

# **High Temperature RTM and VARTM of Phenylethynyl Terminated Imide Composites Based on 2,3,3',4'-Biphenyltetracarboxylic Dianhydride**

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## **Abstract**

Resin transfer molding (RTM) and vacuum assisted resin transfer molding (VARTM) are processes of fabricating composite structures that can be less costly than those fabricated from conventional hand lay-up, autoclave techniques. However, until recently, RTM and VARTM had not been accomplished with high temperature resins because no resins were available having low melt viscosity and long melt stability. With the recent development of RTM and VARTM capable phenylethynyl terminated imide resins (PETIs) and the development of high temperature (371°C) RTM and VARTM techniques, RTM and VARTM of high temperature PETIs composites have now been accomplished. These processes allow for the affordable fabrication of composites having glass transition temperatures ( $T_g$ )  $\geq 300^\circ\text{C}$  and represent the first time that high temperature resins have been successfully fabricated into composites using these techniques. Laminates fabricated from these materials have exhibited high mechanical properties and excellent retention of these properties, such as open hole compressive strength, after aging 1000 hours in air at  $288^\circ\text{C}$ . These resins and fabrication techniques represent a major advancement in materials technology by combining unprecedented processing characteristics, high temperature performance and moderate toughness into one family of matrix resins.

## **Introduction**

New designs for aerospace vehicles clearly show the need for advanced high temperature polymeric composite structures due to their high specific strength and stiffness. The major factor that has limited the growth of composites on high performance aircraft and space vehicles is manufacturing cost and not performance. Improved processing technologies have effectively reduced the cost of fabricating polymeric composites [1-3]. For example, braiding of circumferential frames in conjunction with transfer molding of epoxy composites has been demonstrated to be a lower cost process than that used for the current aluminum circumferential frames [3]. However, only small advances have been made to address the high cost of fabricating high temperature polymeric composites. This is primarily because high temperature resins that lend themselves to resin infusion were not available until recently. The extensive amount of research in the area of PETI technology [4-31] has produced high temperature resins that are capable of being processed via conventional autoclave methods and more recently, resin infusion [25-32].

In a cooperative effort between the NASA Langley and Glenn Research Centers (LaRC and GRC, respectively), Lockheed Martin Aeronautics Company (LM Aero), Clark-Atlanta University, and M&P Technologies, the first significant breakthroughs in the cost-effective manufacture of high temperature polyimide composites via resin transfer molding (RTM) and Vacuum Assisted Resin Transfer Molding (VARTM) have been accomplished. These efforts began under the NASA High Speed Research (HSR) program where composites fabricated from PETIs using resin transfer molding (RTM) technology were successfully accomplished [25-32]. NASA LaRC and LM Aero are continuing efforts to develop affordable manufacturing methods for PETI composites. In this work, LM Aero has been using RTM and VARTM [32] technology to fabricate newly available formulations of the PETI resins. With cured formulations exhibiting  $T_g \geq 300^\circ\text{C}$ , the PETI systems may have many applications in high performance aircraft, reusable launch vehicles, and jet engine components.

## **Results and Discussion**

PETI oligomers were prepared at a calculated number average molecular weight ( $\bar{M}_n$ ) of 750 g/mol by the reaction of the appropriate quantity of aromatic dianhydride(s)

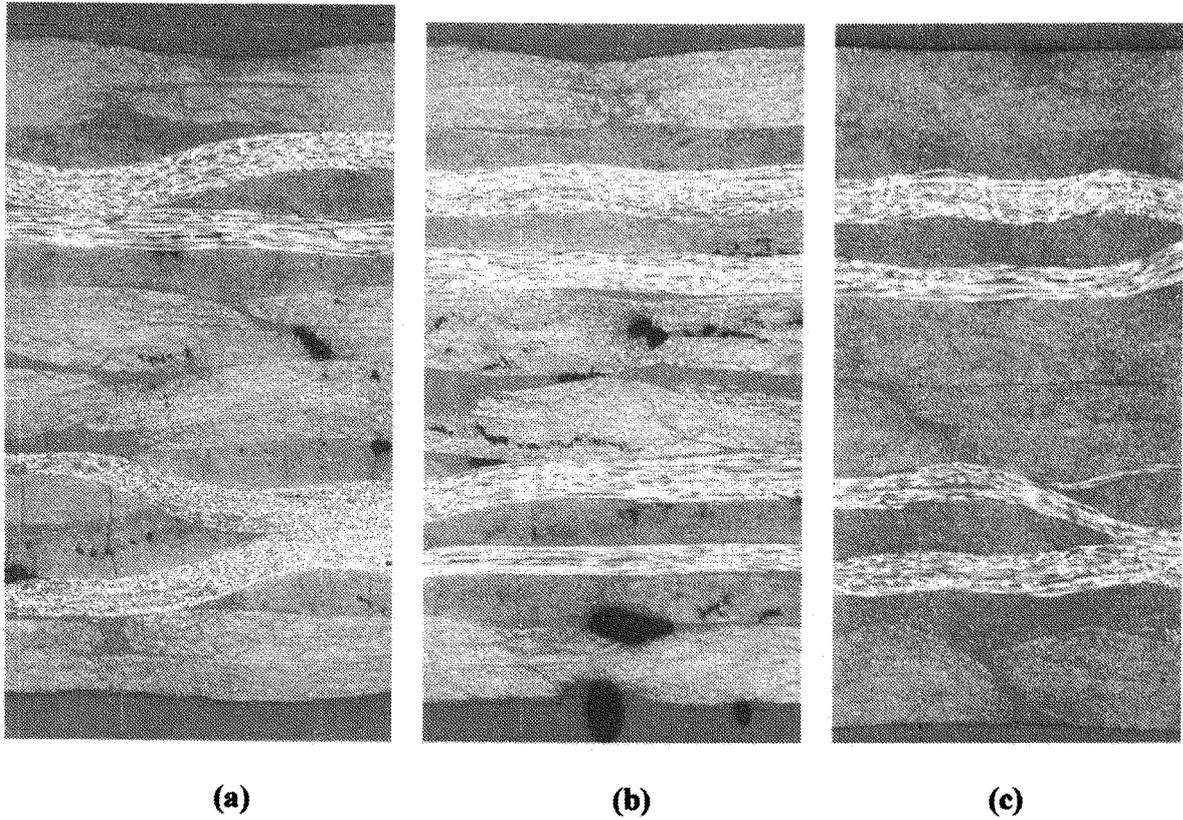
with the appropriate quantity of aromatic diamines and endcapped with 4-phenylethynyl phthalic anhydride (PEPA). The oligomers were prepared by initially dissolving the aromatic diamine(s) in NMP at room temperature under nitrogen. The appropriate quantities of dianhydride(s) and endcapper (PEPA) were 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 oligomers were 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%.

PETI oligomers were 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. For RTM, a high temperature injector was used to initially degass the molten PETI oligomers at 280°C for 1 hour. The molten resins were subsequently injected into the mold at 280°C. Flat laminates were fabricated in a press under ~1.4 MPa hydrostatic pressure during the entire process cycle. The VARTM trials were conducted using a stainless steel tool. Both 6781 glass and 8HS carbon fiber preforms were investigated. The release plys, fabric, and flow medium were laid up on the tool and bagged using Kapton™ and high temperature bagging sealant. An outer bag was then placed over the inner bag. The tool was then preheated to 288°C with both bags under vacuum. The resin was simultaneously heated under vacuum from room temperature to 288°C and allowed to melt and degas. The resin was then transferred to a preheated glass beaker and heated again to 288°C. The inlet valve was then opened and the resin was allowed to infuse within the fabric. Once fully wet-out, the inlet valve was closed and the laminate was heated to 371°C and allowed to cure for 1 hour. The final cure for all laminates fabricated by RTM and VARTM consisted of a 371°C hold for 1 hr. The laminates were cooled under pressure to ~100°C and the pressure subsequently released. The composite panels were ultrasonically scanned (C-scanned), cut into specimens, examined via SEM for microcracks, and tested for mechanical properties according to ASTM procedures.

The objective of this work was to develop and evaluate PETI resins which exhibited cured Tgs  $\geq 300^{\circ}\text{C}$  while maintaining processability by low melt viscosity processes. Previously reported PETI compositions have been based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and diamines containing ether and meta phenylene linkages. One composition designated PETI-298 exhibited a cured Tg of  $\sim 300^{\circ}\text{C}$  and a stable melt viscosity of 0.5 Pa·s at  $280^{\circ}\text{C}$  (29). This material was prepared from 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB), 3,4'-oxydianiline (3,4'-ODA), s-BPDA, and endcapped with PEPA. Flat laminates fabricated by RTM and VARTM of this resin exhibited good mechanical properties, no microcracking, and low void content. Table 1 summarizes the results of panel analyses of PETI-298/AS4 fabric composites fabricated by VARTM. Photomicrographs depicting the best and worst areas of panel #5 are shown in Figure 1. For comparison purposes the photomicrograph of a PETI-298/AS4 fabric panel fabricated by RTM is also shown. The open hole compressive (OHC) properties are compared for the PETI-298/AS4 panels fabricated by RTM and VARTM in Figure 2. The results indicated only a minor difference in strength with the panels fabricated by VARTM exhibiting lower strength. This is probably due to the higher void content in the panels fabricated by VARTM. The compressive moduli were the same.

**Table 1. Summary of resin burn-off and acid digestion results**

Panel	Lay-up / Fiber	Density (g/cc)	Resin Wt. (%)	Fiber Volume (%)	Resin Vol. (%)	Voids (%)
2	[0/90] <sub>2s</sub> /6781	1.7 ± 0.0	41.4 ± 0.2	38.5 ± 0.5	52.6 ± 0.2	8.9 ± 0.7
3	[0/90] <sub>2s</sub> /AS4	1.4 ± 0.0	40.1 ± 0.2	47.9 ± 0.2	43.7 ± 0.2	8.4 ± 0.0
4	Quasi-isotropic/AS4	1.5 ± 0.0	37.1 ± 0.1	51.7 ± 0.4	41.6 ± 0.1	6.6 ± 0.5
5	Quasi-isotropic/AS4	1.5 ± 0.0	37.3 ± 0.2	52.9 ± 0.2	43.0 ± 0.5	4.1 ± 0.7



**Figure 1. Photomicrographs of PETI-298/AS4 panel #5 at 50x showing (a) best and (b) worst areas as determined via C-scan and (c) RTM laminate for comparison.**

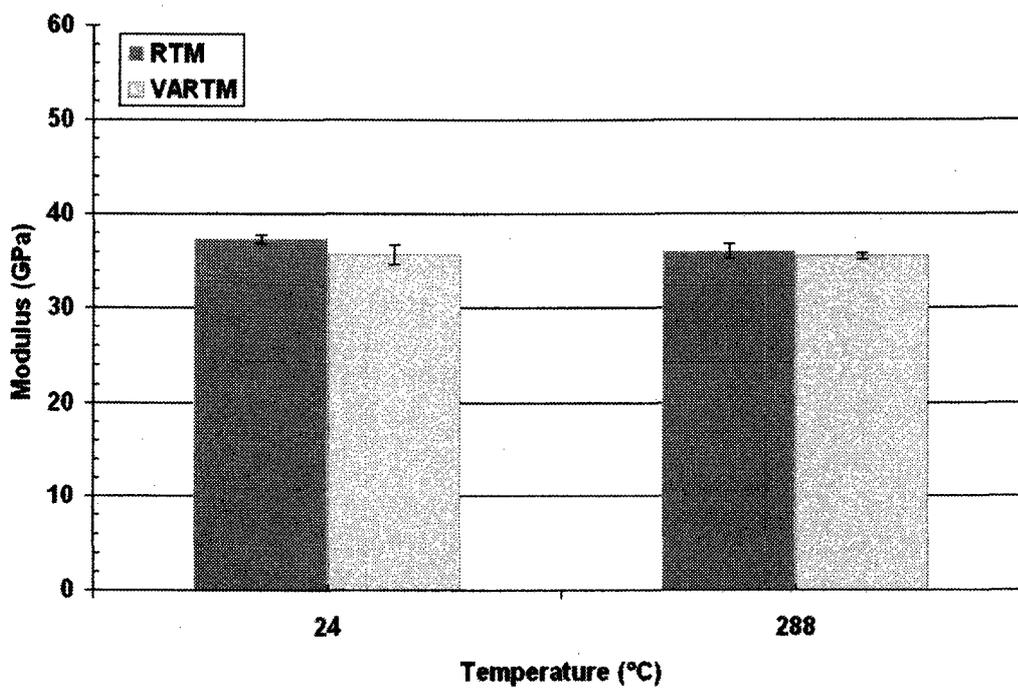
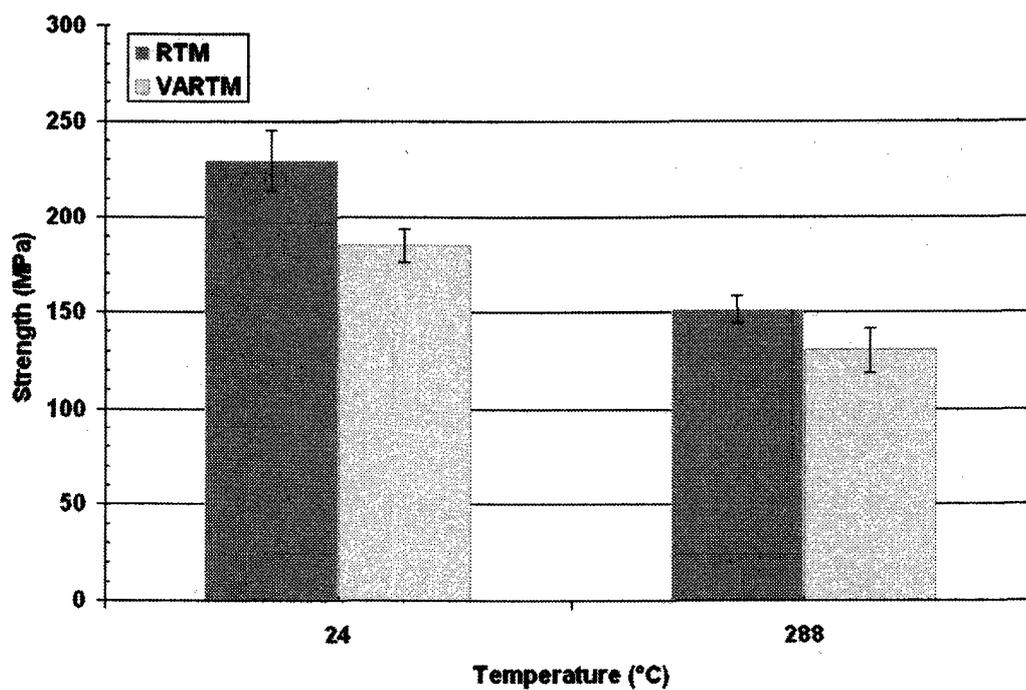
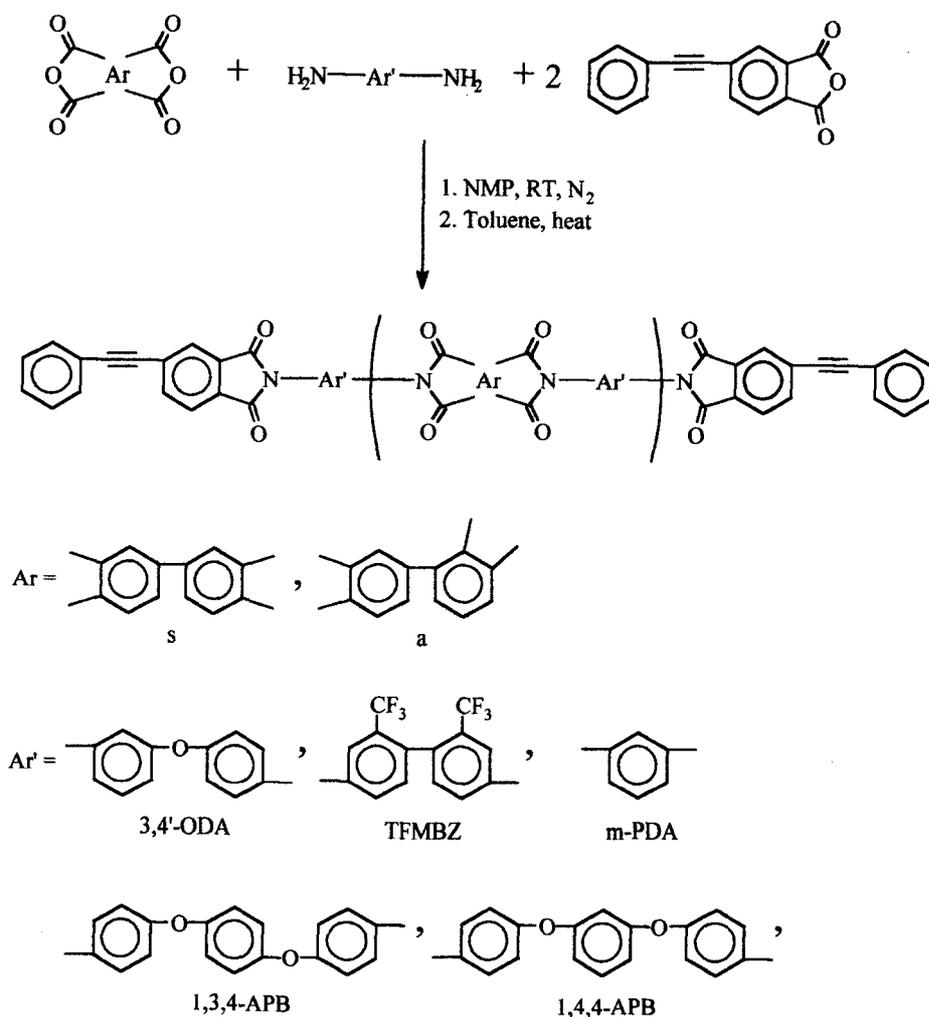


Figure 2. OHC Properties of PETI-298/AS4 RTM and VARTM panels (normalized to 54% FV).

In a recent report an isomer of s-BPDA, 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) provided a PETI based resin with a higher cured T<sub>g</sub> and lower melt viscosity than PETI-5 prepared at a comparable calculated  $\bar{M}_n$ . This composition, however, used a more rigid diamine (4,4'-oxydianiline) [33] than PETI-5 (3,4'-ODA and 1,3,3-APB). The lower melt viscosity 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 results, new compositions of PETI resins amenable to processing by low viscosity techniques were prepared and evaluated based on a-BPDA.

PETI oligomer characterization is presented in Table 2 with PETI-298 included for comparison. The initial T<sub>g</sub>s of the oligomers ranged from ~125-170°C and increased ~160°C upon curing in a DSC pan for 1 hr at 371°C. Several compositions exhibited endotherms [melt transitions (T<sub>m</sub>s)] by DSC. This suggests that some transient



crystallinity was present due to the thermal history of the material. Upon curing at 371°C, no Tms were evident by DSC with cured Tgs  $\geq 300^\circ\text{C}$  being obtained. Compositions P1 and PETI-298 differ only by the 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  $\sim 25^\circ\text{C}$  increase in the cured resin Tg. The Tg of the cured polymer was likewise found to increase  $\sim 20^\circ\text{C}$  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 2. PETI Oligomer Characterization**

Oligomer	Diamine Composition (%)	BPDA	Initial Tg (Tm), °C <sup>1</sup>	Cured Tg, °C <sup>2</sup>
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 <sup>3</sup>	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.

The melt viscosities of the various oligomers are presented in Table 3. In general, the oligomers prepared using a-BPDA exhibited lower melt viscosities than those analogues prepared using s-BPDA. Several compositions gave a good

**Table 3. Melt Viscosities ( $\eta^*$ ) of PETI Oligomers at 280°C**

Oligomer	Diamine Composition (%)	BPDA	$\eta^*$ @ 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

**Table 4. PETI-330/AS4 Laminate Properties (RTM)**

Property	Test Temp., °C	PETI-330 57% Fiber Volume
Un-notched Comp. Str., MPa	23	442
Open Hole Compression Str., MPa	23	250
	288	218
Open Hole Compression Mod., GPa	23	42
	288	40
Short Beam Shear, Str., MPa	23	38
	232	37
	288	34

combination of a high cured  $T_g$  (>325°C), low melt viscosity and based on a qualitative comparison of neat resin plagues, acceptable toughness. One oligomer (P7),

designated as PETI-330 was scaled-up and used to fabricate composites by RTM. Preliminary data is presented in Table 4. The room temperature and elevated temperature composite properties exhibited by PETI-330/AS4 laminates fabricated by RTM were excellent. Due to the low melt viscosity of this resin, it is anticipated that laminate fabrication by VARTM will be readily achievable.

### Summary

A series of resins suitable for composite fabrication by RTM and VARTM based on a-BPDA were prepared and characterized. One resin, PETI-330 exhibited an attractive combination of high cured T<sub>g</sub>, low and stable melt viscosity and good toughness. PETI-330 was scaled-up and used to fabricate composites by RTM. The composite laminates exhibited excellent room temperature mechanical properties and excellent retention of these properties at elevated temperature (288°C).

The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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