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Fatigue of injection molded and 3D printed polycarbonate urethane in solution

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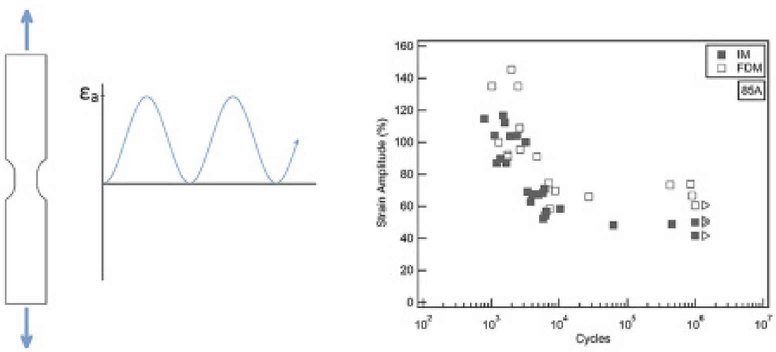
Highlights

- Analyzed properties and tensile fatigue of 3 grades of polycarbonate urethane.
- Compare injection molded samples to 3D printed (fused deposition modeling).
- Increased hard segment improves stress-based tensile fatigue performance.
- 3D printed samples matched or beat injection molded samples across the board.

Abstract

Thermoplastic polycarbonate urethanes (PCUs), have promise in many biomedical applications due to their low stiffness, favorable biocompatibility, and high strength. The long-term performance of PCU implants in load-bearing applications remains to be seen, and will depend in part on the material fatigue properties. Optimizing implants for success in fatigue-prone applications depends on a strong understanding of the relationship between material structure and fatigue performance, a surprisingly understudied area. In this study, we sought to develop relationships between PCU structure and mechanical properties, including fatigue, for three soft PCUs with systematically varied ratios of hard and soft segments. In addition, we compared injection molded controls to 3D printed (fused deposition modeling, FDM) varieties to examine the effects of such processing. Results indicate that increased hard segment content leads to increased stiffness, increased shear failure stress, and improvements in tensile fatigue from a stress-based standpoint despite relatively uniform tensile strength for the tested grades. Effects of hard segment content on tensile failure strain, and strain-based fatigue performance, were more complex and largely influenced by microphase organization and interaction. FDM samples matched or exceeded injection molded controls in terms of tensile failure stress and strain, compressive properties, shear strength, and tensile fatigue. The success of FDM samples is attributed in part to favorable printing parameters and the toughness of PCU which results in lower flaw sensitivity.

Graphical abstract



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Introduction

The use of soft materials for soft tissue replacement in load-bearing, orthopedic applications has been largely unsuccessful due to a lack of adequate materials with sufficient fatigue and wear resistance. Silicone was once purported to be suitable for this purpose, being used in applications ranging from: joint replacements in hand, foot, and wrist applications, radial head implants, temporomandibular joint disc replacements, and even intervertebral disc replacements. However the long term results for these devices demonstrated that there was significant room for improvement, with complications including: implant fracture, deformation, wear, and even synovitis and bone resorption due to the presence of wear particles [1], [2], [3], [4], [5], [6], [7], [8], [9], [10]. More recently, there has been a surge in soft tissue replacement devices based on polycarbonate urethane (PCU), including applications as: intervertebral disc replacements, acetabular cup bearing surfaces, meniscal implants, and osteochondral implants. PCU has gained traction due to its relative biocompatibility and biostability as well as its stiffness and viscoelastic properties, which closely match that of many load-bearing, soft tissues. In addition, the material has proven to be durable through preclinical testing of many of the previously mentioned devices [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [27], [28]. Despite this, caution is warranted as the long-term clinical results of PCU devices have yet to be seen. As was demonstrated in the case of the silicone Acroflex lumbar disc [10], preclinical device testing often represents a non-conservative but unfortunately necessary simplification of loading states and environmental conditions observed *in vivo*. Considering this, there is a clear need for a better fundamental understanding of the fatigue resistance of soft, synthetic polymers in physiological conditions. As was pointed out in our previous study [13], there is a surprising lack of work in this area, and such work would be valuable for materials optimization and long-term success in load-bearing implants.

PCU is one subset of a large family of thermoplastic polyurethanes (TPUs). TPUs are block copolymers, with chains comprised of hard and soft segments. Hard segments typically consist of alternating units of a diisocyanate with a diol chain extender, which join through urethane linkages, while soft segments consist of long, flexible macrodiols [29], [30]. The most popular macrodiols for biomedical use often include ester, ether, or carbonate groups thus yielding polyester, polyether, or polycarbonate urethanes, respectively. Polycarbonate urethane has become especially popular due to its relative biocompatibility, as it has shown to be more resistant to hydrolytic and oxidative degradation than polyester and polyether urethanes [11], [31], [32], [33]. When present in sufficient concentration under the right conditions, the hard segments will aggregate into domains due to thermodynamic incompatibility between the hard and soft segments, leading to microphase separation. These hard domains, held together by hydrogen bonding and thermodynamic forces, provide physical crosslinks for the amorphous matrix of the soft segments. This morphology gives the TPUs many of their favorable properties including its thermoplastic nature, which greatly simplifies processing when compared to conventional, chemically cross-linked rubbers [29], [30]. The morphology and resulting mechanical properties of TPUs can be tailored through a great number of variables including, but not limited to: hard and soft segment chemistry, structure, molecular weight, hard segment content, fillers, and method of preparation and/or processing [29], [30], [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [44], [45], [46], [47], [48], [49], [50], [51], [52], [53], [54], [55], [56]. Further complicating the matter is the fact that these variables can have very nuanced effects and may not necessarily have independent effects on the resulting material properties. For example, as was shown with PCU, an increase in hard segment content generally leads to an increase in tensile strength, but only to a certain extent and only when the soft segment molecular weight is high enough to prevent phase mixing. If soft segment molecular weight is too low, excessive phase mixing prevents crystallization of soft segment under high loads, but excessive phase separation from high hard segment contents may lead to greater localization of shear stresses [55]. As was also noted by Spirkova et al. [51], these structure-property relationships have been somewhat extensively studied for polyester and polyether urethanes [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [44], [45], [46], [47], [48], [56], but only a relatively modest body of work exists for PCUs [49], [50], [51], [52], [53], [54], [55], [56]. Taken a step further, studies on the structure-fatigue properties of PCUs represent a nearly nonexistent subset.

The thermoplastic nature of TPUs makes their processing more convenient than conventional rubbers. It also makes them ideal candidates for additive manufacturing, or 3D printing, through a process known as fused deposition modeling (FDM). 3D printing capabilities for elastomers would provide obvious benefits through cheaper, faster, and easier device prototyping and sometimes final component manufacturing, as well as the potential for complex geometries and architectures. As with any material that is 3D printed, such processing will have implications on the material microstructure and ultimately the mechanical properties, particularly fatigue. A literature review on the fatigue properties of 3D printed polymers turns up a relatively modest amount of work, especially in regards to printed elastomers, a fact that was also noted by Moore and Williams [57]. Currently, regarding the fatigue of 3D printed polymers in general, there are a few studies on the fatigue of FDM ABS which have largely focused on printing direction and the effect of material mesostructure on mechanical performance [58], [59], [60]. In addition, a fair amount of work exists on the fatigue of laser sintered nylons [61], [62], [63], [64], [65], [66], [67], [68], [69], [70], which represents a significantly different process than FDM. One paper exists on the fatigue of a photo-cured elastomer printed through material jetting [57], however the authors could not find any work on the fatigue of FDM elastomers.

While short-term trials and preclinical tests have proven successful for several PCU devices, their long-term success will depend in part on fatigue behavior. The structure-fatigue properties of PCUs represent an understudied area that can potentially provide valuable information for materials optimization. In addition, the convenience of 3D printing techniques has much to offer in terms of device design and manufacturing, but its effects on fatigue properties are also largely understudied. As such, the objectives of this paper are twofold:

1. Examine the fatigue behavior of soft PCUs with systematically varied hardness to develop an understanding of the relationship between material structure and fatigue response.

2. Compare the fatigue behavior of 3D printed (FDM) PCUs with those of traditional, injection molded PCUs to develop an understanding of the effects of such processing on the fatigue behavior of the materials.

Section snippets

Materials and processing

Carbothanes AC-4075A (75A), AC-4085A (85A), and AC-4095A (95A) were obtained from Lubrizol in pellet form. Processing methods utilized in this study include: compression molded (CM), injection molded (IM), and 3D printed (FDM). Compression molded sheets were formed by first drying the pellets in a vacuum oven at 95 °C and −25 inHg for a minimum of 2 h. Dried PCU pellets were then placed in a hot press (Carver, Model 3851-0) (200 °C for 75A and 85A, 210 °C for 95A, 500 lbs pressure, 10 min) and…

Differential scanning calorimetry

Fig. 4 shows representative DSC curves for the tested PCUs, Table 2 shows tabulated transition temperatures for each material calculated from both DSC as well as DMA results. Fig. 4 includes the full first cycle, heating and cooling, on top and then the subsequent heating cycle below for each grade. Each material shows a clear glass transition temperature between −20 °C and −30 °C on the initial heating ramp (T_{gs1}) with the 95A grade being approximately 6 °C higher than both 75A and 85A. Upon…

Discussion

PCU has shown promise in a number of applications in recent years including many load-bearing, orthopedic applications such as intervertebral disc and meniscus replacements. Some of these devices are currently in US clinical trials, while many are already in use in Europe, such as the: TriboFit® Hip System, Elastic Spine Pad® disc replacements, and NUsurface® Meniscus Implant. Preclinical testing and early clinical results for these devices have been promising, however long term results have…

Conclusions

We have investigated the mechanical properties and fatigue performance of three PCUs with systematically varied hard and soft segment contents, processed using both injection molding and 3D printing (fused deposition modeling). The following are the conclusions of the work.

1. Increased PCU hard segment content leads to an increase in monotonic stiffness, increase in shear failure stress, and improvements in tensile fatigue from a stress-based standpoint despite lacking a strong effect on monotonic …

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