

ADDITIVE MANUFACTURING OF THERMOSETTING RESINS

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Keywords: fused deposition modeling, thermosets, additive manufacturing, polyimides, crosslinking

Abstract

The ability to produce previously un-manufacturable designs combined with compelling economic and lead time benefits has led to the investment in additive manufacturing (AM) technology. Even though 3D printing is rapidly growing, the range of materials is fairly limited and mainly consists of thermoplastics. Thermoset polymers that are critical in load-bearing polymer matrix composites have not been widely adopted for AM. The focus of this presentation is on the development of high T_g thermosetting polymer filaments and associated changes in polymer chemistry and the development of printing capabilities that allows the deposition of neat and filled thermosetting resins. The combination of additive manufacturing and reactive extrusion as a continuous production of polymeric materials from a chemical reaction and additional blending of functional and structural fillers may allow in-situ production of thermoset and polymer matrix composite parts. In addition, such a process allows the printing of thermosets from monomeric input as well as the incorporation of functionally graded features. Overall, this work addresses recent demand signals for higher temperature (>250C) and improved thermo-oxidative stability of 3D printed parts.

1. Introduction

Current state-of-the-art (SotA) materials for polymer additive manufacturing exhibit limited temperature capabilities, poor z-directional mechanical properties, poor fatigue behavior, no solvent/oil/fuel resistance and poor thermo-oxidative stability. The problem of current printing techniques, such as Selective Laser Sintering (SLS) or Fused Deposition Modeling (FDM) is that the process is not truly 3D, in that the polymeric material is laid down one layer at a time. This leads to drastic performance loss in the z-direction of printed parts due to weak road-to-road bonding between layers and overall anisotropic material properties.¹

Road-to-road bonding is critical both in thermoplastics and thermosets.² In thermoplastics it is generally chain entanglement depending on the dwell time at a given temperature that leads to enhancement in bonding within interphases between roads. However, these entanglements are reversible and will disappear or become weaker at higher temperatures. This is manifested in accelerated fatigue at temperatures close to T_g or T_{melt}. Thermosets on the other hand provide covalent crosslinks, in which entanglements plus chemical bonds lead to crucial road-to-road bonding. These bonds are irreversible and will not separate even at higher temperatures, offering the best possible strength in all directions in 3D printing (isotropic). Compared to a thermoplastic part (irreversible distortion) a thermoset part will also keep its shape even above T_g and return to its original shape after small deformations (network memory). Key for thermosetting resins is that they behave like thermoplastic resins during the printing process and partially cure or fully crosslink after the roads/filaments are being laid down by the print head. The challenge in all these is to find the right processing/temperature window for either blending or entanglement or a chemical reaction to take

place between the polymer chains during the print process. In addition, these processing details will affect the level and direction of anisotropy in the printed material, as shown in Figure 1.

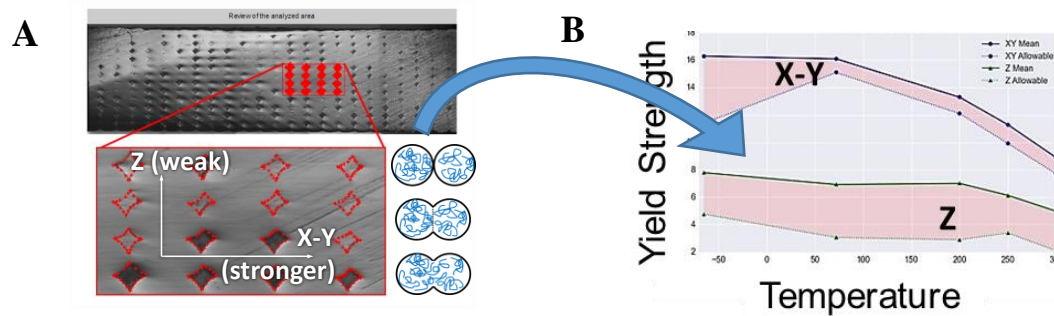


Figure 1. A) Microscopy showing a cross section of printed roads (via fused deposition modeling) and the effect of aligned roads or skewed roads on the resulting AM microstructure (left). The bottom right inset shows the importance of polymer entanglement to ensure good bonding between roads. B) Typical resulting anisotropic mechanical properties of FDM and SLS processing.

Non-optimized AM methods often lead to non-ideal materials with residual porosity that is anisotropic, and the potential for poor bonding between roads, as shown in the microstructure of Figure 1. These microstructural defects can lead to thermal distortion, poor dimensional tolerances and drastically reduced mechanical properties in the finished part. Thermosetting resins address both the limitations of current thermoplastic materials listed above and overcome road-to-road and layer-to-layer bonding limitations via covalent bonds.

To address these shortcomings, thermosetting resins with high crosslink densities (>40mol%) and T_{gs} above 200C were developed that can be extruded into filaments for FDM. It is expected that these new materials will enable additive manufacturing of parts with improved Z-directional mechanical properties with improved thermo-oxidative stability (TOS), key performance parameters that are comparable to current SotA thermosetting resins that are used in conventional composite manufacturing for high temperature applications, namely thermosetting polyimides developed at AFRL. Furthermore, additive manufacturing of tooling for conventional polymer matrix composites is attractive due to cost savings and rapid prototyping. The materials of choice in this work are therefore high performance polyimide thermosetting systems that exhibit both higher temperature capabilities as well as mechanical performance.

While both powder form for SLS and filament for FDM can be applied, the focus in this paper is on FDM. The challenge is to produce a uniform filament via extrusion of the thermosetting polyimide. The accompanying challenges are summarized in Figure 2 and include removal of volatiles, completion of the imidization reaction and the curing reaction (crosslinking) after the extruded filament is used in FDM to print a part. A critical part for thermosetting resins is the post processing step in which the material is transformed into thermoset with complete degree of cure.

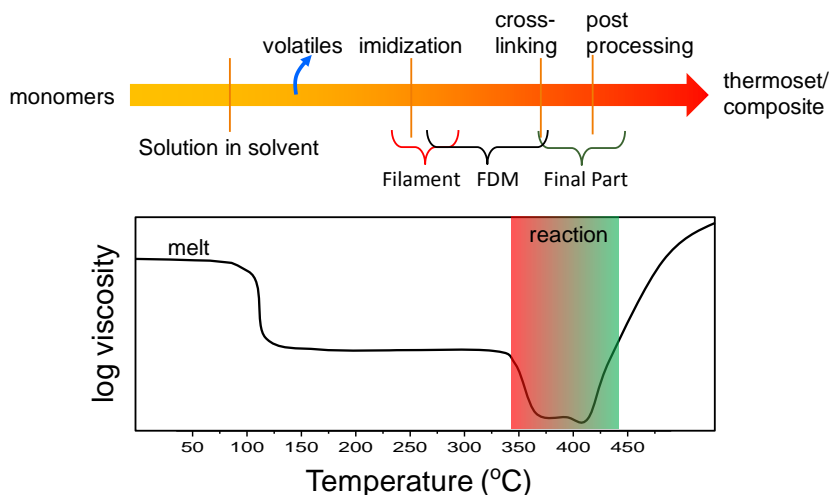


Figure 2. Schematic representation of challenges in 3D printing of thermosetting polyimides.

2. Results

2.1. Thermal Properties

A model polyimide thermosetting system with a phenylethynyl endcap was used to tune processability by varying the endcap concentration and thereby increasing molecular weight of the resulting polymer chains. A schematic of the model polyimide thermoset with simple endcaps is shown in Figure 3 (PAO, blue) and its molecular weight dependence as a function of endcap concentration (Fig. 3B, blue circles).

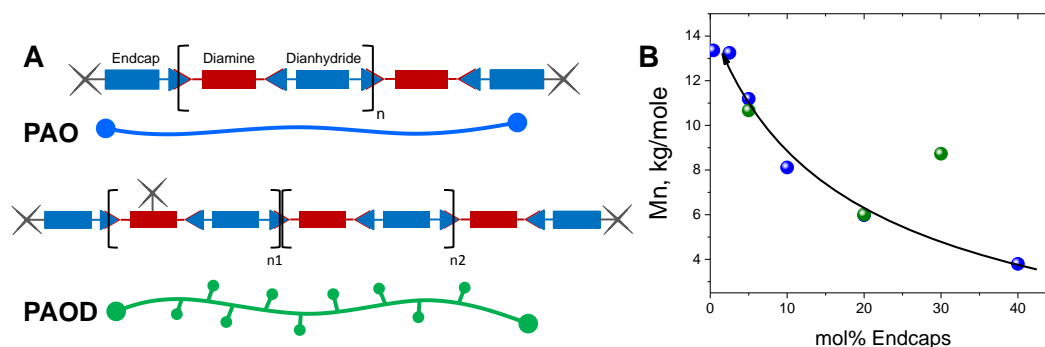


Figure 3. Schematic of thermosetting polyimide structures made from diamine, dianhydride and endcap and molecular weight dependence as function of endcap. A) thermoset system PAO (blue) contains crosslink moieties only in the endcaps, while system PAOD (green) also contains crosslink moieties as pendants along the backbone. B) Molecular weight as a function of endcap concentration.

To compensate for the reduction in crosslink density in system PAO (Fig. 3A blue), pendant crosslink moieties of the same type were included in the polymer backbone to form PAOD (Fig. 3A, green). This allows for the independent tuning of crosslink density and molecular weight, i.e. the crosslink density can be set to 40mol%, while the molecular weight can be increased to obtain optimal processing properties for extrusion and printing. The glass transitions T_g and thermo-oxidative stability of the materials are summarized in Figure 4.

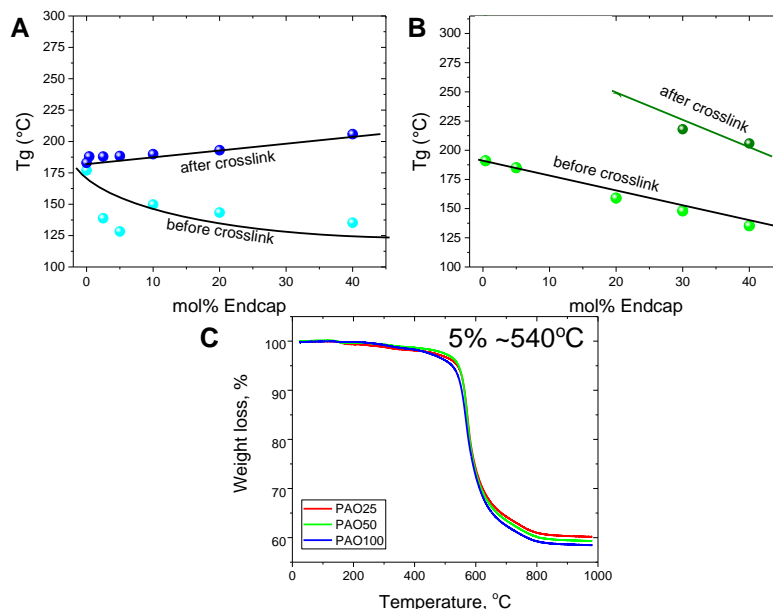


Figure 4. Thermal properties of thermosetting polyimides. A) Glass transition of series PAO before and after crosslinking. B) Glass transition of series PAOD before and after crosslinking. C) Thermo-oxidative stability from TGA experiments.

While the trend in Tg for series PAO increases with higher molecular weights (fewer endcaps) for the uncrosslinked polyimide (Fig. 4A, light blue spheres), the Tg decreases with increased molecular weight in the fully crosslinked materials as expected due to the reduced amount of crosslinking (Fig. 4A, blue spheres). Adding a pendant crosslinker into the backbone to retain the overall crosslink density at 40mol% on the other hand enables an increase in molecular weight while at the same time the Tg of the fully crosslinked thermosets is increasing (Fig. 4B, dark green spheres). The thermo-oxidative stability of all thermosetting resins in this work are comparable to existing high temperature polyimide thermosets and exhibit a 5% weight loss at temperatures of 540°C in air (Fig. 4C).

2.2. Processing

Rheology experiments of both PAO and PAOD thermosetting systems reveal that viscosity is expectedly increased with higher molecular weights as shown in Figure 5A. Moreover, extrusion of the higher molecular weight PAOD samples with 40mol% crosslinker shows exceptional processability and flexible filaments for the FDM process were obtained (Figure 5B, C). The filaments were successfully fed through the fused deposition modeling head of an nScrypt™ 3Dn 500 Quad Head deposition system for printing coupons for mechanical testing.

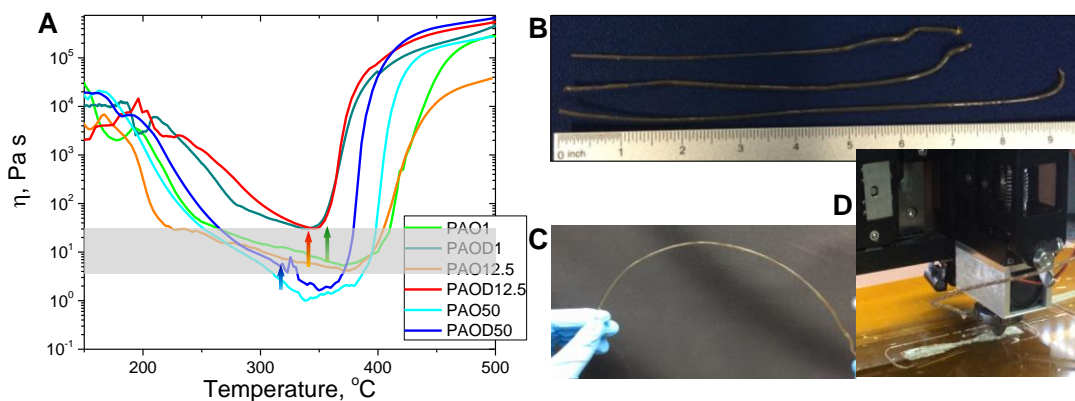


Figure 5. Rheology, extrusion and printing of thermosetting polyimide. A) temperature dependent viscosity demonstrating increase in viscosity with increased molecular weight. B) extruded filaments, C) flexibility/toughness of filament D) Fused deposition modeling of filaments into dogbone specimen.

While FDM has its place for commodity polymeric materials, there are limitations for high performance materials such as the thermosetting polyimides discussed above that are difficult or impossible to extrude into filaments. Enabling direct write assembly to develop “inks” in-situ allows the selective programming of material functionality and reinforcement by locally tuning the physical properties of the extrudate with respect to the desired application as well as the incorporation of functionally graded features into the printed item (for example gradient in crosslink density to reduce localized stresses or to enhance mechanical properties in discrete areas).³ Additionally, in-situ development of inks in the print-head extends the material capabilities of direct write assembly to network forming materials such as thermosetting resins (epoxies, polyimides) without compromising the evolution of the feedstock. The initial focus of testing this approach will be on thermosetting resins that are liquid at room temperature, such as epoxies and Figure 6 summarizes the concept of the printhead development.

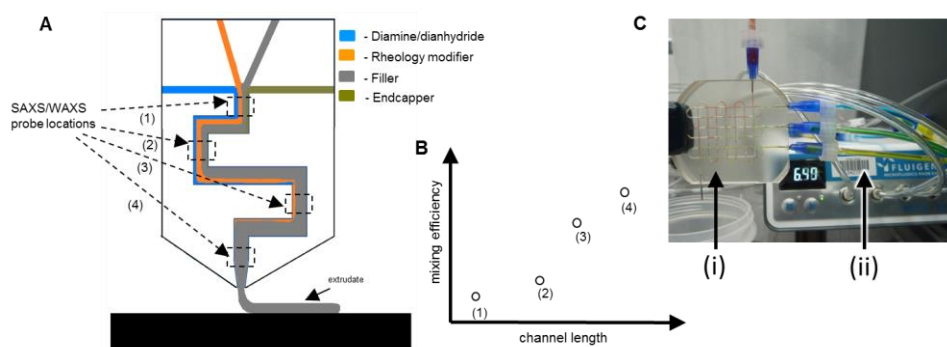


Figure 6. Microfluidic print head with passive mixing of monomeric components that includes in-situ monitoring capabilities. A) schematic of microfluidic cell with transparent windows for in-situ characterization. B) notional plot of mixing efficiency and morphological evolution as a function of printing path. C) prototype of microfluidic cell with multi channel pressure pump.

3. Conclusions

The demand for higher temperature capable materials for additive manufacturing processes requires

design of new materials that can adapt to the printing process. High temperature thermosetting resins, such as polyimides show promise as materials that can provide temperature capabilities, thermo-oxidative stability and improvements in road-to-road bonding. Polymeric additive manufacturing processes rely on specific materials feedstock, e.g. uniform filaments for FDM. Development of new printhead technologies that enable blending and mixing of components such as monomers and functional or reinforcement fillers will pave the way for novel composites with unique emerging properties via gradient and topology optimized morphologies.

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