









# Deformation and fatigue of tough 3D printed elastomer scaffolds processed by fused deposition modeling and continuous liquid interface production

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## Abstract

Polyurethane (PU) based elastomers continue to gain popularity in a variety of biomedical applications as compliant implant materials. In parallel, advancements in additive manufacturing continue to provide new opportunities for biomedical applications by enabling the creation of more complex architectures for tissue scaffolding and patient specific implants. The purpose of this study was to examine the effects of printed architecture on the monotonic and cyclic mechanical behavior of elastomeric PUs and to compare the structure-property relationship across two different printing approaches. We examined the tensile fatigue of notched specimens, 3D crosshatch scaffolds, and two 3D spherical pore architectures in a physically crosslinked polycarbonate urethane (PCU) printed via fused deposition modeling (FDM) as well as a photo-cured, chemically-crosslinked, elastomeric PU printed via continuous liquid interface production (CLIP). Both elastomers were relatively tolerant of 3D geometrical features as compared to stiffer synthetic implant materials such as PEEK and titanium. PCU and crosslinked PU samples with 3D porous structures demonstrated a reduced tensile failure stress as expected without a significant effect on tensile failure strain. PCU crosshatch samples demonstrated similar performance in strain-based tensile fatigue as solid controls; however, when plotted against stress amplitude and adjusted by porosity, it was clear that the architecture had an impact on performance. Square shaped notches or pores in crosslinked PU appeared to have a modest effect on strain-based tensile fatigue while circular shaped notches and pores had little impact relative to smooth samples. When plotted against stress amplitude, any differences in fatigue performance were small or not statistically significant for crosslinked PU samples. Despite the slight difference in local architecture and tolerances, crosslinked PU solid samples were found to perform on par

with PCU solid samples in tensile fatigue, when appropriately adjusted for material hardness. Finally, tests of samples with printed architecture localized to the gage section revealed an effect in which fatigue performance appeared to drastically improve despite the localization of strain.

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## Introduction

Polyurethanes (PUs) represent a large class of materials that are becoming increasingly popular for many biomedical applications. While earlier generations of PUs often suffered from durability and biostability concerns, newer generations such as PCU are gaining in popularity due to their presumably enhanced longevity (Lamba et al., 1997, M. West et al., *Using Polyurethanes in Medical Applications.*, R.W. Treharne, A. Greene, *The case for the use of polycarbonate-urethane in orthopedic implants*, Med-Tech, Spring, 2008, 1, pp. 18–22.). While the biocompatibility of these PUs has been relatively well established (Christenson et al., 2007, Stokes et al., 1995), other aspects such as fatigue performance remain largely understudied. The long-term success of PU in many biomedical applications will depend in part on the material fatigue properties. Therefore, understanding how the fatigue performance of PUs relates to factors such as polymer structure, as well as macroscopic device structure, would be valuable from both basic science and applied technology points of view. In our previous work, we examined the toughness and fatigue performance of a particular PU, polycarbonate urethane (PCU), as a function of both hard segment content and processing via injection molding or 3D printing (fused deposition modeling). The material demonstrated considerable toughness in both compressive and tensile fatigue loading (Miller, 2016, Miller, 2017). In addition, solid 3D printed samples matched or exceeded the performance of injection molded counterparts in terms of tensile and compressive monotonic properties, shear strength, and tensile fatigue performance (Miller, 2017). While the results for the 3D printed solid specimens were on par with injection molded materials, there are many biomedical applications that may require or benefit from the inclusion of pores or three-dimensional architectures.

PUs are available in both bioresorbable as well as nonresorbable varieties that are more resistant to degradation (Santerre, 2005, Zdrahala and Zdrahala, 1999). The case for the use of pores and architectures for bioresorbable materials is rather obvious for the application of tissue engineering, where permeability will assist in cell migration and tissue ingrowth and eventual replacement of the scaffold. Recently, bioresorbable materials with architecture have even been used as temporary supporting systems for bioinks, allowing for dual nozzle printing of cell-laden constructs with custom or complex shapes (Lee, 2014, Shim, 2012, Shim, 2011, Pati, 2014). However, the use of pores and architectures may also be desirable with long-term materials where permeability or ingrowth for permanent attachment is desired, for example. The published literature contains very little information on the fatigue performance of polymer scaffolds, porous polymers, or polymers with architecture. Work includes that by Evans et al., who investigated the fatigue performance of a variety of surface-porous, hard polymers including polyether-ether-ketone (PEEK) and polycarbonate. Generally, they found a substantial decrease in fatigue performance when surface porosity was introduced, and that the ratio of upper to lower yield points of the material could provide insight as to how large of an impact such defects might have (Evans, 2015, N.T. Evans, *Processing-structure-property relationships of surface porous polymers for orthopaedic applications*, 2016.). Hoyt et al. examined the compressive and tensile fatigue of open-cell, porous poly(para-phenylene) scaffolds fabricated through porogen leaching. They found a hundredfold decrease in the tensile endurance limit due to large stress concentrations in their porous architecture (Hoyt et al., 2015). To the best of the

authors' knowledge, few studies exist that have investigated the high cycle fatigue performance of porous polymers or polymer scaffolds. The lack of research in this area for polymers is likely due to the significant impact pores and architecture can have on a material's fatigue performance, leading to a preference for stronger materials for permanent applications, such as metals. In contrast with polymers, considerably more work exists examining the fatigue performance of metal scaffolds and porous metals. For example, several groups have investigated the fatigue performance of porous Ti-6Al-4V. Generally, they have found that the inclusion of pores or architectures leads to a substantial decrease in fatigue strength on the order of approximately 75% (Li, 2012, Hrabe, 2011, Wolfarth and Ducheyne, 1994, Cook, 1988, Yavari, 2013, Cook, 1984, Yue et al., 1984, Kohn and Ducheyne, 1990, Yavari, 2015). Similar work has also been conducted for porous tantalum (Sevilla, 2007, Wernle and Dharia, 2016, Zardiackas, 2001).

Studies on the fatigue performance of scaffolds and porous samples of compliant materials, or elastomers, represents a virtually nonexistent subset. From a more fundamental point of view, the effects of pores and architectures on fatigue performance can be seen as simply a notch sensitivity or stress concentration issue. However, the literature also contains very little information on notch sensitivity and stress concentrations effects in elastomers. This fact also was also noted by McNamara et al., who performed tensile fatigue tests on notched dumbbells of both ethylene propylene diene monomer (EPDM) and natural rubbers. They found that fatigue life was directly influenced by the severity of the notch, notch severity diminishes with increasing deformation, and that notch sensitivity is less pronounced for natural rubber than EPDM due to strain crystallization (McNamara, 2011). Monotonic testing of notch effects for rubbery and rubber-modified materials shows generally promising results, with most displaying small, or even negative, notch sensitivity factors (C. Balazs, Mechanical design and notch sensitivity of molding materials., DTIC Document, 1964, Takano and Nielsen, 1976). Additionally, for materials exhibiting substantial hysteresis, such as PUs, it has been found that stress concentrations at notches are significantly lessened under dynamic loading leading to superior performance as compared to materials with less hysteresis (Andrews, 1963, Whittaker, 1974).

Recent advancements in fabrication techniques, specifically 3D printing, have enabled the construction of more complex, tailored scaffolds and architectures. Designer scaffolds have been found to sometimes better reproduce the mechanical properties of the associated tissue, as well as provide better biologic results, than those made from traditional methods such as porogen leaching (Hollister, 2005). While the majority of work with these polymer scaffolds pertains to bioresorbable varieties (Hollister, 2005, Williams, 2005, Knutsen, 2015), permanent implants will also benefit from the addition or use of such architectures. However, the fatigue performance of such scaffolds must first be investigated, as existing work has demonstrated a significant detrimental impact on fatigue performance with the inclusion of pores or architectures in materials such as PEEK and Ti-6Al-4V. Therefore, the objective of this study is to understand the impact of architecture on the fatigue performance of printed PUs through systematic testing of a variety of biomedically relevant architectures.

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## Section snippets

### Materials

Materials for this study included the physically crosslinked Carbothane AC-4095A obtained from Lubrizol (95A) in pellet form, as well as a photo-cured, elastomeric, chemically crosslinked polyurethane with 68A

hardness obtained from Carbon 3D (EPU40) in liquid resin form. For printed 95A samples, the pellets were first extruded into 3mm printer filament following Lubrizol documentation. For injection molded (IM) 95A samples, the pellets were sent to Lansen Mold Co. Inc. and injection molded...

## microCT and sample characterization

Porosity data for the solid, crosshatch, and advanced architecture samples is summarized in Table 2. Average line width and clear spacing between lines is also reported for crosshatch samples. Samples demonstrated consistency in porosity with 95A crosshatch samples ranging from 17.9% to 58.9% porosity and EPU40 crosshatch samples ranging from 37.2% to 58.9% porosity. Solid printed 95A and EPU40 samples averaged below 2% porosity. Cylindrical pore EPU40 specimens reported 44.0% porosity, while...

## Discussion

Polyurethanes are a popular class of biomaterials that have already found widespread use in a number of biomedical applications. Their popularity will likely continue to increase as the biomedical field pushes for the use of tough, compliant materials to address issues associated with many traditional, stiffer materials. For example, the benefits of a compliant material are becoming apparent in applications ranging from spinal devices (John, 2014) to acetabular cups (Elsner, 2010, Smith et al., ...

## Conclusions

We have investigated the tensile fatigue performance of samples of a printed thermoplastic PCU as well as a photo-cured PU with various architectures. The following are the conclusions of the work:

1. Elastomeric PUs are relatively tolerant of architectures and notches. Introduction of porosity led to a decrease in tensile failure stress based on gross area as expected, without a significant effect on tensile failure strain. Effects on fatigue performance were small, and the EPU40 material proved...

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...Stratasys Inc., USA first introduced FDM in the early 1990 s [18,19]. Generally different thermoplastic materials [20–23] like poly-lactic acid (PLA), reinforced PLA [24], acrylonitrile butadiene styrene (ABS) [25–29], polycarbonate (PC), polyurethanes [31] and PCABS blend are used in FDM process. Recently, the researchers are exploring new materials like ceramics[32], PLA/biphasic calcium phosphate [33], polymer-bioactive glass composites [34], poly-caprolactone (PCL)-based composites [35], biomaterials [36], low melting point alloys [37] etc. for FDM....

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