High-Char Phthalonitrile Resin Blends

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ABSTRACT

Oligomeric phthalonitrile resins exhibit excellent char retention when heated to 1000 °C under nitrogen (> 75%). However, very little is known about the properties and performance of these materials when heated to higher temperatures (> 1500 °C). In addition, blended systems that contain phthalonitrile resins and secondary phases specifically included to enhance char formation at temperatures in excess of 1000 °C have not been previously synthesized. In order to better understand the char forming properties of phthalonitrile resins and identify conditions that maximize char yield, thermogravimetric analysis scans to temperatures exceeding 2000 °C were conducted on a series of different phthalonitrile resins and blended systems. The resulting char from these studies was then characterized *via* powder X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. Ddifferential scanning calorimetry and rheological characterizations were used to determine the proper thermal treatments for curing blended systems and to probe the interactions between different phases of the blend.

1. INTRODUCTION

Because of its use in the aerospace, automobile, alternative energy industries, and many others, the demand for highly graphitic composites is constantlygrowing.[1-2] Given this large scale, new processes which seek to economically produce synthetic graphite is becoming increasingly important.[3] The most common strategy for manufacturing synthetic graphite is to induce graphitization of amorphous carbon, or non-graphitizable carbon (NGC). For example, methods which utilize different metal catalysts (e.g. Fe, Ni, Co, etc.) to precipitate graphitic carbon (~1200 °C) at low temperature have been developed. Because these processes require direct contact between catalyst particles and carbon atoms, only regions near the catalyst form graphitic domains, which limits the practicality of this method.[4]

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Graphitizable carbon (GC) phases such as mesophase pitch exhibit a high degree of graphitization when heated above 2800 °C. As opposed to NGCs, this class of carbon forms highly structured microdomains as they are heated, eventually forming graphitic carbon at sufficiently high temperatures. Graphitic phases, once blended with NGC materials, can be formed given the right conditions. For instance, electrospun nanofiber mats derived from polyimide-mesophase pitch blends form of graphite fibers when heated above 1600 °C.[5] Alternatively, highly graphitized carbon has been formed *via* the mixing of NaOH-treated spherical phenolic resins and various graphitizable cokes.[4]

While these examples demonstrate the ability to form graphitic carbon from NGC, the scope of NGC phases that can be utilized for these processes remains relatively unexplored. Since the char forming properties of NGCs are highly dependent on their chemical structure, it is likely that careful selection of NGC materials could optimize production of synthetic graphite. Along those lines, oligomeric phthalonitrile resins (PN) are highly aromatic and exhibit high char yields as compared to the phenolic resins that are often used as carbon precursor materials.[6] By using higher mass retention carbon precursors, which can undergo successful graphitization through the incorporation of GC phases, the overall yield of graphitic carbon could be greatly improved. This study seeks to evaluate the potential for producing graphitic carbon using a bisphenol A-based PN resins (BisA) blended with mesophase pitch. This resin was selected for study because of its high char yield (> 75%). Before charring at 1000 °C, the thermal properties of the blends were studied. After heating, the resulting carbon materials were characterized using a combination of powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy and scanning electron microscopy (SEM). The thermal properties of the each char was also investigated using thermogravimetric analysis in an oxidizing environment.

2. EXPERIMENTATION

2.1 Materials and Methods

All starting materials were reagent grade and used without further purification. The BisA resins used to fabricate blended samples were synthesized from a previously described method.[7] Mesophase pitch was obtained from Zoltek. Char yield experiments of the polymer or carbonized blends were conducted using thermogravimetric analysis (TGA) on a TA Instruments TGA Q50. Samples were heated to 1000 °C at a constant rate (either 5 or 10 °C min^{-1}) under a nitrogen purge (100 cm^3 min^{-1}). All DSC and TGA thermograms were analyzed using Thermal Analysis software from TA instruments. Raman spectroscopic analysis was completed using a Renishaw inVia spectrometer. The measurement used a 514 nm excitation wavelength in the 900 – 3200 cm^{-1} range and accumulated 12 collections with 10 s exposure time per each collection. WIRE software fit and reduced the resulting data. X-ray diffraction (XRD) was performed with a Rigaku diffractometer in the 20° – 80° 2θ region. PDXL software fit and reduced the resulting data. X-ray photoelectron spectroscopy (XPS) was collected using a K-Alpha (Thermo Scientific) XPS instrument. Scanning electron microscopy (SEM) images were collected using a JEOL SEM. Material samples were mounted on copper tape without sputtering and analyzed using 15 kV accelerating voltage. Skeleton density was measured with a pycnometer (Quantachrome Instruments) and used helium gas to measure the cell volume. Volumetric density was derived by

measuring the apparent weight of samples in air (M_{dry}) and while submerged in water (Ns_{ubm}) and relied on the following calculation (based on Archimedes' principle):

$$Density = 0.0012 + \frac{M_{dry}}{0.9983} \cdot \frac{D_{water} - 0.0012}{M_{dry} - M_{submerged}}$$

Porosity was calculated using the following equation:

$$Porosity = 1 - \frac{Volumetric\ density}{Skeleton\ density}$$

2.2 Preparation Blended Samples

Prior to preparation of blended samples, a BisA pre-polymer was prepared by combining the neat BisA resin with 2.7 wt. % of bis[4-(3-aminophenoxy)phenyl]sulfone (m-BAPS) and heating at 200 °C for 60 min. The staged BisA resin was then blended with mesophase pitch in the proper ratios by grinding using a mortar and pestle for 5 min. Blends were prepared in the following BisA/Pitch ratios: 1:1, 3:1, and 5:1. The ground powder was then placed in a vacuum oven heated to 200 °C and evacuated for 30 min to degas each sample. The blends were then placed in an oven heated to 225 °C in are for an additional 2 hours in order to gel each sample. For comparison, a pure BisA sample was prepared using the same method. Each sample containing BisA was postcured by slowly heating to 350 °C under flowing nitrogen in a tube furnace. The temperature was then held at 350 °C for 2 hours before cooling to room temperature.

2.3 Charring of BisA/Pitch Blends

All samples were charred by heating at 0.8 °C min^{-1} in a tube furnace under flowing nitrogen up to 1000 °C. The temperature was held at 1000 °C for 1 hour before slowly cooling to room temperature over the course of 8 hours. All samples remained intact after charring however, the pure pitch sample exhibited significant foaming after being heated to 1000 °C.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties of BisA/Pitch Blends Heated to 350 °C

Prior to carbonization, the BisA/pitch blends were heated to 700 °C in a nitrogen atmosphere to determine if the concentration of pitch in each sample affected the char yield. According to the TGA results (Figure 1), the char yield ranged between 75% and 78% regardless of the pitch concentration. While the sample containing only BisA begins to lose mass at a lower temperature (425 °C) than the other samples (435-450 °C), the differences are marginal. Given that these TGA scans are similar, this data suggests that that the addition of pitch has very little effect on the mass retention of samples when heated to 700 °C under an inert atmosphere, however, heating to higher temperatures may affect the mass retention of BisA/pitch blends.

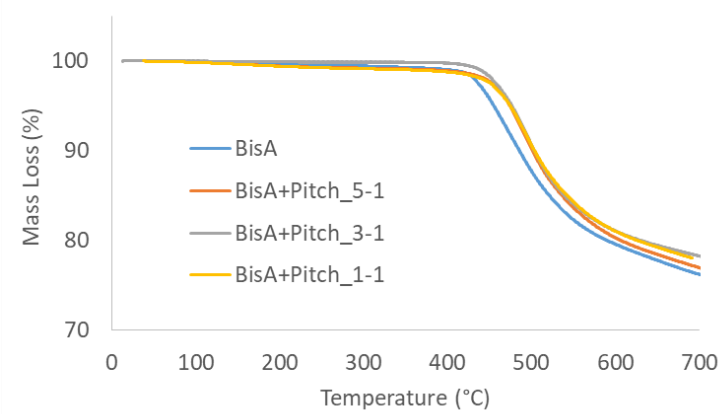

Figure 1. TGA thermograms of BisA/pitch blends heated to 700 °C under nitrogen. (heating rate = 10°C min^{-1}).

3.2 Thermal Characterization of BisA/Pitch Blends Heated to 1000 °C

In order to probe the effect of pitch has on the NGC produced from BisA char, the samples were heated to 1000 °C in a tube furnace. While heating to this temperature will not result in full graphitization, characterization of samples heated to 1000 °C will provide valuable insight into the beginning stages of the graphitization process for BisA/pitch blends. Inspection of the samples by eye after heating showed that porosity developed. In particular, the pure pitch sample formed a carbon foam and therefore could not be characterized using certain techniques. Because heating pitch to 350 °C results in formation of a foam, it is possible that volatile compounds are contained within the pitch which are liberated when heated.

Table 1. Comparison of Volumetric and Skeletal Densities of BisA/Pitch Blends Heated to 350 °C and 1000 °C.

	350 °C			1000 °C		
Material	Volumetric Density	Skeleton Density	Porosity	Volumetric Density	Skeleton Density	Porosity
1:1 BisA:Pitch	0.89 g/cm^3	1.06 g/cm^3	15.4%	1.13 g/cm^3	1.41 g/cm^3	19.9%
3:1 BisA:Pitch	1.02 g/cm^3	1.14 g/cm^3	10.4%	1.29 g/cm^3	1.43 g/cm^3	9.6%
5:1 BisA:Pitch	1.14 g/cm^3	1.16 g/cm^3	2.1%	1.37 g/cm^3	1.49 g/cm^3	8.0%
BisA	1.21 g/cm^3	1.21 g/cm^3	< 1.0%	1.55 g/cm^3	1.56 g/cm^3	1.2%

The density of each sample (with the exception of pure pitch) was determined using pychnometry and Archimedes' method before and after carbonization (Table 1). Examination of the data for the polymer samples heated to 350 °C shows that both the skeleton and volumetric densities decrease with the addition of pitch. The decrease in skeleton density can likely be explained by the rule of mixing, however, the density of pitch heat treated to 350 °C could not be measured due to foaming

of the sample during heating. The addition of pitch also results in the formation of porosity. The pure BisA sample shows less than 1.0 % porosity, which indicates that there is very little off gassing when it as heated at 350 °C. Conversely, the 1:1 BisA/Pitch sample exhibits 15.4% porosity when heated to this temperature. Given this trend, it is likely that the evolution of volatiles produced by heating induces porosity.

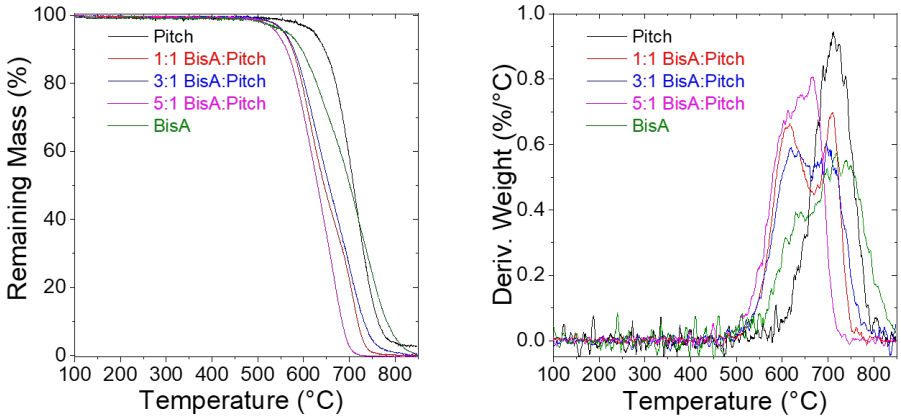

Figure 2. Thermogravimetric analysis scans of BisA/Pitch bledns (left) and their corresponding derivative (right).

Heating to 1000 °C increased the sample density relative to the 350 °C, which corresponded with the samples becoming more graphitized and transitioning closer to the 2.2 g/cm^3 density of graphite. Of note, higher treatment temperatures increased porosity for most compositions. Evolution of unstable oxygen-, hydrogen- and nitrogen- containing organic compounds likely increased the free volume in each material. Furthermore, higher mass fractions of pitch in the blend lowered the densities and increased the porosities of the resulting composites at both 350 °C and 1000 °C curing conditions.

Table 2. Relevant Oxidation Properties of BisA/Pitch Blends Heated to 1000 °C

Material	Oxidation Onset	Peak Oxidation	Oxidation Completion	Ash Content
Pitch	586 °C	711 °C	832 °C	2.81 wt.%
1:1 BisA:Pitch	529 °C	710 °C	812 °C	0.03 wt.%
3:1 BisA:Pitch	533 °C	696 °C	827 °C	0.26 wt.%
5:1 BisA:Pitch	514 °C	667 °C	819 °C	< 0.01 wt.%
BisA	510 °C	718 °C	847 °C	0.35 wt.%

In order to probe the oxidative stability of BisA/pitch blends, TGA scans were collected of each sample (Figure 2, Table 2). Increased pitch content in the composite blend increased the oxidation onset temperature and improved the stability of the material. On the other hand, higher wt.% of BisA extended the temperature range (from onset to completion) during which the composites burned in air. This behavior, in turn, suggests a slower oxidation kinetic process for the cured resin. The derivative TGA plot (Figure 2) shows that the 3:1 and 1:1 BisA/Pitch blends exhibited bimodal oxidation peaks, which suggested that some phase separation was present in those composites.

3.3 Structural and Morphology of BisA/Pitch Blends Heated to 1000 °C

Initial structural characterization was done *via* powder XRD (Figure 3, Table 3). For these measurements, each sample was ground into a fine powder before exposing them to X-rays. The BisA pattern shows two broad peaks centered near 26° and 43° which correspond to [002] and [101]/[100] planes, respectively. By comparison, the pitch pattern clearly contains the [002] peak, however, the peak near 43° is only weakly visible. While the blended samples show evidence of both peaks, the addition of pitch decreases the intensity of the [101]/[100] peak.

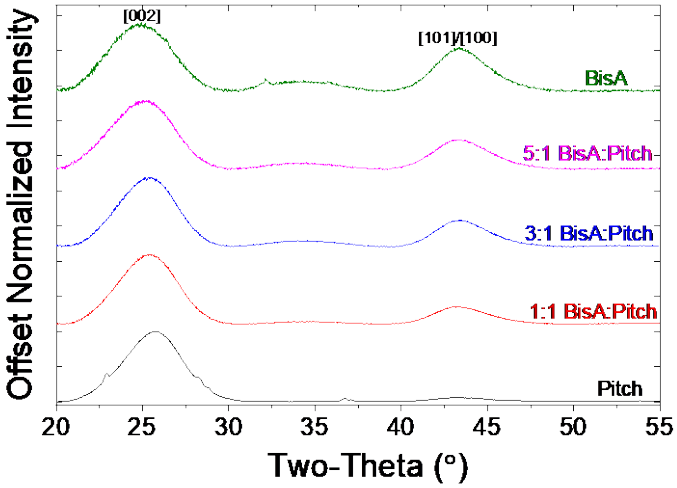

Figure 3. Powder X-ray diffraction (XRD) patterns for BisA/Pitch Samples

The grain sizes were also determined using the powder patterns for BisA/Pitch samples heated to 1000 °C. According to these results, the pitch sample contained the largest grains (1.90 nm), whereas the grains observed for BisA (0.81 nm) were the smallest. Although the background contribution precluded a determination of the grain size for the 3:1 and 5:1 BisA/pitch samples, the grain size for the 1:1 sample (1.63 nm) fell between those extremes.

Table 3. Grain Sizes of BisA/Pitch Samples Determined by Powder XRD

Material	Grain Size
Pitch	1.90 nm
1:1 BisA:Pitch	1.63 nm
3:1 BisA:Pitch	N/A
5:1 BisA:Pitch	N/A
BisA	0.81 nm

The degree of graphitization for the composites treated at 1000 °C was analyzed using Raman spectroscopy (Figure 4). According to these measurements, all materials, including the pure BisA and Pitch, exhibit a strongly graphitized structure after undergoing 1000 °C treatment. However, none of the spectra indicated any resonant 2D or D+G modes (in the 2700 cm^{-1} range).

Subsequently, graphitization of the composited was not complete at 1000 °C and no graphite or graphene-like structure evolved from the blends as a result.

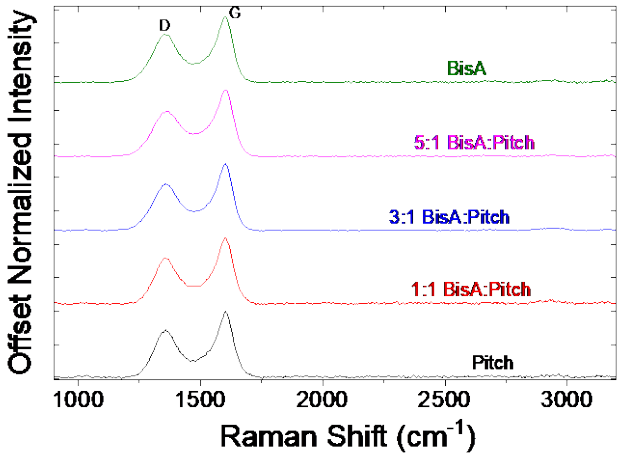

Figure 4. Raman Characterization of BisA/Pitch Samples

The key D and G band properties are summarized in Table 4. The I_D/I_G ratios for the blends of BisA and pitch are slightly lower than those of the respective standalone components, which suggests a possible synergistic influence of the blends on the overall graphitization of the resulting composites. However, neither a positive nor a negative correlation between the weight ratios of Pitch to BisA and the I_D/I_G ratio exists. The full widths at half maxima of the G band do not indicate any influence of pitch composition on the ordering of the graphitic domains in the resulting composites.

Table 4. Raman Data Summary of BisA/Pitch Blends.

Material	I_D/I_G	FWHM of G Band
Pitch	0.75	81.2 cm^{-1}
1:1 BisA:Pitch	0.71	80.7 cm^{-1}
3:1 BisA:Pitch	0.72	77.3 cm^{-1}
5:1 BisA:Pitch	0.71	83.4 cm^{-1}
BisA	0.76	78.1 cm^{-1}

The XPS-derived elemental composition of BisA, Pitch, and several blends after 350 °C and 1000 °C curing cycles is shown in Table 5. As expected, BisA contained a significant amount of oxygen and nitrogen (in the form of functional groups) following the 350 °C cure and, subsequently, lost approximately 40% of those groups during heating up to 1000 °C. Although inclusions of pitch (which has a relatively higher initial carbon content) into the resin blend reduced the overall oxygen and nitrogen compositions, the elemental ratio of carbon to non-carbon did not directly correlate with the mass fraction of pitch in the 350 °C or the 1000 °C blends. While the 1000 °C blends that included BisA had demonstratively higher oxygen than those with higher pitch amounts, the nitrogen content of blends, including 100% BisA and 100% Pitch baselines, was

nearly identical for all compositions. Therefore, both the resin and pitch systems contained strong carbon-nitrogen bonds that withstood 1000 °C thermal treatments. Table 5. Elemental Analysis of Select BisA/Pitch Samples Determined by XPS.

	350 °C						1000 °C					
Material	Carbon		Oxygen		Nitrogen		Carbon		Oxygen		Nitrogen	
	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%
Pitch							94.9	92.9	3.2	4.2	1.3	1.5
1:1 BisA:Pitch	82.5	75.2	12.3	14.9	0.9	1.0	89.2	85.3	7.7	9.8	1.7	1.9
3:1 BisA:Pitch	89.0	85.5	6.0	7.7	3.9	4.3	93.6	90.9	4.7	6.1	1.1	1.3
BisA	81.2	73.8	13.7	16.6	1.9	2.1	88.7	84.3	8.6	10.9	1.7	1.9

The C1s bonding peak for blends cured at 1000 °C is shown in Figure 5. The bonding peak is centered at 284.4 eV for all analyzed blends and suggests a similar carbon-carbon bonding profile for blends treated at that temperature. However, the 100% BisA C1s peak also exhibits a broad shoulder at ~285 eV; this feature is absent in all other peaks, including both 100% pitch and various Pitch/resin blends. This suggests that pure BisA maintained a wide range of chemical functionalities following the 1000 °C cure process. The absence of this bonding behavior in the 3:1 and 1:1 BisA/Pitch blends suggests that the presence of pitch had altered the bonding behavior, and, possibly, growth of graphitic domains in the composite during the 1000 °C thermal treatment.

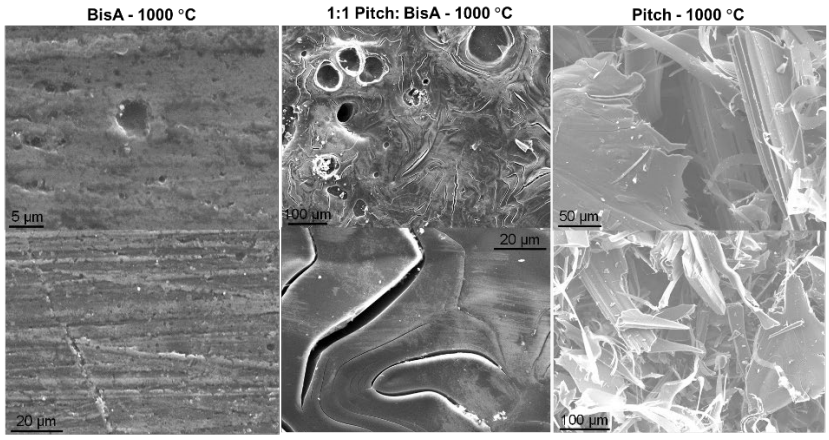

Figure 6. Scanning electron microscope (SEM) images of select BisA/Pitch blends.

The morphology of BisA, pitch, and 1:1 BisA/Pitch was characterized using SEM (Figure 6). The 1:1 BisA/Pitch sample was selected because potential phase separation would be more likely given the larger concentration of pitch compared to the other blends. Examination of the pure BisA sample shows that it is uniform and only a small degree of microporosity was observed. Conversely the pitch sample, which formed a foam when heated to 1000 °C, shows a large degree of microporosity which is consistent with the evolution of gas during heating. In addition, high aspect ratio features were observed, which were not evident in the BisA sample. The SEM images for the 1:1 BisA/pitch sample display characteristics present in both BisA and pitch samples. While the sample appears to be homogenous like BisA, there is significantly more porosity which is presumably due to volatilization of the pitch. Because there is no clear phase separation observed

in the SEM, it suggests that the pitch phase is well dispersed in the blended sample, but there is no co-curing between pitch and BisA.

4. CONCLUSIONS

Blended polymer samples were produced based on combinations of a bisphenol A-based phthalonitrile resin (BisA), a non-graphitizable resin, and graphitizable mesophase pitch. These samples were then heated to 1000 °C in order to convert them to carbon and initiate the graphitization process. Structural characterization of these samples using powder XRD indicated that BisA has smaller grain sizes as compared to pitch after charring. Raman spectroscopy showed that some graphitization had occurred in every sample after heating to 1000 °C. However, it does not indicate that the presence of pitch has any effect on the ordering of graphitic domains in these samples. In addition, XPS characterization showed the presence of strong carbon and nitrogen bonds in BisA even after heating to 1000 °C. Because these bonds were not observed in the blended samples, it suggests that pitch does have some effect on the curing of BisA resin. Although incorporated pitch only marginally enhanced BisA graphitization, initial findings suggest that, with the inclusion of pitch, samples must be heated to high temperatures in order to fully describe the properties of these systems.

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