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# Vinylester and Polyester 3D Printing


Vlastimil Kunc

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**Vinylester and Polyester 3D Printing**

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## ABSTRACT

ORNL collaborated with Polynt Composites USA to evaluate the feasibility of vinylester and polyester 3D printing. Multiple materials were tested and evaluated. The evaluation consisted of rheology measurements, print trials and mechanical testing. Significant effort was devoted to safe handling of large quantities of these materials. The feasibility of using vinylester and polyester materials for large scale 3D printing has been demonstrated with outstanding issues identified in this report.

# 1. VINYLESTER AND POLYESTER 3D PRINTING

This Phase 1 technical collaboration project (MDF-TC-2017-119) started on October 23, 2017 and was completed on April 23, 2018. The collaboration partner Polynt Composites USA is a large business. ORNL successfully showed that Polynt's materials are capable of being used as a 3D printing material for complex geometries in large scale printing format.

## 1.1 Background

Polynt Composites USA Inc. is a leading supplier of gel coats, composite resins and industrial cleaners in the United States. Polynt resins have been optimized to be processed using various application technologies such as hand lay-up, spray-up, casting, pultrusion, filament winding , sheet molding compound (SMC), bulk molding compound (BMC), infusion, injection, resin transfer molding (RTM), etc. This Phase 1 technical collaboration was used to prove feasibility of using Polynt base material chemistries for large scale polymer additive manufacturing (AM). The feasibility was demonstrated by printing complex structures, as well as by test pieces that were mechanically tested.

## 1.2 Technical Results

This project consisted of three tasks. Task 1: rheology and reaction kinetics, Task 2: solvents, build sheets and safety analysis, and Task 3: proof of concept demonstration. These tasks were performed collaboratively by Polynt and ORNL.

### 1.2.1 Rheology and reaction kinetics

The printability of polyester or vinylester resins is driven primarily by the rheology and reaction kinetics of the polymers. These properties can be controlled through chemistry modification and by incorporating additives. The ability to control these properties distinguishes reactive additive manufacturing(AM) from thermoplastic AM, which is driven largely by temperature gradients that can't be controlled. Polymers tested in Phase 1 of this project had viscosity of 300-700 centipose (cP), with reaction times ranging from 9 to 40 minutes. Figure 1 shows an example of rheology measurement results for an initial material trial composition highlighting shear thinning behavior of the polymer.

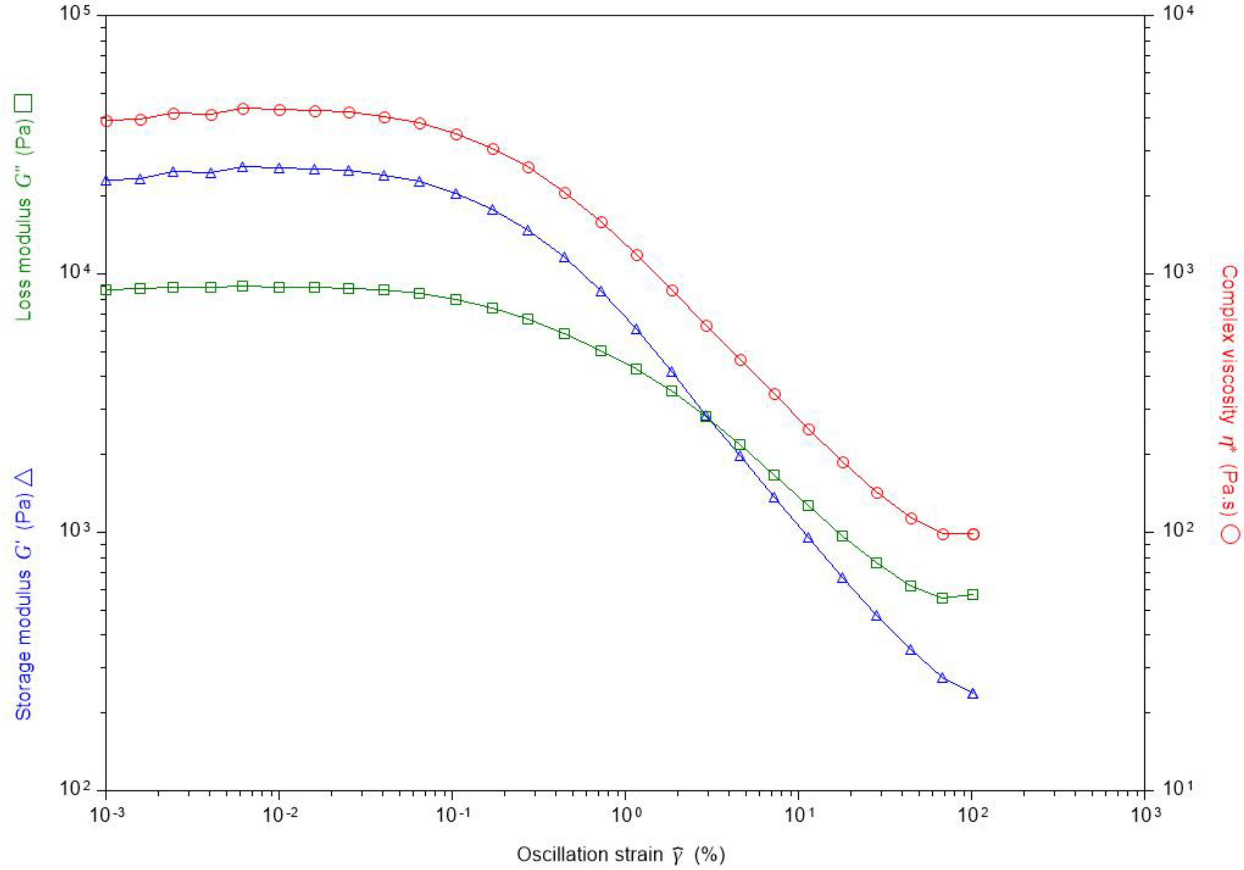


**Figure 1.** Frequency sweep in the linear range of viscoelastic region.

Figure 2 shows reaction of polymer during printing with the reaction demonstrated by the change in color of the three lower layers. The image shows two bead wide, five layer tall honeycomb printed structure.

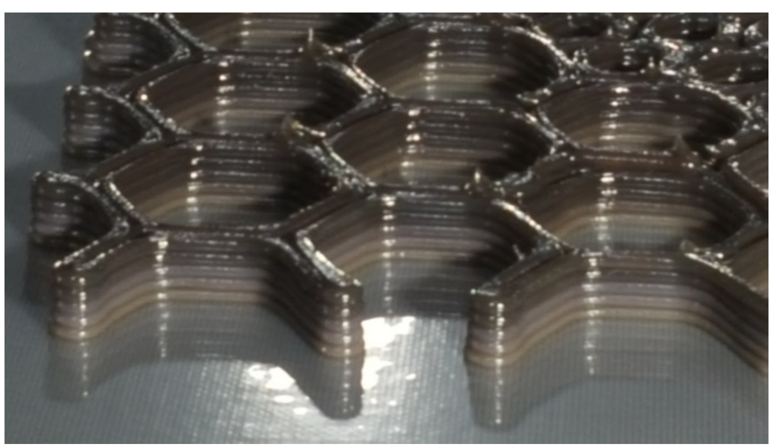

**Figure 2.** Visible polymer reaction during printing.

### 1.2.2 Solvents, build sheets and safety analysis

ORNL and Polynt have evaluated safety considerations for large scale printing of polyesters and vinylesters. Major concerns addressed centered around explosion and health and safety properties of styrene, which is present in the materials evaluated in this work, and volatilizes prior to reaction of the polymer. Catalysts also pose explosion and health risks if treated improperly. The properties of these polymers primarily informed modifications of equipment and facilities used for printing.

Although alternative solvents are available for the materials, acetone is the preferred solvent for cleaning of equipment exposed to catalyzed polymer. Since the system used in this work (shown in Figure 3) was designed to require minimal purging, acetone appears to be acceptable solution for future work. Build sheet selection appears to be less critical compared to thermoplastic printing. Low cost Mylar sheets were successfully used for Phase 1 of this project.


**Figure 3.** Thermobot by Magnum Venus Products was used as testbed for printing trial.

### 1.2.3 Proof of concept demonstration

Demonstration articles were printed on the Magnum Venus Products (MVP) machine as shown in Figure 2 to prove the feasibility of using polyester and vinylester formulations for large scale printing. Tensile coupons were harvested from straight double bead wide samples as shown in Figure 4. Since the height of the build is currently limited, the samples have non-standard profile.

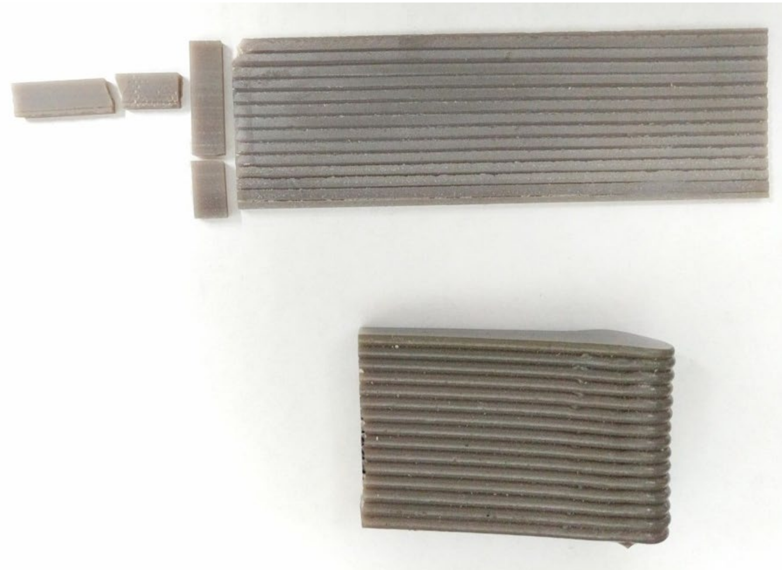

**Figure 4.** Printed samples and extracted test bars.

Quasi-static tensile tests were performed in the print direction (X) and in the build direction (Z). Results shown in Table 1 indicate that this class of reactive polymers will outperform existing thermoplastic materials used for large scale additive manufacturing (strengths for most materials printed in large scale format range from 2 Ksi to 12 Ksi). Moreover, the reduction of properties from print direction to build direction is only 29%, which is less significant decrease than for most thermoplastic materials.

**Table 1. Mechanical test results for vinylester formulation EX-1492**

| Average Strength X | Average Strength Z |
|---|---|
| 21.1 Ksi | 15.1 Ksi |
| Standard Deviation X | Standard Deviation Z |
| 3.2 Ksi | 1.6 Ksi |

Standard toolpath planning strategies were adopted from thermoplastic printers. However, it was demonstrated that materials evaluated in this project allowed greater freedom in toolpath planning since it was possible to cross a previously deposited bead without stopping and pausing the print. Eliminating stops at bead cross-overs will result in significant time savings and possibly an improvement in the mechanical properties of printed structure.

## 1.3 Impacts

This project demonstrated that polyesters and vinylesters have promising properties for large scale additive manufacturing. High strength values compared to existing thermoplastic additive material have been demonstrated along with less than 30% reduction in Z strength compared to print direction strength. These materials require no energy input during printing and have been shown to offer increased freedom in toolpath planning. Additionally, carbon fiber, or other additives with low coefficients of thermal expansion, are not required to achieve large scale prints, presenting the possibility of introducing low cost materials for large scale AM.

### 1.3.1 Subject Inventions

There are no subject inventions associated with this CRADA at this time.

### 1.3.2 Publications

There are no publications at this time.

## 1.4 Conclusions

The goals of this project were met with success in Phase 1 of this project. Leveraging the significant capabilities of Polynt in synthesis of materials and of ORNL in additive manufacturing, the feasibility of using polyesters and vinylesters for large scale additive manufacturing was demonstrated.

The next steps for advancing this technology is to achieve taller builds and optimize material properties for consistent deposition with available equipment. This can be achieved by combination of rheology modification as well as cure kinetic adjustment. With high mechanical properties demonstrated in Phase 1 of this project, it is expected that these materials could be used in applications requiring strength beyond the reach of existing thermoplastic AM materials.

Since the Phase 1 objectives were successfully met, Polynt Composites USA is planning on continuation of this research in Phase 2 as outlined in the original CRADA, if approved by DOE.

## 2. POLYNT COMPOSITES USA INC.

Polynt is one of the leading companies in the production and sale of Unsaturated Polyester Resin (UPR), Urethane Ester, and Vinylester (VE), which is produced under DISTITRON® and other trade names. Polynt Composites USA Inc. is a leading supplier of gel coats, composite resins and industrial cleaners in the United States. Polynt resins have been optimized to be processed using various application technologies such as hand lay-up, spray-up, casting, pultrusion, filament winding , SMC-BMC, infusion, injection, RTM, etc.