

# Fire Resistant, 2<sup>nd</sup> Generation Resorcinol, PEEK<sup>TM</sup>-Like Phthalonitrile Composites For Advanced Applications

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## ABSTRACT

A new oligomeric 2<sup>nd</sup> generation resorcinol-based PEEK<sup>TM</sup>-like phthalonitrile (PN) resin has been developed via a cost-effective method and is being transitioned to an industrial scale. The PN monomer exhibits excellent viscosities comparable to current resin technologies at their respective processing temperatures and was used to prepare composite panels using non-autoclave techniques. The PN composite was tested in accordance with ASTM E1354, which measures the time-to-ignition (TIG), peak heat release (PHR), mass loss rate, and combustion product generation rate of a material exposed to a specified irradiance level. The composite exhibited a TIG and a PHR at 75 and 100 kW·m<sup>-2</sup> of 136 and 58 seconds and 106 and 114, respectively. The flammability results show that the composite is extremely close to passing the Navy's flammability requirements of MIL-STD-2031 for applications in the most extreme fire environments. After exposure to elevated temperature oxidative aging, the composite exhibited very low weight loss and high mechanical strength retention.

**Keywords:** Thermosets, Thermal properties, resin

## 1 BACKGROUND

The NRL developed phthalonitrile (PN)-based polymers/composites exhibit superior flammability, low water absorption, and high temperature properties<sup>1-7</sup> that do not exist in the current marketplace, when compared to traditional high temperature resin systems (e. g. PMR-15 polyimide). Until recently, the only available PN systems were the 1<sup>st</sup> generation PN resins, which consisted of small crystalline molecules synthesized from the salts of bisphenols (e.g. 4, 4'-biphenol, bisphenol A, bisphenol AF, etc.) and 4-nitrophthalonitrile. The early PN resins exhibited high melting points (200-230 °C), which limited the processing/curing to temperatures above their respective melting points. Although the polymers/composites exhibited excellent properties, the resin processing challenges ultimately limited their wide applicability. More recently, in response to a need for a more processable resin system, a series of low molecular weight oligomeric PNs (2<sup>nd</sup> generation) were developed at the NRL and were designed to create a mixture of various length oligomers

within the resin mixture. The new commercially available PEEK<sup>TM</sup>-like PNs<sup>3,4,5</sup> are easily synthesized from environmentally safe compounds/reactants. Being oligomeric in composition, the resins exhibit a glassy structure and have softening temperatures around 70 °C, which enhance the ability to process the resins at a low temperature and open up many more applications than could be realized for the 1<sup>st</sup> generation resins. All PN monomers polymerize through the cyano groups with the aid of an appropriate curing agent such as aromatic diamines<sup>6</sup> to yield a crosslinked polymeric network, which exhibits high thermal and oxidative stability and environmentally inert once fully cured. The fully cured polymers are obtained by heating the PN monomers and a small amount of curing additive in the melt-state at or above 150 °C for various periods of time for conversion to a solid followed by post-curing up to 350 - 425 °C depending on the resin structure and application. Full cure is designated when the PN solid polymer/composite no longer exhibits a glass transition temperature. The fully cured PN polymer is the only known thermosetting resin that does not lose complete structural stability up to its decomposition point. When heated to temperatures over 500 °C, very little outgassing occurs, which enhances the fire resistant properties; the PN composite does not burn in a flame environment. In addition, the high aromatic content of the thermoset affords a high char yield (85-90 %) of composite structures when pyrolyzed to 1000 °C under inert conditions. For instance, the fire performance of the first generation PN-carbon<sup>1</sup> and PN-glass<sup>2</sup> composites are superior to that of any other thermoset-based composites currently in use for aerospace, ship and submarine applications. These 1<sup>st</sup> generation PNs are still the only polymeric material that meets the Navy MIL-STD-2031 for usage inside of a submarine. There is currently much interest in this 2<sup>nd</sup> generation PEEK<sup>TM</sup>-like PN resin/composite especially the resorcinol-based PN as it is much easier to process than the 1<sup>st</sup> generation systems, but more studies are needed to optimize the fire performance.

## 2 EXPERIMENTAL

### 2.1 General Information

Reagent grade starting materials were used without further purification. Differential scanning calorimetric

(DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> and a nitrogen purge of 50 cm<sup>3</sup> min<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen or air purge of 50 cm<sup>3</sup> min<sup>-1</sup>. NMR studies were performed on a Brüker ADVANCE 300 spectrometer. A TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control and torsion fixtures, was used to monitor the response of polymeric samples (50 mm x 13 mm x 2 mm) to oscillatory testing. The measurements were made in nitrogen over the temperature range of ~ 25 to 450 °C. A temperature ramp of 3 °C min<sup>-1</sup> was used to determine the storage modulus and damping factor (tan δ) of the material at a frequency of 1 Hz and a strain of 2.5 x 10<sup>-2</sup> %. Normal force control was utilized throughout the tests to keep the samples taut. The fire performance of the PEEK<sup>TM</sup>-like composite patch system was tested in accordance with ASTM E1354 at NAWCCD.

## 2.2 Resorcinol, PEEK<sup>TM</sup>-Like Phthalonitrile Resin 1 Synthesis

To a 3000 mL, three-necked flask fitted with a thermometer, a Dean-Stark trap with condenser, and a nitrogen inlet were added toluene (200 mL) and dimethylsulfoxide (DMSO) (1000 mL) under nitrogen and the solvents were sparged thoroughly with nitrogen for 15 min. Resorcinol (160 g, 1.45 mol), 4, 4'-dichlorobenzophenone (182.4 g, 0.727 mol), sodium hydroxide (104.6 g, 2.62 mol), and powdered anhydrous K<sub>2</sub>CO<sub>3</sub> (80.2 g, 0.581 mol) were then added. Toluene was used to control the refluxing isotropic removal of water and to control the temperature of the reaction content. Adjustments in the amount of toluene (additions or subtractions) were made in order to achieve reflux around 150-160 °C under a nitrogen atmosphere. The reaction mixture was heated for 8-16h or until a suitable technique to monitor the reaction (e. g. HPLC, NMR, etc.) indicated the disappearance of 4,4'-dichlorobenzophenone and the presence of the hydroxyl terminated oligomer. The toluene was then slowly distilled off and the mixture was cooled below 50 °C. Then, 4-nitrophthalonitrile (253.0 g, 1.46 mol) was added and the reaction mixture was heated at 70-80 °C for 4-8h. The mixture was allowed to cool to 50 °C and poured into a vigorously stirred aqueous HCl solution, resulting in the formation of a solid. The solid was then collected in a Büchner funnel using qualitative filter paper. The brown solid was milled to a fine powder and washed with enough water to reach a neutral pH. The isolated solid was vacuum dried yielding the resorcinol based PEEK<sup>TM</sup>-like oligomeric PN 1 (458 g, 97 %) as a brown powder. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.85-7.70 (m, aromatic-H), 7.57-7.25 (m, aromatic-H), 7.12-6.97 (m, aromatic-H), 6.92-6.78 (m, aromatic-H). IR [cm<sup>-1</sup>]: ν 3074 (C=CH), 2232 (CN), 1650

(C=O), 1587 (C=C), 1477 (aromatic), 1307 (aromatic), 1307 (C-O), 1244 (CH<sub>3</sub>), 1162 (C-O), 928 (C-O), 842 (aromatic).

## 2.3 Preparation of Resin/Amine (1/*m*-BAPS) Mixtures for DSC Analysis and Composite Fabrication

To the powder of the monomer 1 was added 3 weight % of bis(4-[3-aminophenoxy]phenyl)sulfone (*m*-BAPS). After evenly dispersing the curing additive by dry mixing, the sample was used in the DSC and composite fabrication.

## 2.4 Fabrication of Glass Fiber Composites For Testing

7781 E-glass woven fibers sized with a high temperature material were painted with a concentrated acetone solution of the 1/*m*-BAPS mixture calculated to achieve approximately 35 % total resin content on the fibers. The painted fibers were dried at room temperature, trimmed to fit a 10"x10" aluminum plate with a 6"x6" well.

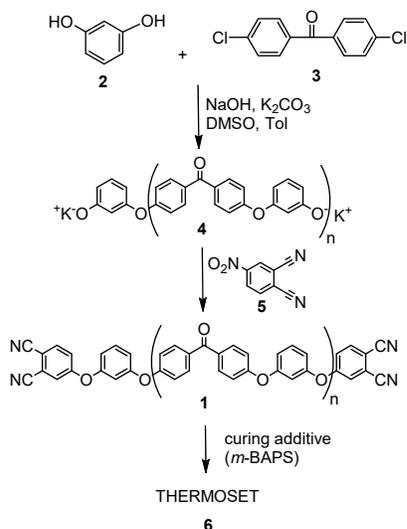
The well and plate were treated with mold release, and then 25 layers of PN painted fibers were placed in the well. A layer of peel ply and a metal cull plate were placed on top. The entire area was vacuum bagged, evacuated and heated in a muffle furnace at 100 °C for 2 hours to remove water, solvent and air from the stack. Fifty lbs of weight was applied to the stack top, and the oven was heated to 200 and then 270 °C for 8h dwells at each temperature. The panel was trimmed using a diamond saw to remove uneven portions

Several 25 ply panels, 1/4" thick, were prepared and studied in terms of their thermal and mechanical properties. The resin content of the final panels were 30-32 % total resin content as determined from TGA air measurement at 800 °C. Several 25 ply glass composite panels were also fabricated for fire testing at NSWCCD.

## 2.5 Machining Composites Test Samples

A high-speed diamond saw was used to cut mechanical test specimens from the 25 ply PN composite panels (7781 E-glass) with dimensions specified for various mechanical property tests. Rectangular test specimens (50 mm x 12.7 mm) were machined for dynamic mechanical measurements. Square specimens (4" x 4") were machined in accordance with ASTM E1354 cone calorimeter testing (MIL-STD-2031). Test specimens were examined visually for flaws, cracks, or delamination introduced during the cutting process, and if found, were not tested. Small samples (2 mm x 2 mm) were used for thermogravimetric analysis (TGA) under nitrogen and air.

### 3 DISCUSSION



Scheme 1: Synthesis of PN monomer **1** and polymer **6**.

The synthesis of the 2<sup>nd</sup> generation resorcinol-based PEEK<sup>TM</sup>-like PN **1** was achieved via a nucleophilic displacement reaction between resorcinol **2** (excess) and 4, 4'-dichlorobenzophenone **3** under basic conditions (Scheme 1) in dimethylsulfoxide (DMSO). The reaction contained a small amount of toluene, which allows the azeotropic distillation of water formed as a by-product in the reaction and a control of the reaction temperature to around 150-160 °C. The first reaction involving **2** and **3** yields a dipotassium phenolate intermediate **4**, consisting of oligomeric multiple aromatic ether ketone phenolates. Formation of the intermediate was considered complete when no more water was observed being azeotropically distilled, and <sup>1</sup>H-NMR spectroscopy confirmed that all of **3** had reacted. Upon cooling to about 50 °C, 4-nitrophthalonitrile **5** was added to the dipotassium phenolate intermediate mixture producing resin **1**. The 2<sup>nd</sup> generation resorcinol-based PEEK<sup>TM</sup>-like PN **1** was readily soluble in common organic solvents such as acetone and DMSO and was isolated in 97 % yield. The structure of the PN resin mixture **1** was confirmed by both FTIR and NMR spectroscopies. Several different formulations of this resin can be produced by simply changing the bisphenol **2** (e.g. bisphenol A, bisphenol AF, etc.) in the synthesis and the ratio of **2** to **3**.

The resorcinol-based PN resin **1** exhibited a melting transition at approximately 70 °C and remained in a melted state until the curing reaction with *m*-BAPS began around 175 °C peaking at 250 °C (Figure 1). A further exothermic transition above 300 °C was the result of the extended cure reaction. The large processing window between the melting and cure reaction of ~105 °C is unusually large from what is seen with comparable high temperature resin systems, allowing for more easily fabricated composite panels.

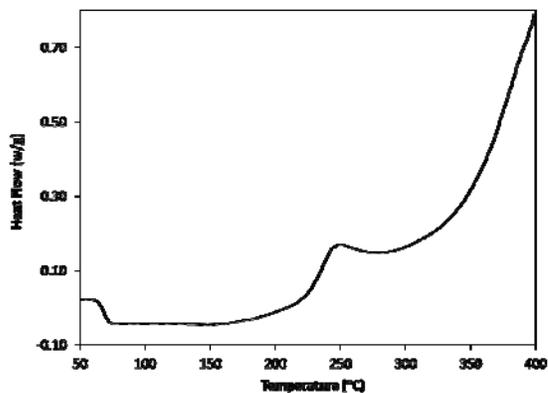


Figure 1: DSC of resin **1** with 3 wt % *m*-BAPS.

After determining the cure conditions for the resin **1**/*m*-BAPS formulation, several 25 ply composite panels were fabricated from 7781 E-glass woven fibers containing the **1**/*m*-BAPS formulations using a non-autoclave technique. The stacked plies were degassed at 100 °C for 2h and cured by heating at 200 °C and 270 °C for 8h under pressure yielding a consolidated panel. Once removed from the mold the composite panels were examined for flaws and cut into various dimensions for testing. The resulting cut pieces of the panel were postcured for an additional 8h at 375 °C to ensure full conversion to thermoset **6**. The char yield at 1000 °C of the composite was determined under nitrogen and found to be around 90 %, and the resin content of several panels ranged from 30-32 % as determined by heating under air to 1000 °C. This char yield is exceptional and composites made from resins with high char should show superior fire performance.

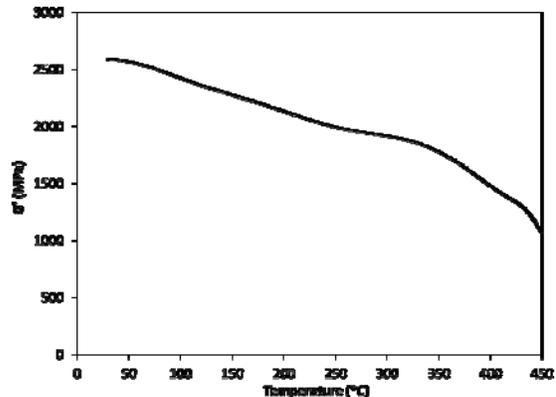


Figure 2: Rheometric analysis of composite **6** with 3 wt % of *m*-BAPS.

Rectangular shaped samples of composite **6** were post-cured at a maximum temperature of 375 °C and analyzed mechanically using a rheometer from 25 to 450 °C (Figure 2). The storage modulus value for **6** gradually changed from 2600 to 1200 MPa over that temperature range indicating a very rigid thermoset within the composite and

no transitions to a rubbery state. This is confirmed by observing the  $\tan \delta$  data which shows a relatively featureless plot (Figure 3). This superb retention of mechanical properties over a wide range is a distinctive feature of PN polymers/composites when fully cured.

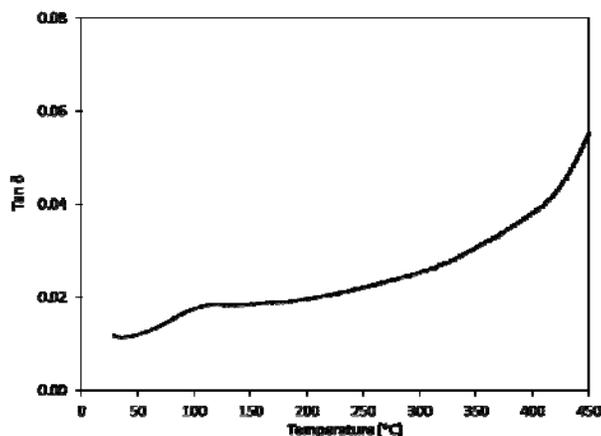


Figure 3:  $\tan \delta$  plot of polymer **6** with 3 wt % of *m*-BAPS.

The rate of heat release is one of the most important parameters in fire growth. The flammability properties of composite **6** was tested in accordance with ASTM E1354. This test measures ignitability, heat release and mass loss rates, and the generation of combustion products of a material exposed to a specified irradiance level. In these tests, samples were exposed to incident heat fluxes of 75 and 100 kW·m<sup>-2</sup>. The 4" x 4" sample is mounted above the heat source and the heat flux is applied. The time to ignition, average heat release for 300 seconds, and peak heat release, are all calculated for each sample. The MIL-STD-2031 requires: TIG greater than 90 and 60 sec at 75 and 100 kW·m<sup>-2</sup>, respectively; greater than 100 and 120 kW·m<sup>-2</sup> average HRR at 300 seconds at 75 and 100 kW·m<sup>-2</sup>, respectively; and greater than 100 and 150 kW·m<sup>-2</sup> peak HRR at 75 and 100 kW·m<sup>-2</sup>, respectively.

These testing results showed that composite **6** was close to passing all the requirements for MIL-STD 2031. The TIG at 75 and 100 kW·m<sup>-2</sup> was 136 and 58 seconds, respectively and the peak HRR at 75 and 100 kW·m<sup>-2</sup> was 106 and 114, respectively. This sample missed the TIG at 100 kW·m<sup>-2</sup> by just 2 seconds and the peak HRR at 75 kW·m<sup>-2</sup> by 6 kW·m<sup>-2</sup>. The performance can be improved further by better sample consolidation during curing and testing multiple samples from multiple panels to improve the error in these results. We are currently in to process of getting several professionally fabricated panels for a more thorough investigation of the fire performance.

## 4 CONCLUSION

The resorcinol-based PEEK<sup>TM</sup>-like PN resin **1** was used to prepare several 7781 E-glass composite panels. From

the experimental studies, we showed that the base resin system has outstanding processability in the preparation of composites. When postcured to elevated temperatures, the composite exhibited excellent dynamic mechanical, thermal, and flammability properties over a large temperature range. The flammability of the composite samples was tested in accordance with ASTM E1354, which measures the ignitability, heat release rate, mass loss rate, and combustion product generation rate of a material exposed to a specified irradiance level. From this data, we showed that composite **6** was close to passing all the requirements for MIL-STD-2031 and has been identified as a promising candidate for the most extreme marine environments. The PN thermosetting composite **6** exhibited low flammability parameters when compared to other thermosetting polymers and offers promise of superior fire performance for potential ship and submarine applications. The ease of processing and excellent properties of the oligomeric PN make it an excellent choice for many advanced composite applications.

## 5 ACKNOWLEDGEMENTS

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