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Material properties of ultra-high molecular weight polyethylene: Comparison of tension, compression, nanomechanics and microstructure across clinical formulations

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ABSTRACT

This is the first study to simultaneously measure material properties in tension, compression, nanoindentation as well as microstructure (crystallinity and lamellar level properties) across a wide variety of clinically relevant ultra-high molecular weight polyethylene (UHMWPE) formulations. Methodologies for the measurement of UHMWPE mechanical properties—namely elastic modulus, yield stress, yield strain, ultimate strength, energetic toughness, Poisson's ratio, hardness and constitutive variables—are evaluated. Engineering stress-strain behavior is compared to true stress-strain behavior for UHMWPE across a range of cross-linking and antioxidant chemistry. The tensile mechanical properties and constitutive behavior of UHMWPE are affected by resin type, antioxidant source and degree of cross-linking. Poisson's ratio is shown to be affected by resin type, antioxidant addition, and cross-linking dosage. Relationships between bulk mechanical properties from different measurement methodologies as well as microstructure are analyzed across all material formulations using Spearman rank correlation coefficients. Modulus and yield strength correlate in both tension and compression. Similarly, tensile and compressive properties including modulus and yield strength correlate strongly with crystallinity (X_c) and lamellar thickness (D). This work has broad application and provides a basis for interpreting the mechanical behavior of UHMWPE used in orthopedic implants.

1. Introduction

For nearly sixty years, medical grade ultra-high molecular weight polyethylene (UHMWPE) has been the longstanding material of choice for use as a bearing surface in total joint arthroplasty (Kurtz, 2015). In its tenure as an orthopedic biomaterial, UHMWPE has undergone numerous iterations in its processing in order to address ongoing clinical challenges faced in total joint replacements (TJRs) including wear-debris induced osteolysis (Bozic et al., 2009; Muratoglu et al., 1999), oxidation embrittlement (Costa et al., 1998; Edidin et al., 2000; Premnath et al., 1996) and fracture associated with high cyclic contact stresses (Baker et al., 2003; Furmanski et al., 2009; Gencur et al., 2006). Contemporary formulations of UHMWPE are owed to decades of research that have addressed challenges of wear, oxidation, and fatigue fracture of this polymer in both laboratory as well as clinical settings (Atwood et al., 2011; Kurtz, 2015).

UHMWPE is a semicrystalline polymer with approximately half of its structure in an ordered crystalline lamellae domain (Atwood et al., 2011; Bistolfi et al., 2009; Turell and Bellare, 2004). The polymer has a very high molecular weight (2–6 million g/mol) that facilitates high entanglement density in its amorphous phase and superior energetic toughness as compared to other homopolymers (Kurtz, 2009; Pruitt, 2005). Despite its excellent energetic toughness and inherent biocompatibility, the polymer in its untailored form is susceptible to wear when articulating against the hard bearings typically used in TJRs (Kurtz, 2015, 2009). Cross-linking through energetic schemes improves wear resistance but comes with a concomitant reduction in mechanical properties (Atwood et al., 2011; Crowninshield and Muratoglu, 2008; Gencur et al., 2006; Rimnac and Pruitt, 2008) as well as susceptibility to oxidation (Costa et al., 1998; Kurtz et al., 1999b; Premnath et al., 1996). Initial improvements to oxidation resistance in cross-linked formulations of UHMWPE utilized thermal annealing methods, yet such treatments either failed to fully eliminate free radicals or altered the microstructure in a way that compromised fatigue resistance (Atwood et al., 2011; Morrison and Jani, 2009; Pruitt, 2005). Antioxidants such as vitamin E have been recently added to UHMWPE in order to improve

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oxidation resistance without detriment to mechanical properties but are known to limit the extent of cross-linking in the polymer (Furmanski and Pruitt, 2007; Oral et al., 2006). With so many options available to tailor medical grades of UHMWPE, it is necessary to understand how these alterations affect structural properties and performance in orthopedic bearing applications.

The purpose of this study was to evaluate the microstructure and mechanical properties of twelve clinically relevant blends of UHMWPE that provided unique combinations of resin type, cross-linking dosage, and antioxidants. We evaluated the microstructure using differential scanning calorimetry (DSC) and small angle x-ray scattering (SAXS). In parallel, we conducted a comprehensive analysis of constitutive behavior and assessment of mechanical properties in both tension and compression. Surface mechanical properties were determined using nanoindentation. Correlations between structure and mechanical properties were then assessed for all material groups. Our study is, to our knowledge, the first unified body of work to provide a comprehensive analysis of microstructure, constitutive behavior in tension and compression, as well as nanomechanical properties across a spectrum of clinical formulations of UHMWPE. Our methods and analysis provide a basis for engineers and designers to better understand and grasp the mechanical performance of UHMWPE used in orthopedic implants.

2. Materials and methods

2.1. Materials

For this study, twelve clinical formulations of UHMWPE were investigated (Table 1). Material was sourced from three different UHMWPE consolidators: Orthoplastics (Lancashire, UK), DePuy (Warsaw, IN), and Quadrant EPP (Fort Wayne, IN). Variations to two base resins, GUR 1020 and GUR 1050, were investigated across a range of cross-link density and antioxidant chemistry. The antioxidants were comprised of 0.1 wt% Vitamin E (VE) and COVERNOX™ (AO) (medical grade version of Irganox™ 1010) which were blended into GUR 1020 resin before consolidation. Lastly, radiation cross-linking dosages at 75 kGy in base resin materials were re-melted (RM) to alleviate free radicals and served as cross-linked samples without antioxidants. Four distinct material categories (Table 1) were explored: 1020 resin (0 kGy, 35 kGy, 75 kGy RM); 1020 resin with AO antioxidant (AO 0 kGy, AO 80 kGy); 1020 resin with 0.1 wt% vitamin E (VE 0 kGy, VE 50 kGy, VE 75 kGy, VE 100 kGy, VE 125 kGy); and 1050 resin (0 kGy, 75 kGy RM). All UHMWPE materials were compression molded except for GUR 1050 75 kGy RM which was ram extruded.

2.2. Methods

2.2.1. Microstructure

The degree of crystallinity in each of the UHMWPE formulations was determined using differential scanning calorimetry (DSC) analysis. DSC measurements were obtained according to ASTM F2625-10 (2016) using a TA Instruments Q2000 DSC (New Castle, DE). The test specimens were cut with a clean razor blade from un-tested tensile specimens into 4.9–5.8 mg pieces and crimped between a standard DSC aluminum pan and lid. DSC specimens were subjected to a heating rate of 10 °C/min up to a temperature of 200 °C. The percent crystallinity was determined using the following relationship:

$$\%X = \frac{\Delta H_s}{\Delta H_f} \times 100\% \quad (1)$$

where ΔH_s is the heat of fusion of the sample in J/g and ΔH_f is the heat of fusion of a 100% crystalline sample (289.3 J/g for polyethylene as per ASTM F2625).

Small angle x-ray scattering (SAXS) was utilized to determine lamellar size distribution across the UHMWPE groups. SAXS data was collected using a laboratory CuKα rotating anode SAXSLAB instrument. The collimated beam had a diameter of approximately 0.4 mm at the sample position. The SAXS scattering intensity was collected by a DECTRIS PILATUS 300 K detector placed at a distance that corresponds to an angular scattering range of $\boldsymbol{q}_{min} = 0.032$ [nm^{-1}] and $\boldsymbol{q}_{max} = 2.5$ [nm^{-1}], and the scattering vector, q, was defined as

$$q = (4\pi/\lambda)\sin\theta \quad (2)$$

where λ is the wavelength of the x-ray used (0.154 nm) and θ is half the scattering angle. The x-ray source was operated at 45 kV and 30 mA. Based on beam diameter and sample thickness, the sampling volume associated with each x-ray measurement was estimated to be 0.06 mm^3. All SAXS samples were 4.5 mm × 10 mm × 1 mm (thickness).

2.2.2. Tension testing and constitutive modeling

Tension testing was utilized to determine the engineering stress-strain and true stress-strain behavior across the UHMWPE formulations.

Table 1
UHMWPE material formulations and consolidators. Darker colors at the top of the table denote base formulations in that group. The following lighter colors denote irradiation cross-link treatments to that material formulation group.

UHMWPE Material Formulation and Manufacturer			
GUR 1020 (Orthoplastics)	GUR 1020 AO (Depuy)	GUR 1020 VE (Orthoplastics)	GUR 1050 (Orthoplastics)
GUR 1020 35kGy (Orthoplastics)	GUR 1020 AO 80kGy (Depuy)	GUR 1020 VE 50kGy (Orthoplastics)	GUR 1050 75kGy RM (Quadrant)
GUR 1020 75kGy RM (Orthoplastics)		GUR 1020 VE 75kGy (Orthoplastics)	
		GUR 1020 VE 100kGy (Orthoplastics)	
		GUR 1020 VE 125kGy (Orthoplastics)	