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Cure studies and thermal stability of an acetylene-functionalized polyphenylene resin

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Summary

Samples of an acetylene-functionalized polyphenylene resin have been thermally cured to determine the effects on char yield and thermooxidative stability. The material's lack of a processing window led to difficulties in handling; it was found that quickly heating small samples above the melting point resulted in complete polymer melting prior to resolidification due to cure. Curing in air and in an inert atmosphere led to decreases and increases in char yields, respectively, at 900°C. Char yields in excess of 90 weight % were obtained at 900°C. The thermooxidative stability of the cured polymer was slightly better than that of the uncured resin, with the biggest improvement being in the 200-400°C range.

Introduction

The use of lightweight, high temperature stable polymeric materials and composites derived from them as replacements for metals, glasses, and ceramics is increasing. The development of new thermally stable polymers which have improved physical and mechanical properties is a desirable goal. We have focused on investigating various acetylene-terminated resins for these specific applications (1-3). Acetylene-terminated resins generally possess the advantages of low viscosity in the prepolymer melt stage, the ability to thermally cure without added catalyst, and a lack of volatile by-product evolution upon curing, leading to good fiber wetting when preparing composites and minimal shrinkage and void formation in the final component (4).

We have obtained samples of a promising new material, an acetylene-functionalized polyphenylene resin, shown in Figure 1. Preliminary reports indicate that samples of this material exhibit high char yields (>80%) on heating to 900°C in a thermogravimetric analyzer (TGA) under a nitrogen atmosphere (5,6). We propose that curing of the polymer prior to TGA analysis will lead to greater char yields and possibly greater thermooxidative stability at elevated temperatures.

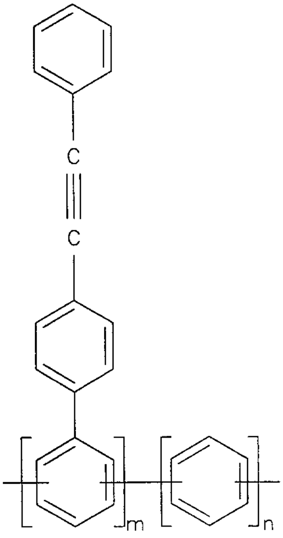

Figure 1: Structure of polyphenylene resin.

This study encompasses the determination of

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the optimum cure conditions, based on highest char yield, for this resin and the comparison of the thermooxidative stability of the cured material versus the original polymer.

Experimental

Samples of the acetylene-functionalized polyphenylene resin were provided by Dr. James M. Tour's laboratory. The accompanying molecular weight data for the polymers used in theis study is as follows: Sample A, Mw = 2960, Mw/Mn = 2.57; Sample B, Mw = 2740, Mw/Mn = 2.59. Differential scanning calorimetry (DSC) experiments were performed on a Dupont 910 Differential Scanning Calorimeter and TGA experiments were performed on a Dupont 951 Thermogravimetric Analyzer. Both were controlled by a Dupont Thermal Analyst 2100 System. All thermal analyses were performed at 10°C/min; DSC experiments were performed under a nitrogen atmosphere while TGA experiments were performed under either a nitrogen or air atmosphere. The melting point apparatus used for the fast heating studies was a National Scientific Melting Point Apparatus, design no. 889339.

Results and Discussion

The two samples of polyphenylene resin were examined initially by DSC to determine melting and reaction exotherm (acetylene cure) behavior. Both exhibited similar behavior; the DSC data for Sample A is shown in Figure 2. The polymer samples show a small melting peak, centered around 185°C, followed by the immediate onset of exothermic curing, which peaks in the 350-360°C range. This data indicates that the polymer does not possess a processing window; that is, the polymer cannot be held in a flowable liquid state for any period of time without curing taking place.

In order to form void free homogeneous samples for further study the polymer needed to be melted completely prior to resolidification due to curing. The method chosen to accomplish this task involved heating the samples very fast to a temperature above that of the melting point and below that of appreciable curing while visually observing the melting and

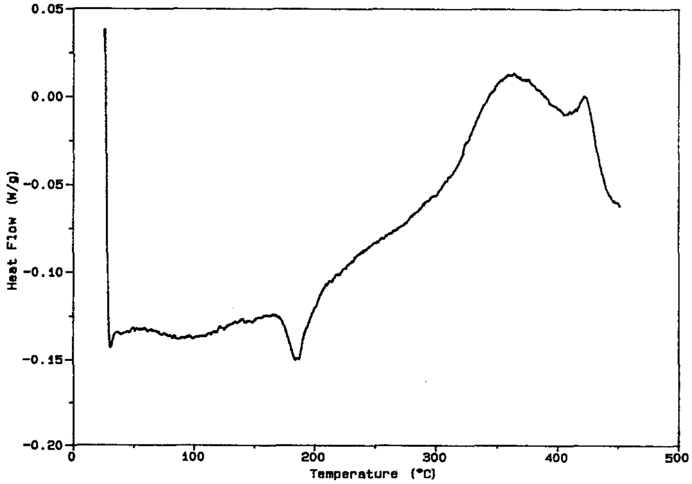

Figure 2: DSC of sample A showing small melting endotherm and large curing (acetylene reaction) exotherm

resolidification. A melting point apparatus equipped with capillary sample tubes allowed these experiments to be performed in air. The temperature on the melting point apparatus was set and equilibrated to within a few degrees, then the samples were introduced and observed while being held at that set temperature. At temperatures above 185°C and below 250°C the samples only partially melted before resolidification due to curing took place; however, at 250°C the samples did fully melt just prior to resolidification. From this data it was concluded that it was possible to totally melt the polymer if done quickly. For larger samples the temperature should be set at 260°C to ensure total sample melting.

TGA data (in nitrogen) was obtained for both of the polymer samples prior to performing cure studies, giving baseline measurements of char yields to compare the cured samples against. These results are given in Table 1. It can be seen that Sample A affords a slightly greater char yield than Sample B at 900°C. The TGA tracing for Sample A is included in Figure 3. Based on this data, cure studies were performed on Sample A.

Initial cure studies were performed in air, since other acetylene-terminated resins have been successfully cured up to 300°C in air (7-9). Aluminum planchettes which contained small amounts of resin were placed on a preheated 260°C hot plate for one hour to quickly melt and precure the polymer. Curing was accomplished by increasing the hot plate temperature to 300°C and allowing the samples to cure for 1-4 hours. Subsequent TGA analyses (in nitrogen) showed greater weight loss at 900°C for these samples than for the original material. In addition the samples lost 2.5-4 wt. % during the precure and cure steps, leading to an even larger cumulative weight loss. Thus, air curing of this polymer leads to a decrease in char yield and thermal stability of the cured resin.

A second series of cure studies was performed in the TGA chamber under a nitrogen atmosphere. All samples, which ranged in size from 14-15 milligrams, were precured by heating quickly to 260°C and holding for 30 min. The samples were then heated at 10°C/min from 250°C to the desired cure temperature and held for the desired time. Subsequent TGA analyses

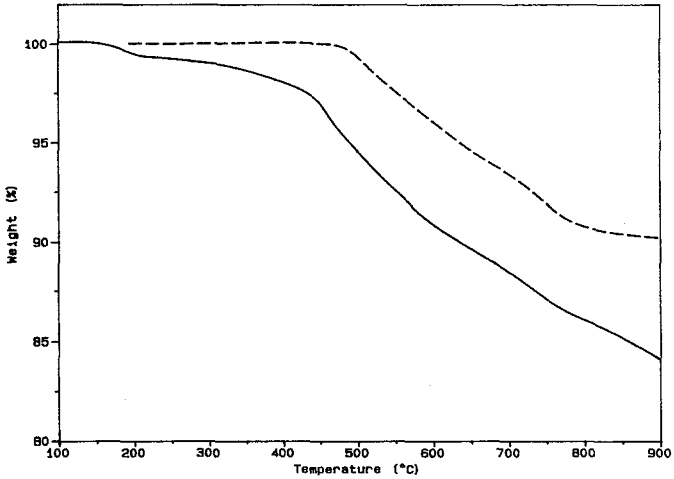

Figure 3: TGA data for sample A (in nitrogen); solid line - uncured resin; dashed line - resin cured 400°C/6 hr (in nitrogen)

Table 1: Cure conditions, weight losses, and char yields at 900°C for samples A and B

			at 900°C			
sample (cure cond.)	wt. % lost during precure	wt. % lost during cure	wt. % lost during TGA	char yield after TGA	cum. wt. % lost	cum. char yield
A (none)	-	-	15.9	84.1	15.9	84.1
B (none)	-	-	16.9	83.1	16.9	83.1
A (300°C/2 hr)	1.0	0.5	13.4	86.6	14.9	85.1
A (350°C/2 hr)	1.1	1.2	12.6	87.4	14.9	85.1
A (400°C/2 hr)	1.0	3.0	9.6	90.4	13.6	86.4
A (400°C/6 hr)	1.1	3.8	9.2	90.8	14.1	85.9
A (400°C/10 hr)	1.0	4.2	9.6	90.4	14.8	85.2
B (400°C/2 hr)	0.8	3.1	11.4	88.6	15.3	84.7

(under nitrogen) provided char yields at 900°C for these cured resins. The results, including weight losses during each step of the cure studies, are given in Table 1.

The weight % lost during precure for all samples was fairly constant, being around 1%. The weight % lost during cure increased as both the cure temperature and time were increased. The weight % lost during TGA analysis to 900°C decreased as cure temperature was increased but remained fairly constant when the 400°C cure time was increased. Sample A cured at 400°C for 6 hours exhibited a char yield of 90.8 weight % at 900°C as determined from TGA analysis. This is a significant improvement of 6.3 weight % over that of the uncured resin. The TGA for this cured sample is shown in Figure 3, along with that of the uncured resin for comparison. If the total weight loss (sum of weight losses during precure, cure, and TGA analysis to 900°C) is taken into account than the best cumulative char yield (86.4 weight %) at 900°C was obtained with Sample A cured at 400°C for 2 hr. This is an improvement of 2.3 weight % over that of the uncured resin. Comparing Samples A and B cured under the same conditions, it can be seen that, as in the case of the TGA analysis of the uncured resins, Sample B affords a lower char yield than Sample A.

Thermooxidative stability tests were performed on Sample A, comparing the uncured resin to a sample cured at 400°C for 6 hr. The TGA results are shown in Figure 4. The uncured resin begins to slowly lose weight in air around 200°C, with 10% weight loss occurring at 523°C. The cured resin commences to lose weight in air at approximately 400°C, with 10% weight loss occurring at 548°C. Thus, at lower temperatures (<400°C), the cured material performs better than the original resin but the onset of catastrophic weight loss for the two resins is similar, in the 520-545°C range.

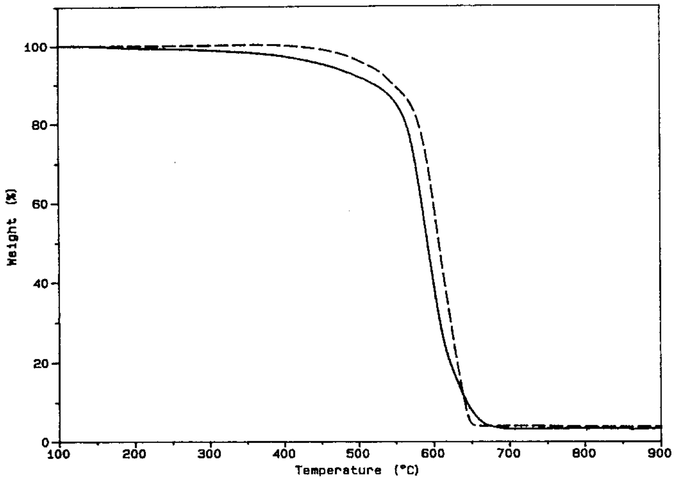

Figure 4: TGA data for sample A (in air); solid line - uncured resin; dashed line - resin cured 400°C/6 hr (in nitrogen)

Conclusions

The samples of acetylene-functionalized polyphenylene resin used for this study posed difficulties in processing due to their lack of a processing window. It was found that quickly heating small samples to 250-260°C did result in complete polymer melting prior to resolidification due to cure. Curing of this polymer in air led to decreases in char yields at 900°C, whereas curing in an inert atmosphere led to increases. The best TGA char yield, 90.8 weight %, was obtained after curing the resin at 400°C for 6 hours while the best cumulative char yield, 86.4 weight %, was obtained after a 2 hour 400°C cure. The thermooxidative stability of the cured polymer was only slightly better than that of the uncured resin, with the biggest improvement being in the 200-400°C range.

Acknowledgments

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