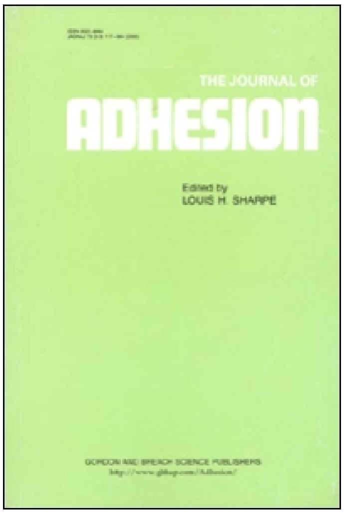

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Chemistry and Adhesive Properties of Phenylethynyl-Terminated Phenylquinoxaline Oligomers

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As part of a program to develop high performance/high temperature structural resins for potential aeronautical applications, phenylethynyl-terminated phenylquinoxaline oligomers were prepared, characterized, thermally cured and the cured resins were evaluated as adhesives. The phenylquinoxaline oligomers were prepared by conventional and aromatic nucleophilic displacement routes and chain terminated with mono or di(phenylethynyl) groups. The oligomers were melt pressed into thin films, compression molded into tensile and compact tension specimens, and fabricated into titanium-to-titanium single lap shear adhesive specimens. The oligomers were generally compression molded for 1 hr at 350°C under pressures ranging from 0.10 to 1.4 MPa. The phenylquinoxaline oligomer prepared *via* aromatic nucleophilic displacement exhibited better processability and higher tensile shear strengths than those of the oligomers prepared *via* the conventional synthetic route. The synthesis, physical and mechanical properties of these oligomers and their cured polymers are presented.

KEY WORDS: Adhesives; phenylethynyl termination; phenylquinoxalines; reactive thermoplastics; high temperature polymers; mechanical properties; titanium; processability; solvent resistance.

INTRODUCTION

High temperature/high performance structural resins with a unique combination of properties are needed for potential use on advanced aircraft. The materials must be readily processable under pressures and temperatures that are compatible with the capabilities of manufacturing equipment presently in use or under development. In addition, they must meet minimum requirements for mechanical performance during operational conditions which include high temperature, high air flow, high stress, cyclic loading, impact resistance, thermal cycling and exposure to moisture (*i.e.* rain, condensation) and aircraft fluids such as hydraulic fluid, deicing fluid, paint stripping solvents, high pH cleaning solutions and aircraft fuels. Recent developments in the area of phenylethynyl-terminated imide oligomer technology have produced some promising results.[1–14] Certain oligomer compositions are readily processable as adhesives and composite matrix resins under pressures less than 1.4 MPa. During compression molding, the material is thermally treated for ~ 1 hr at 350–371°C thereby causing the latent phenylethynyl groups to react and provide a pseudo thermoset. The chemical structure of the cured material is not well known; however, the material exhibits excellent properties including relatively high glass transition temperature (T_g), good thermal stability, good moisture and solvent resistance, high toughness and high mechanical properties.

Polyimides are known to be susceptible to hydrolysis when in contact with high pH aqueous media such as the type used extensively in the aircraft industry for cleaning purposes.[15] Thus, the objective of the work discussed herein was to place phenylethynyl groups onto the chain ends of phenylquinoxaline oligomers and to evaluate these materials subsequently as adhesives for titanium (Ti). Polyphenylquinoxalines are known to be more hydrolytically stable than polyimides.[16]

Phenylquinoxaline oligomers were prepared by two different synthetic routes, conventional[17] and aromatic nucleophilic displacement,[18-20] and subsequently endcapped with mono- and di(phenylethynyl)-containing endcappers.[21] The oligomers were characterized and mechanical properties of thin films, neat resin moldings and Ti-to-Ti single lap shear adhesive specimens were determined.[22] The effects of thermal aging in air and exposure to aircraft fluids were assessed on both neat resin and adhesive specimens. In addition, preliminary evaluation of the effects of processing conditions on final mechanical properties was conducted. The results of this study are discussed herein.

EXPERIMENTAL

Starting Materials

1,4-Bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene and isomers,[18] 4-phenylethynylbenzil,[21] 4,4′-di(phenylethynyl)benzil,[21] and 4-fluoro-4′-phenylethynylbenzophenone[23] were prepared as previously reported. 4,4′-Biphenol was obtained from Aldrich Chemical, Co. and recrystallized from toluene prior to use. All other chemicals and solvents were obtained from commercial sources and used without further purification.

Phenylethynyl-Terminated Phenylquinoxaline Oligomers Via Aromatic Nucleophilic Displacement (target number average molecular weight 5000 g/mole):

Into a 1L three-neck, round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, Dean Stark trap and condenser were placed 1,4-bis (6-fluoro-3-phenyl-2-quinoxalinyl)benzene (and isomers) (38.85 g, 74.35 mmole), 4,4′-biphenol (15.82 g, 85.0 mmole), 4-fluoro-4′-phenylethynylbenzophenone (6.38 g, 21.24 mmole), pulverized anhydrous potassium carbonate (23.6 g, 17.07 mmole), toluene (100 mL) and N-methyl-2-pyrrolidinone (NMP, 225 mL, 20% solids). The reaction mixture was heated to reflux (~ 145°C) for 4 hours in a silicone oil bath to remove water from the reaction mixture. The toluene was removed from the system *via* the Dean Stark trap and the temperature was increased to ~ 165°C and held for 4 hr. The slightly viscous solution was allowed to cool to room temperature and precipitated into acetic acid/water mixture in a high speed blender. The oligomer powder was washed successively in hot water and boiling methanol and subsequently dried for 4 hr at 115°C under vacuum. The oligomer powder exhibited an initial T_g of 246°C which increased to 270°C after curing for 1 hr at 350°C in a sealed aluminum pan in static air. A 0.5% solution of the oligomer in NMP exhibited an inherent viscosity (η_{inh}) of 0.34 dL/g measured at 25°C.

Phenylethynyl-Terminated Phenylquinoxaline Oligomers Via Conventional Synthesis (target number average molecular weight 2500 g/mole):

This serves as a representative example of the procedure used to prepare all of the phenylethynyl-terminated quinoxaline oligomers *via* conventional synthesis. Into a 500 mL three-neck, round bottom flask equipped with a mechanical stirrer, thermometer and nitrogen gas inlet were placed 4,4′-oxydibenzil (15.3286 g, 35.3 mmole), 4-phenylethynylbenzil (5.7097 g, 18.4 mmole) and NMP (50 mL). After the two benzil compounds had dissolved, 3,3′,4,4′-tetraaminobiphenyl (9.5309 g, 44.5 mmole) and additional NMP (65 mL) were added. The solution temperature increased to ~ 35°C due to the exothermic reaction. The solution was stirred at room temperature overnight under nitrogen. The temperature was then increased to ~ 120°C for 3.5 hr and the oligomer began to precipitate from solution. The mixture was poured into water, washed successively in hot water and boiling methanol, and dried at 125°C under vacuum for 5 hr. The powder exhibited an initial T_g of 255 °C which increased to 328°C after curing for 1 hr at 350°C in a sealed aluminum pan in static air. A 0.5% solution of the oligomer in NMP exhibited in η_{inh} of 0.16 dL/g measured at 25°C.

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) solutions in NMP at 25 °C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20 °C/min with the T_g taken at the inflection point of the ΔT *versus* temperature curve. Dynamic thermogravimetric analysis (TGA) was performed on a Seiko Model 200/220 thermal analysis instrument on powder samples, predried for 0.5 hr at 100 °C, at a heating rate of 2.5 °C/min in air and nitrogen at a flow rate of 15 cc/min.

Films

Oligomer powder was melt pressed at 350 °C under 6.9 MPa and held for 1 hr. The films were non-uniform in thickness and contained occluded particulate contaminants. The tensile properties of the thin films were determined according to ASTM D882 using at least four specimens per test condition.

Solvent Exposure of Films

Stressed and unstressed thin films (7.6 cm × 0.51 cm × 0.0127 cm thick) were dried, weighed and subsequently immersed in ethylene glycol, jet fuel, hydraulic fluid, methylene chloride, methyl ethyl ketone and toluene at ambient temperature for 14 days. The samples were blotted dry with a paper towel and weighed to determine solvent uptake. To induce stress on the PETQ-1 specimens they were folded back on themselves to form a circle and held in place with a paper clip. All of the other films were too brittle and could not be bent back on themselves without breaking; thus they could not be exposed in the stressed configuration.

Molded Specimens

Powdered oligomer prepared *via* aromatic nucleophilic displacement (PETQ-1, 5K) was compression molded in a 3.2 cm^2 stainless steel mold under 0.69 MPa by heating to 300°C for 0.5 hr and 350°C for 1 hr. Powdered oligomer prepared *via* conventional synthesis (PETQ-2, 2.5 K) was compression molded under 1.4 MPa by heating to 300 °C for 0.5 hr and 350 °C for 1 hr. Miniature compact tension specimens (1.6 cm × 1.6 cm × 0.95 cm thick) were machined from the moldings and subsequently tested to determine fracture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. G_{Ic} (critical strain energy release rate) was calculated using the mathematical relationship $G_{Ic} = (K_{Ic})^2/E$, where E is the modulus of the material. Flat panels (7.6 cm × 7.6 cm × 0.23 cm thick) were prepared fom PETQ-1 by compression molding under the conditions described above. Dumbbell shaped specimens (ASTM D638V, 6.35 cm × 0.95 cm × 0.23 cm thick) were machined from the panels and subsequently tested to determine neat resin tensile properties according to ASTM D638 using four specimens per test condition.

Viscoelastic Properties

A Rheometrics System 4 rheometer configured in the rectangular torsion mode was used to measure the complex modulus of PETQ-1(5K). The measurement was performed on a molded specimen (6.35 cm × 1.27 cm × 0.11 cm thick) at a constant oscillatory frequency of 10 rad/s and a heating rate of 4 °C/min.

Adhesive Specimens

Adhesive tape was prepared by multiple coating of 112-E glass (A-1100 finish) with NMP solutions of the various oligomers (20% solids) and stage dried (*i.e.* 1 hour at 100 °C, 0.5 hours at 150 °C, 0.5 hours at 200 °C) up to 225 °C for 0.5 hours after each coat. The final volatile content of the tapes was generally ~ 1%. Single lap shear specimens (bond area 2.54 cm wide × 1.27 cm in overlap) using titanium (Ti-6Al-4V) adherends with a Pasa Jell 107® (Products Research and Chemical Corp., Semco Div). surface treatment were fabricated under pressures ranging from 0.10 to 0.7 MPa depending upon the oligomer. The final cure condition was 1 hr at 350 °C. Single lap shear strengths were determined according to ASTM D1002 using four specimens per test condition. Isothermal aging was performed in a forced air oven held at 177°C for 1000 and 5000 hrs.

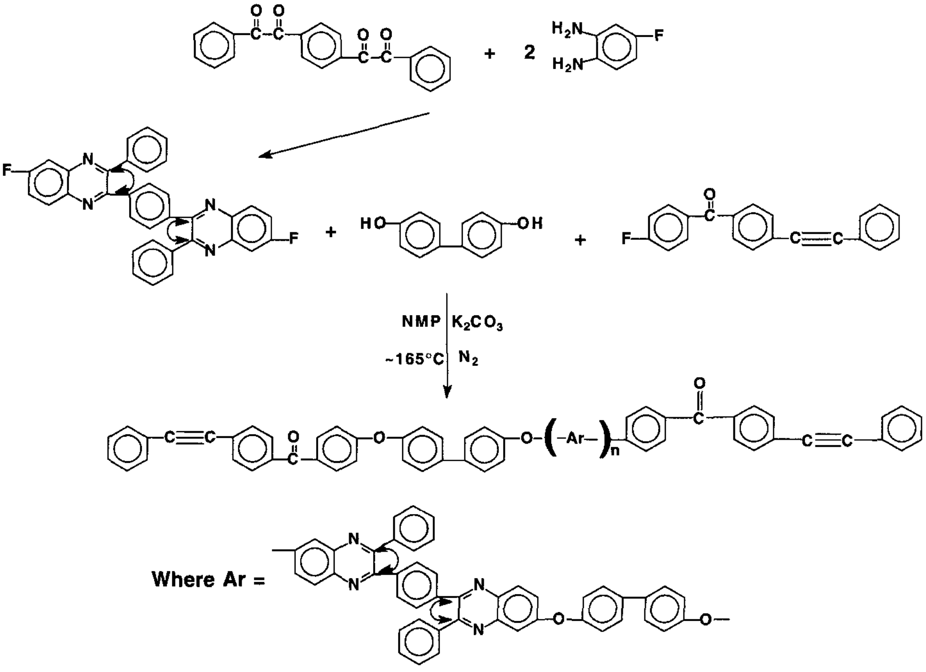
Solvent Exposure of Adhesive Specimens

Unstressed single lap shear specimens were immersed in jet fuel, hydraulic fluid, and methyl ethyl ketone at ambient temperature and water at 100°C for 72 hrs and subsequently removed, blot dried and tested for lap shear strength according to ASTM D1002.

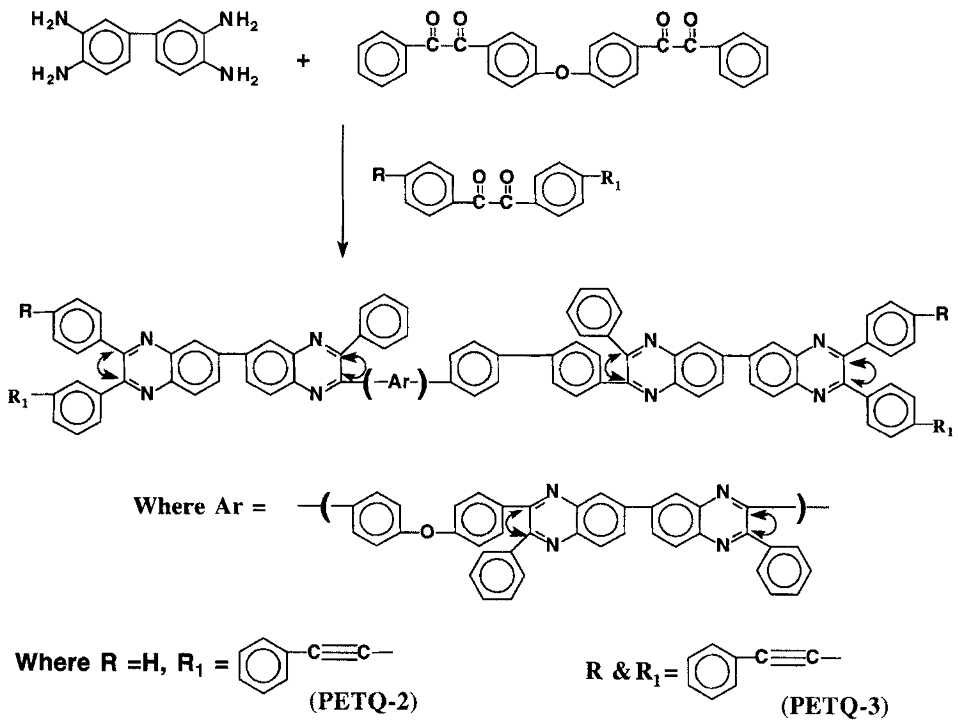
RESULTS AND DISCUSSION

Oligomer Syntheses

The PETQs were prepared by two different synthetic routes in order to determine if one route offered any advantages over the other. The first route involved aromatic nucleophilic displacement of an activated difluoroquinoxaline compound with an aromatic bisphenol[18] using 4-fluoro-4′-phenylethynylbenzophenone as an endcapper. The reactions were carried out in NMP at 165°C using potassium carbonate under nitrogen. The reaction sequence for the preparation of PETQ-1 is presented in Scheme 1. The other PETQs were prepared by the conventional synthetic route from an aromatic bis(1,2-diamine) and an aromatic bis(1,2-diketone).[16] These oligomers were endcapped with mono or di(phenylethynyl) endcapping agents[21] as shown in Scheme 2. PETQ-2 has mono phenylethynyl termination while PETQ-3 has



SCHEME 1 Synthesis of PETQ-1 *via* aromatic nucleophilic displacement route.



SCHEME 2 Synthesis of PETQ-2 and PETQ-3 *via* conventional synthetic route.

TABLE I

Oligomer Characterization

Sample	Calc'd M_n, g/mole	η_{inh}, dL/g[1]	T_g,°C[2] Initial	Cured	Temp. of 5% Weight Loss, °C[3] Air	Nitrogen
PETQ-1	5000	0.34	246	270	497	540
PETQ-2	2500	0.16	249	329	512	532
PETQ-2	5000	0.28	279	340	507	537
PETQ-3	2500	0.16	ND	ND	495	542
PETQ-3	5000	0.32	234	ND	483	541

[1] Inherent viscosities determined on 0.5% (w/v) solutions in NMP at 25°C.

[2] Determined on as-isolated oligomer powders by DSC at a heating rate of 20°C/min. Initial T_g determined on first heat-up, sample cured 1 hr at 350°C and rerun.

[3] Determined by TGA on as-isolated, uncured oligomer at a heating rate of 2.5°C/min.

[4] ND = not detected.

di(phenylethynyl) termination. After thermal curing, PETQ-3 would presumably have higher crosslink density. Oligomers prepared by either synthetic route have configurational isomers distributed randomly along the backbone. Oligomer characterization is presented in Table I. PETQ-1 was prepared at a calculated number average molecular weight ($\bar{M}_n$) of 5000 g/mole, PETQ-2 and PETQ-3 were prepared at $\bar{M}_n$s of 2500 and 5000 g/mole. The initial T_gs ranged from 234 to 279°C. No explanation is offered to account for the higher than expected initial T_g of PETQ-2 (5K). The high molecular weight linear polyphenylquinoxaline of this composition has a T_g of 305°C.[24] After curing for 1 hr at 350°C in a sealed aluminum pan, the T_gs increased markedly due to the thermal reaction (chain extension and crosslinking) of the phenylethynyl groups. The two cured oligomers that contained di(phenylethynyl) termination (PETQ-3) did not exhibit a T_g detectable by DSC presumably due to relatively high crosslink density. The onset of cure of the phenylethynyl groups, as indicated by a broad exothermic peak in the DSC thermogram, was comparable for all of the PETQ oligomers ranging from 350 to 375°C with the temperature of maximum exotherm ranging from 405 to 425°C. The temperatures of 5% weight loss as determined by TGA ranged from 483 to 512°C in air and from 532 to 542°C in nitrogen.

Film Properties

Thin film tensile properties were determined on melt-pressed films of marginal quality; in one case (PETQ-1, 5K), tensile properties were determined on molded dumbbell tensile specimens. Thin films were prepared from oligomer powder by heating to 350°C under 6.9 MPa for 1 hr. Thin film tensile properties are presented in Table II. The data from the melt-pressed films exhibited greater scatter than those obtained from the molded samples, presumably due to film quality and defect sensitivity of the test. Except for those of PETQ-3(2.5K), the tensile properties were comparable with those exhibited by high molecular weight unendcapped polyphenylquinoxalines.[24] The strength retention at 177 °C of PETQ-3(5K) was higher than that of the others but a higher retention of modulus at 177 °C was not observed.

Solvent Exposure of Thin Films

Melt-pressed films of the various oligomers were immersed for 14 days at ambient temperature in solvents that are commonly used on or in the vicinity of aircraft. The PETQ-1(5K) specimens were immersed in both unstressed and stressed configurations.

TABLE II

Unoriented Thin Film Tensile Properties

Sample	Calc'd $\bar{M}_n$, g/mole	Test Temp., °C	Tensile Strength, MPa	Tensile Modulus, GPa	Elong. at Break, %
PETQ-1	5000	23	99.3 ± 3.7	4.12 ± 0.6	4 ± 0.1
		177	51.4 ± 1.5	2.76 ± 0.03	4 ± 0.1
PETQ-2	2500	23	93.5 ± 12.8	2.82 ± 0.10	5 ± 1
		177	64.5 ± 5.5	1.92 ± 0.13	6 ± 2
PETQ-2	5000	23	96.7 ± 11.3	2.66 ± 0.05	5 ± 1
PETQ-3	2500	23	55.1 ± 7.7	2.64 ± 0.03	2 ± 1
		177	54.5 ± 3.8	2.10 ± 0.1	3 ± 1
PETQ-3	5000	23	100 ± 11.6	2.81 ± 0.04	5 ± 1
		177	73.6 ± 0.3	2.00 ± 0.14	6 ± 2

*Test performed on neat resin dumbbell moldings.

To induce stress, the PETQ-1 specimens were folded back on themselves to form a circle and held in place with a paper clip. All of the other films were brittle and could not be bent back on themselves without breaking, thus they could not be exposed in the stressed configuration. The amount of solvent absorbed was determined by the increase in weight of the samples. The solvent uptake information is presented in Table III. In general, the films absorbed significant amounts of methyl ethyl ketone (MEK), methylene chloride and toluene, but only small amounts of jet fuel (JP-IV), deicing fluid (ethylene glycol) and hydraulic fluid (Skydrol®). The stressed film specimens of PETQ-1 absorbed more of the solvent than the corresponding unstressed film. PETQ-3(2.5K) exhibited weight losses when immersed in JP-IV and methylene chloride indicating that some of the material dissolved. The effect of exposure to these solvents on neat resin mechanical properties of these cured oligomers was not determined.

Fracture Toughness

Critical stress intensity factors (K_{Ic}) were determined for PETQ-1(5K) and PETQ-2(2.5K). PETQ-1 moldings were prepared under 0.69 MPa by heating to 300 °C for 0.5 hr and 350 °C for 1 hr. PETQ-2(2.5K) moldings were prepared under 1.4 MPa by heating to 300 °C for 0.5 hr and 350 °C 1 hr. Critical strain energy release rate (G_{Ic}) was calculated using the mathematical relationship $G_{Ic} = (K_{Ic})^2/E$, where E is the modulus of the material. PETQ-1(5K) exhibited a K_{Ic} of 1592 MPa·m$^{1/2}$ and a $G_{Ic}$of 894 J/m^2. PETQ-2(2.5K) exhibited a K_{Ic} of 1200 MPa.m$^{1/2}$ and a G_{Ic} of 744 J/m^2. The linear oligomeric segment in PETQ-1(5K) is essentially twice that of PETQ-2(2.5K) and, therefore, higher K_{Ic} and G_{Ic} were expected. However, it was interesting to note that the differences were not very large.

Viscoelastic Properties

The complex modulus, G', of PETQ-1(5K) was measured as a function of temperature at a constant frequency of 10 rad/s in the rectangular torsion mode. The

TABLE III

Thin Film Solvent Absorption Weight Increase After 14 Days of Immersion, %

Sample	Ethylene Glycol	JP-IV	Skydrol®	Methylene Chloride	Methyl Ethyl Ketone	Toluene
PETQ-1(5k)						
Unstressed	0.5	0.0	0.0	1.8	10.3	4.9
Stressed	0.7	0.0	0.0	2.8	11.2	6.9
PETQ-2(2.5K)						
Unstressed	1.9	0.9	0.0	16.8	13.5	2.8
PETQ-2(5K)						
Unstressed	0.6	0.2	0.5	19.1	10.7	1.5
PETQ-3(2.5K)						
Unstressed	1.0	−1.4	1.1	−4.7	13.0	2.2
PETQ-3(5K)						
Unstressed	1.9	0.6	1.7	15.5	12.7	4.4

rheological behavior of PETQ-1 is presented in Figure 1. PETQ-1(5K) exhibited a G' of 1.271×10^{10} dynes/cm^2 at 50°C, 1.006×10^{10} at 177°C, 9.706×10^9 at 200°C and 7.595×10^9 at 270°C (*i.e.* T_g). These values correspond to relative retentions of 79% at 177°C, 76% at 200°C and 60% at T_g (270°C).

Adhesive Properties

Preliminary Ti-to-Ti tensile shear properties are presented in Table IV. PETQ-1(5K) adhesive specimens fabricated by heating to 350°C under 0.1 MPa and held for 1 hr exhibited good strengths at both room temperature and 177°C with predominantly cohesive failures. PETQ-2(2.5K) adhesive specimens fabricated by heating to 350°C under 0.17 MPa and held for 1 hr exhibited lower than expected strengths with predominantly adhesive failures. It appeared that the PETQ-2(2.5K) oligomer was not compatible with the Pasa Jell 107 titanium surface treatment. Higher pressures (up to 0.69 MPa) and higher cure temperatures (up to 400°C) had no beneficial effects on the tensile shear strengths.

The effect of bonding pressures on the tensile shear strengths and bondline thicknesses for PETQ-1(5K) are presented in Table V. When processed under 0.69 and 0.34 MPa, the bondlines were thin and the scrim cloth fibers were distorted, indicating excessive pressure. Even under 0.10 MPa, PETQ-1(5K) exhibited high flow. Varying the bonding pressure did not have an effect on the tensile shear strengths.

PETQ-1(5K) lap shear specimens were immersed in Skydrol®, JP-IV, MEK and boiling water, blotted dry and immediately tested for tensile shear strengths. In addition, PETQ-1(5K) unstressed lap shear specimens were isothermally aged for 1000 and 5000 hr at 177°C in a forced air oven. The results of both thermal and solvent exposures on PETQ-1(5K) adhesive properties are presented in Table VI.

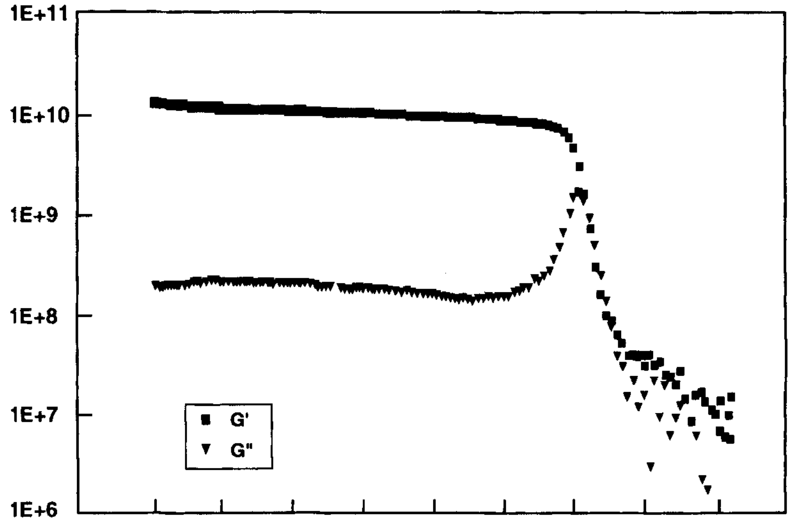


FIGURE 1 Dynamic mechanical spectrum of PETQ-1.

TABLE IV

Ti-to-Ti Tensile Shear Properties

Sample	Test Temperature, °C	Tensile Shear Strength, MPa
PETQ-1(5K)	23	35.2 ± 1.6
	177	27.6 ± 1.5
PETQ-2(2.5K)	23	14.8 ± 1.8
	150	13.6 ± 1.1
	177	12.9 ± 0.3

TABLE V

Effect of Processing Conditions on Room Temp. Tensile Shear Strengths of PETQ-1(5K)

Processing Condtions	Bondline Thickness, cm	Tensile Shear Strength, Mpa
350°C, 1 hr, 0.69 Mpa	0.0061–0.0079	32.9 ± 1.3
350°C, 1 hr, 0.34 MPa	0.0081–0.0107	30.2 ± 1.7
350°C, 1 hr, 0.10 MPa	0.0101–0.0124	35.2 ± 1.6

TABLE VI

Effect of Thermal and Solvent Exposure on Adhesive Properties of PETQ-1(5K)

Exposure Conditions	Test Temperature, °C	Tensile Shear Strength, MPa
none	23	35.2 ± 1.6
	177	27.6 ± 1.5
1000 hr at 177°C	23	28.3 ± 1.7
	177	25.4 ± 0.5
5000 hr at 177°C	23	24.9 ± 0.8
	177	25.4 ± 0.7
JP-IV for 72 hr	23	31.4 ± 0.5
	177	26.5 ± 0.5
Skydrol® for 72 hr	23	29.8 ± 2.1
	177	25.6 ± 0.5
Water Boil for 72 hr	23	25.3* ± 0.3
	177	21.4* ± 0.3
MEK for 72 hr	23	39.3 ± 1.3
	177	28.9 ± 0.8

*Mixed failures, all others exhibited predominantly cohesive failure.

Tensile shear strengths at 23°C declined from 35.2 to 24.9 MPa after aging for 5000 hours at 177°C. The failure modes remained predominantly cohesive. This trend has been observed before with other adhesives such as thermoplastic polyimides[25] and polymers from phenylethynyl terminated oligomers.[26–28] Aged specimens from both Pasa Jell 107 and 5 volt chromic acid anodized surface treated titanium have exhibited this trend. The tensile shear strengths at 23°C for these materials leveled off after aging at 177°C and had essentially the same values at 23 and 177°C. The reason for this is unknown.

The tensile shear strengths of specimens exposed unstressed to JP-IV, Skydrol® and MEK for 72 hours showed only minor changes in the 23°C values and virtually no change in the 177°C strengths relative to the unexposed specimens. A significant loss of strength was seen in specimens exposed to a 72-hour water boil. The failure mode was primarily adhesive. This loss of strength is presumably due to the surface treatment and not to degradation of the adhesive. Adhesive specimens from Pasa Jell 107 surface treated titanium are known to undergo loss of strength after moisture exposure. Specimens exposed to MEK showed no loss in strength. This was unexpected since films of this adhesive [PETQ-1(5K)] absorbed ~ 10% of MEK.

SUMMARY

Controlled molecular weight phenylethynyl-terminated phenylquinoxaline oligomers were prepared by aromatic nucleophilic displacement and conventional synthetic routes. The oligomers were processed into films, moldings and adhesive specimens. PETQ-1(5K) exhibited a favorable combination of properties including high T_g, high neat resin tensile properties and excellent processability under relatively low pressures. Although thin films of all the PETQs absorbed significant amounts of MEK, PETQ-1(5K) exhibited no changes in Ti-to-Ti lap shear strengths after 72-hr immersion in MEK. The PETQ-1(5K), prepared *via* aromatic nucleophilic displacement, exhibited higher mechanical properties in the form of films, moldings and Ti-to-Ti adhesive specimens than the PETQs prepared *via* the conventional synthesis.

References

1. F. W. Harris, S. M. Padaki and S. Vavaprath, *Polym. Prepr.*, **21**(1), 3 (1980).
2. F. W. Harris, A. Pamidimukkala, R. Gupta, S. Das, T. Wu and G. Mock, *ibid*, **24**(2), 324 (1984).
3. F. W. Harris, K. Sridhar and S. Das, *ibid*, **25**(1), 110 (1984).
4. F. W. Harris, A. Pamidimukkala, R. Gupta, S. Das, T. Wu and G. Mock, *J. Macromol. Sci.-Chem. A*, **24**(8/9), 1117 (1984).
5. S. Hino, S. Sato and O. Suzski, *Jpn. Kokai Tokyo Koho JP*, **63**, (196), 564 (1988). *Chem. Abstr.*, **110**, 115573w (1989).
6. C. W. Paul, R. A. Schultz and S. P. Fenelli, in *Advances in Polyimide Science and Technology*, C. Feger, M. M Khoyasteh and M. S. Htoo, Eds. (Technomic, Lancaster, PA 1993), pp. 220; U.S. Patent 5, 138, 028 (1992), to National Starch and Chemical Co.
7. R. G. Bryant, B. J. Jensen and P. M. Hergenrother, *Polym. Prepr.*, **34**(1), 566 (1993).
8. S. J. Haven, R. G. Bryant, B. J. Jensen and P. M. Hergenrother, *ibid*, **35**(1), 553 (1994); U. S. Patent 5,412, 006 (1995), to NASA).
9. P. M. Hergenrother and J. G. Smith, Jr., *ibid*, **35**(1), 353 (1994); *Polymer*, **35**(22) 4857 (1994).
10. B. J. Jensen, P. M. Hergenrother and G. Nwokogu, *Polymer*, **34**(3), 630 (1993).
11. G. W. Meyer, S. Jayaraman and J. E. McGrath, *Polym. Prepr.*, **34**(2), 540 (1993).
12. G. W. Meyer, T. E. Glass, H. J. Grubbs and J. E. McGrath, *ibid*, **35**(1) 549 (1994).
13. J. A. Johnston, F. M. Li, F. W. Harris and T. Takekoshi, *Polymer*, **35**(22), 4865 (1994).
14. T. Takekoshi and J. M. Terry, *ibid*, 4874 (1994).
15. C. I. Croall and T. S. St. Clair, *J. Plastic Film & Sheeting*, **8**(3), 172 (1992).
16. P. M. Hergenrother, *Encycl. of Polym. Sci.*, **Vol. 13**, 2nd Ed. (John Wiely & Sons, New York, 1988), p. 55.
17. P. M. Hergenrother and H. H. Levine, *J. Polym. Sci. Part A-1*, **5**, 1453 (1967).
18. J. L. Hedrick and J. W. Labadie, *Marcomol.*, **21**, 1883 (1988).
19. J. W. Connell and P. M. Hergenrother, *Polym. Prepr.*, **29**(1), 172 (1988); *Polymer*, **33**(17), 3739 (1992).

20. F. W. Harris and J. E. Korleski, *Polym. Matls. Sci. and Eng. Proc.*, **61**, 870 (1989).
21. P. M. Hergenrother, *Macromol.*, **14**(4), 891 (1981).
22. J. W. Connell, J. G. Smith, and P. M. Hergenrother, *Sci. Adv. Mat'ls and Proc. Eng. Ser.*, **40**, 1080 (1995).
23. R. G. Bryant, B. J. Jensen and P. M. Hergenrother, *Polym. Prepr.*, **33**(1), 910 (1992).
24. P. M. Hergenrother and J. W. Connell, *Int'l. Encycl. of Comp.*, **Vol. 4**, S. M. Lee, Ed. (VCH Publishers, New York, 1991), p. 334.
25. T. L. St. Clair and D. J. Progar, *J. Adhesion*, **47**,67 (1994).
26. B. J. Jensen and P. M. Hergenrother, NASA Langley Research Center, unpublished work.
27. R. Mayhew, CYTEC Engineered Products, Inc. unpublished work.
28. M. Rogalski, The Boeing Company, unpublished work.