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Polybenzimidazoquinazolines: High-Temperature Matrix Materials

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Polybenzimidazoquinazolines: High-Temperature Matrix Materials

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ABSTRACT

A series of polybenzimidazoquinazolines (PIQ) were prepared by the condensation of 5,5'-bis[2(o-aminophenyl)benzimidazole] with phenyl esters of various di- and tricarboxylic acids. Thermomechanical and thermooxidative properties of the neat resins and as matrices in reinforced composites were evaluated at 371°C. A benzimidazoquinazoline copolymer, prepared

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from diphenyl bisbenzoate and sym-tris(carbophenoxyphenyl) triazine showed excellent retention of thermooxidative and thermomechanical properties at 371° C after 200 hr at 371° C. For example, a Modmor II unidirectional laminate provided flexural strength and modulus at 371°C, respectively, of 112,000 psi and 15.6×10^6 psi after 1 hr and 108,000 and 16.4×10^6 psi after 200 hr in circulating air.

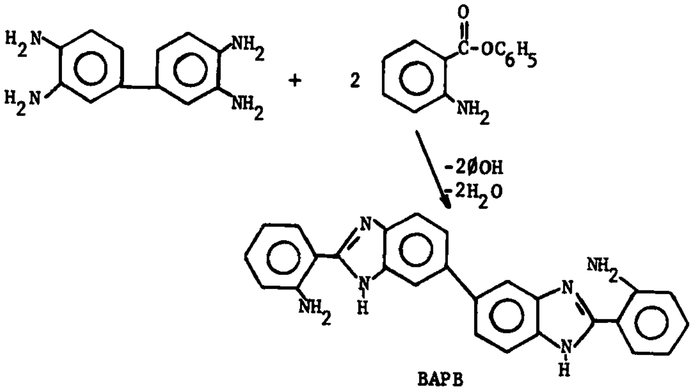
INTRODUCTION

Polybenzimidazoquinazolines have been the subject of several publications and patents during the last decade [1-7]. Several of these articles mention the excellent thermal stability of these polymers [1-4], and one of the patents claims their use as films and wire coatings [7]. The work presented herein was directed toward the development of these polymers as matrix materials for use at temperatures of 371° C and higher. Such material would find use as aircraft engine components where temperatures in this range are encountered and weight savings are critical.

RESULTS AND DISCUSSION

Monomers

The tetraamine used in this study 5,5'-bis[2-(o-aminophenyl)-benzimidazole] (BAPB), was prepared by the condensation of phenyl anthranilate with 3,3',4,4'-tetraaminobiphenyl [Eq. (1)]. After



(1)

washing with methanol and recrystallization from N,N-dimethylformamide–benzene, BAPB was polymer grade purity as indicated by its melting behavior, both visually and by differential scanning calorimetry, and its elemental analysis.

The phenyl esters (listed in Table 1) were either purchased or synthesized through conventional routes. The phenyl esters of the tricarboxylic acids were synthesized by preparing the parent aromatic hydrocarbons [13, 14] whose pendant methyl groups were oxidized to carboxylic acids and esterified [15, 16] as shown in Eq. (2).

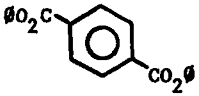
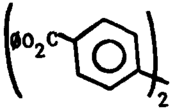
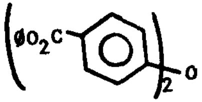
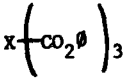
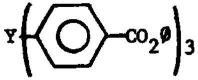
The synthetic routes differed in the preparation of the difunctional esters. 4,4'-Bisbenzoic acid was conveniently prepared by the known coupling [17] of 4-chlorobenzoic acid in the presence of palladium and methanol. The resulting acid was esterified in high yield with diphenyl sulfite [15, 16]. Diphenyl oxybisbenzoate was prepared by acetylating diphenyl ether, followed by oxidation of the acetyl groups to carboxylic groups and esterification.

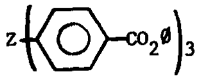
Polymers

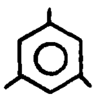
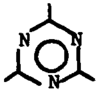
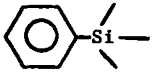
Polymer synthesis [Eq. (3), Ar = arylene] was conducted by heating stoichiometric quantities of BAPB with one or more of the above phenyl esters under an inert atmosphere with either phenol or m-cresol as a flux. The condensations were initiated at temperatures between 230 and 250° C and were allowed to continue until homogeneous viscous melts had formed. These melts were then cooled under vacuum to provide brittle foams which were pulverized and placed in tubes. These were then heated for several hours, either under nitrogen or vacuum, at temperatures gradually rising to ca. 480° C to produce the fully cured polymers. The polymers were yellow, and the linear polymers exhibited inherent viscosities (0.5% solution in H_2SO_4 at 25° C) as high as 1.6 dl/g (polymer prepared from DOBB and BAPB with final cure of 1 hr at 450° C). Thermomechanical studies indicated that the T_g values closely reflect the final cure temperature up to the onset of thermal decomposition, as shown in Table 2.

Benzimidazoquinazoline polymers could also be prepared as films by casting prepolymer solutions in N,N-dimethylacetamide or m-cresol followed by further advancement. In some cases, prepolymer films were cast on sodium chloride cells, and their cures upon exposure to elevated temperature were followed by the disappearance of the carbonyl bands in the infrared spectra (see Fig. 1). Infrared spectral studies such as these gave an indication as to the cure temperatures needed for the polymer system.

TABLE 1. Phenyl Esters

Compound	Designation	Mp (° C)	Lit. mp (° C)	Formula	Elemental analysis[a]			
					C (%)	H (%)	N (%)	Si (%)
	DPiP	138-139	137-138[b] 139[c]	$C_{20}H_{14}O_4$	–	–	–	–
	DPtP	196.5-198	196[c,d]	$C_{20}H_{14}O_4$	–	–	–	–
	DBB	213-214	214-215[e]	$C_{26}H_{18}O_4$	–	–	–	–
	DOBB	193-194	185-187[f]	$C_{26}H_{18}O_5$	–	–	–	–
	TPTM	169-170.5	171[c]	$C_{27}H_{18}O_6$	–	–	–	–
	TCPT	219-221	–	$C_{42}H_{27}N_3O_6$	75.20 (75.32)	4.15 (4.06)	6.16 (6.28)	–

	TCPPS	168-170	—	$C_{45}H_{32}O_6Si$	77.72 (77.56)	4.71 (4.63)	—	3.98 (4.03)

X =  , Y = , Z = 

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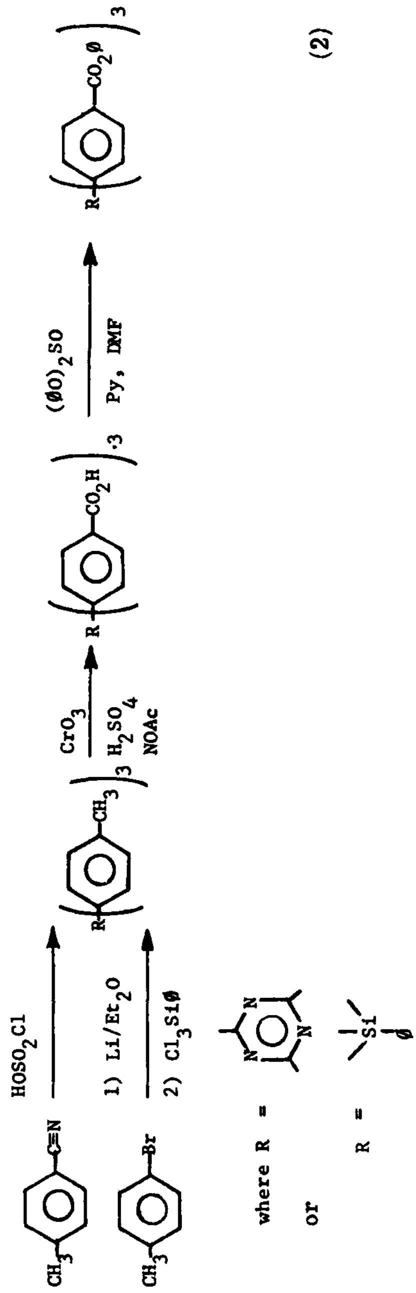
[a] Theoretical values reported in parentheses.
[b] Data of Blicke and Patelski [8].
[c] Data of Sillion and deGuademaris [9].
[d] Data of Schreder [10].
[e] Data of Vogel and Marvel [11].
[f] Data of Marvel et al. [12].


CH3
C≡N
CH3
Br
HOSO2Cl
1) Li/Et2O
2) Cl3SiØ
R
CH3
3
CrO3
H2SO4
NOAc
R
CO2H
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(ØO)2SO
Py, DMF
R
CO2Ø
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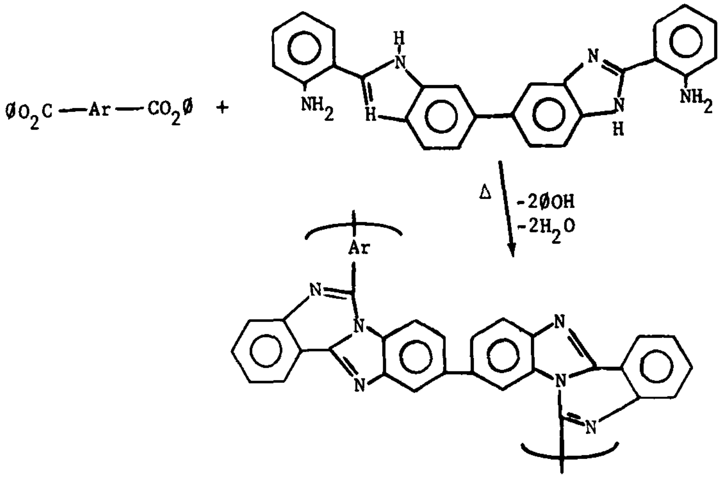
where R =
N
N
N
or R =
Si
Ø

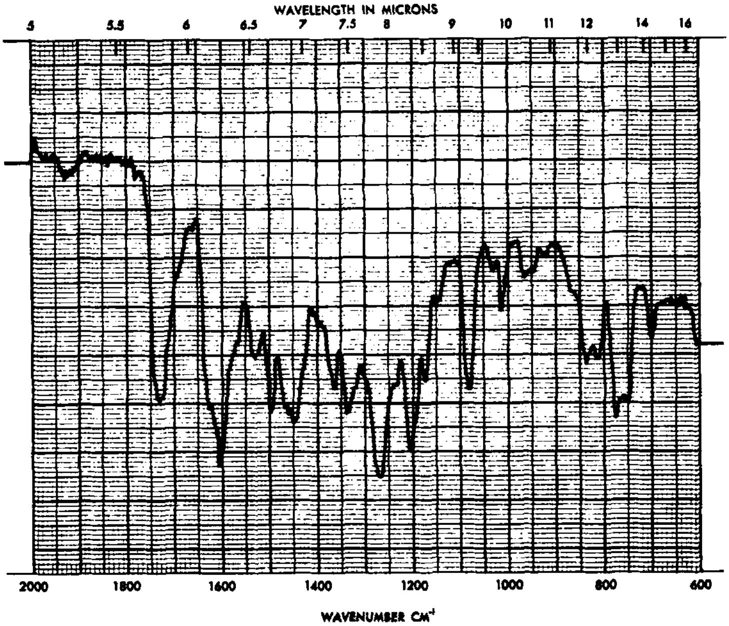
(2)



(3)

TABLE 2. Apparent Glass Transition Temperatures of Polybenzimidazoquinazolines (PIQ) as a Function of Thermal History

Polymer	Thermal history, time/temp (°C)	T_g (°C)
BAPB-DBB	406	396
	+ 60 min/454	494
	+ 60 min/510	495
BAPB-TCPT	60 min/343	350
	+ 60 min/399	410
	+ 120 min/449	451
	+ 120 min/510	~430


WAVELENGTH IN MICRONS
5
5.5
6
6.5
7
7.5
8
9
10
11
12
14
16
2000
1800
1600
1400
1200
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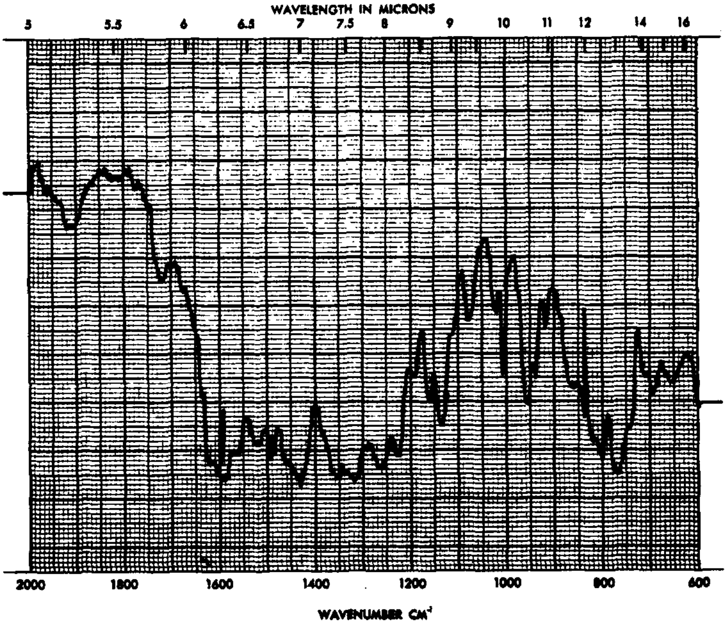
800
600
WAVENUMBER CM⁻¹

(a)


WAVELENGTH IN MICRONS
5
5.5
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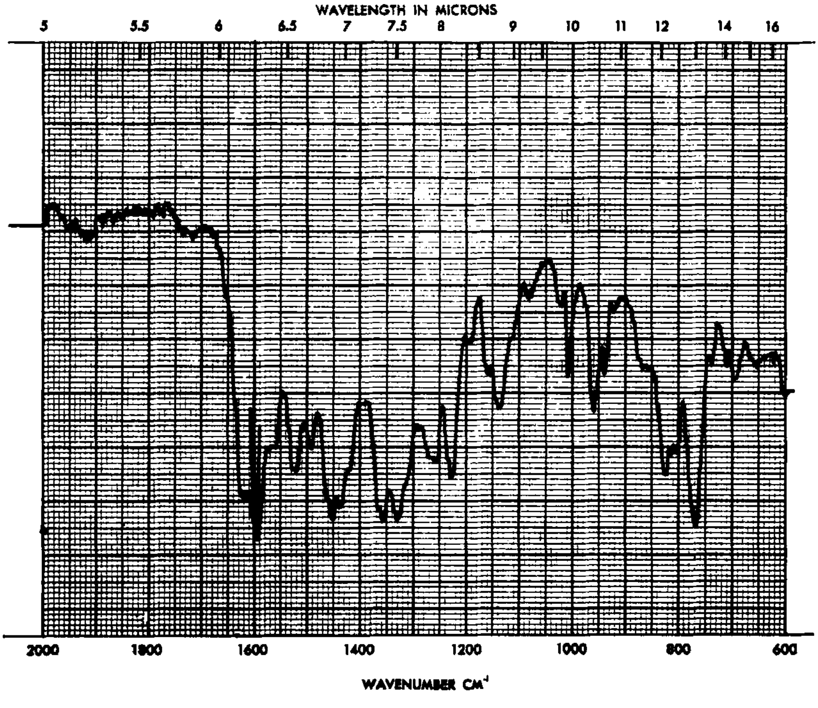
WAVENUMBER CM⁻¹

(b)



(c)

FIG. 1. Infrared spectra of BAPB/DBB film as a function of cure conditions: (a) 1.0 hr/150° C/N_2; (b) 2.0 hr/343° C/N_2; (c) 1.5 hr/468° C/N_2.

The thermooxidative stability of the various polymers in the form of powders (>40 mesh) was determined by isothermal aging at 371° C in circulating air as shown in Fig. 2. The weight retention for all the polymers in Fig. 2 were determined in the same oven at the same time. Table 3 shows the weight retentions after 100 and 200 hr at 371° C for the various polymers.

Laminates

These resins were being developed for use as matrices in reinforced composites. Prepreg was prepared by applying solutions or slurries of the prepolymer in N,N-dimethylacetamide, N-methylpyrrolidione, or m-cresol to a reinforcement and removing the solvent. The prepreg was then cut to the appropriate dimensions, placed in a trap mold, and

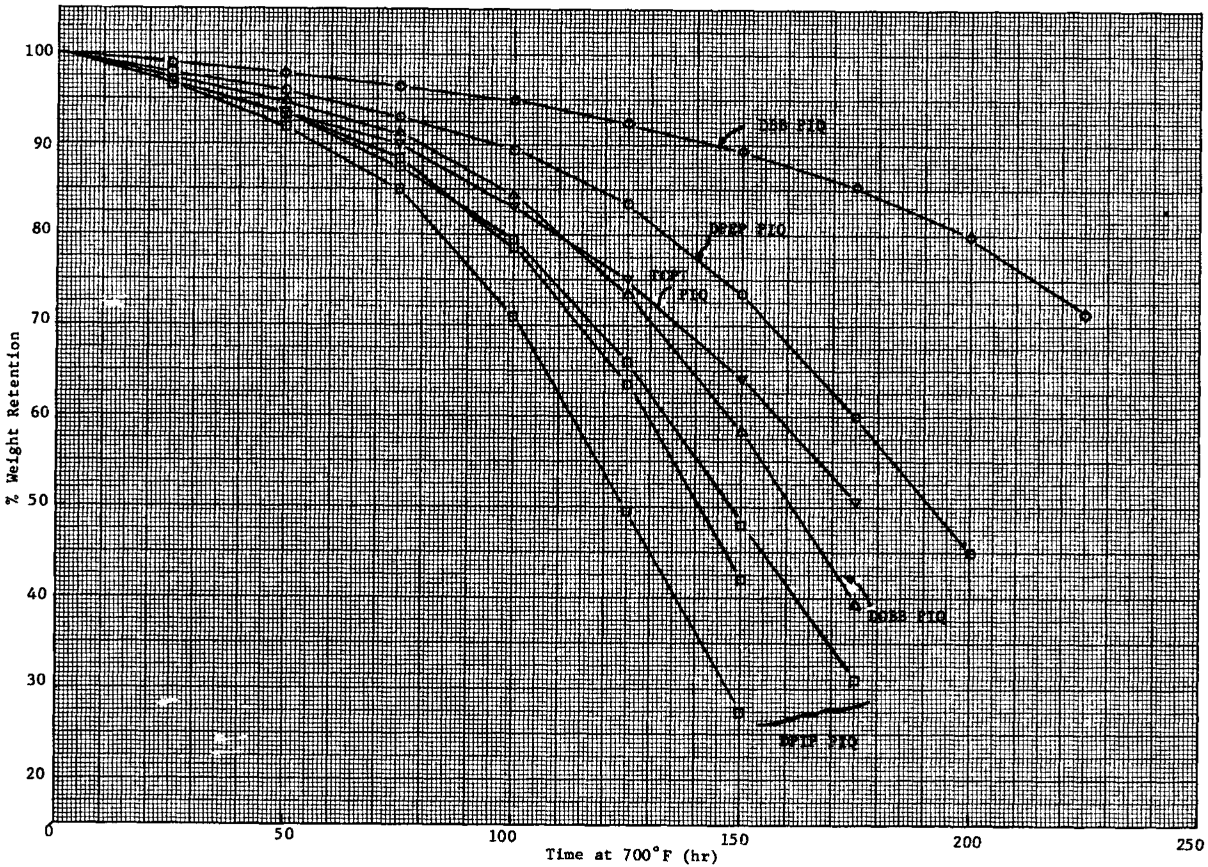


FIG. 2. Simultaneous isothermal aging at 371° C in air of PIQ. Final cure conditions: 1.5 hr/468° C.

TABLE 3. Isothermal Weight Retention of PIQs in Circulating Air at 371° C

Constituent ester[a]	No. of samples	Final cure, time/temp (° C)	Weight retention range (%)	
			100 hr	200 hr
DBB	2	1 hr/454	93.1-93.5 (93.3)	67.7-70.0 (68.9)
	15	1.5 hr/468	88.4-97.3 (94.5)	45.0-84.6 (72.0)
	2	3 hr/468	88.2-92.0 (90.1)	48.3-58.4 (53.4)
	1	3 hr/482	90.3	51.1
DOBB	1	1.5 hr/468	84.1	< 50.0
DPiP	3	1.5 hr/468	72.3-79.5 (76.5)	< 50.0
DPtP	1	1.5 hr/468	89.7	< 50.0
TCPT	6	1.5 hr/468	70.0-87.2 (80.0)	< 50.0
	3	1 hr/482	51.4-94.0 (77.5)[c]	54.0 (< 50.0)
TCPT/DBB[d]	4	1.5 hr/468	93.0-96.4 (94.6)	61.7-83.6 (72.3)

[a] See Table 1.

[b] Values in parentheses are average values.

[c] 94% and 54% weight retention determined at WPAFB by using an Aminco thermal balance under air flow rate of 46 cc/min (G. F. L. Ehlers and K. R. Fisch).

[d] 1 mole TCPT, 6 mole DBB, and 7.5 mole BAPB.

cured at a temperature and pressure sufficient to knit the plies together. The laminate was then removed, cleaned, replaced in the mold and postcured under nitrogen and pressure to a final temperature commensurate with the optimum cure temperature for the polymer.

Specimens from many of these laminates were subjected to flexural testing at 371° C after isothermal aging at 371° C. Table 4 lists the flexural strengths of the PIQs tested under this program as matrices in unidirectional Modmor II laminates. In general, these results paralleled the aging results of the neat resins. However, it was determined by separate 371° C air aging studies that Modmor II fiber, as well as other high-strength carbon fibers tested, lost weight (and presumably strength). This loss was found to vary widely from batch to batch, making it extremely difficult to separate the aging effects of the matrix from those of the reinforcement.

EXPERIMENTAL

Monomers

5,5'-Bis[2-(o-aminophenyl)]benzimidazole

A 5-liter resin flask, equipped with an overhead stirrer, nitrogen inlet, and reflux condenser was charged with 1320 g (6.2 mole) of phenyl anthranilate and 642 g (3.0 mole) of 3,3',4,4'-tetraaminobiphenyl. After the system was thoroughly purged with nitrogen, the resin flask and its contents were heated by means of an oil bath at ca. 220° C for 21 hr. At this point the condenser was replaced with a distillation head and the phenol was distilled off, care being maintained to keep the temperature of the bath below 300° C. Once most of the phenol was removed, the residue was broken up to a powder and washed with methanol to give 870 g (70% crude yield) of tetraamine. This material was recrystallized from N,N-dimethylformamide–benzene to give polymer grade tetraamine, mp 373° C (DSC); lit. [7] mp, 372-373° C).

Analysis. Calculated for $C_{26}H_{20}N_6$:C, 74.98%; H, 4.84, %; N, 20.18, %. Found: C, 74.86%; H, 4.99%; N, 20.12%.

2,4,6-Tris(4-carboxyphenyl)triazine

In a typical oxidation procedure, a 12-liter flask is charged with 4540 g of acetic acid, 275 ml of sulfuric acid, and 174.3 g (0.50 mole) of sym-tri-4-tolyltriazine, prepared by trimerization of p-tolunitrile

TABLE 4. Thermomechanical Properties of PIQ/Modmor II Flat Laminate Specimens

Constituent ester(s)	Resin content (%)	Flexural strength at RT (psi)/modulus (× 10^6 psi)	Flexural strength at 371° C (psi) /modulus (× 10^6 psi)[a]		
			1 hr	50 hr	100 hr
DBB	37.3	106,300/15.1	75,300/11.3	102,200/13.3	–
	30.0	113,300/17.7	104,800/16.8	141,800/16.9	–
DOBB	25.7	193,300/17.3	164,800/17.3	58,500/16.0	–
DPiP	23.8	251,600/18.8	184,000/17.5	121,500/15.7	–
	31.0	243,500/20.3	167,900/17.2	111,500/16.7	–
DPtP	43.5	142,200/13.5	155,800/13.9	86,600/13.0	–
	31.6	173,200/17.0	122,200/15.9	72,500/15.6	–
TPTM	23.2	234,500/20.2	224,600/21.7	27,300/14.1	–
TCPT	26.0	234,400/18.2	200,200/14.6	97,000/9.7	–
	28.8	239,500/19.1	177,400/16.6	64,700/15.5	–
	30.1	281,500/17.2	171,200/18.3	172,000/16.9	143,700/14.5
	33.6	223,200/17.2	117,300/16.9	155,300/16.3	154,100/15.3
TCPPS	43.7	55,400/11.0	16,200/5.3	27,300/4.5	–
	25.8	155,400/17.3	77,400/14.0	18,200/13.2	–

(continued)

TABLE 4. (continued)

Constituent ester(s)	Resin content (%)	Flexural strength at RT (psi)/modulus (× 10^6 psi)	Flexural strength at 371° C (psi)/ modulus (× 10^6 psi)[a]		
			1 hr	50 hr	100 hr
TCPT/DPiP	26.8	239,600/17.4	195,500/17.8	81,800/14.2	–
(1:3)[b]	26.9	218,500/17.4	215,500/18.4	82,400/17.0	–
TCPT/DBB	30.6	162,000/17.2	112,000/15.6	111,000/14.6	108,000/16.4[c]
(1:4)	39.0	170,300/15.6	–	114,000/16.1	105,000/14.8

[a] All were run at temperature after specimens aged in air at 371° C for time intervals listed.

[b] Equivalent ratio, mole ratio 2:9 TCPT:DPiP and 1:6 TCPT:DBB.

[c] After 200 hr; no specimens tested at 100 hr.

[13]. The flask, in a water bath and equipped with an overhead stirring assembly and an immersion thermometer, was then charged slowly with 450 g (4.5 mole) of finely ground chromium oxide and 300 ml of acetic anhydride, care being taken to see the temperature of the reaction medium was kept below 50° C. After the addition was complete the reaction mixture was allowed to stir overnight and was poured into a 12-liter resin flask containing 6 liter ice water. The well mixed contents of the resin flask were then filtered, the filtrate washed with water and taken up in 6 liter 2 N sodium hydroxide. The sodium hydroxide solution was filtered to remove insoluble impurities and acidified with hydrochloric acid to give, after filtration, washing and drying, crude sym-tris-4-carboxyphenyltriazine. The acid may be esterified as is or further purified by recrystallization from N,N-dimethylformamide to give a fine white powder, in 88% yield, mp 403° C, dec (DSC); lit. [18] mp, 374-375° C.

Tris(4-carboxyphenyl)phenylsilane

This compound was conveniently prepared by the oxidation of tri(p-tolyl)phenylsilane by the same procedure outlined for the oxidation of tri-p-tolyltriazine. The product, purified by recrystallization from acetone–hexane, was obtained in a 70% yield and had a mp of 323-325° C.

Esterifications

Both of the trifunctional acids and many of the difunctional acids used in the program were esterified with diphenyl sulfite. A typical procedure is as follows.

A mixture of 800 ml of pyridine and 800 ml of N,N-dimethylformamide in a 3-liter three-necked flask equipped with a heating mantle, overhead stirrer, and immersion thermometer was charged with 150 g (0.34 mole) of sym-tris(4-carboxyphenyl)triazine and the solution warmed until dissolution occurred. To this warm (ca. 50° C) solution, 468 g (2.0 mole) of freshly prepared diphenyl sulfite [15] was added, and the solution was allowed to stir overnight at ca. 90° C. The addition funnel, acting as an air condenser, was replaced with a distillation head and receiver, and a quantity of solvent was removed under aspirator pressure until the product began to precipitate. The solution was allowed to cool and the product separated by filtration and washed with methanol. The triester was then treated as a slurry in warm 10% Na_2CO_3 solution, washed with water and methanol, dried, and recrystallized twice from chloroform-methanol to give 189 g (2.8 mole) of pure sym-tris-(4-carbophenoxyphenyl)triazine, mp 219-221° C, an 80% yield based on the triacid.

The yield of esters prepared by this procedure ranged from 65 to 94%, based on starting acid. Elemental analyses of previously unreported esters are given in Table 1.

Polymers

There is virtually no difference in the preparation of the different PIQs. The following procedure describing the preparation of APBB TCPT polymer is representative.

A 500-ml, three-necked flask equipped with an immersion thermometer, nitrogen inlet, overhead mechanical stirrer, distillation head, and, through that, a receiver and a vacuum take-off, was charged with 66.96 g of tris-4-carbophenoxyphenyltriazine (0.100 mole), 62.46 g of APBB (0.150 mole), and 75 ml of distilled m-cresol. The flask was then alternately evacuated and flushed with nitrogen three times. Heat was applied and, once the ester had dissolved in the m-cresol flux, the stirring motor was turned on. The m-cresol flux was then collected in the receiver. Soon after the reaction commenced, the flask was allowed to heat up to 308-320° C and was held there until the material became uniform and viscous. Heat was then removed, a vacuum was once again applied and, under vacuum, the prepolymer was allowed to solidify. Once cooled to room temperature, the prepolymer was ground, weighed, and the polymer melt temperature (PMT) determined. The yield was 112.8 g, PMT 220-232° C.

Final cure to the polymer was conducted in the following manner. Ground prepolymer was placed in a tared tube in a carefully regulated oven under a flowing nitrogen (argon) atmosphere. Final cure temperatures were generally in the region between 455 and 505° C. Heating rates also varied, but generally they were of the order of 60-100° C/hr from 300° C to the final cure temperature with a 45 min to 3 hr hold at that temperature.

CONCLUSIONS

The potential of two PIQs for use as composite matrices in air at 371° C have been demonstrated. Because of the thermomechanical performance, the BAPB/TCPT system would find applications for short-time (up to 100 hr) use at 371° C. The BAPB/TCPT-DBB copolymer would find longer-term (e.g., $>$ 200 hr) use at 371° C under lower stress conditions. Preliminary results suggest that both systems also give satisfactory results through at least 10 hr at 427° C.

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