HIGH TEMPERATURE TRANSFER MOLDING RESINS BASED ON 2,3,3',4'-BIPHENYLTETRACARBOXYLIC DIANHYDRIDE

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ABSTRACT

As part of an ongoing effort to develop materials for resin transfer molding (RTM) processes to fabricate high performance/high temperature composite structures, phenylethynyl containing imides have been under investigation. New phenylethynyl containing imide compositions were prepared using 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) and evaluated for cured glass transition temperature (Tg), melt flow behavior, and for processability into flat composite panels via RTM. The a-BPDA imparts a unique combination of properties that are desirable for high temperature transfer molding resins. In comparison to its symmetrical counterpart (i.e. 3,3',4,4'-biphenyltetracarboxylic dianhydride), a-BPDA affords oligomers with lower melt viscosities and when cured, higher Tgs. Several candidates exhibited the appropriate combination of properties such as a low and stable melt viscosity required for RTM processes, high cured Tg, and moderate toughness. The chemistry, physical, and composite properties of select resins will be discussed.

KEY WORDS: Resin Transfer Molding, High Temperature Polymers, Polyimides

1. INTRODUCTION

Structural composite applications on advanced aerospace vehicles such as high speed aircraft and reuseable launch vehicles (RLV) require high temperature, high performance resins. One class of materials that has been under extensive investigation for these applications are aromatic polyimides due to their inherent physical and mechanical properties (1,2). However, these polymers are typically difficult to process. A method to improve polyimide processability while retaining the excellent properties is through the use of controlled molecular weight oligomers/polymers containing latent reactive groups.

Since the early 1980's, controlled molecular weight imide oligomers containing phenylethynyl groups have been developed to meet the needs for advanced aerospace vehicles such as a high speed civil transport (HSCT) (3-28). Due to the oligomeric nature of the resins, excellent processability was achieved during fabrication of neat resin moldings, bonded panels, and composites under pressures of 1.4 MPa or less. Thermal cure of the phenylethynyl group, typically for ~1 hr at 350-371°C, resulted in chain extension, branching, and light crosslinking without the evolution of volatile by-products. The cured resin provided an excellent combination of properties including high glass transition temperature (Tg), high toughness, high strength, moderate modulus, and good moisture and solvent resistance.

One phenylethynyl terminated imide (PETI) oligomer composition designated PETI-5 was extensively evaluated as an adhesive (22-24) and composite matrix resin (25-27) for use in structural appilications for the once proposed HSCT. This material, prepared at a controlled molecular weight of 5000 g/mol from 3,4'-oxydianiline, 1,3-bis(3-aminophenoxy)benzene, 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and endcapped with 4-phenylethynylphthalic anhydride, displayed good processability and excellent mechanical properties in adhesive and composite forms processed via traditional autoclave methods.

The lower cost fabrication of complex shaped composite structures though neccesitates the use of techniques such as resin transfer molding (RTM). This method requires a resin with a low and stable melt viscosity. Even though PETI-5 exhibited good processability by autoclave techniques, its use in this method was precluded due to its inherently high melt viscosity. Attempts to lower the PETI-5 melt viscosity to make it amenable to RTM through molecular weight reduction (29) and reactive platicizer incorporation (30) met with limited success. Both approaches afforded PETI-5 based resins with decreased melt viscosity, however, not sufficient to be acceptable for RTM. Additionally, the minimum melt viscosity occurred at temperatures where the phenylethynyl group reacted appreciably leading to an unstable melt.

Therefore, the imide oligomer composition and molecular weight were modified to afford a family of volatile-free resins that displayed low and stable melt viscosities which were amenable

to RTM at temperatures of 250-290°C without the aid of solvents (31-33). At temperatures <290°C the phenylethynyl group is very slow to react and as a consequence the melt viscosity is stable for several hours. One composition designated PETI-RTM prepared from the same monomers as found in PETI-5, albeit at different ratios and lower molecular weight, was successfully used to fabricate high quality 2.4 m long curved F-frames. The cured Tg of PETI-RTM was ~256°C making it an attractive material for the once proposed HSCT where a use temperature of 177°C for 60,000 hours was envisioned.

The fabrication of complex composite structures from this resin family for potential use on a RLV though require materials with higher Tgs. In these applications a higher use temperature for shorter duration would be needed. Modifications of the diamine composition of the PETI-RTM backbone while retaining the dianhydride as s-BPDA afforded a composition designated PETI-298 (34). This material exhibited a comparable melt viscosity to that of PETI-RTM and hence similar processing characteristics. The cured Tg of PETI-298 was ~300°C as compared to 256°C for PETI-RTM. Good mechanical properties were obtained on flat laminates fabricated from this resin. Initial attempts to fabricate panels with this material by vacuum assisted RTM were successful in producing laminates with properties comparable to those via RTM, however with volid contents of ~4% (36). Further work is ongoing using this technique.

Recently polyimides (37, 38) and PETI oligomers (38-40) have been prepared from 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA). These materials exhibited higher Tgs and lower melt viscosities as compared to analogous materials prepared from s-BPDA presumably due to the irregular structure of the dianhydride. Thus, a-BPDA based PETI compositions were prepared and evaluated to meet the objectives to develop a material with a higher Tg than PETI-298, be processable by RTM, and display high mechanical properties in composites. The chemistry and physical properties of the oligomers and the corresponding cured polymers are discussed herein.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: 3,4'-oxydianiline (3,4'-ODA, Mitsui Petrochemical Ind., Ltd., m.p. 84°C), 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB, Chriskev, m.p. 115°C), 1,4-bis(4-aminophenoxy)benzene (1,4,4-APB, Chriskev Co., m.p. 173°C), 1,3-diaminobenzene (m-PDA, Aldrich Chemical Co., m.p. 66°C), 2,2'-bis(trifluoromethyl)benzidine (TFMBZ, Chriskev Co., m.p. 182°C), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA, Allco Chemical Co., m.p. 227°C), 4-phenylethynylphthalic anhydride (PEPA, Imitec, Inc. or Daychem Laboratories, Inc., m.p. 152°C) and N-methyl-2-pyrrolidinone (NMP, Fluka Chemical Co.). 2,3,3',4'-Biphenyltetracarboxylic dianhydride (a-BPDA, Ube Industries Inc., m.p. 197°C) was

recrystallized from toluene and acetic anhydride. All other chemicals were used as-received without further purification.

2.2 Synthesis of Phenylethynyl Terminated Imide (PETI) Oligomers PETI oligomers were prepared at a calculated number average molecular weight ($\overline{M}_n$) of 750 g/mol by the reaction of the appropriate quantity of aromatic dianhydride(s) with the appropriate quantity of aromatic diamines and endcapped with PEPA. The oligomers were prepared by initially dissolving the aromatic diamine(s) in NMP at room temperature under nitrogen. The appropriate quantities of dianhydride(s) and endcapper (PEPA) were subsequently added in one portion as a slurry in NMP. The reactions were allowed to stir for ~24 hrs at ambient temperature under nitrogen. Imide oligomer was prepared directly from the amide acid solution by azeotropic distillation with toluene under a Dean Stark trap to effect cyclodehydration. The imide oligomers remained soluble during the imidization process. Powders were isolated by adding the reaction mixture to water and washing in warm water. The yellow powders were dried to constant weight with yields >95%.

2.3 Composite Specimens PETI oligomers will be used to infiltrate AS4-5HS carbon fiber fabric, where the sizing is thermally removed by heating at 400°C for 2 hr, to fabricate quasi-isotropic 8 ply panels using a high temperature injector. The molten PEI oligomers will be degassed in the injector prior to injection. Flat laminates will be fabricated in a press under ~1.4 MPa hydrostatic pressure during the entire process cycle. The PETI oligomers will be injected at ~280°C. The final cure for all laminates will consist of a 371°C hold for 1 hr. The laminates will be cooled under pressure to ~100°C and the pressure subsequently released. The composite panels will be ultrasonically scanned (C-scanned), cut into specimens, examined via SEM for microcracks, and tested for mechanical properties according to ASTM procedures.

2.4 Other Characterization Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the Tg taken at the inflection point of the ΔT versus temperature curve. PETI oligomers were cured at 371°C for 1 hr in a sealed aluminum pan. Rheological measurements were conducted on a Rheometrics System 4 rheometer at a heating rate of 4°C/min. Specimen disks (2.54 cm in diameter and 1.5 mm thick) were prepared by compression molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a variable strain and a fixed angular frequency of 100 rad/sec while the lower plate was attached to a transducer, which recorded the resultant torque. Storage (G') and loss (G") moduli and complex melt viscosity (η^*) as a function of time (t) were measured at several temperatures.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Phenylethynyl Terminated Amide Acid and Imide Oligomers The objective of this work was to develop and evaluate PETI resins which exhibited cured Tgs >300°C while maintaining processability by low melt viscosity processes such as RTM. Previously reported PETI compositions have been based on s-BPDA and diamines containing ether and meta phenylene linkages. One composition designated PETI-298 exhibited a cured Tg of ~300°C and a stable melt viscosity of 0.5 Pa·s at 280°C (34). This material was prepared from 1,3,4-APB, 3,4'-ODA, s-BPDA, and endcapped with PEPA. Flat laminates fabricated by RTM of this resin exhibited good mechanical properties, no microcracking, and low void content. Attempts to further increase the cured s-BPDA based resin Tg >300°C met with marginal success by using a pendent phenylethynyl containing diamine (DPEB, 3,5-diamino-4'-phenylethynyl benzophenone) (34). Resins with cured Tgs >300°C were obtained that had stable melt viscosities amenable for RTM processing. However, flat laminates prepared from these DPEB containing compositions exhibited microcracking in the as processed panels. The use of diamines containing para phenylene linkages resulted in materials with increased Tgs, but the melt viscosities were out of the range of RTM processing.

In a recent report an isomer of s-BPDA, a-BPDA provided a PETI based resin with a higher cured Tg and lower melt viscosity than PETI-5 prepared at a comparable calculated $\overline{M}_n$. This composition, however, used a more rigid diamine (4,4'-oxydianiline) (39) than PETI-5 (3,4'-ODA and 1,3,3-APB). The lower melt visocisity that was attained was presumably a result of the irregular structure(s) provided by a-BPDA due to the catenation of the dianhydride. Based on these reults, new compositions of PETI resins amenable to processing by low viscosity techniques were prepared and evaluated based on a-BPDA.

The PETI oligomers were prepared via the classic amide acid route at a calculated $\overline{M}_n$ of 750 g/mol. By this approach, the diamine(s) were initially dissolved in NMP with subsequent addition of the dianhydride(s) (a and/or s-BPDA) and PEPA endcapper as a slurry (Fig. 1). The mixture was stirred at ambient conditions for ~24 hrs. Subsequent conversion of the phenylethynyl terminated amide acid oligomer to that of the corresponding PETI oligomer was accomplished by azeotropic distillation in the presence of toluene. The PETI oligomers remained in solution during cyclodehydration and upon cooling to room temperature. Previous work has shown that the high stoichiometric offset employed in the preparation of the calculated $\overline{M}_n$ of 750 g/mol oligomers results in the formation of a complex mixture consisting of oligomers and simple compounds (34). The simple compounds present in this mixture were found to be critical in providing resins with the appropriate melt viscosity required for RTM.

PETI oligomer characterization is presented in Table 1 with PETI-298 included for comparison. The initial Tgs of the oligomers ranged from ~125-170°C which increased ~160°C for powders

cured in a DSC pan for 1 hr at 371°C. Several compositions exhibited endotherms [melt transitions (Tms)] by DSC. This suggests that there was some transient crystallization present based on the materials thermal history. Upon curing at 371°C, no Tms were evident by DSC with cured Tgs ≥300°C being obtained. Compositions P1 and PETI-298 differ only by the

1. NMP, RT, N$_2$
2. Toluene, heat

Ar =

s   a

CF$_3$ CF$_3$

Ar' =

3,4'-ODA   TFMBZ   m-PDA
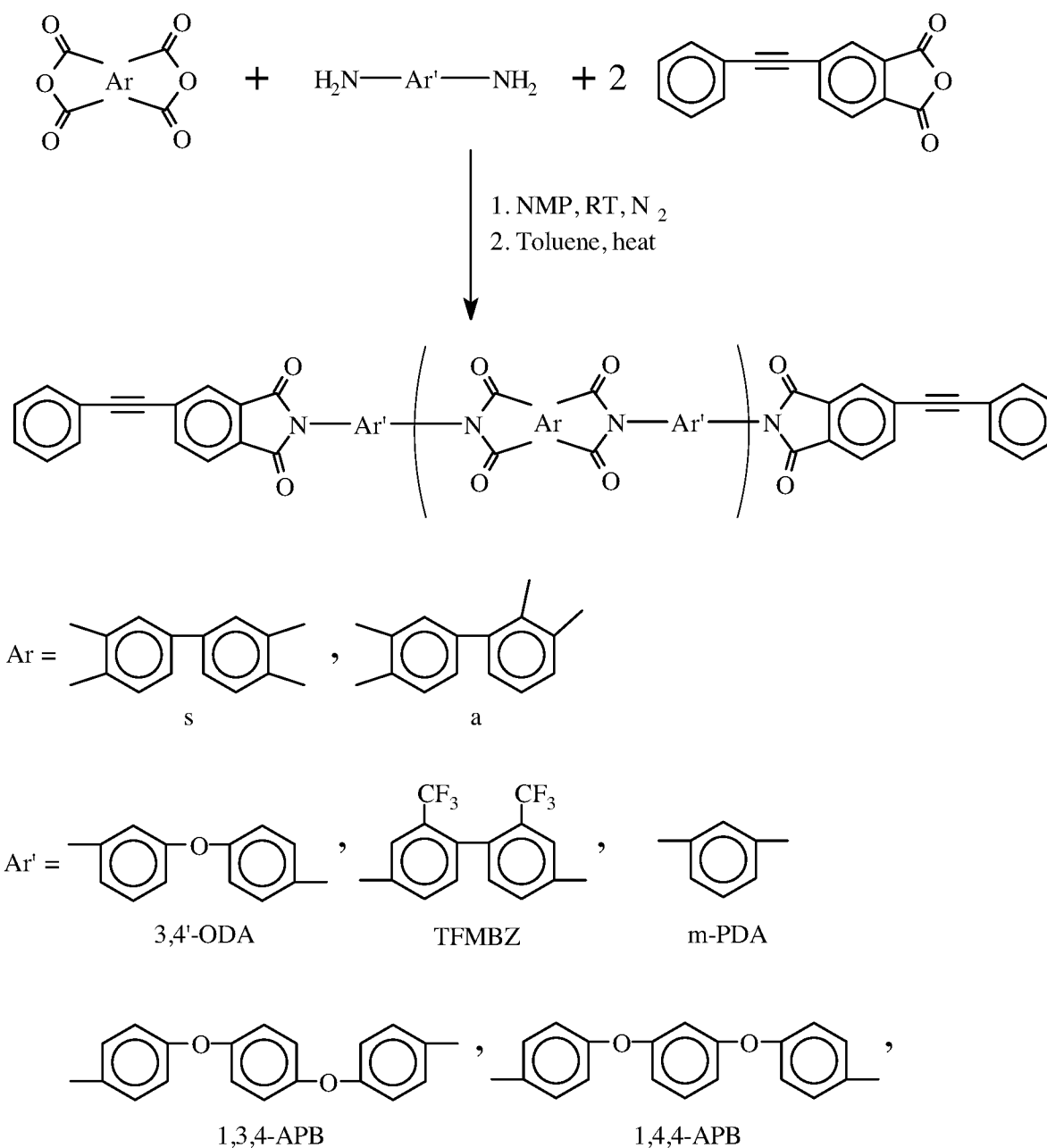
1,3,4-APB   1,4,4-APB

Figure 1: Synthesis of Phenylethynyl containing imide oligomers

dianhydride used: a-BPDA for P1 as compared to s-BPDA for PETI-298. As expected, the cured Tg for P1 (312°C) was greater than that obtained for PETI-298 (Tg of 298°C). Additionally, the cured Tg was observed to increase for increasing amounts of a-BPDA (P4>P3>P2). Oligomer P5,which utilized the more rigid 1,4,4-APB diamine component as compared to 1,3,4-APB used in P1, exhibited ~25°C increase in the cured Tg. The Tg of the cured polymer was likewise found to increase ~20°C for P6 and P8 as compared to P1. In oligomers P6 and P8, the 3,4'-ODA component of P1 was replaced with more rigid diamines. Increasing the mole percentage of the rigid diamine component in P6 and P8 from 25% to 50% in P7 and P9 resulted in a 12 to 25°C increase in the cured resin Tg, respectively.

TABLE 1: PETI Characterization

Oligomer	Diamine Composition (%)	BPDA	Initial Tg (Tm), °C[1]	Cured Tg, °C[2]
PETI-298	1,3,4-APB (75), 3,4'-ODA (25)	s	139	298
P1	1,3,4-APB (75), 3,4'-ODA (25)	a	147	312
P2	1,3,4-APB	s	123 (246)	298
P3	1,3,4-APB	75% s, 25% a	149 (239)	301
P4	1,3,4-APB	50% s, 50% a	168 (222)	307
P5	1,4,4-APB (75), 3,4'-ODA (25)	a	ND[3]	339
P6	1,3,4-APB (75), m-PDA (25)	a	151	318
P7	1,3,4-APB (50), m-PDA (50)	a	ND (182)	330
P8	1,3,4-APB (75), TFMBZ (25)	a	ND (179)	320
P9	1,3,4-APB (50), TFMBZ (50)	a	ND (164)	345

1. Initial Tg determined on powdered samples by DSC at a heating rate of 20°C/min.

2. Cured Tg determined on samples held in the DSC pan at 371°C for 1hr.

3. ND = not detected

3.2 Rheology Dynamic rheological properties, G' (t) and G" (t), were measured using PETI discs compression molded at room temperature. The test chamber of the rheometer was at room temperature prior to specimen introduction. The specimen was heated from 23 to 280°C at a heating rate of 4°C/min and held for 2 hr to assess melt stability. It was then heated to 371°C at the same heating rate and held for 0.5 hr. The results, tabulated in Table 2, are complex melt viscosities (η*) initially and after 2 hrs at 280°C. PETI-298 is included for comparison. A typical melt viscosity curve is shown in Fig. 2 for PETI oligomer P7. The replacement of s-BPDA in PETI-298 with a-BPDA (P1) had a negligible effect on the melt viscosity. The incorporation of a-BPDA in P3 and P4 afforded resins with melt viscosities that were two orders of magnitude

Table 2. Melt Viscosities (η*) of PETI Oligomers

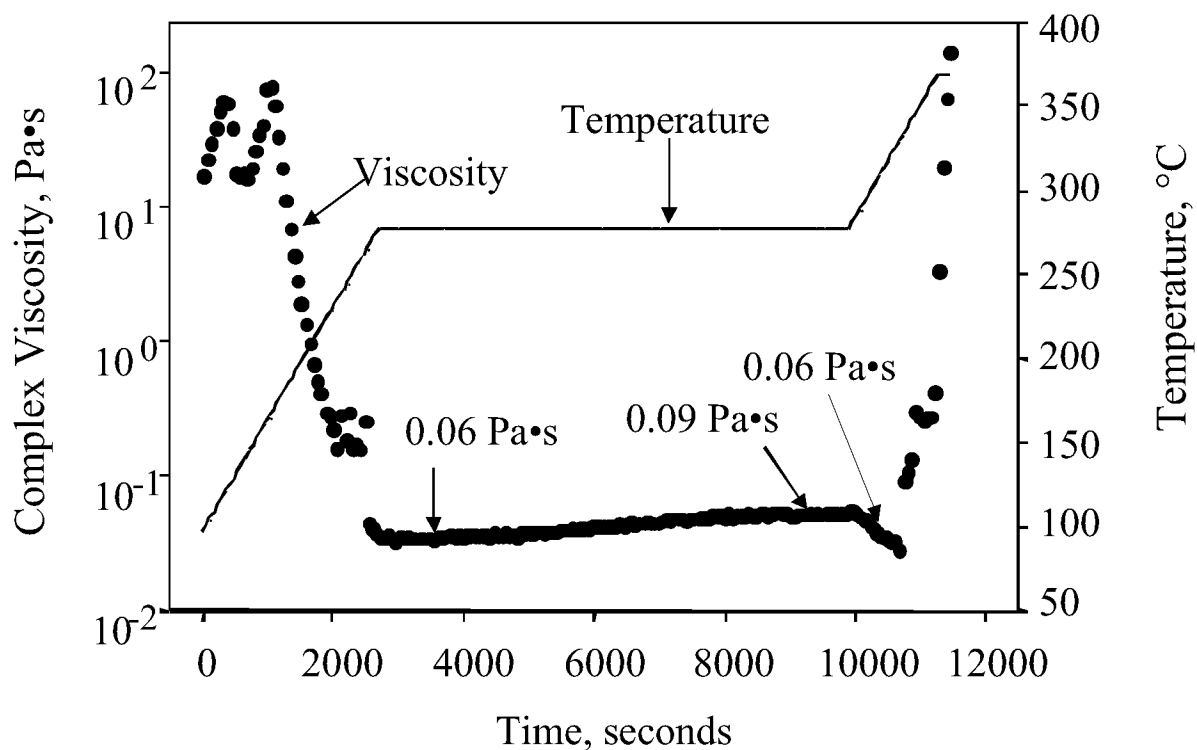| Oligomer	Diamine Composition (%)	BPDA	η* @ 280°C for 2 hr, Pa·s
PETI-298	1,3,4-APB (75), 3,4'-ODA (25)	s	0.6-1.4
P1	1,3,4-APB (75), 3,4'-ODA (25)	a	0.4-3.0
P2	1,3,4-APB	s	13.5-26.0
P3	1,3,4-APB	75% s, 25% a	0.4-0.7
P4	1,3,4-APB	50% s, 50% a	0.8-1.0
P5	1,4,4-APB (75), 3,4'-ODA (25)	a	41-480
P6	1,3,4-APB (75), m-PDA (25)	a	1.2-18
P7	1,3,4-APB (50), m-PDA (50)	a	0.8-3.0
P8	1,3,4-APB (75), TFMBZ (25)	a	0.3-1.4
P9	1,3,4-APB (50), TFMBZ (50)	a	0.6-2.0

Figure 2: Melt viscosity vs. temperature curve of PETI oligomer P7.

lower than P2 which contained only s-BPDA. This was as expected since a-BPDA is known to provide materials with lower melt viscosities as compared to similar materials based on s-BPDA (40). All of the a-BPDA based PETI oligomers except for oligomer P5 exhibited melt viscosities that were acceptable for RTM processing. The 1,4,4-APB component in P5 provided a higher cured Tg material than P1, however, it had a deleterious effect on the melt viscosity rendering the material unprocessable by RTM. The incorporation of 25 mole % of more rigid diamines (P6 and P8) in place of 3,4'-ODA (P1) while holding the 1,3,4-APB component the same though had a negligible effect on the melt viscosity. Increasing the mole percentage of these rigid diamines in P6 and P8 from 25 to 50 in P7 and P9 likewise had no effect upon the melt viscosity. At 280°C, the phenylethynyl groups do not react or react very slowly. Thus, the melt viscosities of these materials are stable for >2 hrs at this temperature.

3.3 Composites At the time of this writing, flat laminates were in the process of being fabricated. The results of the composite fabrication and properties will be presented at the meeting.

4. SUMMARY

New phenylethynyl terminated imide oligomers based on a-BPDA were prepared and evaluated. Oligomers with low and stable melt viscosities amenable to RTM processing were obtained which exhibited higher cured Tgs as compared to similar compositions based on s-BPDA. One composition based on 1,3,4-APB and m-PDA was scaled-up and is undergoing evaluation in flat laminates.

5. ACKNOWLEDGMENT

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