

Improvement in Processing Parameters of 2nd Generation PEEK-like Composites for Advanced Application

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ABSTRACT

A new oligomeric **2nd generation resorcinol, PEEKTM-like** phthalonitrile resin (Res-PEEKTM-PN) has been developed via cost-effective methods and has been transitioned to an industrial scale. This phthalonitrile monomer used to prepare composite components exhibits better processing viscosities relative to the 1st generation resorcinol-based phthalonitrile and is comparable to current resin technologies. When post cured, the composite exhibited excellent mechanical, dynamic mechanical, thermal, and flammability properties over a large temperature range largely due to a lack of a glass transition temperature (T_g). After exposure to elevated temperature oxidative aging, the composites retained a high char yield and high mechanical strength. The new Res-PEEKTM-PN resin has been optimized for facile insertion into industrial-scale production as it is easily scalable and does not require purification. The backbone structure can be tailored for incorporation of various adjuncts geared towards desired mechanical and chemical properties of the final composite.

1 BACKGROUND

The NRL developed phthalonitrile (PN)-based polymers/composites exhibit superior flammability, low water absorption, and high temperature properties¹⁻⁷ 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 1st generation PN resins, which consisted of small crystalline molecules synthesized from the salts of bisphenols (e.g. resorcinol, 4,4'-biphenol, bisphenol A, bisphenol AF, etc.) and 4-nitrophthalonitrile. The early PN resins limited applicability as temperatures above their respective high melting points (200-230 °C) were needed for processing and curing. The difficulty of processing the resin undermined the excellent properties that the polymers/composites exhibited. More recently, a new approach was developed in response to the need for a more

processable resin system. A series of low molecular weight oligomeric PNs (2nd 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 PEEKTM-like PNs^{3,4,5} are easily synthesized from environmentally safe compounds/reactants and rely on simple chemistry to construct. Being oligomeric in composition, the resins exhibit a glassy structure and have softening temperatures around 70 °C, which enhances the ability to process and cure the resins at a low temperature and opens up many more applications than could be realized for the 1st generation resins. Polymerization of the PN monomers occurs through the cyano groups with the aid of a curing agent like aromatic diamines. Once fully cured, the rigid, highly crosslinked polymeric network exhibits high thermal and oxidative stability and is environmentally inert. Due to the ridged nature of the thermoset and subsequent inherent brittle nature of the neat polymers, fiber reinforcement is needed to produce viable components useful in a variety of applications. Two of the most integral factors in carbon or glass fiber reinforcement involve sufficient time and moderate temperatures needed to produce void free composites. After preparation, post curing of the reinforced composite occurs between 350 and 425 °C and is specifically tailored to individual applications. Full cure of the composite is determined through monitoring of the glass transition temperature (T_g) and is considered fully cured when the thermoset no longer exhibits a T_g . PNs are currently the only known thermosetting resin that does not lose complete structural stability up to its decomposition point making it amenable to many emerging applications. The paper will examine the design, preparation and processing parameters for carbon fiber reinforced composite panels made from the 2nd generation Res-PEEKTM-PN resin.

2 EXPERIMENTAL

2.1 General information

Reagent grade starting materials were used without further purification. The 2nd generation Res-PEEKTM-PN resin was

purchased from Chromak Research Inc and dried under vacuum before use. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min⁻¹ and a nitrogen purge of 50 cm³ min⁻¹. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min⁻¹ under a nitrogen or air purge of 50 cm³ min⁻¹. 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⁻¹ 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 10⁻² %. Normal force control was utilized throughout the tests to keep the samples taut.

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

The Res-PEEKTM-PN was heated to 50 °C, under reduced pressure, to remove residual DMSO and water from the resin. To the powder of the monomer, was added 2.7 weight % of bis(4-[3-aminophenoxy]phenyl)sulfone (*m*-BAPS). The curing additive was evenly dispersed via dry mixing making sure to break up any compacted material then b-staged at 175 °C for 50 min. Once cooled to room temperature and hardened, resin was dissolved in acetone (43 % wt) and fully dissolved before evenly applied to the carbon fiber.

2.3 Fabrication of Carbon Fiber Reinforced Composites for Testing

Unsize woven carbon fibers (T650 obtained from BGF Corporation) were dipped in the concentrated acetone solution of the Res-PEEKTM-PN monomer/*m*-BAPS mixture to achieve approximately 35% total resin content on the fibers. The fibers were dried at room temperature, cut into 9.5"x9.5" squares, and further dried at 80 °C, overnight. A 12"x12" aluminum plate was fitted with a 9.5"x9.5" well and subsequently treated with mold release. A thin layer of Kapton followed by perforated peel ply were placed inside the mold. Next, 36 layers of the dried PN painted fibers were placed in the well and covered with another layer of peel ply. The plies were stacked in an alternating array in which the fiber orientation was 0/90. A metal cull plate was placed on top and once everything was aligned, the entire area was vacuum bagged, evacuated and heated to 150 °C for 2 hours to remove residual water, solvent, and air from the stack. Concurrently, low pressure, on the order of 10 PSI, was

placed on the stack using a hydraulic press. Vacuum was subsequently removed, pressure increased to 50 PSI, and temperature was increased to 175 °C for 1 hour followed later by an increase to 230 °C for another hour. Hydraulic press was simply turned off so that pressure and temperature would slowly relax back to room temperature. Once removed from the mold, the composite was inspected for any imperfections, which, if found, the panel was discarded and not used for testing. Approved panels were cut to size and post cured for an additional 8h at 375 °C to ensure full conversion to the thermoset. 12"x12" panels consisting of 9 plies were prepared in a similar manner.

2.4 Machining Composites Test Samples for Mechanical Measurements

A high-speed diamond saw was used to cut specimens from the 9 ply PN composite panels with dimensions specified for various mechanical property tests. Rectangular specimens (55 mm x 15 mm) were machined for rheology measurements. The specimens were visually examined prior to testing to ensure the sample was free from flaws, cracks, or delaminations that may have been introduced during specimen preparation.

2.5 Parr Bomb Acid Digestion

Parr bomb acid digestion was used to determine the fiber volume fraction of the composite. Samples were of 30 mm x 10 mm x 2 mm and dissolved in nitric acid at 120 °C for 48 hours. Dissolved resin was removed from the carbon fiber via vacuum filtration. Samples placed in an oven at 100 °C for 4 hours before they were massed.

2.6 C-Scan Mapping of Carbon Fiber Composites

The carbon fiber reinforced resin composites were evaluated using C-Scan technology at Cincinnati Testing Laboratories using standard techniques to determine porosity of the composite and any delaminations. Data detailing variations in composite density allows for optimization of processing parameters.

Discussion

The 2nd generation Res-PEEKTM-PN resin was structurally reinforced with carbon fiber and pressed into highly compacted, 9 and 36-ply composites. The simpler processing parameters facilitated a higher degree of control over panel fabrication. The melting transition of the resin was approximately 70 °C and remained in a melted state until the curing reaction with *m*-BAPS that began around 175 °C. (Figure 1) Further curing of the resin occurred above 200 °C with another exothermic transition above 300 °C as a result

of the extended cure reaction. This processing window is unusually large for high temperature resin systems.

Assembly of the carbon fiber reinforced composites began with impregnation of the Res-PEEK™-PN monomer/*m*-BAPS into the woven carbon fiber mesh which were then dried under ambient conditions. Individual plies were cut to size, stacked in 0/90 orientation, and pressed at 50 PSI under vacuum. Once completed and debulked, the panels were visually inspected for delaminations and voids before sending for C-scanning. Overall the ease of resin processing allowed for this simple construction of composite panels.

Sample to sample variability is a common problem in construction of fiber reinforced composite panels. The parameters of temperature, time, and pressure must be explicitly controlled or compaction will be suboptimal. A trade-off exists when dealing with resin viscosity as too low of a viscosity can lead to resin flash before compaction and curing, whereas too high of a viscosity greatly limits the ability of the resin to adequately flow throughout the composite and allow air to be removed. This is why proper b-staging of the resin is so vital in this system. Even so, there is generally some variability between samples and within individual composites that may affect mechanical testing. A 36-ply fiber reinforced carbon composite was ultrasonically mapped with C-scanning and revealed that the panels were highly compacted with minimal areas of void-space. Figure 4 depicts a two-dimensional representation of the composite density. Red areas are indicative of lower density, i.e. more void space, whereas blue and green represent areas of greater compaction. Areas of lower density can sometimes be attributed to delamination or air pockets that were not appropriately removed during composite formation. Poorly compacted regions in this composite are attributed to an insufficient amount of time under vacuum at elevated temperature. This likely left minor voids behind in places where the viscosity of the resin was slightly too high for adequate flow. Further optimization of the processing parameters will minimize these voids and delaminations to allow the preparation of quality panels.

With a fiber volume fraction between 60-65% as determined by Parr bomb acid digestion. The thermal stability of the composite was tested with TGA and run in both nitrogen and air. The sample retained upwards of 90 % of its mass when run in a nitrogen atmosphere whereas a steady, gradual dip in mass as a function of temperature occurs when tested in air. The residual mass after 1000 °C is primarily comprised of carbon and the char yield of 90 % (under nitrogen) is superior to those reported in phenolic resin systems. Composites produced with this exceptionally

high char yield exhibit excellent high temperature properties such as thermo-oxidative stability and low flammability.

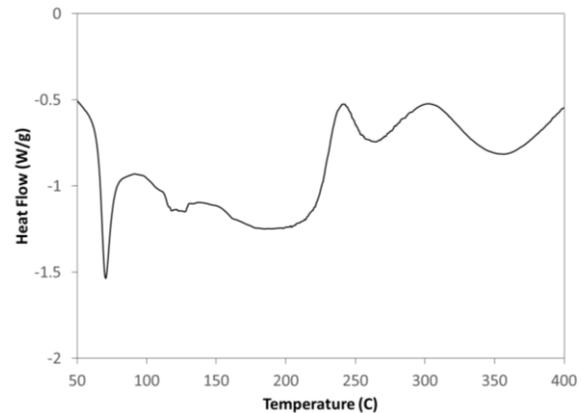


Figure 1: DSC of Res-PEEK™-PN monomer with 3 wt % *m*-BAPS.

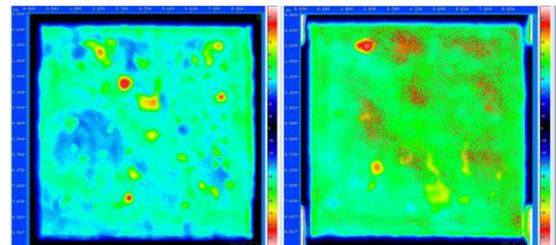


Figure 2: C-Scan of a 36-ply, carbon fiber reinforced Res-PEEK™-PN system, front and back, respectively.

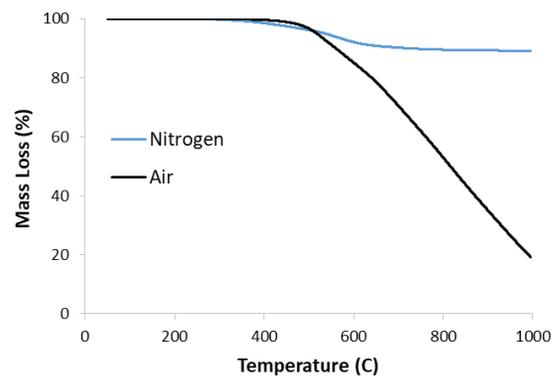


Figure 3: TGA of Res-PEEK™-PN composite under nitrogen (blue) and air (black).

The amount of fiber in the composite generally corresponds to the expected mechanical properties of the material. Theoretically, there is an ideal fiber volume fraction for each resin system that will most efficiently, and uniformly, transfer load between fibers. To examine the mechanical performance, rectangular shaped samples of the 9 ply composite were post cured at a maximum temperature of 375 °C and analyzed mechanically using a rheometer from 25 to 450 °C (Figure 4). The storage modulus value

gradually changed from 2600 to 1000 MPa over the aforementioned temperature range, indicating a very rigid thermoset within the composite and no transitions to a rubbery state typically seen as a plateau in the storage modulus vs. temperature plot. This was confirmed by observing the $\tan \delta$, a way to measure the dampening of the material. As demonstrated in Figure 5, monitoring the $\tan \delta$ over the temperature range revealed a rather featureless plot with $\tan \delta$ values ranging between 0.01 and 0.06 from 30 to 450 °C, respectively. This superb retention of mechanical properties over a wide range is the distinctive feature of fully cured PN composites.

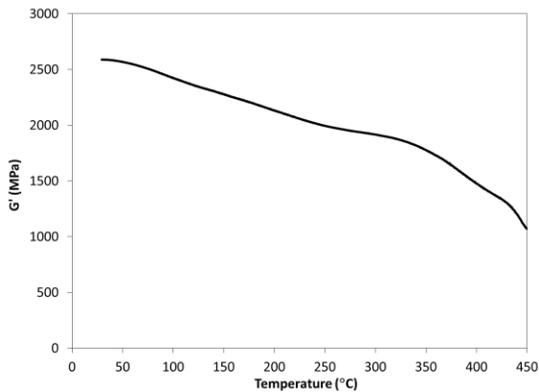


Figure 4: Rheometric analysis of composite formed from the Res-PEEK-PN monomer with 2.7 wt % of *m*-BAPS.

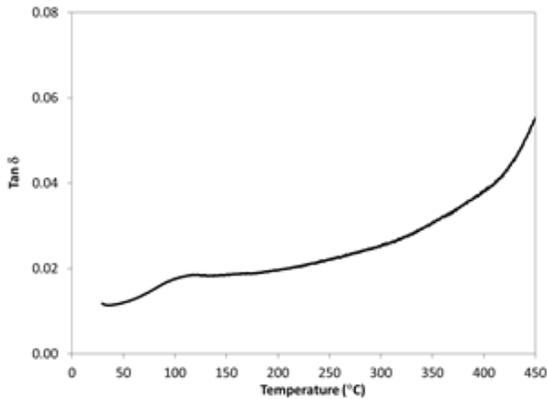


Figure 4: $\tan \delta$ plot of Res-PEEK-PN monomer with 2.7 wt % of *m*-BAPS.

5 CONCLUSIONS

The Res-PEEK™-like PN resin was used to prepare several composites from woven carbon fiber fabric. We have shown through experimental studies that the base resin system has improved processability from the previous generation and can be used to prepare composites with exceptional mechanical, dynamic mechanical, oxidative, and thermal properties. Time and temperature are vitally important processing parameters in the construction of the composites as the viscosity of the material seems to impact panel formation and can leave residual void space. Consolidation of the composite can be improved with increased time under vacuum and a much greater increase in applied pressure during panel formation. As such, the simplicity of processing and exceptional properties of this Res-PEEK™- PN make it an excellent choice for many advanced composite applications.

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