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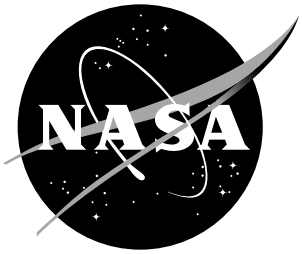

Synthesis and Characterization of Modified Phenylethynyl Terminated Polyimides

Alice C. Chang
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March 1998

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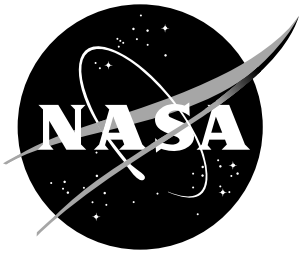

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SYNTHESIS AND CHARACTERIZATION OF MODIFIED PHENYLETHYNYL TERMINATED POLYIMIDES

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1. ABSTRACT

As an ongoing effort to develop structural adhesives for high performance aerospace applications, recent work has focused on phenylethynyl terminated imide (PETI) oligomers[1-10]. The work reported herein involves the synthesis and characterization of a series of phenylethynyl containing oligomers designated as LaRC™MPEI[11] (Modified Phenylethynyl Terminated Polyimide). These oligomers contain mixtures of linear, branched and star-shaped molecules. The fully imidized polymers exhibited minimum melt viscosity as low as 600 poise at 335°C. Ti/Ti lap shear specimens processed at 288°C under 15 psi showed tensile shear strength of ~6000 psi and 5200 psi at ambient and 350°F temperatures, respectively. The chemistry and properties of these new MPEIs are presented and compared to an optimized linear PETI, LaRC™-PETI-5[12].

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), biphenyltetracarboxylic dianhydride (BPDA, m.p. 295-297°C) and phthalic anhydride (PA, m.p. 129-131°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 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 by the slow addition of a calculated stoichiometric offset of BPDA, PA, and PEPA slurried with NMP 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 and spindle #6. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 calorimeter at a heating rate of 20°C/min. The Tg 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 Advanced Rheometric Expansion System 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 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 from Products Research & Chemical Corporation, and primed with the resin solution) were bonded in lap shear configuration under 15 psi by heating rapidly to 288 - 350°C and holding for 1 - 8 h. 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.

Honeycomb sandwich panels (12 in x 6 in) were fabricated by bonding titanium honeycomb to titanium face sheets using MPEI adhesive tape and by heating at either 316°C for 4 hours or 288°C for 8 hours under 15 psi. The resulting sandwich panel was cut into 2 x 2 in specimens and tested according to ASTM C-297 to obtain flatwise tension strength.

3. RESULTS AND DISCUSSION

The structure shown at the bottom of 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 in an order of decreasing TAP and PEPA concentrations, thereby decreasing crosslink densities and branching in the oligomers. Neat resin properties of these MPEIs are listed in Table 1. These compositions utilized BPDA with 85% 3,4-ODA and 15% APB or 75% 3,4'-ODA and 25% APB such that the total theoretical number average molecular weight was 5500 g/mole or 9500 g/mole. The material having 5500 g/mole had received most of the attention because it provided a direct comparison to the completely linear version, PETI-5, of the same theoretical number average molecular weight. As shown in Table 1, MPEI-1 which had highest crosslink density among the oligomers prepared, had the highest Tg of 291°C. A reduction in Tg was observed as crosslink density of the oligomers decreased with values approaching that of the linear PETI-5.

Table 1 also shows both the melt and solution viscosities of the materials. Each of these materials displayed significantly lower melt and solution viscosity than the completely linear version, PETI-5. MPEI-1 had a minimum dynamic melt viscosity of only 600 poise occurring at 335°C, ~35°C lower than the temperature where minimum viscosity for PETI-5 occurred. Furthermore, the Brookfield viscosity (35% solution) was

2000 centipoise versus 30,000 to 40,000 centipoise for linear PETI-5. This difference can be very important during prepregging or adhesive tape fabrication, since lower viscosity solutions wet out individual fibers much better.

Mechanical properties at both RT and 177°C of the cured films 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. There appeared to be a slight reduction in strength and modulus, but higher elongation at lower crosslink densities and branching of the oligomers. MPEI-1, the material with the highest crosslink density exhibited tensile modulus of 570 Ksi at RT and 410 Ksi at 177 °C; while MPEI-5, with the lowest crosslink density had a modulus of 490 Ksi at RT and 300 Ksi at 177°C.

Table 3 shows titanium to titanium tensile shear strengths for the MPEIs when bonded under several different conditions. The adhesive tapes were dried to <2.0% volatile content at a final temperature of 225°C. These materials exhibited excellent processability and adhesive properties at ambient and elevated temperatures as shown in the table. The mild processing condition of low pressure and low temperature was desirable for secondary bonding applications; whereby composites are bonded such that no distortion takes place. Therefore, one condition (15 psi at 288°C for 8 hours) was chosen to fabricate additional Ti/Ti specimens of MPEI-5 (5500 & 9500g/mole). The bonded specimens were exposed to aircraft fluids for 48 hours to investigate the effect of solvent/aircraft fluids exposures on the tensile strengths of the materials. The results are summarized in Table 4. The materials exhibited excellent solvent resistance; virtually no change in tensile strength was observed for the 9500 g/mole material. Only minor changes in strengths were observed at RT and 177°C for the 5500 g/mole material.

4. CONCLUSIONS

Modified phenylethynyl terminated imides, which contain a mixture of linear, branched and star-shaped molecules, were prepared and evaluated for adhesive applications. The polyimides exhibited improved film tensile strength and modulus and low melt and solution viscosities. These resins also had excellent adhesive tensile shear strengths and processability at 288°C and 15 psi. The mechanical properties of these MPEIs were influenced by the concentration of reactive endgroup,

PEPA, and branching point, TAP, as well as the backbone composition, thus allowing tailoring of the materials for various applications. The unique combination of properties in these MPEI materials demonstrated a high potential for future aerospace applications.

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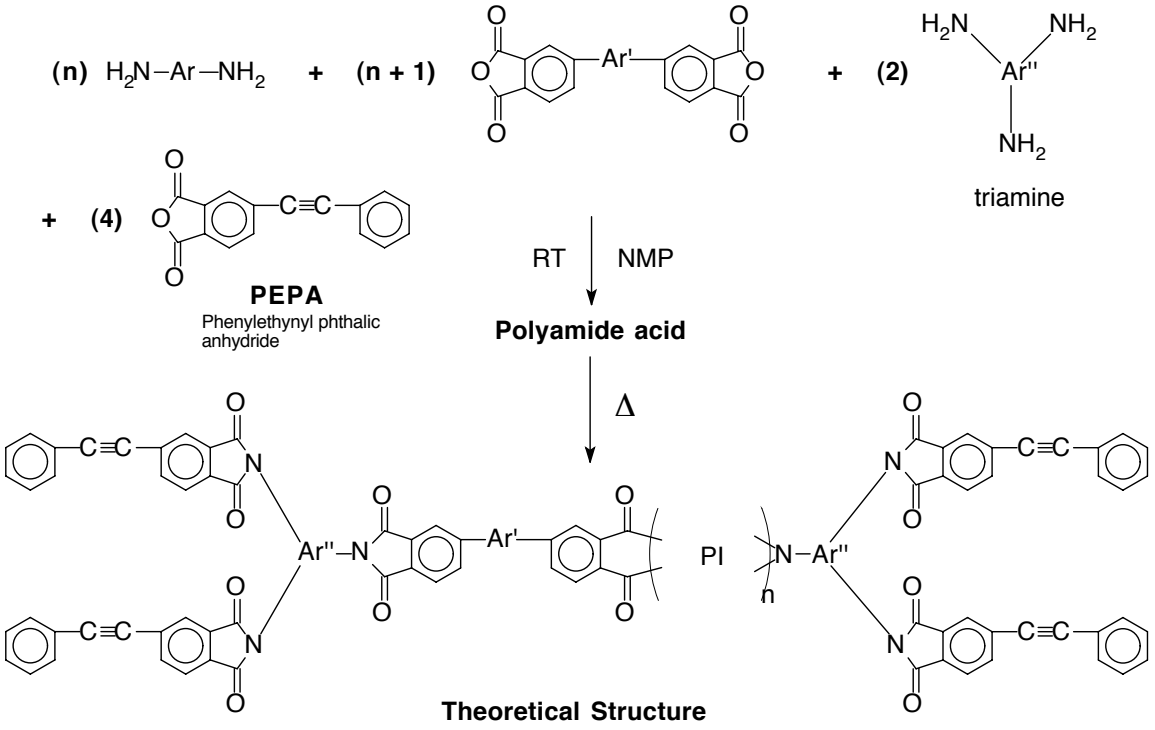
FIGURE 1. SYNTHESIS OF MODIFIED PHENYLETHYNYL IMIDES (MPEI)



Contains mixture of linear, branched and star-shaped molecules

Table 1. Resin Properties of MPEIs

Material (Molecular Wt. g/mole) (Endcappers)	Tg 1h cured @371°C	Minimum melt viscosity poise @ °C	Brookfield viscosity, cps @ % solids @25°C
MPEI-1 (5500) (2 TAP, 4PEPA,0PA)	291	600 @ 335°C	8500 @ 42%s 2000 @ 35 %s
MPEI-2 (5500) (75/25, ODA/APB)	288	700 @340°C	-
MPEI-3 (5500) (2 TAP, 3PEPA,1PA)	279	2000 @360°C	2100 @ 35%s
MPEI-5 (5500) (1 TAP, 3 PEPA,0PA)	271	1000 @340°C	4500 @ 35 %s
MPEI-5 (9500) (1 TAP, 3PEPA,0PA)	272	3000 @365°C	11500 @ 35%s
PETI-5 (5500)	265	60,000 @371°C	35,000 @ 35%s

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-1	23.3 (14.4)	570 (441)	8 (9)
MPEI-2	20.6 (11.6)	520 (400)	8 (5)
MPEI-3	22.0 (11.3)	535 (352)	5.4 (8)
MPEI-5 5500 g/mole	19.0 (11.5)	487 (299)	22 (75)
MPEI-5 9500 g/mole	19.6 (11.5)	477 (386)	8.3 (11)
PETI-5	18.8 (12.2)	455 (332)	32 (84)

Table 3. Ti/Ti Tensile Shear Strength (psi) and Cohesive Failure (%Coh) of MPEIs at RT and (177°C)

Material	15 psi, 8 h 288°C psi/% Coh	15 psi, 4 h@316°C psi/% Coh	15 psi, 1 h 350°C psi/% Coh
MPEI-1	[a]5000/30% [a](4350/20%) Tg: 278°C	[a]4320/70% [a](4800/50%) Tg: 296°C	[b]ND
MPEI-2	[c]5000/30% [c](4800/40%) Tg: 278 °C	4550 (4300)	[b]ND
MPEI-3	[d]4687/80% [d](4812/70%)	4715/70% (5040/70%)	4338/60% (4740/50%)
MPEI-5 (9500 g/mole)	[e]6094/60% [e](5213/100%)	5927/100% 4346/100%)	6715/100% (4700/100%)
MPEI-5 (5500 g/mole)	[f]4693/100% [f](4228/100%)	4686/100% (4062/100%)	4673/100% (4131/100%)

[a] Pasa Jell 107 surface treatment, MPEI-1 primer.

[b] Not determined.

[c] Pasa Jell 107 surface treatment, MPEI-5 primer.

[d] Pasa Jell 107 surface-5 treatment, MPEI-3 primer.

[e] Pasa Jell 107 surface treatment, MPEI-5 5500g/mole primer, 2.5% volatiles in adhesive tape.

[f] Pasa Jell 107 surface treatment, MPEI-5 9500g/mole primer, 1.7% volatiles in adhesive tape.

Table 4. Ti/Ti Tensile Shear Strength (psi) and Cohesive Failure (%) of MPEI-5 at RT and (177°C) After Exposure to Solvents for 48 Hours

Exposure Condition, 48 hours	[a]MPEI-5, 5500 g/mole	[b]MPEI-9, 9500 g/mole
None	6094/60% (5213/100%)	4693/100% (4228/100%)
Hydraulic Fluid	4706/100% (4060/100%)	5157/50% (4974/100%)
Jet Fuel	4631/100% (4090/100%)	5771/80% (5129/100%)
MEK	4613/100% (4273/100%)	5087/50% (4851/80%)

[a] Pasa Jell 107 surface treatment, MPEI-5 5500 g/mole primer, 2.5% volatiles in adhesive tape.

[b] Pasa Jell 107 surface treatment, MPEI-5 9500 g/mole primer, 1.7% volatiles in adhesive tape.

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