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Transfer Molding Imide Resins Based on 2,3,3′,4′-Biphenyltetracarboxylic Dianhydride

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Summary: Phenylethynyl containing imide oligomers have been under investigation as part of an effort to develop resins for non-autoclave composite fabrication processes such as resin transfer molding (RTM). These high performance/high temperature composites are potentially useful on advanced aerospace vehicles such as reusable launch vehicles (RLVs). New phenylethynyl terminated imide oligomers (PETI) based upon 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) were prepared and characterized primarily by rheological behavior and cured glass transition temperature (Tg). In comparison to resins from the symmetrical isomer (3,3',4,4'-biphenyltetracarboxylic dianhydride, s-BPDA), a-BPDA afforded corresponding resins with lower melt viscosities and upon curing, higher Tgs. Several resins exhibited an attractive combination of properties such as low and stable melt viscosities required for RTM composite fabrication, high cured Tgs, and moderate toughness. One resin (P10) was used to fabricate flat, void free laminates by RTM. The laminates exhibited high mechanical properties at temperatures to 288°C. The chemistry and physical properties of these new PETIs and the laminate properties of one composition are discussed.

Keywords: a-BPDA, high temperature polymers, PETI-330, polyimides, resin transfer molding

1 Introduction

Advanced aerospace vehicles such as high speed aircraft and reusable launch vehicles (RLV) require high performance/high temperature resins for use as adhesives and composite matrix resins for structural applications. Due to the excellent physical and mechanical properties of

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aromatic polyimides,[1,2] these materials are under investigation for these applications. However, even moderate molecular weight polyimides are difficult to process into large bonded panels and composites. The monomeric reaction approach, such as used with PMR-15, has been practiced for many years as a means of obtaining processability and accordingly, good quality composites. An alternative approach that is essentially free of toxicity and reduces the problems associated with residual solvent is through the use of controlled molecular weight oligomers containing phenylethynyl groups.

Controlled molecular weight imide oligomers containing phenylethynyl groups have been under investigation for a variety of electronic and structural applications for more than 20 years.[3-28] Phenylethynyl terminated imide oligomers were extensively evaluated as adhesives and composite matrices in the high speed civil transport (HSCT) program.[29-37] To be considered for HSCT applications, the resins had to: (1) be non-toxic, (2) provide bonded panels and composites using conventional fabrication processes, (3) exhibit performance as required by the vehicle, and (4) be cost-effective. The main operational issues for the HSCT included high temperature, high stress, object impact, thermal cycling, and exposure to moisture and aircraft fluids. In addition, components were required to retain acceptable mechanical properties at 177°C for 60,000 hours.

In the HSCT program, many phenylethynyl containing imide oligomers were evaluated. One phenylethynyl terminated imide (PETI), designated PETI–5, was selected as the adhesive and composite matrix resin. The material was prepared from 3,3',4',4-biphenyltetracarboxylic dianhydride (s-BPDA) and an 85:15 ratio of 3,4'-oxydianiline (3,4'-ODA) and 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB) at a calculated number average molecular weight ($\overline{M}n$) of 5000 g/mol and endcapped with 4-phenylethynylphthalic anhydride (PEPA). Due to its oligomeric nature, PETI-5 exhibited good autoclave processability during the fabrication of large bonded and composite structures at 350-371°C for 1 hour under 1.4 MPa (200 psi) or less.[37] The thermal cure of the phenylethynyl group involved chain extension, branching, and light crosslinking without the evolution of volatile by-products. The cured resin with a glass transition temperature (Tg) of ~270°C provided an excellent combination of properties including high toughness, high strength, moderate modulus, good moisture and solvent resistance.

However, the fabrication of support structures (e.g. frames, ribs, stringers) in the HSCT program was preferably performed by resin infusion (RI) and resin transfer molding (RTM) processes due to their low manufacturing costs. These methods required a resin with low (preferably <3 Pa•s) and stable (>2 hr at the injection or infiltration temperature) melt viscosity during part fabrication. Even though PETI-5 exhibited good autoclave processability, the melt viscosity was too high (~6000 Pa*s at 370°C) to fabricate composites by RI and RTM. Initial attempts at lowering the melt viscosity of PETI-5 to make it amenable to RTM through molecular weight reduction[29] and the incorporation of a reactive additive[30] met with limited success. In the first approach, melt viscosities of lower molecular weight versions of PETI-5 decreased relative to that of the $\overline{M}n$= 5000g/mol version, but were still too high for RTM. The second approach reduced the melt viscosity of PETI-5 to acceptable levels, unfortunately, >80 % of the additive was required to be effective. Additionally, the minimum melt viscosities under both approaches occurred at temperatures where the phenylethynyl group reacted appreciably, leading to an unstable melt.

Work continued on the modification of the oligomer composition with the same monomers used to make PETI-5. This was partly due to the desire of the HSCT program which preferred a PETI-5 like material for RTM and RI. The work primarily involved adjustments to the diamine ratio as well as the molecular weight of the oligomer. Results from this effort afforded resins that were processable by RI and RTM.[31-34] These volatile-free oligomers exhibited stable, low melt viscosities at temperatures <290°C where the phenylethynyl group was slow to react. One composition, designated PETI-RTM, was scaled-up to 30 kilogram quantities and successfully used in the fabrication of high quality 2.4 m long curved F-frames by RTM. The cured Tg of PETI-RTM was 256°C, making it an attractive material for the HSCT.

With the closing of the HSCT program in 1999, work continued to develop RI/RTM resins with higher cured Tgs and better mechanical properties than PETI-RTM for future use in composite structures for RLVs. The operational environment for RLV composites differs significantly from that of the HSCT in that higher temperature performance is needed for shorter periods of time. Numerous compositions were evaluated which looked at other diamines than those used in the PETI-5. From this work, RTM resins emerged with higher cured Tgs.[35-36] One composition designated PETI-298 exhibited a cured Tg of ~300°C while retaining excellent RTM processability. It differed from PETI-RTM in that 1,3,3-APB was replaced with 1,3,4-APB. This change provided an improvement over PETI-RTM with better mechanical properties at elevated temperatures due to a higher Tg. Good initial mechanical properties were obtained on flat laminates and excellent retention of room temperature properties were observed after aging at 288°C in air for 1000 hrs.[36] Flat laminates fabricated with this resin by vacuum assisted resin transfer molding (VARTM) gave properties comparable to the RTM laminates, however the void content was ~4%.[38] Work is underway to improve the quality of VARTM/PETI-298 laminates.

Over the past 15 years, polyimides from 2,3',3',4-biphenyltetracarboxylic dianhydride (asymmetric isomer, a-BPDA) were shown to have lower melt viscosities and higher Tgs than the corresponding polymers from s-BPDA.[39-44] This is presumably due to the highly irregular structure of the polyimide emanating from a-BPDA. In addition, a-BPDA based PETIs were shown to have lower melt viscosities and when cured, higher Tgs than the same PETI based upon s-BPDA. [45-47] However, none of these a-BPDA derived PETIs had a melt viscosity low enough for RTM. Thus, a series of low molecular weight PETIs derived from a-BPDA were prepared in an attempt to obtain RTM/VARTM resins with improved processability and when cured, higher Tgs and higher laminate properties.[48] The chemistry, physical and mechanical properties of these new resins and their RTM laminates are described 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., melting point (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. 2,2'-Dichlorobenzidine (CLBZ, m.p. 166°C) [49] was used as-received from Professor Frank W. Harris, The University of Akron. 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 $\overline{M}n$ of 750 g/mol by the reaction of the appropriate amount of aromatic dianhydride(s) with the appropriate amount of aromatic diamines and endcapped with PEPA. The oligomers were prepared by initially dissolving the aromatic diamines 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 and rinsed into the flask with additional NMP. The reactions were allowed to stir for ~24 hrs at ambient temperature under nitrogen prior to thermal imidization. Imide oligomer was prepared directly from the amide acid solution by azeotropic distillation with toluene under a Dean Stark trap to effect cyclodehydration. In general, the imide oligomers remained soluble during the imidization process. Imide powders were obtained by precipitating the reaction mixtures in water and washing in warm water. The yellow powders were dried at ~200°C to constant weight with yields >95%.

2.3 Composite Laminates

Laminates of PETI oligomer were made by RTM using AS-4 8 Harness Satin (AS-4 8HS, Hexcel) carbon fiber fabric. The fabric sizing was removed by bagging the fabric in Kapton™, sealing with a high temperature sealant, and heating at 400°C for 2 hr under vacuum. PETI oligomer was injected into the unsized AS-4 8HS carbon fiber fabric positioned on an Invar tool using a high temperature injector. The maximum processing parameters of the injector, designed and built by Radius Engineering according to Lockheed Martin specifications, are a temperature of 288°C, flow rate of 500 cc/min, and pressure of 2.75 MPa. The tool containing the fabric was loaded into a press, heated to 316°C, and held at 316°C for 1.5 hrs prior to resin injection. PETI oligomer was degassed in the injector by heating to 288°C and holding for 1 hr prior to injection. The degassing step was required primarily to remove moisture, residual solvent, and air from the resin. The molten resin was used to infiltrate 8-ply stacks of unsized AS-4 8HS fabric [equivalent to 16 plies of unitape, lay-up of $(0/90)_{4S}$] in an Invar tool under 1.34 MPa hydrostatic pressure during the entire process cycle. After the resin was injected at 288°C at a rate of 200 cc/min, the part was held under 1.34 MPa of hydrostatic pressure while heating to 371°C and holding at 371°C for 1 hr. The 33 cm x 36 cm laminates were cooled under pressure. The laminates were ultrasonically scanned (C-scanned, pulse echo), cut into specimens, and tested for mechanical properties. The panels were examined for microcracks by a microscope up to 400X magnification. Resin content, fiber volume, and void content were determined by acid digestion using a 1:1 (w/w) solution of concentrated sulfuric acid and 30% hydrogen peroxide. Calculations were based on a density of 1.79 X 10^3 Kg/m^3 (1.79 g/cc) for AS-4 8HS fabric and 1.37 X 10^3 Kg/m^3 (1.37 g/cc) for the cured PETI resin. Open hole compression (OHC) properties (Northrup Grumman Test[25]) were determined on specimens 25.4 cm by 3.81 cm with a 0.64 cm hole in the center. Un-notched compression properties (Boeing Test, BSS 7260) were determined on specimens 8.08 cm by 1.27 cm. Short beam shear (SBS) strength (ASTM D2344-84) was determined on specimens 0.64 cm by 1.91 cm. Unstressed specimens were aged at 288°C in a forced air oven. Five specimens were tested under each condition.

2.4 Other Characterization

Differential scanning calorimetry (DSC) was performed on powdered samples using a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the Tg taken at the inflection point of the differential heat flow (ΔH) versus temperature curve. PETI oligomers were cured at 371°C for 1 hr in a sealed aluminum pan, quenched, and the samples were rerun to obtain the Tgs of the cured resins. Dynamic mechanical thermal analysis (DMTA) was conducted on a Bohlin VOR Rheometer equipped with a solids fixture for measuring rectangular specimens. An oscillatory deformation of ~1% strain, a frequency of 1 Hz which translates to an angular velocity of 6.28 rad/sec, and a stepwise temperature test mode sweep at a heating rate of 10°C/min were used in the analysis. 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. Complex melt viscosity (η^*) as a function of time (t) was measured at several temperatures.

3 Results and Discussion

3.1 Synthesis of Phenylethynyl Terminated Amide Acid and Imide Oligomers

The work reported herein is a continuation of an effort originally begun under the HSCT program to develop PETI resins that could be used to fabricate carbon fiber reinforced composites by low viscosity techniques such as RTM. In addition to being fabricated by RTM, the composites needed to display high cured Tgs and high mechanical properties. The early RTM PETIs were based upon PETI-5 monomers at different calculated $\overline{M}_n$ s and diamine ratios.[31-34] The work resulted in the successful development and article demonstration of PETI-RTM, having a Tg of 256°C when cured.

At the conclusion of the HSCT program, this technology was transitioned to a space transportation program to develop RTM processable resins with high cured Tgs and good mechanical properties for future composite applications on RLVs. This work was still based on s-BPDA, but utilized other diamines than those in PETI-5 to increase the cured Tg while maintaining RTM processability.[35-36] Several attempts at increasing the cured resin Tg through incorporation of a pendent phenylethynyl group (3,5-diamino-4'-phenylethynyl benzophenone) met with limited success. These resins exhibited higher cured Tgs than the early RTM resins but the as-processed laminates exhibited microcracks.

One monomer used in the early RTM PETI resin synthesis was 1,3,3-APB. Although this monomer was known to provide improvement in processability,[50-51] it also contributed to a low Tg. Consequently work was initiated at incorporating the other isomers of APB (1,3,4-APB and 1,4,4-APB) into the oligomer and determining the effects upon RTM processability, cured resin Tg, and laminate properties.[35-36] Compositions containing the 1,4,4-APB monomer increased the cured Tg as expected but the melt viscosity of the resin also increased by several orders of magnitude. Compositions prepared with 1,3,4-APB provided resins with low and stable melt viscosities amenable to RTM processability and high cured Tgs. One composition containing 1,3,4-APB, designated PETI-298, exhibited a cured Tg of ~300°C and a stable melt viscosity of 0.6 Pa•s at 280°C.[35-36] Flat laminates fabricated by RTM from this resin exhibited good mechanical properties, no microcracking, and no detectable void content.

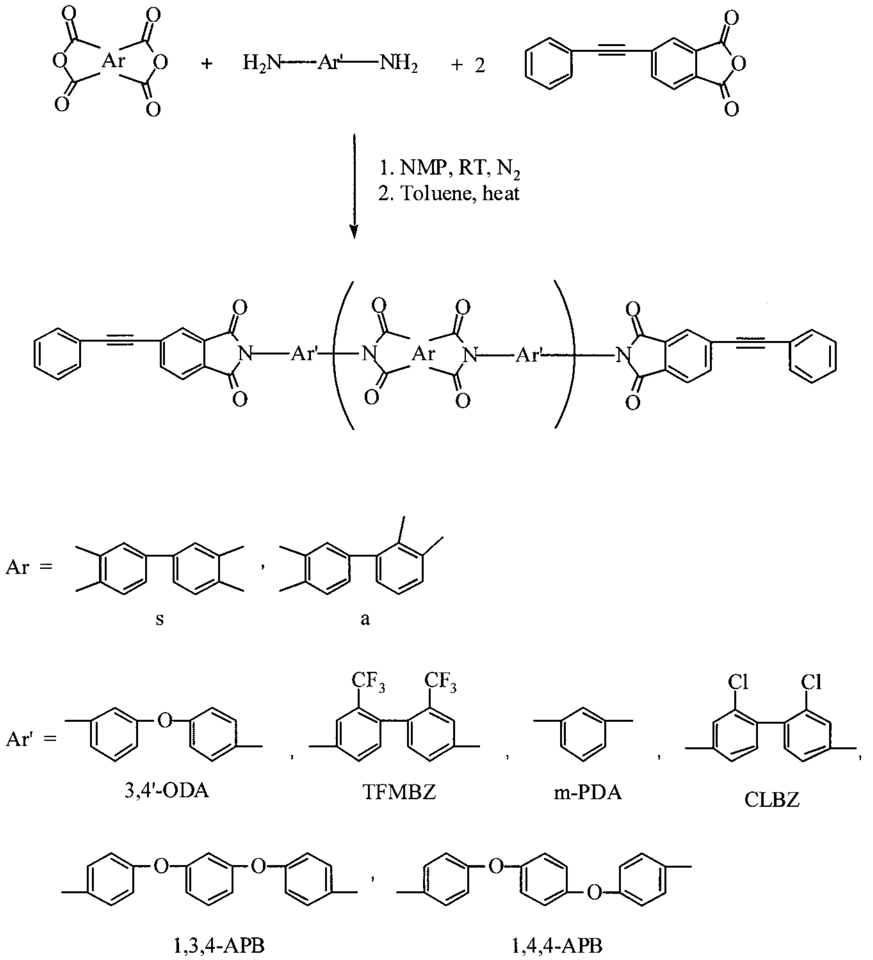

Fig. 1. Synthesis of phenylethynyl containing imide oligomers.

Since a-BPDA derived PETIs were shown to exhibit low melt viscosity and when cured, high Tgs, a series of new PETIs based upon a-BPDA were prepared and evaluated for RTM processability. The PETI oligomers were prepared by the classic amide acid route at a calculated $\overline{M}n$ of 750 g/mol (Fig.1). Initially, the diamine(s) were dissolved in NMP with subsequent addition of the dianhydride(s) (a and/or s-BPDA) and PEPA endcapper as a slurry. The reaction mixture was stirred at ambient conditions for ~24 hrs prior to conversion of the phenylethynyl terminated amide acid oligomer to the corresponding PETI oligomer. Cyclodehydration was accomplished by azeotropic distillation with toluene. The PETI oligomers remained soluble even upon cooling to room temperature. Isolation was performed by precipitation in water. Previous work has shown that the high stoichiometric offset employed in the preparation of these oligomers resulted in the formation of a complex mixture consisting of various molecular weight oligomers and simple compounds.[32-33] The simple compounds in the products were determined to be crucial in providing resins with the appropriate melt viscosity required for RTM.

3.2 Characterization of PETI Resins

The thermal and rheological properties for the PETI oligomers are discussed with respect to the mole % of 1,3,4-APB used. These mole percentages were 50, 75, and 100. Some miscellaneous compositions which did not fit into this delineation are discussed separately.

The initial Tg and crystalline melt transition (Tm) were obtained by DSC. Powdered samples were cured at 371°C for 1 hr in DSC pans and the samples rescanned to determine the cured resin Tg. The complex melt viscosity (η*) was measured using PETI discs compression molded at room temperature. The test chamber of the rheometer was at room temperature for specimen insertion. The specimen was heated from 23 to 280°C at a heating rate of 4°C/min and held for 2 hrs at 280°C to assess melt stability and then heating was continued to 371°C at the same heating rate and held for 0.5 hr to cure the material. The η* is presented initially and after the 2 hr hold at 280°C.

3.2.1 Compositions Based on 100 mole % 1,3,4-APB

To study the effect of a-BPDA content on the cured resin Tg and the melt viscosity of s-BPDA based transfer molding resins, PETIs were prepared using only 1,3,4-APB as the diamine. The a-BPDA was used at 25, 50, and 100 mole % with the difference being s-BPDA. The results are presented in Table 1.

Table 1. PETI Oligomers Based on 100 mole % 1,3,4-APB.

Oligomer	BPDA	Tg (Tm), °C		η* @ 280°C for 2 hr, Pa·s
		Initial[1]	Cured[2]	
P1	s	123 (246)	298	13.5-26.0
P2	75% s, 25% a	149 (239)	301	0.4-0.7
P3	50% s, 50% a	168 (222)	307	0.8-1.0
P4	a	--- (200)	296	0.1-0.4

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.

The cured resin Tg increased as the amount of a-BPDA went from 0 to 50 mole % (P1 – P3). However, the cured Tg of P4 did not increase although it used 100 mole % a-BPDA. This was unexpected, since the a-BPDA based materials have typically exhibited increased Tgs relative to similar resins prepared from the symmetric isomer. The reason for this is unclear, but may be associated with the large stoichiometric offset and the relatively small amount of dianhydride used. The effect of a-BPDA upon the melt viscosity was as expected. For a loading level of 25 mole % a-BPDA (P2), the melt viscosity decreased by 2 orders of magnitude with respect to P1, based solely on s-BPDA. Further reduction in the melt viscosity with increasing a-BPDA was not observed.

3.2.2 Compositions Based on 75 mole % 1,3,4-APB

Based on the results of oligomers from 100 mole % of 1,3,4-APB where a profound effect upon the melt viscosity and cured resin Tg was obtained by the incorporation of a-BPDA, it was of interest to see the effect of replacing s-BPDA in PETI-298 with a-BPDA. PETI-298 is prepared from a 75:25 ratio of 1,3,4-APB and 3,4'-ODA, s-BPDA and endcapped with PEPA. It was anticipated that with a higher cured resin Tg, the melt viscosity would likewise decrease by an order or two in magnitude. The results are presented in Table 2.

The direct replacement of s-BPDA in PETI-298 with a-BPDA to afford P5 resulted in an increase in the cured resin Tg of 14°C. However the melt viscosity remained essentially the same. Similar results to that of PETI-298 and P5 were obtained when m-PDA was substituted for 3,4'-ODA in the PETI-298 and P5 formulations to afford P6 and P7, respectively. The use of a-BPDA appears to have a more pronounced effect upon the melt viscosity in compositions where the melt viscosity is high.

Table 2. PETI Oligomers Based on 75 mole % 1,3,4-APB.

Oligomer	BPDA	25 mole% Diamine	Tg (Tm), °C Initial	Cured	η* @ 280°C for 2 hr, Pa·s
PETI-298[1]	s	3,4'-ODA	139	298	0.6-1.4
P 5	a	3,4'-ODA	147	312	0.4-3.0
P6	s	m-PDA	148 (174, 226, 272)	309	1.9-4.1
P7	a	m-PDA	151	318	1.2-18
P8	a	TFMBZ	ND[2] (179)	320	0.3-1.4
P9	a	CLBZ	193	328	0.2-0.7

1. Data from references 35 and 36.
2. ND = not detected.

As discussed in previous work, the incorporation of 25 mole% of 3,4'-ODA in P1 to afford PETI-298 did not affect the cured resin Tg but did reduce the melt viscosity by two orders of magnitude[35]. Based on these results, it was of interest to evaluate the effect of a-BPDA upon the material properties by replacing 3,4'-ODA in PETI-298 with rigid diamines. Substitution of 3,4'-ODA in PETI-298 and P5 with m-PDA to afford P6 and P7, respectively, increased the cured resin Tg by 6-11°C with the greater effect seen with the s-BPDA based material. As mentioned above, a negligible effect upon the melt viscosity was observed using the more rigid diamine, m-PDA, as compared to the more flexible 3,4'-ODA regardless of BPDA isomer used. Further increases in the cured resin Tgs were observed using TFMBZ (P8) and CLBZ (P9) in the a-BPDA based oligomers with a negligible effect upon the melt viscosity as compared to P5 and P7. The order of increasing cured resin Tgs for the a-BPDA oligomers was: 3,4'-ODA (P5) < m-PDA (P7) < TFMBZ (P8) < CLBZ (P9). The use of TFMBZ and CLBZ was for academic purposes since their high cost prohibits their use in commercial RTM resins.

3.2.3 Compositions Based on 50 mole % 1,3,4-APB

Since the more rigid diamines in P7, P8, and P9 increased the cured resin Tgs without effecting the melt viscosities as compared to PETI-298; it was of interest to further increase the concentration of these diamine components from 25 to 50 mole %. It was anticipated that further increases in the cured resin Tg could be achieved without detrimentally affecting the melt viscosity. The results are presented in Table 3.

Table 3. PETI Oligomers Based on 50 mole % 1,3,4-APB.

Oligomer	50 mole% Diamine	Tg (Tm), °C		η^* @ 280°C for 2 hr, Pa·s
		Initial	Cured	
P10	m-PDA	ND (182)	330	0.06-0.09
P11	TFMBZ	ND (164)	345	0.6-2.0
P12	CLBZ	148	349	7-21

Increasing the mole percentage of m-PDA to 50% in P10 from 25 mole % in P7 resulted in an additional 12°C increase in the cured resin Tg as compared to P7. The melt viscosity decreased by two orders of magnitude in P10 as compared to P7. Similar effects upon the cured resin Tg were observed for increasing the amount of TFMBZ and CLZB from 25 to 50 mole % (P11 as compared to P8 and P12 as compared to P9, respectively). The cured resin Tgs increased ~20-25°C for these polymers as compared to the cured polymers from oligomers containing only 25 mole % of TFMBZ and CLBZ. No effect upon the melt viscosity was observed for increasing the mole % of TFMBZ to 50 (P11 as compared to P8). For compositions containing CLBZ as the diamine, the melt viscosity did increase by one to two orders of magnitude when the mole % was increased to 50 (P12 as compared to P9).

3.2.4 Compositions Based on 50 mole % 1,3,4-APB and 50 mole% m-PDA

Because of the results for oligomers from 100 mole % 1,3,4-APB where the partial replacement of s-BPDA with a-BPDA was evaluated, it was of interest to investigate this with respect to P10. Oligomer P10 was selected due to the combination of low melt viscosity and high cured resin Tg. The a-BPDA in P10 was replaced with 50, 75, and 100 mole % s-BPDA and the effects on the properties are presented in Table 4.

Table 4. PETI Oligomers Based on 50 mole % 1,3,4-APB and 50 mole% m-PDA.

		Tg (Tm), °C		η* @ 280°C
Oligomer	BPDA	Initial	Cured	for 2 hr, Pa·s
P10	a	ND (182)	330	0.06-0.09
P13	50% s, 50% a	139 (173)	332	1.4-4.3
P14	75% s, 25% a	145 (168)	333	1.1-3.1
P15	s	-- (169, 236)	325	$>10^4$

Upon replacement of a-BPDA with 50 and 75 mole % of s-BPDA to afford P13 and P14, respectively, the cured resin Tg remained relatively unchanged with respect to P10. The melt viscosity increased by 2 orders of magnitude for both oligomers as compared to P10. The values for P13 and P14, however, were still within the range useful for resin transfer molding. When a-BPDA in P10 was totally replaced with s-BPDA to afford P15, the melt viscosity increased by 5 orders of magnitude with respect to P10 with a concurrent decrease in the cured resin Tg. This was expected since a-BPDA increases the cured resin Tg and reduces the melt viscosity as reported for other PETIs.[45-47] These results suggest that little a-BPDA is required to have a dramatic impact upon the melt viscosity of high viscosity s-BPDA oligomers.

3.2.5 Miscellaneous Compositions

The Tgs and melt viscosities of other oligomers are presented in Table 5. Oligomers P5, P9, P10, and P12 are included for comparison. Oligomer P16, made with the more rigid 1,4,4-APB as compared to P5 prepared with 1,3,4-APB, exhibited a 27°C increase in the cured resin Tg. However, the melt viscosity increased by 2 to 3 orders of magnitude. Although the melt viscosity of oligomer P5 was out of the range required for RTM, it illustrated that the use of a-BPDA in place of s-BPDA in this composition had the effect of reducing the melt viscosity by 2 to 3 orders of magnitude.[35,36] By reducing the CLBZ content to 40 mole% to afford P17, the melt viscosity was reduced to a comparable level to that of P9 with a minimal reduction in the cured resin Tg as compared to P12. The replacement of 1,3,4-APB in P10 with 3,4'-ODA to afford P18 provided an increase of 12°C in the cured resin Tg. The melt viscosity increased by 2 orders of magnitude using the more rigid 3,4'-ODA and was comparable to that of P13 and P14 where lower amounts of a-BPDA were used.

Table 5. Other PETI Oligomers.

	Diamine	Tg (Tm), °C		η* @ 280°C
Oligomer	Composition, (%)	Initial	Cured	for 2 hr, Pa·s
P5	1,3,4-APB (75), 3,4'-ODA (25)	147	312	0.4-3.0
P16	1,4,4-APB (75), 3,4'-ODA (25)	ND^4	339	41-480
P9	1,3,4-APB (75), CLBZ (25)	193	328	0.2-0.7
P12	1,3,4-APB (50), CLBZ (50)	148	349	7-21
P17	1,3,4-APB (60), CLBZ (40)	145	345	0.3-1.1
P10	1,3,4-APB (50), m-PDA (50)	ND (182)	330	0.06-0.09
P18	3,4'-ODA (50), m-PDA (50)	ND	342	1.4-6.0

3.3 Composites

Based on the combination of cured resin Tg and melt viscosity, oligomer P10 (designated as PETI-330), was selected for evaluation as flat laminates fabricated by RTM. A typical melt viscosity curve for PETI-330 is shown in Fig. 2. At 280°C, the phenylethynyl groups do not react or react very slowly. Thus, the melt viscosities of the material is stable for >2 hrs at this temperature.

The laminates were made with 8 plies of unsized AS-4 8HS carbon fiber fabric with a $(0/90)_{4S}$ lay-up. Fabric sizing was removed by heating at 400°C for 2 hrs under vacuum prior to insertion in the tool. To assess volatile content of the powder, PETI-330 was analyzed by dynamic TGA. At 350°C, <1% mass loss was observed. The PETI-330 powder was charged to the resin chamber and degassed prior to injection into the tool. Laminate fabrication involved injecting the molten oligomer at ~280°C into the preheated tool followed by a cure at 371°C for 1 hr under ~1.4 MPa hydrostatic pressure. All of the laminates were of high quality as determined by C-scan and photomicroscopy.

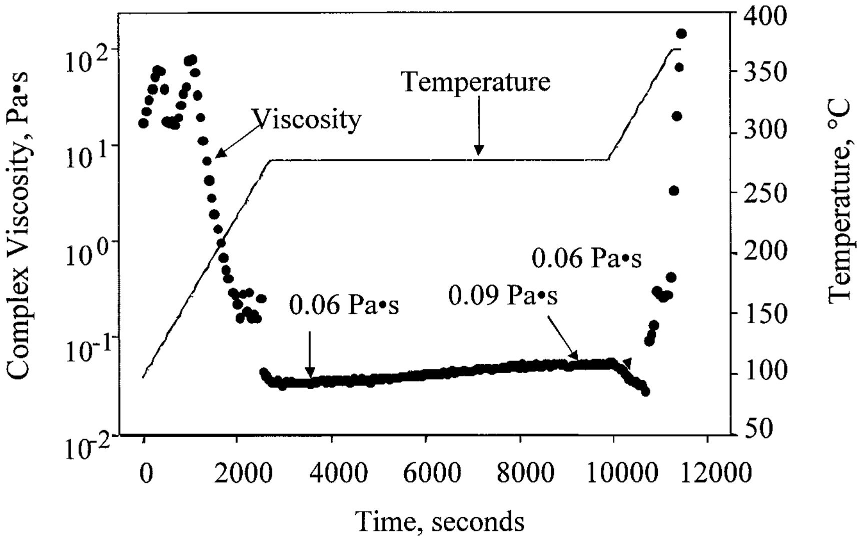

Fig. 2. Melt viscosity vs. temperature curve of PETI-330 (oligomer P10).

The PETI-330 laminate properties are summarized in Table 6 with those of PETI-298 included for comparison. Laminate Tgs were lower for both materials than those obtained for the cured polymers by DSC. Past work has shown that PETIs cured in air exhibited higher Tgs than those cured in a low air environment,[28] as found in the RTM tool. The laminates had ≤2% porosity with fiber volumes of ~57 % as determined by acid digestion. The close fiber volumes allowed for a direct comparison of properties without normalization.

The room temperature (RT) open hole compressive (OHC) strength and short beam shear (SBS) strength of PETI-330 were comparable to those of PETI-298. The retention of OHC and SBS strengths at 288°C was significantly better for PETI-330 than for PETI-298 due to its higher Tg. The OHC modulus was comparable for both materials regardless of test temperature. The RT un-notched compressive strength was lower for PETI-330 as compared to PETI-298. Overall, the mechanical properties of the unoptimized PETI-330 laminates were very good.

Table 6. Laminate Physical and Mechanical Properties.[1]

Property	Test Temp., °C	P10[2] (PETI-330)	PETI-298[3,4]
Cured Tg, °C (DSC of resin)	----	330	298
Cured Tg, °C (TMA of composite)	----	313	289
Fiber Volume, %	----	57	57.3
Un-notched Comp. Str., MPa	23	442	503
OHC Str., MPa	23 288	250 218	244 161
OHC Mod., GPA	23 288	42 40	40 38
SBS Str., MPA	23 232 288	38 37 34	39 32 23

1. 8 plies, quasi-isotropic lay-up.
2. P10 (PETI-330) composition: 50:50 mixture of 1,3,4-APB and m-PDA with a-BPDA and endcapped with PEPA.
3. PETI-298 composition: 75:25 mixture of 1,3,4-APB and 3,4'-ODA with s-BPDA and endcapped with PEPA.
4. Data from references 35 and 36.

4 Conclusion

New PETI 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 (oligomer P10) displayed excellent processability by RTM and provided flat laminates with no voids and free of microcracks that exhibited good mechanical properties at RT with good retention of properties at 288°C. Further development of this composition, designated as PETI-330, is underway.

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