

NOTES

In Situ Polymerization of Monomers for High-Performance Poly(phenylquinoxaline)/Graphite Fiber Composites

Poly(phenylquinoxalines) (PPQ's) are considered to have excellent potential for use as high temperature-resistant matrix resins in advanced fiber/resin composites. However, because of processability problems, their potential as high-temperature matrix resins has not been realized. Current methods used to fabricate PPQ/fiber composites consist of impregnating the reinforcement with high molecular weight PPQ polymer dissolved in a solvent or solvent mixture containing *m*-cresol. Because of the inordinately high viscosity of these solutions, which results from both the high molecular weight of the polymer and the use of *m*-cresol, complete wetting of the fiber during impregnation is difficult to achieve. The approaches used to overcome the viscosity problem are (1) to limit the polymer molecular weight by upsetting the stoichiometry of the system, or (2) to use dilute solutions. Unbalancing the stoichiometry can adversely affect the polymer thermo-oxidative stability and even dilute solutions of high molecular weight polymer are extremely viscous.

This communication describes a new approach to circumvent some of the composite processing problems associated with the use of PPQ polymers as the matrix material. The method used to prepare high-performance PPQ/graphite fiber composites consisted of impregnating the fiber with a freshly made solution of the appropriate monomers instead of a solution of high molecular weight polymer.

Impregnation of the fiber prior to appreciable polymerization completely eliminates the impregnation problems encountered with the use of high-viscosity high molecular weight PPQ solutions. It is important to note that the major part of the polymerization of the reactant mixture is conducted on the fiber during the solvent removal and final curing stages. Although at the time of impregnation the solution is not truly monomeric, we refer to this approach as the *in situ* polymerization of monomers because of its similarity to the monomeric reactant approach developed in our laboratories for A-type polyimides.¹

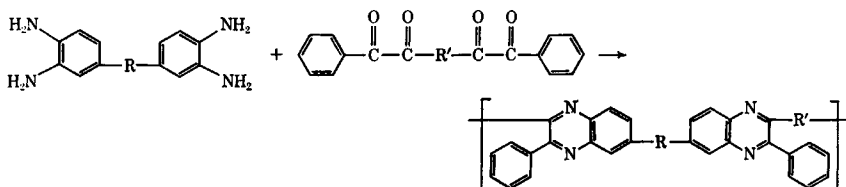
RESULTS AND DISCUSSION

The PPQ systems currently being investigated are listed in Table I. The majority of the work done to date has been with polymer I and Hercules HMS graphite fiber.

In general, the following procedure was used to prepare the composites. Stoichiometric quantities of the bis(*o*-diamine) and the bis(phenylglyoxal) were dissolved separately in N-methylpyrrolidone at a solids content of about 35 wt-%. The two solutions were then mixed and used to impregnate the graphite fiber as it was drum wound. Depending on the reactivity of the monomers, solvent, concentration, etc., the usual life (pot life) of the solution can range between 1/2 and 6 hr. For example, the solution of monomers for polymer I was used 1/2 hour after preparation with no difficulty. Polymerization and simultaneous solvent removal were caused to occur by heating the drum wound prepreg for 45 min at 160°F. Subsequently, the prepreg was removed from the drum, cut into plies 3 × 4 in., stacked (10 plies), wrapped in aluminum foil, and placed into a press heated to the cure temperature. (For polymer I the platen temperature was 625°F). Following a dwell time of about 90 sec, pressures in the range of 200 to 1000 psi were applied and maintained constant for 1/2 to 1 hr. In some instances the composites

TABLE I
Polyphenylquinoxaline Systems^a Investigated

Polymer system	R	R'
I		
II		
III	nil	
IV	nil	



were given elevated-temperature postcures, with and without applied pressure. The complete cure and postcure schedules for the laminates used to generate the data shown in Figure 2 are given in Table II.

Figure 1 is a photomicrograph showing the cross section of the composite from polymer I and HMS graphite fiber. It can be seen that the in situ polymerization of monomers approach permits the fabrication of void-free composites. Figure 2 shows the variation of composite weight loss, flexural strength, and interlaminar shear strength as functions of time in air at 600°F. Also given in the figure are the 75°F mechanical properties. The flexural strength and interlaminar shear strength data are an average of three and six samples, respectively. As can be seen in the figure, the composite exhibited excellent weight retention. The 10% weight loss after 600 hr at 600°F compares favorably with the data for A-type polyimide/HTS composites.¹ After 600 hr of exposure at 600°F, the composite retained ~64% of its 500° flexural strength and ~73% of its 600°F interlaminar shear strength, respectively.

Some preliminary room temperature test results from PPQ polymer I and HTS graphite fiber (52% fiber volume) are as follows: flexural strength, 187 000 psi; interlaminar shear strength, 15 000 psi; transverse tensile strength, 11 600 psi; longitudinal impact strength (miniature Izod), 27 in.-lb. The higher flexural and interlaminar shear strengths can be attributed to the HTS fiber. The most significant point to be made is that the transverse tensile strength is approximately 50% higher than that

TABLE II
PPQ System I/HMS Graphite Fiber Postcure Schedule

2 Hours at 200°C (392°F)
2 Hours at 225°C (437°F)
2 Hours at 250°C (482°F)
2 Hours at 300°C (572°F)
2 Hours at 325°C (617°F)
2 Hours at 350°C (662°F)
3 Hours at 372°C (700°F)



Fig. 1. Photomicrograph of PPQ system I/HMS graphite fiber; $\times 50$.

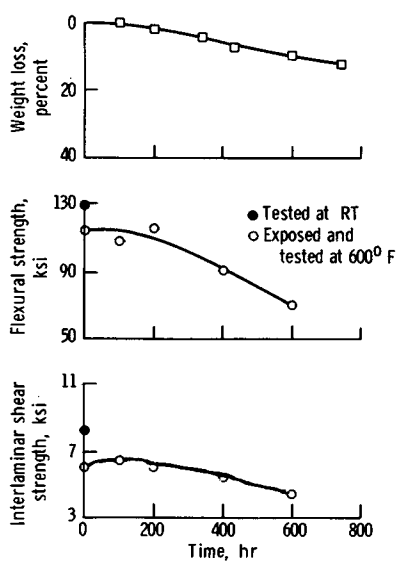


Fig. 2. Properties of PPQ system I/HMS graphite fiber (54% fiber volume) composites as a function of exposure time at 600°F.

for A-type polyimide/HTS composites.² Also significant is the finding that the longitudinal impact strength of the PPQ/HTS composite is three times that of epoxy/HTS composites.³ Additional details and results will be described in a forthcoming publication.

CONCLUSIONS

Based on the results of this preliminary investigation, the following conclusions can be drawn:

1. The in situ polymerization of monomers approach can be used to prepare high-performance PPQ/graphite fiber composites.
2. The in situ polymerization approach greatly simplifies the fabrication of PPQ fiber-reinforced composites.
3. The in situ polymerization approach eliminates the need for polymer synthesis.

References

1. T. T. Serafini, P. Delvigs, and G. R. Lightsey, *J. Appl. Polym. Sci.*, **16**, 905 (1972).
2. M. P. Hanson, personal communication.
3. C. C. Chamis, M. P. Hanson, and T. T. Serafini, *Impact Resistance of Unidirectional Fiber Composites. Composite Materials: Testing and Design*. Spec. Tech. Publ. 497, ASTM, 1972, pp. 324-349.

TITO T. SERAFINI
PETER DELVIGS
RAYMOND D. VANNUCCI

Lewis Research Center
Cleveland, Ohio 44135

Received March 27, 1973