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# The Development of High Temperature Thermoplastic Composite Materials for Additive Manufactured Autoclave Tooling



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Materials Science and Technology Division  
Advanced Manufacturing Office

**The Development of High Temperature Thermoplastic Composite Materials for  
Additive Manufactured Autoclave Tooling**

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## **ABSTRACT**

In this work, ORNL and Techmer investigated and screened different high temperature thermoplastic reinforced materials to fabricate composite molds for autoclave processes using Additive Manufacturing (AM) techniques. This project directly led to the development and commercial release of two printable, high temperature composite materials available through Techmer PM. These new materials are targeted for high temperature tooling made via large scale additive manufacturing.

### **1. THE DEVELOPMENT OF HIGH TEMPERATURE THERMOPLASTIC COMPOSITE MATERIALS FOR ADDITIVE MANUFACTURED AUTOCLAVE TOOLING**

This Phase 2 technical collaboration project (MDF-TC-2016-053) was begun on June 23, 2014 and was completed on August 8, 2017. The collaboration partner Techmer PM is a medium-sized business. The work resulted in two commercially available materials for high temperature tooling that are produced by Techmer PM.

#### **1.1 BACKGROUND**

The Big Area Additive Manufacturing (BAAM) system developed at ORNL has been used primarily for demonstrations and low temperature tooling applications prior to completion of this project. The BAAM system is uniquely suitable for tooling applications, however there were no commercially available materials available for additive manufacturing (AM) printing of elevated temperature tools prior to this project. At the end of the project, there were two printable, high temperature commercially available materials available industry wide through Techmer PM. This new capability creates an opportunity for the US tool and die manufacturing industry to re-establish domestic capabilities, and improve the overall responsiveness and cost-competitiveness of US manufacturing.

#### **1.2 TECHNICAL RESULTS**

In this work, ORNL and Techmer investigated different high temperature materials for their suitability in BAAM printing, see Table 1. This work was tasked into three main sections: a) Thermal properties and rheological parameters, b) Throughput, printability, and thermal stability, and c) Mechanical properties. This detailed characterization resulted in the use of the successful candidate materials in the print of two different size autoclave tools, shown later in this report. It can be noticed from Table 1 that different loadings of carbon fiber (CF) were investigated and their effect on the mechanical properties and printability was monitored. Various grades for Polyphenylene sulfide (PPS) were investigated. The Polyphenylsulfone (PPSU) and Polyethersulfone (PESU) resins were provided by BASF and compounded with different fiber loadings by Techmer PM. The primary focus of this screening was on printability. Major issues encountered during this work were related to thermal degradation of polymers at elevated temperature, inappropriate viscosity for processing and warpage/cracking of printed structures.

Table 1: High temperature materials investigated for additive manufactured autoclave tooling

Material	Description
<b>PPS / CF Family</b>	
PPS / CF 40%	PPS with Carbon Fiber 40% by weight
PPS / CF 50 %	PPS with Carbon Fiber 50% by weight
PPS / CF 60 %	PPS with Carbon Fiber 60% by weight
<b>PPSU / CF Family</b>	
PPSU / CF 25 %	PPSU with Carbon Fiber 25% by weight
PPSU / CF 35 %	PPSU with Carbon Fiber 35% by weight
<b>PESU / CF Family</b>	
PESU / CF 25%	PESU with Carbon Fiber 25% by weight
PESU / CF 35%	PESU with Carbon Fiber 35% by weight

### 1.2.1 Thermal Properties

Rheological tests were performed on candidate materials in the Linear Viscoelastic region (LVE), which can be determined using the strain sweep tests. Both oscillatory shear and transient shear measurements were performed above the melting temperature of these materials. It can be seen in Figure 1a that PPS / CF displays a narrow LVE region that is only up to 0.02%. The PPSU / CF displays a broader LVE region (up to 4%) compared to PPS / CF materials. It should be noted that these two materials have different CF loadings and processing temperatures.

Figure 2a&b show the linear viscoelasticity of PPS / CF composites with different carbon fiber loadings. Two important features should be noted. On one hand, both viscosity and dynamic moduli would be increased with increasing carbon fiber loading. On the other hand, the storage modulus  $G'$  of PPS with 50 wt. % is larger than the loss modulus  $G''$  and this can be attributed to the increases in carbon fiber content. Unlike the linear viscoelastic responses of PPS / CF, the PPSU / CF displayed in Figure 2c&d only shows high viscous behavior, as opposed to than the solid-like behavior the PPS / CF displayed. In addition, it shows less shear-thinning in viscosity plots. With increased carbon fiber loading, the viscosity and modulus increased.

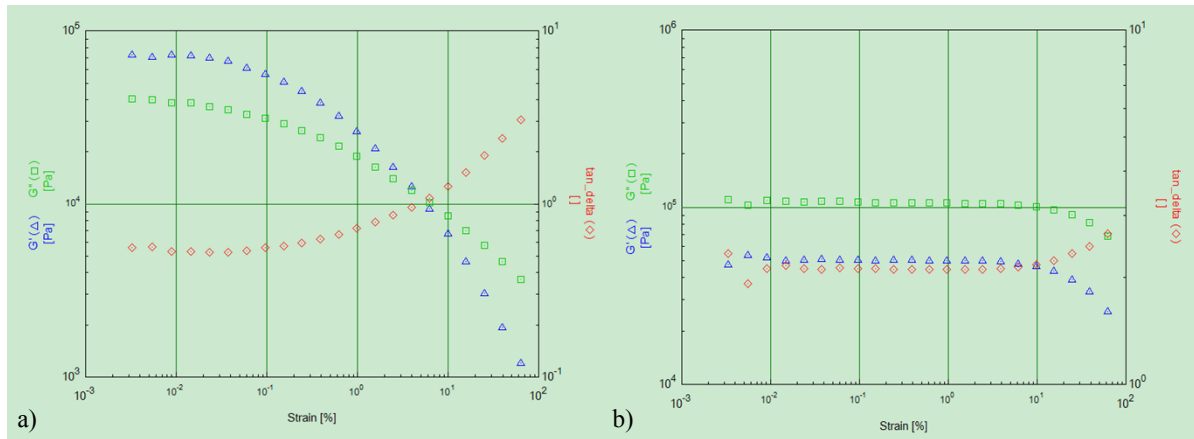
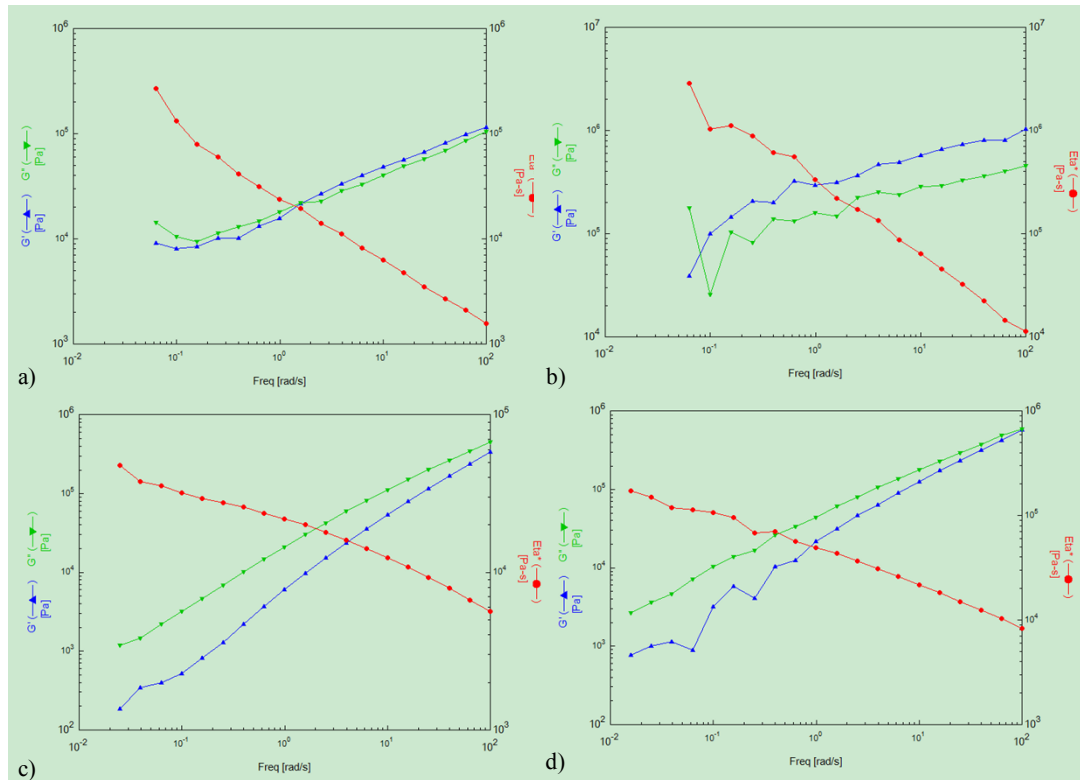


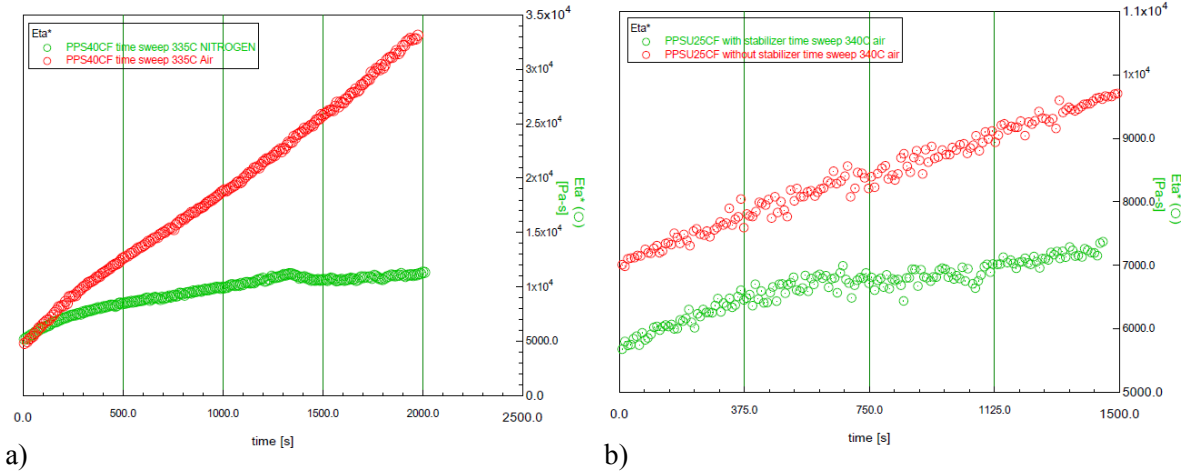
Figure 1: Strain dependent of storage modulus  $G'$  and loss modulus  $G''$  in Nitrogen environment (Frequency is 10 rad/s); a) PPS / CF 40% wt. at 335°C, and b) PPSU / CF 25% wt. at 340°C.



**Figure 2: Frequency dependent of  $G'$  and  $G''$  in Nitrogen environment; a) PPS / CF 40% wt. at 335°C, b) PPS / CF 50% wt. at 335°C, c) PPSU / CF 25% wt. at 340°C, and d) PPSU / CF 35% wt. at 340°C**

### 1.2.2 Throughput, printability, and thermal stability

The thermal stability of the high temperature resins under air atmosphere was investigated. Figure 3a shows that the viscosity and dynamic moduli increased more than 600% over 0.5 hours. This high viscosity will require an extruder operation torque that exceeds the maximum capacity of the extruder. Hence, we investigated two potential solutions, a) Add heat stabilizer to the compounded composite, and b) Print in an inert gas environment. The effect of heat stabilizer on the thermal stability was investigated, as shown in Figure 3b. Heat stabilization is helpful in keeping the viscosity stable during the printing process. Figure 3a shows that it is strongly suggested to use a nitrogen or argon environment while printing these materials as the change in viscosity during printing was significantly reduced.



**Figure 3: Thermal stability of high temperature material; a) PPS / CF 40% wt. under air and Nitrogen environment; ( $T=335\text{ }^{\circ}\text{C}$ , frequency is 10 rad/s, strain is 0.02 %), and b) PPSU / CF 25% wt. with and without heat stabilizer under air; ( $T=340\text{ }^{\circ}\text{C}$ , frequency is 10rad/s, strain is 0.02%).**

### 1.2.3 Mechanical Characterization

To investigate the printability of these high temperature thermoplastic reinforced composites, simple geometry (i.e. wall) with the size of 152.4 cm X 38.1 cm X 1.14 cm (60'' X 15'' X 0.45'') were printed. Printing a double-bead wall is good demonstration of suitable printing process settings. An example wall is depicted in Figure 4.



**Figure 4: Printed composite wall with PPS / CF 50 wt.%.**

The printed walls were used to determine the mechanical characteristics of the material (Figure 5). Different test coupons were extracted out of the printed parts in the bead direction (i.e. X-direction) and perpendicular to the bead direction (Z-direction). It was noticed that PPS samples in the X-direction with 50 % by weight carbon fiber showed an increase of 12.4 % at the tensile strength when compared to the samples with 40% by weight carbon fiber. However, a reduction of 9.9 % in strength by was observed when the carbon fiber weight fraction increased to 60 % when compared to printed parts with 50 % reinforcement.

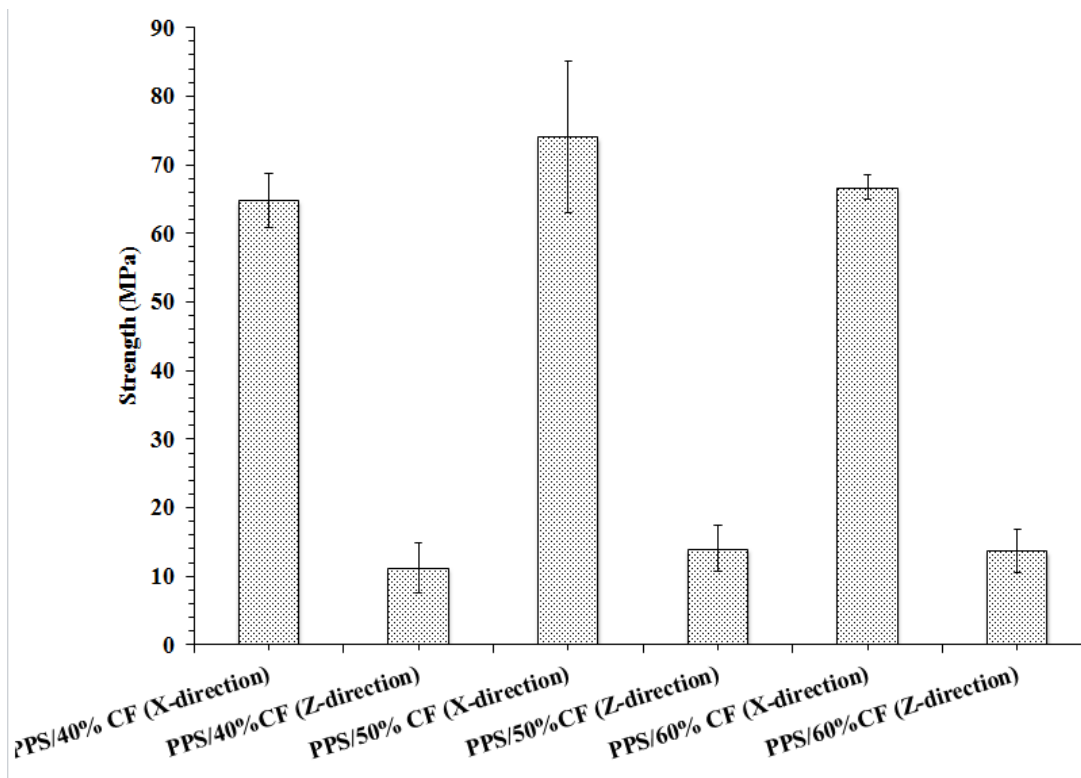


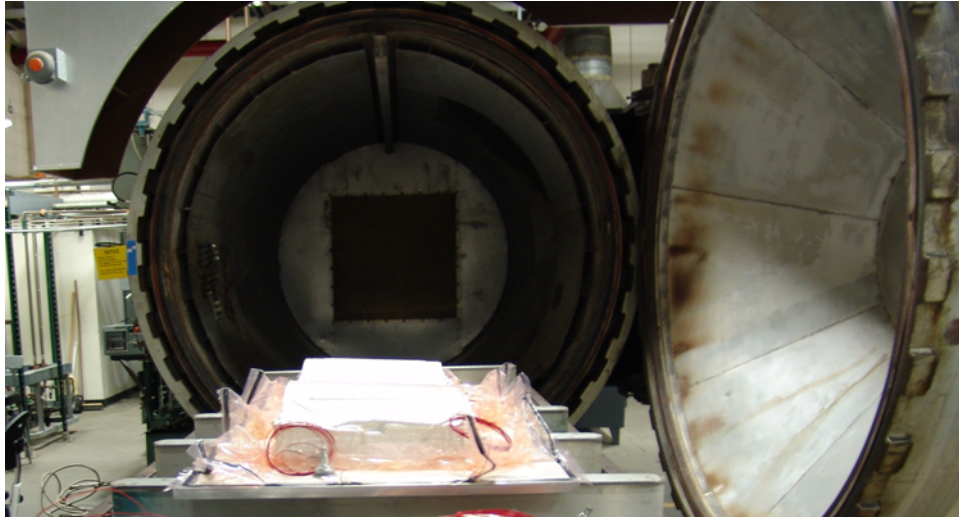
Figure 5: Strength of PPS samples tested in X and Z directions.

#### 1.2.4 Discussion

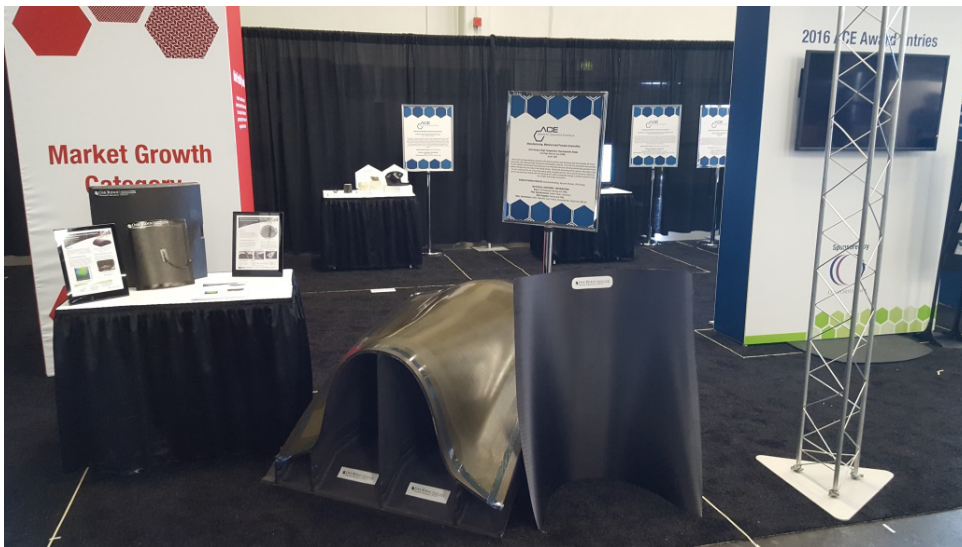
The intensive screening undertaken in this project resulted in the development of two new commercial products, namely PPS / CF 50 wt.% and PPSU / CF 25 wt.%. These products were added to Techmer's current product line as– Electrafil® PPS 3DP line, and Electrafil® PPSU 3DP line in March 2017. It should be noticed that the PPS is a semi-crystalline polymer and the PPSU is an amorphous polymer system.

The new Techmer materials have been used to print autoclave tools. Tools made from the new materials were tested successfully in a Boeing production autoclave under at temperature of 350F and pressure of 90 psi. Work on tooling printed with these materials by Boeing was awarded the American Composites Manufacturer's Association (ACMA) 2016 Materials and Process Innovation Award at the Composites and Advanced Materials Expo (CAMX) (Figures 6 and 7). The Awards for Composites Excellence (ACE), are a prestigious composites industry competition held for over 20 years, recognizes outstanding achievement and innovation in technology, manufacturing and product development

Techmer and ORNL also were named a 2017 R&D 100 Award finalist for their entry TEAMM – Electrafil® PPS 3DP, Electrafil® PPSU 3DP, a new series of new thermoplastic compounds that allow production of autoclave tooling that withstands 350F, 90 psi autoclave cycles,



**Figure 6: TEAMM test molds being loaded into an autoclave at Boeing’s St. Louis facility.**



**Figure 7: AM autoclave midscale tool fabricated using Electrafil® PPS/F CF50 HS 3DP, the image shows the final fabricated composite part (right to the tool).**

### **1.3 IMPACTS**

This project resulted in Techmer PM launching a new family of commercially available Electrafil® products for high temperature tooling applications for large scale additive manufacturing. The ability to rapidly manufacture tools for elevated temperature use creates the opportunity for US tool and die manufacturing to re-establish domestic capabilities and improve the responsiveness and cost-competitiveness of US manufacturing. This work led to a Techmer customer winning Award for Composites Excellence (ACE). Techmer PM and ORNL were named a 2017 R&D 100 award finalist for the development of the materials in this project.

### **1.4 CONCLUSIONS**

Material screening, modification and printing performed in this project resulted in two commercially available product lines offered for large scale additive polymer manufacturing. This new development enables large scale AM to be meaningful tool for elevated temperature tooling applications.

## **2. TECHMER BACKGROUND**

Techmer PM is a leading materials design company that works in partnership with plastics processors, OEMs, and designers to solve some of their most difficult business, manufacturing, and sustainability challenges. The company's solutions modify the aesthetics, as well as extend and maintain the physical properties of plastic products. The company designs custom solutions for customers to maximize performance through collaboration and by leveraging its leading-edge technology. Techmer PM's innovative design and materials solutions for large scale AM have positioned Techmer as the premier supplier in the industry. Techmer PM was recognized by Plastics News "Best Places to Work" for 2014, 2016 and 2017. Learn more by visiting [www.techmerpm.com](http://www.techmerpm.com)