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Adhesive Properties of Cured Phenylethynyl Containing Imides

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ADHESIVE PROPERTIES OF CURED PHENYLETHYNYL CONTAINING IMIDES

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1. ABSTRACT

As part of a program to develop structural adhesives for high performance aerospace applications, several phenylethynyl containing oligomer blends of LaRC™ MPEI[1] (Modified Phenylethynyl Terminated Polyimide) and a reactive plasticizer designated LaRC™ LV-121 were prepared and evaluated. The fully imidized blends exhibited minimum melt viscosity as low as 1000 poise at 371°C. Ti/Ti lap shear specimens fabricated at 316°C under 15 psi gave RT strength of ~4300 psi and no change in strength was observed at 177°C. 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.[2,3]

2. EXPERIMENTAL

2.1 Materials Synthesis

The MPEI was synthesized as previously reported.[1] The LV-121 was synthesized under the same conditions and utilizes similar chemistry as the MPEI but is a lower molecular weight phenylethynyl containing material.

2.2 Characterization

Brookfield viscosity measurements were taken on 35 and 42 wt% 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.

2.3 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.

2.4 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.

2.5 Adhesive Specimens

NMP 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 each bonding condition were tested at RT and 177°C following the guidelines of ASTM D-1002.

3. RESULTS AND DISCUSSION

Although several new 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, 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 similarities in chemistry with the MPEI.

The reactive plasticizers with similar composition to LV-121 but various molecular weights and their dynamic minimum melt viscosities are shown in Table 1. All the plasticizers exhibit low initial Tg and minimum melt viscosity of < 50 poise (below capability of equipment) at a temperature of ~260 °C.

As shown in Table 2, 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 2 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 3 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 4 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.

Neat resin properties of PETI-5/LV-121 blends are shown in Table 5. The dynamic minimum viscosity had reduced from 60,000 to 7,000 poise for PETI-5 containing 10 wt.% of LV-121 plasticizer. The blends exhibit comparable LSS as PETI-5 at 177°C when processed at milder temperature and pressure which are more desirable for secondary bonding applications.

4. CONCLUSIONS

Blends of the MPEI and LaRC™ LV-121 have been prepared and evaluated for adhesive application. The polymer blends exhibit excellent adhesive strengths and processability at 316 °C under low pressure. Blends of PETI-5 and LaRC™ LV-121 also exhibit excellent Ti/Ti lap shear strength retention at 177 °C and lower melt viscosities than the pure PETI-5, providing easier processing conditions.

5. REFERENCE

1. B. J. Jensen, Poly. Prepr; 37(2), 222 (1996).
2. B. J. Jensen, R. G. Bryant, J. G. Smith and P.M. Hergenrother, J. of Adhesion, 54 (1), 57 (1995).

3. T. H. Hou, B. J. Jensen and P. M. Hergenrother, J. of Composite Materials, 30(1), 109 (1996).

Table 1. Resin Properties of Reactive Plasticisers

Material	Molecular Wt g/mole	Initial Tg °C	Cured Tg °C	Minimum Melt Viscosity, poise
LaRC™ LV121	1266	132	[a]ND	<50 @ ~250°C
LaRC™ LV122	1817	134	232	<50 @ ~260°C
LaRC™ LV123	2367	150	219	<50 @ ~270°C
LaRC™ LV124	2918	155	213	<50 @ ~280°C

[a] not detectable.

Table 2. Properties of MPEI[1] Compared to PETI-5.

Property	MPEI	PETI-5
Tg (350°C, 1h cure) °C (371°C, 1 h cure)	281 291	260 263
Film Tensile Strength, Ksi	23.3 @ RT;14.4 @ 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	60,000 @ 371 °C
Brookfield Viscosity of Poly(amide acid) (25°C), centipoise	~2000 @ 35% solids ~8500 @ 42% solids	30,000-40,000 @ 35 % solids

Table 3. Adhesive Properties of MPEI Compared to PETI-5.[2]

Material	Processing Conditions	Tg, °C	Ti/Ti Tensile Shear Strength, psi % Cohesive Failure 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 4. 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% LV-121	3300 80% (3230 70%)	3400 80% (3550 90%)		3760 70% (4000 70%)

Table 5. Neat Resin Properties of PETI-5/LV 121 Blends and Ti/Ti Lap Shear Strength(LSS) at RT and (177°C)

% LV 121	Tg °C	Minimum melt η poise	Ti/Ti LSS (psi)	Bonding condition
0	265	60,000 @371°C	7000 (4350)	75 psi, 350°C, 1h
10	258	7,000 @371°C	5900 (4227)	15 psi, 316°C, 4h
15	255	1,600 @371°C	5125 (4311)	15 psi, 316°C, 4h
20	253	1,000 @371°C	5130 (3980)	15 psi, 316°C, 4h

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As part of a program to develop structural adhesives for high performance aerospace applications, several phenylethynyl containing oligomer blends of Larc™ MPEI and a reactive plasticizer designated LaRC™ LV-121 were prepared and evaluated. The fully imidized blends exhibited minimum melt viscosity as low as 1000 poise at 371°C. Ti/Ti lap shear specimens fabricated at 316°C under 15 psi gave RT strength of ~4300 psi and no change in strength was observed at 177°C. 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.

14. SUBJECT TERMS
LaRC™-PETI-5, Polyimides, LaRC™ MPEI, LaRC™ LV-121, Lap Shear Strength.

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