EXTRUSION DEPOSITION ADDITIVE MANUFACTURING UTILIZING HIGH GLASS TRANSITION TEMPERATURE LATENT CURED EPOXY SYSTEMS

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ABSTRACT

This paper investigates the formulation, chemo-rheological properties, and extrusion deposition additive manufacturing (AM) of high glass transition temperature epoxies. Currently there are two methods of using thermoset materials in extrusion deposition AM. The first approach uses a reactive material that will fully cross-link during the build process. The second approach, which is explored in this paper, uses a reactive material that requires a thermal curing cycle after deposition is completed. Yield stress fluids for successful deposition were produced by blending various ratios of rheology modifying fillers into latent curing epoxy systems. After analyzing the rheological properties of the various blends via shear, temperature, and cure rate, the preferred formulation was selected. Test specimens for flexural analysis and dynamic mechanical analysis were printed from down selected combinations. This work resulted in the identification of key parameters for printing latent cured epoxy systems that will be scaled for the first large scale 3D printed epoxy for composite tooling applications.

1. INTRODUCTION

Extrusion deposition additive manufacturing is one of the most prevalent plastic AM technologies. Typically, a thermoplastic is melted and deposited in a specific path to build parts sequentially layer by layer. Recently thermosets have begun to be utilized in a similar fashion known as direct write [1,2,3]. These materials can be deposited at room temperature avoiding the temperature gradients associated with the heated extruder required to print thermoplastics. Further, thermosets offer a wider range of performance and applications to their thermoplastic counterparts. They also introduce with a host of new challenges. In extrusion deposition AM there are two different methods of controlling the final cure of the part. Materials can be mixed prior to deposition and subsequently react at ambient conditions to form a solid [4,5,6]. This method requires high control of rate of cure, temperature of reaction, and rheological properties during the reaction. However, it provides additional resistance to structural instabilities caused by depositing on top of a

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viscoelastic material [7]. In this paper we utilize the alternative method where the reaction is either non-existent or extremely slow after mixing, and a subsequent thermal cure after deposition is used to create a final rigid part. This method has decreased structural stability during the print and cure process when compared to its ambiently reactive counterpart. However, materials with high, post-cure thermal performance can be accessed by using this method.

Motivation for this work comes from the development of a new system for large scale thermoset additive manufacturing at the Manufacturing Demonstration Facility by Magnum Venus Products (MVP) and the Oak Ridge National Laboratory (ORNL). Similar to the BAAM process developed at ORNL [8,9], the MVP system known as the "Thermobot" is capable of depositing thermoset materials in a large build envelope, 2.44 m x 6 m x 1 m. One goal for the Thermobot is to produce composite tooling. A portion of the composite tooling market requires elevated temperatures, up to 205 °C, to produce the final composite part such as in an autoclave [10]. However, the materials currently being used on this do not meet this temperature requirement.

To investigate the production of elevated temperature tooling on the Thermobot, Dixie Chemical Company and ORNL partnered to evaluate Dixie Chemical Company's anhydride curatives for epoxy. This paper outlines the initial phase of research to achieve the overarching goal of using extrusion deposition AM to produce elevated temperature composite tooling. Dixie Chemical Company provided ORNL with four different anhydride curatives labeled ANH1, ANH2, ANH3, and ANH4. ORNL and Dixie Chemical Company investigated rheology modifying additives and evaluated the subsequent composite materials in extrusion deposition AM. Produced AM parts also had the mechanical and thermomechanical performance analyzed. Results of this lab scale work will be utilized to transition the material systems to use on the MVP Thermobot.

2. EXPERIMENTATION

Various epoxy bases were explored at the beginning of this work such as, Epon 828, Epon 826, Epon 862, and Diacel Celloxide 2021P. Diacel Celloxide 2021P was chosen as the base epoxy for further study due to its superior thermal properties post cure compared to the other candidate materials using ANH1-ANH4 [11].

2.1 Material Preparation Technique

Composite material combinations outlined in this paper were prepared by planetary centrifugal vacuum mixing in a THINKY ARV-310LED. Epoxy resin and anhydride curatives were initially mixed at 1200 RPM for 60 seconds. Garamite 7305 from BYK Additives and Instruments was then added and mixed at 1200 RPM for 60 seconds. Finally, the combined composite mixtures were mixed under vacuum at 1200 RPM for 60 seconds. The composite materials used for extrusion deposition AM were loaded into 10 CC syringes using a THINKY ARC-40H vacuum syringe loader.

Two different curing procedures were used to crosslink the final deposited parts. In the case of epoxy with ANH1, ANH2, and ANH4 the following procedure was used: a 2 °C ramp from room temperature to 120 °C, an isothermal hold at 120 °C for 1 hour, a 2 °C ramp from 120 °C to 220 °C, an isothermal hold at 220 °C for 1 hour, and a slow ramp down to room temperature. In the case of epoxy with ANH3 the procedure was identical except the initial isothermal hold was changed from 120 °C to 150 °C.

2.2 Extrusion Deposition Additive Manufacturing

The composite material combinations were deposited using a custom-built extrusion deposition AM system shown in Figure 1. The system motion is provided from a ShopBot 2418 router. The router head was removed and replaced with a Nordson EFD HPx syringe dispenser. Gcode is used to prescribe the path of the dispensing head and signal the syringe dispenser when to extrude material. The build substrate was a glass panel covered with Bytac, a Saint Gobain product.

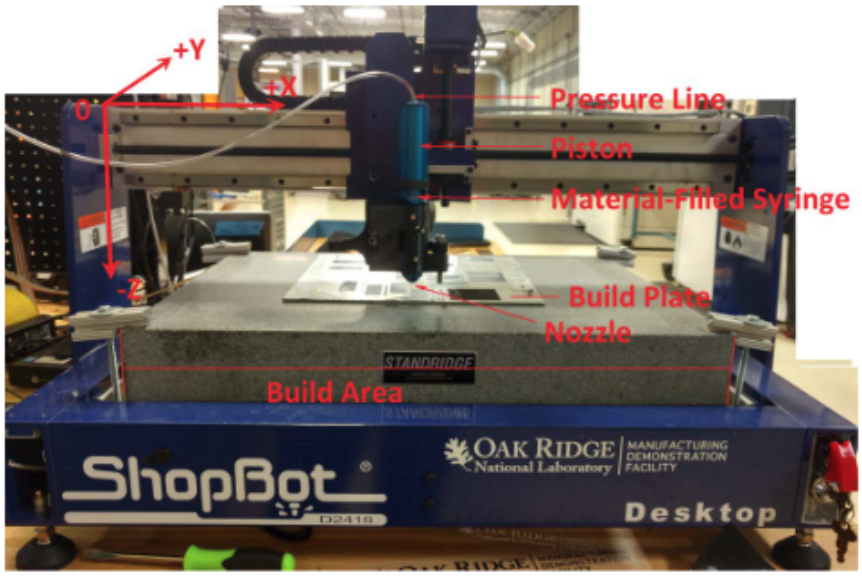

Figure 1. Custom-built extrusion deposition AM system for thermoset materials

2.3 Rheological Test Procedures

Testing of the epoxy composites were performed using a TA Instruments DHR-2 rheometer. Samples were tested within 6 hours of mixing to minimize the effect of ageing on the results. Each test used 25 mm disposable aluminum parallel plates with Norton 600 grit sandpaper adhered to each plate surface to prevent slip. Strain sweep tests were conducted from 0.01-100% at 1 rad/s and ambient temperature. Frequency sweep tests were conducted from 0.1-100 rad/s at 0.03% strain and ambient temperature. Yield stress was determined using a steady shear stress sweep at ambient temperature. A non-isothermal temperature sweep from 25-120 °C at 10 rad/s and 0.03% strain was used to determine the minimum viscosity and curing behavior.

2.4 Mechanical and Thermomechanical Testing Procedure

Testing samples were printed to size for both 3-point bend flexural analysis and dynamic mechanical analysis. 3-point bend samples were sized in accordance with ASTM D790 [12] (70 mm x 12.7 mm x 3 mm). After curing they were broken in 3-point bend flexure on an MTS electromechanical load frame using a 55.8 mm span with a crosshead speed of 5 mm/min. Deposition paths were oriented along the length of the sample specimen. Dynamic mechanical analysis (DMA) specimens were sized at 55 mm x 12.7 mm x 3 mm. They were tested in torsion on a TA Instruments DHR-2 at a strain rate of 0.01%, an angular frequency of 10 rad/s, and a temperature ramp of 2 °C from 40 °C to 240 °C.

3. RESULTS AND DISCUSSION

3.1 Rheological Analysis

Several epoxy/anhydride formulations were proposed and down-selected based on both rheological and mechanical properties. Base viscosities of each formulation were too low for printing and required the addition of filler to increase viscosity and hence modulus. Strain sweep tests were used to interpret the effect of the platelet filler, shown in Figure 2.

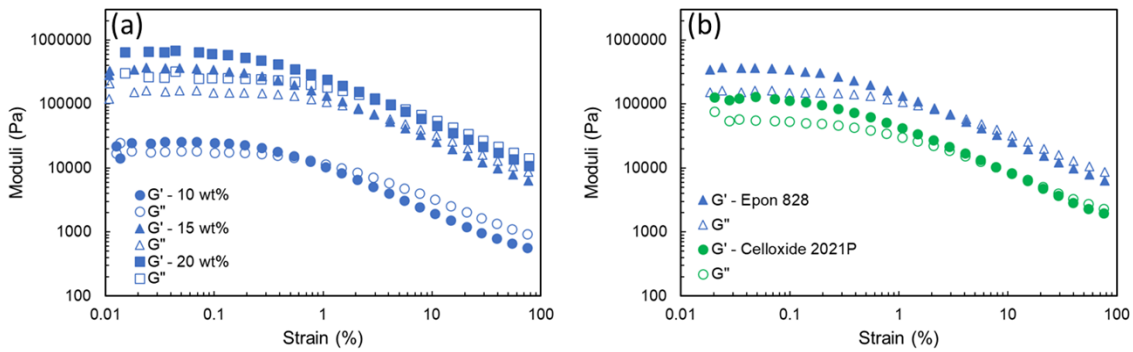

Figure 2. Strain sweep tests showing (a) effect of filler addition on Epon 828 resin and (b) effect of 15 wt% clay on Celloxide 2021P with ANH1.

The addition of up to 20 wt% clay is shown in Figure 2a. for Epon 828 resin. The modulus was greatly improved up to 15 wt% with minor effects at higher loadings. The choice of 15 wt% was made for the remainder of the study using Celloxide 2021P as the epoxy of interest. A comparison of Epon 828 to Celloxide 2021P is made in Figure 2b. The onset of nonlinear occurred near 0.3% strain in all cases suggesting that the filler dominated the rheology.

Bead stability during a print is critical which requires a material to have a yield stress. Addition of the clay filler was found to impart a yield stress onto the epoxy-anhydride systems. A shear stress sweep to determine yield stress for Celloxide 2021P/ANH1/ with 15 wt% clay is shown in Figure 3.

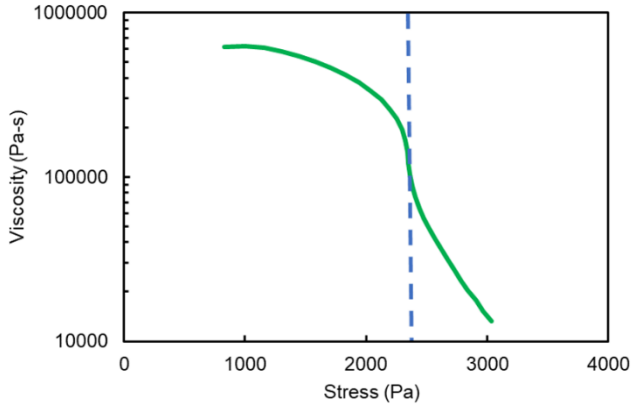

Figure 3. Shear stress sweep of Celloxide 2021P with ANH1 and 15 wt% clay. Yield stress was found to be 2300 Pa.

Yield stress for the Celloxide 2021P system was 2300 Pa. The yield stress is a measure of stress required for a material to flow. Since the system under investigation does not cure during deposition, it is important to have a high yield stress to support a load of subsequent layers. More importantly, it is important that the structure maintain its integrity while curing in an oven. To test the temperature dependence and rate of cure, a non-isothermal temperature sweep was conducted and presented in Figure 4.

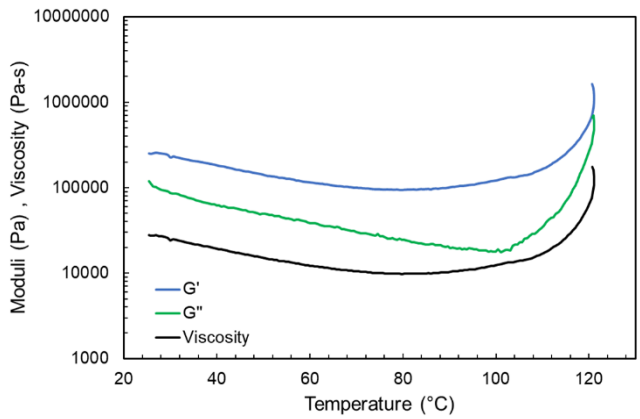

Figure 4. Non-isothermal curing of Celloxide 2021P with ANH1 and 15 wt% clay.

The temperature sweep was found to reduce the viscosity by nearly 2.5 its initial value. This would suggest that the yield stress would have a similar decrease.

3.2 Extrusion Deposition Additive Manufacturing

Diacel Celloxide 2021P epoxy mixed with ANH1-ANH4 containing 15 weight percent Garamite 7305 were all successfully used to print test samples for DMA and flexural analysis. During the deposition a linear speed of 2000 mm/min was used. Depending on the material combination, pressures used to extrude the material from the syringes in the Nordson EFD HPx dispenser ranged from 0.55 MPa to 0.83 MPa (80 psi to 120 psi). A tapered nozzle with an inner diameter of 0.6 mm was used during the deposition process.

These materials all showed similar ability to flow under pressure and recover quickly after extrusion to allow the subsequent layers to be deposited on top. This gives great confidence that the systems can be successfully used for large scale processing. Besides the testing geometries the material was used to print various other parts. A thin-walled box in Figure 5 shows the materials ability to print tall free-standing features.

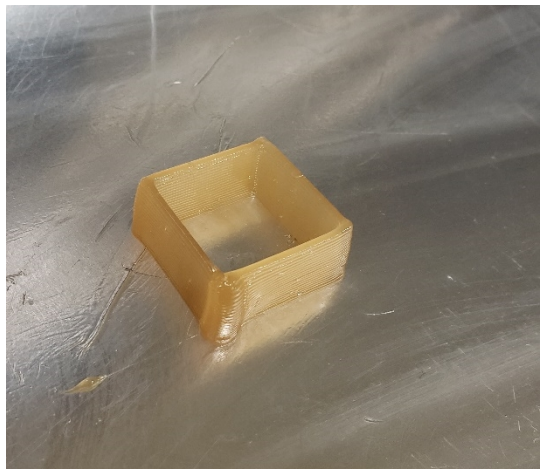

Figure 5. Thin-walled box printed using Celloxide 2021P and ANH1 with 15 wt% Garamite 7305

3.3 Thermomechanical Analysis

For post-cured printed parts used in applications such as tooling, it is important to have a high glass transition temperature, T_g. Four epoxy formulations were made using Celloxide 2021P mixed with ANH1-ANH4 and 15 wt% clay to compare the effect of anhydride on T_g. A DMA test using cured 3D printed bars for each formulation is shown in Figure 6. The dynamic T_g values from the onset *G'* and maximum of tan(δ) are summarized in Table 1.

From the DMA results it was found that Celloxide 2021P with ANH3 and 15 wt% clay offered the highest glass transition temperature from printed parts.

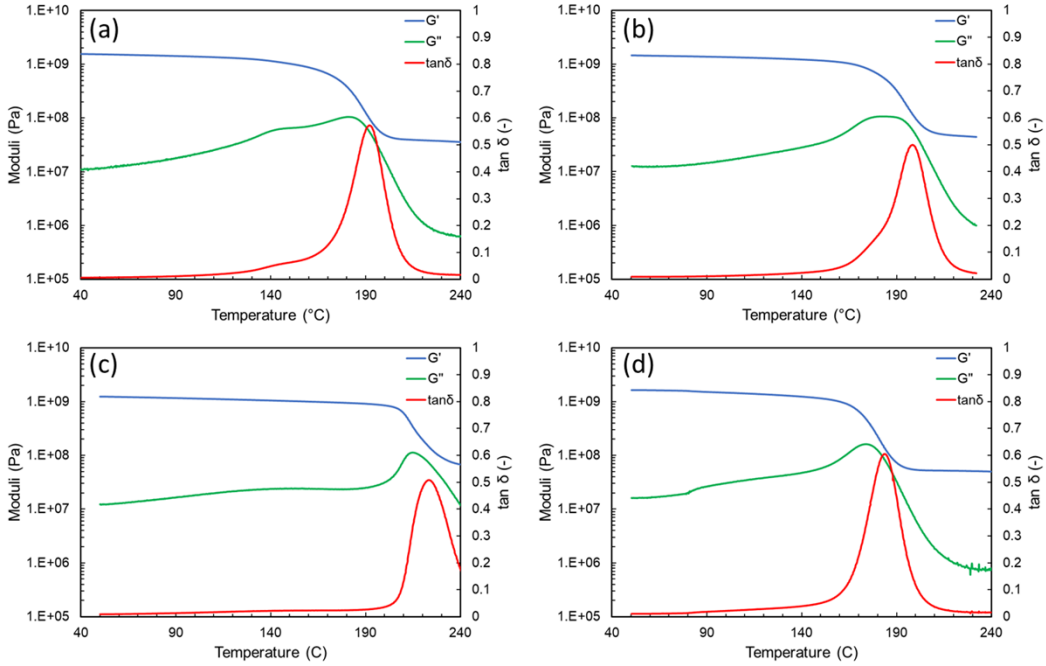

Figure 6. Dynamic mechanical analysis for Celloxide 2021P and 15 wt% clay using (a) ANH1 (b) ANH2 (c) ANH3 and (d) ANH4.

Table 1. Glass transition temperatures for Celloxide 2021P with 15 wt% Garamite 7305

Curing Agent	Onset T_g (°C)	Tan δ T_g (°C)
ANH1	177	192
ANH2	180	198
ANH3	206	223
ANH4	166	184

3.4 Flexural Analysis

Results of the 3-point bend testing can be seen in Table 2. Strength and modulus values correspond to the flexural strength and flexural modulus calculate as prescribed in ASTM D790 [12]. Based on the results of this testing all the anhydride curatives used in this study yielded similar values for flexural strength and modulus. Given the mechanical testing results, when scaling the technology anhydride curatives will be chosen based on thermomechanical performance and processability.

Table 2. 3-point bend flexural analysis results of Celloxide 2021P with 15 wt% Garamite 7305

Curing Agent	Strength (MPa)	Modulus (GPa)
ANH1	96.23 ± 5.05	4.27 ± 0.11
ANH2	95.84 ± 7.48	3.42 ± 0.51
ANH3	99.16 ± 6.9	3.69 ± 0.29
ANH4	90.45 ± 10.13	4.13 ± 0.17

4. CONCLUSIONS

In summary, we have shown the ability to take off the shelf epoxy with anhydride curative systems and turn them into yield stress fluids capable of being utilized in extrusion deposition additive manufacturing. Rheological evaluation was used to quantify the effect of Garamite 7305 at various weight percentages on the epoxy and anhydride mixtures. Rheology also validated that the mixtures now had high enough yield stress to be used in extrusion deposition additive manufacturing. Thermomechanical and mechanical testing results proved the end use parts would have adequate ability to be used in elevated temperature tooling applications. Future work on these systems will involve transferring the technology to the large-scale thermoset additive system developed by MVP and ORNL. This will include investigation of further additives to the epoxy

mixtures and evaluation of the deposited structures as tooling for autoclave composite materials production.

5. ACKNOWLEDGEMENTS

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