Synthesis, Characterization, and Cure of Propargyl-Functionalized Cyclopentadiene for Use in Carbon−Carbon Composites

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A new composite resin was synthesized by reaction of cyclopentadiene with propargyl bromide and base under phase transfer conditions to give a mixture of products with two to six propargyl functionalities per cyclopentadiene ring. DSC analysis of the propargylated cyclopentadiene resin (PCP) showed thermal cure with no added initiator over a broad temperature range with a peak at 250 °C. FT-IR analysis of the cured resin showed the generation of new unsaturated and saturated species through a hydrogen transfer ene-like reaction and polyaddition of the propargyl groups to give oligomers and/or cyclotrimers. X-ray analysis showed no long-range graphitic order. Neat PCP resin cured at 250 °C gave a room-temperature flexural modulus of 2.9−3.0 GPa by DMA and showed no thermal transitions up to 300 °C while PCP/carbon fiber composites gave a room-temperature flexural modulus of 115−120 GPa and a flexural strength of approximately 950 MPa. TGA showed exceptional carbon yield at 1000 °C with 75% weight retention in both air and N_2, while composites with 40 wt % resin showed 90% carbon yield. Interlaminar shear strengths of carbonized samples were comparable to those of presently used materials.

Introduction

Interest in carbon/carbon composites has grown exponentially in recent years. These unique materials offer a combination of high specific strength retention at elevated temperatures (500−2500 °C) and chemical inertness. In addition, they provide excellent thermal energy transfer, which has led to their use in applications such as aircraft brakes, space vehicle heat shields, and rocket nozzles.[1] Although the properties of carbon/carbon composites make them very useful, there are inherent problems with typical matrix precursors (such as pitch and various thermoset resins) used to fabricate them. One of the most severe limitations is low char yields during pyrolysis. Typical thermoset precursors yield only 50−65 wt % carbon after pyrolysis at 800 °C; i.e., roughly half of the matrix is lost.[2] This results in the need for repeated impregnation cycles with resin to achieve a high-density sample. Such repetitive treatment greatly increases the time and expense of fabrication. Another problem with typical thermoset and some pitch-based carbon precursors arises from their high viscosities and intractable nature. This often results in poor wetting of the reinforcing fiber and/or the need for high pressures and temperatures during impregnation cycles. The ideal precursor for carbon/carbon composites would be a low viscosity resin that can be thermally cured to a suitable viscosity for a given application that then cures and chars with overall yields greater than presently used materials.

The polymerization of cyclopentadiene-based monomers has long been used to generate inexpensive hydrocarbon materials.[3,4] These materials have inherently low dielectric constants, due to their nonpolar hydrocarbon nature, and good mechanical properties. In addition to their polymerizability, the ability to substitute various moieties for the acidic protons on cyclopentadiene (and similar cyclic hydrocarbons such as indene and fluorene) has prompted numerous synthetic studies. Cyclopentadienes substituted with linear aliphatic,[5] cyano[6] or *tert*-butyl[7] groups have been made and evaluated for use as chemical reagents and lubricants, for example.

Although much work has been devoted to substituted and unsubstituted cyclopentadiene as end products, there has been very little work done in using functionalized cyclopentadienes as new monomer systems. Past effort in our group has focused on the synthesis and characterization of multiply allylated cyclopentadiene (ACP) for use as an all-hydrocarbon thermoset composite matrix.[8] This resin is composed of various isomers with two to six allyl groups per cyclopentadiene ring. It was somewhat surprising to discover that this novel resin could be cured with or without added catalyst to give composites with excellent chemical, thermal, and mechanical properties. In this paper we describe the extension of this work to propargyl-functionalized cy-

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Table 1. Results of Varous Reaction Conditions on the Product Mixture of the Phase Transfer Reaction of Propargyl Bromide and Cyclopentadiene

PB:CP ratio	solvent/base	addition conditions	PB present	PE present	di	tri	tetra	penta	hexa
2:1[a]	H_2O/NaOH	batch	no	no	21	19	12		
4:1	H_2O/NaOH	batch	yes	slight	13.5	26.5	25	19	16
6:1	H_2O/NaOH	batch	yes	yes	12.5	24.5	26.5	19	17.5
6:1	H_2O/NaOH	heated	no	yes	10	24	27	20	19.5
8:1	H_2O/NaOH	batch	yes	yes	7.5	23.5	27	23	19
6:1	THF/K_2CO_3	batch	yes	slight			no reaction		
6:1[b]	THF/K_2CO_3	heated	yes	slight	37	12	5.5		

[a] 48% mono. [b] 45% mono.

clopentadienes for use as matrix materials in carbon–carbon composites.

Experimental Section

Dicyclopentadiene was obtained from Aldrich Chemical Co. and cracked to cyclopentadiene at 175 °C with a 30 in. Vigreux column. Fluorene, propargyl bromide, and tetrabutylammonium bromide were obtained from Aldrich Chemical Co. and used without further purification. All solvents were obtained from Fisher or Aldrich. AS-4 unsized carbon fiber was donated by Hercules Chemical Co. (Wilmington, DE) and T-300-3K plain weave woven carbon fiber mats were donated by Textile Products Inc. (Anaheim, CA).

Cure analysis was accomplished using a TA Instruments DSC 2920 differential scanning calorimeter, and TGA data were obtained with a TA 2960 TGA unit, both operated with a TA 2100 data collection unit. IR spectra were collected on a Mattson ATI Galaxy Series FTIR 5000 FT-IR spectrometer. Solution ^{13}C spectra were obtained on a Bruker AC-300 instrument. A Polymer Laboratories DMTA Mark III was used for thermomechanical analysis operating in the three-point bending mode. Three-point bending fracture tests were carried out on a Materials Testing System (MTS) mechanical analyzer with a sample length-to-thickness ratio of 24:1 and a transverse speed of 2 mm/min. Scanning electron micrographs (SEM) were obtained with an Electroscan environmental scanning electron microscope. Wide-angle X-ray diffraction data was obtained with a Siemens XPD-700P polymer diffraction system equipped with a two-dimensional area detector with a sample distance of 10 cm. Composite cure was done in a Dake heated press. Microanalyses (for carbon and hydrogen) were carried out by M-H-W Laboratories (Phoenix, AZ); oxygen content was calculated based on the difference between carbon and hydrogen and the total sample. Resin content in the composites was determined as the difference in weight between the fibers before impregnation and the total cured sample. Density was estimated based on volume displacement for weighed samples.

Synthesis of Propargylated Cyclopentadiene. A 50% aqueous NaOH solution (30 g, 756 mmol) and tetrabutylammonium bromide (0.731 g, 2.27 mmol) were combined in a three-neck flask equipped with a magnetic stir bar, addition funnel, and N_2 inlet and outlet. The mixture was cooled with an ice bath and the air in the reaction vessel was evacuated with a vacuum pump. The reaction vessel was then charged with N_2. The procedure was repeated twice to ensure complete evacuation of O_2, which causes oxidation and side reactions during synthesis, from the vessel. Freshly distilled cyclopentadiene (5 g, 75.6 mmol) was added to the flask with rapid stirring. The ice bath was then removed and the reaction was allowed to warm to room temperature. The reaction gradually turned a deep red color (after approximately 15 min), signifying generation of the cyclopentadienyl anion. Propargyl bromide (54.0 g, 454 mmol) was then added through the addition funnel dropwise over 30–45 min. As addition of propargyl bromide proceeded, the mixture gradually changed from red to bright yellow. The reaction was continued for 16 h at room temperature with constant stirring. Variations in reaction conditions to optimize yield and overall results are discussed in the Results section and listed in Table 1.

After reaction, the organic phase was separated from the aqueous phase and a small amount of hydroquinone or *tert*-butylcatachol was added to act as oxidation inhibitor during workup. The organic phase was then washed twice with H_2O (150–200 mL) and once with a brine solution (150–200 mL) to remove the phase transfer catalyst. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure: yield ca. 90%; IR (NaCl Disk) 3292, 3054, 2902, 2837, 2117, 1423, 1365, 1297, 1081, 890, 848, 721, 649 cm^{-1}.

Dipropargylfluorene (DPF) Synthesis. Synthesis of the dipropargylfluorene (DPF) was carried out according to a literature procedure.[9] Fluorene (10 g, 60.2 mmol) and propargyl bromide (21.47 g, 180 mmol) were combined in a three-neck flask with a 50% aqueous NaOH solution and benzyltrimethylammonium chloride (0.559 g, 3 mmol). The mixture was heated at 70 °C for 3 h with rapid stirring. It was then diluted with 20 mL of toluene, washed once with dilute acid (150–200 mL) and twice with water (200 mL). The organic layer was separated and dried over magnesium sulfate. Toluene was removed under reduced pressure and the product was purified by recrystallization from ethanol followed by sublimation to give a white crystalline monomer in ca. 90% overall yield: IR (solvent cast film on NaCl disk) 3275, 3040, 2905, 2830, 2120, 1477, 1446, 1425, 1344, 1298, 1263, 1220, 763, 736, 671 cm^{-1}; ^1H NMR ($CDCl_3$) 2.0 (s, 2H), 2.83 (s, 4H), 7.35 (m, 4H), 7.73 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$) 27.46, 49.90, 70.69, 80.91, 119.88, 123.24, 128.01, 139.94, 148.37 ppm. Anal. Calcd for $C_{19}H_{16}$: C, 94.2; H, 5.8; Found: C, 94.1; H, 6.0.

Composite Formation. Unidirectional composites were made in a stainless steel mold with three compartments measuring 60.5 mm × 13 mm. The mold surfaces were sprayed with Fluo-Kem (Aldrich) to facilitate removal of the composites from the mold after cure. Composites were formed by placing a layer of carbon fiber bundles in the mold cavities and wetting them with PCP resin. The fibers were spread out to achieve homogeneous distribution of the fibers. This process was repeated until the desired thickness (usually 1.75–2.00 mm) was achieved. Stainless steel plugs, machined to have a small amount of clearance around the sides of the cavity, were then inserted. A mechanical press was then used to squeeze excess resin and voids from the composite (approximately 100 psi). The composites were cured in a heated press at 175 °C for 6 h and at 250 °C for 6 h under 500–1000 psi of mechanical pressure.

In the formation of the 2-D woven carbon fiber laminate composites, a stainless steel mold with a 63.5 mm × 63.5 mm cavity was used. Pieces of T300 carbon mat were cut to size. Composites were laid up by placing a piece of carbon fiber mat into the mold and wetting it with PCP resin. The process was repeated to produce carbon fiber laminates with 12–16 layers of carbon mat. A stainless steel plug machined to fit into the mold cavity was then placed over the composite in the mold. Mechanical pressure (ca. 100 psi) was used to squeeze out excess resin and voids. The composite laminates were then cured under the same conditions as the unidirectional carbon composites.

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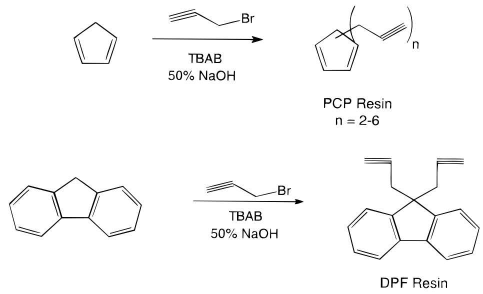

Figure 1. Synthesis scheme for propargylated cyclopentadiene (PCP) and dipropargylfluorene (DPF).

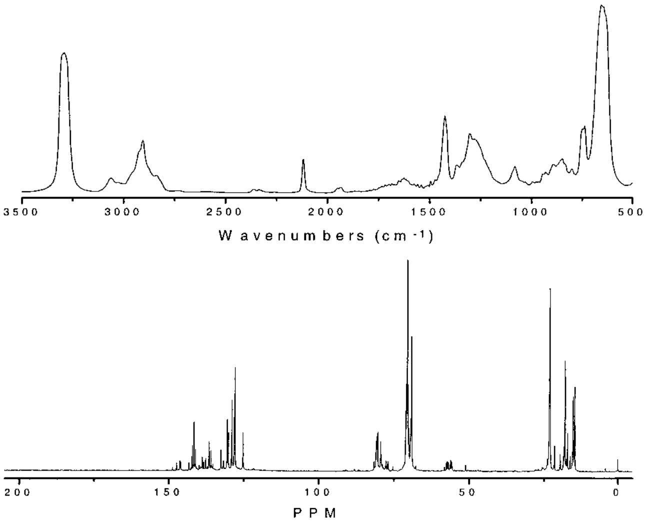

Figure 2. FTIR (top) and ^{13}C NMR (bottom) spectra of neat, uncured PCP.

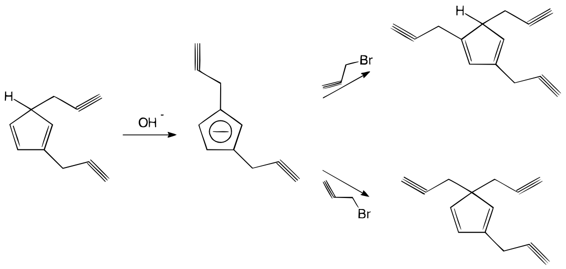

Figure 3. Reaction pathways for additional substitution of a disubstituted PCP.

Results and Discussion

Propargylated Cyclopentadiene (PCP) Resin Synthesis. The general reaction scheme is shown in Figure 1. Auto-oxidation in propargylated cyclopentadiene leading to cross-linking and gelling of the resin in the presence of oxygen was a major concern, due to the high concentration of propargyl units. It is important to exclude air from the reaction vessel and from the isolated product mixture.

The reaction of propargyl bromide and cyclopentadiene was monitored using gas chromatography (typical conditions), which showed a mixture of substituted cyclopentadienes with degrees of substitution (DS) ranging from two to six substituents per ring; this is consistent with more detailed analysis carried out on allylated cyclopentadiene.[8] An increase in higher retention time products was seen up to 8 h at room temperature. The ^{13}C NMR spectrum (Figure 2) of the PCP resin confirmed the complex nature of this mixture, resulting from formation of products with both different DS values and isomeric structures. Multiple peaks can be seen for the acetylenic carbons at 78−80 and 68−74 ppm and for the quartenary carbon of the substituted cyclopentadiene rings at 55−58 ppm

As was found for allylated cyclopentadiene (ACP), the generation of such a complex product mixture is due to a number of factors. First, as substitution proceeds, the reaction of a propargyl electrophile with an already substituted cyclopentadiene carbon (which would terminate further reaction of the ring) is unfavorable, due to steric inhibition. Also, the electronic charges on the β and γ carbons of a substituted cyclopentadiene position are higher, making them more reactive toward nucleophilic substitution than the α carbon. On the other hand, termination of reaction for a given DS product is favored by the high concentration of reactants. These competing factors lead to a complex mixture of multiply substituted products, all with the core cyclopentadiene ring incapable of further reaction due to disubstitution on one carbon. Figure 3 illustrates these points for a disubstituted intermediate; the upper path gives a product that can react further, while the lower path gives an unreactive product that becomes part of the final mixture.

Variations in reaction conditions and reagent ratios were evaluated in an attempt to control substitution and side reactions (e.g., propargyl ether formation). The results of these variations are summarized in Table 1. Gas chromatography was used to monitor the reactions and determine final product composition. In all cases, mixtures of products with two to six substituents per ring were produced. For the reaction with a 2:1 propargyl bromide-to-cyclopentadiene ratio, the absence of propargyl ether or propargyl bromide, plus an average functionality of 2.0 for the PCP product, demonstrates that all of the propargyl bromide was consumed in reaction with cyclopentadiene. In addition, the presence of tri- and tetra-substituted products indicates a propensity to give higher DS. An increase in higher DS products was observed upon addition of more propargyl bromide to this mixture, demonstrating incomplete termination of the ring with limiting propargyl bromide. Increasing the propargyl bromide-to-cyclopentadiene ratio from 2:1 to 4:1 increased the DS significantly. In addition, the presence of propargyl bromide at the end of the reaction indicated that complete termination of the cyclopentadiene rings had taken place. As the ratio of propargyl bromide to cyclopentadiene was increased further (from 4:1 to 6:1 and 8:1), the percentage of higher DS products increased only slightly, from 3.8 to 4.0 to 4.2, respectively, with no significant change in overall yield. These average DS values are slightly lower than those observed for the allylated cyclopentadiene resins.[8] Heating the reaction had very little effect on the average DS of the resin, increasing it from 4.0 to 4.15 on going from 25 to 50 °C. In fact, heating the reaction increased the amount of propargyl ether formed and decreased the yield of PCP resin.

Attempts to apply phase transfer conditions in tetrahydrofuran using solid K_2CO_3 as the base were not successful. At room temperature, no generation of cyclopentadienyl anion (signified by a red-colored solution) was seen. When heated to reflux, some reaction

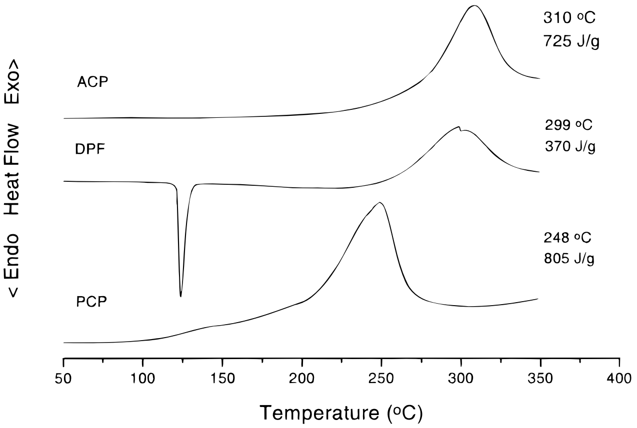

Figure 4. DSC analysis of ACP, DPF, and PCP.

occurred after approximately 16 h, although only products with DS values of 1−4 were obtained. Exposure of this product mixture to more propargyl bromide under normal phase transfer conditions resulted in typical DS values. Attempts to use stronger bases such as NaH in THF resulted in a thick tarlike product, possibly due to alkyne proton abstraction and reaction, which would lead to cross-linking.

Dipropargylfluorene (DPF) Synthesis. Synthesis of DPF was straightforward. Heat was needed in order to generate the fluorenyl anion due to the higher pK_a of the acidic protons on the middle fluorene ring compared to cyclopentadiene (pK_a = 23 and 16, respectively).[10] When the reaction was carried out at room temperature, incomplete reaction was seen after 24 h.

Thermal Cure of Propargylated Resins. Figure 4 shows the DSC thermograms of neat PCP and DPF compared to the thermogram of allylated cyclopentadiene (ACP) previously reported.[8] The thermal cure of PCP gives a very broad exotherm, beginning at approximately 125 °C and ending at approximately 275 °C, implying that a number of processes and/or mechanisms with different energies of activation occurred throughout the cure. The majority of reaction took place between 200 and 275 °C with the peak occurring at 250 °C. The peak of the thermal cure of ACP resin occurred at approximately 300 °C; that is, 50 °C higher than for PCP resin. This demonstrates the higher reactivity of the propargyl groups over allyl groups toward bulk thermal cure. In addition, the difunctional DPF resin showed an increase in peak temperature of approximately 60 °C compared to PCP resin, indicating that the reactivity of the propargyl functional resins is effected by the degree of substitution (local concentration) of reactive groups.

The energy of cure for neat PCP resin was over 800 J/g compared to 725 J/g found for neat ACP resin. This further demonstrates the greater reactivity of the propargyl groups toward thermal cure in these resins, especially in light of the average DS being higher in ACP than in PCP resins. The heat of cure for DPF was proportional to the heat of cure for PCP with respect to the relative DS; i.e., it was roughly one-half the PCP value.

Spectroscopic Evaluation of Thermal Cure. The thermal cure of PCP resin was monitored using FT-IR.

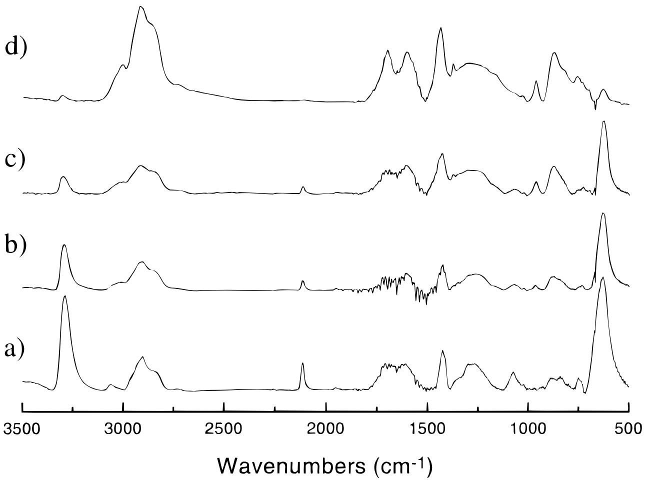

Figure 5. FTIR spectra of four PCP resin samples cured for 4 h each at (a) 150 °C, (b) 175 °C, (c) 200 °C, and (d) 250 °C.

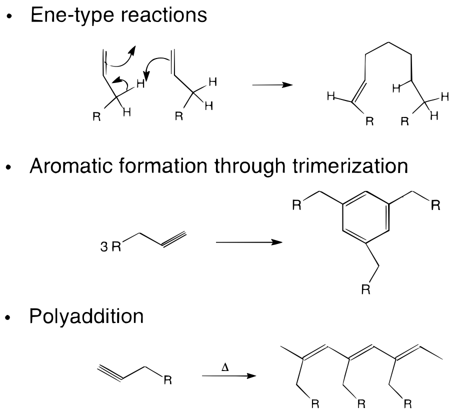

Figure 6. Three probable mechanisms of cure for propargylated resins.

Figure 5 shows the IR spectra of PCP resin samples cured for 4 h each at the given temperatures. Reaction of the propargyl groups can be seen most dramatically through the reduction in relative intensity of the peak at 3290 cm^{-1}, which is assigned to the C−H stretch of the terminal alkyne groups. Also the disappearance of the bands at 2115 and 630 cm^{-1}, which correspond to the C≡C stretch and ≡C−H bend, respectively, demonstrates the near complete reaction of the propargyl groups. Further evidence of the mechanisms and products of the thermal cure is found in the broad band from 2750 to 3000 cm^{-1} due to C−H stretches of alkanes. As cure continues, this band intensifies and sharpens, suggesting further alkyl segment formation through mechanisms involving hydrogen transfer in an ene-type reaction (Figure 6) similar to what is found in allyl systems. In addition to changes in the alkane band, five new bands are seen in the IR spectra as the cure proceeds. The new bands appear at 3010, 1695, 1598, 692, and 866 cm^{-1}. The first band is associated with the C−H stretch of alkene groups. The peaks at 1695 and 1598 cm^{-1} correspond to C=C stretches of nonconjugated and conjugated C=C bonds, respectively,[11] and are assigned to newly generated C=C bonds. In addition, the new peaks at 962 and 866 cm^{-1} are consistent with the C−H bending of alkene protons. This spectro-

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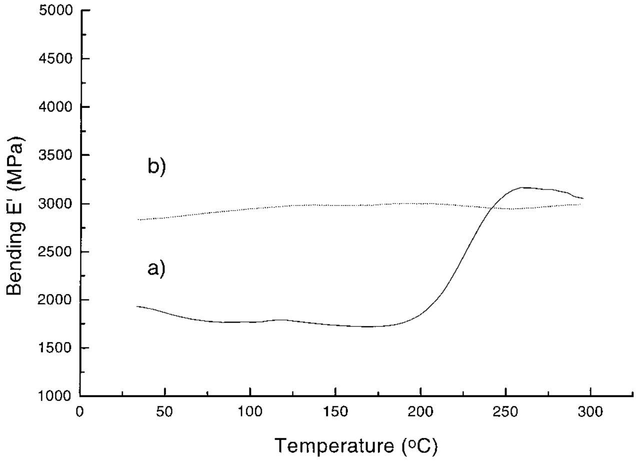

Figure 7. DMA trace of neat PCP resin cured at (a) 175 °C and (b) 250 °C.

scopic evidence suggests that the major mechanisms of cure in the PCP systems involve hydrogen transfer (which forms new alkane and alkene bonds) and oligomerization/cyclotrimeraztion, the latter involving the formation of linear polyalkenes and aromatic species (Figure 6).

Solid-state ^{13}C NMR of cured PCP resin supports the proposed mechanisms of cure. A broad peak is seen in the 100−150 ppm range, indicating that a number of unsaturated species are present. These groups, in addition to the alkenes of the cyclopentadiene nucleous, are the result of proton shifting and/or polyadditon of propargyl groups to generate polyalkenes or aromatic species, as shown in Figure 6.

Physical Properties of PCP. PCP resin is a low to medium viscosity liquid with a golden red color and a room-temperature density of 0.96 g/cm^3. Once cured, the material produces a brittle, black, glassy material with a density of 1.5 g/cm^3. X-ray analysis of the cured PCP material shows that a completely amorphous morphology is produced; i.e., there is no evidence for extended graphitic structures.

Figure 7 shows the DMA spectra of neat PCP resin cured at 175 and 250 °C. The former gives a room temperature modulus of approximately 2.0 GPa. However, further cure of the sample takes place at approximately 200 °C, resulting in a maximum modulus of 3.1 GPa and a modulus of 3.0 GPa at the final temperature. The sample cured at 250 °C showed no further cure or transition, maintaining a modulus of 2.9−3.0 GPa up to 300 °C. These values are comparable to the values of ca. 2.7 GPa found in common epoxy materials (values measured in our laboratory for *m*-phenylenediamine cured bisphenol A diglycidyl ether with the same carbon fiber reinforcement[8]).

Thermal Stability and Char Yields of PCP and DPF Resins. The TGA thermographs of cured PCP and DPF resins are given in Figure 8. Cured PCP resin showed a 5% weight loss up to 410 °C. However, the most unique property of this material is its carbon yield of 75% when ramped to 1000 °C. This is far greater than what has been seen for other simple hydrocarbon systems such as polystyrene, polybutadiene, and polyethylene, which generally decompose below 400 °C and produce carbon yields of less than 10%. In addition, the carbon yield of cured PCP at 1000 °C is 15−20% higher than comparable thermoset systems such as phenolics and polyimides (Table 2). While polyphenylenes give higher char yields, these materials are very difficult to synthesize and process, and involve expensive precursors, making them impractical for routine composite formation.

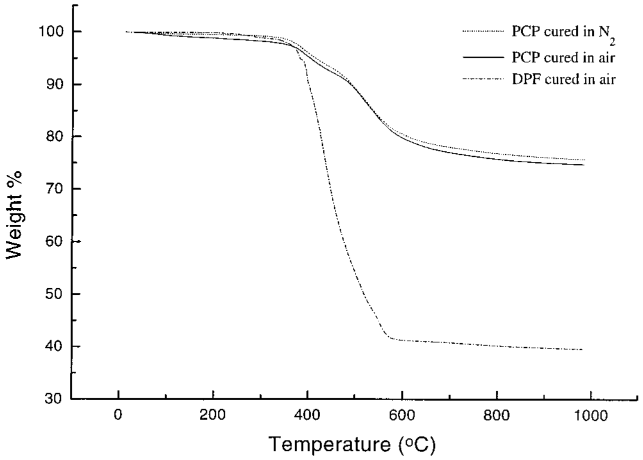

Figure 8. TGA of PCP resin cured in air and N_2 and DPF resin cured in air.

Table 2. Typical Carbon Yield of Thermoset Resins[2]

furan resins	50−60%
phenolic resins	50−60%
polyimide	60%
polyphenylene	85%
PCP resin	75%

A small difference in char yield was seen between PCP cured in air and PCP cured in N_2. This difference may be due to the difference in oxygen-containing moieties in the final product caused by oxidation during cure. Elemental analysis of the two systems showed approximately 2% more oxygen (by inference from differences in carbon and hydrogen results) in the air-cured sample than the N_2-cured sample (elemental analysis: C, 87.5; H, 7.2 and C, 89.8; H, 7.9, respectively). The difference in char yield is therefore attributed to the expelling of more oxygen-containing byproducts, such as CO_2, generated during rearrangement to the carbon product. This proposed explanation is in agreement with the mechanism of rearrangement found in comparable systems such as phenolic resins, in which carbonization also generates hydrocarbon and oxygen-containing byproducts.[12]

In contrast to the exceptionally high char yield of the PCP resin, cured DPF resin decomposed beginning at approximately 400 °C and continuing to approximately 600 °C in N_2. The char yield at 1000 °C was approximately 40%. This value is again higher than what is seen for typical hydrocarbon materials but lower than what is found for traditional thermoset precursors for carbon−carbon composites.

PCP/Carbon Fiber Composites. The PCP/carbon fiber composites made here all contained approximately 40% resin by weight (30% volume fraction). DMA analysis of the composites showed no thermal transi-

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Table 3. Flexural Storage Modulus and Strength Values for PCP/Carbon Fiber, Phenolic Resin/Carbon Fiber[13] and Epoxy Resin/Carbon Fiber[14] Composites

composite system/ resin fiber	% fiber	flexural modulus, E_f (GPa)	flexural strength, σ_f (MPa)
PCP/AS-4	65–70	115–120	920
epoxy/T300	65–70	122	1383
phenolic/carbon	50	110	1200

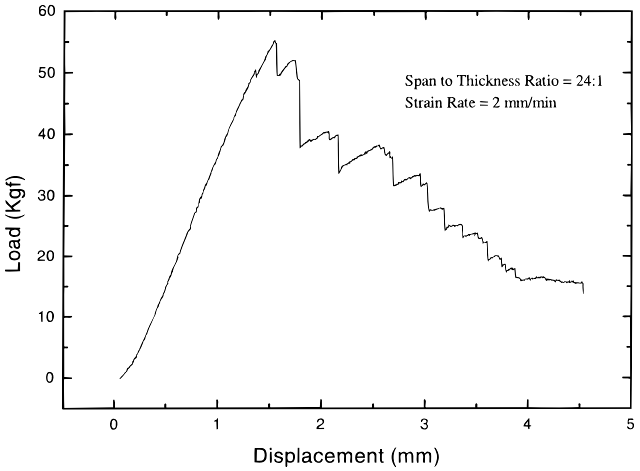

Figure 9. Three-point bend analysis of a unidirectional PCP/carbon fiber composite.

tions or significant loss in modulus up to 300 °C. This is consistent with the extremely high cross-link density developed in these systems.

Room-temperature three-point bending gave flexural modulus and flexural strength values of the various composites and are shown in Table 3, which also includes literature values for an epoxy/carbon system and a phenolic/carbon system. The PCP/carbon composite displayed a modulus of 115–120 GPa, which is approximately equal to the modulus reported for the epoxy composite and higher than that reported for the phenolic material. Figure 9 shows a representative graph of load versus displacement for a PCP/carbon composite. Initial loss of strength at failure was drastic, as would be expected in a highly cross-linked material. After the initial loss of strength, failure of the composite continued in a stepwise fashion as the displacement increased. Failure occurred mainly through delamination of the composite along the fiber axis under load due to interphase and matrix failure caused by the extremely high cross-link density and brittleness of the cured PCP resin. This was confirmed by scanning electron micrographs of the fracture surfaces of PCP/carbon composites tested in three-point bend, which showed moderate to poor adhesion of the matrix to the fiber. Small fractured pieces of matrix were seen attached to the fiber, indicating brittle failure of the matrix under load.

Carbonization and Interlaminar Shear Strength of PCP Composites. Carbonization of composites of PCP reinforced with T300 woven fiber were performed with in a carbonization furnace at Wright-Patterson Air Force Materials Laboratory. The samples were approximately 40% PCP by weight and were temperature ramped to 1000 °C at 1 °C/min. The composites retained 90% of their initial weight during carbonization. Assuming minimal loss from the carbon fiber in the composite, matrix loss is approximately 25%, which is equal to what is found in the neat material at a ramp rate of 20 °C/min.

Preliminary interlaminar tensile measurements of carbonized PCP/T300 composites gave shear strength values of 1.46 MPa. These values are slightly lower than typical phenolic resin composites after carbonization. This is the result, in part, of the high cross-link density and brittleness of the resin, although a contributing factor is the poor resin adhesion to the fiber. This is probably due to the lack of chemical bonding of the type that can form with epoxy and phenolic resins, where ether and ester bonds, for example, will develop that hold the resin and fiber together during gradual carbonization. We have made no attempts so far to deliberately generate such chemical linkages and develop a tailored interphase that would enhance low- and high-temperature behavior. Such work is needed, along with efforts to enhance the toughness of the matrix resin itself; this would in turn enhance the flexual strength and toughness of the final composite.

Conclusions

Propargylated cyclopentadiene is a promising matrix material for generating carbon–carbon composites. The resin is inexpensive, with medium to low viscosity and is easily synthesized via phase transfer reaction of propargyl bromide with cyclopentadiene. The high concentration and reactivity of propargyl groups in the PCP resin allows a relatively low temperature cure that apparently involves multiple mechanisms: hydrogen rearrangement in an ene-type reaction, polyaddition, and/or generation of aromatic species through cyclotrimerization. These mechanisms produce a material with carbon yields as good or higher than presently used carbon precursors. Composite properties are comparable to phenolic/carbon and epoxy/carbon systems with flexural modulus values of 115–120 GPa and interlaminar shear strengths of 1.46 MPa.

Cure of DPF resin proceeded at higher temperature due to the lower concentration of functional groups, which increased the apparent activation energy. The energy of cure was proportional to the number of alkyne units present. A major difference in carbon yield was also seen with DPF, due to the lower functionality reducing the number of thermally stable products formed during the cure reaction. Thus, DPF is not a good candidate for carbon–carbon composites since its carbon yields are 20% below currently used materials.

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