechanical properties remain unknown.

The aim of this paper is to provide a review of the deformation, yielding, fracture and fatigue behavior of conventional and highly cross-linked medical grade UHMWPE. These properties play an important role in determining the long-term success of UHMWPE components used in total joint replacements. The

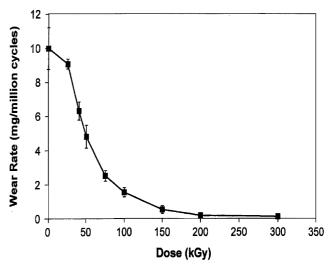


Fig. 1. Wear rate as a function of radiation dose. Adapted from [4].

mechanical properties discussed include the deformation behavior of UHMWPE, the yielding associated with quasi-static tension and compression, fracture toughness, cyclic loading, and fatigue resistance. The findings in this paper will be discussed in the context of total joint replacements.

2. Deformation behavior of UHMWPE

Polyethylene wear generated at the articulating surface remains the primary concern in total knee and hip replacement components, however, the mechanisms of wear are different depending on the location of the components. These differences are linked to disparities in conformity and cyclic contact stresses [22]. However, cyclic deformation and plasticity mechanisms have been linked to wear processes in both tibial and acetabular components [9,10]. In UHMWPE tibial inserts, the components are subjected to high cyclic contact stresses resulting in pitting and delamination associated with fatigue and fracture processes. These fatigue and fracture mechanisms have been directly related to the yield stress and ultimate stress associated with the plastic flow of the polymer [23]. The generation of submicron wear particles in acetabular components has been linked with the local accumulation of plastic strain and attainment of a critical strain under multiaxial loading conditions [24,25]. The clinical performance of UHMWPE orthopedic implants has also been associated with large-scale deformation and plasticity induced damage layers that develop under the articulating surface due to sliding and high contact stresses [26]. Thus much of the surface deformation and wear damage observed in clinical components is linked to plastic flow and yielding behavior of UHMWPE.

3. Plastic flow and yielding behavior of conventional and cross-linked UHMWPE

Uniaxial quasi-static mechanical properties are important parameters for UHMWPE as these properties are the basis of comparison for resins with different process conditions, cross-link dosages, thermal treatments and sterilization protocols. All UHMWPE materials used in total joint replacements must adhere to strict to national (ASTM) and international (ISO) requirements, which designate acceptable ranges of yield strength, elastic modulus, ultimate strength, ductility, and impact resistance [3].

Previous research on the plastic flow behavior of semi-crystalline polymers capable of large deformations has shown that the true stress-strain curve provides the most useful information about the yielding behavior, the true rate of strain hardening, and texture development [27–35]. Thus for the characterization of UHMWPE at large deformations, it is most appropriate to utilize true stress and true strain to describe its constitutive behavior. Kurtz and co-workers [8,9,11,36–38] have best demonstrated this characterization and have found that the following two-segment elastic-plastic material model represents the true stress–strain data in tension as well as compression:

$$\sigma(\varepsilon) = E \text{ for } \varepsilon \leqslant \varepsilon_{y},$$

$$\sigma(\varepsilon) = \alpha + \beta \exp(\gamma \varepsilon) \text{ for } \varepsilon_{y} < \varepsilon < 0.12,$$
 (1)

where σ (MPa) and ε represent the true stress and strain, E (MPa) is the Young's modulus, ε_y is the yield strain, α is the asymptotic true stress at infinite strain, β is the rate at which the stress approaches the asymptotic limit, and γ represents the curvature of the true stress—strain curve. α can be eliminated by constraining segments to intersect at the yield point. Prior to yielding, the material response is described by linear elasticity. Once the material yields and plasticity ensues, the true stress—strain curve becomes non-linear and stress follows an exponential form of strain.

Kurtz et al. [36] found the true yield stress to be 23.0 MPa in tension and 21.7 MPa in compression. His study indicates that the true stress-strain behavior of UHMWPE up to 0.12 true strain is nearly the same in both tension and compression, and is captured by the exponential model described above. A typical true stress-strain plot for conventional UHMWPE is shown in Fig. 2. Fractography of these tensile specimens revealed slow crack growth mechanisms associated with void coalescence and fibrillation. Transmission electron microscopy of uniaxially deformed UHMWPE revealed crystalline texture and orientation of the lamellae parallel to the direction of loading. Lamellar orientation at high strains has been shown to result in anisotropic strain softening, in which the ultimate response of UHMWPE is decreased in a direction normal to the applied load [10]. Further, plasticity induced texture has

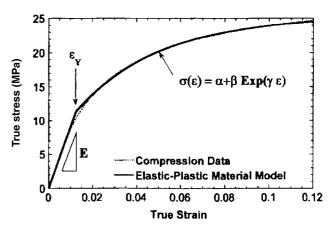


Fig. 2. Typical true stress–strain curve for UHMWPE. Adapted from [36].

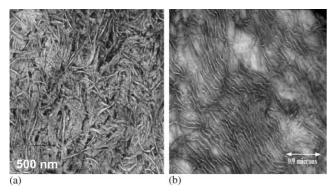


Fig. 3. Transmission electron micrograph of: (a) random lamellae organization in UHMWPE without mechanical deformation; and (b) texture development of lamellae in direction of sliding in UHMWPE.

been observed in retrievals and linked to delamination wear mechanisms [9]. An example of this texture development in UHMWPE is shown in Fig. 3.

More recently, Kurtz and co-workers [8] examined the role of coupled cross-linking and thermal processing on the uniaxial tensile and compressive properties of UHMWPE. In this study, two conventional and two highly cross-linked UHMWPE resins were examined. Quasi-static uniaxial properties were assessed at room temperature and at body temperature (37°C). A standard non-irradiated GUR 1050 resin represented conventional polyethylene and that same resin subjected to a 30 kGy gamma radiation dose in an inert (nitrogen) environment represented a sterile version. The two highly cross-linked groups were both irradiated to 100 kGy using gamma radiation but post processed with different thermal treatments. One highly crosslinked group was annealed at 110°C, which is below the melt transition temperature (135°C), and the other group was remelted above the melt transition temperature at 150°C. This enabled the researchers to look at the effects of crystallinity and radiation dose on mechanical properties. These materials were tested under uniaxial compression and tension conditions, and over a range of strain rates and temperatures. Their findings revealed that thermal treatment affected crystallinity and that this morphological change affected yielding, flow, and fracture properties of the polymer. They found that under uniaxial tension the highly crosslinked groups exhibited a decrease in ultimate strength and strain, ultimate true stress, and ultimate true strain (Table 2). They found that enhanced crystallinity brought about through thermal processing increased the yield strength and modulus of the material. Their compression studies revealed that increased temperature resulted in a decrease in elastic modulus, yield strength, and ultimate true stress. This study provided evidence that radiation dose and crystallinity dictate yielding, plastic flow, and ultimate properties of conventional and cross-linked polyethylene.

Gomoll et al. [14] performed a similar study and investigated the effect of cross-link dose on the mechanical properties of UHMWPE. In their analysis, they investigated four gamma radiation dosages (25, 50, 100, and 200 kGy) along with conventional UHMWPE. In their study, all cross-linked resins were subjected to a remelting treatment at 138°C following irradiation (in nitrogen). They found that elastic modulus, ultimate true stress, and ultimate true strain decreased monotonically with radiation dose. The physical properties of UHMWPE resins as a function of radiation dose are summarized in Table 3. In their study, very little change was noted in crystallinity for the various cross-link dosages. They attribute the monotonic reduction in elastic modulus with a higher number of smaller fragmented lamellae in the cross-linked polymer. The fragmentation of lamellae is believed to reduce the tensile modulus of UHMWPE. This theory is supported by other morphological studies in which transmission electron microscopy of conventional and highly crosslinked UHMWPE showed smaller lamellae with shorter lengths in highly cross-linked resins [11]. In Gomoll's study, the greatest reduction in mechanical properties was found in strain-to-break and ultimate tensile strength properties. These findings indicate that for a given crystallinity, enhanced cross-linking results in loss of modulus, strength, and ductility.

4. Fracture behavior of conventional and cross-linked UHMWPE

Fracture toughness is the mechanical property that describes a material's intrinsic resistance to fracture and captures the coupled sensitivity to flaws and stresses. There are two basic parameters used to describe fracture toughness: K_{IC} and J_{IC} . The first of these parameters, $K_{\rm IC}$, is known as the plane strain mode I fracture toughness. The plane strain condition assures that the fracture toughness is independent of material thickness, and mode I refers to a tensile "opening" mode of fracture. $K_{\rm IC}$ is based on a stress intensity factor, K, derived from linear elastic fracture mechanics. The stress intensity factor describes the magnitude of the stresses, strains and displacements in the region ahead of the crack tip. The linear elastic solution for the normal stress in the y-direction (σ_{yy}) for the mode I loading case incorporates K_I as a scaling parameter and is written as a function of distance, r, and angle, θ , away from the crack tip [39]:

$$\sigma_{yy} = \frac{K_1}{\sqrt{2\pi r}} \cos\frac{\theta}{2} \left\{ 1 + \sin\frac{\theta}{2} \sin\frac{3\theta}{2} \right\}. \tag{2}$$

Here $K_{\rm I}$ is the mode I (opening mode) stress intensity factor, which incorporates the boundary conditions of the cracked body and is a function of loading, crack

L.A. Pruitt | Biomaterials ■ (■■■) ■■■-■■■

Table 2 Physical properties of conventional and highly cross-linked GUR 1050

Property	GUR1050	30 kGy (N ₂)	100 kGy (110°C)	100 kGy (150°C)
Crystallinity (%)	50.4±3.3	51.3±1.0	60.8 ± 0.9	45.7 ± 0.3
Tensile properties (20°C)				
Yield strength (MPa)	23.5 ± 0.3	24.1 ± 0.14	24.79 ± 0.12	21.36 ± 0.13
Yield strain (%)	14.4 ± 0.6	13.4 ± 0.6	12.7 ± 0.6	14.5 ± 0.9
Ultimate strength (MPa)	50.2 ± 1.6	47.1 ± 4.2	46.4 ± 3.4	37.1 ± 3.2
Ultimate strain (%)	421 ± 11	373 ± 8	248 ± 11	232 ± 8
True yield stress (MPa)	26.9 ± 0.4	27.35 ± 0.24	27.94 ± 0.10	24.47 ± 0.24
True yield strain (%)	0.134 ± 0.005	0.126 ± 0.005	0.120 ± 0.005	0.136 ± 0.008
True ultimate stress (MPa)	262 ± 12	223 ± 22	162 ± 16	123 ± 13
True ultimate strain (%)	1.65 ± 0.02	1.55 ± 0.02	1.25 ± 0.03	1.20 ± 0.02
Compressive properties (20°C)				
Elastic modulus (MPa)	833.0 ± 9.1	932.1 ± 21.2	994.3 ± 29.2	778.9 ± 6.8
Offset yield (MPa)	12.0 ± 0.2	12.8 ± 0.1	13.2 ± 0.1	11.6 ± 0.1
Maximum true stress (MPa)	39.6 ± 0.1	39.8 ± 0.1	40.3 ± 0.1	37.2 ± 0.1
Maximum true strain (MPa)	0.446 ± 0.002	0.444 ± 0.003	0.431 ± 0.002	0.507 ± 0.004
Compressive Properties (37°C)				
Elastic modulus (MPa)	648.2 ± 23.5	737.2 ± 15.8	771.4 ± 30.6	570.0 ± 15.2
Offset yield (MPa)	9.7 ± 0.2	10.3 ± 0.1	10.8 ± 0.2	8.8 ± 0.1
Maximum true stress (MPa)	35.7 ± 0.1	35.6 ± 0.4	36.4 ± 0.2	32.7 ± 0.3
Maximum true strain (MPa)	0.548 ± 0.002	0.552 ± 0.011	0.529 ± 0.051	0.631 ± 0.006
Fracture toughness				
$K_{\rm C}~({\rm MPa}\sqrt{\rm m})$	4.0 ± 0.5	4.5 ± 0.02	2.8 ± 0.4	3.0 ± 0.6

Mechanical properties are taken from engineering and true stress-strain plots. Adapted from [8,12].

Table 3 Physical properties of UHMWPE as a function of radiation dose

Property	GUR 1050	25 kGy	50 kGy	100 kGy	200 kGy
Crystallinity (%)	50.7 ± 0.5	45.4 ± 0.7	46.2 ± 0.7	46.9 ± 0.8	47.7 ± 0.4
Yield stress (MPa)	20.2 ± 1.0	19.0 ± 0.4	19.9 ± 0.8	18.9 ± 0.7	21.2 ± 1.0
Modulus (MPa)	495 ± 56	433 ± 14	412 ± 50	386 ± 23	266 ± 30
True stress at break (MPa)	315.5 ± 31.6	284.8 ± 18	237.6 ± 12.3	185.7 ± 7.5	126.0 ± 14
True strain at break	1.82 ± 0.01	1.74 ± 0.03	1.59 ± 0.01	1.50 ± 0.02	1.37 ± 0.06
Fracture toughness (J_{IC} , kJ/m^2)	2.1	23.8	76.2	$=J_{ m SS}$	$=J_{ m SS}$
Steady-state fracture toughness $(J_{SS}, kJ/m^2)$	116.9 ± 0.1	101.2 ± 0.1	98.5 ± 0.2	87.6 ± 0.1	79.3 ± 1.9

Mechanical properties are taken from true stress–strain plots. Fracture toughness is determined from Rice and Sorenson *J*-integral method. Adapted from [14].

length, and specimen geometry. The stress intensity factor can be found for a wide range of specimen geometries and is used to scale the effect of the far-field load, crack length and geometry of the flawed component [40]:

$$K_1 = \sigma^{\infty} \sqrt{\pi a} F\left(\frac{a}{W}\right). \tag{3}$$

Here σ^{∞} is the remote far-field stress, F is the geometric factor for the specimen or component geometry. F is a function of crack length, a, normalized by the specimen width, W. The efficacy of the stress intensity parameter derives from its ability to correlate the inception and growth of cracks contained in

different specimens through a concept known as similitude. This concept states that two cracks with the same stress intensity factor experience the same driving force for crack growth. The similitude concept enables fracture toughness data taken from laboratory specimens to be used for strength predictions of load bearing components. When the value of $K_{\rm I}$ attains a critical value unstable crack growth ensues and fast fracture occurs:

$$K_{\rm I} \geqslant K_{\rm IC},$$
 (4)

where K_{IC} is the fracture toughness of the material containing the crack. Fracture toughness is a true material property that provides a measure of resistance

to crack growth for an intrinsic flaw subjected to an applied stress.

The other parameter used to describe fracture toughness of a material is $J_{\rm IC}$. The resistance of ductile materials, such as polymers, to plane-strain brittle crack initiation is often characterized by the J-integral method (ASTM E 813). This parameter utilizes non-linear fracture mechanics (J-integral) to measure the change in energy per unit area of new crack surface for a tensile (mode I) mode of fracture. The J-integral describes the stresses and strains ahead of the crack tip under elastic-plastic conditions. The stress field is written as [39]:

$$\sigma_{ii} = \sigma_0 (J/(\alpha \sigma_0 \varepsilon_0 l_n r))^{1/(n+1)} \sigma(\theta, n)$$
 (5)

where σ_0 and ε_0 represent the yield stress and strain, n is a strain hardening coefficient, l_n is a material parameter that depends on the strain hardening coefficient, and r and θ represent the radial and angular coordinates ahead of the crack tip. Using a Rice and Sorenson Model [14,39], the J-integral takes the form:

$$J = \alpha \varepsilon_0 \sigma_0 \operatorname{ch}_1(a/b, n) (P/P_0)^m, \tag{6}$$

where ε_0 and σ_0 represent the strain and stress from a power-law fit, strain hardening expression $\varepsilon_e =$ $\alpha \varepsilon_0 (\sigma_e / \sigma_0)^n$, with a fitting constant $\alpha \varepsilon_0$. The tensile yield stress is used for σ_0 , a is the crack length, b is the distance from the loading line to the free end of the specimen, and c is the uncracked ligament length, n is the strain hardening exponent, m = 1/n, and h_1 is a tabulated function of a/b and n. P is the maximum pin load per unit specimen thickness and P_0 is $1.455\eta c\sigma_0$ where η is a polynomial function of a and c. J_{IC} captures the initial crack driving force needed to initiate crack growth (resistance to crack initiation). While a steadystate value of J-integral, J_{SS} , is used to assess the resistance of the crack to propagation or growth. Under linear elastic, plane strain conditions, this parameter can be related to fracture toughness:

$$J_{\rm IC} = K_{\rm IC}^2 (1 - v^2) / E, \tag{7}$$

where E is the elastic modulus and v is the Poisson ratio. From a structural standpoint, the mode I fracture toughness, $K_{\rm IC}$, provides the most utility in UHMWPE material design. This parameter captures defect sensitivity and indicates the combinations of flaw size and stress that will result in fracture of the material. However, due to its high ductility, little is known about the plane strain fracture toughness, $K_{\rm IC}$, for UHMWPE. Most efforts to characterize the fracture toughness of UHMWPE have focused on $J_{\rm IC}$ testing [39–41]. But these energetic methods are not without limitations. Predictions of toughness can be overestimated due to crack tip blunting and variations in testing methods can cause discrepancies in reported values of $J_{\rm IC}$. For conventional UHMWPE, the critical fracture energy

parameter is reported to range from 66.5 to $99 \,\mathrm{kJ} \,\mathrm{m}^{-2}$ [41–43].

To date, no direct experimental measurements of $K_{\rm IC}$ for UHMWPE have been made. The fracture toughness can be estimated with certain limitations by indirect methods from $J_{\rm IC}$ tests, tensile tests, or fatigue crack propagation tests. Using an elastic assumption one can estimate the fracture toughness from $J_{\rm IC}$ values. Using values from the literature [41–43], one obtains an upperbound estimate of fracture toughness on the order of 9– $10.5 \,\mathrm{MPa} \,\mathrm{m}$. The fracture toughness may also be approximated from monotonic tensile tests provided that the true ultimate stress and the critical flaw size at the time of failure can be measured. Using a relationship derived from LEFM, $K_{\rm C} \approx \sigma_{\rm ULT} \sqrt{a_{\rm c}}$, Kurtz and coworkers found the average fracture toughness of conventional UHMWPE to be 4.7 MPa \(\sqrt{m} \). They also found that the fracture toughness was linearly related to the ultimate true stress of conventional UHMWPE. Fracture toughness can also be approximated from the fast fracture regime of fatigue crack propagation tests. Using the fast fracture regime of published fatigue data provides an inferred value of $K_{\rm IC}$ on the order of $3.5 \,\mathrm{MPa} \,\sqrt{\mathrm{m}}$ for conventional UHMWPE [44]. These indirect experimental measurements of $K_{\rm IC}$ serve as an estimate of the fracture toughness of conventional UHMWPE.

As with any material, fracture toughness is sensitive to changes in its microstructure. Alterations to crystal-linity, molecular weight, and cross-linking will affect the fracture toughness of a polymer. Generally speaking, any microstructural changes that result in a decrease of plasticity will have a concomitant reduction in fracture toughness. As described above, cross-linking of UHMWPE results in a loss in ultimate strength and ductility. Thus it is expected that cross-linking will also degrade the fracture toughness of UHMWPE.

In a recent study by Gencur et al. [12], fracture toughness of highly cross-linked UHMWPE was estimated based on the size of the flaw, location and the true ultimate strength of the material. They noted a 32% reduction in fracture toughness in the highly crosslinked (100 kGy) UHMWPE. Their work demonstrated that radiation dose was linearly related to fracture toughness (Table 2). Duus et al. [21] utilized the Jintegral approach to quantify fracture toughness as a function of radiation dose for highly cross-linked resins. They found a 50% decrease in the J-resistance curve for the highly cross-linked polyethylene (100 kGy) as compared to conventional polyethylene. Gillis et al. [13] also found a reduction in J-integral fracture toughness with radiation dose. Similarly Gomoll et al. [14] utilized the Rice and Sorenson model to measure $J_{\rm IC}$ and J_{SS} for a range of dosages up to 200 kGy. They found that for low dosages (<50 kGy) cross-linking benefited $J_{\rm IC}$ and provided more resistance to crack initiation while steady-state values, $J_{\rm SS}$, decreased monotonically with radiation dose. They observed that for 0–50 kGy, UHMWPE exhibited a ductile tearing behavior with stable crack growth; while highly crosslinked polyethylene (>50 kGy) exhibited spontaneous unstable fracture once $J_{\rm IC}$ was attained. These findings are consistent with the fracture studies performed by Gencur et al. [12]. A summary of the J-integral fracture toughness as a function of radiation dose is provided in Table 3.

5. Fatigue of conventional and cross-linked UHMWPE

Fatigue refers to the degradation of material properties as a result of cyclic loading and accumulated damage. Fatigue failure often occurs as a result of accumulated damage or growth of a defect to a critical dimension. The fatigue behavior of UHMWPE is sensitive to the molecular structure and depends on factors such as molecular weight, crystallinity, lamellae size, chain entanglement, and cross-link density [45]. In addition to molecular factors, the fatigue life of a polymeric component is controlled by a number of mechanical factors including the stress or strain amplitude of the loading cycle, the mean stress of the cycle, and the presence of stress concentrations or initial defects in the component. All of these factors are of considerable interest and practicality for the safe design of UHMWPE components subjected to fatigue loading. Understanding the fatigue resistance of conventional and highly cross-linked polyethylene used in orthopedics is of utmost importance due to the cyclic nature of physiological loading and the large contact stresses acting along the articulating surface. This is especially important in total knee replacements where cyclic contact stresses can range from 1 to 15 MPa in tension to $-40 \,\mathrm{MPa}$ in compression [22,46].

Cyclic damage leading to softening accompanied by a reduction in elastic modulus and yield stress is also a concern. Polymers subjected to cyclic loading typically experience a hysteresis and softening phenomena when a critical cyclic strain is attained [45]. Krzypow and Rimnac [47] have investigated the effect of cyclic loading the stress-strain behavior of conventional UHMWPE. In this work full reversed loading was examined and UHMWPE was found to soften under cyclic loading conditions. Another study by Meyer and Pruitt [48] examined the role of cyclic true strain on the structure, morphology, and relaxation behavior of conventional and gamma radiated UHMWPE. They noted cyclic softening and found that residual strain was more dependent on the amount of plastic strain in the strain amplitude than the number of loading cycles. An example of this cyclic softening on the stress-strain behavior is shown in Fig. 4. Another interesting finding

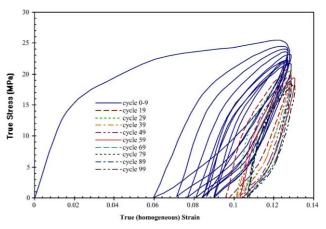


Fig. 4. Softening in UHMWPE stress-strain behavior due to cyclic loading at 0.12 true strain. Adapted from [48].

of this study was that density decreased monotonically with true plastic strain. This relationship between density and residual true strain provides remarkable evidence of a morphological evolution in UHMWPE directly related to the cyclic strain behavior. Electron microscopy revealed microvoid formation and fibrillation associated with cyclic damage. This finding was similar to that noted by Kurtz and co-workers [36]. Field emission microscopy of the etched surfaces revealed substantial texturing in the UHMWPE due to cyclic loading. Fig. 5 shows this failure mode of void nucleation and fibrillation. The findings of these studies indicate that UHMWPE undergoes significant changes in its morphology, structure and mechanical behavior as a result of cyclic loading. These findings suggest that the cyclic true stress–strain curves may be more appropriate when developing models that predict long-term stability of UHMWPE in orthopedic applications where cyclic contact stresses are expected.

Characterization of the fatigue behavior of a structural polymer entails the use of one of two distinct design philosophies. The first of these, commonly used in non-critical applications is the total life approach. This design methodology assumes that the component is initially defect free. Fatigue characterization is performed with unnotched specimens that are assumed to be free of flaws or substantial stress concentrations. This methodology is based on the notion that fatigue failure is a consequence of crack nucleation and subsequent growth to a critical size. The other philosophy is based on a defect tolerant approach in which the fatigue life of a component is based on the number of loading cycles needed to propagate a crack of an initial size to a critical dimension.

In the total life philosophy, it is assumed that no flaws pre-exist in the polyethylene resins and that the majority of the fatigue life will be spent in the initiation phase. In total life stress-based fatigue testing, the applied stress,

L.A. Pruitt | Biomaterials ■ (■■■) ■■■-■■■

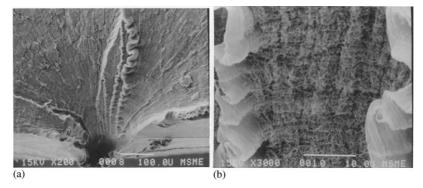


Fig. 5. Cyclic tensile fracture surface showing void nucleation and fibrillation at (a) low and (b) high magnification.

 σ_a , is typically described by the stress amplitude of the loading cycle and is defined as:

$$\sigma_{\rm a} = \frac{\sigma_{\rm max} - \sigma_{\rm min}}{2},\tag{8}$$

where σ_{max} is the maximum stress and σ_{min} is the minimum stress of the fatigue cycle. The stress amplitude is generally plotted against the number of cycles to failure on a linear-log scale. This plot is termed the S-N plot, where S represents the stress amplitude and N denotes the cycles to failure. This process is continued at increasingly smaller values of stress amplitude until an endurance limit is reached. An endurance limit is defined as the stress level that results in no failure (defined with a minimum of 10 million cycles). The assumption is that if the device is exposed to stress values below the endurance limit then the device is safe from fatigue failure. S-N curves enable life to be predicted based on the stress amplitude or range of stress amplitudes that the device is expected to encounter.

In contrast, the defect tolerant philosophy is based on the implicit assumption that structural components are intrinsically flawed and that the fatigue life is based on propagation of an initial flaw to a critical size. Fracture mechanics is used to characterize the propagation of fatigue cracks in these materials. The stress intensity factor, K, derived from linear elastic fracture mechanics is the parameter used to describe the magnitude of the stresses, strains and displacements ahead of the crack tip. There are three distinct regimes of crack propagation under constant amplitude cyclic loading conditions. Fig. 6 schematically illustrates the sigmoidal curve that captures the crack growth rate as a function of stress intensity range (illustrated on log-log scale). The plot captures three distinct regions: the slow crack growth or threshold-regime, the intermediate crack growth or Paris regime, and the rapid crack growth or fast fracture regime. The velocity of moving fatigue crack subjected to a constant stress amplitude loading is determined from the change in crack length, a, as a function of the number of loading cycles, N. This velocity represents the

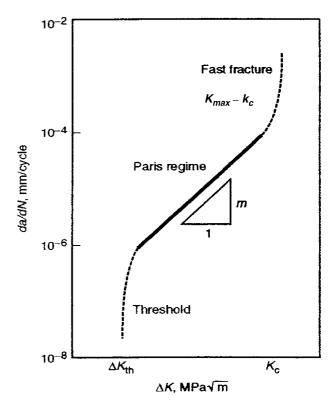


Fig. 6. Schematic of fatigue crack propagation plot showing near-threshold regime, Paris regime, and fast-fracture regime.

fatigue crack growth per loading cycle, da/dN, and is found from experimentally generated curves, where a is plotted as a function of N. The stress intensity factor range, $\Delta K = K_{\text{max}} - K_{\text{min}}$, which itself captures the far-field stress, crack length, and geometry, is the characteristic driving parameter for fatigue crack propagation. This is known as the Paris law, and it states that da/dN scales with ΔK through the power-law relationship:

$$\frac{\mathrm{d}a}{\mathrm{d}N} = C \,\Delta K^m,\tag{9}$$

where C and m are material constants. While this linear regime is most often used for life prediction, the fatigue

threshold is key for designing against the inception of crack growth.

The Paris law is commonly employed for fatigue life prediction of polymer components that have known stress concentrations or safety critical applications. It is implied in this defect-tolerant approach that the device or component contains an initial defect or crack size, a_i . Assuming that the fatigue loading is performed under constant stress amplitude conditions, that the geometric factor, $f(\alpha)$, does not change within the limits of integration, and that fracture occurs when the crack reaches a critical value, a_c , one can integrate the Paris equation in order to predict the fatigue life of the component:

$$N_{\rm f} = \frac{2}{(m-2)Cf(\alpha)^{m}(\Delta\sigma)^{m}\pi^{m/2}} \times \left[\frac{1}{a_{i}^{(m-2)/2}} - \frac{1}{a_{\rm c}^{(m-2)/2}}\right] \quad \text{for } m \neq 2.$$
 (10)

A complicating factor in the assessment of the fatigue resistance of conventional and cross-linked polyethylene lies in choosing a design philosophy. Variations in philosophical approach and associated experimental

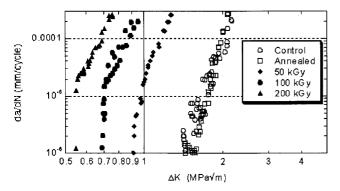


Fig. 7. Plot of crack velocity, da/dN vs. crack driving force, ΔK showing the effect of radiation dose on fatigue crack propagation resistance.

methodologies result in vastly different findings in the literature [16-20]. For example, O'Connor et al. reported that no failures were observed in their crosslinked specimens after 20 million fatigue cycles [17] while Baker et al. reported that cross-linking resulted in a significant decrease in the resistance to fatigue crack propagation [20]. The apparent dichotomy in these results is due to differences in testing philosophy. The O'Connor study utilized a total-life philosophy with unnotched samples while the Baker study utilized a defect tolerant philosophy with pre-cracked specimens to measure the material's resistance to crack propagation. The former measures the resistance to crack initiation (and subsequent propagation) while the latter measures resistance to crack growth. Both types of information are important for the design and prediction of the performance of the orthopedic device.

Recent work by Baker et al. [20] examined both the fatigue initiation and propagation resistance of UHMWPE with varying cross-link doses. A stressbased total-life test and a fracture mechanics approach was used to determine the effect of radiation dose (crosslinking) on the fatigue crack initiation and propagation resistance of polyethylene. Three doses of gamma radiation (50, 100 and 200 kGy) were used. Additionally, two conventional groups were examined and included an untreated GUR 1050 rod stock and rod stock with the same thermal treatment as the crosslinked groups. Fatigue crack propagation results for this study are provided in Fig. 7. Radiation cross-linking resulted in a monotonic decrease in crack propagation resistance and crack inception values (Table 4). For clinical comparison, the fatigue crack inception values for gamma-air sterilized and accelerated aging conditions for GUR 1050 are also included [19]. Note the similar relative decreases in the crack growth inception values for the gamma sterilized and gamma sterilized, aged conditions as compared to the highly cross-linked groups. The stress-life results from this study indicate that cross-linking is beneficial to fatigue initiation.

Table 4
Summary of fatigue crack propagation data

Paris regime fatigue $da/dN = C(\Delta K)^m$	GUR 1050	50 kGy	100 kGy	200 kGy		
(A) Fatigue crack inception data for conventional and cross-linked UHMWPE						
$\Delta K_{\rm incep} ({\rm MPa} \sqrt{\rm m})$	1.41	0.91	0.69	0.55		
% Decrease in ΔK_{incep}	_	35	51	61		

(B) Fatigue crack inception data for gamma radiation sterilized GUR 1050, gamma irradiated GUR 1050 subjected to accelerated aging, and non-sterile 1050 control

Paris regime fatigue $da/dN = C(\Delta K)^m$	Control ^a	25 kGy air ^a	25 kGy aged ^a
$\Delta K_{\text{incep}} \text{ (MPa } \sqrt{\text{m})}$	2.01	1.51	0.90
% Decrease in $\Delta K_{\rm incep}$	_	24	55

Adapted from [19,20].

^a Data is provided here to show the relative decreases in fatigue resistance owing to gamma radiation sterilization and accelerated aging.

Cross-linking resulted in an increased resistance to cyclic yield for any given stress range. The results of these studies indicate that the high degree of cross-linking is detrimental to fatigue propagation resistance but aids in crack initiation resistance. A subtlety in fatigue behavior is that microstructural improvements that aid fatigue initiation will generally degrade fatigue crack propagation. The question is then whether the design and material components are likely to have stress concentrations and defects that will render them susceptible to crack propagation.

It is clear that optimizing the microstructure is key to developing an UHMWPE resin that will provide both the needed wear and fatigue resistance in total joint replacements. Recent studies have investigated the coupled effects of cross-linking and enhanced crystallinity via high-pressure methods to improve the mechanproperties of UHMWPE. This microstructure provides a material with good wear resistance due to the cross-linking and improved fatigue resistance due to higher crystallinity and larger lamellae [49]. Such material developments are especially important for applications involving high cyclic stresses (i.e. tibial inserts) that can contribute to the propagation of subsurface cracks and can eventually lead to fatigue wear mechanisms.

6. Summary and clinical perspective

Highly cross-linked UHMPWE has shown great promise as an orthopedic bearing in total hip replacements. However, the enhanced resistance to plastic deformation that benefits wear behavior comes at the expense of other mechanical properties. Ultimate tensile strength, ductility, modulus, toughness, and crack propagation resistance are degraded at high cross-linking doses. The degradation in fracture properties indicates that highly cross-linked polyethylene should not be used in applications where high stresses are expected. Lower degrees of cross-linking may be more appropriate when designing for both wear and fatigue in total joint replacements.

References

- [1] Li S, Burstein AH. Ultra-high molecular weight polyethylene. The material and its use in total joint implants. J Bone Jt Surg Am 1994;76:1080–90.
- [2] Premnath V, Harris WH, Jasty M, Merrill EW. Gamma sterilization of UHMWPE articular implants: an analysis of the oxidation problem. Biomaterials 1996;17:1741–53.
- [3] Kurtz SM, Muratoglu OK, Evans M, Edidin AA. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. Biomaterials 1999;20:1659–88.

- [4] Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH, Gul R, McGarry F. Unified wear model for highly crosslinked ultra-high molecular weight polyethylenes (UHMWPE). Biomaterials 1999;20(16):1463–70.
- [5] McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. J Orthop Res 1999;17(2):157–67.
- [6] Jasty M, Bragdon CR, O'Connor DO, Muratoglu OK, Premnath V, Merrill EW, Harris WH. Marked improvement in the wear resistance of a new form of UHMWPE in a physiologic hip simulator. In: Transactions of 43rd Annual Meeting of the Orthopedic Research Society, San Francisco, 1997. p. 785.
- [7] Sun DC, Wang A, Stark C, Dumbleton JH. The concept of stabilization in UHMWPE. In: Transactions of the Fifth World Biomaterials Congress, vol. 1, 1996. p. 195.
- [8] Kurtz SM, Villarraga ML, Herr MP, Bergstrom JS, Rimnac CM, Edidin AA. Thermomechanical behavior of virgin and highly crosslinked ultra-high molecular weight polyethylene used in total joint replacements. Biomaterials 2002;23:3681–97.
- [9] Edidin AA, Pruitt L, Jewett CW, Crane DJ, Roberts D, Kurtz SM. Plasticity-induced damage layer is a precursor to wear in radiation-cross-linked UHMWPE acetabular components for total hip replacement. J Arthroplasty 1999;14(5):616–27.
- [10] Wang A, Sun DC, Yau SS, Edwards B, Sokol M, Essner A, Polineni VK, Stark C, Dumbleton JH. Orientation softening in the deformation and wear of ultra-high molecular weight polyethylene. Wear 1997;203:230–41.
- [11] Kurtz SM, Pruitt LA, Jewett CW, Foulds JR, Edidin AA. Radiation and chemical crosslinking promote strain hardening behavior and molecular alignment in ultra high molecular weight polyethylene during multi-axial loading conditions. Biomaterials 1999;20(16):1449–62.
- [12] Gencur SJ, Rimnac CM, Kurtz SM. Failure micromechanisms during uniaxial tensile fracture of conventional and highly crosslinked ultra-high molecular weight polyethylenes used in total joint replacements. Biomaterials 2003;24:3947–54.
- [13] Gillis AM, Schmiegg JJ, Bhattacharyya S, Li S. An independent evaluation of the mechanical, chemical and fracture properties of UHMWPE crosslinked by 34 different conditions. In: Proceedings of the 45th Annual Meeting of the Orthopaedic Research Society, vol. 24, Anaheim, CA. 1999. p. 908.
- [14] Gomoll A, Wanich T, Bellare A. J-Integral fracture toughness and tearing modulus measurement of radiation cross-linked UHMWPE. J Orthop Res 2002;20:1152–6.
- [15] Greenwald AS, Bauer TW, Ries MD. New polys for old: contribution or caveat. In: Transactions of 68th Annual Meeting of the American Academy of Orthopaedic Surgeons, San Francisco, 2001.
- [16] Baker DA, Hastings RS, Pruitt L. Study of fatigue resistance of chemical and radiation crosslinked medical grade ultrahigh molecular weight polyethylene. J Biomed Mater Res 1999;46(4):573–81.
- [17] O'Connor DO, Muratoglu OK, Bragdon CR, Lowenstein J, Jasty M, Harris WH. Wear and high cycle fatigue of highly crosslinked UHMWPE. In: Transactions of 44th Annual Meeting of the Orthopaedic Research Society, Anaheim, CA, 1999. p. 816.
- [18] Krzypow DJ, Bensusan J, Sevo K, Haggard W, Parr J, Goldberg V, Rimnac C. The fatigue crack propagation resistance of gamma radiation or peroxide crosslinked UHMW polyethylene. In: Transactions of Sixth World Biomaterials Congress, Hawaii, 2000. p. 382.
- [19] Baker DA, Hastings RS, Pruitt L. Compression and tension fatigue resistance of medical grade ultra high molecular weight polyethylene: the effect of morphology, sterilization, aging and temperature. Polymer 2000;41(2):795–808.

L.A. Pruitt | Biomaterials ■ (■■■) ■■■—■■■

- [20] Baker DA, Bellare A, Pruitt L. The effects of degree of crosslinking on the fatigue crack initiation and propagation resistance of orthopedic grade polyethylene. J Biomed Mater Res 2003;66A:146–54.
- [21] Duus LC, Walsh HA, Gillis AM, Noisiez E, Li S. The effect of resin grade, manufacturing method, and cross linking on the fracture toughness of commercially available UHMWPE. Trans Orthop Res Soc 2000;25:544.
- [22] Bartel DL, Bicknell VL, Wright TM. The effect of conformity, thickness, and material on stresses in ultra-high molecular weight components for total joint replacement. J Bone Jt Surg Am Vol 1986;68(7):1041–51.
- [23] Pascaud RS, Evans WT, McCullagh PJ, Fitz Patrick DP. Influence of gamma-irradiation sterilization and temperature on the fracture toughness of ultra-high-molecular-weight polyethylene. Biomaterials 1997;18:727–35.
- [24] Wang A, Stark C, Dumbleton JH. Role of cyclic plastic deformation in the wear of UHMWPE acetabular cups. J Biomed Mater Res 1995;29:619–26.
- [25] Jasty M, Goetz DD, Bragdon CR, et al. Wear of polyethylene acetabular components in total hip arthroplasty. An analysis of one hundred and twenty-eight components retrieved at autopsy or revision operations. J Bone Jt Surg Am 1997;79:349–58.
- [26] Kurtz SM, Rimnac CM, Pruitt L, Jewett CW, Goldberg V, Edidin AA. The relationship between the clinical performance and large deformation mechanical behavior of retrieved UHMWPE tibial inserts. Biomaterials 2000;21:283–91.
- [27] Bartczak Z, Cohen RE, Argon AS. Evolution of the crystalline texture of high-density polyethylene during uniaxial compression. Macromolecules 1992;25:4692–704.
- [28] Galeski A, Bartczak Z, Cohen RE, Argon AS. Morphological alterations during texture-producing plastic plane strain compression of high density polyethylene. Macromolecules 1992;25: 5705–18.
- [29] G'Sell C, Jonas JJ. Determination of the plastic behaviour of solid polymers at constant true strain rate. J Mater Sci 1979;14:583.
- [30] G'Sell C, Hiver JM, Dahoun A, Souahi A. Video-controlled tensile testing of polymers and metals beyond the necking point. J Mater Sci 1992;27:5031–9.
- [31] G'Sell C, Dahoun A. Evolution of microstructure in semicrystalline polymers under large plastic deformations. Mater Sci Eng 1994;A175:183–99.
- [32] G'Sell C, Paysant-Le Roux B, Dahoun A, et al. Plastic behaviour and resistance to wear of ultra-high molecular weight polyethylene. Deformation Yield Fracture Polym 1997;10:57–60.
- [33] Kitagawa M, Zhou D, Qiu J. Stress-strain curves for solid polymers. Polym Eng Sci 1995;35:1725–32.

- [34] Lee BJ, Argon AS, Parks DM, Ahzi S, Bartczak Z. Simulation of large strain plastic deformation and texture evolution in high density polyethylene. Polymer 1993;34:3555–75.
- [35] Lin L, Argon AS. Review: structure and plastic deformation of polyethylene. J Mater Sci 1994;29:294–323.
- [36] Kurtz SM, Pruitt L, Jewett CW, Crawford RP, Crane DJ, Edidin AA. The yielding, plastic flow and fracture behavior of ultra high molecular weight polyethylene used in total joint replacements. Biomaterials 1999;19/21:1989–2003.
- [37] Kurtz SM, Rimnac CM, Bartel DL. A predictive model for the tensile true stress-strain behavior of chemically and mechanically degraded ultra-high molecular weight polyethylene. J Biomed Mater Res (Appl Biomater) 1998;350:209–20.
- [38] Kurtz SM, Rimnac CM, Santner TJ, Bartel DL. Exponential model for the tensile true stress-strain behavior of as-irradiated and oxidatively degraded ultra high-molecular weight polyethylene. J Orthop Res 1996;14:755-61.
- [39] Suresh S. Fatigue of materials. Cambridge: Cambridge University Press; 1992.
- [40] Tada H, Paris PC, Irwin GR. The stress analysis of cracks handbook. Hellertown, PA: Del Research Corporation; 1973.
- [41] Rimnac CM, Wright TM, Klein RW. J integral measurements of ultra-high molecular weight polyethylene. Polym Eng Sci 1988;28:1586–9.
- [42] Mai Y-W, Cotterell B, Horlyck R, Vigna G. The essential work of plane stress ductile fracture of linear polyethylenes. Polym Eng Sci 1987;27:804–9.
- [43] Pascaud RS, Evans WT. Critical assessment of methods for evaluating J_{IC} for a medical grade ultra-high molecular weight polyethylene. Polym Eng Sci 1997;37:11.
- [44] Pruitt L, Bailey L. Factors affecting the near-threshold fatigue behavior of surgical grade ultra high molecular weight polyethylene. Polymer 1998;39:1545–53.
- [45] Hertzberg RW, Manson JA. Fatigue of engineering plastics. New York: Academic Press; 1980.
- [46] Kennedy FE, Currier JH, Plumet S, Duda JL, Gestwick DP, Collier JP, Currier BH, Dubourg M-C. Contact fatigue failure of ultra high molecular weight polyethylene bearing components of knee prostheses. Trans ASME 2000;122:332–9.
- [47] Krzypow DJ, Rimnac CR. Cyclic steady-state stress-strain behavior of UHMW polyethylene. Biomaterials 2000;21:2081–7.
- [48] Meyer R, Pruitt L. The effect of cyclic true strain on the morphology, structure, and relaxation behavior of ultra high molecular weight polyethylene. Polymer, 2001;42:5293–306.
- [49] Simis K, Bellare A, Pruitt L. The effect of high pressure crystallisation and crosslinking on the fatigue crack inception behaviour of medical grade ultra high molecular weight polyethylene. In: Proceedings of the 12th International Conference on the Deformation, Yield and Fracture of Polymers, Cambridge, UK, 2003. p. 69–72.