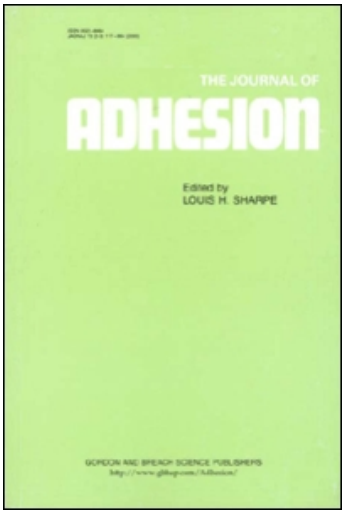

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B. J. Jensen[a]; R. G. Bryant[a]; J. G. Smith Jr.[a]; P. M. Hergenrother[a]
[a] NASA Langley Research Center, Hampton, VA, USA

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Adhesive Properties of Cured Phenylethynyl-Terminated Imide Oligomers*

B. J. JENSEN, R. G. BRYANT, J. G. SMITH Jr. and P. M. HERGENROTHER

NASA Langley Research Center, MS 226, Hampton, VA 23681-0001, USA

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As part of a program to develop structural adhesives for high performance aerospace applications, phenylethynyl-terminated imide oligomers are under evaluation. Imide oligomers with different molecular weights and compositions endcapped with either 4-(3-aminophenoxy)-4'-phenylethynylbenzophenone (3-APEB) or 4-phenylethynylphthalic anhydride (PEPA) have been prepared and characterized. These oligomers exhibit excellent processability. After heating to 350°C for 1 hour, the terminal phenylethynyl groups have reacted to provide chain extension, branching and crosslinking. The cured polymers exhibit excellent solvent resistance and high mechanical properties as neat resins and in various adhesive forms (tensile shear, sandwich flatwise tension and climbing drum peel specimens). The chemistry and properties of these phenylethynyl-terminated imide oligomers are discussed.

KEY WORDS Adhesion; phenylethynyl-terminated imides; polyimides; high performance adhesives; pseudo thermoset resins; lap shear strength; tensile strength; tensile modulus; peel strength.

1 INTRODUCTION

Over the past two decades, acetylene-terminated oligomers have been studied and their cured resins used in various applications.[1] Recently, this work has been directed towards ethynyl-terminated arylene ether oligomers[2-6] including phenylethynyl-terminated arylene ether oligomers[7-10] and arylene ethers with pendent ethynyl groups.[11] The phenylethynyl endcap offers distinct advantages over the simple ethynyl endcap. The phenylethynyl group is more chemically and thermally stable allowing it to remain unchanged during harsh synthetic conditions, affording more synthetic options in preparation as well as oligomers with greater processing windows.

Polyimides containing pendent ethynyl groups[12] and phenylethynyl-terminated imide (PETI) oligomers have been reported,[13-22] with current work focusing on the

* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

latter. The work reported herein concerns the use of 4-(3-aminophenoxy)-4′-phenylethynylbenzophenone (3-APEB) and 4-phenylethynylphthalic anhydride (PEPA) as endcappers for two imide oligomers and their evaluation as structural adhesives.

2 EXPERIMENTAL

2.1 Materials

4,4′-Oxydiphthalic anhydride (ODPA, mp 225–226°C, Occidental Chemical Co.), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, mp > 300°C, Ameribrom Inc.) were used as-received. 3,4′-Oxydianiline (3,4′-ODA, mp 72–74°C, Mitsui Toatsu Chemical Inc.), 4-(3-aminophenoxy)-4′-phenylethynylbenzophenone (3-APEB, mp 137–139°C, Daychem Labs Inc.), and 1,3-bis(3-aminophenoxy)benzene (APB, mp 105.5–107°C, Mitsui Toatsu Chem. Inc.) were used as-received. N-methylpyrrolidinone (NMP) and toluene were obtained commercially and used as-received. 4-Phenylethynylphthalic anhydride (PEPA) was prepared following a known procedure.[20] The chemical structure of each monomer and endcapper used in this study is shown in Figure 1.

2.2 Synthesis of Phenylethynyl-Terminated Imide Oligomers (PETI)

In a resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap and condenser, were placed the required amount of BPDA or ODPA,

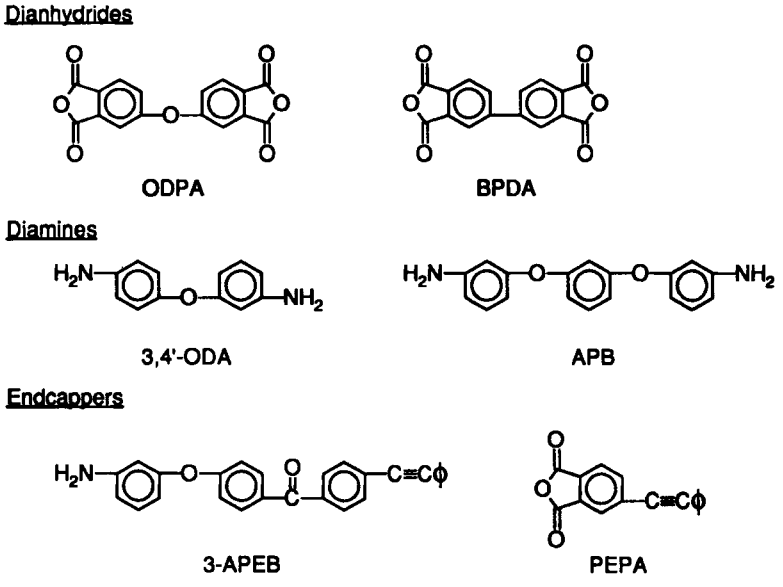

FIGURE 1 Chemical structures of the monomers and endcappers.

APB and/or 3,4′-ODA, PEPA or 3-APEB, and NMP to afford a 30% solids solution containing a phenylethynyl-terminated amic acid oligomer (PETAA) with a calculated number average molecular weight of either 5000 or 9000 g/mol. The mixture was stirred overnight at room temperature under nitrogen. A portion of the amic acid oligomeric solution was doctored onto plate glass. Another portion of the solution was used to coat 112 E-glass fabric (A 1100 finish) to prepare adhesive tapes. Toluene was added to the remaining solution and the mixture was heated to ~165°C for 7 to 12 h during which time the amic acid was converted to imide and toluene/water was removed by azeotropic distillation. The mixture was cooled to room temperature and poured into water. The resulting solution-imidized powder (white to yellow) was collected by filtration, washed with methanol and dried *in vacuo* at 180°C for 10 h. Detailed synthetic procedures have been described previously.[16,18–22]

2.3 Characterization

Inherent viscosities (η_{inh}) were obtained on NMP solutions (0.5 g/dL) at 25°C. Brookfield viscosities were determined at 25°C using a Brookfield LVT #2 viscometer. Differential scanning calorimetry (DSC) was performed on imidized powders or polyimide films using a DuPont 9900 Thermal Analyzer equipped with a 910 cell base or a Shimadzu DSC-50 calorimeter at a heating rate of 20°C/min with the T_g taken at the inflection point in the heat flow *vs.* temperature curve.

2.4 Films

The amic acid solutions doctored onto glass plates were dried in a dust-free chamber until tack-free. The resulting films were cured at 100, 225 and 350°C for 1 h each in an air circulating oven. The films were removed from the glass plates by soaking in water after carefully lifting a corner with a razor blade. The 0.0025–0.005 cm (1–2 mil) thick films were cut into 15.2 × 0.51 cm (6 × 0.20 in) strips and the tensile properties were determined on five specimens at several temperatures according to ASTM D-882.

2.5 Neat Resin Moldings

PETI powder(s) containing <0.1% volatiles were sandwiched between Kapton™ film in a steel mold treated with Frekote™ release agent. The mold was placed in a preheated press, quickly heated up to 350°C and held at 350°C for 1 h under 1.0 to 1.4 MPa (150 to 200 psi). The resulting consolidated resin plaques were then machined into test specimens. Four compact tension specimens 1.57 × 1.57 × 0.76 cm (~0.62 × 0.62 × 0.30 in) were cut from the molding and tested according to a known procedure to determine fracture toughness.[23]

2.6 Adhesive Specimens

PETI adhesive tape was prepared by coating 112 E-glass fabric (A 1100 finish) with PETAA solution in NMP and dried to a final temperature of 250°C (volatile

content of < 1.5%). Several coats were required to obtain the desired tape thickness of 0.305 nm (12 mils). Titanium (Ti-6 Al-4V) with a PasaJell 107™ surface treatment was primed with the corresponding dilute PETAA/NMP solution (~ 5% solids) and dried at 100 and 225°C for 1 h each. Titanium (Ti-3 Al-2.5 V) honeycomb 1.27 cm (0.5 in) thick with a 0.64 cm (0.25 in) cell size was acid etched, primed with the corresponding dilute PETAA/NMP solution and dried at 100 and 225°C for 1 h each.

Single lap shear specimens were fabricated at 350°C for 1 h under pressures ranging from 0.17 to 1.4 MPa (25 to 200 psi). Four single lap shear specimens of each resin were tested according to ASTM D-1002.

Honeycomb sandwich panels 30.5 cm × 15.2 cm (12 in × 6 in) were fabricated by bonding titanium honeycomb to titanium face sheets using PETI adhesive tape and by heating at 350°C for 1 h under 0.34 MPa (50 psi). The resulting sandwich panel was cut into 5.08 cm × 5.08 cm (2 in × 2 in) specimens and tested according to ASTM C-297.

Climbing drum peel panels were fabricated using titanium sheets 30.5 cm × 30.5 cm (12 × 12 inch) with thickness of 0.25 mm (0.01 inch) and 1.3 mm (0.05 inch) by heating at 350°C for 1 h at 0.34 MPa (50 psi). The cured panel was cut into 2.54 cm (1 inch) wide specimens and tested according to ASTM D-1781.

3 RESULTS AND DISCUSSION

The synthesis of the PETI oligomers was carried out by adding the monomers and the endcapper at the start of the reaction. After the reaction(s) had stirred for at least 16 h, some of the PETAA/NMP solution was removed for inherent viscosity, film casting, and adhesive tape preparation. When the dianhydrides were added in the powder form to a solution of diamine(s), they sometimes formed balls due to inadequate stirring. In these instances the reactions were stirred for longer times to obtain solutions. More recently, the dianhydrides have been added as a slurry in NMP and dissolution is much more rapid. Toluene was added to the remaining solution which was then heated to form the PETI oligomers which precipitated from solution. The oligomeric imides designated PETI-1 and PETI-2 were based on ODPA and 3,4'-ODA and have a calculated molecular weight of 9000 g/mol, while PETI-4 and PETI-5 were based on BPDA and 85/15 mole percent ratio of 3,4'-ODA/APB and have a calculated molecular weight of 5000 g/mole. The PETI-1 and 4 use 3-APEB as the endcapper and PETI-2 and 5 use PEPA as the endcapper. The chemical structures of the imide oligomers are shown in Figure 2. After drying in vacuum at 180°C, the resulting PETI powder(s) were compression molded into neat resin plaques.

Selected properties of the PETAA and PETI oligomers and the cured polymers are presented in Table I. The inherent viscosities of the PETAAs range from 0.27 to 0.58 dL/g while the Brookfield viscosities range from 14 to 80 KPa·s at 30% solids in NMP. The T_gs of the uncured oligomers were below 230°C while the T_gs of the cured polymers were 23 to 60°C higher. The DSC curves for PETI-1 are shown in Figure 3 with the top curve being that of a solution-imidized powder and the bottom

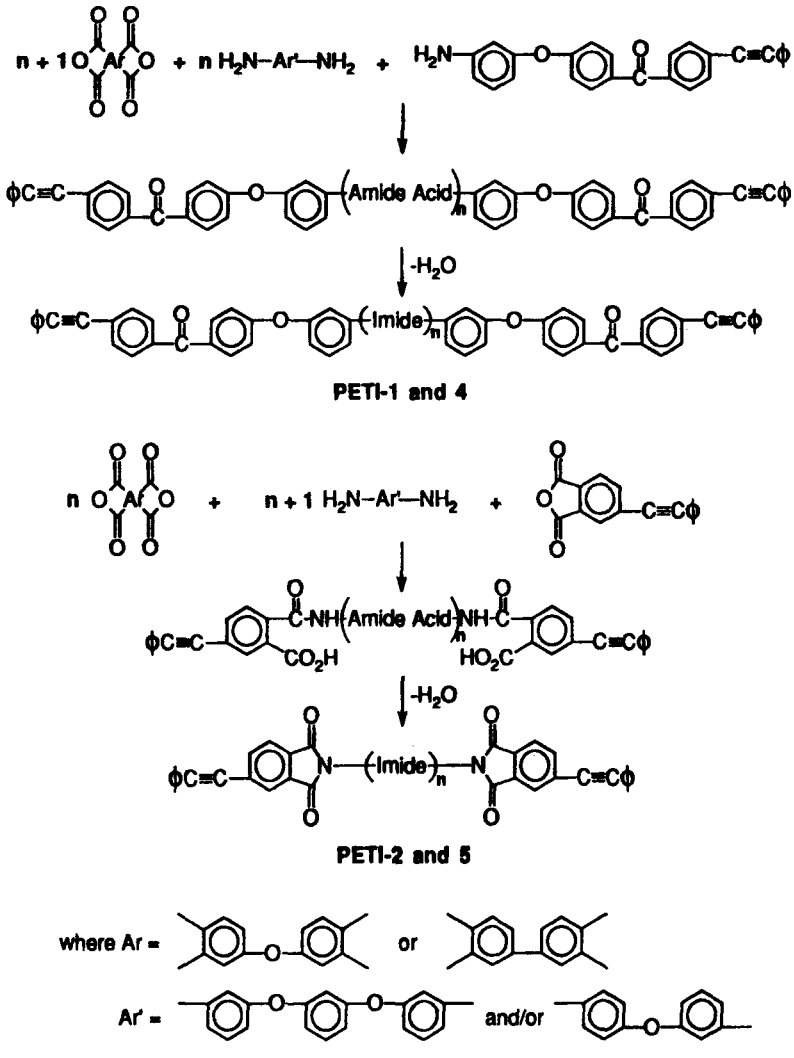

FIGURE 2 Structures of phenylethynyl-terminated imide oligomers.

curve being that of a film. In some cases, it was necessary to heat the samples to the melting points and quench in order to better detect the uncured T_gs. The crystallinity is present in material only as prepared, with the polymers being completely amorphous after heating above these transient melting points. The mechanical properties of the cured PETI films are shown in Table II. The PETI-1 and 2, of calculated molecular weights of ~ 9000 g/mole, consistently formed uniform films which did not crack after drying in a dust-free chamber until tack-free. However, the PETI-4 and 5, of calculated molecular weight of ~ 5000 g/mole, formed brittle tack-free films, with occasional cracks. After the 350°C cure, the films were tough and

TABLE I
Solution and T_g Properties of PETAAs, PETIs and Cured Polymers

Oligomer	Calcd. MW (g.mol)[a]	Viscosity (Polyamic acid) η_{inh} (dL/g)	Brookfield (KPa•s)	Tg°C (DSC) Uncured	Cured[b]
PETI-1	9000	0.58	80	215	249
PETI-2	9000	0.46	52	236	251
PETI-4	5000	0.31	30	228	251
PETI-5	5000	0.27	14	210	270

[a] Calculated using a modified Carother's equation.
[b] Taken from cured films.

creasible and the cracks healed. Previous work has shown that curing for 1 h at 350°C provides a fully-cured material as demonstrated by no residual exotherm in the DSC.[7] The tensile properties of these cured imide films are in the expected range for amorphous polyimides. The modulus drops 20 to 40 percent and the tensile strength drops 35 to 50 percent at 177°C relative to room temperature values. The films from PETI-4 and 5 exhibited the highest retention at 177°C. The endcapper has a dramatic effect on the elongation of the cured film. When the endcapper is 3-APEB, the ultimate elongation of the resulting films is below 12 percent at all temperatures. When PEPA is used, the elongation of the films was significantly higher. This could indicate that the PEPA endcap affords more linear chain extension while the 3-APEB endcap generates a higher crosslink density during cure. However, this was not apparent from the T_gs.

The PETI powders exhibited excellent flow during the compression molding of neat resin plaques. The neat resin properties obtained from machined microdumbell and compact tension specimens are shown in Table III. The tensile strengths of the

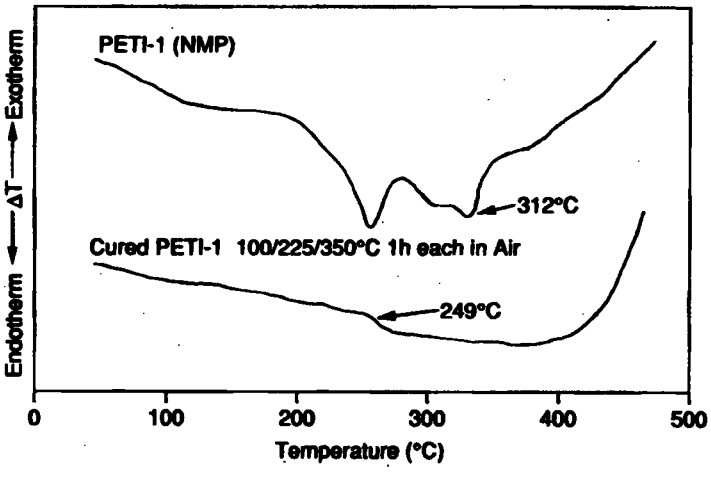

FIGURE 3 DSC curves for PETI-1, where the top curve corresponds to a solution-imidized powder and the bottom curve corresponds to a film.

TABLE II
Thin Film Properties of Cured Polymers

Oligomer	Test Temp. (°C)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)
PETI-1	RT	113	3.19	6.8
	150	67	2.02	9.2
	177	56	1.94	12
PETI-2	RT	119	2.90	38
	177	64	2.19	60
PETI-4*	RT	116	3.24	5.3
	177	69	2.65	4
PETI-5	RT	129	3.13	32
	177	84	2.29	83

*0.13 nm compression molded film.

molded specimens of PETI-1 and 2 are slightly lower and display a greater drop in properties at 177°C when compared with the specimens from films. The tensile moduli for the moldings are greater than those for films and they display a drop-off in properties of 20% from room temperature to 177°C. Neat resin moldings of PETI-1 aged for 1000 hours at 177°C and tested at 177°C showed essentially no drop in tensile properties with a strength of 39 MPa (5.7 Ksi) and a modulus of 3.06 GPa (444 Ksi). The fracture toughness (K_{Ic}) and fracture energy (G_{Ic}) of the curred resins are much higher than expected and show that they display toughness usually associated with amorphous, high-performance thermoplastics.

The tensile shear strengths obtained for PETI-1, 2, 4 and 5 are shown in Table IV, V, VI and VII, respectively. Significant amount of flash was observed in the tensile shear specimens which is a further indication of the excellent processibility of these systems. Each specimen displayed essentially complete cohesive failure with the exception of the 72-hour water boil specimen which displayed mixed failures. The

TABLE III
Neat Resin Molding Properties

Oligomer	Test Temp (°C)	Tensile Strength (MPa)	Tensile Modulus (GPa)	K_{Ic} ($GN \cdot m^{-3/2}$)	G_{Ic} (KJ/m^2)
PETI-1[a]	RT	109	3.86	3.03	2.38
	177	41	3.10	ND	ND
PETI-2[b]	RT	97	3.60	3.38	4.03
	177	34	2.85	ND	ND
PETI-4[b]	RT	116[d]	3.24[d]	3.77	4.38
	177	69[d]	2.65[d]	ND	ND
PETI-5[b]	RT	129[d]	3.13[d]	3.87	4.79
	177	84[d]	2.29[d]	ND	ND

[a] Molded at 350°C for 1 h at 1 MPa.
[b] Molded at 350°C for 1 h at 1.4 MPa.
[c] ND = Not Determined.
[d] Taken from Table II.

room temperature data for PETI-1 and 2 show that these systems are unaffected by hydraulic fluid and jet fuel. The 177°C properties are excellent. Specimens of PETI-1 aged for 1000, 3000, 5000 and 10,000 hours at 177°C in air showed strengths of 27, 27, 29, and 27 MPa (3.3, 3.9, 4.2 and 3.3 Ksi), respectively, when tested at 177°C,

TABLE IV
Ti/Ti Tensile Shear Strengths of PETI-1 bonded 1 h at 350°C under 50 psi

Test Temp (°C)	Dry (MPa)	Wet (MPa)[a]	Hydraulic Fluid (MPa)[b]	Jet Fuel (MPa)[c]
RT	51	37	47.2	50
150	30	26	ND	ND
177	27	25.8	ND	ND
204	21	ND[d]	ND	ND

[a] After 72 h water boil, tested wet.
[b] After 72 h soak in Chevron HyJet IV™, tested wet.
[c] After 72 h soak in Jet fuel, tested wet.
[d] ND = Not Determined.

TABLE V
Ti/Ti Tensile Shear Strengths of PETI-2 bonded 1h at 350°C under 100 psi

Test Temp (°C) (Aging Time, h)	Dry (MPa)	Wet (MPa)[a]	Hydraulic Fluid (MPa)[b]	Jet Fuel (MPa)[c]
RT	49	41	50	48
177	30	23	30	31
177 (1000 h)[d]	33	ND[e]	ND	ND

[a] After 72 h water boil, tested wet.
[b] After 72 h soak in Chevron HyJet IV™, tested wet.
[c] After 72 h soak in Jet fuel, tested wet.
[d] Aged in a forced air oven at 177°C.
[e] ND = Not Determined.

TABLE VI
Ti/Ti Tensile Shear Strengths of PETI-4

Test Temp (°C) (Aging time, h)	Fabrication Pressure[a] (MPa)/(psi)	Shear Str. (MPa)
RT	0.17/(25)	39
RT	0.69/(100)	42
177	0.17/(25)	30
177	0.69/(100)	31
177 (1000)[b]	0.69/(100)	32
177 (3000)[b]	0.69/(100)	30
204	0.69/(100)	26

[a] At 350°C, 1 h.
[b] Aged in a forced air oven at 177°C.

TABLE VII
Ti/Ti Tensile Shear Strengths of PETI-5 bonded 1 h at 350°C under 75 psi

Test Temp (°C)	Dry (MPa)	Wet (MPa)[a]	Methyl Ethyl Ketone (MPa)	Hydraulic Fluid (MPa)[b]	Jet Fuel (MPa)[c]
RT	49	41	38	50	48
150	34	ND[d]	ND	ND	ND
177	30	23	ND	30	31
204	24	ND	ND	ND	ND

[a] After 72 h water boil, tested wet.
[b] After 72 h soak in Chevron HyJet IV™, tested wet.
[c] After 72 h soak in Jet fuel, tested wet.
[d] ND = Not Determined.

TABLE VIII
Flatwise Honeycomb Tensile and Climbing Drum Peel Strength* for PETI-1

Test Temp (°C)	Flatwise Tensile Strength (MPa)	Peel Strength (N·m/m)[a]
−54	6.7	152
RT	5.9	149
150	4.9	ND[b]
177	4.2	149

[a] Tested by Mark Rogalski at the Boeing Commercial Airplane Group.
[b] ND = Not Determined.
* ASTM D-1781.

demonstrating the outstanding thermooxidative stability of the polymer. Specimens of PETI-4 displayed lower RT adhesive strength than those of PETI-1 or 2 but equivalent strength at 177°C, whereas specimens of PETI-5 displayed adhesive properties similar to PETI-1 and 2 cured polymer. Specimens of PETI-5 aged for 1000 hours at 177°C in air showed a strength of 33 MPa (4.8 Ksi) when tested at 177°C, displaying a slight increase over the unaged specimen. All of the cured PETI resins show excellent resistance to jet fuel and hydraulic fluid. The flatwise tensile and climbing drum peel values obtained for PETI-1 are excellent as shown in Table VIII. Most of the failure in the honeycomb sandwich specimens was adhesive but there were instances of failure occurring at the mounting fixtures and through the titanium honeycomb. The results obtained from the climbing drum peel specimens of PETI-1 show that the strength is outstanding and remained relatively constant over a temperature range of −54 to 177°C.

4 CONCLUSIONS

Several novel, lightly-crosslinked, thermoplastic polyimides were synthesized which display excellent processibility, excellent solvent resistance, high mechanical properties

and outstanding adhesive properties. These resins exhibit a wide processing window, affording excellent flow and processability. The mechanical properties of these PETIs are influenced by the phenylethynyl endcapper and the backbone composition, thus allowing tailoring of the materials for various applications. The attractive combination of properties in these PETI resins demonstrates that they have a potential for future aerospace applications.

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