Polyquinoxalines. I. Synthesis and Preliminary Mechanical Properties as Laminating and Adhesive Resins*

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Synopsis

A study on polyquinoxaline synthesis was conducted which provided a method of obtaining processable, reproducible high molecular weight polymers as solutions in *m*-cresol; these solutions had excellent storageability at ambient temperatures. Polyquinoxaline solutions in *m*-cresol were readily used for prepreg and tape preparation. Laminate and adhesive data showed the excellent potential of the polyquinoxalines for high temperature applications.

INTRODUCTION

The drastic need for new improved high-temperature structural resins created a major research effort in the field of high-temperature organic and heterocyclic polymers. Since Vogel and Marvel[1] reported their work on the preparation of thermally stable polybenzimidazoles in 1961, a wide variety of thermally stable organic heterocyclic polymers have been reported. The major portion of work on these polymers was confined to the synthesis and preliminary characterization and usually involved little or no development work to demonstrate their true potential use. This may have been due, in many instances, to a number of contributing factors. For example, many of these polymers or their intermediate forms were not readily amenable to processing, owing to certain inherent limitations such as high melt temperature, poor solubility, limited flow characteristics, and hydrolytic and oxidative instability.

Although the synthesis of polyquinoxalines was the subject of previous publications,[2-8] this publication presents the synthetic efforts which emphasized polymer processability and reproducibility directed toward utilization in application work. The major synthetic effort concerned two polymers, a monoether and a diether polyquinoxaline, although other polyquinoxalines can also be synthesized as processable polymers. The poly-

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quinoxalines are potentially useful, multipurpose resins which exhibit out-standing hydrolytic, oxidative, and thermal stability.

Several investigators[2-8] reported the successful preparation of high molecular weight, thermally stable polyquinoxalines from the reaction of aromatic bis(o-diamines) with aromatic diglyoxals, as shown in the following general equation:
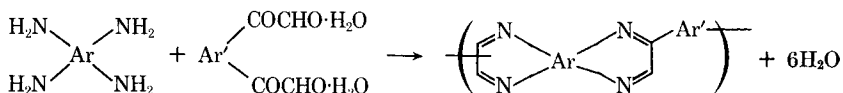

where Ar and Ar' are aromatic.

Our work involved principally two polymers prepared from the reaction of 4,4'-oxybis(phenyleneglyoxal hydrate) (OBPG, I) with 3,3'-diaminobenzidine (DAB, II) and with 3,3',4,4'-tetraaminodiphenyl ether (TADE, III) to yield poly[2,2'-(p,p'-oxydiphenylene)-6,6'-diquinoxaline] (monoether PQ) and poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxydiquinoxaline] (diether PQ), respectively, as shown in the following equation:

monoether PQ

diether PQ
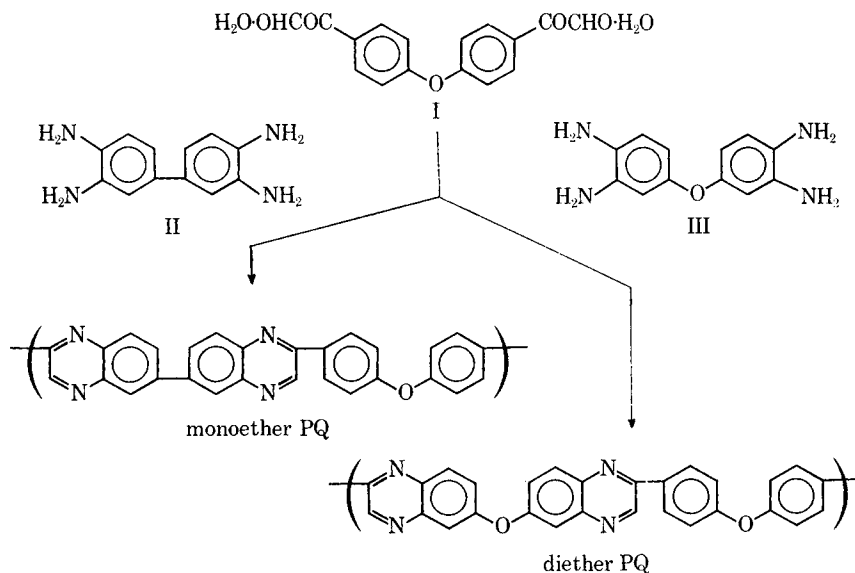
Very recently, the synthesis of a copolymer was carried out by the reaction of 75 mole-% OBPG and 25 mole-% p-phenylene diglyoxal dihydrate with DAB as a first effort to increase the glass transition temperature of the polyquinoxalines, without resorting to crosslinking. The resultant structure is unknown regarding the periodicity of the p-phenylene moiety, but an ideal structure would be
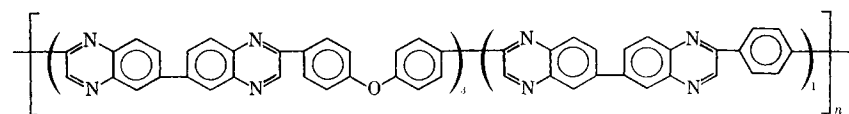
Use of the p-phenylene moiety should introduce greater rigidity and crystallinity into the polymer. Hence it is not surprising that the polymer had poorer solubility and decreased thermoplasticity.

The characterization of these polymers has been previously reported.[8] The possibility of isomers does exist; however, Stille and Williamson[2] have indicated that the 2,2'-isomer is predominantly formed.

EXPERIMENTAL

Reactants

4,4'-Oxybis(phenyleneglyoxal Hydrate) (OBPG). Following a known procedure,[3] diphenyl ether was acetylated and the resulting 4,4'-diacetyl-diphenyl ether oxidized with selenium dioxide to provide a crude product which was recrystallized once from a mixture of dioxane and water. The resulting white crystals were dried at 60°C over phosphorus pentoxide, in vacuo, for 24 hr to afford OBPG (60% overall yield) melting at 140.5°–142°C (lit.[3] mp 122°C). Calculated for $C_{16}H_{14}O$: C, 60.38; H, 4.43; found: C, 60.14; H, 4.35. This reactant was stored in a sealed brown bottle prior to use in polymer formation.

p-Phenylene Diglyoxal Dihydrate. Commercially available p-diacetyl-benzene was oxidized with selenium dioxide in refluxing aqueous dioxane to provide a crude pink solid. Recrystallization twice from water provided white plates of p-phenylene diglyoxal dihydrate (55% overall yield) melting at 163°–164°C (lit.[9] mp 110°–111°C) and exhibiting the following elemental analysis: Calculated for $C_{10}H_{16}O_6$: C, 53.10; H, 4.46; found: C, 53.34; H, 4.26. Prior to use in polymer synthesis, this reactant was stored in a sealed brown bottle.

3,3'-Diaminobenzidine (DAB). This tetraamine was obtained commercially and recrystallized once from deoxygenated water under an inert atmosphere. The resulting near-white crystals were dried for 24 hr at 80°C over phosphorus pentoxide, in vacuo, and melted at 177.5°–178°C (lit.[1] mp 179°–180°C). This monomer was stored in a sealed brown bottle under an inert atmosphere prior to use in polymer preparation.

3,3',4,4'-Tetraaminodiphenyl Ether (TADE). Following the general procedure as described by Foster and Marvel,[10] TADE was prepared as near-white crystals in an overall yield of 54%, melting at 150°–151°C (lit.[9] mp 150°–151°C) after recrystallizing from deoxygenated water in an inert atmosphere. Drying and storage were performed as previously described for DAB.

m-Cresol. Reagent-grade m-cresol was redistilled at atmospheric pressure in an inert atmosphere prior to use in polymer synthesis.

Polymers

The following procedure is a representative preparation of the diether PQ solution for application work. Monoether PQ synthesis was also per-

formed following this procedure. All inherent viscosities (η_{inh}) were determined as 0.5% sulfuric acid solutions at 25°C.

A slurry of OBPG (636.5 g, 2.0 mole) in m-cresol (1.5 l) was added during 5 min to a vigorously stirred slurry of TADE (460.5 g, 2.0 mole) in m-cresol (2 l) at ambient temperature under nitrogen. Following the addition, m-cresol (888 ml) was added to quantitatively wash down the residual glyoxal and to obtain the desired concentration. The reaction mixture was stirred for 1 hr, increasing the temperature from 32°C to 64°C. The resulting clear orange-brown viscous solution was stirred at 61° ± 4°C for 1 hr. This solution, which was used directly in application work, contained 20% solids based upon starting material, or 16.8% solids based upon the final polymer. The m-cresol solution was stored in a sealed brown bottle prior to use.

A small portion of the m-cresol solution was poured into a Waring blender containing methanol to precipitate a beige, fibrous solid. Thorough washing with methanol followed by drying for 1 hr at 170°C, in vacuo, provided a beige polymer having an η_{inh} of 0.66 and a polymer melt temperature (PMT) of 265°–270°C. A portion of the beige material was advanced in a polymerization tube under nitrogen to final polymer by introducing into a preheated oil bath at 350°C and increasing the temperature to 400°C during 1 hr and maintaining at 400°C for 1 hr. A volatile weight loss of 2.0% was recorded and an η_{inh} of 1.59 (0.5% solution in sulfuric acid) was obtained for the final polymer. During this thermal treatment, the polymer melted, foamed, and resolidified. The excellent adhesive power of the polymer was shown when glass was torn from the polymerization tube during cooling.

DISCUSSION

The primary objective of this work was to demonstrate the potential application of the PQ, especially as a high-temperature laminating resin and adhesive. Since a development effort of this type requires a significant quantity of polymer, it was necessary to develop a polymerization method which would provide an adequate supply of processable, reproducible polymer. Therefore, initial work concerned a study on polymer preparation and subsequently on the stability or shelf life of the polymer. Although the literature reports the preparation of PQ via melt and solution polymerizations, these methods were inappropriate for obtaining relatively large quantities ($\sim$1200 g) of processable, reproducible polymer.

A synthetic study which devised a method for preparing polymer suitable for evaluation in application work also provided a general method for polymer formation in m-cresol. Polymerization in m-cresol provided both a convenient means of controlling the molecular weight of the polymer and also a stable solution which could be readily employed directly in application work.

An investigation of the polymerization procedure in m-cresol was conducted using TADE and OBPG and is summarized in Table I. Since the

TABLE I
Polymerization Study of Diether Polyquinoxaline

Method no.	Mode of addition[a]	Prepolymer[b]			Final polymer[f]			
		η_{inh}[c] dl/g	PMT[d] °C	Volatile content[e] %	η_{inh}, dl/g	Isothermal wt loss[g], %, at 600°F in air after		Film[h]
						100 hr	200 hr	
1	TADE slurry to OBPG solution	0.50	~270	5.3	Insol.	4.5	14	fails fingernail crease
2	OBPG solution to TADE slurry	0.51	~260	3.8	Insol.	23.0	44	fails fingernail crease
3	OBPG slurry to TADE slurry	0.73	~265	1.9	1.68	0.5	2.0	tough and flexible
4	TADE slurry to OBPG slurry	0.68	~265	1.7	1.59	1.0	2.0	tough and flexible

[a] Addition time ~3 min at 55° ± 3°C, followed by stirring to 75° ± 3°C during 4 hr; reaction scale 0.10 mole and concentration of 20% solids in m-cresol.

[b] Isolated by dilution with methanol and drying 1 hr at 170°C under pump vacuum.

[c] Inherent viscosity (0.5% H_2SO_4 at 25°C).

[d] Polymer melt temperature.

[e] Determined by heating for 1 hr at 400°C under nitrogen.

[f] One hr at 400°C under nitrogen.

[g] Particle size <30 mesh.

[h] Prepared by doctoring m-cresol solution onto glass plate and drying to 200°C during 8 hr in vacuo.

tetraamine exhibited only limited solubility in *m*-cresol, it was used as a slurry in *m*-cresol whereas OBPG was employed in the form of a solution and also as a slurry in *m*-cresol. In addition, other modes of addition were evaluated where the OBPG as a solid was added to the tetraamine slurry. Although good polymer was obtained in this manner, a few particles of OBPG remained undissolved apparently due to the high viscosity of the *m*-cresol solution which failed to provide adequate wetting. All polymer preparations were conducted using exact stoichiometric balance. Prior to the polymerization study, it was determined that OBPG could be dissolved in *m*-cresol with warming and recovered unchanged.

Poor-quality polymer was obtained when a *m*-cresol solution of OBPG was used for polymer synthesis using the indicated reaction conditions in Table I. However, when the OBPG was used as a *m*-cresol slurry, good-quality polymer was formed as indicated by its inherent viscosity, isothermal weight loss, and film-forming ability.

The difference was apparently due to a concentration factor; too much OBPG in solution reacts rapidly with the TADE to yield a crosslinked polymer as indicated by insolubility and film of the final polymer. It is theorized that the slow addition of the OBPG solution would provide a more orderly and controlled reaction to yield good-quality polymer in the following manner:
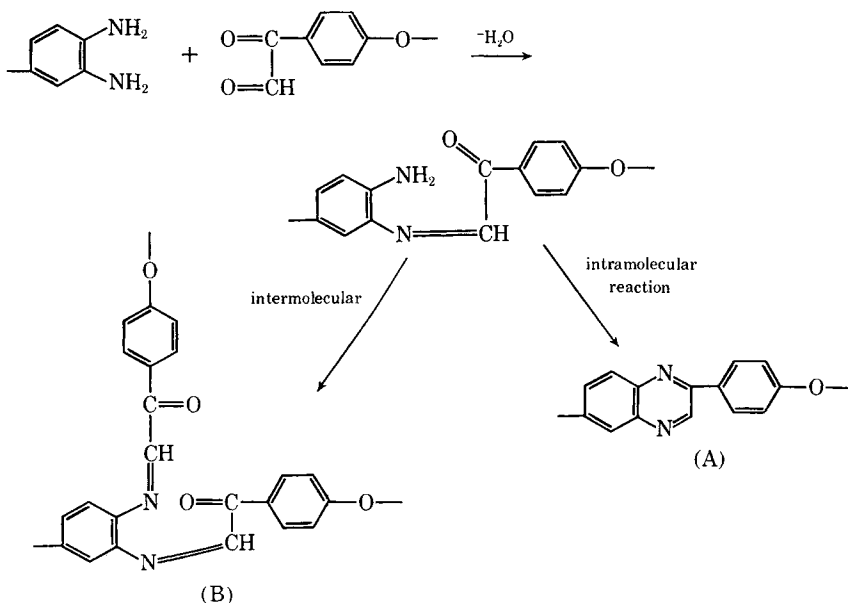
With the slurry there is little if any excess of bisglyoxal in solution, consequently the less reactive keto group of the intermediate has the opportunity to react intramolecularly to form the desired product (A). With the bisglyoxal completely in solution, the opportunity arises for the more reactive aldehyde portion of the glyoxal group to react intermolecularly

with an unreacted amine group and consequently to lead to crosslinking, low molecular weight polymers (brittle films), and poorer oxidative stability because of unclosed rings.

Regardless, this study provided a method for preparing processable, reproducible polymer. A basic study of PQ synthesis, including kinetic data, would have failed to contribute significantly to the overall primary objective of the program, which was demonstration of potential PQ application.

Although methods 3 and 4 of Table I provided essentially identical polymer, method 3 was selected for large-scale polymer synthesis because of the relative ease of manipulation. The m-cresol solutions of the polymers so formed were used directly in application work for film casting or prepreg and tape preparation.

A m-cresol solution of the diether PQ exhibited excellent shelf life as shown by characterizing the polymer solution and isolated polymer therefrom periodically up to 90 days. The film-forming ability of the solution and the physical properties such as η_{inh} and PMT of the isolated polymer remained essentially constant, which indicated no apparent change in the characteristics of the polymer. In addition, prepreg and tape prepared from a m-cresol polymer solution provided good laminates and adhesive panels after being stored in a polyethylene bag up to 120 days at ambient temperature. This further demonstrated the excellent stability of the PQ both in solution and in a more applied state.

Both polyquinoxalines, isolated as described in the experimental section, generally exhibited an η_{inh} of 0.6 to 0.8 dl/g with a PMT of 260° to 300°C. Advancement of this isolated material by heating for 1 hr at 400°C in nitrogen provided final polymer which generally exhibited an η_{inh} of >1.5. The final polymer is somewhat thermoplastic as shown by the formation of a clear yellow, extremely tough polymer disc when a powdered sample was placed between preheated press platens at 427°C and 2000 psi. However, the thermoplastic nature of the polyquinoxalines in a composite or as an adhesive can be almost completely overcome as demonstrated by the excellent mechanical properties discussed later in this paper. In addition, further improvement can be realized by the preparation of quinoxaline copolymers which will be discussed in a forthcoming publication.

Polymers were evaluated for thermal and oxidative stability by thermogravimetric analysis (TGA) and isothermalgravimetric analysis (ITGA). In our laboratories emphasis is placed on ITGA data because it more closely approaches heat-aging conditions generally required for structural polymers and because it is a more discriminatory technique than TGA. Polymers whose TGA curves are virtually identical can display considerable differences in stability under ITGA conditions. Polymer oxidative degradation is a time-dependent reaction, hence the rapidity of the TGA test is one possible reason for the technique's inability to differentiate between some polymers. The differences in stability by TGA and ITGA are illustrated in Figures 1 and 2. By TGA, the A-B polybenzothiazole synthe-

sized from 3-amino-4-mercaptobenzoic acid in polyphosphoric acid has a polymer decomposition temperature 50°C higher than that of the diether polyphenylquinoxaline[8] synthesized from oxydibenzil and 3,3',4,4'-tetra-aminodiphenyl ether.   However, isothermally at 371°C in air the positions are reversed, with the polyphenylquinoxaline being considerably more stable.
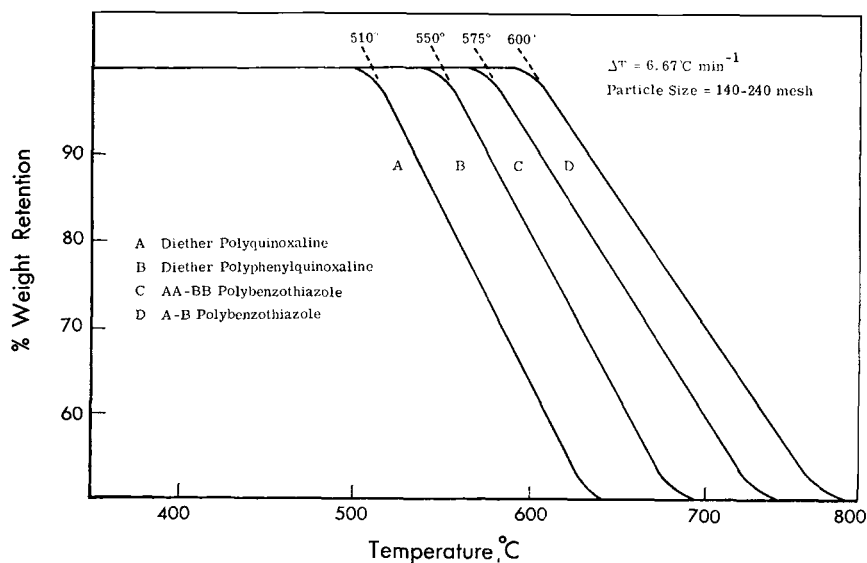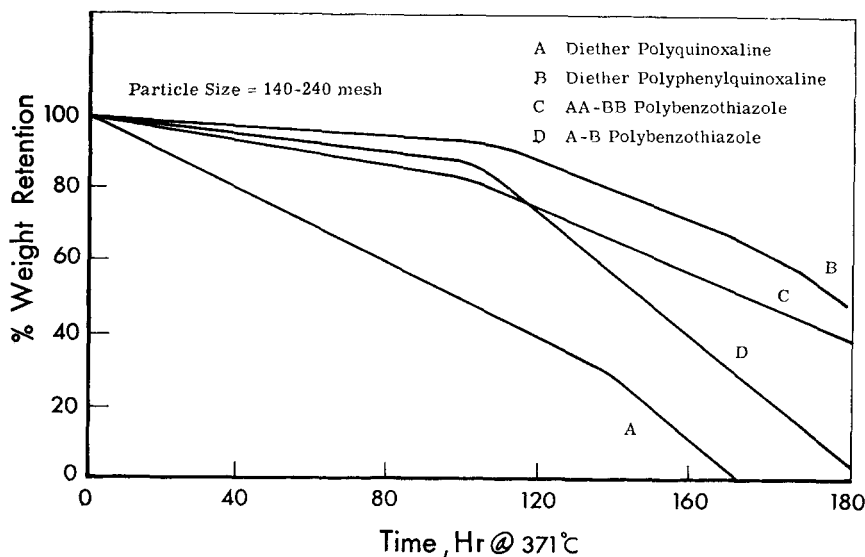

Fig. 1. Thermograms in air.

Fig. 2. Isothermal weight loss in air at 371°C.

APPLICATION

The primary purpose of this work was to demonstrate a potential of the polyquinoxalines as laminating resins and structural adhesives. Other potential uses were given cursory examinations. The diether and monoether PQ were selected for application studies because these were the best-known polymers in all respects.

Polyquinoxalines are noteworthy for their processability when compared to other aromatic-heterocyclic polymers. The most significant advantage is the retention of processability while having very low volatiles evolution. For example, laminates have been fabricated from prepreg containing only 0.8% total volatiles under 500 psi at 371°C. When the prepreg total volatile content was adjusted to 2%–3%, high-density laminates were fabricated under 200 psi. Generally, laminates were fabricated from prepreg having a total volatile content of 6%–9% under 200 psi pressure starting at 232°C and increasing the press temperature to 371°C.

With such a low level of condensation-volatiles evolution, it is necessary for the polymer in the prepreg to be of substantially high molecular weight and also almost totally ring closed; the high molecular weight was indicated by inherent viscosities of about 0.8. The processability of the polymer apparently results from the presence of tenaciously held m-cresol which serves as a plasticizer. This was indicated by analysis of the trapped volatiles evolved from prepreg varying in total volatile content from 0.8% to 9.0%. A piece of the prepreg was placed in a polymerization tube under argon and heated at 400°C for 1 hour. The evolved volatiles were collected by means of cooling in a dry ice-acetone bath and analyzed by vapor phase chromatography. The composition of the volatiles from prepreg (resin pickup 32%) having a total volatile content of 0.8% was 0.3% water and 0.5% m-cresol. This corresponded to a volatile content of 2.5% for the resin of which 0.8% and 1.7% were water and m-cresol respectively. In addition, analysis of volatiles from prepreg (resin pickup 42%) with a volatile content of 9.0% showed that 0.8% was water and 8.2% was m-cresol.

Initial heating in the press removes the remaining m-cresol but now, the porous resin matrix is still sufficiently thermoplastic to be compressed prior to complete loss of condensation volatiles. Such behavior provides the polyquinoxalines with superior processability and heat aging performance superior to that anticipated from TGA and ITGA evaluations.

FABRICATION AND MECHANICAL PROPERTIES

Unless indicated otherwise, all composites were prepared with 1581 style AF-994 glass having an HTS finish. The dimensions of the laminates were 4.5 in. $\times$ 6 in. $\times$ 7 ply and all test data are reported as averages of triplicate tests. All tests including aging were done at temperature.

Prepreg was prepared from a diether PQ solution (20% resin) by using three dip coats with forced air drying for 10, 15, and 60 min at 130°C, re-

spectively. This prepreg was used to make a 7-ply laminate by curing for 10 min at 232°C, followed by raising the temperature as rapidly as possible (~45 min) to 407°C and maintaining at 407°C for 4 hr, all at 200 psi. The entire laminate was postcured for 4 hr each at 205°C and 232°C, 10 hr at 260°C, 8 hr at 288°C, and 4 hr each at 316°C, 344°C, 371°C, and 398°C, all under nitrogen. The final laminate had a 24.8% resin content, a density of 1.92, and a calculated void content of 4.0%. Test data are shown in Table II.

TABLE II
Flexural Strength and Modulus of Diether Polyquinoxaline

Test condition	Flexure, psi[a]	Modulus, psi $\times$ 10^6
RT	111,500	3.87
1 hr/371°C	55,900	3.49
50 hr/371°C	35,750	2.62
10 min/538°C	29,800	3.20

[a] All values are averages of triplicate tests.

Prepreg was made with monoether PQ solution (20% resin) by the identical treatment as above. This was used to fabricate a 7-ply laminate by curing in the same way as above for the diether polymer. After the identical postcure as above, the laminate was postcured an additional 8 hr at 371°C, in nitrogen. The final laminate had a resin content of 33.1%, a density of 1.71, and a calculated void content of 8.6%. Table III lists the test data.

TABLE III
Flexural Strength and Modulus of Monoether Polyquinoxaline

Test condition	Flexure, psi[a]	Modulus, psi $\times$ 10^6
RT	99,600	3.64
1 hr/371°C	61,600	2.44
50 hr/371°C	44,000	2.51
10 min/538°C	16,900	2.19

[a] All values are averages of triplicate tests.

Examination of the monoether flexure specimens tested at 538°C after 10 min at 538°C in air indicated that some thermoplastic failure had occurred. In an attempt to overcome this thermoplastic failure, an exploratory copolymer was synthesized using 75:25 mole-% of OBDG and p-phenylenediglyoxal respectively with DAB.

As anticipated, the resultant polymer was less soluble in m-cresol and was therefore used as a 12% solution to prepare prepreg. Seven dip coats were needed, using forced air drying for 10 min at 130°C between coats and a final dry of 1 hr at 130°C. The resulting prepreg on AF-994 HTS was used to fabricate a 7-ply laminate which was cured and postcured as for the monoether PQ. The laminate had a resin content of 27.8%, a density of

TABLE IV
Flexural Strength and Modulus of Copolymeric Monoether Polyquinoxaline

Test conditions	Flexure, psi	Modulus, psi $\times 10^6$
RT	105,600	3.45
1 hr/317°C	75,000	3.09
200 hr/317°C	57,700	3.35
1 hr/371°C	50,800	2.49
50 hr/371°C	49,900	2.83
10 min/538°C	31,750	3.23
60 min/538°C	12,700	1.97

1.77, and a calculated void content of 9.2%. Data are presented in Table IV.

Preliminary data were obtained on a unidirectional boron filament composite using monoether polyquinoxaline. Cure was accomplished by a 5-min contact at 382°–394°C, then 4 hr at 394°C and 500 psi in air. Postcure was accomplished with the same schedule used for the diether laminate (Table I). Test data given in Table V were obtained after 3 min at temperature.

TABLE V
Flexural Strength and Modulus of Monoether Polyquinoxaline,
Boron Filament, Unidirectional Composite

Test Temperature	Flexure, psi	Modulus, psi $\times 10^6$
RT	253,000	42.3
133°C	197,000	36.2
177°C	200,600	37.5
212°C	180,200	37.0
316°C	220,800	24.2
361°C	241,500	12.1

TABLE VI
Tensile Shear on Stainless Steel of Diether Polyquinoxaline

Test conditions	Tensile shear, psi
RT	3320
1 hr/371°C	1567
50 hr/371°C	1670
10 min/538°C	1283

Efforts aimed at structural adhesives were less extensive; nevertheless, the data indicated a definite potential. As indicated in the following discussion the monoether PQ provided somewhat better performance after aging at elevated temperature.

Adhesive prepreg tapes were made from 112 E glass fabric having A-1100 finish. The polymer solution in m-cresol was mixed with elemental boron, applied to the fabric, and dried to a volatile content of 3.8%. Bonding was

TABLE VII
Tensile Shear on Stainless Steel of Monoether Polyquinoxaline

Test conditions	Tensile shear, psi
RT	3350
1 hr/316°C	2930
200 hr/316°C	2280
1 hr/371°C	1870
50 hr/371°C	2540
10 min/538°C	1325

to 17-7 stainless steel, given the phosphate etch. Cure was achieved by heating 1 hr each at 426°C and 455°C at 200 psi in nitrogen. There was no postcure (see Table VI).

Processing at 200 psi and 1 hr each at 344°C, 426°C, and 455°C, the monoether adhesive tape containing 11.3% volatiles was used to make bonds. Test data are shown in Table VII.

The temperatures and pressure used to prepare the bonds were too stringent, but the potential of the PQ as structural adhesives was demonstrated. A reduction in processing conditions is highly desirable and most likely can be achieved by either more processing studies and/or modification of the polymer properties.

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