Micromechanisms of fatigue crack growth in polycarbonate polyurethane: Time dependent and hydration effects

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A B S T R A C T

Polycarbonate polyurethane has cartilage-like, hygroscopic, and elastomeric properties that make it an attractive material for orthopedic joint replacement application. However, little data exists on the cyclic loading and fracture behavior of polycarbonate polyurethane. This study investigates the mechanisms of fatigue crack growth in polycarbonate polyurethane with respect to time dependent effects and conditioning. We studied two commercially available polycarbonate polyurethanes, Bionate® 75D and 80A. Tension testing was performed on specimens at variable time points after being removed from hydration and variable strain rates. Fatigue crack propagation characterized three aspects of loading. Study 1 investigated the impact of continuous loading (24 h/day) versus intermittent loading (8–10 h/day) allowing for relaxation overnight. Study 2 evaluated the effect of frequency and study 3 examined the impact of hydration on the fatigue crack propagation in polycarbonate polyurethane. Samples loaded intermittently failed instantaneously and prematurely upon reloading while samples loaded continuously sustained longer stable cracks. Crack growth for samples tested at 2 and 5 Hz was largely planar with little crack deflection. However, samples tested at 10 Hz showed high degrees of crack tip deflection and multiple crack fronts. Crack growth in hydrated samples proceeded with much greater ductile crack mouth opening displacement than dry samples. An understanding of the failure mechanisms of this polymer is important to assess the long-term structural integrity of this material for use in load-bearing orthopedic implant applications.

1. Introduction

Polyurethane copolymers have a broad range of elastomeric and biocompatible properties that make them good candidates for use in medical applications. Polyether polyurethane and polyester polyurethanes were first introduced in medical applications, but unforeseen oxidative and hydrolytic degradation mechanisms led to their premature failure (Stokes, 1995; Christenson et al., 2007). Polycarbonate polyurethane was subsequently developed in the 1990s as a more biostable alternate (Tanzi et al., 2000; Khan et al., 2005a; Chandy et al., 2009; Christenson et al., 2004).

Polycarbonate polyurethane (PCU) is a block copolymer. Thermodynamic interactions between the polyurethane (hard) and polycarbonate (soft) segments create phase separation into amorphous regions of mixed hard and soft segments and regions of ordered hard segments that dictate the structure of the material (Eceiza et al., 2008; Guo et al., 2007; Martin et al., 1997). The exact degree of phase separation is dependent on thermal and temporal processing (Martin et al., 1997; Cipriani et al., 2012). Correspondingly, the mechanical properties of PCU are dependent on the degree of phase separation (Guo et al., 2007; Martin et al., 1997, 1996; Santerre et al., 2005). The ordered hard segments effectively create a quasi-rubber-reinforced energetic toughening mechanism that enables an increased ductility while maintaining strength in the polymer. Hard segments form highly ordered structures with a high degree of hydrogen bonding within the domain. The remaining amount of hard segments in the amorphous mixture of soft segments determines the degree of phase separation of the material (Stokes, 1995; Christenson et al., 2007; Eceiza et al., 2008; Cipriani et al., 2012; Geary et al., 2008).

Polycarbonate polyurethane is also hygroscopic. Absorbed water disrupts the hydrogen bonding in the ordered domains of PCU and has a plasticizing effect on the polymer. Water absorption has been shown to significantly decrease the ultimate strength, ultimate elongation, and modulus of PCU (Khan et al., 2005a; Geary et al., 2008); yet, little is known about the effects of hydration on fatigue and fracture resistance of PCU.

The cartilage-like modulus and elastomeric properties of PCU make it an attractive material for orthopedic joint replacement application.

More recently, PCU has been introduced as an alternative bearing polymer to ultra-high molecular weight polyethylene in hip, knee, and spinal implants (Siebert et al., 2008; Sonntag et al., 2012; Wippermann et al., 2008; Ianuzzi et al., 2010; Cipriani et al., 2013; St. John, 2014). Initial data on PCU is promising (Siebert et al., 2008; Ianuzzi et al., 2010; Cipriani et al., 2013; Kurtz et al., 2009; Fan et al., 2012), though long-term clinical data is lacking. Although isolated cases of fracture have been observed in vivo (Ianuzzi et al., 2010; Khan et al., 2005b), little work on the fatigue properties of PCU exists (Miller et al., 2017; Wiggins et al., 2003).

This study uses a safety-critical, defect-tolerant approach to characterize fatigue in PCU. This approach investigates the mechanisms that control and propagate a flaw under fatigue conditions that mimic orthopedic implant applications. By understanding the mechanisms that propagate a flaw under cyclic loading we can better predict potential long-term failure mechanisms of this material. The objective of this study was to explore the impact of time-dependent effects and hydration on the ability for cracks to propagate in PCU.

2. Methods

2.1. Materials

Polycarbonate polyurethanes, tradename Bionate® 75D and 80 A (named for their respective Shore hardness values), were obtained from DSM Biomedical, Berkeley, CA.

2.2. Tensile testing

Tensile specimens (ASTM D638, Type IV, Fig. 1A) were cut from injection molded plaques by waterjet as shown in Fig. 1A. These dog-bone specimens were soaked in phosphate-buffered saline (PBS) at room temperature for at least 12 days prior to testing to ensure equilibrium had been reached (Geary et al., 2008). Tensile testing was performed on an Instron 5566 (Norwood, MA) using two protocols. First, the effect of 'drying time' was assessed by testing samples after variable removal times from the PBS bath of 1, 5, and 10 min. Specimens were extended at a rate of 1 mm/min until 0.25% strain, and then 500 mm/min until break (n = 3, ISO 527-1 and ASTM D638). Second, the effects of strain rate on the mechanical response was assessed using crosshead displacement rates of 10, 75, and 150 mm/min, all with a dry time of 5 min (n = 3). These displacement rates translate to strain rates of 0.52%/s, 3.91%/s, and 7.83%/s, respectively.

For all tests, excess water was removed from the sample immediately after removal from PBS. Samples were then placed on an absorbent material in air until testing. Because tensile tests were relatively fast (between 1 and 2 min at 500 mm/min), additional

evaporation during testing was considered negligible. However, at low strain rates of 10 mm/min, tests lasted up to 30 min, therefore the effects drying must be considered along with of strain rate. Code was constructed in MATLAB to extract relevant tensile properties in accordance with ASTM D638: elastic modulus, yield stress, yield strain, ultimate stress, and strain to failure.

2.3. Fatigue crack growth

Compact tension disc specimens were machined from injection molded Bionate® 75D discs (3.3 mm thick, 38 mm in diameter) as guided by ASTM E1820 and E647 (Fig. 1B). Sample thickness was limited by the cooling rate following injection molding that would provide homogenous phase separation through the thickness. A 1.0 ± 0.2 mm pre-crack was started with a razor blade in the 0.005 in radius notch. The samples were cyclically loaded in tension (14–140 N, R = 0.1, n = 3–4) using a servohydraulic Instron 8871 (Norwood, MA). Unless otherwise specified, testing was done in air at room temperature with a forced air-cooling system to reduce hysteretic heating. Crack growth was recorded optically (Infinivar CFM-2/S, 5 µm/pixel and Sony XCD-SX910) and a custom MATLAB code was used for image processing.

Three test groups were evaluated to test the effects of relaxation, frequency, and conditioning respectively as outlined in Table 1. First, samples were tested both intermittently and continuously at 5 Hz. Intermittently loaded samples were loaded 8–10 h/day and unloaded completely overnight. Continuously loaded samples were loaded 24 h/day. Second, the effect of frequency was evaluated by testing samples at 2, 5, and 10 Hz. Samples tested at 2 Hz were tested intermittently while samples tested at 5 and 10 Hz were tested continuously. Third, the effect of hydration was evaluated by testing conditioned samples fully submerged in a PBS bath. Crack measurements were performed while samples were loaded in the environmental bath chamber (acrylic walls). Conditioned samples were soaked in PBS and the mass was measured daily (to ensure that equilibrium had been reached). All samples were tested after more than 30 days of conditioning.

After fatigue failure, the fracture surfaces were sputter coated and imaged with a Hitachi 2460 Scanning electron microscope (SEM). To compare the fatigue fracture surfaces to monotonic failure, a single compact tension specimen of equivalent geometry was tested at a strain rate of 50 mm/min until failure, sputter coated and imaged with the SEM. Results are presented as average ± standard deviation. A Students t-test and one-way ANOVA with post hoc analysis were used to compare means.

3. Results

3.1. Tensile testing

The results of the tensile testing are summarized in Table 2. Drying time up to 10 min did not have a statistically significant effect on the tensile properties of Bionate® 75D (Fig. 2D). In the case of Bionate® 80 A, the ultimate strain was lower for the 1 min dry time compared to
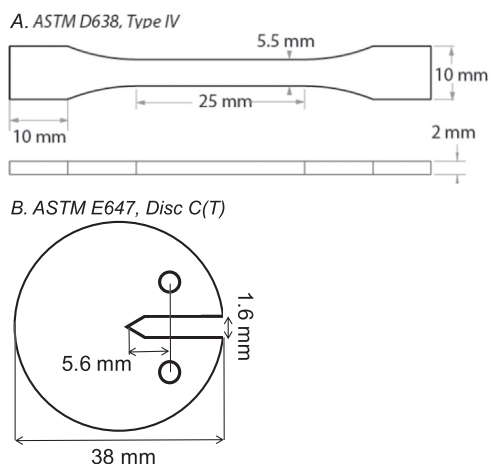

Fig. 1. Geometry of tension testing dogbones (A) and compact tension disc specimens (B).

Table 1
Outline of testing done in Studies 1 – 3.

	Loading	Frequency	Conditioning
Study 1	Intermittent (8–10 h/day) Continuous (24 h/day)	5 Hz	Dry
Study 2	Intermittent Continuous	2 Hz 5 Hz 10 Hz	Dry
Study 3	Continuous	5 Hz	Dry Hydrated