Chemistry and Properties of a Phenylethynyl-Terminated Polyimide

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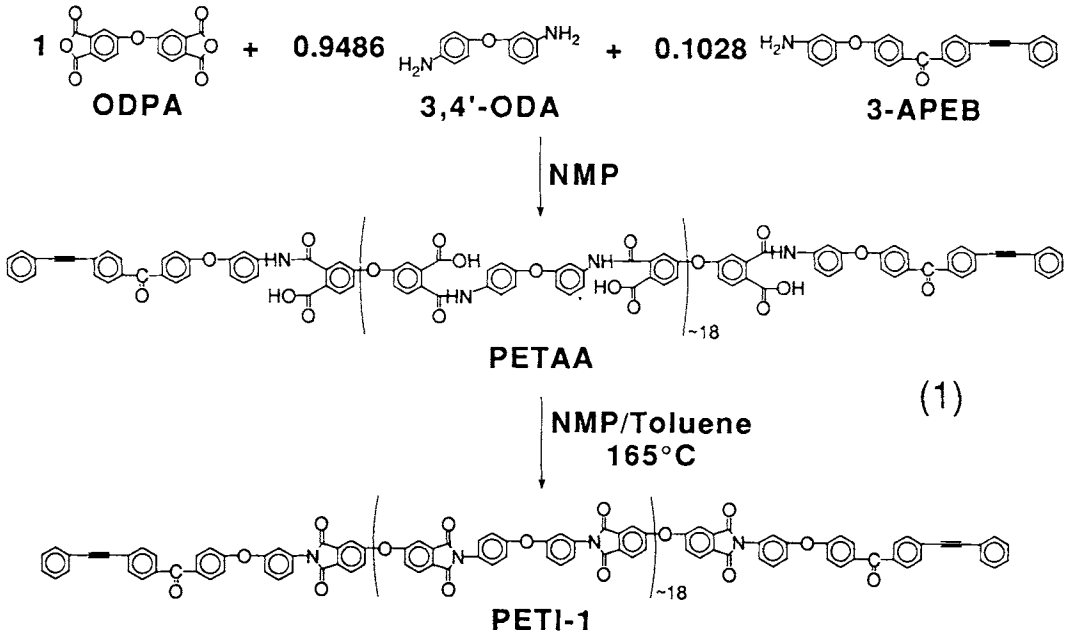
SYNOPSIS

As part of an ongoing effort to develop processable, high-performance resins for aerospace applications, a phenylethynyl-terminated imide (PETI) oligomer designated LaRC^{MT} PETI-1 was developed. This reactive oligomer has a number-average molecular weight of 6300 g/mol and a T_g of 218°C. Upon curing the reactive oligomer at 350°C for 1 h, a tough material with a T_g of 249°C was obtained. The properties of cured PETI-1 in the form of composites, adhesive specimens, thin films, and neat resin moldings are excellent. The synthesis, characterization, and mechanical properties of this polyimide are discussed.

INTRODUCTION

Over the past two decades, acetylene-terminated oligomers, particularly imides, have been developed and their cured resins used in certain specialty applications.[1] Recently, this work was directed toward ethynyl[2-6]- and phenylethynyl[7-10]-terminated arylene ether oligomers. The phenylethynyl endcap offers distinct advantages over the ethynyl endcap, which include better chemical and thermal stability, allowing it to remain unchanged during harsh synthetic conditions. In addition, the phenylethynyl-terminated oligomer affords a wider processing window than does the corresponding ethynyl-terminated oligomer. These phenylethynyl-terminated oligomers also thermally cure without the evolution of volatile byproducts. Once cured, the resulting polymers display high glass transition temperatures (T_g's) and excellent solvent resistance and mechanical properties. Phenylethynyl-terminated imide oligomers have been previously reported.[11-23] This article describes the chemistry and preliminary neat resin, adhesive, and composite properties of one particular phenylethynyl-terminated imide oligomer designated LaRC^{TM} PETI-1:



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EXPERIMENTAL

Materials

4,4′-Oxydiphthalic anhydride (ODPA, mp 225–226°C, Occidental Chemical Co.), 3,4′-oxdianiline (3,4′-ODA, mp 72–74°C, Mitsui Toatsu Chem., Inc.), and 4-(3-aminophenoxy)-4′-phenylethynylbenzophenone (3-APEB, mp 137–139°C, Daychem Labs Inc.) were used as-received. *N*-Methylpyrrolidinone (NMP), *m*-cresol, isoquinoline, and toluene were obtained commercially and used as-received.

Synthesis of PETI-1

NMP Solvent

In a 2 L flask equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser, ODPA (186.1633 g, 0.6001 mol), 3,4′-ODA (113.9718 g, 0.5692 mol), 3-APEB (24.0209 g, 0.0617 mol), and NMP (760 g) were stirred at ambient temperature for 16 h under nitrogen to afford a 30% solids amber-colored solution (w/w) of the phenylethynyl-terminated amic acid oligomer (PETAA). A portion of the amic acid oligomer solution was doctored onto plate glass. Another portion of the solution was used to coat 112-E glass (A1100 finish) to prepare adhesive tape or impregnate IM-7 carbon fiber to form unidirectional prepreg. Toluene (100 g) was slowly added to the remaining stirred solution and the stirred solution was heated to ~ 165°C for 7 h, during which time the amic acid was converted to imide and water and toluene were removed by azeotropic distillation. A precipitate formed and the resulting slurry was cooled to room temperature and poured into water. The resulting light yellow PETI oligomeric powder was collected by filtration, washed with methanol, and dried *in vacuo* at 180°C for 10 h to afford an oligomer with a calculated molecular weight of 9000 g/mol.

m-*Cresol Solvent*

In a 1 L flask equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser, ODPA (31.0227 g, 0.1000 mol), 3,4′-ODA (18.9935 g, 0.0949 mol), 3-APEB (3.9726 g, 0.0102 mol), and *m*-cresol (306 g) were stirred at ambient temperature for 16 h under nitrogen to afford a 15% solids amber-colored solution (w/w). Isoquinoline (3 drops) was added to the solution and the solution was heated to ~ 195°C for 6 h. The mixture was cooled to room temperature and a portion of the PETI-1 oligomeric solution was doctored onto plate glass. The remaining solution was slowly poured into methanol in a large blender. The resulting light yellow PETI oligomeric powder was collected by filtration, washed with methanol, and dried *in vacuo* at 180°C for 10 h to afford an oligomer with a calculated molecular weight of 9000 g/mol.

Characterization

Inherent viscosities (η_{inh}) of the PETAA and PETI-1 were determined in NMP and *m*-cresol at 0.5 g/dL at 25°C, respectively. Brookfield viscosities were determined at 25°C using a Brookfield LVT#2 viscometer. Differential scanning calorimetry (DSC) was performed on PETI-1 powders and cured films using a DuPont 9900 thermal analyzer equipped with a 910 cell base at a heating rate of 20°C/min with the T_g taken at the inflection point in the heat flow vs. temperature curve. Gel permeation chromatography (GPC) was performed at 60°C using Permagel™ columns (10^6, 10^5, 10^4, 10^3 Å), NMP/LiBr (0.02*M*) solution as the eluent flowing at 1 mL/min, and a differential viscosity detector. Molecular weights were determined using a universal calibration curve generated with polystyrene standards.

Films

Wet films of PETAA and PETI-1 doctored onto glass plates were dried in a dust-free chamber until tack-free, then cured at 100, 225, and 350°C for 1 h each in air. The ~ 0.25 mm-thick films were removed from the glass plates by soaking in water and were cut into 15.3 cm (6 in.) × 0.51 cm (0.20 in.) specimens. The tensile properties were determined at several temperatures according to ASTM D-882 using four specimens at each condition. Solvent resistance was determined on circular specimens (1.27 cm diameter) of the above film strips secured with a metal paper clip. These were placed in ethylene glycol, jet fuel, toluene, methyl ethyl ketone (MEK), and hydraulic fluid for 10 days. The loss in shape and solvent pickup was noted.

Neat Resin Moldings

PETI-1 powder sandwiched between Kapton™ film was placed in either a 3.2 × 3.2 cm (1.25 × 1.25 in.) or a 7.6 × 7.6 cm (3 × 3 in.) steel mold treated with Frekote™ release agent. The mold was heated in a press and held for 1 h at 350°C under 1.4 MPa (200 psi). The resulting consolidated resin plaques were then machined into test specimens. Neat resin tensile properties were determined according to ASTM

D-882 and fracture toughness using compact tension specimens was measured according to ASTM E-399 using four specimens for each condition in both tests.

Adhesive Specimens

PETI-1 adhesive tape 0.3–0.5 mm (12–20 mil) thick was prepared by coating 112 E-glass (A1100 finish) with the PETAA/NMP solution and drying at a final temperature of 250°C to a volatile content of < 1.5%. Several coats were required to obtain adequate tape thickness. Titanium (Ti,6AI-4V) coupons and sheets pretreated with Pasagel 107™ were primed with the corresponding PETAA/NMP solution and dried at 100 and 225°C for 1 h each. Titanium (Ti,3AI-2.5V) honeycomb 30.5 × 15.2 cm (12 × 6 in.) sheets 1.27 cm (0.5 in.) thick with a 0.64 cm (0.25 in.) cell size were acid-etched, primed with the corresponding PETAA/NMP solution, and dried at 100 and 225°C for 1 h each. Lap shear specimens were fabricated in a press with a final temperature of 350°C for 1 h under 0.35 MPa (50 psi). Four tensile shear specimens were tested at each condition according to ASTM D-1002. Honeycomb sandwich panels 30.5 × 15.2 cm (12 × 6 in.) were fabricated by bonding Ti honeycomb sheets to Ti face sheets using PETI-1 adhesive tape and by heating to and holding at 350°C for 1 h under 0.34 MPa (50 psi). The resulting sandwich panel was cut into 5.08 × 5.08 cm (2 × 2 in.) specimens and tested according to ASTM C-297. Climbing drum peel panels were fabricated using Ti sheets 30.5 × 30.5 cm (12 × 12 in.) with thickness of 0.25 and 1.3 mm by heating to and holding at 350°C for 1 h at 0.34 MPa. The cured panel was cut into 2.54 cm (1 in.)-wide specimens and three specimens were tested at each condition according to ASTM D-1781.

Composite Panels

Unidirectional prepreg (tape) was prepared by impregnating unsized IM-7 carbon/graphite fiber on a tape machine with 30% NMP solution of the PETAA. The volatile content of the tape was ~ 12% and was controlled by the residence time and temperature of the in-line furnaces in the tape machine. Resin content of the tape (minus volatiles) was 33.4% by weight and fiber areal weight was 142 ± 2 g/m^2. Small composite panels (7.6 cm × 15.2 cm × 10–24 plies) were fabricated in a stainless-steel mold by heating to 350°C under 1.4 MPa for 1 h. Larger lanminates (15.2 cm × 15.2 cm × 10–14 plies) were fabricated in an autoclave by heating to 350°C under 1.4 MPa for 1 h. Composite panels for flexural strength and modulus determination were 7.0 × 1.9 cm (2.75 × 0.75 in.) × 10 plies using a unidirectional lay-up and specimens were tested according to ASTM D-790. Short beam shear strengths were determined from 1.9 × 0.64 cm (0.75 × 0.25 in.) × 22 ply undirectional composite panels tested according to ASTM D-2344. Unidirectional compressive strength (IITRI) was determined according to SACMA SRM 1-88. Open hole compression strengths were determined on a 7.6 × 2.54 cm (3 × 1 in.) × 24 ply specimen with a 0.64 cm (0.25 in.) hole and a $[+45,-45,90,0,0,+45,-45,0,0,+45,-45,0]_5$ lay-up and tested according to Northrup Specification 3.1.3. Compressive strength after impact was determined on 15.24 × 10.1 cm (6 × 4 in.) × 24 ply panels with a quasi-isotropic lay-up and tested according to Boeing Specification BSS 7260. Four specimens at each condition were used for each of the composite tests.

RESULTS AND DISCUSSION

The work on LaRC™-PETI-1 emanated from LaRC™-IA,[24] a linear thermoplastic polyimide obtained from the reaction of ODPA and 3,4′-ODA. Although LaRC™-IA has many attractive attributes, a phthalic anhydride endcapped, controlled molecular weight form exhibited solvent sensitivity under stress. In an attempt to improve the solvent resistance of LaRC™-IA and also to obtain a material with better compression moldability and elevated temperature properties, LaRC™-IA at a calculated molecular weight of 9000 g/mol was endcapped with phenylethynyl groups. A calculated molecular weight of 9000 g/mol was selected initially because it was thought that a reasonably high molecular weight linear segment would be required to obtain high toughness in the cured polymer. Since this early work, it has been found that significantly lower molecular weight imide oligomers endcapped with phenylethynyl groups provided cured polymers with high elongation and toughness.

The reaction sequence to form the PETAA and PETI oligomers is depicted in eq. (1). The synthesis of the PETAA oligomer was carried out by adding all the monomers at the start of the reaction. The stoichiometric offset ratio, determined from the modified Carother's equation,[25] was adjusted to afford an imide oligomer with a molecular weight of 9000 g/mol. After the reaction was stirred overnight, some of the PETAA/NMP solution was removed for inherent viscosity, film casting, adhesive tape, or prepreg preparation. Toluene was added to the

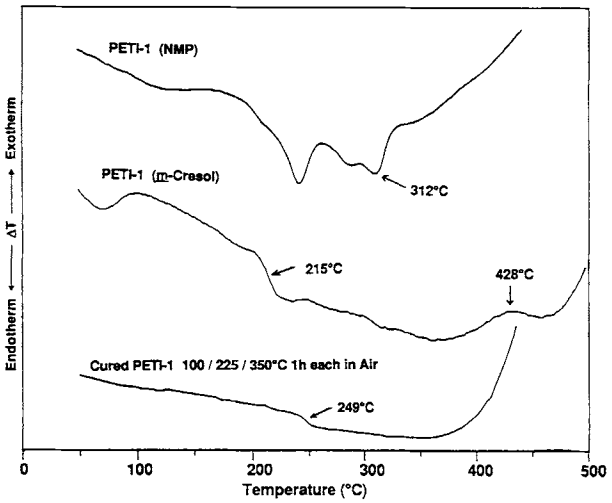

Figure 1 Differential scanning calorimetric curves.

remaining solution which was then heated to form PETI-1 which precipated from the solution. The resulting imide powder was semicrystalline and displayed multiple melting endotherms on its DSC thermogram with the highest one at 315°C (Fig. 1). The semicrystalline PETI-1 was not completely soluble at room temperature in NMP or *m*-cresol. However, the PETI-1 made in *m*-cresol remained soluble when cooled to room temperature and the resulting isolated powder showed no melting endotherm by DSC (Fig. 1). When either of these imide powders was molded and cured at 350°C, the resulting neat resins were amorphous and clear orange.

The solution and/or thermal properties of the PETAA and PETI oligomers are presented in Table I. The inherent viscosity of the PETAA was 0.58 dL/g and the Brookfield viscosity of the 30% solids content NMP solution was 8.0 Pa-s. The inherent viscosities of the PETI-1 made in *m*-cresol and NMP were 0.36 and 0.32 dL/g, respectively. The T_g of the PETI-1 made in *m*-cresol was 215°C, while the PETI made in NMP was semicrystalline. Curing the PETI from *m*-cresol or NMP for 1 h in air produced a polymer with a T_g of 249°C. The calculated molecular weight of PETI made in *m*-cresol was ~ 9000 g/mol, whereas GPC provided a value of 6300 g/mol. The stressed circular film specimens exhibited excellent solvent resistance as evidenced by not losing their shape and absorbing < 1% by weight of any one solvent (<4% for MEK, see Experimental on films). The thin films from the PETAA/NMP or PETI-1/*m*-cresol solution after curing at 350°C for 1 h in air were amorphous. The mechanical properties of the cured PETI-1 films are reported in Table II. The properties of the film cast from an *m*-cresol solution of the PETI-1 were higher than those of film cast from an NMP solution of the PETAA. The modulus drops 20% and the tensile strength drops 50% at 177°C relative to room temperature values.

Table II Thin-film Properties

Test Temp (°C)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
RT[a]	3.19	113	6.8
RT[b]	4.05	135	6.1
150[a]	2.02	67	9.2
177[a]	1.94	56	12

[a] Cast as PETAA from NMP.
[b] Cast as PETI-1 from *m*-cresol.

Table I Solution and Thermal Properties of PETI-1

Material	Property	Value
PETAA made in NMP	η_{inh} (dL/g)[a]	0.58
PETAA as 30% solids in NMP at 25°C	Brookfield viscosity (Pa-s)	8.0
PETI-1 made in *m*-cresol (NMP)	η_{inh} (dL/g)[b]	0.36 (0.32)
PETI made in *m*-cresol	Initial T_g (°C)	215
Polymer cured at 350°C	Cured T_g (°C)[c]	249
PETI-1 made in *m*-cresol	Number-average mol wt calcd,[d] found[e] (g/mol)	9000 (6300)
Stressed films, cured at 350°C	Solvent resistance	Excellent

[a] PETAA in NMP at a concn of 0.5 dL/g at 25°C.
[b] PETI-1 in *m*-cresol at a concn of 0.5 dL/g at 25°C.
[c] Taken from cured film.
[d] Calculated using a modified Carother's equation.
[e] From *m*-cresol polymerization, determined by GPC in NMP/2% LiBr at 30°C.

Table III Neat Resin Molding Properties

Test Temp (°C)	Tensile Modulus (GPa)	Tensile Strength (MPa)	K_{1c} (GN $m^{-3/2}$)	G_{1c} (kJ/m^2)
RT	3.86	109	3.03	2.38
150	3.17	55	ND[a]	ND
177	3.10	41	ND	ND
177/1000 h	3.06	39	ND	ND

[a] ND = not determined.

The PETI-1 powders exhibited excellent flow during the fabrication of neat resin moldings. The neat resin properties obtained from machined tensile and compact tension specimens are shown in Table III. The tensile moduli of specimens from moldings were greater than those obtained from the specimens of the thin films. However, the tensile strengths of the specimens from moldings are lower than the specimens from the films. This may be due to the presence of impurities or edge defects in the machined resin specimens which can cause premature failure. The fracture toughness (K_{1c}) and fracture energy (G_{1c}) of the resins are high and indicate that these cured resins display toughness usually associated with amorphous high-performance thermoplastics.

The tensile shear strengths are shown in Table IV. A significant amount of flash was observed in the tensile shear specimens, which is a further indication of the excellent processibility of this system. The room-temperature data for the cured PETI-1 specimens suggest that this resin is unaffected by hydraulic fluid and jet fuel. The elevated temperature properties are outstanding and specimens aged at 177°C in air for 10,000 h showed no loss in shear strength, demonstrating the excellent thermooxidative stability of cured PETI-1. The flatwise tensile and climbing drum peel values obtained for cured PETI-1 are presented in Table V. Most of the failure in the honeycomb sandwich was adhesive but some failure occurred at the mounting fixtures and through the Ti honeycomb. The results obtained from the climbing drum peel specimens are excellent and show that the peel strength remains relatively constant over a wide temperature range.

Unidirectional prepreg was prepared on a tape machine by coating a 30% solids PETAA/NMP solution onto IM-7 carbon fiber, then drawing the wet fibers through several ovens and nip rolls to afford a boardy tape with a ~ 12% volatile content and a 33.4% dry resin content. Although the quality of the tape was only moderate, primarily because of nonuniformity in resin content and some splitting, high-quality laminates were fabricated in a press and autoclave. The composites were well consolidated as evidenced by ultrasonic scanning. The mechanical properties of the cured PETI-1 composites are presented in Table VI. The room temperature 0° compressive and flexural strength of 1338 and 1868 MPa, respectively, are excellent. The open hole compres-

Table IV Titanium Tensile Shear Strengths

Test Conditions	Strength (MPa)
23°C dry	51
23°C wet (after 72 h water boil)	37
23°C hydralic fluid[a] (after 48 h soak)	47.2
23°C jet fuel (after 48 h soak)	50
150°C dry	30.4
150°C wet (after 72 h water boil)	26
177°C dry	26.9
177°C wet (after 72 h water boil)	25.8
177°C (1000 h at 177°C, air)	27.2
177°C (3000 h at 177°C, air)	26.8
177°C (5000 h at 177°C, air)	29.0
177°C (10000 h at 177°C, air)	26.9
204°C dry	21

[a] Chevron HyJet IV™.

Table V Flatwise Honeycomb Tensile and Climbing Drum Peel Strength

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.

Table VI IM-7 Composite Properties

Property	Test Temp (°C)	Data Obtained
Flexural strength (MPa) [Mod, GPa]	23	1868 [149.6]
	177	1199 [131.7]
Short beam shear strength (MPa)	23	111.7
	177	55.2
Compressive strength (MPa)	23	1358
Open hole compressive strength (MPa)[a]	23	372.3
	177 (wet)	234.4
Compressive strength after impact (MPa)[a]	23	302.0

[a] From Monica Rommel at Northrop Grumman Corp.

sive strengths of 372.3 MPa at 23°C and 234.4 MPa at 177°C wet are impressive as well as was the compressive strength after impact of 302 MPa at 23°C.

CONCLUSION

LaRC™ PETI-1 is a processable reactive oligomer that cures and provides a versatile, high-performance, pseudothermosetting resin. PETI-1 offers relatively easy compression moldability. The mechanical properties of cured adhesive, film, molding, and composite specimens tested under a variety of conditions were excellent. In addition, the cured polymer exhibited good solvent resistance.

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