HIGH TEMPERATURE TRANSFER MOLDING RESINS: PRELIMINARY COMPOSITE PROPERTIES OF PETI-375

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ABSTRACT

As part of an ongoing effort to develop materials for resin transfer molding (RTM) of high performance/high temperature composites, a new phenylethynyl containing imide designated as PETI-375 has been under evaluation. PETI-375 was prepared using 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), 1,3-bis(4-aminophenoxy)benzene and 2,2'-bis(trifluoromethyl)benzidine and endcapped with 4-phenylethynylphthalic anhydride. This material exhibited a stable melt viscosity of 0.1-0.4 Pa·sec at 280°C. High quality, void-free laminates were fabricated by high temperature RTM using unsized T-650 carbon fabric and evaluated. After curing for 1 hour at 371°C, the laminates exhibited a glass transition temperature of ~375°C by thermomechanical analysis. The laminates were essentially void and microcrack free as evidenced by optical microscopic examination. The chemistry, physical, and composite properties of PETI-375 will be discussed.

KEY WORDS: Resin Transfer Molding, High Temperature Polymers, Phenylethynyl Terminated Imides, 2,3,3',4'-Biphenyltetracarboxylic Dianhydride

1. INTRODUCTION

Development of resins that could be processed into composites by resin transfer molding (RTM) or resin infusion (RI) techniques and have thermooxidative stability superior to bismaleimides (BMIs) began in the late 1990's [1-3]. This work was conducted under NASA's High Speed Civil Transport (HSCT) Program where the requirement for structural composites was high retention of mechanical properties after 60,000 hours at 177°C. Resin transfer moldable oligomeric imides containing phenylethynyl groups were developed. These materials exhibited cured glass transition temperatures (Tgs) in the 230-250°C range and an acceptable combination of processability (e.g. low and stable melt viscosity), thermal and mechanical performance, cost, and low toxicity. However, when the HSCT program ended in 1999, there were no applications that required long term performance at 177°C. Since these materials offered no advantage and were not cost competitive with BMIs or epoxies for shorter-term applications at 177°C, the goal of the work shifted towards increasing the use temperature.

The approach to increase the use temperature involved advancing the cured Tg without detracting from processing characteristics or mechanical properties (e.g. toughness). More specifically, research has focused on high temperature transfer molding resins with potential use temperatures above 288°C [4-12]. These materials have potential applications in and around hot areas on advanced aerospace vehicles and engines. The chemistry has focused on phenylethynyl terminated imide (PETI) oligomers with low and stable melt viscosities (e.g. 0.1-0.3 Pa·sec at ≤280°C), that cure without volatile evolution and yield cured resins with acceptable toughness (e.g. microcrack resistance) and high Tgs (e.g. ≥300°C). PETI-298, a high temperature transfer moldable oligomer prepared from 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB), 3,4'-oxydianiline (3,4'-ODA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and 4-phenylethynylphthalic anhydride (PEPA), was the first material reported to exhibit acceptable processing characteristics, a cured Tg near 300°C and good toughness. This material has been evaluated in composites fabricated by RTM [5,6] and vacuum assisted RTM (VARTM) [6]. Composites fabricated from PETI-298 have exhibited high mechanical properties up to 288°C with good retention of composite properties after aging for 1000 hrs at 288°C in flowing air [5,6]. PETI-298/nanosilicate carbon fiber reinforced laminates have been fabricated and characterized [13]. PETI-298 has been used to fabricate composite components that are part of an integrated composite tank design for a reusable launch vehicle [14].

More recently, the work has focused on further increasing the use temperature of the composites to >300°C by increasing the cured Tg, without sacrificing processability or toughness. This empirical approach has involved combining two or more diamines with a dianhydride at a high stoichiometric offset and endcapping with PEPA [15]. Due to the high stoichiometric offset and use of anhydride endcapping agent, the diamines are in large excess and therefore have a significant impact on cured Tg, toughness and processability of the imide oligomer. Thus, the

combination of appropriate quantities of a flexible diamine and a more rigid diamine with a rigid dianhydride and endcapping with PEPA has resulted in the development of a number of potentially useful PETI resins [8]. The use of a unique dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) has provided an increase in the cured Tg to 330°C without sacrificing processability or toughness in the cured resin. Over the past 15 years, polyimides from a-BPDA were shown to have lower melt viscosities and higher Tgs than the corresponding polymers from s-BPDA [16-21]. The lower melt viscosity is presumably due to the highly irregular structure of the polyimide emanating from a-BPDA. In the structure/property relationship of polyimides, it is highly unusual for a monomer to provide both an increase in Tg and a decrease in melt viscosity. Work with PETI oligomers using a-BPDA resulted in the development of PETI-330. PETI-330 is prepared from 1,3,4-APB, 1,3-phenylenediamine (1,3-PDA), a-BPDA and PEPA. The excellent properties of PETI-330/carbon fiber fabric composites fabricated by RTM have been reported [7-12]. Due primarily to the attributes of a-BPDA, PETI-330 offers improved processability and higher temperature performance than PETI-298. The focus of this paper is the further advancement of this technology through the development of an even higher cured Tg PETI resin that is processable by RTM. The chemistry, physical and composite properties of PETI-375 are discussed herein.

2. EXPERIMENTAL

2.1 Starting Materials The following chemicals were obtained from the indicated sources and used without further purification: 1,3,4-APB (Chriskev Co., m.p. 115°C), 2,2'-bis(trifluoromethyl)benzidine (TFMBZ, Chriskev Co., m.p. 182°C), PEPA (Imitec, Inc. or Daychem Laboratories, Inc., m.p. 152°C), a-BPDA (Ube Industries Inc., m.p. 197°C) and N-methyl-2-pyrrolidinone (NMP, Fluka Chemical Co.).

2.2 Synthesis of PETI-375 PETI-375 was prepared at a calculated number average molecular weight ($\overline{M}_n$) of 750 g/mol by the reaction of the appropriate quantities of 1,3,4-APB (50 mole%) and TFMBZ (50 mole%) with a-BPDA and PEPA. Into a 4 L reaction kettle equipped with a mechanical stirrer, thermometer, nitrogen gas inlet, moisture trap and reflux condenser were placed 1,3,4-APB (292g, 1.0 mole), TFMBZ (320g, 1.0 mole) and NMP (450g). The TFMBZ did not readily dissolve and the flask was warmed to dissolve the material. A slurry of a-BPDA (267g, 0.906 mole) and PEPA (543g, 2.19 moles) in NMP (1200g) was added to the diamine solution. The residual solid was rinsed in with additional NMP (350g) to give a final solids content of 40%. The mixture was warmed to ~60°C with a heating mantel to give a dark brown solution. Toluene (250 mL) was subsequently added and the reaction heated to reflux (~175°C) overnight under nitrogen. The toluene was removed from the solution via the moisture trap and the solution was allowed to cool to ~60°C. The solution was poured into water in a high speed blender to precipitate the imide oligomer. The solid was collected, washed three times in

water and air dried overnight. The solid was subsequently heated to 125°C in a forced air oven for 24 hrs to give 1300g of imide powder.

2.3 Composite Specimens Quasi-isotropic 8-ply panels were fabricated by infiltrating T650-35 8 harness satin (HS) carbon fiber fabric on an Invar tool with PETI-375 using a high temperature injector. The sizing on the carbon fiber was removed by a 0.5 to 1 hour hold at 288°C under vacuum prior to injection. The injector designed and built by Radius Engineering according to Lockheed Martin specifications, operates at a maximum 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 288°C, and held at 288°C for 0.5 to 1 hrs prior to resin injection. PETI-375 was degassed in the injector by heating to 288°C and holding for 1 hr prior to injection. The degassing step is generally required in RTM primarily to remove moisture, residual solvent, and air from the resin. The molten resin was used to infiltrate 8-ply stacks of un-sized T650-35 8HS fabric with $[+45/0/90/-45]_s$ orientation in an Invar tool. The tool was clamped in the press in order to assure adequate sealing. After the resin was injected at 288°C at a rate of 200 cc/min, the part was held at a minimum of 1.34 MPa of hydrostatic pressure and heated to 371°C and held at 371°C for 1 hr + 10 min. The 33 cm x 36 cm laminates were cooled in the mold. 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. Open hole compression (OHC) properties (Northrup Grumman Test [22]) were determined on specimens 22.9 cm by 3.81 cm with a 0.64 cm hole in the center. Short beam shear (SBS) strength (ASTM D2344-84) was determined on specimens 0.64 cm by 1.91 cm. Five specimens were tested under each condition.

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 ΔH versus temperature curve. The cured Tg was determined by heating the sample to 371°C in an open aluminum pan and holding for 1 hr. The sample was cooled and subsequently re-heated to record the Tg. Thermogravimetric analysis (TGA) was performed on uncured imide powder in air at a heating rate of 2.5 °C/min and a flow rate of 50 mL/min. The samples were heated to 100°C at 20°C/min, held for 0.5 hr and subsequently heated to 600°C at 2.5°C/min. Rheological measurements were conducted on a Rheometrics System 4 rheometer at a heating rate of 4°C/min. Specimen discs (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. Dynamic mechanical thermal analysis (DMTA) was conducted on a SEIKO DMS equipped with a solids fixture for measuring rectangular specimens. An oscillatory deformation of ~1% strain, a frequency of 20 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.

3. RESULTS AND DISCUSSION

3.1 Synthesis of PETI-375 PETI compositions such as PETI-298 and PETI-330 exhibited cured Tgs of 298 and 330°C, respectively, excellent processability, good toughness and good retention of room temperature composite properties after aging for 1000 hours at 288°C in air [5-12]. Several approaches undertaken to increase the cured Tg while maintaining processability and toughness have not been successful. For example, increasing the rigidity of the oligomer to significantly increase the cured Tg resulted in loss of processability. Likewise, increasing cross-link density resulted in loss of toughness. The work described herein was focused on the development and evaluation of PETI resins which exhibit cured Tgs ≥350°C while maintaining the processing characteristics of PETI-298 and PETI-330. The approach involved using diamines that were more rigid than 1,3-PDA (used in PETI-330). After synthesizing and characterizing a number of different PETI oligomers [8], PETI-375 was selected for scale-up and evaluation in composites.

PETI-375 was prepared via the classic amide acid route at a calculated $\overline{M}_n$ of 750 g/mol. By this approach, the diamines (1,3,4-APB and TFMBZ) were initially dissolved in NMP with subsequent addition of the dianhydride (a-BPDA) and PEPA as a slurry in NMP (Fig. 1). The mixture was stirred at ambient conditions for several hrs. Subsequent conversion of the phenylethynyl terminated amide acid oligomer to that of the corresponding imide oligomer was accomplished by azeotropic distillation in the presence of toluene. The PETI-375 oligomer remained in solution during cyclodehydration and upon cooling to ~60°C. The powder was isolated by pouring the NMP solution into water to precipitate the oligomer followed by washing in water and drying. The imide powder exhibited a Tg of 350°C by DSC after curing for 1 hr at 371°C in an open aluminum pan in static air. The oligomeric powder exhibited less than 1% weight loss by TGA at 350°C. This synthesis is analogous to that of PETI-298 and PETI-330 both of which have been scaled-up to a multi kilogram batch sizes [23].

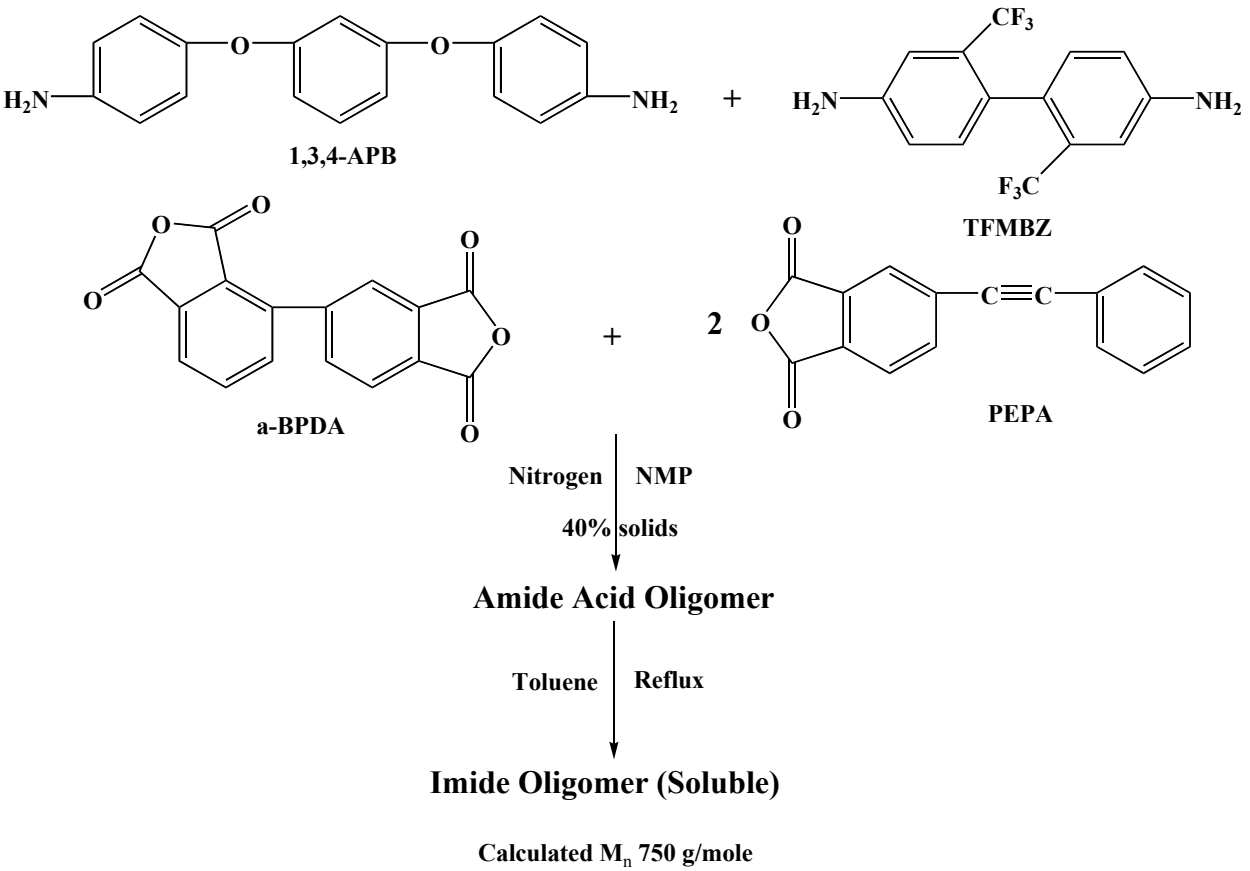

Figure 1: Synthesis of PETI-375

3.2 Rheology Dynamic rheological properties, G' (t) and G" (t), were measured using PETI-375 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 in air. The results, tabulated in Table 1, are complex melt viscosities (η^*) initially and after 2 hrs at 280°C. The melt viscosities of PETI-298 and

Table 1. Melt Viscosities (η^*) of PETI Oligomers

Oligomer	Diamine Composition (%)	BPDA	η^* @ 280°C, initial, Pa·sec	η^* @ 280°C, after 2 hr, Pa·sec
PETI-298	1,3,4-APB (75), 3,4'-ODA (25)	s	0.6	1.4
PETI-330	1,3,4-APB (50), 1,3-PDA (50)	a	0.06	0.9
PETI-375	1,3,4-APB (50), TFMBZ (50)	a	0.1	0.4

PETI-330 were included for comparison. All oligomers were prepared at the same calculated $\overline{M}n$ (750 g/mole) so the crosslink density should be comparable. It is significant to note that the melt viscosity of both PETI-330 and PETI-375 are lower than that of PETI-298, but the cured Tgs are significantly higher. This is primarily due to the contribution of a-BPDA since it is known to provide imides with lower melt viscosities and higher Tgs as compared to similar materials based on s-BPDA. In addition, because of the unique properties of a-BPDA, more rigid diamines such as 1,3-PDA or TMFBZ can be used to increase the overall rigidity of the oligomer and consequently the cured Tg and still exhibit a low melt viscosity. In our previous work, all of the a-BPDA based PETI oligomers exhibited lower melt viscosities compared to the s-BPDA analogues [7,8]. It is also important to note that all of the PETI oligomers have exhibited excellent melt stability at 280°C because at this temperature the phenylethynyl groups have low reactivity. Thus, the melt viscosities of these materials are stable for >2 hrs at this temperature.

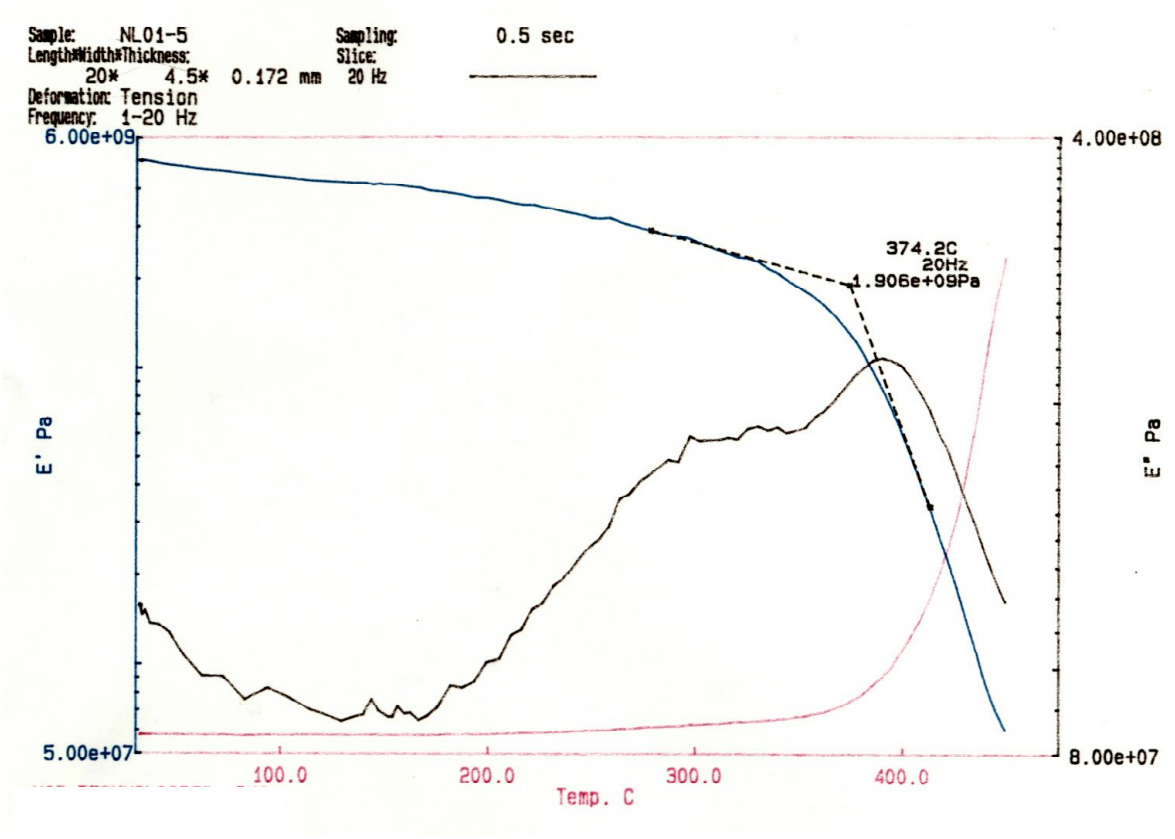

Figure 2. DMTA of neat resin sample of PETI-375

DMTA was conducted on cured composite specimens using a SEIKO DMS equipped with a solids fixture for measuring rectangular specimens. An oscillatory deformation of ~1% strain, a frequency of 20 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. Neat resin samples obtained from inside the mold during composite fabrication exhibited a Tg of ~375°C by this technique (Figure 2.). This is somewhat higher than the cured Tg of 350°C determined by curing the PETI-375 sample in a DSC cell. However, the DMTA was performed at 20 Hz, this typically gives a higher Tg than when performed at 1 Hz (1 Hz is more comparable to DSC). Other possible explanations for this difference are that the two techniques use different methods of detecting the Tg and that the resins were thermally cured under different conditions.

3.3 Composites PETI-375 T650-35 8HS fabric laminates were prepared by initially loading the dry powder into the injector and heating to 280°C under vacuum to degas the resin. The mold was placed in a platen press, heated to ~288°C and the resin injected under ~1.34 MPa hydrostatic pressure. The mold was then heated to 371°C for 1 hr, subsequently cooled to ~100°C and the pressure released. The laminates were ultrasonically scanned, machined into specimens and tested according to ASTM procedures. In general, PETI-375 exhibited excellent processability and provided laminates of excellent quality as evidenced by the C-scans and microscopic analysis. The laminates exhibited fiber volumes of 57-59% and void contents less than 0.75% as determined by acid digestion. Properties were determined at room temperature, 232, 288 and 316°C for PETI-375/un-sized T650-35 8HS laminates fabricated by RTM and are presented in Table 2. For comparative purposes, the properties of PETI-330/T650-35 8HS laminates fabricated by RTM are included [12]. The PETI-330 laminates had an average fiber volume of ~58% and a void content of ~1%. The data is not normalized for fiber volume. The PETI-375 laminates exhibited relatively high room temperature properties with greater than 50% retention of room temperature properties when tested at 316°C. The as-processed laminates showed no microcracking as evidenced by microscopic examination.

Table 2. PETI/un-sized T650 8HS Laminate Properties

Property	Test Temp., °C	PETI-375	PETI-330
OHC Strength, MPa	23	297	270
	288	235	200
	316	160	----
OHC Modulus, GPa	23	46	47
	288	45	44
	316	42	----
SBS Strength, MPa	23	52	56
	232	40	43
	288	32	35
	316	29	----

4. SUMMARY

PETI-375/un-sized T650-35 8HS laminates were fabricated by RTM using a high temperature injector. The laminates exhibited excellent quality with void contents less than 0.75%. The composites exhibited high mechanical properties at room temperature with good retention of properties up to 316°C. The preliminary laminate properties of PETI-375 compared well with those of PETI-330, a leading candidate for a number of aerospace applications requiring an unprecedented combination of processing characteristics and high temperature performance.

5. ACKNOWLEDGMENT

The authors would like to acknowledge the Clark Atlanta University facilities at the High Performance Polymer and Composite Center (HiPPAC), Professors Eric A. Mintz, David R. Veazie and Mr. Brian Shonkwiler for the mechanical testing and Dr. Michael Meador of NASA Glenn Research Center for partial financial support of this work. Dr. Rikio Yokota of the

Institute of Space and Astronautical Sciences for helpful technical discussions and Dr. Ryoichi Sato of Ube Industries for supplying the a-BPDA.

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