PROCESSING AND CHARACTERIZATION OF PETI COMPOSITES FABRICATED BY HIGH TEMPERATURE VARTM[§]

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ABSTRACT
The use of composites as primary structures on aerospace vehicles has increased dramatically over the past decade, but so have the production costs associated with their fabrication. For certain composites, high temperature vacuum assisted resin transfer molding (HT-VARTM) can offer reduced fabrication costs compared to conventional autoclave techniques. The process has been successfully used with phenylethynyl terminated imide (PETI) resins developed by NASA Langley Research Center (LaRC). In the current study, three PETI resins have been used to make test specimens using HT-VARTM. Based on previous work at NASA LaRC, larger panels with a quasi-isotropic lay-up were fabricated. The resultant composite specimens exhibited void contents of ~ 3% by volume depending on the type of carbon fabric preform used. Mechanical properties of the panels were determined at both room and elevated temperatures. Fabric permeability characterizations and limited process modeling efforts were carried out to determine infusion times and composite panel size limitations. In addition, new PETI based resins were synthesized specifically for HT-VARTM.

1. INTRODUCTION
Polyimide composites are very attractive for applications requiring a high strength to weight ratio and performance at use temperatures above 177 °C. Recent work at NASA LaRC has concentrated on developing new polyimide resin systems that can be processed out of the autoclave for advanced aerospace applications. Using controlled molecular weight imide oligomers containing phenylethynyl endcaps, PETI resins are readily processed into neat resin moldings, bonded panels and composites using resin transfer molding (RTM) and resin infusion (RI) processing. Commercially available resins include LaRC™ PETI-330 (T_g ~ 330 °C and calculated number average molecular weight (M_n) ~1290 g/mole) and LaRC™ PETI-8 (T_g ~ 300 °C and

M_n ~1125 g/mole). PETI-330 laminates exhibit good mechanical properties up to 288 °C [1,2] and have retained approximately 98% of room temperature open hole compression (OHC) strength after aging 500 h at 288 °C [3]. PETI-8 produces good tensile and flatwise tensile strengths when processed under vacuum bag pressure only [4] and mechanical properties including short beam shear (SBS) strength, flexural strength and modulus have been evaluated at various temperatures [5].

VARTM was developed as a variation of RTM over twenty years ago and has shown potential to reduce manufacturing costs. The Controlled Atmospheric Resin Infusion Process (CAPRI) patented by The Boeing Company [6] is a variation of the Seemans Composite Resin Infusion Molding Process (SCRIMP) [7]. The CAPRI VARTM process has been extended to the fabrication of composite panels from various LaRC polyimides by employing HT-VARTM. Although these resins exhibit the necessary melt flow characteristics for HT-VARTM processing, the resulting laminates had void contents greater than 7% by volume [8,9]. By adjusting the processing cycle the void content was reduced to <3%, while still achieving sufficient fiber volume (>58%) [10,11].

This paper focuses on the HT-VARTM processing trials using a quasi isotropic lay-up. Limited computational work, based on experimental inputs, was performed to help establish initial processing parameters. This enabled a better understanding of the process requirements that lead to the subsequent generation of larger composite panels. Work is being carried out to generate a more extensive database of mechanical properties that include SBS and OHC. Research is also underway to synthesize new imide based resins designed specifically for HT-VARTM.

2. EXPERIMENTAL
2.1 Materials
PETI-8 was purchased from Imitec, Inc., Schenectady, NY, USA and PETI-330 from Ube Chemicals Ltd, Japan. The third resin, a new material designated PETI-9, was synthesized specifically for HT-VARTM and purchased from Imitec, Inc. The following chemicals were obtained from the indicated sources and used without further purification: 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB, Mitsui Toatsu), 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB, Chriskev), 1,3-diaminobenzene (m-PD, Sigma-Aldrich), 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA, Ube Industries Inc.), 4-phenylethynylphthalic anhydride (PEPA, Imitec, Inc.) and N-methyl-2-pyrrolidinone (NMP, Fluka Chemical Co.). Three types of carbon fiber fabrics (C-fabric) were used for this work: IM7-6K 5-harness satin woven fabric (GP sizing, 280 gsm), T650-35-3K 8-harness satin woven fabric (309 sizing, 366 gsm), and IM7-6K unidirectionally woven fabric (GP sizing, 160 gsm, Sticky String 450 1/0 fill fiber). All fabrics were obtained from Textile Products, Inc., Anaheim, CA, USA.

2.2 New Resin Synthesis
A new PETI resin, based on a modification to the currently used PETI-8, was synthesized. The resin, designated as PETI-9, is a phenylethynyl endcapped aromatic polyimide (M_n ~1125 g/mole) based on 3,3',4,4'-biphenyltetracarboxylic dianhydride and a 25:75 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy) benzene. In-house work has focused on the synthesis of new PETI resins described in previous work [12]. PETI oligomers were prepared by the reaction of a-BPDA with the appropriate quantity of aromatic diamines and endcapped with PEPA.

2.3 Resin characterization

Differential scanning calorimetry (DSC) was performed to determine the cured T_g using a Setaram DSC 131 at a heating rate of 20 °C/min. Dynamic rheological measurements were obtained using an Advanced Rheometric Expansion System (ARES) Rheometer from Rheometrics, Inc. under nitrogen atmosphere in an oscillatory shear mode using parallel plate geometry (25 mm diameter) at a heating rate of 4 ºC/min from 100 to 371 ºC at a fixed angular frequency of 10 rad/s.

2.4 Simulation/Fabric Characterization

Flow simulation and preform characterization was conducted at the University of Delaware – Center for Composite Materials (UD-CCM). The permeabilities of the three types of C-fabric and the distribution medium (DM) were determined. The in-plane permeability of the fabric was evaluated using standard flow experiments where the fabric layers were placed under the bag and the flow location versus time was recorded via an automated camera system. 1-D Darcy's law was used to calculate the permeability. For the out-of-plane permeability of the fabric and in-plane permeability of the DM, a technique of Gokce et al. [13] was utilized. Here, video of both flow surfaces (DM and tool side) was recorded and the flow data was matched to a finite element simulation. The data reduction provided the effective permeability of the materials, while considering all the process effects, such as nesting of the fabric into the DM and compaction changes. In addition, lead length (the difference between the saturated flow distances on the DM and tool surface) of the non-saturated flow and non-uniform fill through the thickness of the fabric could be observed.

The permeability of the C-fabrics and the DM was also investigated at Michigan State University (MSU). The in-plane and through thickness permeabilities of each carbon fiber preform and the aluminum (Al) distribution medium were measured. The approach that was used initially compacted the sample to a known thickness or fiber volume fraction. A fluid of known viscosity and flow rate was then passed through the sample using either an in-plane or through thickness fixture [14]. The corresponding pressure drop was recorded and the permeability calculated using the 1-D Darcy's Law. The experiments were repeated for different fiber volume fractions between 35 and 60% and a curve of permeability versus fiber volume fraction was constructed. Since the materials are orthotropic, three experiments in three directions were required for each material to complete the characterization. Two samples for each measurement were run. The fluid used in the tests was SAE 40W motor oil.

2.5 High Temperature VARTM

The HT-VARTM set-up utilized in this work has been described in previous work [15]. During the fabrication of 33 cm x 33 cm panels, a quasi isotropic lay-up of 8 fabric plies with [±45/(0/90)**/**±45**/**(0/90)]$_s$ orientation was used for IM7-6K 5HS and the T650-35-3K 8HS C-fiber fabrics. In the case of the uniweave fabric, a quasi isotropic lay-up {[-45/0/45/90]$_{2s}$} of 16 plies was used.

Prior experience demonstrated [10] that the process worked best using a two-oven set-up where a heated tube connected the two ovens to each other. Infusion was carried out at 260 ºC and depending on the type of carbon fabric, the infusion time varied. However, all samples were typically allowed to infuse for up to 2 h or longer after the start of infusion to ensure that the resin had flowed through the thickness of the panel. A staged cure cycle was used for all resins as previously described [11].

2.6 Composite characterization

C-scan inspections of the composite panels utilized a 3 axis (x, y and z) Ultrasonic Scanner from SONIX Advanced Acoustic Solutions. Acid digestion of cured composites was carried out following ASTM D3131. Calculations were based on a 1.77 g/cc fiber density and a 1.31 g/cc resin density [10].

2.7 Composite Mechanical Properties

Mechanical properties of the composites tested were SBS according to ASTM D2344 and OHC according to ASTM D6484. Both SBS and OHC tests were performed at room (RT) and elevated temperatures (ET). For SBS, a Sintech 2W mechanical testing machine with a 4.45 kN load cell and a heating chamber (Thermcraft) was used. The crosshead speed was 0.127 cm/min. For OHC, an Instron test stand with a 88.96 kN load cell was used. The speed of testing was 1.27 cm/min.

3. RESULTS AND DISCUSSION

3.1 Resin properties

The newly synthesized PETI-9 had a T_g of 265 °C, as determined by DSC. During a 4 h hold at the infusion temperature of 260 °C, the complex melt viscosity (η^*) was between 1 and 2 Poise. This value is lower than that of PETI-8 (~5 Poise) and PETI-330 (~20 Poise) and hence the resin offers the capability to manufacture larger and thicker parts.

While it is possible to process PETI-330 by VARTM, there was a desire to further reduce the η^* of the material and expand its processing window. The first method to achieve this was by reduction of the M_n of the material which typically results in improved melt flow. PETI-330 was prepared in-house so as to have a direct comparison between the materials. The calculated M_n was reduced by 25 g/mol increments so as to limit the effect of M_n reduction upon the mechanical properties of the material while decreasing the η^*. The same molar proportion of m-PD to 1,3,4-APB was used in the synthesis as described for PETI-330 while the molar amounts of a-BPDA and PEPA were varied based on the calculated M_n. The η^*s for all these materials were greater than that for PETI-330 presumably due to lesser amounts of a-BPDA at the lower M_ns or the increased M_ns relative to PETI-330. Besides the dependence upon molecular weight, the melt viscosity can also be affected by the molecular weight distribution. For the materials discussed here the molecular weight distributions have not yet been determined, so a definitive assessment cannot be made at this time.

The second method to reduce the η^* was through the incorporation of a flexible diamine, an all meta isomer of 1,3,4-APB (i.e. 1,3,3-APB), at 12.5 mol % increments with a commensurate reduction of 1,3,4-APB to maintain the overall 50 mol % quantity of APB in the PETI material. The calculated M_n for all materials was maintained at ~1290 g/mol. As expected, the cured T_g decreased with an increasing amount of 1,3,3-APB. The expected η^* trend however was not observed regardless of temperature.

3.2 Simulation/Fabric Characterization

The results obtained from UD-CCM's investigation of the permeability of the three types of carbon fabric and the DM are presented in Figure 1. The lead length increased significantly for the uniweave compared to the other fabrics, reflecting the lower out-of-plane permeability of the uniweave system. In addition, race-tracking

along the stitches securing alignment of the uniweave tows allowed for preferential flow paths through the thickness potentially resulting in dry areas. The effective permeability values calculated from the flow experiments are shown on Figure 1(a). The DM permeability is 4-5 orders of magnitude larger than the out-of-plane permeability of the fabric.

UD-CCM used the obtained permeability values in their Liquid Injection Molding Simulation (LIMS) software and ran simulations of the total infusion length and the lead length. Calculations showed that the DM permeability significantly affected both maximum infusion length as well as lead length. Total infusion length increased with an increase in DM permeability while also increasing lead length and potential for dry spot development. The most significant information obtained from the simulation work related the viscosity of the resin and the permeability of the carbon fabric to the thickness of the infused part (Figure 1(b)). As evident from the Figure, the out-of-plane flow time should be significantly shorter than the two hour gel time (or infusion time) to allow larger panel fabrication. Otherwise, the fabric thickness becomes a major limitation during the infusion process for resins with higher viscosities.

The permeability results from MSU for 5 layers of T650-35-3K 8HS are shown in Figure 2. As expected, the through thickness permeability is about two orders of magnitude lower than the in-plane values. The symbols represent the measured permeabilities while the solid line is the best fit to MSU data. The data were fit to a power law mathematical equation for use in the MSU-VARTM simulation model:

$$S = d(V_f)^e \qquad\qquad\qquad (1)$$

where S is the permeability, V_f is the fiber volume fraction, d and e are power law fit constants.

For 10 layers of IM7-uniweave, at low fiber volume fractions, the in-plane permeabilities are similar. However, as the fiber volume fraction increases, the permeability along the fibers, Sxx, becomes much lower than the permeability normal to the fibers, Syy. This is most likely due to the fibers tows nesting and the bundles compacting under higher compaction loads. As expected, the through thickness permeability is about three orders of magnitude significantly lower than the in-plane values. The low transverse permeability is most likely due to the fact that resin flows slowly through the nested and highly compacted tow bundles.

Results from the simulation experiments helped guide infusion of larger 33 cm x 33 cm panels. It was expected that with PETI-8, infusion of larger and thicker panels would not be an issue. However, the viscosity of PETI-330 is almost an order of magnitude higher than that of PETI-8 at the infusion temperature. As evident from Figure 1(b), this would, essentially, limit the thickness of the composite and for larger panels, limit the part size as well.

3.3 HT-VARTM
Based on the simulation data from UD-CCM and MSU, larger panels were processed using HT-VARTM. All three resins, PETI-8, PETI-9 and PETI-330 were used for making these panels following a quasi isotropic lay-up. For the two biaxial fabrics, IM7 and T650, the scale-up did not have any issues. However, with PETI-330 and the IM7-uni fabric, there was incomplete infusion with 16 plies. Hence, for this particular sample, it was decided to infuse only 8 plies. For every cycle, the infusion was carried out 2 to 2½ h. Table 1 discusses the processing conditions as well as void contents

of the HT-VARTM panels. Although the composite area and volume have quadrupled with respect to initial panel sizes, the void contents still averaged just under 3.5%.

3.4 Mechanical properties
The SBS data for the newly developed resin, PETI-9, are shown in Figure 3(a). Since the resin is a variation of PETI-8, the data have been compared to PETI-8 [11] as represented by Figure 3(b). Preliminary data indicate higher SBS strength for PETI-9 composites fabricated with both IM7-5HS and IM7-uni C-fabric. The strength data for the T650 specimens are comparable. SBS strength retention at 177 °C was between 80 and 90% for both resins. The PETI-9 had a lower T_g compared to PETI-8 but the composite specimens had lower voids and better SBS strength.

OHC provides a controlled simulation of a natural defect in a composite structure, and served as a method for testing fastener holes. Figure 4 denotes the OHC strength of the VARTM samples at RT and ET. The OHC strength of PETI-330/T650 made by RTM was reported as 270 MPa at 23 °C [3]. For the VARTM samples, the value measured was lower by 7.5%. The PETI-8/T650 and PETI-9/T650 composites were similar to those of PETI-330, but produced significantly higher OHC strengths when fabricated with IM7 biaxial fabrics. Preliminary data show OHC strength retention at ET between 75 and 90%. Select samples have also been aged at ET (177 °C for PETI-8 and PETI-9 and 288 °C for PETI-330) for 1000 hours and the OHC strength of these aged samples will be determined at RT.

4. SUMMARY
Experimental work was carried out at both UD-CCM and MSU to determine the permeabilities of the different carbon fabrics and simulation work from both universities was used to guide the NASA HT-VARTM experiments. Based on modeling results, large panels were fabricated with void contents slightly higher than previous smaller panels but still averaging just below 3.5%. A new resin, PETI-9, was developed specifically for the HT-VARTM process and the composite panels exhibiting promising results. Work is also ongoing to develop new resins based on PETI-330 that would exhibit lower melt viscosities at the infusion temperature without compromising the T_g.

FIGURES AND TABLES
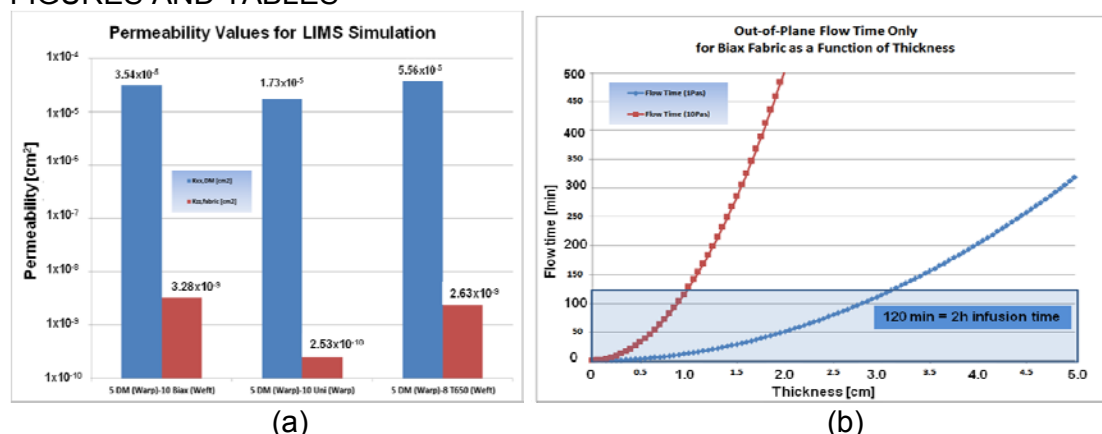

(a)   (b)

Figure 1: Permeability values obtained by UD flow experiments used in the LIMS simulation (a) and effect of fabric thickness on infusion length for two resins with different viscosities(b) (UD simulation)

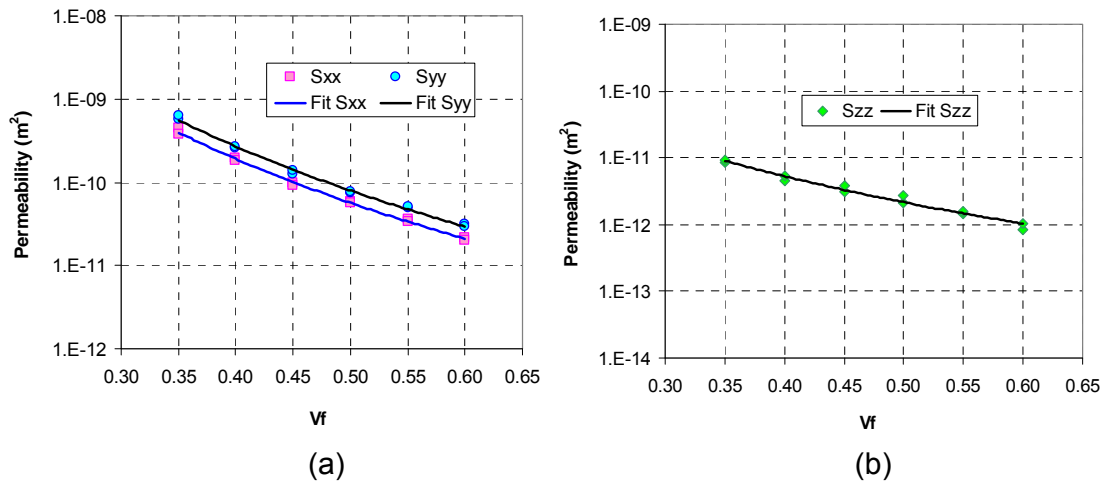(a)   (b)

Figure 2: In-plane (a) and transverse (b) permeability versus fiber volume fraction for 5 layers of T650-35-3K 8-harness satin fabric.

Table 1: Composite characteristics for VARTM of PETI resins for 33 cm x 33 cm panels:

Resin	C-fabric	Void content, %	Fiber volume, %
PETI-8	T650	3.63	63.3
PETI-8	IM7	3.46	57.8
PETI-8	IM7-uni	3.58	57.5
PETI-9	T650	3.63	63.7
PETI-9	IM7	2.68	58.7
PETI-9	IM7-uni	2.91	57.5
PETI-330	T650	3.28	62.7
PETI-330	IM7	2.95	57.5
PETI-330	IM7-uni	1.73	55.7

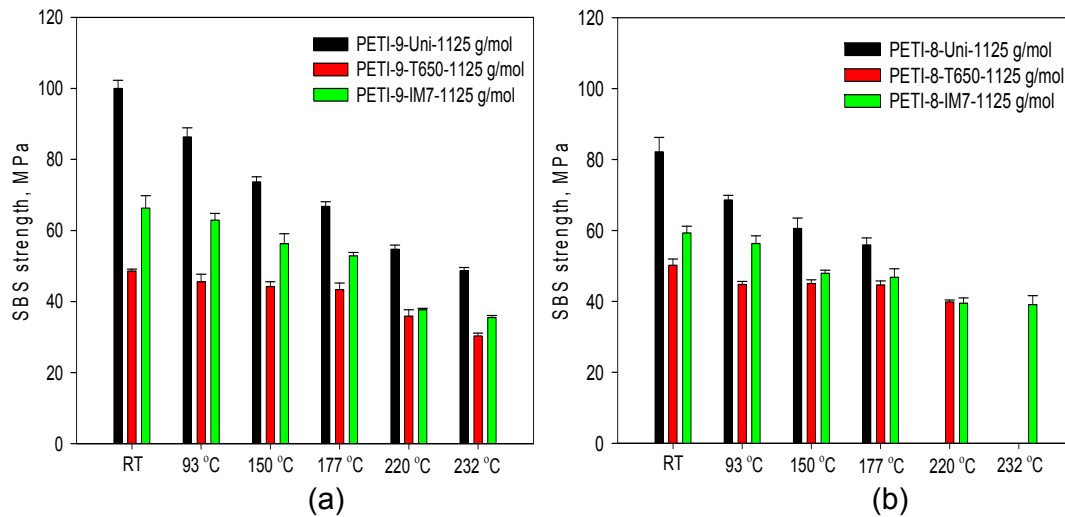(a)   (b)

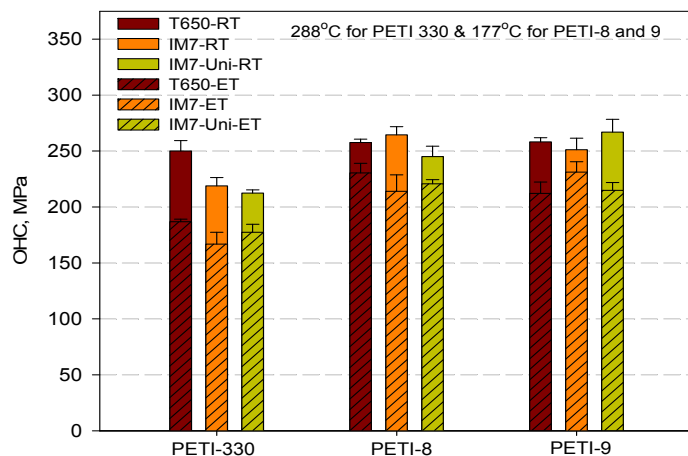Figure 3: SBS strength of PETI-9 (a) and PETI-8 (b) composites.

Figure 4: OHC strengths of PETI/C-fabric panels at RT and elevated temperatures.

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