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DEVELOPMENT OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

By

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June, 1976

The Boeing Aerospace Company
Seattle, Washington 98124

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16. Abstract

Six polyphenylquinoxalines (PPQ) containing pendant cyano (CN) groups were synthesized. The polymers were characterized in terms of inherent viscosity, glass transition temperature, softening temperature and weight loss due to aging in air at 316°C (600°F). The potential for crosslinking PPQs by trimerization of pendant CN groups was investigated. A polymer derived from 1 mole 3,3',4,4'-tetraaminobenzophenone, .2 mole p-bis(p'-cyanophenoxyphenylglyoxalyl)benzene and .8 mole p-bis(phenylglyoxalyl)benzene was selected for more extensive characterization in HM-S graphite fiber-reinforced composites. Mechanical properties were determined using composites made from HM-S fiber and polymer and composites made from HM-S fiber, polymer and a potential CN group trimerization catalyst. Composite mechanical properties, interlaminar shear strength and flexure properties, were determined over the temperature range of +21°C to 316°C.

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FOREWORD

This report presents the work accomplished by the Boeing Aerospace Company during the period of November 14, 1974 to March 15, 1976, on NASA Contract NAS 3-18927, "Development of Polyphenylquinoxaline/Graphite Composites." The work is administered by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, with Dr. P. Delvigs as Project Manager.

Performance of this contract is under the direction of the Structures/Mechanical Engineering Branch, Boeing Aerospace Company; Mr. G. E. Hughes is Program Supervisor, Mr. J. T. Hoggatt is Program Manager. Dr. Jose' G. Shdo is Technical Leader and Principal Investigator on polymer synthesis and characterization and composite studies.

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1.0 INTRODUCTION AND SUMMARY

During performance of NASA contract NAS3-16799 (Reference 1) a polyphenylquinoxaline (PPQ) containing cyano (CN) groups pendant along the polymer's backbone was synthesized. Although the polymer demonstrated excellent resistance to degradation at 316°C (600°F), its potential for use in high temperature composites was not investigated because of a tendency to form gels within one-half hour after mixing of ingredients thus making it difficult for processing into composites. Since the CN containing PPQ system had both the potential for extended service at elevated temperature and CN groups which could enter into crosslinking reactions, investigations to improve processing characteristics and gain a better understanding on crosslinking the polymer through reactions at the CN groups were warranted.

This program was divided into two technical tasks. The first task was devoted to the synthesis and characterization of new polyphenylquinoxaline derivatives containing different quantities of pendant CN groups. Six CN containing PPQs were synthesized and characterized. The PPQs were derived from different combinations of 3,3'-diaminobenzidine, 3,3',4,4'-tetraaminobenzophenone, p-bis(phenylglyoxalyl)benzene and para-bis(p'-cyanophenoxyphenylglyoxalyl)-benzene. Studies were conducted to determine if the CN containing PPQ could be crosslinked by treatment with catalysts which cause CN groups to trimerize. Polymer mechanical, or flow characteristics due to exposure to elevated temperatures and CN crosslinking catalysts were determined. One polymer was selected for Task II studies.

Task II was devoted to composite fabrication and evaluations. Two sets of composites were investigated in Task II. One set of composites was derived from the selected polymer, using Hercules HM-S graphite fiber, without added catalyst. The second set of composites incorporated a small amount of tetraisopropyltitanate crosslinking catalyst.

1.0 (Continued)

The PMR (Polymerization of Monomeric Reactants) approach was used for preparation of CN PPQ composites. In the PMR approach an ethanol/xylene mixture was used as carrier for polymer ingredients thus opening the potential for future processing of PPQ composites without use of toxic or corrosive solvents. Mechanical properties of composites were determined at 21°C (70°F) and 316°C (600°F). CN PPQ/HM-S graphite composites exhibited flexure strength of 7.12×10^8 N/m^2 (103.3 Ksi) at room temperature, and 3.50×10^8 N/m^2 (50.8 Ksi) at 316°C. After exposure in air for 600 hours at 316°C, the composites retained 100 percent of their initial 316°C flexural strength.

2.0 TASK I - SYNTHESES AND CHARACTERIZATION

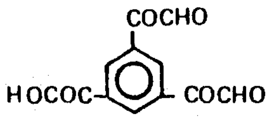
The objectives of Task I were to synthesize and characterize polyphenylquinoxalines (PPQ) which have latent cyano (CN) crosslinking groups pendant along the polymer back bone and to investigate potentials for crosslinking the PPQs through chemical reactions at the CN groups.

2.1 Synthesis and Characterization

This section is divided into two parts. The first part describes generalized reactant synthesis while the second part describes generalized polymer synthesis. Details on reactant and polymer syntheses are given in the Appendix.

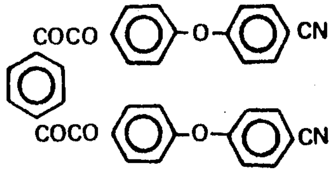
2.1.1 Reactant Synthesis

The carbonyl compounds shown below were initially selected for synthesis of the PPQs.



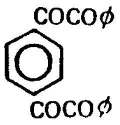
tris-glyoxalylbenzene

TGB (I)



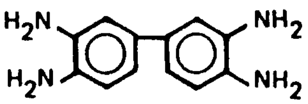
para-bis(p'-cyanophenoxy-
phenylglyoxalyl)benzene

p-CPGB (II)



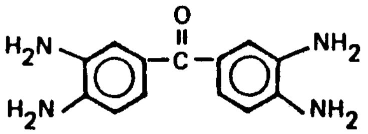
para-bis(phenylglyoxalyl)-
benzene

p-BPGB (III)



3,3'-diaminobenzidine

DAB (IV)



3,3',4,4'-tetraaminobenzophenone

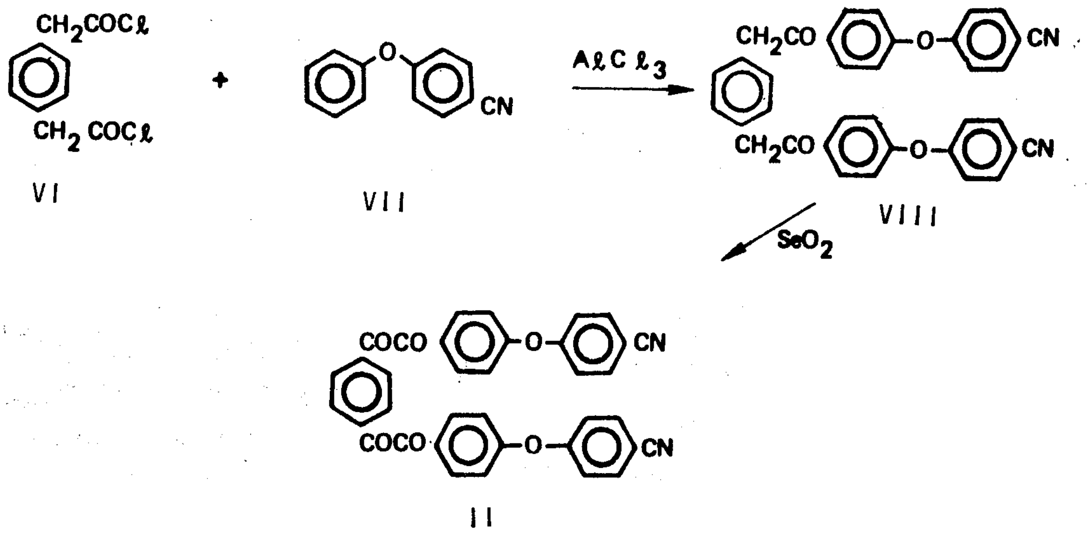
TAB (V)

2.1.1 (Continued)

A minor effort was devoted to an attempted synthesis of TGB(I) early in Task I. Results of the work suggested that synthesis of I would be difficult and beyond budget and schedules allowed for Task I. Therefore, the remainder of Task I concentrated on synthesis of PPQs derived from various combinations of monomers II through V. Below are generalized descriptions on monomer synthesis approaches:

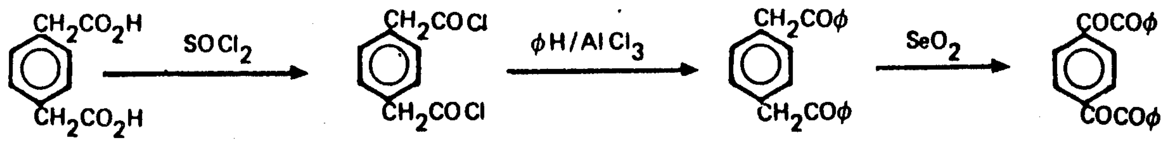
Trisglyoxalylbenzenene, TGB(I) Attempted Synthesis: A brief investigation was conducted to synthesize TGB(I) by oxidation of 1, 3, 5-triacetylbenzene with selenium dioxide in dioxane and water. The reaction's liquid phase yielded a substance which, after precipitation and drying could not be purified because of lack in solubility in common solvents such as acetic acid, m-cresol and chloroform.

Para-bis(p'-cyanophenoxyphenylglyoxalyl)benzene, p-CPGB(II): The tetracarbonyl compound p-CPGB(II) was synthesized in general accord with the following previously reported reaction sequence (Reference 1):



2.1.1 (Continued)

Para-bis(phenylglyoxalyl)benzene, p-BPGB (III): The tetracarbonyl compound p-BPGB(III) was prepared in accord with the following previously reported reaction sequence (Reference 1 and Reference 2).



IX X XI III

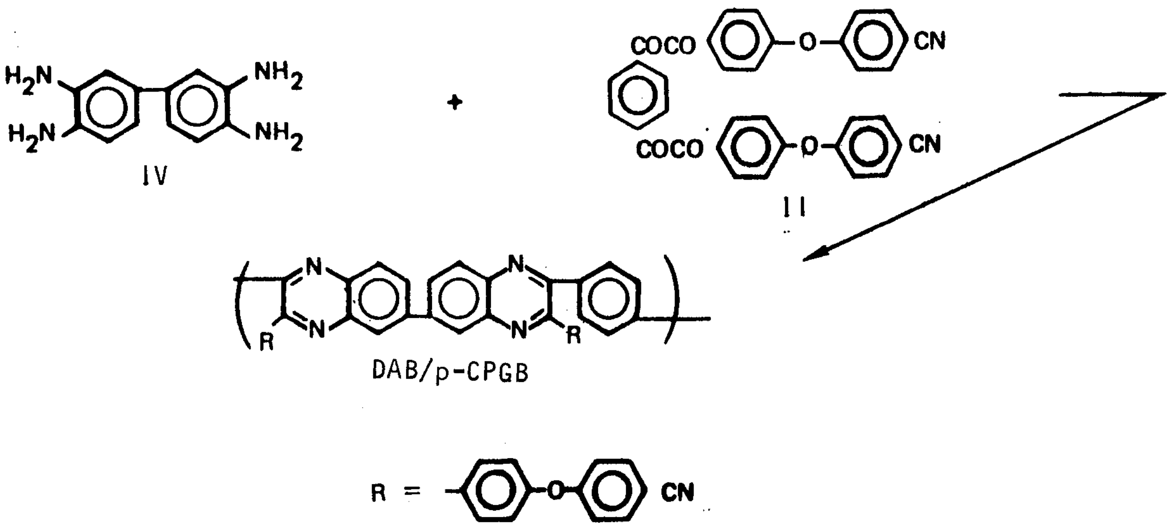
Tetraamines: The two tetraamines 3,3'-diaminobenzidine DAB (IV) and 3,3',4,4'- tetraaminobenzophenone TAB (V) were purchased from commercial sources and purified in-house. DAB (IV) was recrystallized from water and TAB (V) was recrystallized from dimethylformamide (DMF).

2.1.2 Polymer Synthesis

Seven different PPQs were synthesized and characterized in Task I. The polymers are listed in Table 1 and are briefly discussed below. The following approaches were investigated to prepare CN containing PPQs derived from p-CPGB: 1. Variation in amine/tetracarbonyl stoichiometry; 2. Copolymerization of p-CPGB and a second tetracarbonyl compound (p-BPGB, III) with DAB (IV) and/or TAB (V); and 3. Incremental addition of tetraamines to dispersions of tetracarbonyl compounds.

2.1.2 (Continued)

<u>DAB/p-CPGB:</u> Two polymers, each derived from different stoichiometric ratios of DAB (IV) and p-CPGB (I) were synthesized. The polymers and polymer parameters are listed under Item 1 and Item 2, Table 1.



In a preliminary synthesis, the polymer listed under Item 1, Table 1 was prepared using an excess of p-CPGB. A ratio of DAB/p-CPGB = 1/1.05 yielded a gel within 2 hours after mixing ingredients in m-cresol. Previously (Reference I) a ratio of DAB/p-CPGB=1 yielded gels 1/2-1 hour after ingredient mixing.

A different approach was used in the synthesis of the DAB/p-CPGB polymer listed under Item 2, Table 1: The amine DAB was added incrementally over a period of 3 hours to a m-cresol dispersion of p-CPGB. A greater imbalance

TABLE 1: CHARACTERIZATION OF POLYPHENYLQUINOXALINES

Item No.	Polymer No. JS-	Polymer [1]	Stoichiometry (CO/NH_2) [2]	Solids Concentration (%) [3]	η_{inh} dl/g [4]	DSC Tg °C [5]	PST °C [6]
1	25-1	DAB/p-CPGB	1/1.05	15	[7]	340	>316
2	28-1	DAB/p-CPGB	1/1.08	10	[7]	355	312
3	25-2	DAB/p-CPGB/p-BPGB	1/.5/.5	20	[7]	300	>316
4	25-3	DAB/p-CPGB/p-BPGB	1/.2/.8	20	[7]	315	>316
5	25-4	TAB/p-CPGB/p-BPGB	1/.5/.5	20	.96	275	310
6	25-5	TAB/p-CPGB/p-BPGB	1/.2/.8	10	.84	304	320
7	44	DAB/TAB/p-BPGB	.5/.5/1	15	1.76	265	280

[1] DAB = 3,3'-diaminobenzidine; p-CPGB = p-bis(p'=cyanophenoxyphenylglyoxalyl)benzene; p-BPGB = p-bis(phenylglyoxalyl)benzene TAB = 3,3',4,4'-tetraaminobenzophenone.

[2] Mole ratio of tetraamine to tetracarbonyl monomers.

[3] Based upon weight of polymer and weight of m-cresol solvent

[4] Inherent viscosity in 0.5% m-cresol solution at 25°C.

[5] Glass transition temperature, determined by DSC (ΔT = 20°C/min in N_2)

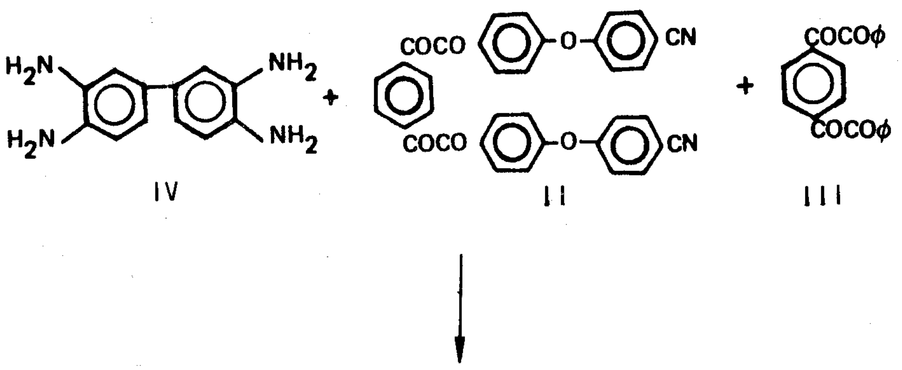
[6] Polymer softening temperature, determined on Fisher-Johns melting point apparatus under slight pressure on polymer.

[7] Polymer inherent viscosity could not be determined due to polymer partial insolubility in m-cresol or concentrated sulfuric acid.

2.1.2 (Continued)

in reactants' stoichiometry was also used. Inasmuch as the overall reaction time was extended to 3 hours, a gel began forming 1/2 hour after the final increment of DAB was added to the reaction mixture.

<u>DAB/p-CPGB/p-BPGB:</u> Two random type copolymers derived from different stoichiometric ratios of DAB (IV), p-CPGB (II) and p-BPGB (III) were synthesized. The copolymers and their parameters are listed under Item 3 and Item 4, Table 1.

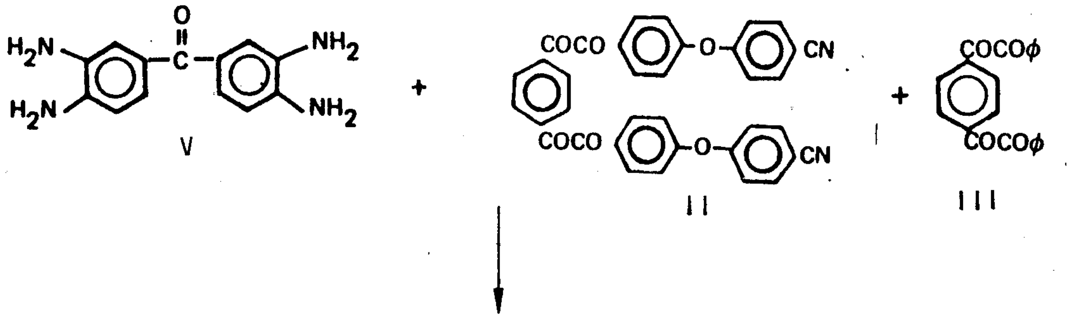


DAB/p-CPGB/p-BPGB
Random PPQ Copolymer

The copolymers were prepared by adding DAB to individual dispersions of p-CPGB and p-BPGB in <u>m</u>-cresol. Onset of gel formation was evident two hours after DAB addition.

2.1.2 (Continued)

TAB/p-CPGB/p-BPGB: Two random type copolymers derived from different stoichiometric ratios of TAB (V), p-CPGB(II) and p-BPGB (III) were synthesized. The copolymers and their parameters are listed under Item 5 and Item 6, Table 1.



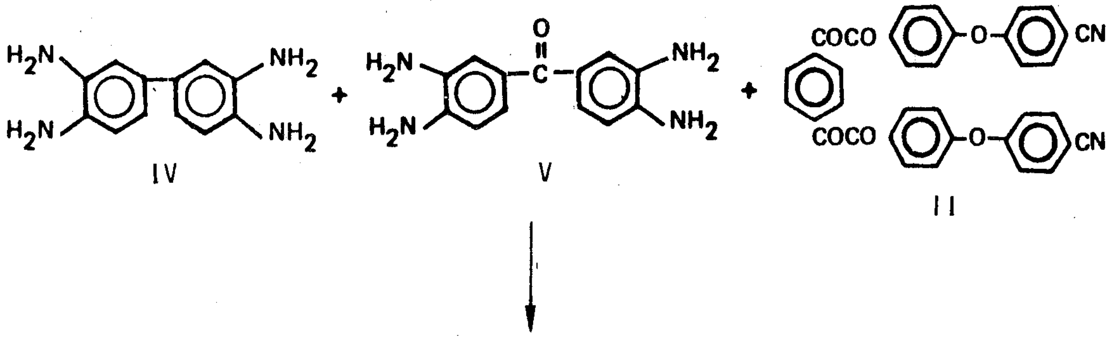
TAB/p-CPGB/p-BPGB
Random PPQ Copolymer

The copolymer listed under Item 5 was prepared using the same procedure as described for the previous two copolymers. Onset of gel formation was evident two hours after TAB addition.

Different results were obtained in the synthesis of the copolymer listed under Item 6, Table 1 inasmuch as gel formation was suppressed. Two factors were varied in the polymer's synthesis: (1) The amine (TAB) was added incrementally over a period of 24 hours to a m-cresol dispersion of the two tetracarbonyl compounds; and (2) The quantity of p-CPGB used was decreased to the ratio listed under Item 6, Table 1. A small sample of the polymer solution stood approximately 30 days without apparent gellation.

2.1.2 (Continued)

DAB/TAB/p-CPGB: Two tetraamines and one tetracarbonyl compound were used in synthesis of this PPQ. The copolymer is listed under Item 7, Table 1. The random copolymers described in the previous paragraphs were synthesized from reactions of one tetraamine and two tetracarbonyl compounds.



DAB/TAB/p-CPGB

Random PPQ Copolymer

A mixture as fine powder of the two tetraamines was added to a m-cresol dispersion of p-CPGB. The amine mixture was added incrementally over a period of 3 hours to a m-cresol dispersion of p-CPGB. Gellation was not observed 30 days after polymer synthesis.

2.2 Polymer Evaluations

This section is divided into two parts. The first part is on general polymer characterization tests and includes elevated temperature [316°C (600°F)] aging test results obtained with six of the seven polymers listed in Table 1. The second section is devoted to crosslinking studies.

2.2.1 Polymer Characterization

General characterization tests were conducted on the polymers described under paragraph 2.1.2. The polymers were characterized in terms of inherent viscosity (η_{inh}), glass transition temperature (T_g) and polymer softening temperature. Results of these characterization tests are summarized in Table 1.

Isothermal aging of polymer films in air at 316°C (600°F) was conducted. Table 2 summarizes results of the elevated temperature aging tests. Six of the seven polymers listed in Table 1 were subjected to heat aging. Because of structural similarity between the two DAB/p-CPGB polymers listed under Item 1 and Item 2, Table 1, only one of the two polymers (polymer No. JS28-1) was included in the elevated temperature aging tests. Greatest weight retention, after aging 500 hours in air at 316°C (600°F), was displayed by the DAB/TAB/p-CPGB polymer listed under Item 7, Table 2. The second highest weight retention was displayed by the two copolymers derived from TAB/p-CPGB/p-BPGB. These polymers are listed under Item 5 and Item 6, Table 2.

2.2.2 Polymer Crosslinking Studies

An investigation was conducted to attempt to crosslink the PPQs containing CN groups. The initial objective of the investigation was to determine if chemical conditions known to be conducive to trimerization of CN groups were effective in increasing Tg and elevated temperature aging life of CN PPQs. Two CN containing PPQ polymers derived from TAB/p-CPGB/p-BPGB were selected for the initial part of the investigation. The selected polymers are listed under Item 5 and Item 6, Table 1. Selection of these polymers was based on the following factors: high polymer softening temperature, high Tg and high resistance to degradation at 316°C (600°F). Of the polymers listed

TABLE 2: ISOTHERMAL AGING OF POLYPHENYLQUINOXALINE POLYMER FILMS IN AIR AT 316°C (600°F)

Item No.	Polymer No. JS-	Polymer [1]	Stoichiometry (CO/NH_2) [2]	Weight Loss (%) [3] hours at 316°C (600°F)			
				50	100	250	500
1	25-1	DAB/p-CPGB [4]	1/1.05	-	-	-	-
2	28-1	DAB/p-CPGB	1/1.08	3.1	4.2	6.4	25
3	25-2	DAB/p-CPGB/p-BPGB	1/.5/.5	2.3	3.4	7.1	37
4	25-3	DAB/p-CPGB/p-BPGB	1/.2/.8	2.9	4.2	7.8	40
5	25-4	TAB/p-CPGB/p-BPGB	1/.5/.5	2.3	3.3	4.9	14
6	25-5	TAB/p-CPGB/p-BPGB	1/.2/.8	1.5	3.3	3.8	16
7	44	DAB/TAB/p-CPGB	.5/.5/1	2.4	3.0	4.9	9.4

[1] DAB = 3,3'-diaminobenzidine; p-CPGB = p-bis(p'-cyanophenoxyphenylglyoxalyl)benzene; p-BPGB = p-bis(phenylglyoxalyl)benzene; TAB = 3,3',4,4'-tetraaminobenzophenone.

[2] Mole ratio of tetraamine to tetracarbonyl monomers.

[3] Films were aged inside beakers in an air circulating oven.

[4] Not included in the aging program.

in Table 1, the DAB/TAB/p-CPGB polymer (item 7) exhibited the highest resistance to degradation at 316°C (600°F). This polymer was not selected for this study because of its very low polymer softening temperature and Tg.

Para-toluenesulfonic Acid and 2-pyrrolidinone as Potential Crosslinking Catalysts: Preliminary screening tests were conducted to identify a chemistry to effect crosslinking through reactions at the CN groups in the selected PPQs. Crosslinking by treatment of each polymer with 2-pyrrolidinone and p-toluenesulfonic acid was investigated. The monomers p-toluenesulfonic acid and 2-pyrrolidinone have been used by others (Reference 3 and Reference 4) to effect CN trimerization. Films, cast from m-cresol/polymer solutions containing the above monomers, were aged 500 hours at 316°C (600°F). The results are summarized in Table 3. The systems which had been exposed to the above monomers exhibited weight losses of 22% to 37%. For comparisons, the control polymers, also listed in Table 3, only lost 14% and 16% on aging 500 hours at 316°C (600°F). Control polymers' heat aging data listed in Table 3 were abstracted from Table 2. The above monomers accelerated polymer degradation at 316°C.

Organometallics as Potential Crosslinking Catalysts: Investigations were conducted to determine if CN groups in PPQs could be crosslinked by organometallic monomers such as tri-n-propyltin oxide, ethylborate and tetraisopropyltitanate. The monomer tri-n-butyltin oxide (a homolog of tri-n-propyltin oxide) has been previously used in studies related to trimerization of pendant CN groups (Reference 5). One polymer was used in this part of the investigations. The selected polymer was JS 25-5, listed under Item 6, Table 1. This polymer remained soluble and did not gel on standing for an extended period of time. The investigations are described below:

Tri-n-propyltin Oxide--A chloroform solution containing 10% of polymer and 1% tri-n-propyltin oxide was shaken over a period of 72 hours. Apparent

TABLE 3. ISOTHERMAL (316°C) AGING OF CROSSLINK CATALYST TREATED PPQ FILMS

ITEM NO.	POLYMER NO. JS-	POTENTIAL CROSSLINK CATALYST	% WEIGHT LOSS AFTER AGING IN AIR AT 316°C [1]
1	25-4	none (control)	14
2	25-4	p-toluenesulfonic acid	36
3	25-4	2-pyrrolidinone	37
4	25-5	none (control)	16
5	25-5	p-toluenesulfonic acid	33
6	25-5	2-pyrrolidinone	22

[1] Films were aged inside beakers in an air circulating oven (500 hours)

TABLE 4. ORGANOMETAL/PPQ SOLUTION COMPOSITION

ITEM NO.	$CHCl_3$ SOLVENT WEIGHT (g)	POLYMER WEIGHT (g)	ORGANOMETAL		
			COMPOUND	WEIGHT (g)	% [1]
1	3.8	0.2	tetraisopropyltitanate	.004	2
2	3.8	0.2	tetraisopropyltitanate	.008	4
3	3.8	0.2	tetraisopropyltitanate	.016	8
4	3.8	0.2	ethylborate	.004	2
5	3.8	0.2	ethylborate	.008	4
6	3.8	0.2	ethylborate	.016	8

[1] % by weight relative to polymer weight.

changes in solution viscosity and infrared spectrum were not observed during the 72 hour shaking. Addition of the tri-n-propyltin oxide did not cause any observable change in the infrared spectrum of the solution. It was concluded that the tin oxide was ineffective for the desired reaction.

Tetraisopropyltitanate and Ethylborate-- Chloroform solutions of the selected polymer were treated individually with three different quantities of each tetraisopropyltitanate and the Lewis acid ethylborate. The solutions were agitated vigorously for 120 hours. The CN infrared absorption band at 4.45μ was monitored during this period of time. Significant changes in the absorption band intensity were not noticed. After 120 hours agitation, the titanate containing solution exhibited viscosity increases. Although viscosity was not monitored, the rising viscosity roughly corresponded with quantity of added titanate: the solution with highest titanate content exhibited the highest viscosity. The increases in viscosity of titanate-containing solutions suggested occurrence of some type of crosslinking reaction. The borate containing solutions did not exhibit any noticeable viscosity increase. Table 4 lists polymer, solvent and catalyst content.

Additional investigations were conducted to determine effects of tetraisopropyltitanate on elevated temperature aging characteristics and thermomechanical properties of the selected copolymer TAB/p-CPGB/p-BPGB.

Elevated temperature aging of TAB/p-CPGB/p-BPGB films containing 2% to 8% tetraisopropyltitanate was conducted. Table 5 summarizes film preparation parameters and film weight losses after aging 500 hours in air at 316°C (600°F). Least weight losses were exhibited by the control (Item 1, Table 5) and the system containing 2% titanate (Item 2, Table 5).

TABLE 5: Isothermal Aging of Tetraisopropyltitanate Treated TAB/pCPGB/pBPGB Polyphenylquinoxaline Films in Air at 316°C (600°F)

ITEM NO.	FILM CASTING SOLUTION PARAMETERS				POLYMER FILM WEIGHT LOSS (%) [4]			
					Hours at 316°C (600°F)			
	Polymer Weight (g)	Solvent [1] Weight (g)	Titanate [2] Weight (g)	% Titanate [3]	50	100	250	500
1	.75	4.25	None	-	1.10	1.61	3.10	4.93
2	↕	↕	.014	2	1.08	1.58	3.05	4.80
3			.028	4	1.59	2.10	4.73	8.14
4			.042	6	1.76	2.32	4.77	8.80
5	.75	4.25	.056	8	2.80	3.81	8.86	17.9

[1] $CHC\ell_3$ was used as solvent.

[2] Tetraisopropyltitanate was immediately mixed after weighing into polymer solution.

[3] % Titanate by weight relative to polymer weight.

[4] Polymer films were cast from $CHC\ell_3$ solutions.

Table 6: THERMOMECHANICAL ANALYSES OF TITANATE CONTAINING TAB/pCPGB/pBPGB FILMS

Item No.	Titanate Content (%)	TMA Analysis [1]	
		Polymer Flow or Softening Temperature °C (°F) [2]	
		Unaged Specimens [3]	Heat Aged Specimens [3] [4]
1	0 (Control)	310 (590)	345 (652)
2	2	315 (598)	328 (622)
3	4	325 (617)	330 (626)
4	6	328 (622)	322 (611)
5	8	298 (568)	330 (626)

[1] E. I. DuPont deNemours and Company, 941 Thermo Mechanical Analyzer (TMA) was used. Heat-up rate, 20°C min; N_2 atmosphere; penetration probe 5g load, .064 sq. cm. flat tip.

[2] Temperature at which polymers exhibit maximum flow rate change.

[3] Polymer films were first exposed to 350°C ($\frac{1}{2}$ hr.) and cooled to room temperature under [1] conditions in the TMA analyzer. The reported values were obtained on re-runs without displacing test specimens from the sample holder.

[4] Specimens were aged 250 hrs at 316°C inside beakers in an air circulating oven.

2.2.2 (Continued)

It is postulated that weight losses due to actual polymer degradation of the titanate-containing systems are lower than the obtained values listed in Table 5. The obtained values include weight losses due to volatilization of titanate and partial volatilization of titanate thermolysis products. On the basis where titanate is totally converted into non-volatile titanium dioxide and volatile isopropoxide fragments, approximately half of the weights of added tetraisopropyltitanate are manifest in the weight loss values listed in Table 5. By adjusting for partial volatilization of titanate as isopropoxide fragments, the system listed under Item 2, Table 5, would have an approximate weight loss of 3.8% after 500 hours at 316°C. Although the weight loss differences are small, the control and the 2% titanate-containing PPQ, in film form, exhibited the lowest weight losses.

Thermo Mechanical Analyses (TMA) were conducted on TAB/p-CPGB/p-BPGB polymer films containing the four different levels of titanate and the control listed in Table 5. The tests were conducted to determine effect of added titanate on polymer flow characteristics before and after aging at elevated temperature. Table 6 lists TMA test results before and after heat aging the polymers in film form 250 hours in air at 316°C. The results summarized in Table 6 are irregular: Before heat aging at 316°C (600°F), specimens exhibited gradual increases in their TMA flow temperature as titanate content increased from 0% to 6%. However, the system with 8% titanate exhibited the lowest TMA flow temperature. A less consistent pattern in TMA flow temperature was obtained after heat aging: The control exhibited the greatest change in TMA flow temperature. The titanate-containing systems did not display any consistent trend in TMA flow temperature.

2.3 Polymer Selection for Task II

The TAB/p-CPGB/p-BPGB random PPQ copolymer (described in Item 6, Table 1) was selected for evaluation in high temperature graphite reinforced composites. This selection was based primarily on the polymer's elevated temperature aging characteristics, high Tg and potential for ease in processing into composites.

The composites prepared in this section had a nominal fiber volume content of 60% based on weights of fiber and polymer used. A fiber specific gravity of 1.94 (Reference 6) and resin specific gravity of 1.25 were used in the calculations. Resin density was determined gravimetrically.

3.0 TASK II - COMPOSITE FABRICATION AND EVALUATION

Task II was divided into two parts: Preliminary Composite Fabrication Studies and Final Composite Evaluation. The Preliminary Composite Fabrication Studies were conducted to provide a basis for selecting a process for fabrication of final composites. Additional TAB/p-CPGB/p-BPGB random PPQ copolymer selected for Task II composite studies was synthesized (paragraph 6.1.2).

3.1 Preliminary Composite Fabrication Studies

Preliminary Composite Fabrication Studies were comprised of two parts: Impregnation Studies and Composite Cure Studies. Results of the Studies are summarized in Table 7. Details of composite preparation parameters and interlaminar shear test results are also listed in Table 7. The Studies were conducted to evaluate the selected polymer's characteristics for processing into composites. Preliminary composites were derived from the selected polymer and HM-S graphite. All composites had a fiber content of 60% by volume. Three different solvents and two different impregnation methods were investigated in this study: Methanol, m-cresol and chloroform (with 2% tetraisopropyltitanate) were used as media for the selected polymer. An effort was devoted to a composite cure and postcure study. The cure and postcure studies were conducted to provide a basis for selection of parameters for use in preparation of composites for final evaluations. Impregnation studies and cure and postcure studies are briefly described in paragraph 3.1.1 and paragraph 3.1.2. Paragraph 6.1.3, Appendix describes details of each impregnation method used.

TABLE 7. SHORT BEAM INTERLAMINAR SHEAR STRENGTH OF PRELIMINARY COMPOSITES

Laminate Series No.	Test Temp. °C (°F)	ILS Strength		Impregnation Technique and Solvent	Lamination Parameters	
		10^6 N/m^2	(psi)		Cure	Postcure
A-1	21 (70)	31.6	(4588)	[1]	[2]	None
A-2		31.3	(4540)	↑	↑	↑
A-3	↓	31.2	(4530)			
		31.4	(4552)			
A-4	316 (600)	24.6	(3568)			
A-5		25.4	(3682)	↓	↓	↓
A-6	↓	24.7	(3588)	[1]	[2]	None
		24.9	(3612)			
B-1	21 (70)	30.8	(4467)	[1]	[2]	[3]
B-2		32.0	(4638)	↑	↑	↑
B-3	↓	29.9	(4336)			
		30.9	(4480)			
B-4	316 (600)	21.1	(3065)			
B-5		22.9	(3326)	↓	↓	↓
B-6	↓	26.7	(3871)	[1]	[2]	[3]
		23.6	(3420)			
C-1	21 (70)	18.4	(2672)	[4]	[2]	None
C-2		18.2	(2640)	↑	↑	↑
C-3	↓	18.1	(2636)			
		18.3	(2649)			
C-5	316 (600)	5.8	(842)			
C-6		9.1	(1326)	↓	↓	↓
C-7	↓	7.4	(1082)	[4]	[2]	None
		7.5	(1083)			
D-1	21 (70)	14.7	(2136)	[4]	[2]	[3]
D-2		15.8	(2291)	↑	↑	↑
D-3	↓	16.7	(2447)			
		15.8	(2291)			
D-4	316 (600	11.8	(1708)			
D-5		9.9	(1441)	↓	↓	↓
D-6	↓	13.3	(1930)	[4]	[2]	[3]
		11.7	(1693)			
E-1	21 (70)	13.8	(1997)	[5]	[2]	None
E-2		16.2	(2356)	↑	↑	↑
E-3	↓	17.1	(2491)			
		17.2	(2281)			
E-4	316 (600)	10.1	(1468)			
E-5		8.5	(1227)	↓	↓	
E-6	↓	10.4	(1511)	[5]	[2]	None
		9.7	(1402)			
F-1	21 (70)	17.4	(2525)	[5]	[2]	[3]
F-2		16.5	(2397)	↑	↑	↑
F-3	↓	13.2	(1918)			
		15.7	(2280)			
F-4	316 (600)	9.4	(1365)			
F-5		10.6	(1532)	↓	↓	↓
F-6	↓	12.1	(1760)	[5]	[2]	[3]
		10.7	(1552)			
G-1	21 (70)	35.1	(5100)	[4]	[2]	[6]
G-2	↓	39.1	(5670)	↑	↑	↑
G-3		42.0	(6080)			
		38.7	(5611)			
G-4	316 (600)	11.4	(1655)			
G-5	↓	8.1	(1175)	↓	↓	↓
G-6		9.0	(1312)	[4]	[2]	[6]
		9.5	(1380)			
H-3	21 (70)	45.6	(6616)	[4]	[2]	[7]
H-4	↓	44.1	(6392)	↑	↑	↑
		44.8	(6504)			
H-1	316 (600)	19.1	(2774)	↓	↓	↓
H-2	↓	17.7	(2561)	[4]	[2]	[7]
		18.4	(2667)			

[1] PMR impregnation technique was used. TAB/p-CPGB/p-BPGB in the ratio of 1/.2/.8, respectively, as a fine powder mixture was stirred five minutes in a boiling solution of 4 parts ethanol to 1 part xylene. The mixture was poured evenly onto preweighed graphite fibers, dried one hour at room temperature and laminated.

[2] Cured 1/2 hour at 316°C (600°F) and one hour at 343°C (650°F) under a pressure of 1.4×10^6 N/m^2 (200 psi).

[3] Post cured two hours at 343°C (650°F) under a pressure of 1.4×10^0 N/m^2 (200 psi).

[4] Standard impregnation technique was used for prepreg preparation. Appropriate quantity of polymer/meta-cresol solvent was metered into preweighed fibers.

[5] Standard impregnation technique was used for prepreg preparation. Appropriate quantity of polymer/chloroform and 2% tetraisopropyltitanate was metered into preweighed fibers.

[6] Post cured 6-1/2 hours at 343°C (650°F) under a pressure of 1.4×10^6 N/m^2 (200 psi).

[7] Post cured two hours at 399°C (750°F) under a pressure of 1.4×10^6 N/m^2 (200 psi).

3.1.1 Impregnation Studies

Polymerization of Monomeric Reactants (PMR) Impregnation Method. Laminates were prepared using the PMR method (Reference 7). A fine powder mixture of TAB/p-CPGB/p-BPGB in the ratio 1/.2/.8, respectively, was stirred five minutes in a boiling solution of 4/1 ethanol/xylene. The mixture was poured rapidly and evenly onto preweighed graphite fibers. After drying 1 hour a boardy, fragile prepreg resulted. The prepreg had the semi-dry polymer ingredient mixture on one of its sides only. Although the solids in the PMR mixture failed to permeate the fibers during impregnation, improved fiber permeation was accomplished during laminate cure at 343°C (650°F). Table 7 lists, under Laminate No. A-1 through Laminate B-6, the resulting composite's short beam interlaminar shear strength (ILS) at ambient temperature and 316°C. The values listed in Table 7 under the Series B laminates are within 10% of values previously reported (Reference 1) for laminates which were post cured at 455°C (850°F). The ILS values obtained in this work are considered exceptionally high, considering their void content (~8% estimated) as evident from photomicrographs. Figure 1 and Figure 2 show the cross section of a representative of the Series A- and Series B- laminates listed in Table 7.

The PMR system described above represents a new approach for preparation of PPQ/graphite prepregs. To our knowledge ethanol/xylene mixtures have not been used as carrier medium for ingredients in the PMR impregnation method. Additional work was not conducted to improve processing characteristics because of budget and schedule considerations.

Standard Impregnation. The standard fiber impregnation method was used to impregnate graphite fibers with chloroform/tetraisopropyltitanate solutions of the selected polymer and to impregnate graphite fibers with m-cresol solutions of the selected polymer. The standard fiber impregnation method consisted of

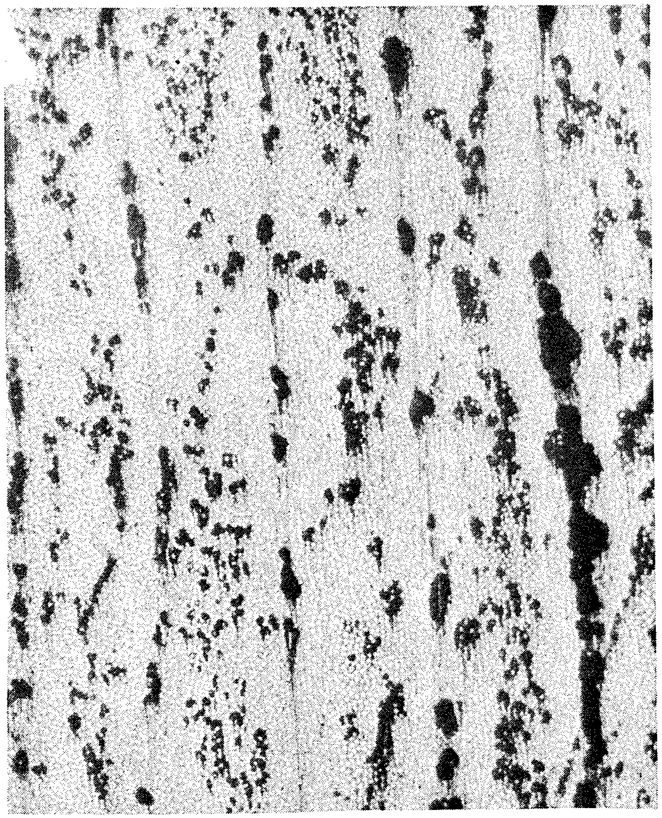


FIGURE 1.
Cross Section Photoenlargement of Laminate A, Table 7 (X100)

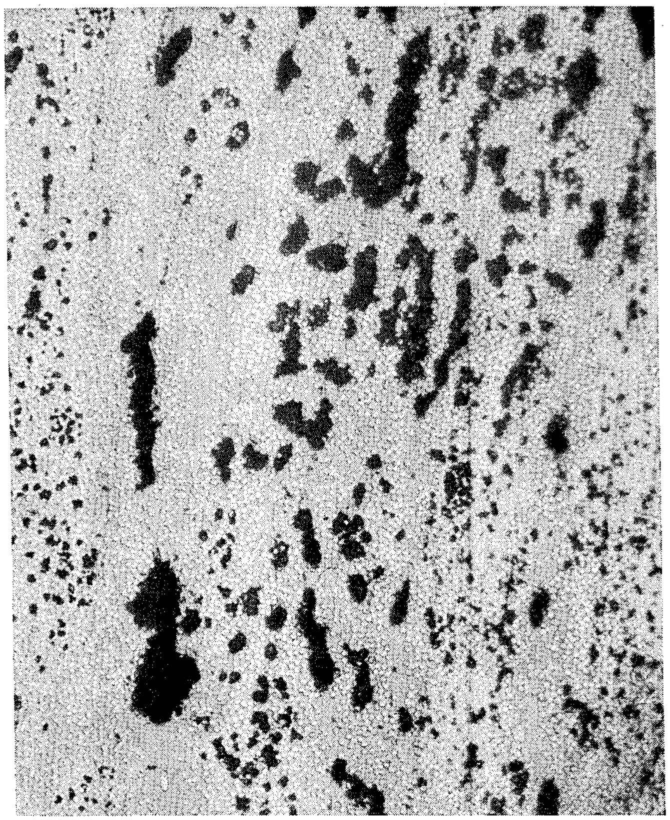


FIGURE 2.
Cross Section Photoenlargement of Laminate B, Table 7 (X100)

adding a known quantity of resin to preweighed, drum-wound fibers. Laminates C-1 through laminates H-1, Table 7, were prepared using the standard fiber impregnation method. The laminates listed in Table 7 are more fully discussed below.

3.1.2 Composite Cure Studies.

The initial objective of Task II was to achieve composite cure at temperatures ≤343°C (650°F). Table 7 laminates A-1 through A-6, C-1 through C-6 and E-1 through E-6 were cured 1/2 hour at 316°C (600°F) and 1 hour at 343°C (650°F). High ILS strength values were obtained from laminates A-1 through A-6. The series A laminates were prepared by the PMR method. Laminates C-1 through C-6 and E-1 through E-6 exhibited low ILS strength; this was attributed to insufficient polymer cure. Even though the series E and series C laminates were cured using the same conditions, the series E laminates exhibited higher ILS strength at 316°C (600°F) than did the series C laminates. The higher ILS strength at 316°C of the series E laminate was partly attributed to added titanate. The lower ILS strength at 316°C (600°F) of series C laminates may be partly attributed to the solvent (m-cresol) used for fiber impregnation. As described in Table 7, the E laminates were prepared using polymer, chloroform solvent and 2% added tetraisopropyltitanate. Further extending laminate exposure to 343°C (650°F) for 2 hours and 6-1/2 hours additionally did not lead to significant changes in elevated temperature ILS strength (refer to laminate series B, D, F and G, Table 7). Significant increases in laminate ILS strength were obtained from the series H laminates listed in Table 7. The series H laminates were postcured 2 hours at 399°C (750°F) after receiving a cure of 1/2 hour at 316°C (600°F) and one hour at 343°C (650°F).

Figure 1 through Figure 8 are cross section photoenlargements of a representative of each laminate series listed in Table 7. Table 8 lists laminate specific gravity.

FIGURE 3.

Cross Section Photoenlargement of Laminate C, Table 7 (X100)

FIGURE 4.

Cross Section Photoenlargement of Laminate D, Table 7 (X100)

FIGURE 5.

Cross Section Photoenlargement of Laminate E, Table 7 (X100)

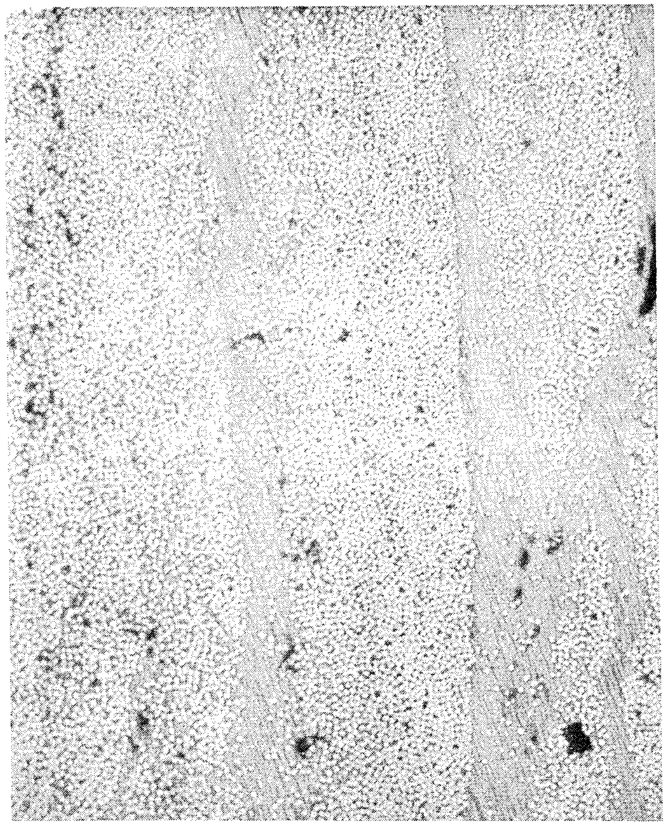


FIGURE 6.

Cross Section Photoenlargement of Laminate F, Table 7 (X100)

FIGURE 7.

Cross Section Photoenlargement of Laminate G, Table 7 (X100)

FIGURE 8.

Cross Section Photoenlargement of Laminate H, Table 7 (X100)

TABLE 8. SPECIFIC GRAVITY OF TASK II PRELIMINARY COMPOSITES

Item No.	Laminate Series [3]	Specific Gravity (25°C) [1]
1	A	1.48
2	B	1.48
3	C	1.49
4	D	1.49
5	E	1.40 [2]
6	F	1.35 [2]
7	G	1.46
8	H	1.47

[1] Specific gravity was determined by dividing specimen weight in air by its apparent weight loss in water at 25°C.

[2] 2% tetraisopropyltitanate was added to polymer prior to fiber impregnation.

[3] Laminate series correspond with laminate designations listed in Table 7.

3.1.2 (Continued)

Examination of the cross section photo enlargements reveal a high void content for series A and B laminates. Calculations made from composite constituents densities (polymer $\rho = 1.25$ g/cc, fiber $\rho = 1.94$ g/cc) and fiber volume (60%) indicate that series A and B laminates, Table 7, have a theoretical void content of 9 % and these values are substantiated by the photoenlargements shown in Figures 1 and 2. Calculations also lead to theoretical void contents of 8% to 16% for series C through H laminates however examination of cross section photographs of series C through H suggests void contents estimated at 2% to 7%, indicating the theoretical calculations are in error, at least for the series C through H laminates. A basis to explain the disagreement between calculated and actual values was not established.

3.2 Final Composite Evaluations

The initial objective of this phase of Task II was to conduct more extensive characterization of composites derived from one system comprised of the selected polymer, crosslinking catalyst and HM-S graphite. A review of the above work under Task II suggested that evaluation of two composite systems would lead to better understanding of the role of the selected polymer behavior in composites and tetraisopropyltitanate on composite elevated temperature aging characteristics. Thus it was decided to evaluate two sets of composites. One set was derived from the PPQ polymer and the second set was the same except 2% tetraisopropyltitanate was added to the polymer before fiber impregnation. Both sets were reinforced with HM-S fibers.

3.2.1 Lamination Parameter Selection

The selected cure/posture schedule for lamination of Task II composite consisted of press curing the prepreg 1/2 hour at 316°C (600°F), 1 hour at 343°C (650°F) and 2 hours at 399°C (750°F) under a pressure of 1.4 x 10^6 N/m^2 (200 psi). These lamination parameters were used to prepare the series H laminates (Table 7) which exhibited the highest ILS strength at room temperature and second highest ILS strength at 316°C of the composites listed in Table 7. Poorly compacted laminates were obtained when the above parameters were used to prepare larger laminates from chloroform/titanate containing prepregs. The poor compaction was tentatively attributed to interplay of the following factors: poor resin flow due to excessive solvent loss; too rapid polymer molecular weight advancement due to crosslinking by the titanate; and insufficient lamination pressure. Therefore two factors were changed to alleviate the compaction problem with the titanate containing system: prepreg solvent content was increased (see paragraph 6.1.3) and lamination pressure was increased to 2.07 x 10^6 N/m^2 (300 psi). These changes enabled preparation of composites with much improved compaction discussed in paragraph 3.2.2.

3.2.2 Final Composite Testing

Two types of composites were fabricated using HM-S graphite yarn and the selected polymer. One type composite was prepared from the selected PPQ in m-cresol, (laminates I and J, Table 9). The second type composite was prepared from the polymer containing 2% tetraisopropyltitanate and dissolved in chloroform (laminates K and L, Table 10). The cure cycle of 1/2 hour at 316°C (600°F), 1 hour at 343°C (650°F) and 2 hours postcure at 399°C (750°F) under 2.07 x 10^6 N/m^2 (300 psi) was used for lamination. Specific gravity, cross section photomicrographs, weight loss due to aging in air at 316°C (600°F), and ILS and flexure properties were determined for each laminate. Below is a brief discussion on each of the test results.

TABLE 9. INTERLAMINAR SHEAR AND FLEXURE PROPERTIES OF TASK II FINAL COMPOSITES

Specimen No. [1] [2]	Exposure Time (hrs)	Exposure Temp. °C(°F)	Test Temp. °C(°F)	Flexure Properties [3] Strength $10^8 N/m^2$	Flexure Properties [3] Strength (10^3 psi)	Flexure Properties [3] Modulus $10^{10} N/m^2$	Flexure Properties [3] Modulus (10^6 psi)	Interlaminar Shear [4] Strength $10^6 N/m^2$	Interlaminar Shear [4] Strength (psi)
1	None	21(70)	21(70)	6.57	(93.8)	9.1	(13.2)	38.6	(5380)
2	↓	↓	↓	7.34	(106.5)	7.4	(10.8)	38.2	(5533)
3				7.55	(109.5)	7.7	(11.2)	40.7	(5907)
				7.12	103.3	8.1	11.7	38.6	5606
4	.1	316(600)	316(600)	3.31	(48.1)	3.2	(4.6)	10.8	(1563)
5	↓	↓	↓	3.67	(53.2)	4.3	(6.2)	13.0	(1886)
6				3.52	(51.0)	4.6	(6.6)	11.1	(1611)
				3.50	50.8	4.0	5.8	11.6	1680
7	100			4.13	(59.8)	4.8	(7.0)	22.7	(3298)
8	↓			4.22	(61.2)	5.5	(8.0)	22.7	(3293)
9				4.08	(59.2)	5.0	(7.3)	24.8	(3596)
				4.14	60.0	5.1	7.4	23.4	3395
10	300			3.92	(56.8)	6.8	(9.8)	20.2	(2935)
11	↓			4.43	(64.3)	5.9	(8.6)	19.3	(2802)
12				4.70	(68.2)	6.9	(10.0)	21.5	(3116)
				4.35	63.1	6.5	9.4	20.3	2951
13	600			3.88	(56.3)	5.5	(7.9)	10.9	(1577)
14	↓			3.56	(51.7)	5.0	(7.2)	11.9	(1731)
15				3.26	(47.4)	3.6	(5.3)	3.3	(476)
				3.57	(51.8)	4.7	6.8	8.7	1260
16	1000			—	—	—	—	—	—
17	↓	↓	↓	—	—	—	—	—	—
18				—	—	—	—	—	—

[1] TAB/p-CPGB/p-BPGB and HM-S graphite laminates (without added titanate)

[2] Fiber volume: 60% by weight

[3] Flexure properties laminate I

[4] ILS properties laminate J

TABLE 10. INTERLAMINAR SHEAR AND FLEXURE PROPERTIES OF TASK II FINAL COMPOSITES

Specimen No. [1] [2]	Exposure Time (hrs)	Exposure Temp. °C(°F)	Test Temp. °C(°F)	Flexure Properties [3] Strength $10^8 N/m^2$	Flexure Properties [3] Strength (10^3 psi)	Flexure Properties [3] Modulus $10^{10} N/m^2$	Flexure Properties [3] Modulus (10^6 psi)	Interlaminar Shear Strength [4] $10^6 N/m^2$	Interlaminar Shear Strength [4] (psi)
1	None	21(70)	21(70)	3.85	(55.9)	5.0	(7.3)	24.9	(3613)
2	↓	↓	↓	3.72	(53.9)	5.3	(7.6)	19.6	(2837)
3				4.12	(59.7)	7.6	(11.0)	22.6	(3280)
				3.90	56.5	6.0	8.6	22.3	3243
4	.1	316(600)	316(600)	2.19	(31.8)	4.0	(5.8)	15.9	(2301)
5	↓	↓	↓	2.76	(40.0)	3.0	(4.3)	16.0	(2328)
6				2.28	(33.0)	3.0	(4.3)	14.5	(2103)
				2.41	34.9	3.3	4.8	15.5	2244
7	100			2.61	(37.9)	2.7	(3.9)	17.4	(2528)
8	↓			2.37	(34.4)	2.8	(4.0)	17.7	(2572)
9				2.79	(40.5)	3.4	(4.9)	10.4	(1501)
				2.59	37.6	3.0	4.3	15.2	2200
10	300			2.34	(34.0)	2.3	(3.3)	13.8	(2007)
11	↓			2.17	(31.5)	3.2	(4.6)	11.0	(1600)
12				2.53	(36.7)	3.0	(4.4)	14.2	(2059)
				2.35	34.1	2.9	4.2	13.0	1889
13	600			2.22	(32.2)	5.7	(8.4)	7.8	(1132)
14	↓			2.04	(29.6)	3.7	(5.4)	7.6	(1098)
15				2.20	(31.9)	3.4	(5.2)	5.1	(738)
				2.15	31.2	4.3	6.3	6.8	990
16	1000			1.55	(22.5)	1.2	(1.7)	3.7	(537)
17	↓			1.89	(27.5)	2.2	(3.2)	6.2	(895)
18		↓	↓	1.14	(16.5)	1.2	(1.8)	6.2	(901)
				1.52	22.1	1.5	2.2	5.3	778

[1] TAB/p-CPGB/p-BPGB, 2% added tetraisopropyltitanate and HM-S fibers

[2] Fiber volume: 60% by weight

[3] Flexure properties laminate K

[4] ILS properties laminate L

3.2.2 (Continued)

Table 9 lists ILS and flexure properties of laminates derived from prepregs containing m-cresol solvent/polymer/HM-S fibers. Table 10 lists ILS and flexure properties of laminates derived from prepregs containing chloroform solvent/2% titanate/polymer/HM-S fibers. In general the system containing titanate gave lower initial flexure and ILS properties at room temperature and after aging in air at 316°C (600°F). This response was attributed to the high void content (discussed below) of titanate containing composites. Parenthetically, after aging 600 hours at 316°C, the laminates without titanate (Table 9) exhibited the highest flexure strength of any PPQ/graphite composite tested under the previous contract (Reference 1).

Table 11 lists the specific gravity of Task II laminates. In general, the values were lower than the ideal specific gravity for the composites (see paragraph 3.2.1). Examination of the laminates under a microscope revealed that laminates I, J and L were of very low void content (estimated $<2\%$ void content), laminate K, however, had very small, occasional voids. The void content of laminate K was estimated at $<8\%$. Figure 9 through Figure 12 are cross section photoenlargements of I, J, K and L laminates. Figure 13 is a cross section photoenlargement of small voids(~1/mm diam) in laminate K.

Table 12 lists isothermal weight losses of the final Task II composites. In terms of weight retention on aging in air at 316°C (600°F), the TAB/p-CPGB/pBPGB/HM-S graphite composites exhibited the highest weight retention of any PPQ/HM-S graphite composite tested in this laboratory (Reference 1 and Reference 8).

TABLE 11. SPECIFIC GRAVITY OF TASK II FINAL COMPOSITES

Item No.	Laminate Series [2]	Specific Gravity (25°C) [1]
1	I	1.47 [3]
2	J	1.40 [3]
3	K	1.34 [4]
4	L	1.43 [4]

[1] Specific gravity was determined by dividing specimen weight in air by its apparent weight loss in water at 25°C.

[2] Laminate series correspond with laminate designations listed in Table 9 and Table 10.

[3] TAB/p-CPGB/p-BPGB and HM-S fibers.

[4] TAB/p-CPGB/p-BPGB, 2% tetraisopropyltitanate and HM-S fibers.

TABLE 12. ISOTHERMAL AGING OF TASK II FINAL COMPOSITES AT 316°C (600°F)

Item No.	Hours Aging 316°C (600°F)	WEIGHT LOSS (%)	
		[1]	[2]
1	100	.2	.5
2	300	.5	1.0
3	600	1.8	2.5
4	1000		

[1] TAB/p-CPGB/p-BPGB and HM-S fibers.

[2] TAB/p-CPGB/p-BPGB, 2% tetraisopropyltitanate and HM-S fibers.

FIGURE 9.
Cross Section Photoenlargement of Laminate I,
(X100)

FIGURE 10.
Cross Section Photoenlargement of Laminate J
(X100)

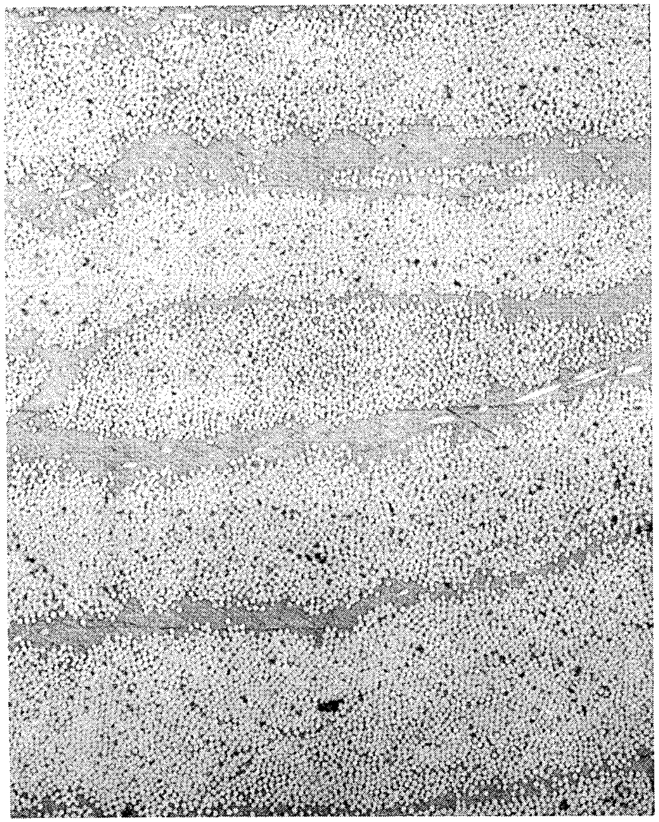


FIGURE 11.

Cross Section Photoenlargement of Laminate K (X100)

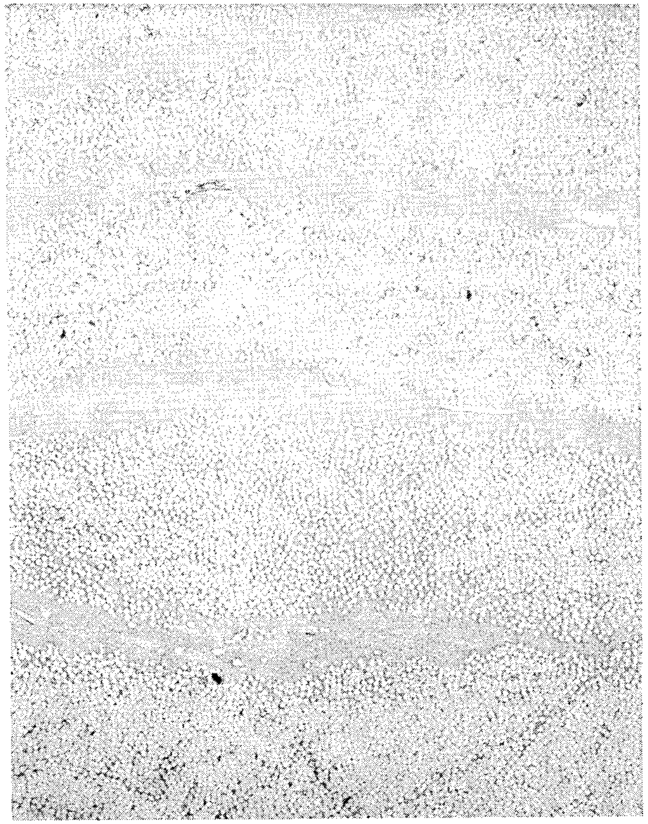


FIGURE 12.

Cross Section Photoenlargement of Laminate L (X100)

FIGURE 13.
Cross Section Photoenlargement of Small Voidsin
Laminate K (X100)

4.0 CONCLUSIONS AND RECOMMENDATIONS

1. The use of catalysts such as p-toluenesulfonic acid, 2-pyrrolidinone, and tetraisopropyltitanate to effect crosslinking of polyphenylquinoxalines (PPQ) by trimerization of pendant cyano (CN) groups did not yield graphite fiber-reinforced composites with improved elevated temperature properties.

2. HM-S graphite fiber-reinforced composites using a CN-containing PPQ derived from 1.0 TAB/0.2p-CPGB/0.8p-BPGB [TAB, 3,3',4,4'-tetraaminobenzophenone; p-CPGB, p-bis(p'-cyanophenoxyphenylglyoxalyl)benzene; p-BPGB, p-bis(phenylglyoxalyl)benzene] could be fabricated at lower temperatures than previously used. The composites exhibited improved flexural strength retention after extended aging at 316°C (600°F).

3. The potential for using a solvent mixture such as ethanol/xylene for the PMR method of fiber impregnation was demonstrated. The approach yielded composites which could be cured at lower temperatures than previously used.

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6.0 APPENDIX

6.1 Experimental

6.1.1 Reactants

The following are representative syntheses and purification of polymer reactants used in this program:

1,3,5-Triglyoxalylbenzene TGB, I (attempted synthesis): 51 g. (.25 mole) of 1,3,5-triacetylbenzene was added to a suspension of 83 g (.75 mole) of SeO_2 in 500 ml dioxane and 25 ml H_2O. The reaction mixture was heated to ~95°C and kept at this temperature 16 hours. The mixture was filtered hot. After solvent removal from the filtrate a brick red solid was obtained. The solid could not be redissolved in solvents such as water, acetic acid, m-cresol or chloroform.

Para-phenoxybenzonitrile, VII: 184 g. (1 mole) of p-phenoxyaniline (Aldrich Chemical) was dissolved in 1.4ℓ of hot water containing 250 ml concentrated hydrochloric acid. After cooling (0°C), the system was diazotized with 71 g (1.2 moles) of $NaNO_2$ in 200 ml water. After stirring approximately 1/2 hour the solution was carefully neutralized with finely ground Na_2CO_3. The neutral solution was added during 30 minutes to a vigorously stirred, cold (0°C) suspension of 125 g (1.4 moles) CuCN, 1.6ℓ water and 208 g (3.2 moles) KCN. The cyanide suspension was kept at 0°C during addition of the diazonium salt solution. After addition was completed, the resulting system was kept 2 hours at 0°C to 5°C. The system was allowed to warm to ambient temperature (~ 6 hours) and then 500 ml CH_2Cl_2 was added. After stirring overnight at room temperature the system was heated and kept at 50°C for 2-3 hours. The system was subsequently extracted with CH_2Cl_2 (tedious step). After acidification, neutralization and washing with water, the CH_2Cl_2 solution was concentrated. The resulting dark gum was distilled rapidly (short path distillation) under reduced pressure. The desired nitrile was collected in crude form at 130 - 170°C under 2 mm Hg (lit. b.p. 170-174/4mm, Reference 9) yield, crude 50%. After redistillation the pure nitrile was obtained, m.p. 41-43°C (lit., m.p. 46°C, Reference 10).

Para-bis[p'-phenacyl (p'-cyanophenoxy)] benzene: A solution of p-phenylenediacetyl dichloride (16.1 g, .07 mole), p-phenoxybenzonitrile (29 g, .149 mole) and 100 ml CS_2 was added under nitrogen to 50 g (.37 mole) of aluminum chloride in 100 ml of CS_2. Addition was effected at 15°C to 20°C and vigorous stirring. After addition, the system was stirred at room temperature for ~1 hour and then heated to reflux (N_2 atmosphere) for 16 hours. The dark solid and solvent were poured into ice/HCl and stirred until the dark color disappeared. The aqueous mixture was extracted 3 times with methylene chloride (tedious step). The organic phase was neutralized with sodium bicarbonate. To facilitate handling, the solvents were removed by evaporation at room temperature. The remaining dry solids were crystallized 3 times from minimum volume of boiling chloroform. Solvents such as boiling acetone may be used instead of boiling chloroform, however large volumes of acetone are required to dissolve the diketone. Yield of diketone: 19 g (50%); melting point: 223°-227°. Lit melting point: 223° - 227°C (Reference 1). Addition of the organic chloride and cyano compound to equivalent quantities of aluminum chloride led to 16% yield of diketone. Similar yields were obtained by adding aluminum chloride in equivalent quantity to the organic chloride and cyano compound, or by using sym-tetrachloroethane as solvent.

Para-bis(p'-cyanophenoxyphenylglyoxalyl)benzene, p-CPGB, II: The diketone para-bis[p'-phenacyl(p'-cyanophenoxy)]benzene (14.2 g, 0.026 mole) was oxidized with selenium dioxide (5.77 g, 0.052 mole) in glacial acetic acid to the corresponding bis (1,2-dicarbonyl) compound. After filtering the solids, the acetic acid

6.1.1 (Continued)

solution was cooled and crude p-CPGB was collected. A reaction yield of ~50% crude p-CPGB was obtained. After purification from benzene/hexane, yields of ~25% p-CPGB (m.p. 208° - 211°C) were obtained. Lit. m.p. 211.5° - 213°C (Reference 1).

Para-bis(phenylglyoxalyl)benzene p-BPGB, III: The following is a representative procedure for synthesis of p-BPGB (Reference 2). Para-phenylenediacetic acid (566 g, 2.9 mole) melting at 249° - 253°C (softened at 245°C) was stirred in thionyl chloride (1.7ℓ) at RT for 48 hours to form a turbid orange solution. The orange solution was concentrated to near dryness at 50°C under vacuum to yield a yellowish orange solid which was washed with n-hexane and dried to yield the diacid chloride as yellow crystals (610g). The diacid chloride (619g, 2.6 mole) was dissolved in dry benzene (1.6ℓ) and added dropwise during 3 hours under nitrogen to a slurry of anhydrous powdered aluminum chloride (842g, 6.3 mole) in dry benzene (2.0) at < 10°C. After complete addition, the brown reaction mixture was stirred at <10°C for 3 hours, and then overnight at ambient temperature. The resulting dark brown reaction mixture was poured onto ice in hydrochloric acid and stirred 4 hours to yield a gray emulsion. The thick emulsion was transferred to large evaporating dishes and allowed to sit overnight. After decanting the water and drying the residue at 75°C, the resulting solid was pulverized and washed successively with dilute aqueous hydrochloric acid, water, aqueous sodium carbonate, and water. The resulting dry gray solid (872g) was dissolved in DMF (5ℓ), filtered, and cooled to yield light tan crystals which were washed with methanol and dried to afford p-diphenacylbenzene (573g), mp 204-207°C. To a slurry of selenium dioxide (404g, 3.6 mole) in glacial acetic acid (3ℓ), p-diphenacylbenzene (573g) was added and the mixture refluxed for 18 hours. The black mixture was filtered hot, and the yellow filtrate was treated with Celite and charcoal, refiltered, and cooled to provide p-bis-(phenylglyoxalyl)benzene(499g) as yellow crystals m.p. 124.5-126°C, [lit. m.p. 125-126°C (Reference 2)].

3,3'-Diaminobenzidine DAB, IV: This material as received (Burdick and Jackson) melted at 174-176.5°C. Recrystallization was accomplished by dissolving 150g portions in deoxygenated water (~6ℓ) containing a pinch of sodium dithionite under nitrogen. The yellowish solution was treated with charcoal, filtered, and cooled to provide light tan needles (105g, 70% recovery) of the tetraamine, m.p. 176-177 .5°C, [lit m.p. 179-180°C (Reference 11)].

3,3',4,4'-Tetraaminobenzophenone TAB V: This tetraamine as received (Burdick and Jackson) melted at 214-217.5°C was recrystallized by dissolving 150g in DMF (1.5ℓ) and adding hot water (~3.0ℓ) to near turbidity. The yellowish solution was treated with charcoal, filtered, and cooled to afford the tetraamine (120g, 70% recovery) as yellow needles, m.p. 216-217.5°C, [lit m.p. 217°C, Reference 12)].

6.1.2 Polymers

Task 1 Polymers. The following is a representative polymer synthesis for the polymers listed under Items 1, 3, 4 and 5, Table 1: The amine, as fine powder, was added to a stirred mixture of the tetracarbonyl compound(s) and m-cresol solvent. Amine addition was effected over a period of three to five minutes. The reaction scale ranged from a total solids content of ~.81 g to 4 grams. Gellation was observed in all cases within 2 hours after mixing ingredients.

The following is the polymerization procedure used to prepare the polymers listed under Item 2 and Item 7, Table 1: The amine or mixture of amines, as fine powder, was added incrementally to a stirred mixture of p-CPGB and m-cresol. The rate of addition which was used is listed below:

TIME (Minutes Elapsed After Adding 1st Amine(s) Increment)	Approximate Percentage of Added Amine(s)
0	28
30	23
60	28
90	9
120	2
185	5

The following is the polymerization procedure used to prepare the polymer described under Item 6, Table 1: TAB was added in three increments to a stirred mixture of m-cresol and the tetracarbonyl compounds p-CPGB and p-BPGB. The rate of TAB addition which was used is listed below.

TIME (Hours Elapsed After Adding 1st Increment of TAB)	TAB added as Approximate Percentage of Total TAB Used
0	97.6
16	2.0
24	0.4

Polymer Films: Polymer films containing 2-pyrrolidinone and p-toluenesulfonic acid were prepared as follows: during polymer synthesis an aliquot of polymer solution was removed from the synthesis pot just prior to visible onset of gellation. The polymer aliquot was weighed on a glass plate and the desired quantity of 2-pyrrolidinone or p-toluenesulfonic acid was weighed on the glass plate. The system was thoroughly mixed, allowed to dry in a quiescent atmosphere (24 to 48 hours) and subsequently heated 24 hours at 160°C for removal of residual solvent.

6.1.2 (Continued)

Titanate containing films were prepared as follows: Films were cast from $CHCl_3$ solutions of the polymer and appropriate quantity of titanate. After adding the titanate, each solution was thoroughly mixed before casting on glass plates. After casting, each solution was covered with loose-fitting watch glass to allow slow evaporation of $CHCl_3$. Drastic increases in viscosity were observed during mixing the systems containing 4%, 6% and 8% titanate. For example, within 3 minutes after titanate addition, the solution containing 8% titanate could not flow freely and had a gel-like appearance. This rapid increase in viscosity after titanate addition suggests occurrence of cross-linking reactions.

Task II Polymer. The polymer selected for Task II composites was synthesized. The polymer was prepared from TAB/p-CPGB/p-BPGB in the molar ratio of 1 TAB to .2 p-CPGB to .8 p-BPGB. The synthesis approach used in Task I was used with one minor modification: After addition of 60% of needed TAB to the mixture of p-CPGB/p-BPGB in m-cresol, a rapid exotherm developed. This exotherm was not noticed in the small-scale synthesis conducted in Task I. To avoid possible gellation the reaction mixture was quickly cooled to ~18°C and stirred overnight at ~18°C. After overnight stirring, the remaining portion of TAB was added in three parts. The reaction mixture was subsequently stirred for six hours more at ~18°C. The resulting polymer was precipitated with methanol, washed in boiling methanol, dried under vacuum and stored in dry form. On redissolving, a m-cresol solution of the polymer exhibited a drastic increase in viscosity after standing 8 hours. This behavior was attributed to the exotherm described above.

6.1.3 Impregnation Procedure

The standard method of impregnation consisted of winding a known weight of one tow HM-S graphite onto a 30.48 cm (12") diameter drum at 3 tows per cm (8 tows per inch). When m-cresol was used as solvent, a freshly made polymer solution (see below) was poured and distributed on the fiber. When the desired quantity of resin had saturated the fibers, heat lamps were directed on the drum to drive off the solvent. With the drum continuously rotating (~8 rpm) the prepreg was maintained at 93°C (200°F) until the prepreg was tacky. Subsequently the prepreg was cut from the drum and kept under heat lamps for additional drying to ~12% solvent content. This procedure was used to prepare a prepreg using the $CHCl_3$/titanate/polymer system. After adding 2% titanate to the $CHCl_3$/polymer solution, the system's viscosity increased very rapidly. The resulting solution was too viscous for thorough fiber permeation. Therefore, the drum wound fibers (of known weight) were impregnated in sections: a portion of needed catalyst/solvent/polymer was prepared (see below) and poured on the fibers. The system was immediately covered with FEP film (copolymer of perfluorinated ethylene/propylene) to prevent rapid solvent loss. The fibers were impregnated by sweeping over the FEP film manually with a smooth piece of plastic such as polyethylene. This process was repeated (4 times) until the entire graphite tape was totally impregnated. The prepreg layup had ~30% solvent content.

The m-cresol/polymer solution used for fiber impregnation was prepared as follows: The polymer, as a fine powder, was added to m-cresol under rapid stirring. A Waring blender was used to promote polymer dispersion. Blender speed was kept sufficiently low to prevent heating of the liquid due to mechanical agitation. The solution was used immediately after the last traces of solids dissolved (~20 minutes).

Chloroform/tetraisopropyltitanate/polymer solutions were prepared as follows: the desired quantity of polymer, as fine powder, was added to chloroform under rapid stirring. A Waring blender was used to promote polymer dispersion.

6.1.3 (Continued)

During blending the system was kept under a blanket of argon. Blender speed was kept sufficiently low to prevent heating of the liquid due to mechanical agitation. After the last traces of polymer dissolved, 2% tetraisopropyltitanate (relative to polymer content) was added to the polymer solution. The titanate was added as a chloroform solution containing 10% (w/w) of the titanate. A drastic rise in solution viscosity was observed after titanate was added to the dissolved polymer. After blending ~2 minutes the system was used for fiber impregnation. Four such batches were prepared and used to incrementally impregnate a tape 37" x 24" wide.

6.2 Test Methods

6.2.1 Interlaminar Shear Strength (Short Beam)

Interlaminar shear (ILS) strength tests were conducted per ASTM Test Method D2344.at a span-to-depth ratio of 5.

6.2.2 Flexural Properties

Flexural properties were determined per ASTM Test Method D790 using a specimen 1.27 cm (0.5 inches) wide at span-to-depth ratio of 16.

6.2.3 Isothermal Aging

Isothermal aging of laminates was conducted in an air circulating oven preheated to the desired temperatures. Air velocities (non-recirculating) were controlled to a nominal 150 $m\ell$/min.

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