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IN SITU POLYMERIZATION OF MONOMERS FOR POLYPHENYLQUINOXALINE/GRAPHITE FIBER COMPOSITES

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ABSTRACT

Methods currently used to prepare fiber reinforced, high temperature resistant polyphenylquinoxaline (PPQ) composites employ extremely viscous, low solids content solutions of high molecular weight PPQ polymers. An improved approach, described in this report, consists of impregnating the fiber with a solution of the appropriate monomers instead of a solution of previously synthesized high molecular weight polymer. Polymerization of the monomers occurs in situ on the fiber during the solvent removal and curing stages. The in situ polymerization approach greatly simplifies the fabrication of PPQ graphite fiber composites. The use of low viscosity monomeric type solutions facilitates fiber wetting, permits a high solids content, and eliminates the need for prior polymer synthesis.

INTRODUCTION

Polyphenylquinoxalines (PPQ) are considered to have excellent potential for use as high temperature resistant matrix resins in advanced fiber-resin composites (ref. 1). 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. Prior approaches used to overcome the viscosity problem are: (1) to limit the polymer molecular weight by unbalancing the stoichiometry of the system or (2) to use dilute solutions. Unbalancing the stoichiometry can adversely affect the polymer thermooxidative stability and even dilute solutions of high molecular weight polymer are extremely viscous.

This report 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 consists 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 (ref. 2).

This report describes a screening study of six different PPQ/HMS graphite fiber composite systems fabricated by the in situ polymerization approach. Composite mechanical properties and thermooxidative stability characteristics were determined at 600° F over an extended time period. Also presented are weight loss measurements of PPQ films fabricated by conventional polymerization procedures.

EXPERIMENTAL PROCEDURE

Monomers

The monomers used in this study are shown in Table I. 3,3'-Diaminobenzidine(DAB), 3,3',4,4'-tetraaminobenzophenone (TABP), 1,4-bis(phenylglyoxalyl)benzene(PPGB), 1,3-bis(phenylglyoxalyl)benzene(MPGB), and 4,4'-oxydibenzil(ODB) were obtained from commercial sources, and used as received.

3,3',4,4'-Tetraaminodiphenyl sulfone(TADPS) was prepared according to the method of Stille and Arnold (ref. 3).

3,3',4,4'-Tetraaminodiphenylmethane(TADPM) was prepared essentially according to the method of Bell and Jewell (ref. 4).

Film Fabrication and Testing

The PPQ polymers were prepared according to the following representative procedure. A stoichiometric quantity of the tetraketone was added during 5 minutes to a stirred slurry of the tetraamine in m-cresol. The solids content was in the range of 10 to 15 weight percent. The reaction mixture was stirred for 18 hours at room temperature to provide a viscous solution. Films were cast by doctoring the solution on a glass plate followed by drying in air at 70° C for 4 hours, then in vacuum at 130° C for 4 hours. The film thickness was in the range of 1 to 2 mils.

Isothermal exposure of the PPQ films was performed at 600° F in a circulating air oven. The air change rate was 100 cm^3/min. The film size was 2 in. x 2 in.

Composite Fabrication and Testing

Solutions of systems I to VI (fig. 1) were prepared by separately dissolving stoichiometric quantities of each monomer in N-methylpyrrolidone(NMP) at a solids content of 25 to 35 weight percent. The solutions were then combined, stirred for 30 seconds, and applied within one half hour to drum wound Hercules HMS graphite fiber. The prepregs were then dried with heat lamps as the drum was rotated to yield prepreg tape containing a volatile content of approximately 28 weight percent. The quantities of fiber and solution were calculated to yield composite containing 40 weight percent resin. Volatile content was determined by placing a 3 in. x 3 in. section of dried prepreg into a 600° F oven for 30 minutes and measuring weight loss. At a volatile content of 28 percent, the tapes were flexible but not tacky. The prepreg tapes were then removed from the drum, cut, stacked unidirectionally 8 to 12 plies thick and wrapped in 2 mil stainless steel foil. Composites were then molded by placing the wrapped prepreg stack into a preheated matched metal die in a press also heated to the desired cure temperature. Following a dwell time which ranged from 45 to 130 seconds, pressures ranging from 500 to 900 psi were applied for times of 30 to 60 minutes. In most instances, the composites were given elevated temperature postcures without applied pressure.

Flexural strength tests were performed using a three point loading fixture with a fixed span of 2 inches. The specimen size was 1/4 inch by 2-3/8 inch. The thicknesses of the laminates ranged from 0.070 inch to 0.090 inch. The resultant span/depth ratio used ranged from 22 to 28. The rate of center loading for flexural testing was 0.05 inch/min. The interlaminar shear strength tests were conducted at a constant span/depth ratio of 5 using the interlaminar shear test fixture described in reference 5. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests the load was applied after a 15 minute soak at 600° F. Composite weight loss was determined using the apparatus and conditions previously described for the PPQ film. Generally, specimens were tested in triplicate.

RESULTS AND DISCUSSION

The monomer combinations used for the fabrication of PPQ/graphite fiber composites are shown in figure 1. Synthesis and properties of PPQ polymers from several of these monomer systems have been reviewed (ref. 6).

In the prior studies the polymers were synthesized using carefully controlled laboratory procedures. Polymers from monomer systems I and VI have also been evaluated as matrix resins in graphite fiber composites (ref. 1). Some difficulty was experienced in obtaining void-free composites, employing solutions of high molecular weight PPQ polymers. The processing difficulties could be attributed to a number of factors, such as the inability to achieve complete fiber wetting, and to remove completely the m-cresol/xylene solvent mixture. To eliminate these processing problems, we used the approach of conducting the polymer synthesis step on the surface of the fiber reinforcement. This approach utilizes a low-viscosity solution of monomer mixtures in N-methylpyrrolidone (NMP) as the prepreg varnish. Because of the fast reaction rate of the tetraamine/tetracarbonyl monomer system, some reaction occurs immediately upon mixing the two separate monomer solutions. The pot life of the prepreg varnish is limited by the solubility of the reaction products, perhaps oligomers, in the NMP solvent. The solution, however, has sufficient pot life for use as a prepreg varnish.

The conventional fabrication method employs m-cresol because high molecular weight PPQ polymers remain soluble in this solvent. Apparently, due to the formation of polymer/solvent complexes, the m-cresol serves as an internal plasticizer, providing flow during processing. Consequently, the m-cresol is difficult to remove during precuring, and therefore volatilizes during the final cure, producing voids. The voids in composites prepared from high-viscosity polymer solutions can also be attributed to incomplete fiber wetting during impregnation, combined with little or no resin flow after the precure step.

The various monomer combinations shown in figure 1 were selected on the basis of improved processability without sacrificing the thermo-oxidative stability of the PPQ resin.

Isothermal exposure of PPQ films was performed in air at 600° F to obtain an estimate of polymer thermo-oxidative stability. The isothermogravimetric analysis (ITGA) results for the films are shown in figure 2. The data shown in the figure were obtained on PPQ films cast from m-cresol solutions of high molecular weight polymers. The m-cresol solutions were used because of the ease of film preparation. The curves shown in figure 2 do not take into account the initial weight loss experienced by the films during the first hour of exposure at 600° F. The investigators of reference 1 attribute the initial weight loss to volatilization of retained solvent. The film weight loss after the one-hour exposure is given in table II. The data in table II also point out the difficulty in completely removing the m-cresol. Figure 2 shows that polymers I and II lost considerably less weight after 600 hours than polymers III-V. Films of polymer VI were reported to exhibit a thermo-oxidative stability comparable to polymer I (ref. 1).

As previously mentioned, ITGA of polymer films provides only a "best first guess" of polymer thermo-oxidative stability. Therefore, composites were fabricated and evaluated using Hercules HMS graphite fiber and all six monomer systems. Solutions of monomers in NMP having a solids content of 25-35 weight percent were used. All six of the monomer combinations provided low-viscosity solutions that possessed an adequate pot life, ranging from about 1/2 hour for system VI to more than 7 hours for system I. Excellent to good fiber wetting was obtained using systems I-IV. Void-free composites resulted from systems I-III. System V provided fair wetting, while system VI was rated as poor. As used in this investigation, the relative ratings of fiber wetting were determined by microscopic examination of sectioned composite specimens. It is possible that some of the observed voids, attributed to poor wetting, might have resulted from volatilization of entrapped solvent.

Figure 3 compares photomicrographs of cross-sectioned composites obtained from systems I and VI. The photomicrographs clearly show that a void-free composite was obtained from system I. Photomicrographs of composites from systems II and III were very similar to that of system I. Several attempts to improve the quality of composite VI were unsuccessful. Difficulty was also encountered in the fabrication of composites from system V. Monomer systems V and VI are highly reactive, and it is possible that upon mixing the monomer solutions oligomers were formed that were unable to penetrate the fiber bundle. It needs to be emphasized that the overall processability of all of the PPQ monomer fiber systems were considerably better than that of conventional methods which employ solutions of high molecular weight polymer. It is entirely possible that further improvement in solvent-monomer systems, impregnation techniques etc., would result in void-free composites for all of the systems.

Table III indicates the processing parameters that were selected after preliminary experimentation. The cure temperatures were selected to be above published Tg values of each polymer system, where available (ref. 7). The dwell time given for each system is the time interval required for complete evolution of volatile material. During the dwell time a cloud of vapor was observed. Means are currently being developed to utilize instrumental methods to establish the proper dwell time. As shown in table III, the cure pressures ranged from 500 to 900 psi, and cure times from 30 to 60 minutes. The composites were given an additional cure for 60 minutes at 700° F at the pressure.

Preliminary evaluation of composite properties at 600° F indicated that elevated temperature post-curing was required to decrease thermoplastic behavior at elevated temperatures. Thermoplasticity was manifested as continued yielding of the composite without failing during application of load. After some experimentation, the post-cure cycle shown in table IV was adopted.

The room temperature and short-time 600° F properties of the post-cured composites are shown in table V. The data show that even after the extensive post-cure cycle composite systems II, III, and VI exhibited thermoplastic behavior at 600° F. In addition to the flexural strength values, the failure mode resulting from the three-point flexural test is indicated. In the room temperature flexural test composite system II exhibited a tension type failure, which is responsible for its higher flexural strength. All other flexural test specimens, tested at room temperature or at 600° F, exhibited a compression type of failure, indicating that the resin matrix did not completely transfer the applied loads to the fiber reinforcement. Except for composite system II, which had a fiber translation efficiency (FTE) of 96% based on a nominal fiber tensile strength of 300 ksi, the other composites exhibited FTE values of approximately 75%. The 600° F retention of flexural strength ranged from 22% for system III to 68% for system IV.

The specimens tested for interlaminar shear strength did not exhibit shear failures. Instead, they exhibited a bearing type of failure. The interlaminar shear strength, therefore, is at least equal to, or greater than the interlaminar shear stress values given in table V. Even after the thermal postcure composite systems II, III, and VI displayed thermoplasticity at 600° F. The thermoplastic nature of systems II and III can perhaps be attributed to relatively low Tg values for the resin matrix. This argument, however, it not valid for system VI, because the Tg value for the polymer resulting from the DAB/PPGB combination is 702° F (ref. 7). The Tg value for the TABP/PPGB polymer used in system I is appreciably lower (619° F), yet composite system I did not exhibit thermoplasticity at 600° F.

Data are not presented for sytem V in table V because of previously discussed fiber wetting problems in the fabrication of composites. Similar problems were encountered with system VI, therefore further investigation of composite systems V and VI was terminated.

Figure 4 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 room temperature mechanical properties. All data points are an average of three samples except the room temperature flexural strength for system II, which is an average of two samples. Figure 4 shows that the composite weight retention ranged from good to poor. A correlation between weight loss for the composites and weight loss for the corresponding PPQ films was not apparent.

The results of flexural tests after isothermal exposure in air at 600° F showed that composite systems I and II exhibited good retention of their short-time 600° F strength. System III exhibited an increase of flexural strength after 100 hours of exposure. This could be attributed to further post-curing during the exposure. The flexural strength of system IV decreased rapidly during exposure. Microscopic examination of sectioned specimens of system IV showed the presence of interply voids rather than intraply voids which would have resulted from poor fiber wetting. The formation of interply voids is attributed to degradation of the polymer during the elevated temperature cure.

The interlaminar shear data show excellent retention of short-time 600° F values on exposure at 600° F in air. It should be pointed out that composite system III lost thermoplasticity somewhere between 0 and 100 hours of exposure. System II lost its thermoplasticity between 100 and 200 hours. The interlaminar shear strength test is conducted in a manner which precludes taking a thermoplastic specimen to failure. Therefore, no failure points for composite systems II and III were observed until the indicated test times.

The weight loss and mechanical property tests were discontinued at various times at which appreciable surface degradation of the resin matrix had occurred, as indicated by the appearance of loose fibers.

Of all the monomer combinations investigated in this study, composite system I (TABP/PPGB) displayed the best overall performance. In fact, the data obtained in this investigation using the in situ polymerization of monomers approach are significantly better than the data reported in reference 1, using conventional methods for a PPQ copolymer/HMS fiber composite. The composition of the copolymer was TABP,DAB and PPGB in a molar ratio of 3:1:4. This particular combination had been selected as the PPQ polymer which had the best balance of processability and thermo-oxidative stability. Our results show that the in situ polymerization of monomers approach can be used to fabricate PPQ/fiber composites. However, considerable work still needs to be done to eliminate thermoplasticity of PPQ composites without using elevated temperature post-cure cycles. In addition to introducing cross-links, the elevated temperature post-cure undoubtedly causes degradation of the resin matrix or introduces reactive sites for subsequent degradation. Cross-links introduced by chemical reactions at milder conditions would eliminate resin degradation resulting from exorbitantly high post-cure temperatures.

CONCLUSIONS

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

The in situ polymerization approach greatly simplifies the fabrications of PPQ fiber reinforced composites. This approach eliminates the need for polymer synthesis, improves fiber wetting and results in an overall improvement in processability. Our results show that the PPQ monomer combination which provided the best performance at 600° F in air was TABP/PPGB.

Further work needs to be done to eliminate the high temperature thermoplasticity of PPQ polymers by introducing cross-linking by chemical means rather than thermally induced cross-linking during elevated temperature post-curing.

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Table I. - Monomers used for polyphenylquinoxaline synthesis.

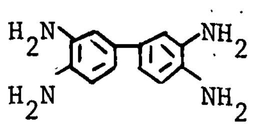
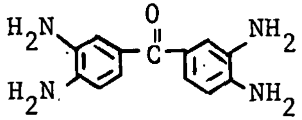
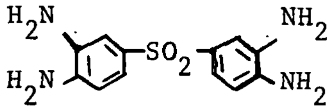
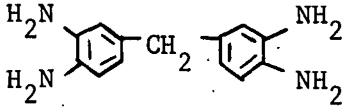
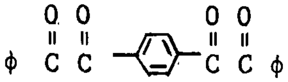
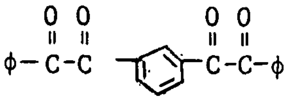
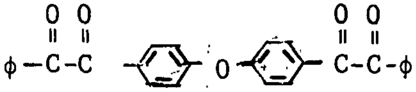
Structure	Name	Abbreviation
	3,3'-Diaminobenzidine	DAB
	3,3',4,4'-Tetraaminobenzophenone	TABP
	3,3'4,4'-Tetraaminodiphenyl sulfone	TADPS
	3,3',4,4'-Tetraaminodiphenylmethane	TADPM
	1,4-Bis(phenylglyoxalyl)benzene	PPGB
	1,3-Bis(phenylglyoxalyl)benezene	MPGB
	4,4'-Oxydibenzil	ODB

Table II. - Weight loss of polyphenylquinoxaline films exposed in air at 600° F for 1 hour.

PPQ film sample	Weight loss, percent
I (TABP/PPGB)	5.8
II (TABP/MPGB)	8.4
III (TABP/ODB)	9.8
IV (TADPS/PPGB)	7.7
V (TADPM/PPGB)	6.2

Table III. - Summary of PPQ/graphite fiber composite processing conditions.

System	Monomers[a]	Volatiles,[b] W%	Fiber,[c] V%	Cure parameters[d] Temperature, °F	Dwell time, sec	Pressure, psi	Cure time, min
I	TABP/PPGB	28.0	54.0	625	90	900	60
II	TABP/MPGB	25.0	50.0	625	60	900	60
III	TABP/ODB	28.0	52.4	610	90	800	30
IV	TADPS/PPGB	22.0	55.0	650	45	600	30
V	TADPM/PPGB	30.0	----	625	105	500	30
VI	DAB/PPGB	36.0	51.0	720	130	900	60

[a] Solids content of impregnating solutions 25-35 weight percent.

[b] Volatile content of prepreg before curing.

[c] Resin content determined by H_2O_2/H_2SO_4 digestion.

[d] All laminates except No. VI subjected to additional curing for 60 min. and 700° F at processing pressure.

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Table IV. - Schedule for elevated temperature post-cure in air.

2 Hours at 392° F

2 Hours at 437° F

2 Hours at 482° F

2 Hours at 572° F

2 Hours at 617° F

2 Hours at 662° F

2 Hours at 700° F

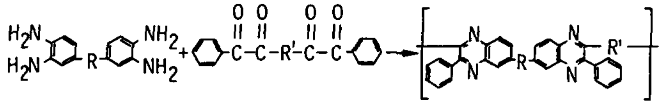
Table V. - Mechanical properties of PPQ/graphite fiber composites at room temperature and 600° F.

Composite system	Flexural str., / Modulus x 10^{-6}, psi		Interlaminar shear stress at failure, psi	
	R.T.	600° F	R.T.	600° F
I	123000/20.7(C)	70000/10.2(C)	7600	4250
II	143000/20.6(T)	69000/9.8(C)	8000	(TP)
III	122000/19.8(C)	26500/---(C)	8500	(TP)
IV	114000/21.2(C)	79000/13.2(C)	4730	3940
VI	--------------	-------------	3600	(TP)

(C) Failed in compression.

(T) Failed in tension.

(TP) Thermoplastic



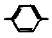
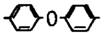
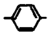
PPQ SYSTEM	R	R'
I	$-\overset{O}{\overset{\Vert}{C}}-$	
II	$-\overset{O}{\overset{\Vert}{C}}-$	
III	$-\overset{O}{\overset{\Vert}{C}}-$	
IV	$-SO_2-$	
V	$-CH_2-$	
VI	NIL	

Figure 1. - Polyphenylquinoxaline systems investigated.

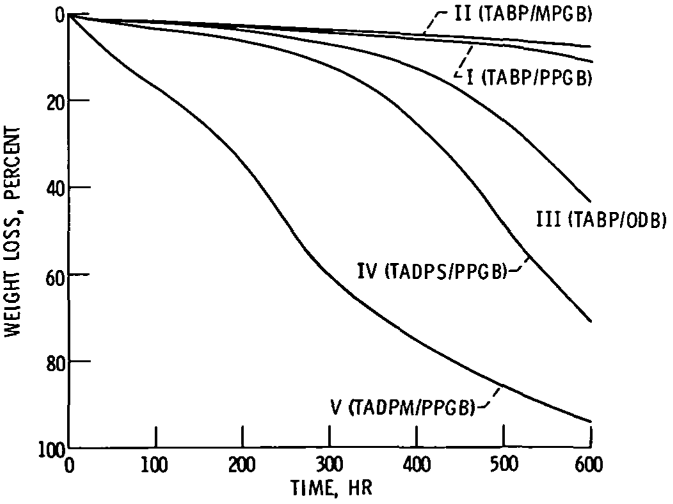
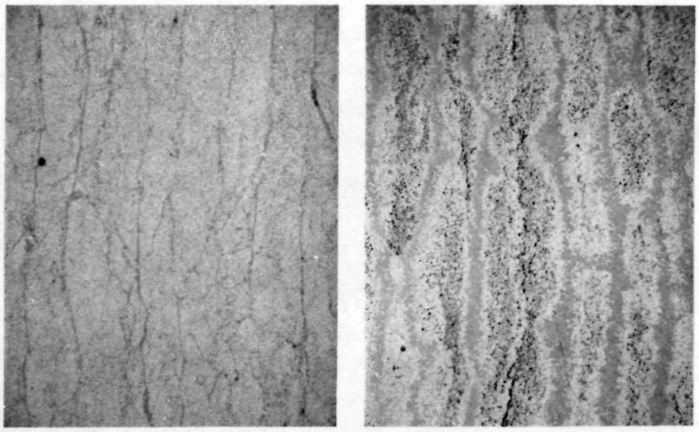


Figure 2. - Weight loss of polyphenylquinoxaline films exposed in air at 600° F.



I VI

Figure 3. - Photomicrographs of PPQ/HMS graphite fiber composite systems I and VI. X50.

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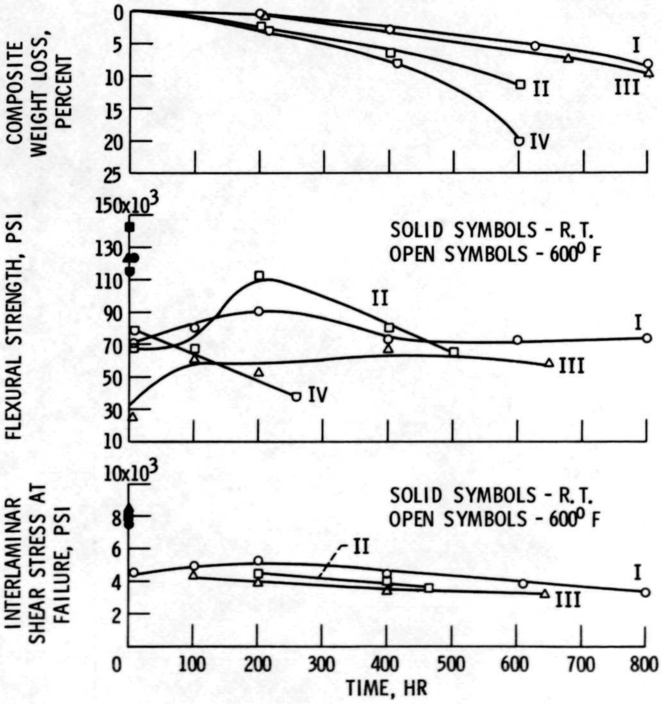

Figure 4. - Properties of PPG/HMS graphite fiber composites as a function of exposure time at 600° F.

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