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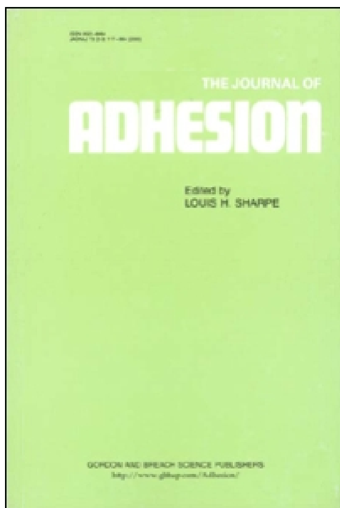

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A. C. Chang[a]; B. J. Jensen[b]
[a] Lockheed Martin Engineering and Science Corporation, Hampton, Virginia, USA [b] NASA Langley Research Center, Hampton, Virginia, USA

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Adhesive Properties of Cured Phenylethynyl-Containing Imides*

A. C. CHANG[a] and B. J. JENSEN[b,†]

[a] *Lockheed Martin Engineering and Science Corporation, Hampton, Virginia 23666, USA;*
[b] *NASA Langley Research Center, Hampton, Virginia 23681-0001, USA*

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As part of a program to develop structural adhesives for high-performance aerospace applications, work has continued on phenylethynyl-containing imides. Initial work on linear phenylethynyl-terminated imides (PETI), led to a material called LaRC™ PETI-5, which is now commercially available and was selected as the composite matrix resin and adhesive on the High Speed Research Program. In this report, the preparation and evaluation of a series of modified phenylethynyl-containing imides, which are being developed as secondary bonding adhesives, will be discussed. The modification of these materials compared with the linear material involves the use of a small amount of trifunctional monomer to introduce branching. These adhesives exhibit excellent processability at pressures as low as 15 psi and temperatures as low as 288°C. The cured polymers exhibit excellent solvent resistance and high mechanical properties. Polymer properties can be controlled by varying the molecular weight, the amount of branching, and the phenylethynyl content. This research involves changing the flexibility in the copolyimide backbone of the branched, phenylethynyl-terminated adhesives and determining the effect on properties.

Keywords: Polyimides; phenylethynyl; adhesives; processability; high temperature; thermoset; thermal stability

1. INTRODUCTION

Considerable attention has been directed towards ethynyl-terminated oligomers over the last 20 years and recent work has focused on

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†Corresponding author. Tel.: (757) 864-4271, Fax: (757) 864-8312, e-mail: b.j.jensen@larc.nasa.gov

phenylethynyl-terminated imide (PETI) oligomers [1–13]. Because these reactive oligomers have relatively low melt viscosities, compared with completely linear versions, and thermally cure without the evolution of volatile by-products, they are attractive candidates for composite matrices and adhesives. Once cured, they display moderately high glass transition temperatures (T_g), excellent solvent resistance and high mechanical properties.

As an ongoing effort to develop high-performance resins for aerospace applications, several new modified phenylethynyl-terminated imide (LaRC™ MPEI) oligomers [12, 14, 15] with different imide backbones were synthesized utilizing a small amount of trifunctional amine. The addition of small amounts of triamine produces a mixture of linear, star-shaped and branched polymer chains that has lower melt and solution viscosities than an equivalent molecular weight linear phenylethynyl-terminated imide oligomer. Previous work focused on linear phenylethynyl-terminated imides (PETI) and led to a material called LaRC™ PETI-5, which is now commercially available. This material was selected as the composite matrix resin and adhesive on the High Speed Research (HSR) Program, which has as a goal the development of a Mach 2.4 High Speed Civil Transport (HSCT). These MPEI materials were developed as secondary bonding adhesives, which are limited to lower-temperature and lower-pressure bonding than LaRC™ PETI-5 requires, for bonding composites together without distortion. Phenylethynyl-containing materials typically display increased T_gs when cured at higher temperatures and longer times; however, the focus of this work is to develop materials with high use temperatures that are cured at temperatures of 300°C or below. They are believed to be fully imidized after this cure, but would display higher T_gs if cured at higher temperatures. The chemistry and properties of these new MPEIs are presented herein.

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2. EXPERIMENTAL[1]

2.1. Starting Materials

3,4′-Oxydianiline (3,4′-ODA, m.p. 82–84°C), 1,3-bis(3-aminophenoxy)benzene (APB, m.p. 105.5–107°C), 2,4,6-triaminopyrimidine

[1]Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

(TAP, m.p. 241–243°C), biphenyltetracarboxylic dianhydride (BPDA, m.p. 295–297°C) were obtained commercially and purified as needed. 4-Phenylethynyl phthalic anhydride (PEPA, m.p. 151–152°C) was obtained from Imitec, Inc., Schenectady, New York, USA and used as received. N-Methylpyrrolidinone (NMP) and toluene were obtained commercially and used as received.

2.2. General Procedure for Oligomer Synthesis

The poly(amide acid)s were prepared as shown in Scheme 1 by the slow addition of a calculated stoichiometric offset of BPDA and PEPA slurried with NMP, to a mechanically-stirred mixture of the ODA, APB, TAP and NMP under a nitrogen atmosphere at room temperature (RT). The ratio of ODA to APB was varied from the stiffer 85 : 15 to the most flexible 70 : 30. The exothermic reaction raised the temperature to ~60°C where it was held overnight to produce poly(amide acid) solutions. Imide powders were prepared by adding toluene, heating to reflux and removing the toluene/water mixture by azeotropic distillation. The temperature of the reaction was held at

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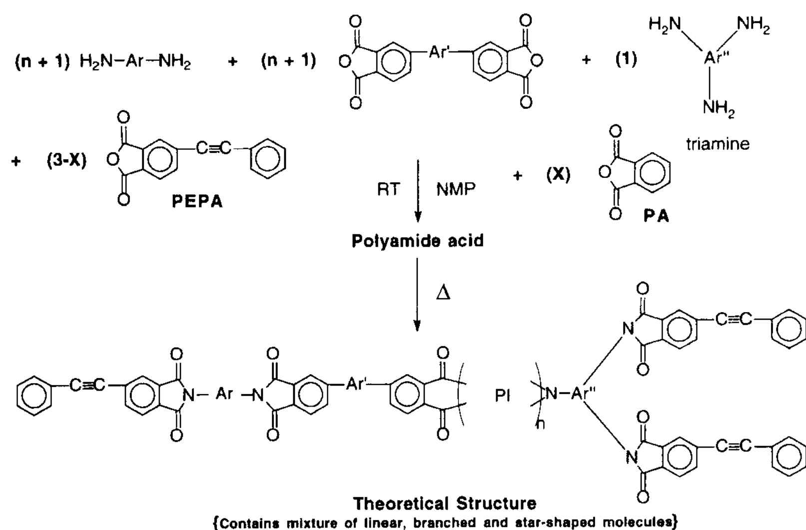

SCHEME 1 Synthetic route and theoretical structure of Modified Phenylethynyl Imides (MPEIs).

~185°C for 16 h, then ~200°C for ~3 h to remove the last traces of water and toluene. After cooling, the solution was poured into water in a blender stirring at a high rate. The precipitate was collected by filtration, washed with water and dried *in vacuo* at 220°C for 12 h to yield yellow powders. All MPEIs utilized a stoichiometric offset such that theoretical number average molecular weight (Mn) of 5500 g/mole was obtained, assuming complete reaction.

2.3. Characterization

Inherent viscosities (η_{inh}) for the poly(amide acid)s were obtained in NMP (0.5 g/dL) at 25°C. Brookfield viscosity was measured on 35% and 42% solids solutions for the poly(amide acid)s in NMP at 25°C. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 calorimeter at a heating rate of 20°C/min. The T_g was taken at the inflection point of the heat flow *vs.* temperature curve.

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2.4. Melt Rheology

Melt viscosity measurements were performed on a Rheometrics ARES rheometer. Sample specimen disks, 1 inch in diameter and ~0.06 inch thick, were prepared by press molding of solution-imidized powder at RT. The top plate was oscillated at a fixed strain rate of 5% and a fixed angular frequency of 10 rad/sec, while the lower plate recorded the resultant torque. Storage (G') and loss (G'') moduli as a function of time (t) were measured at several temperatures.

2.5. Films

Poly(amide acid) solutions were poured onto clean glass plates and spread to ~15 mils thickness, then placed in a level, dust-free dry chamber until tack free. Films were cured in a circulating air oven for 1 hour each at 100, 225 and 350°C, removed from the glass plates and the thin film properties were tested according to ASTM-D882 at a crosshead speed of 0.2 inches/minute. This cure schedule provided quality films which were fully imidized and essentially fully cured.

2.6. Adhesive Specimens

NMP/oligomer solutions were used to brush coat by hand 112 E-glass with a standard A1100 finish (BGF Industries, Greensboro, NC). Each coat was dried in a circulating air oven at 100 and 225°C for 1 h each. Several coats were used to provide a 12 – 14 mil thick tape with final volatile content measured to be < 2%. Titanium (Ti, 6Al-4V) coupons prepared using a Pasa-Jell 107™ surface treatment (PRC-DeSoto International, Mt. Laurel, NJ) and primed using a dilute solution of the adhesive were bonded under 15 psi in a press by heating rapidly to 288 – 300°C and holding for 1 – 8 h. Several specimens utilized an autoclave (for heating only) or a temperature-programmable oven and a vacuum bag for application of atmospheric pressure. Four specimens per bonding condition were tested for Ti/Ti tensile shear strength at RT and 177°C following the guidelines of ASTM D-1002.

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3. RESULTS AND DISCUSSION

The structure shown at the bottom of Scheme 1 is a theoretical structure used to calculate stoichiometric ratios of the reactants. The product of this synthesis contains a mixture of linear, branched and star-shaped molecules with a theoretical number average molecular weight of 5500 g/mole. The degree of branching was determined by the concentration of trifunctional amine (TAP) while the degree of crosslinking and/or chain extension was determined by the concentration of reactive endcapper, PEPA. Many versions of the MPEIs have been prepared and characterized. The MPEIs reported herein were prepared such that the theoretical molecule contains one TAP and three PEPA units (with no phthalic anhydride), resulting in the same degree of branching and crosslinking. The backbone flexibility of the oligomers is determined by the molar ratio of 3,4′-ODA to APB when the polymers are prepared, with the higher amounts of APB producing more flexible oligomers. Melt and solution viscosities (measured on 35 wt% solids solutions in NMP) decrease with increasing chain flexibility, while T_gs decrease, as shown in Table I. MPEI-6, which has the highest amount of APB among the oligomers prepared, exhibited a dynamic melt viscosity of 700 poise at 288°C and a Brookfield

TABLE I Properties of MPEIs

Materials (*3,4′-ODA/APB*)[1]	*Cured T_g, °C* 1 *h* @ 371°*C*	*Melt viscosity* @ 288°*C* (*poise*)[2]	*Brookfield viscosity* (*centipoise*)
MPEI-5 (85/15)	277	200,000	4600 @ 25°C
MPEI-8 (80/20)	276	10000	2000 @ 25°C
MPEI-7 (75/25)	272	7800	6000 @ 22°C
MPEI-6 (70/30)	263	700	950 @ 25°C
PETI-5	263	Does not melt	30,000 @ 25°C

[1] Ratio of 3,4′-ODA/APB used in synthesis.
[2] Measured on 35 wt% solids solutions in NMP.

TABLE II Thin film tensile properties of MPEIs

	Tensile strength (ksi)		*Tensile modulus (ksi)*		*% Elongation*	
Materials	*RT*	(177°*C*)	*RT*	(177°*C*)	*RT*	(177°*C*)
MPEI-5 (85/15)	20.0	(11.5)	520	(385)	7.7	(8.3)
MPEI-8 (80/20)	19.0	(10.0)	549	(361)	6.8	(11)
MPEI-7 (75/25)	18.5	(11.4)	520	(350)	7.6	(16)
MPEI-6 (70/30)	20.0	(10.7)	520	(380)	7.6	(15)
PETI-5	18.8	(12.2)	455	(332)	32	(84)

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viscosity of 950 centipoise at 25°C and 35% solids. For reference, the PETI-5 does not melt until well above 288°C and has a Brookfield viscosity of 30,000 centipoise at 25°C and 35% solids. The target processing conditions specified by the HSR Program for secondary bonding, where composites are bonded without distortion, are 288°C and 50 psi. While these conditions still require an autoclave for pressurization, 15 psi processing can be accomplished in a vacuum bag using an oven for heating. The low melt viscosity and relative melt stability of MPEI-6 allow processing under these mild conditions.

Mechanical properties of the cured films at both RT and 177°C are shown in Table II. When cured at 350°C, each MPEI produced tough, creasible films that displayed high tensile strength and modulus at both RT and 177°C. Compared with PETI-5, these materials have similar strength but higher modulus and lower elongation. While the elongation has decreased significantly, it is still similar to or higher than epoxy adhesives.

Table III shows Ti/Ti tensile shear strengths (average of four specimen) and a visual estimate of the % cohesive failure for the MPEIs press bonded under 15 psi at 288°C and held for 8 hours to cure. These tensile shear data ware typical, displaying a scatter of +/− ~ 10%. The adhesive tapes were dried at a final temperature of 225°C

TABLE III Ti/Ti tensile shear strength (psi) and failure mode (%) of MPEIs (press bonded @ 15 psi, 288°C for 8 hr)

Material	*Room temperature*	*177°C*
MPEI-5 (85/15)	4700/100% Coh	4230/100% Coh
MPEI-8 (80/20)	5850/80% Coh	4600/50% Coh
MPEI-7 (75/25)	5230/90% Coh	4130/80% Coh
MPEI-6 (70/30)	5260/100% Coh	4220/80% Coh
	[1]4150/80% Coh	[1]3850/80% Coh
	[2]5160/100% Coh	[2]4400/60% Coh

[1] Bonded in a vacuum bag in an autoclave with no external pressure at a heating rate of 2.6°C/min until 288°C, then held for 8 hours at 288°C.
[2] Bonded in a vacuum bag in a temperature-programmable oven at a heating rate of 2.6°C/min until 300°C, then held for 8 hours at 300°C.

TABLE IV Ti/Ti tensile shear strength[1] (psi) and cohesive failure (%) of MPEI-5 and MPEI-6 at RT and (177°C) after exposure to solvents for 14 days

Solvents	*MPEI-5*	*MPEI-6*
Control	5620/100% Coh	5260/100% Coh
Jet Fuel	5350/100% Coh	5100/100% Coh
Hydraulic Fluid	5550/100% Coh	5100/100% Coh
MEK	5510/100% Coh	5200/100% Coh
Toluene	5550/100% Coh	4580/90% Coh
Ethylene Glycol	5490/100% Coh	5310/100% Coh
Alkaline	5280/100% Coh	ND[2]

[1] Adhesive tape < 2.1% volatiles; bonding condition 15 psi/288°C/8 h.
[2] Not determined.

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until a < 2.0% volatile content was measured, which is necessary to produce quality large-area bonds. These materials exhibit excellent processability and adhesive properties at RT and 177°C, with MPEI-8 displaying unexpectedly high values. Also shown are autoclave- and oven-bonded specimens of MPEI-6 using vacuum bag pressure only and a slow heating rate of 2.6°C/min. When large parts are fabricated or when large autoclaves are utilized, only slow heating rates are possible. Even with the slow heating rates, excellent strengths were obtained. Although the bonding conditions are not optimized, this work shows the potential for MPEIs to be bonded under vacuum bag pressure in an oven, thereby eliminating autoclave processing, which is expensive and limits the size of the parts available for bonding.

The Ti/Ti lap shear specimens of MPEI-5 and MPEI-6 were exposed to aircraft fluids for 14 days according to the HSR Phase I screening test for secondary bonding adhesives. They exhibited excellent solvent resistance as shown in Table IV. No significant degradation was

observed, except for exposure to toluene of MPEI-6, which showed a decrease in strength of $\sim 12.5\%$. Improved solvent resistance is relatively easy to obtain for these types of materials by increasing crosslink density (by decreasing molecular weight or increasing cure temperature) or by increasing the stiffness of the polymer backbone.

4. CONCLUSIONS

Modified phenylethynyl-terminated imides with various backbone chemistries (and flexibilities) were prepared and evaluated for adhesive applications. The backbone flexibility was determined by the molar ratio of the diamines, 3,4′-ODA and APB. The MPEIs exhibited excellent processability at 288°C and 15 psi and retained excellent mechanical properties at elevated temperature. The combination of high mechanical properties and low-temperature/low-pressure processing demonstrates a high potential for future aerospace applications. The ability to process in a vacuum bag using an oven for heating instead of an autoclave presents the possibility of substantial cost savings in bonding parts.

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