ADHESIVE PROPERTIES OF CURED PHENYLETHYNYL CONTAINING IMIDES

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INTRODUCTION

Considerable attention has been directed towards acetylene terminated oligomers over the last 20 years[1] and recent work has focused on phenylethynyl terminated imide (PETI) oligomers.[2-12] These reactive oligomers possess several features which make them attractive candidates for use as composite matrices and adhesives. The phenylethynyl group can be readily incorporated into many different functionalized oligomers. The reactive oligomers possess relatively low melt viscosities and thermally cure without the evolution of volatile by-products. Once cured, they typically display high glass transition temperatures (T_gs), 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] were synthesized at various molecular weights utilizing a small amount of trifunctional amine. As long as the amount of triamine is relatively small, this approach produces a mixture of linear, star-shaped and branched polymer chains that has lower melt and solution viscosity than an equivalent molecular weight linear phenylethynyl terminated imide oligomers. The work reported herein involves the synthesis and characterization of a copolymer using this approach and the preparation of blends utilizing a phenylethynyl containing reactive plasticizer of lower molecular weight called LaRC LV-121. The chemistry and properties of this new MPEI as well as some blends of MPEI with LV-121, are presented and compared to the linear version, LARC™-PETI-5.[10,11]

EXPERIMENTAL

Materials Synthesis - The MPEI was synthesized as previously reported.[12] The LaRC LV-121 was synthesized under the same conditions and utilizes similiar chemistry as the MPEI but is a lower molecular weight phenylethynyl containing material.

Characterization - Inherent viscosities (η_{inh}) were obtained on poly(amide acids) in NMP (0.5 g/dL) solution at 25°C. Brookfield viscosity measurements were taken on 35 and 42% solids solutions 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.

Rheology - Melt viscosity measurements were performed on a Rheometrics System IV 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 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 at several temperatures.

Films - Poly(amide acid) solutions were poured onto clean glass plates and spread to ~30 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.

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 225°C for 1 h each. Several coats were used to provide a 12-14 mil thick tape with final volatile content of <1.5%. Titanium (Ti,6Al-4V) coupons (Pasa-Jell 107™ surface treatment, primed with PETI-5 solution) were bonded under 1.7 - 50 psi by heating rapidly to 288 - 371°C and holding for 1 - 8 h. Four specimens of bonding condition were tested at RT and 177°C following the guidelines of ASTM D-1002.

RESULTS AND DISCUSSION

Although several new LaRC MPEI compositions and different molecular weights (from 1500 to 7000 g/mole theoretical number average molecular weights) have been prepared, the work presented herein describes only one composition and at only one molecular weight. This composition utilizes BPDA with 85% 3,4-ODA and 15% APB such that the total theoretical number average molecular weight is 5500 g/mole. This particular material has received most of the attention because it provides a direct comparison to the completely linear version, LARC-PETI-5 of the same theoretical number average molecular weight. Likewise, many different LaRC LV compositions and molecular weights have been prepared, the LV-121 composition was chosen for the blends because of the similiarities in chemistry with the MPEI.

As shown in Table 1, the MPEI has a higher cured T_g than PETI-5 by about 20°C when cured at either 350 or 371°C for 1 h. Furthermore, film properties are higher at both RT and 177°C for the MPEI. Tensile strength at RT has improved by almost 25% while strength at 177°C has improved by over 15%. Tensile moduli at both RT and 177°C have increased by ~25% to very high values of 570 and 411 Ksi, respectively, when compared to PETI-5. There is a significant reduction in film elongation from 32% at RT for PETI-5 to 8% elongation for the MPEI material at RT.

Table 1 also shows both the melt and solution viscosities for the two materials. As shown, the MPEI has a minimum dynamic melt viscosity of 600 poise occurring at 335°C, a lower temperature by ~35°C than the minimum for PETI-5. Furthermore, the concentrated solution viscosity (35% solids) is ~2000 centipoise versus 30,000 to 40,000 centipoise for the linear PETI-5. This difference can be very important when making prepreg or adhesive tape.

Table 2 shows titanium to titanium tensile shear strengths for the MPEI when bonded under several conditions. The adhesive tape had been dried to <1.5% volatile content at a final temperature of 250°C. Very good strengths were obtained at RT and there was little to no drop off in strengths when tested at 177°C. The 177°C strengths are comparable to PETI-5.

Table 3 shows titanium to titanium tensile shear strengths for the blends when bonded under several conditions. The RT strengths are lower than the MPEI in most cases but the 177°C strengths are comparable under some bonding conditions. The blends have lower melt viscosity and actually have significant adhesive strength when bonded under only 1.7 psi at 316°C.

CONCLUSIONS

Modified phenylethynyl terminated imides have been prepared which have improved film tensile strength and modulus and lower melt and solution viscosities. The MPEI studied most extensively also shows excellent tensile shear strength even when bonded under relatively mild conditions. Blends of the MPEI and LaRC LV-121 also have excellent tensile shear strength at 177°C and lower melt viscosities than the pure MPEI.

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Table 1. Properties of MPEI Compared to PETI-5.

Property	MPEI	PETI-5
Tg (350°C, 1h cure) (371°C, 1h cure)	281 291	260 263
Film Tensile Strength, Ksi	23.3 @ RT; 14.1 @ 177°C	18.8 @ RT; 12.2 @ 177°C
Film Tensile Modulus, Ksi	570 @ RT; 411 @ 177°C	455 @ RT; 332 @ 177°C
Film Elongation, %	8 @ RT; 9 @ 177°C	32 @ RT; 84 @ 177°C
Minimum Dynamic Melt Viscosity, poise	600 @ 335°C	10,000 @ 371°C
Brookfield Viscosity of Poly (amide acid) (25°C), centipoise	~2000 @ 35% solids ~8500 @ 42% solids	30,000-40,000 @ 35% solids

Table 2. Adhesive Properties of MPEI Compared to PETI-5.[10]

Material	Processing Conditions	Tg, °C	Ti/Ti Tensile Shear Strength, psi	
			RT	177°C
MPEI	15 psi, 288°C, 8 h	278	5000 30%	4350 20%
MPEI	50 psi, 288°C, 8 h	278	4600 40%	4550 40%
MPEI	15 psi, 316°C, 8 h	290	4800 70%	4800 50%
MPEI	50 psi, 316°C, 8 h	290	4800 70%	4400 40%
MPEI	15 psi, 371°C, 1 h	299	4750 50%	---
PETI-5	75 psi, 350°C, 1 h	265	7000 80%	4350 80%

Table 3. Ti/Ti Tensile Shear Strength (psi) and Cohesive Failure (%) of MPEI/LV-121 Blends at RT and (177°C).

Material	1.7 psi, 8h, 316°C	15 psi, 8h, 288°C	15 psi, 8h, 316°C	15 psi, 4h, 316°C
MPEI	2320 50% (2630 20%)	5000 30% (4350 20%)	4800 70% (4800 50%)	5320 70% (5150 90%)
MPEI + 15% LV-121	4050 70% (3500 70%)	4500 100% (4480 80%)		4220 90% (4650 90%)
MPEI + 20% LV-121	2975 80% (3790 80%)	3510 80% (4315 70%)		3865 80% (4370 70%)
MPEI + 25% LV-121	2810 70% (3740 70%)	3500 90% (4030 90%)		4360 90% (4270 80%)
MPEI + 30%	3300 80%	3400 80%		3760 70%