High Temperature VARTM of Phenylethynyl Terminated Imides

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Abstract

Depending on the part type and quantity, fabrication of composite structures using vacuum assisted resin transfer molding (VARTM) can be more affordable than conventional autoclave techniques. Recent efforts have focused on adapting VARTM for the fabrication of high temperature composites. Due to their low melt viscosity and long melt stability, certain phenylethynyl terminated imides (PETI) can be processed into composites using high temperature VARTM (HT-VARTM). However, one of the disadvantages of the current HT-VARTM resin systems has been the high porosity of the resultant composites. For aerospace applications, the desired void fraction of less than 2% has not yet been achieved. In the current study, two PETI resins, LaRC PETI-330 and LaRC PETI-8 have been used to make test specimens using HT-VARTM. The resins were infused into ten layers of IM7-6K carbon fiber 5-harness satin fabric at 260 ºC or 280 ºC and cured at temperature up to 371 ºC. Initial runs yielded composites with high void content, typically greater than 7% by weight. A thermogravimetric-mass spectroscopic study was conducted to determine the source of volatiles leading to high porosity. It was determined that under the thermal cycle used for laminate fabrication, the phenylethynyl endcap was undergoing degradation leading to volatile evolution. This finding was unexpected as high quality composite laminates have been fabricated under higher pressures using these resin systems. The amount of weight loss experienced during the thermal cycle was only about 1% by weight, but this leads to a significant amount of volatiles in a closed system. By modifying the thermal cycle used in laminate fabrication, the void content was significantly reduced (typically ~ 3% or less). The results of this work are presented herein.

Keywords: phenylethynyl terminated imides, VARTM, voids, acid digestion

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1. Introduction

Due to their excellent physical and mechanical properties, aromatic polyimides are finding use in a variety of aerospace applications. Polyimide composites are very attractive for applications that require a high strength to weight ratio and excellent thermal stability. Recent work at NASA Langley Research Center (LaRC) has concentrated on developing new polyimide resin systems for advanced aerospace applications that can be processed without the use of an autoclave. Researchers have developed several polyimides from various aromatic diamines and dianhydrides that can be melt processed into coatings, adhesives, composites and films. Controlled molecular weight imide oligomers containing phenylethynyl groups [phenylethynyl terminated imide (PETI), e.g. PETI-8, PETI-330] have exhibited exceptional processability during fabrication of neat resin moldings, bonded panels and composites, albeit typically under 2.4 MPa (200 psi).

LaRC PETI-330 is a low molecular weight imide oligomer (M_n ~1250 g/mole with end caps) with a low, stable melt viscosity and a glass transition temperature (T_g) of around 330 °C after curing for 1-2 h at 371 °C. It was prepared using 2,3,3'4'-biphenyltetracarboxylic dianhydride, 1,3-bis(4-aminophenoxy)benzene and 1,3-phenylenediamine and endcapped with 4-phenylethynylphthalic anhydride. The resin was designed specifically for resin transfer molding (RTM) and resin infusion (RI) processing and has been used for making composites by RTM and RI. PETI-330 laminates exhibit excellent thermal and mechanical properties [1,2]. PETI-330 laminates have exhibited excellent retention of room temperature open hole compression strength and short beam shear strength after aging 1000 h at 288 °C [3].

LaRC PETI-8 is an aromatic polyimide (M_n ~1125 g/mole with end caps) based on 3,3',4,4'-biphenyltetracarboxylic dianhydride, a 50:50 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy) benzene, with 4-phenylethynylphthalic anhydride as the endcapping agent. PETI-8 has a T_g of around 300 °C after curing for 1 h at 371 °C and produces excellent tensile shear strengths and flatwise tensile strengths when processed with vacuum bag pressure only [4], eliminating the need for costly autoclave processing. Composites were processed using standard and double-vacuum-bag process and mechanical properties including short beam shear strength, flexural strength and modulus were evaluated at various temperatures [5].

Vacuum assisted resin transfer molding (VARTM) process was developed as a variation of RTM over ten years ago for application in commercial and military, ground-based and marine composite structures [6,7].VARTM has shown potential to reduce the manufacturing cost of composite structures. The upper tool of the matched metal mold used in RTM is replaced in the VARTM process by a formable vacuum bag material. Both transfer of the matrix resin and compaction of the part are achieved using atmospheric pressure alone. Flow of the resin into the part is improved through the use of a resin distribution medium [8]. The highly-permeable medium induces resin flow through the thickness of the part, reducing filling times. In VARTM, the fibrous preform is infiltrated on a rigid tool surface contained beneath a flexible vacuum bag. Both resin injection and fiber compaction are achieved under pressures of 101.3 KPa or less. Studies have demonstrated the feasibility of the VARTM process for fabrication of void free structures utilizing epoxy resin systems with fiber volume fractions approaching 60% [9]. VARTM using vinyl ester resins have traditionally yielded composites with low void contents as well and have found applications in the marine industry for making yacht hulls [10] and for rotorline wind turbine blades [11]. However, it should be noted that the focus so far has been on VARTM at room temperature. The Seemans Resin Infusion Molding Process (SCRIMP), patented by TPI Composites [8], is a vacuum infusion process using a high-permeability layer to rapidly distribute the resin on the part surface and then allow through-thickness penetration. The Controlled Atmospheric Resin Infusion Process (CAPRI) patented by The Boeing Company [12], is a SCRIMP variation where vacuum debulking and a reduced pressure difference is used to minimize thickness gradients and resin bleeding.

The CAPRI VARTM process has been extended to the fabrication of composite panels from polyimide systems developed at LaRC. Work has focused on processing various LaRC polyimides (PETI-330, PETI-8) by VARTM at *high temperatures*, hence forth referred to as HT-VARTM. In this case the resins are infused at temperatures above 250 ºC, and cured at 371 ºC. In HT-VARTM, resin flow lines, tools, sealants and bagging materials must be able to tolerate the high temperature processing cycle. Preliminary evaluation of these resins has shown that they exhibit the necessary melt flow characteristics for HT-VARTM processing, but the laminates typically have void contents greater than 7% by volume [13, 14]. The focus of this study has been to reduce the void content in composite parts and achieve sufficient fiber volume (>58%).

This paper focuses on the HT-VARTM processing trials carried out under several conditions by control of the process variables in an effort to reduce voids. Initial work focused on identifying the source of the volatiles leading to void formation. It was determined that due to the high temperature required for infusion and the low pressure, a small amount of degradation of the phenylethynyl group was occurring leading to volatile by-products. By adjusting the processing cycle, void content was reduced to routinely achieve 3% or less. In an attempt to further reduce porosity, optimization of the cure cycle by introducing higher fidelity control of the temperature and pressure is underway.

2. Experimental

2.1 Materials

Two PETI resins were used for the HT-VARTM processing trials. PETI-8 was purchased from Imitec Inc., Schenectady, NY, USA and PETI-330 from Ube Chemicals Ltd, Japan.

2.2 Melt Rheology

Dynamic rheological measurements were obtained using an Advanced Rheometric Expansion System (ARES) Rheometer from Rheometrics, Inc. The measurements were carried out under nitrogen atmosphere in an oscillatory shear mode using parallel plate geometry (30 mm diameter) at a heating rate of 4 ºC/min from 100 to 371 ºC. The top plate was oscillated at a variable strain and a fixed angular frequency of 10 rad/s while the lower plate was attached to a transducer that recorded the resultant torque. The as-received powders were press molded at room temperature (RT) into 2.54 cm diameter and ~ 1.5 mm thick disks. PETI-8 specimens were heated from 100 to 280 °C at 4 °C/min and held for 2 h while the PETI-330 was held for 2 h at both 260 °C and 280 °C. Storage (G') and loss (G") moduli were measured as a function of time during the temperature ramp. The minimum viscosity was identified from the measurements.

2.3 High Temperature VARTM

The HT-VARTM set-up utilized in this work is shown in Figure 1. A 1.27 cm thick steel plate was utilized as a tool. Three holes were drilled and tapped into the plate to provide one resin inlet and two vacuum outlets. Aluminum (Al) screen material was utilized as the flow medium. Polyimide bagging material and high temperature sealant were used to seal both an inner bag that contained ten layers of IM7-6K carbon fiber 5-harness satin fabric (GP sizing, Hexcel), five layers of Al screen flow media, Release Ease™ fabric, a breather material, and an outer bag that provided redundancy should a leak occur in the inner bag after infiltration.

During the initial runs only one oven containing both the resin pot and the tool was used. The tool was placed in an air circulating oven and heated to 280 °C. The resin pot was heated in a separate oven to melt the resin powder and cooled to create a seal for the inlet tube. It was then placed in the air circulating oven once the tool had reached temperature to minimize time-at-temperature effects on the resin. The resin pot was then plumbed to the tool and allowed to heat in the same oven. Vacuum was pulled on both the inner and outer bags (101.6 kPa or 30" of Hg) and the resin pot (101.6 kPa or 30" of Hg) as the resin was heated in order to degas the resin and remove air from the preform. Infiltration began when the resin reached 280 °C, corresponding to its minimum viscosity, by releasing the vacuum on the resin pot to 50.8 kPa (15" of Hg) and allowing the pressure differential to push the resin into the fabric stack. Once the panel was filled, the entire system was then cured at 371 °C for 1 h.

To improve the process, two ovens connected to each other by a heated tube were used. The resin pot was placed in the first oven and heated to the injection temperature under full vacuum. The tool was heated separately in the second oven under full vacuum, to the injection temperature. Upon reaching the infusion temperature, the resin was degassed for 5 min, vacuum on the pot was released to 50.8 kPa (15" of Hg) and the connecting valve between the pot and heating tube was opened to allow the resin to flow till infusion was complete. The connecting tube comprised of a 0.64 cm (¼") diameter stainless steel tube encased in a 1.27 cm (½") diameter tube around which the heating coil was wrapped. The connecting tube was kept at a temperature 2-5 ºC above the infusion temperature. Once infusion was completed, the connecting valve was shut off and the cure cycle was started.

2.4 Density Gradient Column

In order to construct a density gradient column (DGC) of desirable range, two separate solutions of ZnCl/H_2O with densities of ~1.278 g/cc and ~1.376 g/cc, respectively, were mixed. A jacketed glass column was filled with the two miscible solutions to create a linear density gradient, according to ASTM D1505 Method C. Calibrated density beads

(American Density Materials Inc.) were then introduced into the column, using a slowly descending basket to prevent turbulence in the column, and were allowed to stabilize in the column overnight. The positions of the calibrated beads were recorded and plotted versus their known densities to show that a linear gradient of range 1.3000-1.3338 g/cc had been established.

The samples of unknown density were then introduced into the column and allowed to stabilize overnight. Their respective positions were then measured, and their densities calculated, using the following calculation found in ASTM D1505:

$$\text{Density at } x = a + [(x - y)(b - a)/(z - y)]$$

where:

a and b = densities of the two calibrated beads,
y and z = distances of the two calibrated beads in cm, respectively, bracketing the sample from an arbitrary level, and
x = distance of sample above the same arbitrary level.

Densities are reported in grams per cubic centimeter.

2.5 Thermal Characterization

2.5.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on cured samples in a sealed aluminum pan using a Setaram Instrument DSC 131 thermal analyzer at a heating rate of 20 ºC /min with the T_g taken as the mid-point of inflection of the differential heat flow (ΔH) versus temperature curve.

2.5.2 Dynamic Mechanical Analysis

In order to obtain material stiffness as a function of temperature, dynamic mechanical analysis (DMA) was performed on all solid polymer samples where DMA provided a measure of dynamic storage modulus over a range of temperatures [15]. The bar samples were cut to be between 5 and 15 mm in width and 25 and 30 mm in length to conform to the dimensional limits required for the test fixture, using a calibration standard template provided with the DMA apparatus (DMA Q800 by TA Instruments). The average thickness for each bar sample was based on three separate measurements, taken along the length of the specimen with a digital micrometer, not to exceed 5 mm. A sample was mounted across the 3-point bend supports, and the moveable clamp placed in position at the center of the bar. The furnace was then sealed, and the sample allowed to equilibrate at 25 °C. The sample was then heated at 3 °C/min to 400 °C. All samples were tested with an applied preload force of 0.5 N, using a dynamic force with a single frequency oscillation of 1 Hz and amplitude of 20 µm. The storage modulus for each run was calculated as a function of increasing temperature, using thermal analysis software included with the DMA apparatus.

2.5.3 Thermogravimetric Analysis-Mass Spectroscopy, Pyrolysis-Gas Chromatography/ Mass Spectroscopy

Thermogravimetric analysis-mass spectroscopy (TGA-MS) experiments were conducted on uncured powder samples using a standard TGA-MS setup with a total purge flow of 100 mL/min of ultra high purity (UHP) nitrogen gas. The TGA portion was performed on a TA Instruments 2950 TGA with an evolved gas furnace and the MS portion was ran on a Pfeiffer Thermostar mass spectrometer with a mass range of 1-200 amu. The samples were held at RT for 30 min to evacuate all residual air. The samples were subsequently heated at 20 °C/min to 280 °C with a 45 min isothermal hold. This was followed by the experimental segment of interest: 5 °C/min to 371 °C with a 4 h isothermal hold.

For Pyrolysis-Gas Chromatography/ Mass Spectroscopy (Pyrolysis-GC/MS), uncured powder samples were run in a CDS 5200 Pyrolyzer attached to a Varian GC/MS. The samples were heated according to the same temperature profile used in the TGA-MS experiments. The purge gas was helium. The only chromatogram obtained was for the species evolved during the second heating ramp and isothermal hold at 371 °C. The sample size was 2.5 mg.

In another set of experiments, instead of using a TGA, a horizontal tube furnace was employed to heat the samples. A 2.54 cm stainless steel tube with Swagelok connections on both ends was inserted into the tube furnace. Approximately 3 g of uncured powder was loaded into an aluminum boat, which was inserted into the SS tube. UHP nitrogen flowing at 100 mL/min was connected to one side of the SS tube while the MS capillary probe was inserted into the other end. The MS scan range was 1-200 amu. The second heating rate was changed to 10 °C/min for these experiments, and the set points were about 8 °C lower than desired due to temperature variations between TGA and furnace.

2.6 C-Scan

C-scans of the composite panels were carried out using a 3 axis (x, y and z) Ultrasonic Scanner from SONIX Advanced Acoustic Solutions with a WIN IC (C-Scan) Version 4.1.0k software. A Panametrics transducer of 15 MHz/0.635 cm (0.25") diameter and 3.175 cm (1.25") focal length was used. A conventional ultrasonic pulse-echo C-scan method was used for detecting and characterizing delaminations in composites with a gain set to about 54 dB. The C-scan mode, however, had limitations because it provided only planar information and could not display the depth of flaws in the thickness direction.

2.7 Acid Digestion

Acid digestion of cured composites was carried out following ASTM D3131. Each specimen was weighed to the nearest 0.0001 g and placed into a 100-mL beaker and 30 mL concentrated sulfuric acid was added. The beaker was placed on a hot plate and heated until the mixture started to fume; heating was continued for 5 h. The beaker was then removed from the hot plate and 30 mL of 30% hydrogen peroxide was slowly added down the side of the beaker to oxidize the matrix. The solution was allowed to cool to RT; at this point the fibers floated to the top of the solution and the solution appeared clear. If the matrix was not completely digested, the solution could be filtered and reintroduced into the beaker to repeat the digestion procedure. Otherwise the contents were filtered into preweighed crucibles, washed with ~400 mL distilled water and rinsed with acetone. The crucibles were dried in an oven at 160 °C for 4 h, cooled to RT in a dessicator and weighed. Equations discussed in ASTM 3131 were used to calculate resin and fiber contents and volume fraction of voids using the obtained weights.

3. Results and Discussion

Figures 2 and 3 show the rheology behavior of the PETI resins used for VARTM runs. The complex viscosity (η^*) was measured as a function of time and temperature with a temperature hold at potential infusion temperatures. Typically, a viscosity ~ 10 Poise or less is necessary for successful resin infusion during VARTM. But it is also important that the viscosity remains low for at least a couple of hours so as to give sufficient time for degassing and infusion. As evident from Figure 2, η^* for PETI-8 stayed between 1 and 5 Poise for 4 h at 280 °C, providing a long processing window. However for the PETI-330, at the same temperature, η^* remained around 10 Poise for only 20 min hence reducing the window of operation (Figure 3a). Complex viscosity was then measured at 260 °C (Figure 3b) and it was found that although η^* was slightly above 10 Poise, it remained constant at that value for a much longer period of time. Based on these rheology curves, infusion temperature for PETI-8 was set at 280 °C and for PETI-330 at 262-266 °C.

For the first set of HT-VARTM runs, infusion was carried out at the chosen infusion temperature with the cure cycle started once infusion was completed. This involved heating the resin from the infusion temperature to 371 °C at 2.77 °C (5 °F)/min and curing at that temperature for 1 h. The void content of the composite panels obtained were determined by photomicrographs and acid digestion. Small pieces of void free samples obtained by RTM and VARTM were used to determine the densities of the resins using the density gradient column. For both PETI-8 and PETI-330, the resin density was found to be 1.31 g/mL. Figure 4 shows the micrographs of the two PETI resins. Using acid digestion, it was found that PETI-8 had a void content of 6.7 % while that of PETI-330 was 7.5%.

Based on the initial set of data, several approaches to reduce the void content were investigated. These included varying the processing parameters such as vacuum level, degassing time, and the temperature cycle. In conjunction with these approaches, TGA/MS experiments were conducted in an attempt to identify volatile species and their source.

To study possible resin degradation, TGA-MS was carried out on PETI-330. Water, carbon dioxide, toluene, benzene and benzaldehyde were evolved during the ramp from infusion temperature to cure temperature and subsequent hold (Ramp 2). Pyrolysis-GC/MS data also confirmed the release of benzene and toluene. Also several nitrogen containing compounds were detected including NMP. Figure 5(a) shows the Pyrolysis-GC/MS data where 18 peaks were detected but 7 were not identified. Results from the tube furnace experiments showed that as in the TGA-MS experiments, benzene, toluene, water, and carbon dioxide evolved during Ramp 2. They also evolved during the first ramp (Ramp 1) which was the heating up to the infusion temperature. With the larger sample size used in this experiment, benzonitrile, benzaldehyde, and styrene were also detected during both ramps. Figure 5(b) denotes the possible source of volatiles that were released upon degradation of PETI compounds. Newly detected species also included diphenylmethane, 1,2-diphenylethylene, and 1-methyl-2-pyrrolidinone (NMP). These species evolved only during Ramp 2. These chemical species appear to have evolved due to minor degradation of the phenylethynyl endcaps with the exception of NMP which was the solvent used in the synthesis of PETI-330. During these experiments, approximately 0.5-1% weight was lost, but this leads to a significant volume of gas in a closed system. It appears that this degradation occurred predominately when the pressure was low. In previous studies involving laminate fabrication by RTM, the high pressure (1379 kPa) used during RTM effectively suppressed volatilization and void-free panels were made [3]. However, in VARTM, the pressure differential was only 50.8 kPa (15" of Hg) which was apparently not enough to fully suppress evolution and volatilization of these low molecular species.

With regards to void formation in VARTM panels, researchers at the University of Delaware have conducted several experiments on room temperature VARTM of vinyl ester and other similar resins [16,17]. They reached a conclusion that the root cause of void formation was the vaporization of the components of the resin due to the application of the vacuum resulting in the partial pressure drop within the control volume. Their work has shown that effective control of the vacuum on the tool leads to a reduction of voids. Based on this work, for certain VARTM runs, the tool was not kept at full vacuum but at ~60 kPa after the infusion was completed. However, upon acid digestion of the obtained specimen, no reduction in void content was observed. Attempts were also made to increase the degassing time, but this hindered the infusion of the resin by reducing the processing window. Even though degassing times up to 30 min were tried, it was found that it made no difference when compared to a degassing time of 5 min. Another attempt at process optimization was to wash the neat resins (PETI-8 and PETI-330) with various solvents like methanol, isopropanol or acetone in an attempt to remove low molecular weight components from the resin that may contribute to void formation. Typically about 10% by weight of the resins was removed by these washings. Rheology carried out on these solvent washed samples found that the viscosity was increased by 1-2 orders of magnitude due to the removal of lower molecular weight species. The results showed the importance of the contribution of low molecular weight species to melt flow behavior.

The final set of process optimization tests involved modification of the cure cycle. Typically, once infused, the resin is heated directly to the cure temperature of 371 ºC and held for 1 h. Since the TGA-MS data showed that most of the resin degradation occurred during this stage of the process, curing the resins at lower temperatures but for a longer time was studied. Figure 6 shows the images of the resin when cured in a vacuum oven under different cure cycles. In each case, the resin was heated from RT to 280 ºC, held there for 90 min and then ramped to 310 ºC and held there for 2, 4 or 6 h. As seen in Figure 6a, when the resin was cured at 371 ºC, numerous voids are present. However, when the cure was carried out at a lower temperature and for a longer time, 4 h in case of Figure 6b and 6 h in case of 6c, the porosity decreased. DSC was also carried out on these samples to assess the extent of cure and the cured T_g values are given in Table 1. It is evident from the values that at 4 h, the resin was not fully cured and had a lower T_g. Based on this data, the resin was cured at 310 ºC for 8 h instead of the traditional 1 h cure at 371 ºC. A second approach was to stage the cure cycle - cure the resin at 310 ºC for 8 h and then take it to 371 ºC and cure for 1 h.

VARTM runs on the PETI resins were then carried out based on the modified cure cycles. In order to have better control of the processing parameters, the two-oven set up was used. PETI-8 was infused at 280 ºC after degassing at that temperature for 5 min. Typically, infusion took about 20 min and after 1 h the inlet valve connecting the pot to the tool was shut off and the cure cycle started. After an 8 h cure at 316 ºC, the sample was cooled down to RT and taken out of the tool. The panel was C-scanned and then cut into specimens for photomicrography and acid digestion. Figure 7 shows the C-scan of the panel and the photomicrograph of one section. Acid digestion yielded a void content of 3.3% with a fiber volume of 57 %.

To further reduce the void content of PETI-8 panels, a modified infusion and cure cycle was employed. Since PETI-8 maintains a viscosity of approximately 1.5 Poise for several hours at 260 °C, the infusion temperature was lowered to this value. Also, a modified cure cycle was used which utilizes intermittent holds. Therefore, a 10 ply panel was laid up as previously described and infused at 260 °C using CAPRI. Once the panel was fully wet out, the resin supply valve was closed and the modified cure cycle was employed. The cure cycle was a 0.27 °C (0.5 °F) ramp to 290 °C, a 2 h hold at 290 °C, a 0.27 °C ramp to 300 °C, a 2 h hold at 300 °C, a 0.27 °C ramp to 316 °C, an 8 h hold at 316 °C, and then cooled to RT. Figure 8 shows the C-scan of the panel and the photomicrograph of one section. This modified infusion/ cure procedure resulted in a high quality part with a void volume fraction of 3.0 %. It should be noted that three of the four specimens used to determine this measured value by acid digestion resulted in values below 3.0%. Another approach was then investigated where the above-described procedure was followed except that the CAPRI conditions were modified. Typically, CAPRI utilizes full vacuum of 101.6 kPa (30” of Hg) on the part and a partial vacuum of 50.8 kPa (15” of Hg) on the resin pot. In order to provide slightly more compaction force and thus further reduce the void volume formation, a PETI-8 panel was infused at 260 °C while maintaining full vacuum on the part and 74.5 kPa (22” of Hg) of vacuum on the resin pot. A high quality panel having a void content of 3.4% and a fiber volume of 56.7% was successfully fabricated with this modified procedure. Figure 9 shows the photomicrographs and C-scan from this panel.

For the PETI-330 resin, similar processing conditions were followed. Using a single oven, an infusion temperature of 280 ºC was used and the resin was cured for 8 h at 310 ºC instead of 316 ºC. A second HT-VARTM run with a staged cure cycle was also carried out. In this cycle, the resin was infused at 280 ºC and then taken to 310 ºC and held for 8 h. After that it was taken to 371 ºC and held for another 1 h before being cooled down to RT. Figure 10 shows the photomicrographs of samples obtained from the two panels. It was apparent from the images that the void content was reduced in Figure 10(b). Acid digestion results further corroborated this observation – the first sample exhibited a void content of 5.5% and a fiber volume of 59% while the second sample had a void content of 3% and a fiber volume of 58%. It should be noted that the samples for acid digestion are typically taken from four corners of the panel as it is likely that the outermost regions of the samples would have the highest voids. For the panel in Figure 10(b), void content was also measured from two samples taken from the center of the panel and the value was 10% lower. Since in the case of PETI-330, staging the cure cycle produced better results, the HT-VARTM run was repeated with the two-stage cure cycle – this time using the double oven set-up, and a void content of 3% was obtained. DMA was carried out on the PETI-330 composites and a T_g of ~355 ºC was obtained. For the next run a lower infusion temperature 260 ºC was used. Figure 11 shows the photomicrograph of this panel and the corresponding C-scan. The panel had a void content of 3.4 % with a fiber volume of 55%.

Several other approaches were investigated in an attempt to further reduce the void content. In the first experiment, an additional layer of breather cloth was placed above the Al screen flow media in an effort to reduce the voids. This was based somewhat on the use of porous membranes [18] for VARTM, a process carried out at the University of Delaware. Figure 12(a) shows a section from this panel. The average void content was 3.1% with 2 of the four samples having a void content <3%. In the second experiment, in addition to the extra layer of breather cloth, the carbon fibers were heat treated (tool with C-fibers taken to 400 °C, held for 1 h and cooled down to 260 °C) to remove any low molecular weight residue that may have remained behind on the fibers during manufacture. Figure 12(b) shows the photomicrograph of this sample and the average void content was 2.5%. In the third experiment the vacuum on the bags was adjusted. Upon completion of infusion of the resin at 260 °C, the vacuum on the outer bag was removed and the vacuum on the inner bag was brought down to 50.8 kPa (15” of Hg) and taken back to 101.6 kPa. This vacuum fluctuation or “bumping” was done twice on the inner bag. The vacuum on the outer bag was then brought back to 101.6 kPa and the normal cure cycle was started. As in the previous two runs, here too, an extra layer of breather cloth was placed above the flow media. A very high quality panel was obtained and Figure 13 shows the photomicrographs from this panel. Samples from this panel gave the lowest void content obtained to date – 2.3% with one of the four samples having a void content <2.0%.

Table 2 summarizes the various processing conditions that have been used so far to reduce the void content of the PETI-8 and PETI-330 panels.

4. Summary

One of the toughest challenges faced in HT-VARTM is the reduction of void content to 2.0% or less required for aerospace applications. To date it has not been possible to fabricate composite panels with less than 2.0% voids from high temperature polyimide resins by conventional HT-VARTM in spite of the fact that these resins have been successfully fabricated into high quality panels using RI or RTM. The current research has focused on in-depth studies to determine the volatile source and when volatile evolution occurs followed by appropriate modification of the process cycle. Thermal degradation studies demonstrated that the phenylethynyl group in these resins undergoes slight degradation at the processing temperatures and pressures used for HT-VARTM. Process modification involved curing at a lower temperature but for a longer period of time, and staging the cure cycle resulted in composites with void content <3.0%, substantially lower than any other reported polyimide composite panels made by HT-VARTM.

Future work will involve implementation of higher fidelity temperature and pressure controls for the HT-VARTM process followed by additional processing trials, as well as evaluation of mechanical properties of the composites.

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6. Figures

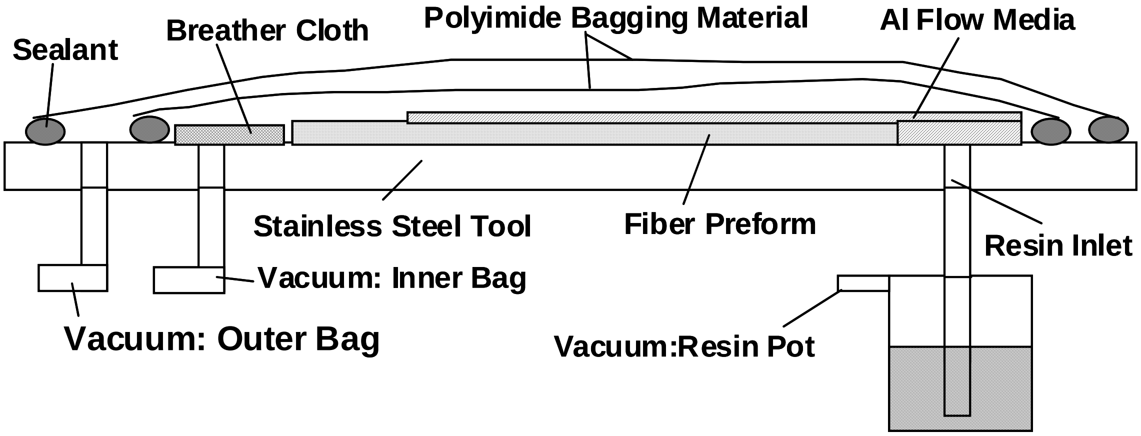


Figure 1: Schematic of HT-VARTM set up

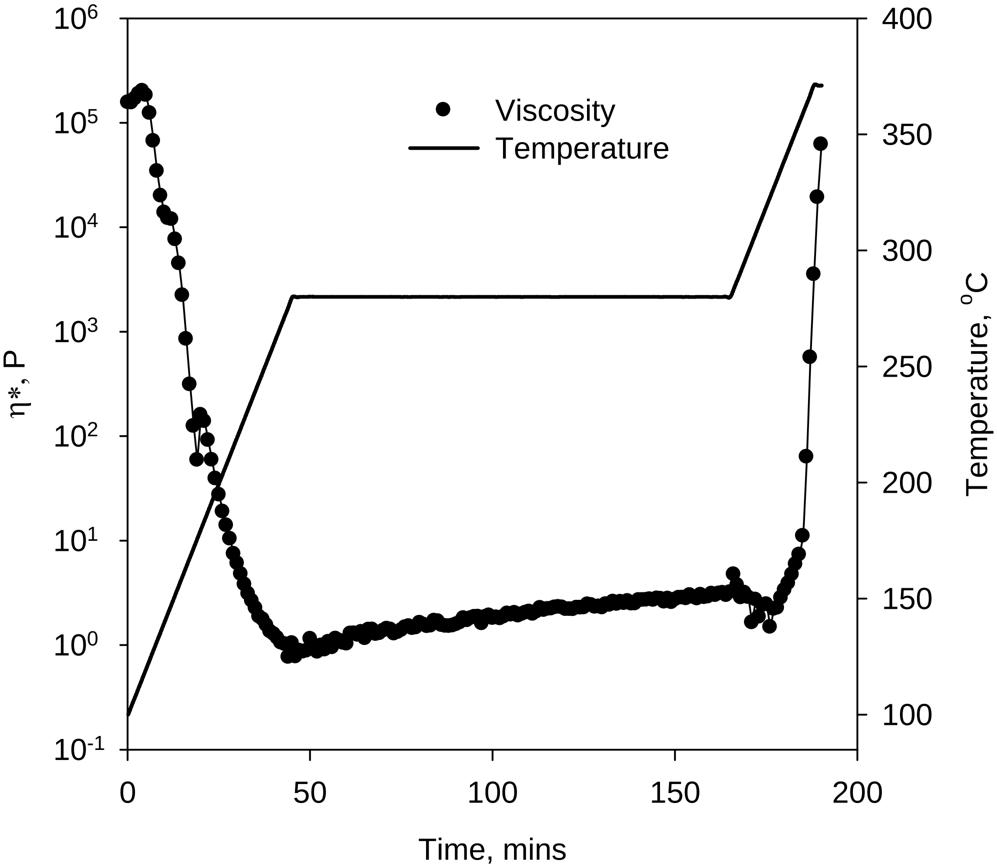


Figure 2: Rheology profile of PETI-8; 2 hour hold at 280 ºC

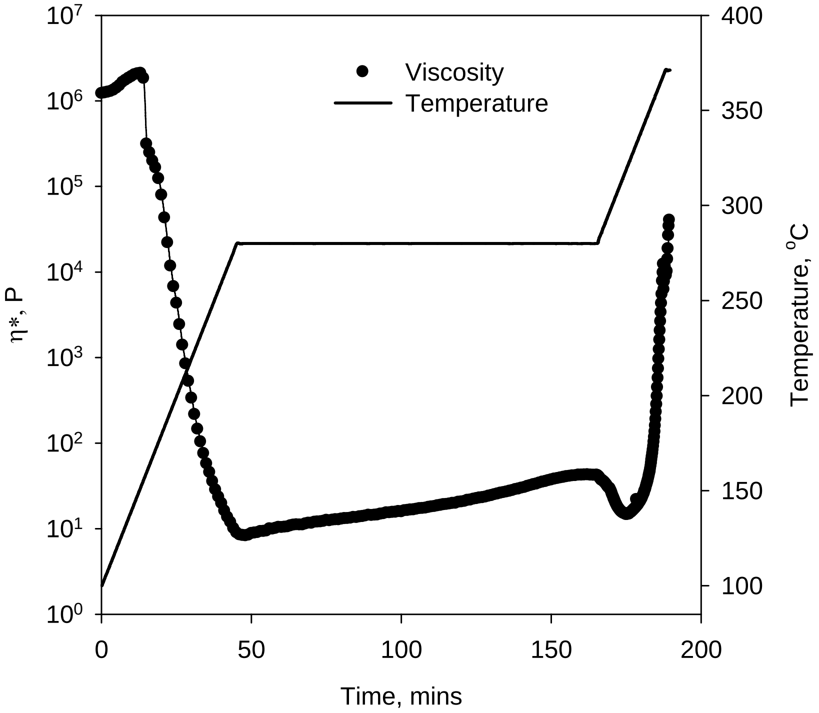


Figure 3a: Rheology profile of PETI-330; 2 hour hold at 280 ºC

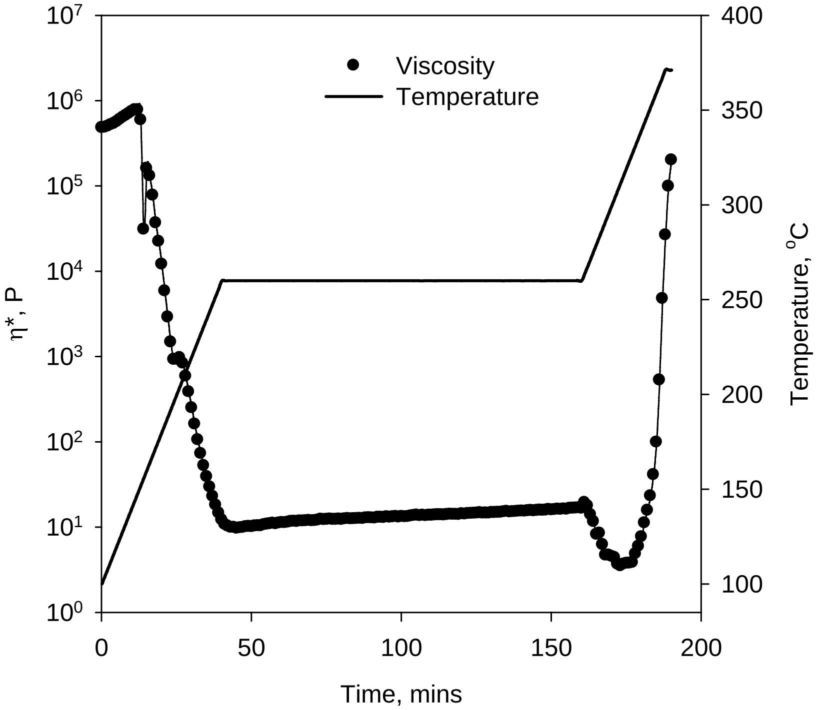
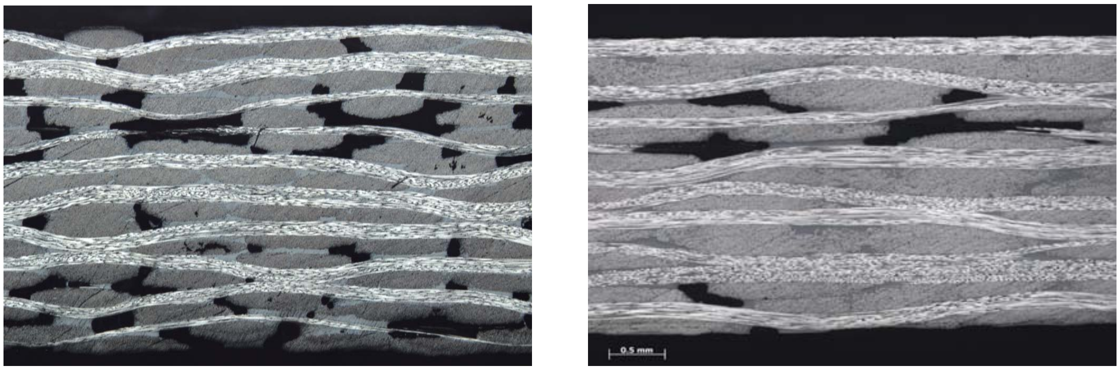
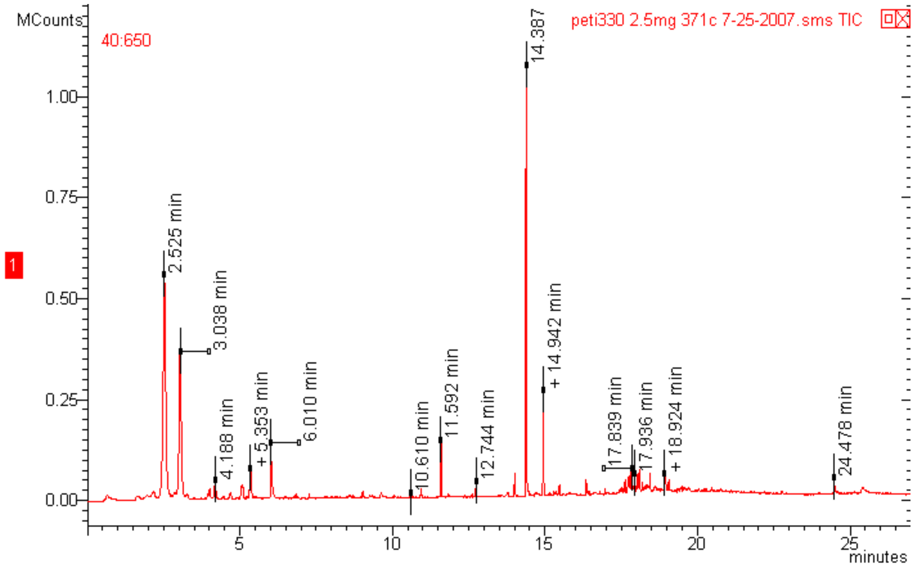


Figure 3b: Rheology profile of PETI-330; 2 hour hold at 260 ºC



(a) (b)

Figure 4: Photomicrographs of (a) PETI-330 and (b) PETI-8



Retention Time	**Compound**
2.5	Benzene
3	Toluene
4.2	Styrene
5.1	Benzaldehyde
5.4	Benzonitrile
6	1-methyl-2-pyrrolidinone
11.6	Diphenylmethane
12.7	Stilbene
14	Benzophenone
14.4	Benz[a]azulene
14.9	1,2-diphenylethylene

Figure 5(a): Pyrolysis-GC/MS data for PETI-330

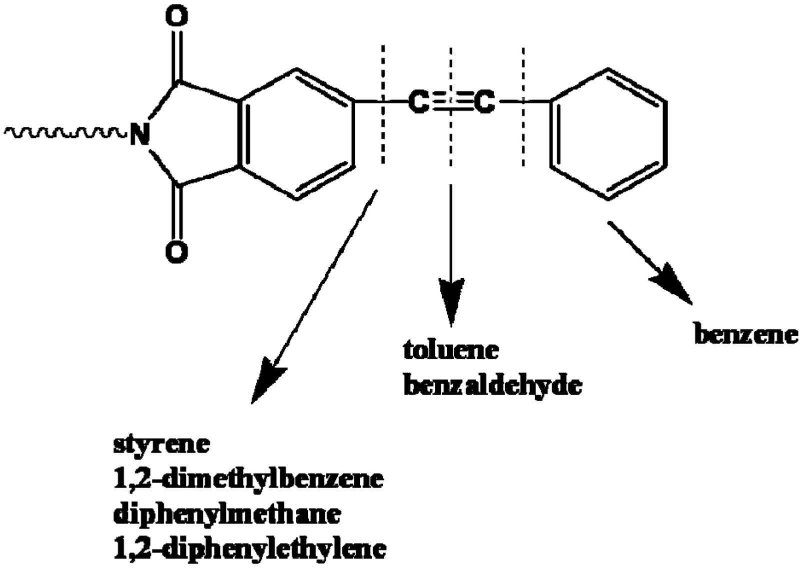
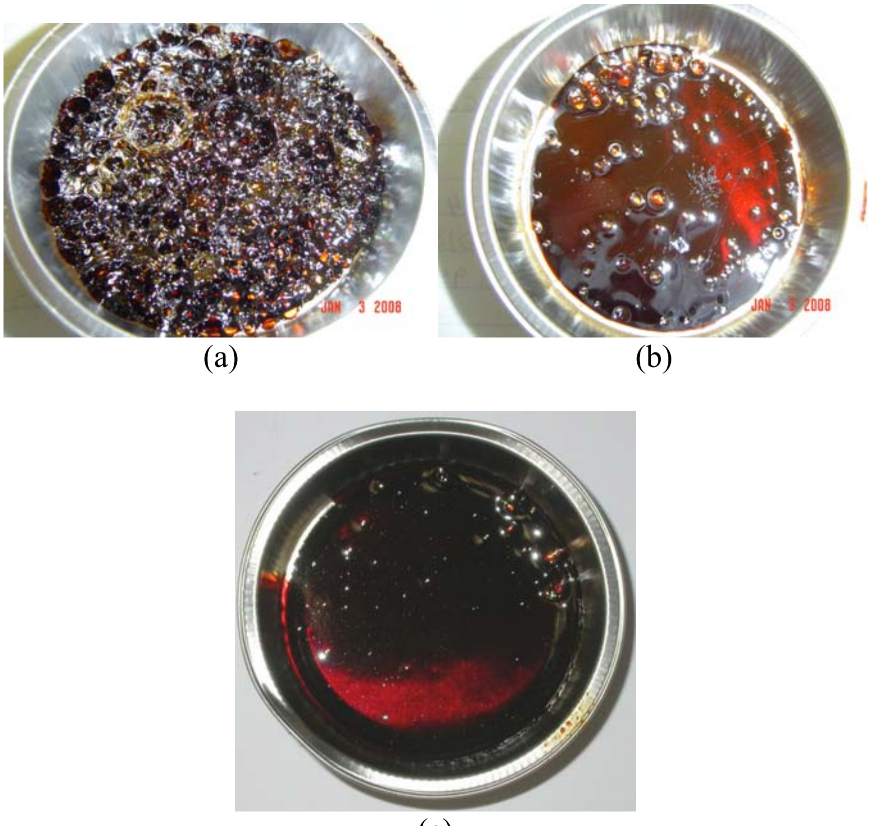


Figure 5(b): Possible sources of volatiles in PETI compounds



(a) (b)

(c)

Figure 6: PETI-330 cure tests under vacuum;
(a) 280 ºC to 371 ºC, 1 hour hold at 371 ºC
(b) 280 ºC to 310 ºC, 4 hour hold at 310 ºC
(c) 280 ºC to 310 ºC, 6 hour hold at 310 ºC

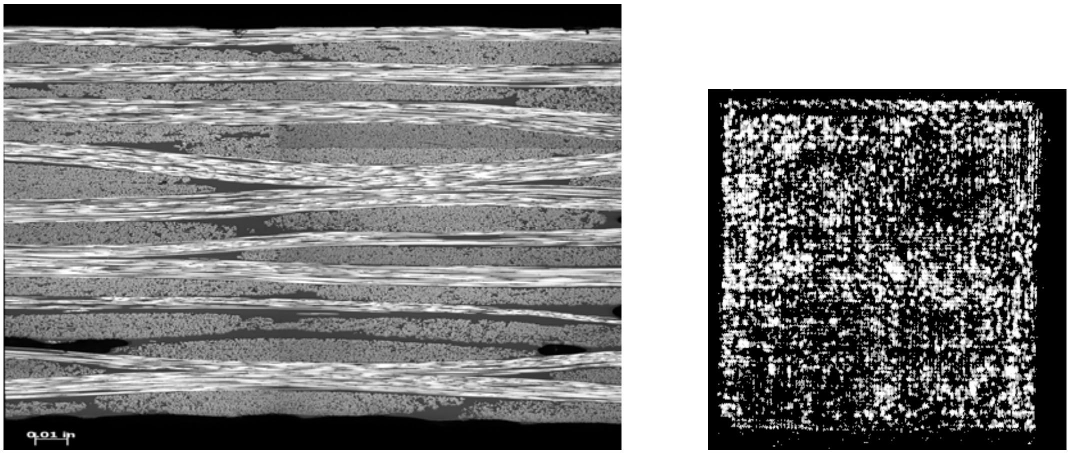


Figure 7: Photomicrograph of PETI-8 composite panel with 3.3% void content and its corresponding C-scan

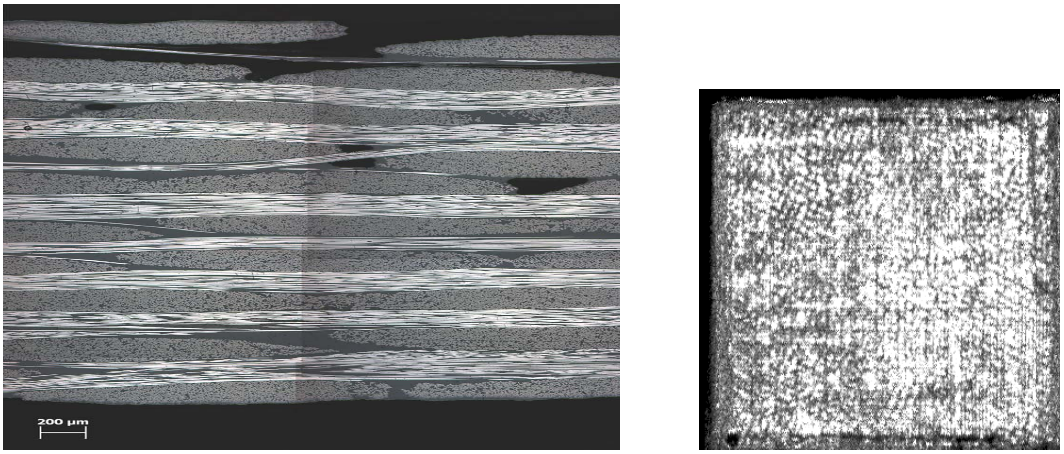


Figure 8: Photomicrograph of PETI-8 composite panel with 3% void content and its corresponding C-scan

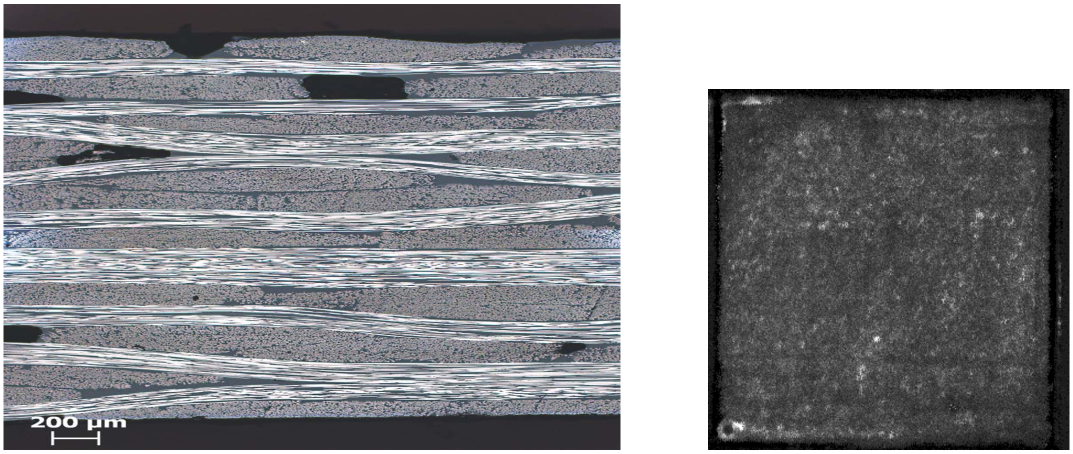
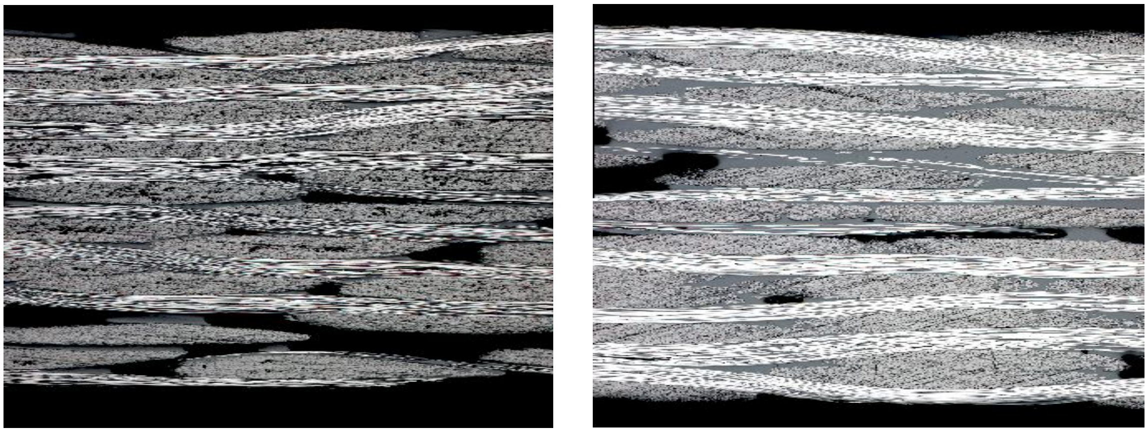


Figure 9: Photomicrograph of PETI-8 composite panel with 3.4% void content and its corresponding C-scan



(a) (b)

Figure 10: Photomicrograph of PETI-330; 8h at 310 ºC (a), 8h at 310 ºC followed by 1h at 371 ºC (b)

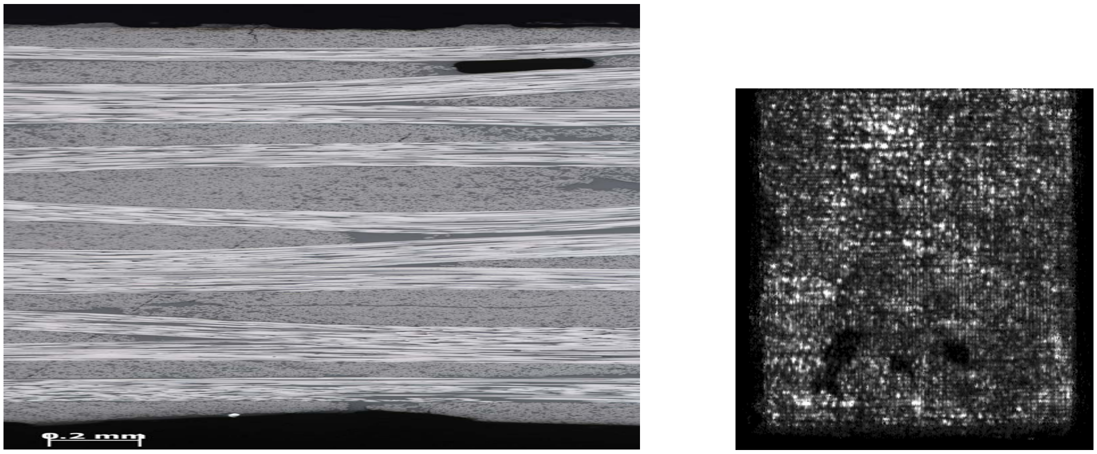
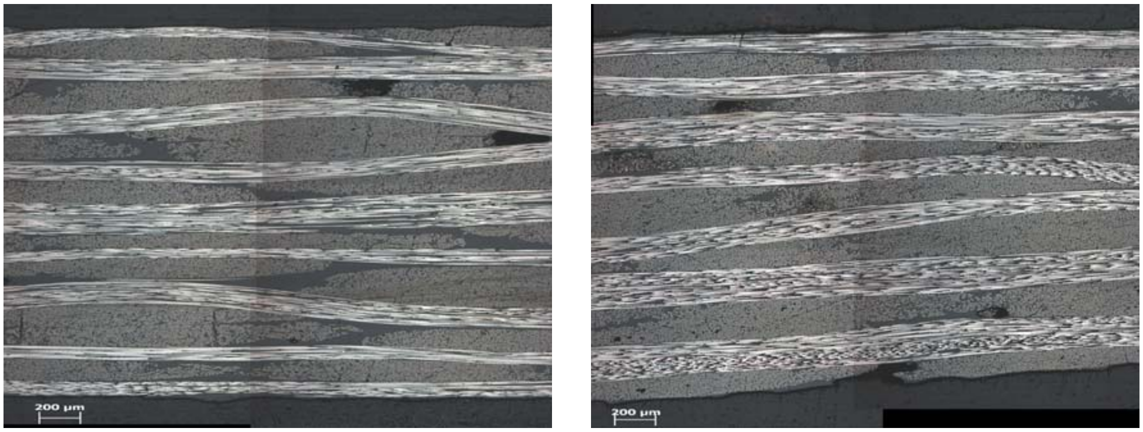


Figure 11: Photomicrograph of PETI-330 composite panel with 3.4 % void content and its corresponding C-scan



(a) (b)

Figure 12: Photomicrograph of PETI-330; with extra breather cloth (a), heat treatment of C-fibers (b)

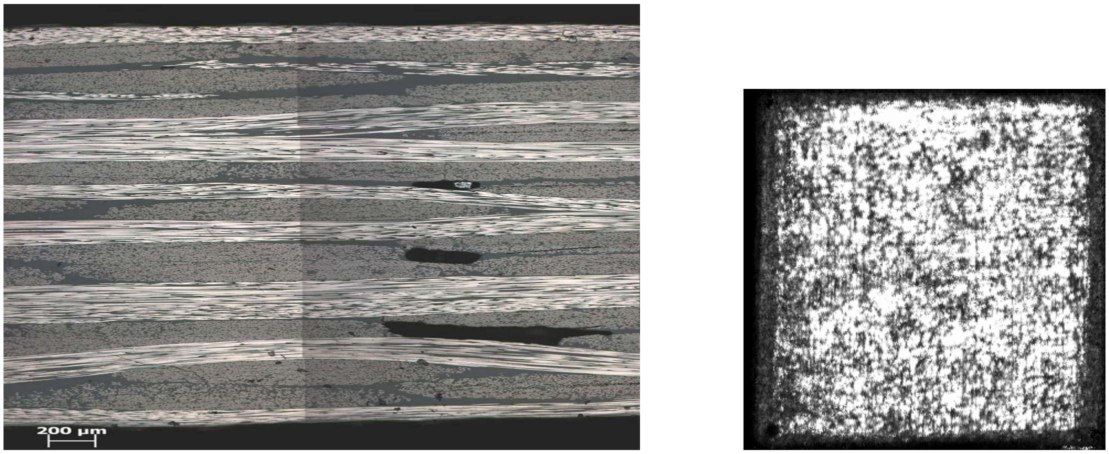


Figure 13: Photomicrograph of PETI-330 composite panel with 2.3% void content and its corresponding C-scan

Table 1: T_g of PETI-330 samples at different cure cycles

Sample	**Cured T_g (ºC)**
PETI-330, 280 ºC to 371 ºC, 1h hold at 371 ºC	343
PETI-330, 280 ºC to 310 ºC, 4h hold at 310 ºC	318
PETI-330, 280 ºC to 310 ºC, 6h hold at 310 ºC	331

Table 2: Processing conditions for VARTM of PETI resins

Sample	Oven	Infusion Temp, °C	Pot vacuum during infusion, kPa	Staging	Void content, %	Fiber volume, %
PETI-8	Single	280	50.8	No	6.7	55.0
PETI-8	Double	280	50.8	8h hold @ 316°C	3.3	57.0
PETI-8	Double	260	50.8	2h hold @ 290°C, 2h hold @ 300°C 8h hold @ 316°C	3.0	55.4
PETI-8	Double	260	74.5	2h hold @ 290°C, 2h hold @ 300°C 8h hold @ 316°C	3.4	56.6
PETI-330	Single	280	50.8	No	7.5	50.3
PETI-330	Single	280	50.8	8h hold @ 310°C	5.5	58.7
PETI-330	Single	280	50.8	8h hold @ 310°C, 1h hold @ 371°C	3.0	58.1
PETI-330	Double	280	50.8	8h hold @ 310°C, 1h hold @ 371°C	3.0	56.0
PETI-330	Double	260	50.8	8h hold @ 310°C, 1h hold @ 371°C	3.4	54.7
PETI-330	Double	260	50.8	Extra breather cloth, 8h hold @ 310°C, 1h hold @ 371°C	3.1	56.7
PETI-330	Double	260	50.8	Extra breather cloth, heat treatment of C-fibers, 8h hold @ 310°C, 1h hold @ 371°C	2.5	57.3
PETI-330	Double	260	50.8	Extra breather cloth, “Bumping” @ 260°C, 8h hold @ 310°C, 1h hold @ 371°C	2.3	54.7

* Tool vacuum was 101.6 kPa for all runs

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