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On reducing anisotropy in 3D printed polymers via ionizing radiation

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ABSTRACT

The mechanical properties of materials printed using fused filament fabrication (FFF) 3D printers typically rely only on adhesion among melt processed thermoplastic polymer strands. This dramatically limits the utility of FFF systems today for a host of manufacturing and consumer products and severely limits the toughness in 3D printed shape memory polymers. To improve the interlayer adhesion in 3D printed parts, we introduce crosslinks among the polymer chains by exposing 3D printed copolymer blends to ionizing radiation to strengthen the parts and reduce anisotropy. A series polymers blended with specific radiation sensitizers, such as trimethylolpropane triacrylate (TMPTA) and triallyisocyanurate (TAIC), were prepared and irradiated by gamma rays. Differential scanning calorimetry (DSC), tensile testing, dynamic mechanical analysis (DMA) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were employed to characterize the thermomechanical properties and the chemical structure of the various polymers. TAIC was shown to be a very effective radiation sensitizer for 3D printed sensitized polylactic acid (PLA). The results further revealed that crosslinks induced by radiation temperatures near T_g of shape memory systems have prominently enhanced the thermomechanical properties of the 3D printed polymers, as well as the solvent resistance. This enables us to deliver a new generation of inexpensive 3D printable, crosslinked parts with robust thermomechanical properties.

1. Introduction

The ability to rapidly manufacture materials into complex shapes presents compelling opportunities in a variety of areas: medical and dental instruments [1], medical and dental implants [2–8], consumer products [9,10], food [11,12], electronics [13–15], industrial machines [16,17], aerospace applications [18,19], motor vehicles [20], architectural [21], consumer hobbyist arenas [22] and shaping national policy [23]. The materials that can be formed into these complex shapes range from metals to ceramics to polymers to natural materials to living cells and tissues. Within the field of additive manufacturing for polymers, several types of systems enable printing of different materials by different processes [24] such as variations on fused filament fabrication (FFF)/fused deposition modeling [25–28], stereolithography (SLA) [29,30], and selective laser sintering (SLS) [31,32].

FFF 3D printing is increasingly becoming a vital tool in many industries for its ability to produce a wide range of physical parts quickly, but the quality of the printed parts are lacking the strength, toughness and reliability of parts manufactured through injection molding or milling [33–35]. Many of the challenges with 3D printed polymers are due to anisotropy caused by the method in which FFF printers lay down the material. In FFF, the polymer is typically melted or melt-extruded through the print head and deposited onto a growing substrate layer by layer. 3D printed polymers by FFF are not as reliable as traditional manufactured parts because poor interlayer adhesion limits toughness and robustness, especially perpendicular to printed layers. Since materials are typically melt processed during FFF, crosslinked polymers systems are traditionally not viable. Unlike FFF, SLA does not require melt processing but liquid photo-reactive polymers which can be cured by ultraviolet laser or other source. SLS is a technology with very similar setup to SLA except that it uses laser with higher energy than UV and prints from powder materials instead of liquid

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photopolymers. Neither SLA nor SLS has the degree of anisotropy challenges as FFF does since the liquid photo-reactive polymers used in SLA are crosslinked during printing and SLS creates a more homogenous melt at the surface.

The layer-by-layer process of the aforementioned 3D printing technologies allows thermoplastics to be printed in various orientations relative to the print direction. While this can allow for great freedom in part design and stacking within a print space, this comes at a cost. Previous works have shown the significant effect of print orientation on the mechanical properties of the 3D printed parts [33,34,36–41]. While orthogonal directions are commonly tested [18,33,36,41], some work has investigated the intermediate orientations as well as the effect of the pathing of the printing [33,34,39]. These efforts have focused on differing polymers printed via different printers and printing technologies, indicating the issue of anisotropy is a broad concern for 3D printed polymer components. The effect of anisotropy, the percent difference in property due to print orientation, on tensile properties has been as much as 85% [33], compression as much as 20% [33], and impact strength as much as 90% [39]. Not every polymer and printer will exhibit anisotropy behavior to this extent, but it is a stark indicator of the challenges that anisotropy can present in 3D printed polymer components. While anisotropy is a leading challenge with additive manufacturing, other challenges include residual stress and dimensional errors [37,38]. Residual stress can lead to warping and delamination of printed components if appropriate post processing steps are not taken while dimensional printing errors lead to part that no longer meet the dimensional specifications. These challenges inhibit the use of this technology to make complex polymer parts that can withstand multi-axial mechanical loads.

To mitigate the layer-to-layer adhesion challenge, crosslinks can be created among layers. Crosslinks in polymers are traditionally formed by chemical reactions during the initial cure of the material or by the addition of a chemical crosslinking agent, approaches that are impractical for this application. Alternatively, high energy ionizing irradiation, such as electron beam, gamma, or X-ray radiation, may be used to induce crosslinking in certain polymers. Irradiation generates radicals on the main chain (scission) or on side chains (crosslinking). The radicals recombine or trigger further reactions potentially improving the adhesion between layers and enhancing thermomechanical properties. However, scission reduces polymer molecular weight and leads to poor properties and should be avoided in this paradigm. Whether the chain scission or the crosslinking is dominant during the irradiation process determines the degree of crosslinking and thermoset behavior. This in turn, determines whether the properties of polymeric materials are enhanced or lowered by the irradiation.

One way to control the degree of crosslinking is to change the irradiation dosages. Depending on different types of materials, higher dosages of irradiation may result in higher or lower crosslinking densities [42]. In addition, the effects of irradiation are temperature-dependent as the two competing processes, crosslinking by radical combination and chain scission, are also both temperature-sensitive, and polymer segment or chain mobility is increased when the temperature exceeds the glass transition temperature (T_g) of the material, or crystallite melting point (T_m) for some polymers [43]. Pioneering work in radiation physics and chemistry [44,45], set the stage for better control of sol/gel curves relative to dose [46] and has allowed thorough recent work in elucidating responses of specific polymer systems [47–51]. Specifically ionizing radiation has been used to crosslink polyacrylates [52,53], polyurethanes [54,55], poly (lactic) acid [56,57] and other polymers [58,59]. PLA has been widely explored as a biological scaffold [60] and in a wide variety of 3D printing applications [61].

The application of 3D printing to biomedical applications enables the rapid prototyping and development of complex geometries, necessary for tissue engineering and specialized components, not easily accessible by traditional methods. Additionally, 3D printed SMPs can be widely used for advanced manufacturing of smart materials. This technology allows for the 3D printing of flexible electronics or devices, after which the device can be deformed into a secondary shape for efficient packing and shipping, and later undergo shape recovery to return to its complex 3D geometry [62]. Moreover, 3D printed SMP foams are very promising materials for aerospace applications, where the high porosity reduces the density of the polymers as well as the cost, and offsets the relatively lower mechanical properties [63].

Complex parts possess features at various depth profiles which make their uniform treatment difficult for various radiation sources. Gamma rays, as uncharged high energy rays, are attenuated little by the molecular structure of materials as they propagate, leading to a significant depth of penetration. As long as the dimensions of the complex parts are within the depth of penetration of gamma rays, the consistency of the radiation exposure across the parts will not be significantly affected by the geometry of the parts. Therefore, gamma radiation is an excellent technique for curing materials in complex geometries. Additionally because of their excellent penetrating ability, gamma rays are a popular method for sterilizing medical devices [64].

Shape memory polymers (SMPs) are so-called “smart” materials with a rapid response of modulus to small temperature variations which enable large shape changes and rapid softening or stiffening. Shape memory polymers have been proposed for biomedical applications [65–67], for implantable bioelectronics [68,69], for control of surface morphology [70], for multiple shape recoveries [71–75] and as a two-way effect [76,77]. Multi-functional materials have even branded themselves as 4D materials in which shape change (time) is another dimension of control for 3D printed parts [78]. 3D printed shape memory polymers such as PLA and polyacrylates or other specialty polymers that are enhanced by radiation crosslinking have the potential to play a unique role in emerging applications in oil and gas applications, in defense applications, in medical applications [79] and as composites [80].

To support the use of 3D printing of medical devices, a working group within the Center for Devices and Radiological Health of the US Food and Drug Administration is investigating the challenges of using the technology to manufacture medical devices [http://www.gpo.gov/fdsys/pkg/FR-2014-05-19/pdf/2014-11513.pdf]. Furthermore, the agency has provided an emergency use exemption for a 3D printed bronchial splint [81], and with similar emergency uses of additive manufacturing reported in Europe [82,83]. A cursory review of the publicly available 510(k) Summary Database [84,85] showed that the Agency has cleared at least 13 devices manufactured via 3D printing, which indicates that the FDA's current premarket notification process, 510(k), can address 3D printed devices similar to device submissions manufactured using traditional techniques that would otherwise be eligible for premarket notification. These cleared devices have spanned from dental implants, K120792, to patient matched cutting guides, K120956, to patient specific knee replacement system, K133560 revealing the breadth of applications for 3D printed medical devices.

The distributed manufacturing ability of additive manufacturing allows for local manufacturing of components and a potentially simplified supply chain [86]. This aspect of the technology makes it attractive to the FDA Medical Countermeasure Initiative [87,88] as a way to ensure a ready supply of medical devices to hospitals in case of a natural disaster or CBRN (Chemical, Biological, Radiological, or Nuclear) event. Of specific interest to the program in this area is to develop a printable polymer system that is cross linkable post

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