

# CARBON-CARBON COMPOSITES FROM A NEW CLASS OF HIGH-CHAR YIELD RESINS

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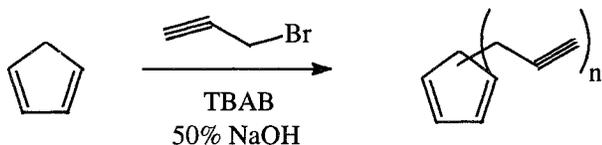
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## Introduction

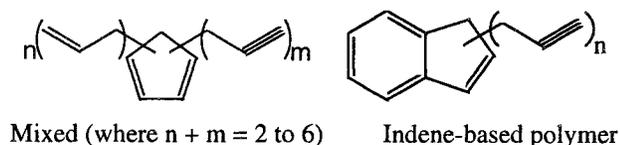
Carbon-carbon composites are composed of carbon fibers held together by a carbon matrix. A fiber preform and a matrix capable of carbonizing are pyrolyzed. The char yield or carbon remains of the matrix determines how many times a resin is reimpregnated into the composite and pyrolyzed. The lower the char yield of the matrix, the more reimpregnation and pyrolysis steps are needed to fully densify the carbon-carbon composite.

The class of polymers examined here is based on propargyl substituted cyclopentadiene. This resin is composed of 95% carbon by weight and has the potential of producing a very high-char yield composite. TGA measurements showed up to 95% char yield in the composites and over 80% in neat resin samples.

Propargyl- and mixed allyl-/propargyl-cyclopentadiene and propargyl-indene polymers form the family of high-char yield resins examined as potential matrices for carbon-carbon composites. The resins are synthesized using a five-membered unsaturated ring base, a propargyl halide, and a phase change catalyst in a basic environment [1]:



Several ( $n = 2$  to  $6$ ) of the propargyl groups add to the ring. The unsaturated additions thermally decompose to form free radicals which can add to other triple or double bonds producing a crosslinked polymer network. Some polymerization begins during the original synthesis, but if kept away from oxygen, the resin remains as a low-viscosity fluid for a long time at room temperature.



Mixed (where  $n + m = 2$  to  $6$ )

Indene-based polymer

Allyl halides can be substituted for propargyl or a mix used. Other five-member unsaturated rings can be used instead of cyclopentadiene, such as indene.

## Experimental

The basic resins were synthesized and infiltrated into the fibers or preforms which had been placed in a mold. The resin was poured into the mold over fibers and additional fibers and resin added to complete the composite. The mold was heated under sufficient pressure to squeeze out some resin to ensure the fibers were completely wet by the resin. The mold was heated to 250°C and then to 350°C and held for 4-6 hours to completely cure the resin [1-2].

The three resins examined in this study were a propargyl-substituted cyclopentadiene (PCP), a 3:1 allyl:propargyl-cyclopentadiene (APCP) and a propargyl-indene (PI). The three fiber forms examined were the ThermalGraph® 6000X preform from AMOCO, a uniaxial AS-4 hand lay-up, and a T-300 plain-weave multi-ply lay-up.

Interlaminar tensile strength (ILT) specimens (average of three for each composite) were cut after carbonization for a modified button measurement. The composites were carbonized by heating at 2°C/min. to ~900°C in a nitrogen atmosphere.

Microscopy samples were cut from samples before and after carbonization. The samples were vacuum infiltrated with a fluorescently-dyed potting resin and then polished by ordinary resinographic techniques. The polished plugs were examined with a Nikon Optiphot FXL microscope in both bright-field and fluorescent illumination. Images were obtained using 35-mm film and a CCD digital camera. Image-1 image processing software was used to measure the fiber volumes and void content in the composites.

Density measurements were made on composite specimens using the Archimedes displacement method with water and on cured neat resin specimens using a pycnometer and toluene.

## Results and Discussion

The results of this study are summarized in the table below for the carbonization char yields, microscopy, and interlaminar tensile testing.

Fiber volumes were measured in the as-cured composites and are shown for within bundles for the woven fiber composites or in the regions away from large voids for the other fiber composites. The overall fiber volumes are also calculated. Reasonable fiber volumes were obtained in these composites: 54 to 62% in woven bundles and 51 to 66% in the other composites.

Char yields for the composites were calculated from weight loss during carbonization. The matrix char yields were calculated based on the total char yield, measured fiber volumes and measured resin density (1.54 g/cm<sup>3</sup>). The density of the resin had to be measured using toluene because the resin was highly hydrophobic.

The apparent material density of the composites was measured and, because of the high resin density and high fiber content, was dominated by the density of the respective fibers. The cured composites had bulk densities of 1.4 g/cm<sup>3</sup> (AS-4 and T-300 composites) and 1.65 g/cm<sup>3</sup> (ThermalGraph® 6000X composites).

The percent voids in the as-cured composites were high relative to typical composites indicating that the processing was less than optimum. After carbonization the void level increased as expected. The PCP composites all had void contents typical of that found in carbonized phenolic composites (14-19%). The PI composites had a larger void volume of 32%, and the APCP composites was even higher (see micrographs).

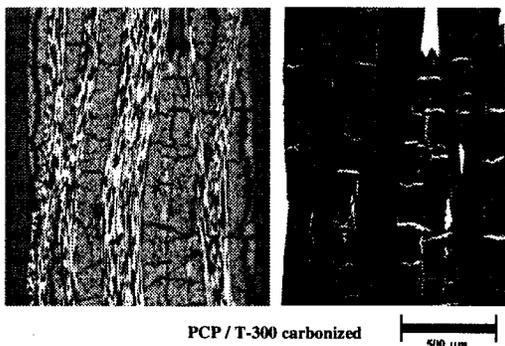


Fig. 1. Bright-field and fluorescence optical micrographs.

Table - Summary of Results for Composites

Resin	Fiber	Fiber volume (%)		Matrix char (%)	Voids (%)		Interlaminar tensile strengths	
		overall	bundle		as-cured	carbonized	(MPa)	(psi)
PCP	ThermalGraph®	63.2	66.0	80	4.3	19.2	2.07	300
PCP	AS-4	48.2	51.2	77	5.9	17.6	1.00	145
PCP	T-300	55.2	62.0	75	6.4	13.6	1.30	189
APCP	T-300	48.6	54.0	55	5.6	58.0	na	na
PI	T-300	52.8	58.0	68	5.0	32.4	na	na

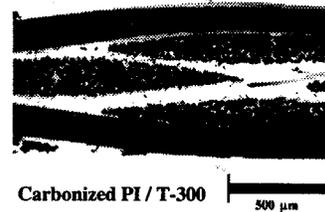


Fig. 2. Fluorescence optical micrograph.

After carbonization the PI and APCP composites could not be tested for ILT; the composites fell apart during cutting. The PCP composites were tested and found to have reasonable strengths (1 to 2 MPa). These are the same general strengths as carbonized phenolic composites.

## Conclusions

Propargyl-substituted resins (PCP) do show promise as carbon-carbon composite matrix resins with ILT strengths of the carbonized composite better than similar carbonized phenolic composites. This matrix has 77% resin char yield in the composites. The mixed allyl- and propargyl-cyclopentadiene and propargyl-indene matrices lost too much mass in their composites for use as carbon-carbon matrix resins.

Additional work needs to be performed to reduce voids during the cure process. This may allow other resins in this family to function as carbon-carbon matrices. Also, densified articles need to be produced and characterized as carbon-carbon composites to fully evaluate the potential of these resins.

## Acknowledgments

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## References

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