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Gamma radiation effects on siloxane-based additive manufactured structures

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HIGHLIGHTS

- Results of radiation effect on pads produced by DIW technique are reported.
- Radiation exposures were provided by Co-60 sources.
- Changes in chemistry, microstructure, and mechanical response were analyzed.
- DIW resins containing phenyl groups showed good resistance to radiolysis.

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ABSTRACT

Siloxane-basedadditive manufactured structures prepared by the direct ink write (DIW) technology were exposed to ionizing irradiation in order to gauge radiolysis effects on structure-property relationships. These well-defined 3-D structures were subjected to moderate doses of gamma irradiation in an inert atmosphere and characterized by a suite of experimental methods. Changes in thermal, chemical, microstructure, and mechanical properties were evaluated by DSC, TGA, FT-IR, mass spectroscopy, EPR, solvent swelling, SEM, and uniaxial compressive load techniques. Our results demonstrated that 3-D structures made from aromatic-free siloxane resins exhibited hardening after being exposed to gamma radiation. This effect was accompanied by gas evolution, decreasing in crystallization levels, decreasing in solvent swelling and damage to the microstructure. Furthermore, long-lived radiation-induced radicals were not detected by EPR methods. Our results are consistent with cross-link formation being the dominant degradation mechanism over chain scission reactions. On the other hand, 3-D structures made from high phenyl content siloxane resins showed little radiation damage as evidenced by low off gassing.

1. Introduction

Additive manufacturing (AM) technology allows for the production of complex materials with customized design and improved performance, along with reducing manufacturing time, costs, and the amounts of feedstock and waste (Gibson et al. 2010). Recently, such technology gained considerable attention since it enabled the design of new and exciting devices, ranging from self-healing materials to artificial organs (Toohey et al., 2007; Durmus et al., 2013). A commercially available siloxane-based adhesive known as Dow Corning® SE1700, was identified by Duoss et al. (2014) as a suitable polymeric resin to be used in the direct ink writing (DIW) process (Fig. 1). Their elegant DIW approach produced well-defined 3-D porous elastomeric architectures that exhibited directional load response together with negative stiffness. The authors demonstrated that the mechanical response of these 3-D structures was a function of the micro-architected design, which for instance, could be tailored in interesting ways to prevent damage to the material when under stress.

These novel AM siloxane pads may be used in applications that require exposure to harsh environmental conditions such as ionizing radiation. Thus, the present work investigated the resilience of such AM structures when exposed to relatively moderate doses of gamma radiation, namely less than 250 kGy. As mentioned above, the DIW resin of interest is based on poly(dimethyl siloxane) (PDMS), a polymer that is non-toxic and well-known for its thermal and chemical stability. Exposure of PDMS to high energy irradiation such as gamma rays has been the subject of several investigations over the years, showing that the polymer is susceptible to radiation-induced structural changes. For instance,

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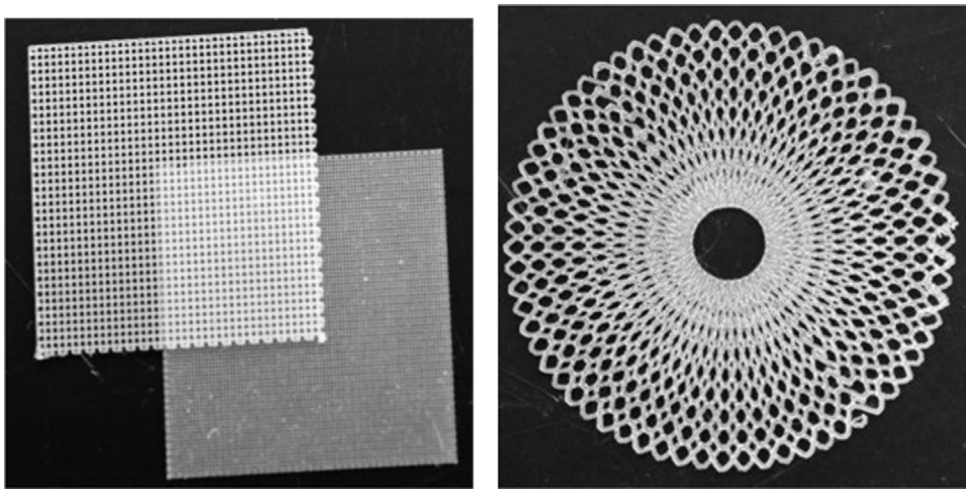

Fig. 1. Examples of AM pads produced using the SE1700 resin.

Charlesby and others described formation of a cross-linked network accompanied by gas evolution (Charlesby, 1955a; Stpierre et al., 1959; Miller, 1960). Radiation-induced changes in cross-link density are expected to influence the material's mechanical response by enhancing tensile properties and increasing hardness, as it was certainly observed by Warrick (1955) and Basfar (1997).

To our knowledge, the current work represents the first study on radiolysis of 3-D structures produced by the DIW technique. Radiation-induced changes in chemistry, thermal properties, microstructure, and mechanical response were assessed by a combination of diverse experimental techniques, providing valuable insights on the radiolysis in inert atmospheres of AM siloxane pads.

2. Materials and characterization methods

2.1. Materials

One of the materials of interest to this study is a commercial two-part silicone adhesive, known as Dow Corning® SE 1700. Preparation of the resin requires mixing "Part A" and "Part B" in a 10–1 ratio, respectively. This is a non-flowing (yield stress) resin that cures after 30 min at 150 °C, allowing for good working time after the mixing. This curing procedure was investigated by varying the curing time from 30 min at 150 °C to up to 48 h at 150 °C. TGA results showed that the weight loss was mostly independent of the curing time, indicating that curing for 30 min is largely sufficient. According to the material data sheet provided by the vendor, part A is composed, by weight, of 55–75% dimethylsiloxane (dimethylvinyl-terminated), 15–35% trimethylated silica, 5–10% dimethyl vinylated and trimethylated silica, 1–5% titanium oxide, and less than 1% methylvinyl, (dimethoxy(glycidoxypropyl)-terminated). Part B is composed of 30–50% dimethylsiloxane (dimethylvinyl-terminated), 30–50% dimethyl methylhydrogen siloxane, and 15–35% dimethyl vinylated and trimethylated silica. ^{1}H NMR analysis of the uncured resin confirms that it contains vinyl and silane groups. Analysis by inductively coupled plasma mass spectrometry (ICP-MS) reveals that several metals are also found in small quantities in parts A and B, as listed in Table 1. The platinum detected in part A is assumed to be the catalyzing agent for the curing process of the SE 1700 resin.

Another material of interest to this work is a commercially available Dow Corning® siloxane resin known as OE6636. This is a two part optical encapsulant with high diphenyl content and high viscosity (7500 cP). The uncured resin was modified to prevent the material from flowing under its own weight during 3-D printing. Untreated fumed silica (Cab-o-sil® HS-5) was added to uncured OE6636 using a Thinky planetary mixer. The addition of 8.5 wt% silica made this material printable through a 600 μm nozzle. The 3-D printed pad was cured following the same procedure as for the SE1700 resin.

Table 1
ICP-MS data obtained for parts A and B (in ppm). Other metals that were detected in the resin included osmium, nickel and gold in part A, and silver in both parts.

	Sn	Ca	Ti	Cu	Pt
Part A	2.83	24.16	2.4	0.54	7.2
Part B	4.70	0	1.45	0.32	0

AM pads were produced using the DIW process, which differs from traditional 3D printing methods by using a thermosetting shear-thinning yield-stress resin that holds its shape during the printing and curing process. This technique has been recently demonstrated to manufacture structure-controlled materials (Duoss et al. 2014). DIW allows for microstructural control of the final material, as opposed to blown closed cell foams that have stochastic cellular structures. The AM pads investigated in this study were printed using a Nordson Ultimus V engineered fluid dispenser (EFD) and Aerotech 3 axis linear positioning stage. The EFD provides a constant pressure drop to a syringe filled with uncured SE1700, which is mounted on the z-axis of the Aerotech stage. The x, y, and z axes are controlled by the Aerotech Npaq, and operated according to a gcode based program written in the Aerotech A3200 Motion Composer Software.

Once the printed material was cured, approximately 21 g samples were cut from the full pad, and placed in aluminum canisters. The canisters were sealed with copper gasket, evacuated to 10^{-3} Torr and then backfilled with 650 Torr of high purity nitrogen gas. These canisters were exposed to cobalt-60 sources at a constant dose rate of 1 Gy/sec. The samples were irradiated for different time periods to achieve total doses of 10, 50, 100 and 200 kGy. These exposures were performed at the Gamma Irradiation Facility (GIF) at Sandia National Laboratories in New Mexico.

2.2. Thermal analyses

TGA experiments were carried out using a commercial TA Instruments Q5000. 10–20 mg samples were heated from 30 °C to 750 °C at 2 °C/min under nitrogen atmosphere. DSC experiments