The Journal of Adhesion

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Adhesive and Thermo-Mechanical Behavior of Phosphorus-Containing Thermoplastic Polyimides*

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Thermally stable, soluble and amorphous bis(m-aminophenoxy) triphenylphosphine oxide (m-BAPPO) based polyimides were synthesized in controlled high molecular weight *via* solution imidization. Several dianhydrides were used to establish chemical-structure-physical property behavior. The m-BAPPO based polyimides were characterized by several techniques, including intrinsic viscosity, thermal analysis, single lap shear adhesive bond strength and thermo-mechanical behavior. The resulting phosphorus-containing polyimides were demonstrated to be thermally stable *via* dynamic TGA in air up to 500°C and showed 10 ~ 20% char yield at 750°C, suggesting improved fire resistance. In addition, these polyimides showed good tensile modulus, ductile stress-strain behavior and excellent adhesion to a Ti-6Al-4V substrate, as determined by single lap shear tests. The rheological behavior was investigated by using a parallel plate type viscometer which confirmed that the materials were true thermoplastics. Tailoring the polyimides with the non-reactive phthalimide end group inhibited crosslinking and chain extension and, hence, was essential for the observed good processability.

KEY WORDS Polyimides; triphenyl phosphine oxide diamine monomer; thermal oxidative stability; adhesion; tensile behavior; thermoplastic, end-capped polyimides.

INTRODUCTION

Many new polymers have been discovered and evaluated as high temperature, high performance materials. Among these, polyimides appear to possess many favorable characteristics. For example, the outstanding mechanical properties of polyimides make them excellent candidates to replace metals, glass, and other materials in high performance applications. In addition, properly designed polyimides are known to be excellent high temperature structural adhesives and composite matrix resins, which can

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be used in a variety of industrial areas, including aerospace and microelectronics.[1,2] Their other attractive properties include high glass transition temperature, good thermal oxidative stability, and excellent thermo-mechanical properties. There is a continuing need to produce high performance materials that meet the increasingly rigorous demands of new applications. One attempt to improve certain properties involves the development of phosphorus-containing polyimides. Polymers containing phosphorus in the backbone are thermally stable and several efforts have been made to synthesize phosphorus containing polyimides,[3−6d] which are processible *via* melt or solution and possess good thermal and mechanical behavior.

Phosphorus substituents are known to impart fire retardancy to macromolecular systems and, in fact, phosphorus-containing polyimides have exhibited high char yields upon thermo-oxidative degradation in air. In addition, it was earlier demonstrated that these materials show excellent adhesion to Ti alloys, an important substrate in the aerospace industry. The triphenyl phosphine oxide moiety in the polyimide backbone chain is non-coplanar and promotes enhanced solubility in many common solvents, which helps to overcome one of the principal disadvantages of polyimides.

Polyimide performance is highly dependent on a number of variables. Possible chemical variables include monomer and solvent purity, reactivity, and stoichiometry. Other factors include solubility of the monomer, intermediates and catalysts, and the required reaction temperature and times. Therefore, careful molecular design is necessary to produce high molecular weight, fully imidized, processible polyimides for high performance structural adhesives applications. While the physical properties of most polymers are highly dependent on achieving optimum molecular weight, processibility can be improved by molecular weight control and endgroup functionalization.[7,8]

The principal objective of this research was to synthesize and characterize highly soluble, processible, flame retardant polyimides from hydrolytically stable phosphorus-containing monomers employing molecular weight and end group control and solution imidization. These phosphorus-containing polyimides were then investigated for their adhesion behavior and film and rheological properties, as a function of several dianhydride structures. Molecular weight was controlled by adding the monofunctional endcapper phthalic anhydride and by altering the ratio of diamine to dianhydride employing the Carothers equation.[7,8] Processability was also investigated by melt viscosity measurements.

EXPERIMENTAL

Materials

N-methyl pyrrolidinone (NMP) and N,N'-dimethyl acetamide (DMAc) were stirred over P_2O_5 (phosphorus pentoxide), refluxed for 1-2 hours, then fractionally distilled under reduced pressure. 1,2-Dichlorobenzene (DCB) was purified by vacuum distillation after drying over P_2O_5.

Pyromellitic dianhydride (PMDA) and phthalic dianhydride (PA) were sublimed and dried before use. Their purity was confirmed by NMR and *via* melting point measure-

ments. The other dianhydrides, including 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), 3,3′,4,4′-bensophenone tetracarboxylic dianhydride (BTDA), 5,5′-[2,2,2-trifluoro-1-(trifluoromethyl)ethyliden]-bis-1,3-isobenzofuranedione(6FDA), 4,4′-oxy-diphthalic dianhydride (ODPA) were dried prior to use without additional purification.

Synthesis

Synthesis of Bis(m-aminophenoxy) triphenyl Phosphine Oxide

The synthesis of phosphorus-containing monomers, such as bis(m-amino phenoxy) triphenylphosphine oxide (m-BAPPO), was already briefly reported.[9] It was achieved *via* the nucleophilic aromatic substitution of m-amino phenolate on 4,4′-bis(fluorophenyl)phenyl phosphine oxide (BFPPO) in the aprotic dipolar solvent DMAC.[10]

The m-BAPPO was synthesized by the reaction of 3-aminophenol (2 moles) with BFPPO (1 mole) in the presence of potassium carbonate (5 mol% excess) in a flame-dried, 4-neck, round bottom flask with a mechanical stirrer, a Dean-Stark trap with a condenser and a nitrogen inlet. The monomers were dissolved to a 20 w/v% solids concentration in a cosolvent system of DMAc (70 v.%) and toluene (30 v.%) and the reaction was conducted at 165–170°C. The water formed during the reaction was removed from solution by the toluene/water azeotrope and, subsequently, a nitrogen gas purge and additional heat were used to remove the toluene. After 20 hours, the solution was light brown in color and the toluene/water in the trap were discarded. The solution was then further reacted for an additional 4 hours.

The resulting m-BAPPO was precipitated into cold distilled water in a blender. The product was collected by filtration and then dried in a vacuum oven at 150°C for 24 hours. The diamine was dissolved in a saturated, heated DMAc solution, and then allowed to crystallize overnight in a refrigerator. It was then filtered, washed with cold DMAc, dissolved in ethanol (20 w/v%), and precipitated into excess water in a blender. After two crystallizations from DMAc, followed by precipitating the ethanol solution into cold distilled water, pure white m-BAPPO was obtained and dried at 70°C for 48 hours in a vacuum oven. The structure was confirmed by NMR, elemental analysis, melting point and thin layer chromatography.

Synthesis of m-BAPPO Based Polyimides

All polyimides using m-BAPPO and various dianhydrides were prepared *via* the two-step poly(amic acid) precursor route,[1,2] followed by a subsequent solution imidization as described below and illustrated in Figure 1. The number average molecular weight (< Mn >) was controlled to about 20,000 g/mol. by upsetting the stoichiometry. Phthalic anhydride (PA) was used to provide stable phthalimide end groups by employing an excess of the diamine, relative to the dianhydride.

SYNTHETIC PROCEDURE

The poly(amic acid)s were synthesized in a 4-neck, round bottom flask equipped with a mechanical stirrer, a reverse Dean-Stark trap with a condenser, and an argon inlet. The

DIANHYDRIDE   **m - BAPPO**   **P A**

NMP/CHP 80:20
R.T., 8 Hours
Nitrogen

POLY(AMIC ACID)

SOLUTION IMIDIZATION
160° C, 24 Hours
Nitrogen

PA—BAPPO

Ar = BPDA, BTDA, ODPA, PMDA, and 6FDA
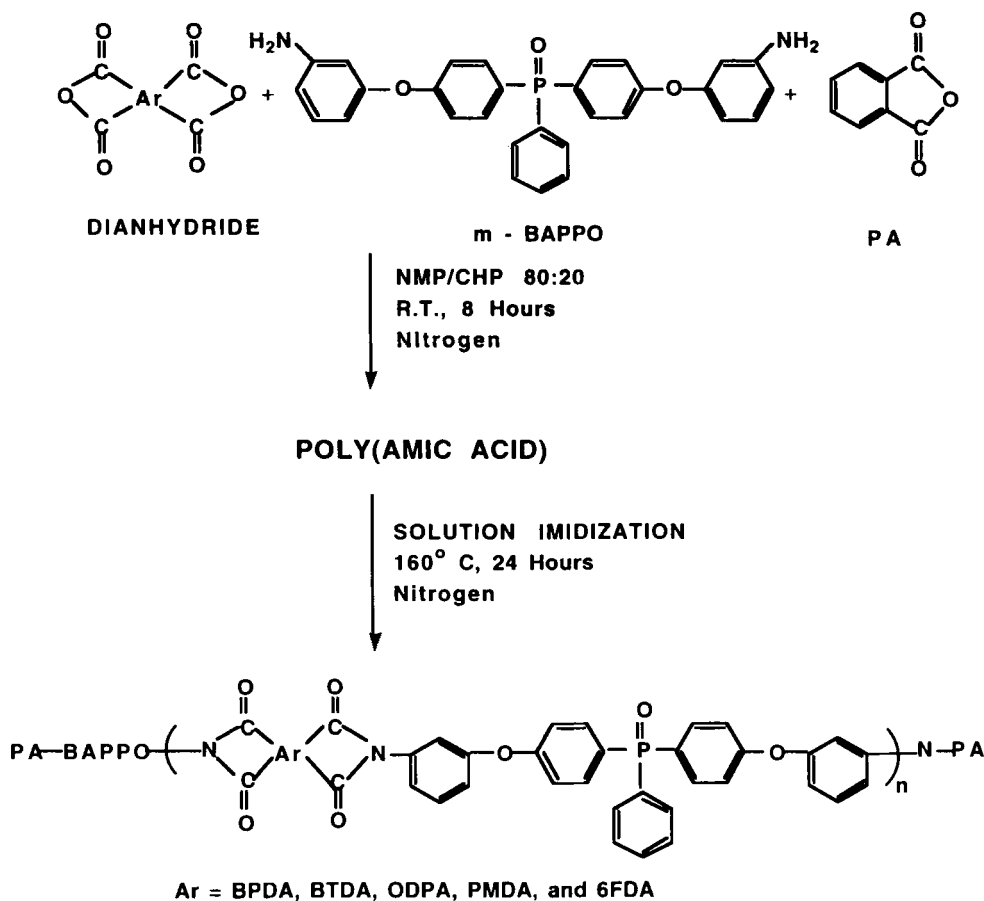
FIGURE 1   Synthesis of m-BAPPO based polyimides.

setup was flame-dried to minimize moisture and well-purged with argon. The diamine (m-BAPPO) was first charged to the flask and dissolved in dry NMP. A calculated amount of PA was then added to the flask to afford non-reactive endgroups. The dianhydrides were added in small increments to the stirred NMP solution.

The poly(amic acid) reaction was conducted at 20 w/v% solids concentration and stirred for 8 hours at room temperature to complete the reaction and insure a uniform molecular weight distribution. The solution imidization of the poly(amic-acid)s was performed in a cosolvent system of 80% NMP and 20% o-DCB (both volume percent). The o-DCB was added as an azeotropic agent to remove the water formed during the imidization step. The reaction mixture was heated to 180–190°C for 24 hours under an argon flow. The reaction was then cooled to room temperature and the product precipitated by slowly adding the solution into excess stirred methanol in a blender. The polymers were collected by filtration and dried, dissolved in chloroform (20–30 w/v%) and precipitated into methanol to remove NMP. Finally, the polymers were isolated by filtration and vacuum dried at 150°C for 24 hours.

Characterization

Proton (NMR) was used to confirm the structure and purity of these monomers and polymers. A Varian 400 MHz spectrometer was utilized and tetramethyl silane was used as the internal reference and $CDCl_3$ or deuterated DMSO were used as solvents.

Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet MX-1 FTIR) was used to confirm the presence of imide groups in the polymers.

Monomer melting points were determined on a Lab a Devices Melt-Temp II.

The intrinsic viscosity of the polyimides was measured in NMP at 25°C using a Cannon-Ubbelohde viscometer. Three or four concentrations were analyzed and linear extrapolation to zero concentration produced intrinsic viscosity or limiting viscosity number values, $[\eta]$.

The solubility of the polyimides was determined in several solvents, by addition of dried polymer powders to the appropriate solvents at a concentration of 10 w/v%. The solutions were stirred at room temperature for 2–6 hours, and solubility of the polymers was assessed by visual observation.

Differential Scanning Calorimetry (DSC) was used to determine glass transition temperatures with a Perkin-Elmer DSC-7 at 10°C/minute. The T_g values of the amorphous thermoplastic polyimides were obtained from the second scan after the first heating and rapid cooling.

Thermal Gravimetric Analysis (TGA) was performed on a Perkin-Elmer TGA-7 at 10°C/minute in air. The char yield at designated temperatures and the 5% weight loss temperatures were recorded.

Thermo-mechanical Properties Measurements

Stress-Strain Measurements

Thermoplastic polyimide films were prepared by compression molding well-dried powders above the T_g (using a Pasadena hydraulic press) or by solution casting. These compression molded films were also used as adhesives. Well-dried thermoplastic polymer powder was placed between two Teflon films and steel plate backings and the plates were then placed inside the preheated press and compressed for 10 minutes at low pressure to allow the powder to soften and flow. The resulting smooth films were bubble-free and could be controlled to approximately 5-10 mils thick. The molding temperatures were optimized at 80–100°C above the T_g values of the polymers.

Thermoplastic films were also obtained *via* solution casting. In this method, 3 grams of the polymer were dissolved in approximately 15 ml of $CHCl_3$ and filtered through a glass frit to remove any dust or gel and doctored onto a clean and chloroform-washed glass plate. The resulting films were dried very slowly under glass cover at room temperature in a vacuum oven for 24 hours, then finally in a vacuum oven at 100°C for 48 hours, in an attempt to remove all the solvent.

Stress-strain measurements to determine tensile properties were conducted on both compression molded and solution cast thermoplastic films, (all with a thickness of ~ 5 mil). Dog-bone type samples, punched randomly from the films, were prepared using an ASTM D638 type V die. The samples were tested using an Instron 1123 at a crosshead speed of 0.13 cm/min. (0.05 inch/min.) at room temperature. Tensile proper-

ties were generated using an Instron strain gauge (extensometer), Model 2630. About 4–6 samples were tested for each film and the average values are reported.

Adhesive Bond Strength Measurement

The adhesive films were prepared by compression molding at different conditions, depending on T_g and properties of the polymer, as explained above.

The adherends, Ti-6A1-4V alloys, $5 \times 1''$ (12.7×2.5 cm), were first sand-blasted to provide a clean and relatively rough surface, and were then treated with Pasa Jell 107®(from Products Research and Chemical Corporation, Semco Division). The adherends were washed with distilled water, followed by ultrasonic cleaning. After being dried at 100°C for 10 minutes in a vacuum oven, the samples were coated with a chloroform solution of the same polymer as the adhesives in order to preserve the post-treatment surface, then further dried at 200°C for 24 hours and stored in a desiecator.

The single lap shear specimens were prepared by sandwiching the compression molded film adhesives between the two adherends. The specimens were heated from 25 to 280°C under contact pressure, and then 500 psi was applied, although this value was not critical, since the melt viscosities were relatively low (Table II). The specimens were heated to 340, 350, or 360°C and were held there for 10 or 30 minutes, followed by cooling to room temperature under pressure.

Single lap shear specimens were tested with an Instron Model 1123 at room temperature or at elevated temperature according to ASTM Standard D-1002. The adhesive bond strength data were collected at a crosshead speed of 0.13 cm/min. (0.05 inch/min.). An environmental chamber was used to obtain elevated temperature stress-strain measurements. About 10 minutes was allowed to equilibrate the temperature of the specimens. The average value of 4 specimens are reported.

X-ray Photoelectron Scattering (XPS or ESCA) surface analysis was used to provide elemental concentrations. The failure mode of single lap shear specimens were initially tested by visual observation. To obtain a more precise analysis, some of the Ti alloy test specimens were analyzed using a Perkin Elmer 5300 XPS, with magnesium $K_{\alpha-a}$, X-ray source at 250 mW at a take-off angle of 90 and 15 degrees. Chemical changes were detected from the change in atomic concentration and from the binding energy shift, which were de-convoluted values from C1s peaks. Since XPS provides a relative percentage of atomic concentrations, the ratios of oxygen and nitrogen to carbon were calculated and are reported.

Melt Viscosity Measurements

Samples to determine melt viscosity measurements were prepared *via* compression molding at 300°C under vacuum. The vacuum-dried polymers were then used to prepare 2.5 cm diameter samples with about 0.2 cm thickness. The melt viscosities of the thermoplastic polyimides were determined on a Bohlin rheometer by temperature-frequency sweeps in nitrogen. Tests were performed using parallel plates over a range of frequencies (0.01–100 Hz) at a constant temperature, and over a dynamic temperature scan at a constant frequency (5 Hz) and amplitude (10%) at 5°C/minute.

RESULTS AND DISCUSSION

Characteristics of Materials

The purity of the m-BAPPO was confirmed by proton NMR, melting point, thin layer chromatography (TLC) and elemental analysis. Proton NMR spectroscopy was also used to verify the structure of the m-BAPPO, as confirmed by the characteristic peak due to amino protons at 3.78 ppm, as well as by the multiple aromatic peaks between 6 and 7 ppm. A sharp melting was obtained at 76–78°C and by TLC using a mixture (9:1) of MeOH and diethyl ether. The molecular weight as determined *via* an amino group titration technique was 493.6 g/mol., which is in good agreement with the theoretical molecular weight of 492.5 g/mol. The overall yield based on BEPPO was 65–70%.

The molecular weight of the m-BAPPO based polyimides made from several different dianhydrides was controlled to 20,000 g/mol., which affords both good processibility and mechanical behavior. The use of a cosolvent system during the synthesis was valuable. Essentially quantitative imidization was confirmed by observation of the characteristic imide bands in the region of 1770–1780 cm^{-1} (asymmetrical) and 1710–1735 cm^{-1} (symmetric), as well as by the disappearance of the amic acid stretch at 1535 cm^{-1}. One of the major advantages in synthesizing m-BAPPO based polyimides in this manner is that the normally insoluble high molecular weight polyimides are soluble, while maintaining good mechanical properties and high glass transition temperatures. Summers *et al.* were among the first to demonstrate that solution-imidized materials are more soluble than analogous bulk-imidized poly-imides.[11] The enhanced solubility of m-BAPPO containing systems appears to result from the presence of the flexible ethes linkages, as well as from the non-coplanar phenyl phosphine oxide structure. It should be noted that the systems were quite soluble in both polar aprotic solvents and chloroform, and the 6FDA polyimidimides showed good solubility even in THF. Solubility data for these polyimides are provided in Table I.

The intrinsic viscosities in NMP at room temperature ranged from 0.36 to 0.43 dl/g, which appear to correlate with the desired number average molecular weight of 20 kg/mol. Intrinsic viscosity measurements [12, 13] can be related to the viscosity average molecular weight as determined by the Mark-Houwink equation, $[\eta] = KM^a$, when K and *a* are available and this was further established by Netopilik *et al.*[24] and Konas *et al.*[25] for soluble, fully-cyclized polyimides. Proton NMR was also used to estimate molecular weight, when appropriate endgroups were utilized (*e.g.* t-butyl phenyl).

TABLE I
Solubilities of Phosphorus-Containing Polyimides

	NMP	CHCl$_3$	CB	THF
PMDA-mBAPPO	S	S	IS	IS
BPDA-mBAPPO	S	S	IS	IS
6FDA-mBAPPO	S	S	gel	S
BTDA-mBAPPO	S	S	IS	IS
ODPA-mBAPPO	S	S	IS	IS

Note: S = Soluble; IS = Insoluble; PS = Partially soluble; CB = Chlorobenzene

All m-BAPPO based polyimides demonstrated higher char yields in air, as judged by TGA experiments (Table II). Five percent weight loss temperatures for these polyimides were all greater than 500°C.

Glass transition temperatures for these homopolyimides are provided in Table II. The T_gs ranged from 216–255°C, depending on their backbone structure. The observed T_g increased as follows: ODPA < BTDA < 6FDA < BPDA < PMDA.

It should be pointed out that while the use of the m-BAPPO diamine in polyimide formation lowers the T_g relative to p-phenylene diamine or 4,4-diaminodiphenyl ethes derived polyimides, the presence of the phosphine oxide group in the backbone structure does provide increased flame retardant properties[3, 14, 15].

Tensile Properties

Table III summarizes the stress-strain results for the thermoplastic m-BAPPO based polyimides, all of which were prepared by compression molding or solvent casting.

TABLE II

Instrinsic Viscosity and Thermal Behavior of Phthalic Anhydride Terminated 20K m-BAPPO Based Polyimides

Polyimide	I.V. (dl/g)*	T_g (°C)**	5% wt. loss TGA, air, °C
PMDA-mBAPPO-PA	0.39	255	522
BPDA-mBAPPO-PA	0.43	239	562
BTDA-m-BAPPO-PA	0.43	223	506
6FDA-mBAPPO-PA	0.36	228	530
ODPA-mBAPPO-PA	0.37	216	519

*NMP, 25°C
**DSC

TABLE III

Tensile Properties of m-BAPPO Based 20,000 Mn Polyimides:
(a) Compression Molded

Dianhydride	Modulus MPa (ksi)	Tensile Stress MPa (ksi)
Ultem (control) 1000	3599(522 ± 45)	110(16.0 ± 0.8)
PMDA	3813(553 ± 23)	112(16.2 ± 0.3)
BPDA	3613(524 ± 8)	116(16.9 ± 0.4)
BTDA	3792(550 ± 27)	117(17.0 ± 1.62)
6FDA	3834(556 ± 23)	107(15.5 ± 0.5)
ODPA	3634(527 ± 50)	99(14.3 ± 2.0)

(b) Solution Cast from Chloroform

Dianhydride	Modulus Mpa (ksi)	Tensile Stress MPa (ksi)
PMDA	3068(445 ± 21)	102(14.8 ± 0.9)
BPDA	3930(570 ± 31)	125(18.1 ± 0.4)
BTDA	4006(581 ± 25)	103(15.0 ± 1.3)
6FDA	3682(534 ± 16)	80(11.6 ± 0.6)
ODPA	3723(540 ± 13)	114(16.6 ± 0.7)

Compression-molded films exhibited reasonable modulus values of about 550 ksi, which was comparable with the commercial Ultem® system.

The solvent-cast polymer films demonstrated tensile behavior comparable with compression molded films, except for the PMDA based polymer (Table III). Since 20,000 g/mol Mn is known to be sufficiently high for many thermoplastic materials to form chain entanglements,[17,18] these results are considered to be representative of what can be achieved.

Adhesion Properties

The phosphorus-containing thermoplastic polyimides exhibited excellent adhesive bond strength to Ti-6A1-4V alloy, as shown in Table IV, with the PMDA-mBAPPO-PA polyimide demonstrating the highest adhesive bond strength. High adhesive bond strength was observed when the PMDA based polyimide was bonded at 360°C for 30 minutes, to provide a strength of approximately 7000 psi (48.3 MPa) at 25°C. In contrast, the 6FDA based polyimide displayed good bond strength at a slightly lower bonding temperature (350°C/30 min.), but still not as high as the PMDA based polyimide. These systems offered two distinct advantages for thermoplastic processing and improved adhesion. First, controlled molecular weight polyimides exhibited lower viscosity and more stable melt behavior without diminished mechanical properties than did higher molecular weight polyimides; they also produced good adhesive bond consolidation. Second, non-reactive endgroups prevented additional reactions which might inhibit wetting of the adhesives to the substrate.

The polyimide based on BTDA-mBAPPO showed higher lap shear strength than the more common BTDA-mDDS polyimide, which also has a T_g of 259°C.[16,19] Furthermore, the phosphorus-containing polyimides appear to be more ductile and reveal a possible interaction between the P = O bond and the Ti adherends. In order to achieve maximum adhesive bond strength, good wetting and optimum bond line thickness are improtant,[20,22] which are all influenced by bonding conditions such as temperature, pressure, time and the pretreatment of the adhesives and adherends. The sample thickness was controlled to 0.02–0.04 cm (0.008–0.016 inch). Most of the samples fell within this range by controlling the initial adhesive film thickness ($\sim$ 10 mil, 0.025 cm), as well as by applied pressure. However, even though other factors could

TABLE IV

Adhesive Bond Strength of m-BAPPO Based Polyimides at Room Temperature Adhesive Bond Strength MPa (ksi)

Lamination Condition	340°C 30 min.	350°C 10 min.	350°C 30 min.	360°C 10 min.	360°C 30 min.
	31.8	38.1	39.2	41.9	48.1
PMDA-mBAPPO	(4611 ± 399)	(5531 ± 183)	(5692 ± 154)	(6072 ± 216)	(6982 ± 193)
	27.8	31.3	31.5	29	28.7
6FDA-mBAPPO	(4033 ± 106)	(4537 ± 97)	(4563 ± 89)	(4218 ± 226)	(4168 ± 129)
	18.5		25.3	22.8	20.1
BTDA-mBAPPO	(2689 ± 180)	—	(3669 ± 221)	(3311 ± 144)	(2921 ± 492)

affect bond performance, such as the bonding holding time, pressure, and temperature, these were not optimized. As expected, bonding time and temperature played critical roles for improving adhesive bond performance. These parameters must be carefully determined in order to avoid thermal degradation, as well as to achieve good flow.

Rigidity and strength decrease as a function of temperature, whereas ductility is increased. In Table V, the adhesive bond strength of polyimides tested at 200°C and at room temperature are compared. All adhesive specimens were prepared at 350°C for 30 minutes. The PMDA-mBAPPO polyimide showed much lower values at 200°C than at room temperature. The 6FDA based polyimide was unchanged, and the BTDA based system demonstrated slightly higher values.

The brittle-ductile behavior of polymers influences adhesive bond strength, since the latter is governed not only by ductility but also by the rigidity and stiffness of the adhesives. Thus, maximum bond strength is obtained from an optimum combination of these two variables. Since polyimides are naturally quite rigid, they can fail at low elongation and result in low adhesive bond strength at room temperature. In contrast, because ductility increases at higher temperatures, adhesive bond strength may increase. The adhesive bond strength will, of course, decrease when the test temperature approaches T_g. The 6FDA and BTDA polyimides showed good bond strength, even at 200°C. The presence of residual solvents can also play an important role in bond strength. For example, even though the PMDA-mBAPPO probably contained trace amounts of residual solvents, the adhesive bond strength at room temperature was still good. However, it is possible that the remaining residual solvent may have reduced the strength of the adhesive bond at 200°C.

Investigation of bond failure loci was conducted by both visual observation and XPS (ESCA) (Table VI). It appears that most of the bond failure occurs between the primer coating and the bulk adhesive. The justification for this statement is that a trace amount of Ti was detected, which suggests that the bond failure did not occur at the surface of the Ti adherend. Moreover, the presence of fluorine from the Teflon release sheet confirmed that the fluorine was adsorbed to the adhesive films during compression molding.

Rheological Properties

The rheological behavior of PMDA-m-BAPPO thermoplastic polyimide was investigated *via* parallel plate rheometry, in order to determine the processibility of the

TABLE V

Adhesive Bond Strength of m-BAPPO Based Polyimides at Room Temperature and at 200°C

| | Adhesive Bond Strength Mpa (ksi)* | |
	R.T.	200°C
PMDA-mBAPPO	39.2(5692 ± 154)	22.2(3214 ± 122)
6FDA-mBAPPO	31.5(4563 ± 89)	29.5(4284 ± 80)
BTDA-mBAPPO	25.3(3669 ± 221)	26.2(3800 ± 215)

* Bonding Condition: 350°C/30 min.

TABLE VI
Bonding Failure Investigation of Single Lap Shear Samples

	O/C	F/C	Si/C	N/C	P/C	Ti/C
Ti-6A1-4V*	1.549	0.038	0.551	—	—	0.324
6FDA-BAPPO (CM film, 90°C)	0.162	0.113	0.045	0.045	Trace	—
(CM film)	0.191	0.212	0.011	—	—	—
(Cast film)	0.285	0.090	0.169	Trace	Trace	—
6FDA-BAPPO (Ti side)	0.305	0.121	0.016	0.035	0.018	Trace
(Ads. side)	0.223	0.097	0.096	0.032	0.015	—
BTDA-BAPPO (CM film)	0.218	0.187	0.134	—	—	—
(Ti side)	0.169	0.043	—	0.034	0.021	—
(Ads. side)	0.148	0.084	—	0.032	0.022	—
PMDA-BAPPO (Ti side)	0.189	0.039	—	0.040	0.021	—
(Ads. side)	0.154	0.171	—	0.037	0.020	—

*Sand blasted and Pasa Jell® treated; Take-off angle of 15°

thermoplastic polyimides (20 kg/mol.). The rheological behavior of an uncontrolled high molecular weight polyimide was used as a control. Frequency and temperature effects on the complex melt viscosity were studied *via* temperature sweeps, both at a constant frequency and at frequency sweeps at several constant temperatures. During temperature sweeps, the sample was heated from 260 to 370°C at a heating rate of 5°C/min. and a frequency of 5 Hz in nitrogen. When studied at a range of frequencies (0.01–75 Hz), the test temperature was held at 300, 320, 340 and 360°C. In both sweeps, the strain was held constant and 10% amplitude was used because the polyimides demonstrated linear viscoelastic responses up to this level, which was determined from separate strain sweep experiments. Melt viscosity *versus* temperature of the PMDA-mBAPPO-PA (20K, $T_g = 255$°C) demonstrated typical thermoplastic behavior.

Above T_g, melt viscosity decreased with increasing temperature. Melt viscosity showed a minimum of ~ 1000 Pas at approximately 310°C, which is within a practical processing range (Figure 2).

The frequency sweep experiments involved cycling a single sample through various frequency sweeps at different temperatures. In doing so, the sample was exposed to elevated temperatures for approximately 30–40 minutes. In Figure 2, the complex viscosity values are plotted *versus* frequency for the 20K PMDA polyimide. In order for the viscosity to decrease to a feasible range for processing at lower temperatures, such as 320°C, a relatively high frequency (> 10 Hz) or higher torque was needed. This dependence of viscosity on frequency indicated that the sample was shear thinning, as is usually observed for true thermoplastics. Meanwhile, in these experiments, zero shear viscosity could be obtained from the extrapolation of frequency to zero by applying the Cox-Merz rule,[23] as shown in the following equation:

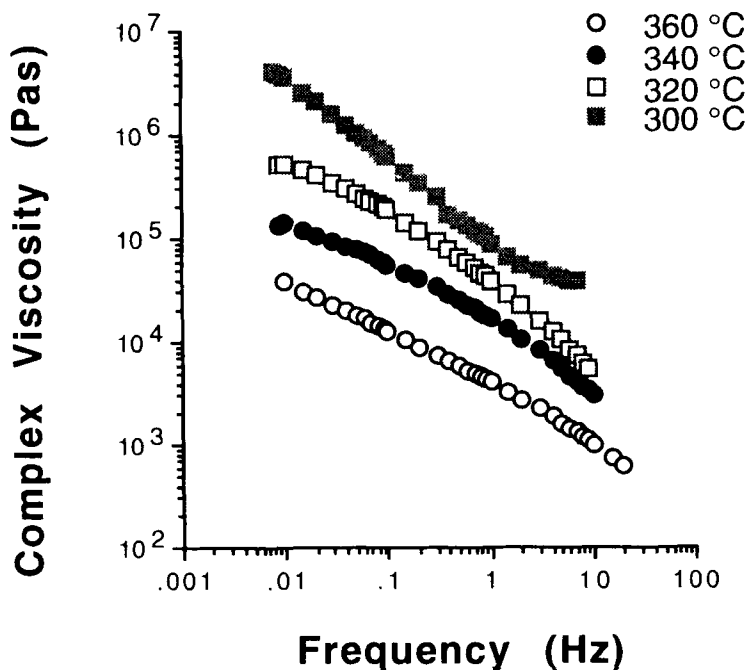$$\eta(\omega)|_{\omega \to 0} = \eta(d\gamma/dt)|_{d\gamma/dt} \to 0.$$

FIGURE 2   Effect of frequency and temperature on the melt viscosity of thermoplastic 20K PMDA-mBAPPO-PA.

SUMMARY AND CONCLUSIONS

Soluble, thermally stable, phosphorus-containing polyimides were sucessfully synthesized *via* the poly(amic acid) precursor route, followed by solution imidization. Poly(amic acid) from m-BAPPO and several dianhydrides were prepared in polar aprotic solvents. Subsequently, fully cyclized, soluble m-BAPPO based polyimides were formed within 24 hours. Controlled molecular weight and end groups were achieved by endcapping with monofunctional phthalic anhydride.

The resulting m-BAPPO based polyimides were thermally stable up to 500°C (TGA) and generated a 10~20% char yield at 750°C, suggesting improved fire resistance. The T_g values contributed to the excellent structure-property behavior of the polyimides, such as their attractive tensile and processing properties.

These polyimides showed good to excellent adhesion to Ti-6A1-4V substrate, as judged by single lap shear tests. In particular, single lap shear samples of PMDA-mBAPPO-PA polyimides exhibited about 7000 psi (48.3 MPa) tensile shear strength at room temperature. This was attributed to both the interaction between P = O bond and the Ti adherends, which may provide good wetting, and also to the relative ductility of m-BAPPO based polyimides.

Tailoring the polyimides with non-reactive end group (PA) served to control melt viscosity, which was essential for good processibility. Possible applications could

include aircraft interiors, where good adhesion and fire resistance are needed and only moderate solvent resistance is required.

Acknowledgments

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