HIGH TEMPERATURE VARTM OF PHENYLETHYNYL TERMINATED IMIDES

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SUMMARY

LaRC phenylethynyl terminated imide (PETI) resins were processed into composites using high temperature vacuum assisted resin transfer molding (VARTM). Although initial runs yielded composites with high void content, process modifications reduced voids to <3%. Photomicrographs were taken and void contents and T_gs of the panels were determined.

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

INTRODUCTION

Polyimide (PI) composites are used in the aerospace industry due to their high strength to weight ratio and excellent thermal stability. Researchers at NASA Langley Research Center (LaRC) have developed several PIs from various aromatic diamines and dianhydrides that can be melt processed into coatings, adhesives, composites and films without the use of an autoclave. 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. LaRC PETI-330 was designed specifically for resin transfer molding (RTM) and resin infusion (RI) processing and laminates exhibited excellent properties [1 - 3]. LaRC PETI-8 also produced excellent mechanical properties when processed with vacuum bag pressure only [4] as well as using standard and double-vacuum-bag processes [5].

VARTM was developed as a variation of RTM for application in commercial and military sectors [6,7] to reduce manufacturing costs. Both resin injection and fiber compaction are achieved under pressures of 101.3 KPa or less [8] and void free or low void content structures utilizing epoxy resins [9] and vinyl ester resins have been used in the marine industry [10]. 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 [11], is a SCRIMP variation where vacuum debulking and a reduced pressure difference is used to minimize thickness gradients and resin bleeding.

To date the focus has been on VARTM at room temperature (RT). The CAPRI VARTM process has been extended to composite panel fabrication from various LaRC PIs (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 °C, and cured at 371 °C. 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 > 7% by volume [12,13]. The focus of this study has been to reduce the void content in composite parts and achieve sufficient fiber volume (>58%) by control of process variables. Initial work focused on identifying volatile sources leading to void formation after which the processing cycle was adjusted resulting in void content of <3% being routinely achieved. In an attempt to further reduce porosity, cure cycle optimization by higher fidelity control of temperature and pressure is underway.

EXPERIMENTAL

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.

Melt Rheology

Dynamic rheological measurements were obtained using an Advanced Rheometric Expansion System (ARES) Rheometer from Rheometrics, Inc. Measurements were performed under N_2 in an oscillatory shear mode using parallel plate geometry with variable strain and a fixed angular frequency of 10 rad/s. Uncured resin specimens were heated from 100 to 260 or 280 °C at 4 °C/min and held for 2 h and then heated to 371 °C. Storage (G') and loss (G") moduli were measured as a function of time and the minimum viscosity identified from the measurements.

High Temperature VARTM

The HT-VARTM set-up utilized in this work is shown in Figure 1. PI 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 aluminum (Al) screen flow media, Release Ease™ fabric, a breather material, and an outer bag for redundancy should a leak occur in the inner bag after infiltration. Initial trials used only one oven containing both the resin pot and the tool. 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 and cooled to create a seal for the inlet tube. It was then placed in the main oven once the tool reached temperature and plumbed to the tool and allowed to heat up. Vacuum (101.6 kPa or 30" of Hg) was pulled on both inner and outer bags and the resin pot 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 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.

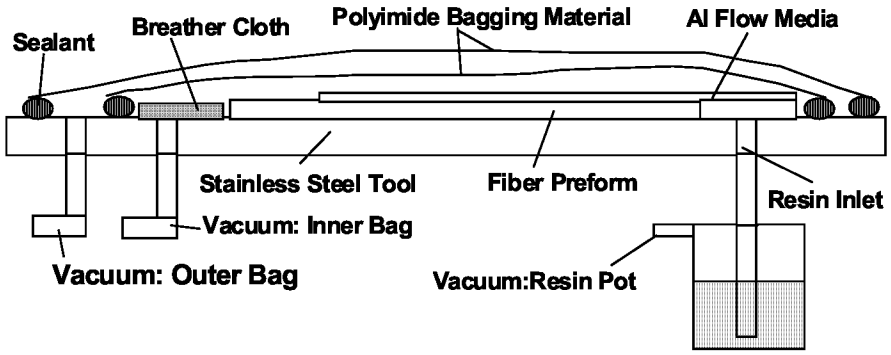


Figure 1: Schematic of HT-VARTM set up

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, also under full vacuum, was heated separately in the second oven 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 and the connecting valve between the pot and heating tube opened to allow for resin flow till infusion was complete. The connecting tube was a 0.64 cm diameter stainless steel (SS) tube encased in a 1.27 cm diameter tube around which a heating coil was wrapped. It 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.

Density Gradient Column

A density gradient column was set up according to ASTM D1505 Method C. Samples of unknown density were introduced into the column and allowed to stabilize overnight. Their respective positions were then measured, and their densities (in g/cc) calculated.

Thermal Characterization

Differential Scanning Calorimetry(DSC)

DSC was performed on cured samples in a sealed Al 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.

Dynamic Mechanical Analysis (DMA)

In order to obtain material stiffness as a function of temperature, DMA was performed using a DMA Q800 by TA. The sample was heated at 3 °C/min to 400 °C. 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 was used on all samples. The storage modulus for each run was calculated as a function of increasing temperature, using thermal analysis software included with the DMA apparatus.

Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS), Pyrolysis-Gas Chromatography/ Mass Spectroscopy(Pyrolysis-GC/MS)

TGA-MS was conducted on uncured powder samples using a standard setup with a total purge flow of 100 mL/min of ultra high purity (UHP) N_2 gas. The TGA portion was performed on a TA Instruments 2950 TGA with an evolved gas furnace with the MS portion run 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 (Ramp 1). This was followed by the experimental segment of interest: 5 °C/min to 371 °C with a 4 h isothermal hold (Ramp 2). For Pyrolysis-GC/MS, uncured powder samples were heated in a CDS 5200 Pyrolyzer attached to a Varian GC/MS following 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. In another case, a 2.54 cm SS tube with Swagelok connections on both ends was inserted into a horizontal tube furnace. Uncured powder was loaded into an Al boat, which was inserted into the SS tube. UHP N_2 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 second heating rate was changed to 10 °C/min for these experiments.

C-Scan

C-scans of the composite panels were performed 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 diameter and 3.175 cm 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.

Acid Digestion

Acid digestion of cured composites was carried out following ASTM D3131with the resin and fiber contents and volume fraction of voids calculated.

RESULTS AND DISCUSSION

Figures 2 and 3 show the rheological behavior of the PETI resins used for HT-VARTM. The complex viscosity (η^*) was measured as a function of time and temperature with a temperature hold at potential infusion temperatures. Typically, a viscosity of $\leq$10 Poise is necessary for successful resin infusion. But it is also important that the viscosity remains low for ~ 2 h so as to give sufficient time for degassing and infusion. For PETI-8 (Figure 2), η^*stayed between 1-5 Poise for 4 h at 280 °C, providing a long processing window. However for PETI-330, at 280 °C, η^* remained at 10 Poise for only 20 min hence reducing the operational window (Figure 3a). Measurements at 260 °C (Figure 3b) showed that although η^* was slightly >10 Poise, it remained constant for a much longer period of time. Based on these results, infusion temperature for PETI-8 was set at 280 °C and for PETI-330 at 262-266 °C.

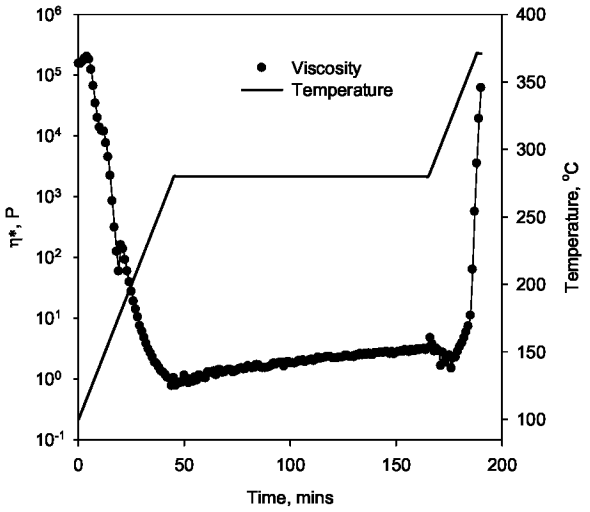


Figure 2: Rheology profile of PETI-8; 2 hour hold at 280 °C

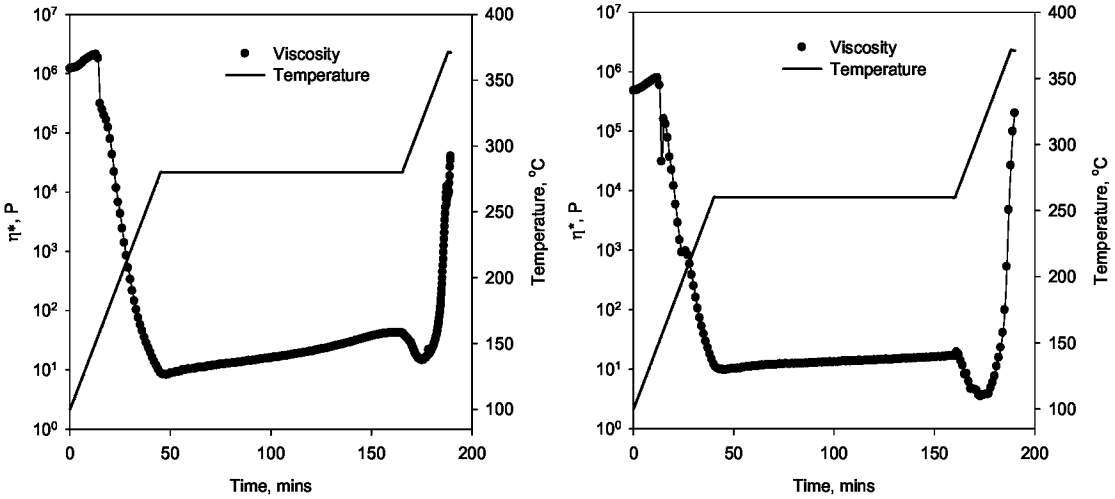
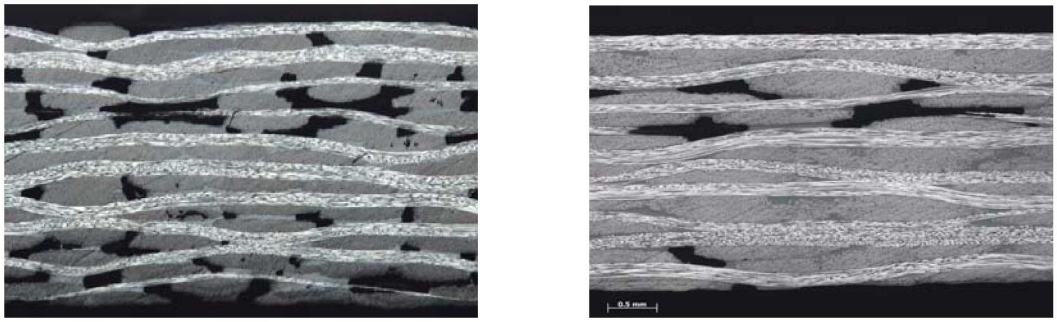


Figure 3: Rheology profile of PETI-330; a) 2 hour hold at 280 °C; b) 2 hour hold at 260 °C

For initial HT-VARTM runs, infusion was carried out at the chosen infusion temperature after which the cure cycle was started by heating the resin from the infusion temperature to 371 °C at 2.77 °C/min and curing at that temperature for 1 h. The void content of the composite panels obtained were determined by photomicrographs and acid digestion. Void free samples obtained by RTM and VARTM were used to determine the densities of the resins using a density gradient column and for both resins the density was found to be 1.31 g/cc. 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 including varying processing parameters such as vacuum level, degassing time, and the temperature cycle, were investigated to reduce the

void content. In conjunction with these approaches, TGA/MS experiments were conducted in an attempt to identify volatile species and their source.



(a) (b)

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

To study possible resin degradation, TGA-MS was carried out on PETI-330. Water, carbon dioxide, toluene, benzene and benzaldehyde were evolved during Ramp 2. Pyrolysis-GC/MS data confirmed the release of benzene and toluene. Also several nitrogen containing compounds were detected including 1-methyl-2-pyrrolidinone (NMP). Results from the tube furnace experiments also showed evolution of benzene, toluene, water, and carbon dioxide evolution during Ramp 2. They also evolved during Ramp 1. With the larger sample size used in this experiment, benzonitrile, benzaldehyde, and styrene were also detected during both ramps. Figure 5 denotes the possible source of volatiles that were released upon degradation of PETI compounds. Newly detected species also included diphenylmethane, 1,2-diphenylethylene, and 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, the solvent used in PETI synthesis. During these experiments, ~0.5-1% weight was lost, but this leads to a significant volume of gas in a closed system. In previous studies involving laminate fabrication by RTM, the high pressure (1.4 MPa) used effectively suppressed volatilization resulting in void-free panels [3]. In VARTM, the pressure differential was only 50.8 kPa which was apparently not enough to fully suppress evolution and volatilization of these low molecular species.

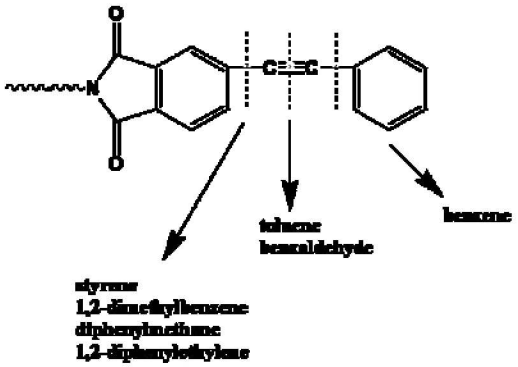


Figure 5: Possible sources of volatiles in PETI compounds

With regards to void formation in VARTM panels, researchers at the University of Delaware reached a conclusion that the root cause of void formation was the vaporization

of the components of the resin due to application of vacuum resulting in a partial pressure drop within the control volume and an effective control of the vacuum on the tool would lead to a reduction of voids [14,15]. Based on this work, for certain runs, the tool was not kept at full vacuum but at ~60 kPa after the infusion was completed. However no reduction in void content was observed. Attempts were also made to increase degassing time, but this hindered resin infusion 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 PETI resins with various solvents like methanol, isopropanol or acetone in an attempt to remove low molecular weight components that may contribute to void formation. Typically ~10% by weight of the resin was removed by these washings and as a result η^* increased by 1-2 orders of magnitude. This result showed the important contribution of low molecular weight species to melt flow behavior.

The final set of process optimization tests involved cure cycle modification. Typically, once infused, the resin was heated directly to the cure temperature of 371 °C and held for 1 h (T_g ~ 343 °C). Since TGA-MS data showed that most of the resin degradation occurred during this stage, curing the resins at lower temperatures but for longer times was studied. In each case, the resin was heated to 280 °C, held for 90 min and then ramped to 310 °C and held for 2 h, 4 h (T_g ~ 318 °C) or 6 h (T_g ~ 331 °C). When the resin was cured at 371 °C, numerous voids were present. But when cured at a lower temperature and for a longer time (4 or 6 h), the porosity decreased. As evident from the T_g, at 4 h, the resin was not fully cured. Consequently, the resin was cured at 310 °C for 8 h. A second approach was to stage the cure cycle - cure the resin at 310 °C for 8 h and then take it to 371 °C and cure for 1 h.

VARTM runs were carried out based on the modified cure cycles. For better control of processing parameters, the two-oven set up was used. PETI-8 was infused at 280 °C 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 closed and the cure cycle started. After an 8 h cure at 316 °C, the sample was cooled to RT, taken out and C-scanned and then cut into specimens for photomicrography and acid digestion. 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 lower infusion temperature of 260 °C and a modified cure cycle with intermittent holds were used. Using a heating rate of 0.27 °C/min, temperature was ramped to 290 °C, held for 2 h, ramped to 300 °C, held for 2 h, ramped to 316 °C, held for 8 h, and then cooled to RT. Figure 6 shows the C-scan of the panel and the photomicrograph of one section. This modified procedure resulted in a high quality part with a void volume fraction of 3.0 %. It should be noted that 3 of the 4 specimens used to determine this measured value by acid digestion resulted in values <3.0%. Another approach was then investigated where the above-described procedure was followed except that the CAPRI conditions were modified. In order to provide slightly more compaction force and thus further reduce the void formation, a PETI-8 panel was infused while maintaining full vacuum on the part and 74.5 kPa (22" of Hg) of vacuum on the resin pot. A panel having a void content of 3.4% and a fiber volume of 56.7% was successfully fabricated.

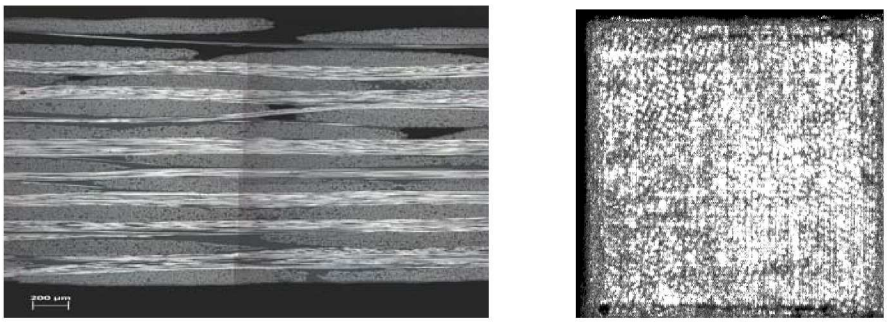
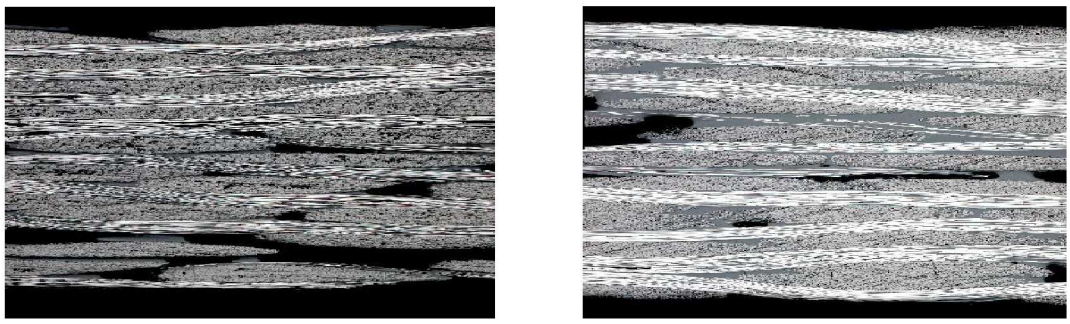


Figure 6: PETI-8 composite panel with 3% void content and its corresponding C-scan

For PETI-330, similar processing conditions were followed. Using a single (S) 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 run with a staged cure cycle was performed where the resin was infused at 280 ºC, then taken to 310 ºC and held for 8 h with a final 1 h hold at 371 ºC before being cooled to RT. Figure 7 shows the photomicrographs of samples obtained from the two panels. It was apparent from the images that the void content was reduced in Figure 7(b). Acid digestion results further corroborated this observation – the first sample exhibited a void content of 5.5% while the second sample had a void content of 3%. 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 7(b), void content was also measured from two samples taken from the center of the panel with the value being 10% lower. Since in the case of PETI-330, staging the cure cycle produced better results, the run was repeated with the two-stage cure cycle – this time using the double oven set-up, resulting in a void content of 3%. DMA on the PETI-330 composites indicated a T_g of ~355 ºC. Another run used a lower infusion temperature of 260 ºC. The panel had a void content of 3.4 % with a fiber volume of 55%.



(a) (b)

Figure 7: Photomicrograph of PETI-330; 8 h at 310 ºC (a), 8 h at 310 ºC, 1 h at 371 ºC (b)

Several other approaches were investigated in an attempt to further reduce the void content. In the first experiment, based somewhat on the use of porous membranes [16] for VARTM, an additional layer of breather cloth was placed above the Al screen flow media. For this panel the average void content was 3.1% with 2 of the 4 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

to 260 °C) to remove any residue that may have remained behind on the fibers during manufacture. For this sample 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 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 resumed. As in the previous two runs, an extra layer of breather cloth was placed above the flow media. A very high quality panel was obtained and Figure 8 shows the photomicrograph and C-scan. Samples from this panel gave the lowest void content obtained to date – 2.3% with 1 of the 4 samples having a void content <2.0%. The various processing conditions are summarized in Table 1.

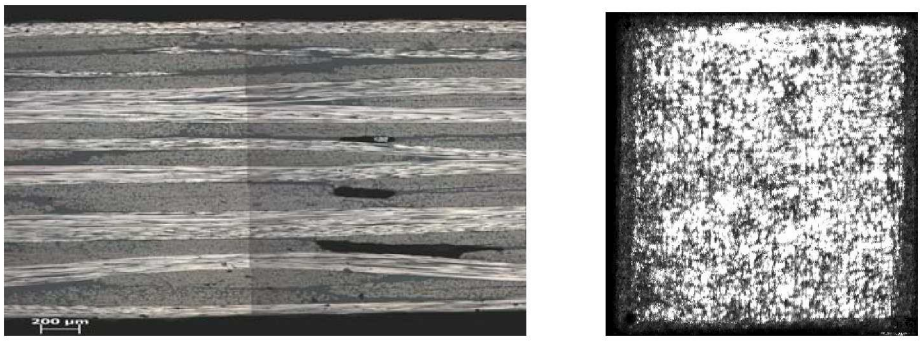


Figure 8: PETI-330 composite panel with 2.33% void content and its corresponding C-scan

Table 1: Processing conditions for VARTM of PETI resins

Sample, PETI-	Oven	Infusion Temp, °C	Pot vacuum, kPa	Staging	Void %	Fiber vol., %
8	S	280	50.8	No	6.7	55.0
8	D	280	50.8	8h @ 316°C	3.3	57.0
8	D	260	50.8	2h @ 290°C, 2h @ 300°C, 8h @ 316°C	3.0	55.4
8	D	260	74.5	2h @ 290°C, 2h @ 300°C,8h @ 316°C	3.4	56.6
330	S	280	50.8	No	7.5	50.3
330	S	280	50.8	8h @ 310°C	5.5	58.7
330	S	280	50.8	8h @ 310°C, 1h @ 371°C	3.0	58.1
330	D	280	50.8	8h @ 310°C, 1h @ 371°C	3.0	56.0
330	D	260	50.8	8h @ 310°C, 1h @ 371°C	3.4	54.7
330	D	260	50.8	+1 breather cloth, 8h @ 310°C, 1h @ 371°C	3.1	56.7
330	D	260	50.8	+1 breather cloth, heat treatment of C-fibers, 8h @ 310°C, 1h @ 371°C	2.5	57.3
330	D	260	50.8	+1 breather cloth, "Bumping"	2.3	54.7

				@ 260°C, 8h @ 310°C, 1h @ 371°C		

* Tool vacuum was 101.6 kPa for all runs, S – Single, D - Double

CONCLUSIONS

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 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 staging the cure cycle that 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 additional processing trials as well as evaluation of mechanical properties of the composites.

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