



## AN INVESTIGATION OF THE RHEOLOGICAL BEHAVIOR OF PHENOLIC RESINS CONSIDERED FOR PRODUCTION OF CARBON BONDED CARBON FIBER INSULATION

Glenn Romanoski<sup>1</sup>, Kyle Lach<sup>2</sup>, Kyle Monaghan<sup>3</sup>, Ashli Clark<sup>1</sup>, Nidia Gallego<sup>1</sup>, and George Ulrich<sup>1</sup>

<sup>1</sup>Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831, 865-574-4838, [romanoskigr@ornl.gov](mailto:romanoskigr@ornl.gov)

<sup>2</sup>University of Dayton Research Institute, 300 College Park Ave., Dayton, OH, 45469, 937-255-0521,  
[Kyle.Lach@udri.udayton.edu](mailto:Kyle.Lach@udri.udayton.edu)

<sup>3</sup>Western Carolina University, 1 University Way, Cullowhee, NC 28723, 215-589-9380, [kylemonaghan@gmail.com](mailto:kylemonaghan@gmail.com)

*CBCF insulation is made from chopped and carbonized rayon fibers bonded by carbonized phenolic resin. The rheological behavior of several resins was investigated to determine if alternative resins would be more effective in forming carbon-bond precursors.*

### I. INTRODUCTION

The requirement for containment and thermal protection of the isotopic fuel in Radioisotope Power Systems led to a design and material selection for the General Purpose Heat Source that relied principally on carbon materials (Ref. 1). A unique Carbon Bonded Carbon Fiber (CBCF) insulation was developed to provide thermal protection during the extremes of unlikely reentry scenarios. The microstructure of CBCF, shown in Fig. 1, is comprised of carbonized rayon fibers bonded at intersections by carbonized phenolic resin.



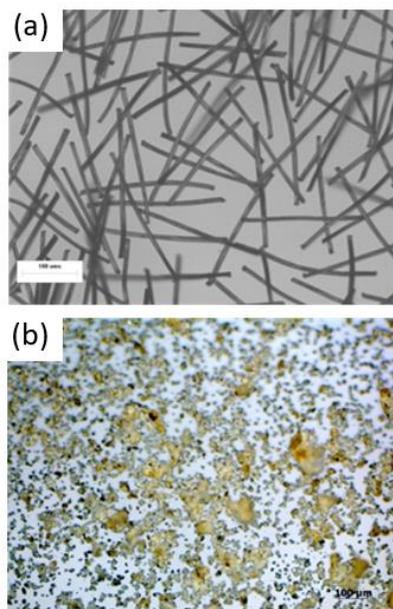
**Fig. 1.** Microstructure of CBCF

The principal physical properties that define the performance of CBCF as an insulator in the GPHS include: density, thermal conductivity and compressive strength. The CBCF production process was detailed by Wei and Robbins in Ref. 2.

### II. MATERIALS

The two essential constituents of CBCF insulators are carbonized rayon fibers and phenolic resin. As described

previously in Ref. 3, the rayon fibers are an apparel-grade viscose rayon chopped to uniform length and carbonized at high temperature under a protective atmosphere. The standard phenolic resin used in the production of CBCF, hereinafter - “qualified resin”, is a thermosetting resin consisting principally of Novolac powder. Novolacs  $[(C_6H_4OHCH_2)_n]$  are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one. The resin contains ~8% hexamethylenetetramine  $[(CH_2)_6N_4]$  as an activator for polymerization. Images of the fibers and the resin powder used in CBCF production are shown in Fig. 2. The mean length of the carbonized rayon fibers is ~250  $\mu m$ . The mean diameter of the resin powder is ~20  $\mu m$ . The standard CBCF process includes a drying and curing heat treatment accomplished in a convection oven. Drying at 50  $^{\circ}C$  is followed by a slow-stepwise increase to final curing at 130  $^{\circ}C$ .



**Fig. 2.** (a) Image of chopped and carbonized rayon fibers and (b) Image of phenolic resin powder

The specific phenolic resins investigated in this study are given in Table 1, including two separate lots of the qualified resin produced in 2012 and 2017 as indicated by the first two digits of the lot numbers. Several alternative commercial phenolic resins that exhibit greater inclined plate flow values were included as potential alternatives to the currently qualified resin.

**Table 1. Specification for Commercial Resins**

Resin	Hexa (%)	Cure Time (s)	Inclined Plate Flow (mm)
Qualified Resin <sup>§</sup> Lot 12HH1163	7.6	23 @ 165 °C	28 @ 60°
Qualified Resin <sup>§</sup> Lot 17CC8322	7.8	23 @ 165 °C	35 @ 60°
GP-5520 <sup>§</sup>	8.1	74 @ 150 °C	46 @ 60°
GP-652D55*	0	90 @ 150 °C	50 @ 30°
Varcum 29217*	0	40 @ 160 °C	55 @ 60°

<sup>§</sup>Novolac type resin      \*Resole type resin

### III. EXPERIMENTAL

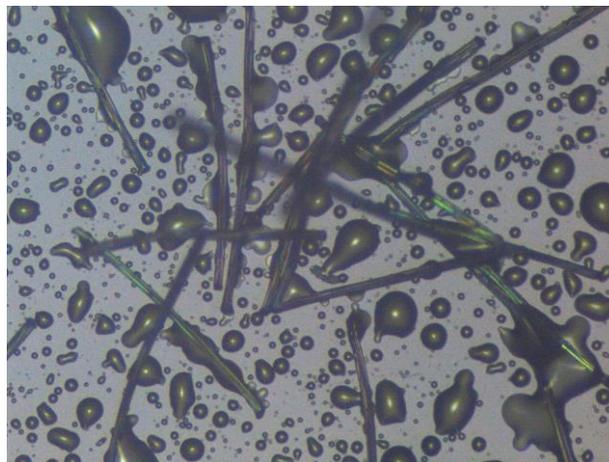
Commercial resin suppliers characterize the macroscopic flow and curing behavior of resin using an industry standard “Inclined Plate Flow” test as shown in Fig. 3. A pressed resin pellet is heated on a glass slide to 125 °C and elevated to a 60° angle while maintaining isothermal conditions in air. The test result is the distance, in mm, to which the leading edge of the resin advances. This test provides a dynamic measure of resin flow and curing kinetics as the flow is finally arrested when crosslinking makes the resin too viscous to continue. Several commercial resins listed in Table 1 and considered here have greater inclined plate flow results and would be expected to have lower viscosity and/or slower curing rate.



**Fig. 3.** Inclined plate flow test at 125 °C in air

In addition to inclined plate flow tests, the melting behavior of the resin was investigated using a hot stage microscope under ambient air. Time-lapsed images revealed fiber-resin interactions from room temperature to 375 °C. Incipient melting of resin particles begins at 100

°C and is complete by 130 °C. As shown in Fig. 4, the molten spheres dominate the resin morphology as the internal and resin-air surface tension forces withstand surface tension forces between the “molten” resin and the carbonized rayon fibers.



**Fig. 4.** Qualified resin and fiber interaction during a hot stage microscope experiment at 130 °C

To better understand the melt, flow and cure behavior of several resins, an Advanced Rheometric Expansion System (ARES) like that shown in Fig. 5 was employed to quantify the rheologic behavior of resin candidates.



**Fig. 5.** Advanced Rheometric Expansion System

In a strain-controlled viscosity test of the phenolic resin, a small volume of resin powder is compacted in a die to form a cylindrical disc. The disc is placed between the

platens of the rheometer under a light compressive load. The sample and test fixtures are heated rapidly to an isothermal condition by enclosing within a pre-heated clam-shell furnace. After achieving the desired uniform temperature, the sample is sheared by rotating the lower platen at a constant rate while the resulting torque is measured by a transducer attached to the upper platen.

#### IV. RESULTS AND DISCUSSION

The image shown in Fig. 1 illustrates the nature of bonding throughout the CBCF microstructure. Successful bonding at carbon fiber contact locations requires that the resin, as a carbon precursor, flows to these sites and remains during heat treatments. The physical requirements for resin flow and fiber wetting is further illustrated in the hot stage microscopic image of Fig. 4. Molten resin particles form spherical “drops” due to weak intermolecular forces within the resin liquid/gel. Resin-fiber surface tension (shear forces) must overcome the intermolecular forces within the softened resin to result in flow and wetting. Rheology is the science of flow and deformation of matter such as molten or semi-molten resin. Flow is a special case of deformation. Viscosity is a fluid’s internal resistance to flow. Thus, in the simplest terms:

$$\text{Shear Stress } (\tau) / \text{Strain Rate } (\dot{\gamma}) = \text{Viscosity } (\eta) \text{ Eq. (1)}$$

Rheological characterization of the qualified resin was performed at a constant strain rate in ORNL’s ARES rheometer at temperatures of 100, 110, 120 and 130 °C. The results are presented in Fig. 6 as viscosity versus time for times ranging from a fraction of a second to approximately 15 minutes for the lower temperature tests. The lowest initial viscosity was measured at 130 °C since the resin readily melted at that temperature, but also showed a rapid increase in viscosity within 10 seconds due to rapid crosslinking promoted by the higher temperature. Tests at lower temperatures exhibited higher initial viscosities due to the semi-molten state of the resin and showed a more extended period of slowly rising viscosity until about one minute where cross-linking became evident for the 110 and 120 °C tests. Cross linking began at around 10 minutes in the 100 °C tests. If one considers the very short time scale of crosslinking and resulting high viscosities to the duration of the standard CBCF curing cycle (several hours), it is immediately apparent why incomplete flow of resin particles were previously observed during CBCF processing (Ref. 3).

In total; two separate lots of the qualified resin, two different Georgia Pacific resins and one Varcum 29217 resin were characterized in the constant strain rate rheometer at several temperatures. The results for 130 °C

tests are shown in Fig. 7. Although resins exhibited some separation in viscosity values throughout, all began to exhibit a rapid increase in viscosity within 100 seconds due to cross-linking. Considering the temperature versus time profile that has become the standard for CBCF processing, none of these resin options could be expected to result in a significant improvement in final product if used to make CBCF.

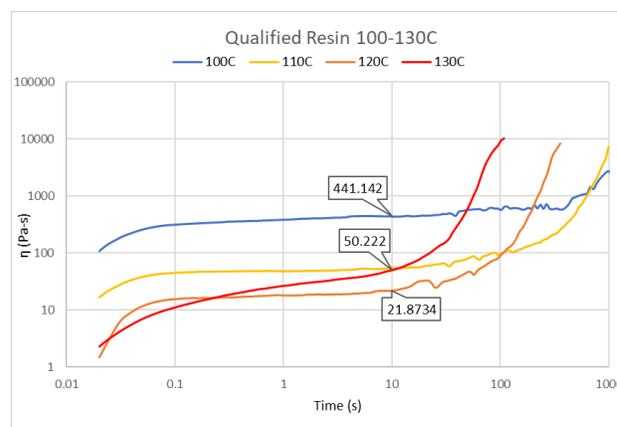


Fig. 6 Apparent viscosity vs time for the qualified resin

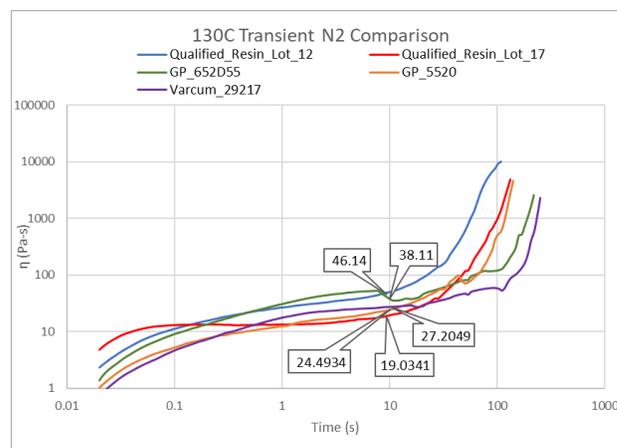


Fig. 7 Apparent viscosity vs time for several commercial resins

#### V. CONCLUSIONS

The evidence presented here verifies that the resin does not become sufficiently fluid during the standard cure cycle specified for CBCF processing. Improved resin flow and greater bonding could be achieved in CBCF using a resin that exhibits significantly lower viscosity and slower curing rate compared to the qualified resin.

## **VI. A PATH FORWARD**

Improved bonding of carbonized rayon fibers within CBCF may be achieved with a non-curing resin or a very slow curing resin. Our vendor for the qualified resin has agreed to produce a trial batch of an identical Novolac resin with different levels of the curing agent, hexamethylenetetramine (0%, 0.5%, 1%, 2.5% and 5%). Rheological characterization and fiber/resin wetting experiments will be conducted. A few experimental lots of CBCF will be produced.

## **ACKNOWLEDGMENTS**

This work was sponsored by the United States Department of Energy Office of Nuclear Facilities Management (NE-31). Primary funding was provided by the NASA Science Mission Directorate. Second and third authors were supported in part by an appointment to the Higher Education Research Experiences Program at Oak Ridge National Laboratory.

## **REFERENCES**

1. A. SCHOCK, "Design Evolution and Verification of the General Purpose Heat Source," Proceedings of the Intersociety Energy Conversion Engineering Conference, pp. 1032-1042, American Institute of Aeronautics and Astronautics, 1980.
2. G. C. WEI and J. M. ROBBINS, "Carbon-Bonded Carbon Fiber Insulation for Radioisotope Space Power Systems," Ceramic Bulletin, Vol. No. 64, Nov. 5, 1985.
3. G. Romanoski, K. Lach, A. Clark, N. Gallego, S. Adhikari and G. Ulrich, "An Investigation of the Melt, Flow and Cure Behavior of Phenolic Resin During Processing of Carbon Bonded Carbon Fiber Insulation," ANS NETS 2018 – Nuclear and Emerging Technologies for Space, Las Vegas, NV, February 26 – March 1, 2018, ANS on CD-ROM