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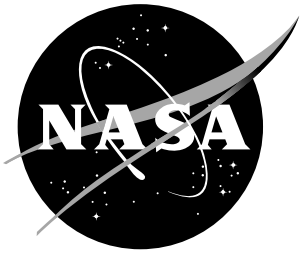

Modified Phenylethynyl Containing Imides for Secondary Bonding: Non-Autoclave, Low Temperature Processable Adhesives

Alice C. Chang
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February 1999

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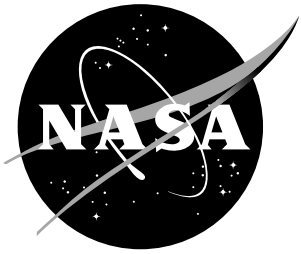

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1. ABSTRACT

As part of a program to develop structural adhesives for high performance aerospace applications, research continued on the development of modified phenylethynyl containing imides, LaRC™ MPEIs[1-5]. In previous reports[6-7], the polymer properties were controlled by varying the molecular weight, the amount of branching, and the phenylethynyl content and by blending with low molecular weight materials. This research involves changing the flexibility in the copolyimide backbone of the branched, phenylethynyl terminated adhesives. These adhesives exhibit excellent processability at pressures as low as 15 psi and temperatures as low as 288°C. The Ti/Ti lap shear specimens are processable in an autoclave or a temperature programmable oven under a vacuum bag at 288-300°C without external pressure. The cured polymers exhibit high mechanical properties and excellent solvent resistance. The chemistry and properties of these adhesives are presented.

2. EXPERIMENTAL

2.1 Materials Synthesis

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

General Procedure for Oligomer Synthesis- The poly(amide acids) were prepared as shown in Figure 1 at a concentration of 35% solids, calculated stoichiometric offset of BPDA and PEPA slurried with NMP were slowly added to a mechanically stirred mixture of the APB, TAP and NMP under a nitrogen atmosphere at room temperature. The exothermic reaction raised the temperature to ~60 °C where it was held to dissolve all the reactants. After stirring overnight at ~60°C, toluene was added and the solution was heated to reflux. The toluene/water mixture was removed by azeotropic distillation. The temperature of the reaction was held at ~185°C for 16 h, then increased to ~200°C for ~3 h to remove the last traces of water and toluene. The solution was cooled to 23°C and poured into water in a blender. The precipitate was collected by filtration, washed with water in a blender and dried in vacuo at 225 °C for 12 h to yield yellow powders.

2.2 Characterization

Brookfield viscosity measurements were taken on 35 wt% solids solutions at 25°C using a Brookfield Digital Rheometer with spindle #6. 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.

2.3 Rheology

Melt viscosity measurements were performed on a Rheometric Scientific ARES rheometer. Sample specimen disks, 1 inch in diameter and ~0.06 inch thick, were prepared by press molding the solution imidized powder at RT and high pressure. The compacted resin disk was then loaded in the rheometer fixture with 1 inch parallel plates. 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 was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G'') moduli as a function of time (t) were measured from 100°C to 371°C.

2.4 Films

Poly(amide acid) solutions were poured onto clean glass plates and spread to ~15 mils thickness using a doctor's blade, 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 tested for tensile properties according to ASTM-D882.

2.5 Adhesive Specimens

NMP/oligomer solutions (35% solids) were used to coat 112 E-glass (A1100 finish). Each coat was dried in a circulating air oven at 100 and 200°C for 1 h each. Several coats were used to obtain MPEI adhesive tape 12-14 mil thick with final volatile content of <2.0%. Titanium (Ti, 6Al-4V) coupons (Pasa-Jell 107™ surface treatment, primed with the resin solution) were press bonded in lap shear configuration under 15 psi by heating rapidly to 288°C and holding for 8 h. The Ti/Ti lap shear specimens were bonded in an autoclave or a temperature programmable oven in a vacuum bag without external pressure and were heated at 2.6°C/min and held at 288-300°C for 8 hours. Four specimens of each bonding condition were tested at RT and 177°C following the guidelines of ASTM D-1002 to obtain lap shear strengths.

3. Results and Discussion

Figure 1 is a theoretical structure used to calculate stoichiometric ratios of the reactants. The structure contains a mixture of linear, branched and star-shaped molecules. The degree of branching was calculated 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. The MPEIs reported herein were prepared using the same molar ratio of TAP and PEPA; therefore same degree of branching and crosslinking. The backbone flexibility of the oligomers are 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. Each of these materials displays significantly lower melt and solution viscosity than the baseline MPEI-5 resin as shown in Table 1. MPEI-6, which has the largest amount of APB among the oligomers prepared, has the most flexible backbone. The polymer exhibited a dynamic melt viscosity of only 700 poise at 288°C and a Brookfield viscosity of 950 centipoise at 25°C and 35% solid contents. The High Speed Research (HSR) Program target processing temperature for secondary adhesive bonding is 288°C.

Mechanical properties of the cured films at both RT and 177 °C are shown in Table 2. Each of the MPEIs produced tough, creasible films when cured at 350°C. The films displayed high tensile strength at yield and break at both RT and 177°C. No

distinct difference in the thin film tensile modulus was observed among the four oligomers.

Table 3 shows titanium to titanium tensile shear strengths and failure mode for the MPEIs bonded under 15 psi at 288 °C for 8 hours. The mild processing condition of low pressure (15 psi, vacuum bag pressure) and low temperature (288°C) is desirable for secondary bonding applications whereby composites are bonded such that no distortion takes place. The adhesive tapes were dried to <2.0% volatile content at a final temperature of 225°C. These materials exhibit excellent processability and adhesive properties at ambient and elevated temperatures.

Table 4 shows the Ti/Ti lap shear strengths processed under different bonding conditions: press cure, autoclave, and conventional oven cure. The autoclave and oven cure were processed in a vacuum bag without any external pressure at a heating rate of 2.6°C/min and with a hold at 288 or 300°C for 8 hours. Good Ti/Ti bondlines were observed and the tensile shear strengths data are comparable to the data obtained from press cure.

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. The results are summarized in Table 5. The material exhibited excellent solvent resistance; no significant effect on strengths was observed after soaking in the solvents for two weeks, with the possible exception of toluene soak on MPEI-6.

4. CONCLUSIONS

Modified phenylethynyl terminated imides, which theoretically should contain a mixture of linear, branched, and star-shaped molecules and which have various backbone flexibilities were prepared and evaluated for adhesive applications. The polymer backbone flexibility was determined by the molar ratio of the diamines 3,4'-ODA and APB. The polyimides exhibited excellent processability at 288°C and 15 psi and retained the baseline mechanical properties on film tensile modulus and Ti/Ti adhesive tensile shear strength. The flexibility of the polymer backbone can be tailored for various applications. The unique combination of high mechanical properties and low temperature/low pressure processing in these MPEI materials demonstrate a high potential for future aerospace applications.

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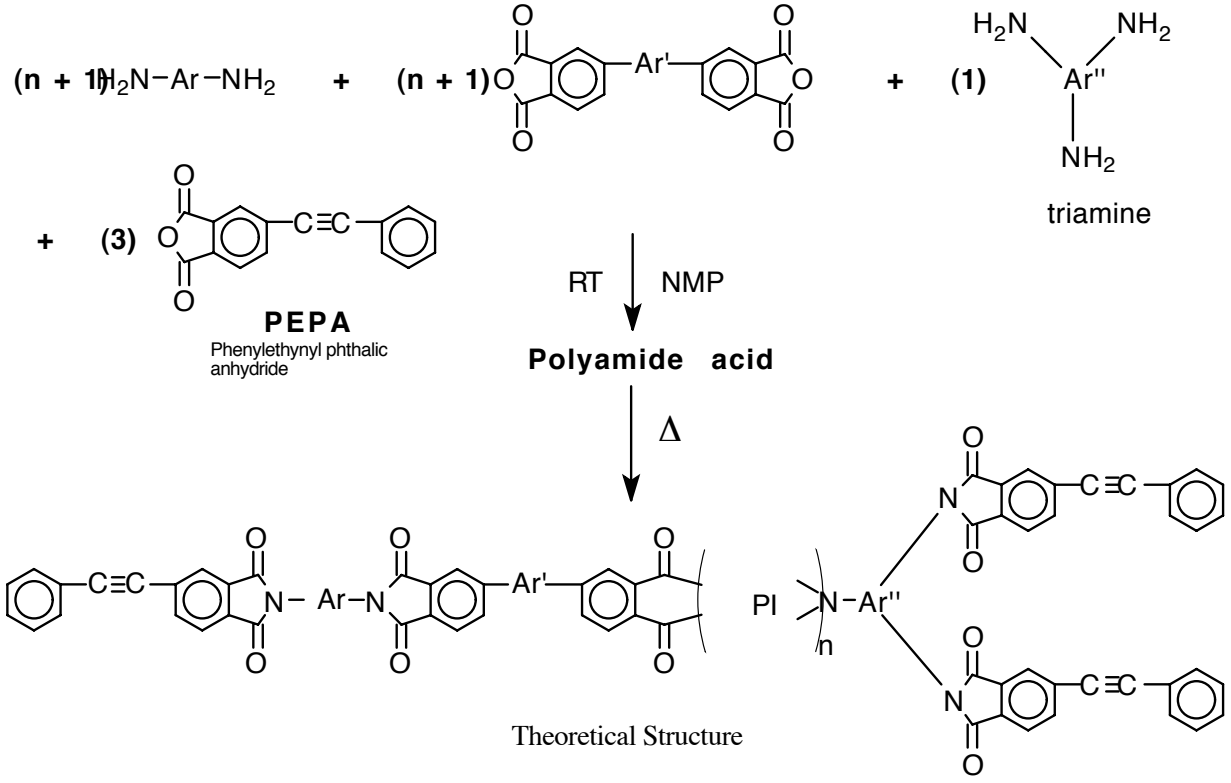
FIGURE 1. SYNTHESIS OF MODIFIED PHENYLETHYNYL IMIDES (MPEI)



PI = Polyimide

Table 1. Properties of MPEIs

Materials (3,4'-ODA/APB)[1]	Tg °C Cured 1h@371°C	Melt viscosity @288°C (poise)	Brookfield Viscosity (centipoise)
MPEI-5 (85/15)[1]	277	200,000	4600 @ 25°C
MPEI-8 (80/20)[1]	276	10000	2000 @25°C
MPEI-7 (75/25)[1]	272	7800	6000 @22°C[2]
MPEI-6 (70/30)[1]	263	700	950 @ 25°C

[1] Diamine ratio of 3,4'-ODA/APB.

[2] No data was available @ 25°C.

Table 2. Thin Film Tensile Properties of MPEIs

Materials	Tensile strength(ksi) RT (177°C)	Tensile modulus(ksi) RT (177°C)	% Elongation 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 (10.7)	520 (380)	7.6 (15)

Table 3. Ti/Ti Tensile Shear Strength (psi) and Failure Mode (%) of MPEIs (Press bonded @ 15psi, 288°C for 8 hr)

Material	Lap Shear @ RT (psi)	Lap Shear @ 177 °C (psi)
MPEI-6 (70/30)	5260/100 % Coh	4220/80%Coh
MPEI-7 (75/25)	5230/90% Coh	4130/80% Coh
MPEI-8 (80/20)	5850/80% Coh	4600/50% Coh
MPEI-5 (85/15)	4693 /100% Coh	4228/100% Coh

Table 4. Ti/Ti Tensile Shear Strength (psi) and Cohesive Failure (%) of MPEI-6 (Bonded under different conditions)

Bonding Condition	Lap Shear @ RT (psi)	Lap Shear @ 177 °C (psi)
Press Cure[1]	5260/100% Coh	4220/80% Coh
Autoclave Cure[2]	4150/ 80% Coh	3850/80% Coh
Oven Cure[3]	5160/100% Coh	4400/60% Coh

[1] 8 hours @288°C,15 psi.

[2] Bonded in a vacuum bag at a heating rate of 2.6°C/min until 288°C, then held for 8 hours at 288°C.

[3] 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 5. Ti/Ti tensile shear strength[1] (psi) and cohesive failure (%) of MPEI-5 and MPEI-6 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 15psi/288°C/8h.

[2] Not determined

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