Infusion Processing of Phenylethynyl Terminated Imides by High Temperature RTM and VARTM

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Abstract

Fabrication of composite structures using infusion processes such as resin transfer molding (RTM) and vacuum assisted resin transfer molding (VARTM) is generally more affordable than conventional autoclave techniques. Recent efforts have focused on adapting both technologies for the fabrication of high temperature (HT) resistant composites. Due to their low melt viscosity and long melt stability, certain phenylethynyl terminated imides (PETI) can be processed into composites using these high temperature out-of-autoclave processes. In the current study, two PETI resins, LARC™ PETI-330 and LARC™ PETI-8 have been used to make test specimens using both RTM and VARTM. For aerospace applications, a void fraction of less than 2% is desired. Traditionally, RTM has had the advantage over VARTM for generating composites with low void content. However, the process is limited in terms of size. Work at NASA LaRC has incorporated modifications to the thermal cycle used in laminate fabrication that have reduced the void content significantly (typically 1-3%) using the current HT-VARTM process. For composite fabrication by both RTM and VARTM, the resins were infused into three carbon fiber preforms (T650-35-3k 5HS, IM7-6k 5HS, and IM7-6k Uniweave) at 316 ºC and 260 ºC respectively and cured up to 371 ºC. The details of the RTM processing carried out at the University of Akron are discussed in this work along with a brief description of the HT-VARTM processing carried out at NASA-LaRC. Photomicrographs of the panels were taken and void contents were determined by acid digestion. Mechanical properties (short beam shear, SBS) of the panels fabricated by both infusion processes were determined at room temperature as well as at various elevated temperatures. The results of this work are presented herein.

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1. Introduction

Polyimide composites are very attractive for applications requiring a high strength to weight ratio and performance at use temperatures above 177 °C. With the combination of thermal and mechanical properties along with improvements in processability, aromatic polyimides are now finding increased use in aerospace applications. Recent work at NASA Langley Research Center (LaRC) has concentrated on developing new polyimide resin systems for advanced aerospace applications that can be processed out of the autoclave. Using controlled molecular weight imide oligomers containing phenylethynyl endcaps, phenylethynyl terminated imide (PETI) resins are readily processed into neat resin moldings, bonded panels and composites. PETI oligomers for high temperature resin transfer molding (RTM), vacuum assisted RTM (VARTM) and resin infusion (RI) have been under investigation since the late 1990s. To demonstrate the versatility and processing robustness of these resins, complex composite parts such as I-beams, F-frames and skin stringer panels have been fabricated using RTM and RI [1, 2].

LaRC™ PETI-330 is a low molecular weight imide oligomer (calculated number average molecular weight (M_n) ~1290 g/mole) that exhibits a low melt viscosity and a post cure glass transition temperature (T_g) around 330 °C. It was prepared using 2,3,3'4'-biphenyltetracarboxylic dianhydride, 1,3-bis(4-aminophenoxy)benzene and 1,3-phenylenediamine and endcapped with phenylethynylphthalic anhydride. The resin was specifically designed for making composites using RTM and RI processing. PETI-330 laminates exhibit good mechanical properties up to 288 °C [3,4] and have retained approximately 98% of room temperature open hole compression (OHC) strength after aging 500 h at 288 °C [5]. LaRC™ PETI-8 is a phenylethynyl endcapped aromatic polyimide (M_n ~1125 g/mole) based on 3,3',4,4'-biphenyltetracarboxylic dianhydride, and a 50:50 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy) benzene. PETI-8 has a post cure T_g around 300 °C and produces excellent tensile shear strengths and flatwise tensile strengths when processed under vacuum bag pressure only [6], eliminating the need for costly autoclave processing. PETI-8 resin composites from prepreg tape have been processed using standard and double-vacuum-bag (DVB) processes. The resulting mechanical properties including short beam shear (SBS) strength, flexural strength and modulus have been evaluated at various temperatures [7].

RTM is an out-of-autoclave, closed molding process which offers high-quality dimensional and surface finish composite moldings using liquid thermoset polymers reinforced with various forms of fiber reinforcements. The high temperature RTM (HT-RTM) system consists of a high temperature injector that is used to inject the resin into a tool containing the preform. The closed mold is then placed into a high temperature press and the laminate is fabricated. HT-RTM has been highly successful with PETI-330 resins but it has not been utilized with PETI-8. 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 [8] is a variation of the Seemans Composite Resin Infusion Molding Process (SCRIMP) [9]. The CAPRI VARTM process has been extended to the fabrication of composite panels from polyimide systems developed at NASA LaRC. Work has focused on processing various LaRC polyimides by employing a high temperature VARTM process referred to as HT-VARTM. Although the evaluation of these resins has shown that they exhibit the necessary melt flow characteristics for HT-VARTM processing, the initial laminates fabricated

by this process had void contents greater than 7% by volume [10,11]. It was determined that the high temperature required for processing resulted in degradation of some of the phenylethynyl groups, forming volatile by-products during low pressure consolidation. By adjusting the processing cycle the void content was reduced to <3%, while still achieving sufficient fiber volume (>58%) [12,13].

This paper focuses on the fabrication of PETI laminates by two out-of-autoclave processes: HT-RTM and HT-VARTM. RTM has had the advantage over VARTM for generating composites with low void content but this high pressure process is limited in terms of part size. Although PETI-330 laminates have been fabricated using HT-RTM, this was the first effort at generating PETI-8 specimens. The details of the HT-RTM processing carried out at the University of Akron are discussed in this work along with a brief description of the HT-VARTM processing carried out at NASA-LaRC. Work involved the fabrication of laminates using three different types of carbon fabrics. Void contents of the laminates generated by both processes were determined and short beam shear strength values of both sets of composites were compared.

2. Experimental

2.1 Materials

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

Three types of carbon fiber fabrics 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 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 (General Sealant, A-800-3G from Airtech) were used to seal both an inner bag that contained the appropriate number of layers of carbon fiber preform, 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. For the IM7 biaxial fibers, ten layers were used with both resins whereas for the T650, ten layers were used with PETI-8 and eight layers with PETI-330. For the IM7 uniweave fabric, twenty and ten layers were used with PETI-8 and only ten layers with PETI-330. Prior to infusion, each type of carbon fabric was heat treated at 400 °C for 1 h to remove sizing.

It was previously demonstrated [12] that the process worked best using a two-oven set-up where the two ovens were connected to each other by a heated tube. 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 an additional 5 minutes, the vacuum on the pot

was reduced to 50.8 kPa pressure and the connecting valve between the pot and heating tube was opened to allow the resin to flow until infusion was complete. 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.

2.3 High Temperature RTM

The HT-RTM set-up is depicted in Figure 2. It consisted of a mold and an injection system. The mold consisted of a top and a bottom platen (34.3 cm x 34.3 cm x 1.3 cm) made of 4140 steel. A steel frame, made of the same material, inserted between platens had various thicknesses based on the laminate being fabricated. The frame thickness was calculated based on fabric densities provided by the manufacturer and the desired fiber volume fraction that was a minimum of 58% by volume. The preform lay-up consisted of carbon fabric plies and breather fabric and a sealant tape (General Sealant, A-800-3G from Airtech) placed along the periphery of the frame. The injection point was located at the center of one edge of the frame and was 0.3 cm wide with a thickness corresponding to the thickness of the frame. The top platen had vent holes (0.3 cm in diameter) at each corner. The injection system consisted of an 8.9 cm pneumatic cylinder with pressure control attached to a heated injection chamber (3.8 cm in diameter). A pressure of 0.28 MPa was used at the cylinder to provide an injection pressure of approximately 1.52 MPa. The mold was placed between 30.5 cm x 30.5 cm platens of a high temperature compression molding press (Carver, Wabash, IN) that had a maximum temperature of 400^{o}C and a clamping force of 107 kN. Insulation was used on all exposed areas for uniform temperature control.

2.4 C-Scan

C-scan 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 with 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 defects in composites with a gain set to about 54 dB. The C-scan mode, however, has limitations because it provides only planar information and cannot display the depth of flaws in the thickness direction.

2.5 Acid Digestion

Acid digestion of cured composites was carried out following ASTM D3131. Each specimen was weighed to the nearest 0.1 mg and placed into a 100-ml beaker and 30 ml 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 added down the side of the beaker to oxidize the matrix. The solution was allowed to cool; at this point the fibers floated to the top of the solution and the solution appeared clear. If the matrix is not completely digested, the solution may 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 to remove all moisture. The crucibles were dried in an oven at 160 °C for 4 h, cooled to room temperature in a dessicator and weighed. Equations were used to calculate resin and fiber contents and volume fraction of voids using the obtained weights. Calculations were based on a 1.77 g/cc fiber density and a 1.31 g/cc resin density.

2.6 Composite Mechanical Properties

Mechanical properties of the composites were tested in shear to determine their short beam shear strength (SBS) following ASTM D2344. SBS tests were carried out at room temperature (RT) and several elevated temperatures (ET). A Sintech 2W mechanical testing machine with a 454 kg (1000 lb) load cell and a heating chamber (Thermcraft) was used. The specimens were tested at a displacement rate 1.27 mm/min.

3. Results and Discussion

3.1 Manufacture of HT-RTM Laminates

Four different laminates were manufactured by the HT-RTM process as described in Section 2.3 at the University of Akron. Laminate #1 was composed of PETI-8 resin and ten plies of IM7-6K 5HS fabric. A mold thickness of 2.727 mm was used based on calculations for a required fiber volume of 58%, as shown below.

$$Fabric\ Areal\ Weight = 280\frac{g}{m^2}$$

$$Area\ per\ ply = 31.75cm * 31.75cm = 1008.0625cm^2$$

$$Total\ Area = 1008.0625cm^2 * 10\,plies = 10080.625cm^2 = 1.0080625m^2$$

$$Weight = 280\frac{g}{m_2} * 1.0080625m^2 = 282.2586g$$

$$FiberVolume = \frac{1cm^3}{1.77g} * 282.2586g = 159.4681cm^3$$

$$Total\ Volume = \frac{159.4681cm^3}{0.58} = 274.945cm^3$$

$$Plaque\ Thickness = \frac{274.945cm^3}{(31.75cm)^2} = 0.2727cm = 2.727mm$$

Plies were cut to 31.75 cm x 31.75 cm, using a cutting board, to fill up the mold as completely as possible. Plies were stacked on top of each other in the mold with the same weave orientation. High temperature sealant tape was compressed to a thickness of 1.6 mm. Then it was cut into 3.18 mm strips and placed along the edges of the mold between the plies. This sealed area prevented race tracking of the infused resin during injection. The preform consisted of sealant tape, two layers of carbon fabric and sealant tape repeated five times for a total of ten plies. The perform was sandwiched between a layer of breather fabric on top and another layer at the bottom. The sealant tape was placed a minimum of 3 cm away from all vents and the injection point to prevent blockage. After assembling the preform, the mold was placed in the compression molding press and clamped using the maximum force. The vents were closed and vacuum was drawn through the injection port. The temperature was raised to 400^{o}C and held for two hours under vacuum to pull off any volatiles. Then the mold temperature was lowered to 316 °C for injection.

A container with 240g of PETI-8 powder was placed in a vacuum oven and degassed at 288 °C for 30 minutes. The material was then transferred to the injection chamber maintained at 316 °C. The vents were opened on the top platen and the resin was injected. As the resin reached each vent they were closed. After injection, the temperature was raised to 371 °C and cured for 1 hour at an injection pressure of 1.52 MPa. After curing, the heating was turned off and the laminate was left to cool to room temperature.

The remaining three laminates were manufactured in the same manner with the following noted differences. Laminate #2 was composed of PETI-330 and ten plies of IM7-6K 5HS fabric. A mold thickness of 2.727 mm was used with the same lay-up configuration as in Laminate #1. The PETI-330 resin was degassed for 40 minutes. Laminate #3 was composed of PETI-8 and ten plies of T650-35-3K 8HS fabric. A mold thickness of 3.28 mm was used with the same lay-up configuration as in Laminate #1. Laminate #4 was composed of PETI-8 and twenty plies of IM7-6K unidirectionally woven fabric and a mold thickness of 3.07 mm was used. The lay-up was as follows: one layer of breather fabric, sealant tape, two layers of carbon fabric, sealant tape, three layers of carbon fabric, sealant tape, five layers of carbon fabric, sealant tape, five layers of carbon fabric, sealant tape, three layers of carbon fabric, sealant tape, two layers of carbon fabric, sealant tape and one layer of breather fabric. The plies were all oriented perpendicular to the injection point.

3.2 Problems Encountered During HT-RTM Process

The platens must be heat treated and stress relieved. At the high devolatilization and curing temperatures, the mold warped in the center that created a thickness variation with a reduction of thickness near the center of the platen. This led to high resistance to the flow during injection causing the resin to circumvent this area and entrap air.

The high temperature sealant was needed to prevent race tracking of the resin along the wall. Without the sealant tape, the infused resin ran along the wall and encapsulated air. Maintaining a constant pressure gradient throughout the mold is important for uniform flow of the resin during infusion.

3.3 Problems Encountered During HT-VARTM Process

One of the toughest challenges faced in HT-VARTM is the reduction of void content to 2% or less required for aerospace applications. It was determined that due to the high temperature required for infusion and the low pressure, a small amount of degradation of the phenylethynyl groups was occurring leading to volatile by-products [12]. Over the last few years researchers at NASA LaRC have successfully processed HT-VARTM panels with low void contents by various process modifications. These involved using a two oven set-up, curing at a lower temperature but for a longer period of time, and staging the cure cycle [13]. As a result, with biaxial carbon fabric, composites with void content <3% have been routinely fabricated. With the uniweave carbon fabric, the void content was lowered to <2%, thereby meeting the requirement for aerospace applications.

3.4 Characterization of Laminates

The HT-RTM panels had dry spots and only specimens from relatively well infused areas were examined. All of the HT-VARTM panels, on the other hand, were fully wet out with no

observable dry spots. Both C-scans and photomicrographs were used to obtain a qualitative analysis of the void contents in the specimens. Photomicrographs of the specimens obtained by the two out-of-autoclave processes are shown in Figures 3 and 4. It is evident from the photos that the HT-VARTM specimens have higher void contents than the well wet-out portions of the HT-RTM specimens and this observation is supported by the quantitative analysis carried out using acid digestion. Table 1 summarizes that void volumes and the fiber volumes of the PETI/C-fabric composites. With the exception of PETI-8/T650, all composite specimens fabricated by HT-RTM (well wet-out sections) had void contents of less than 1% while only the IM7-uni specimens made by HT-VARTM had void contents lower that 2%. Previous experiments have shown that during the curing reaction of the PETI resins, minor degradation of the phenylethynyl endcaps led to an approximate 0.5-1% weight loss, but this led to a significant volume of volatiles in a closed system. It appears that the phenomenon becomes an issue when the processing pressures are very low. During laminate fabrication by HT-RTM, the high pressure (1379 kPa) used during RTM effectively suppressed volatilization and void-free panels are possible. However, in HT-VARTM, the net pressure on the part of only 50.8 kPa was not enough to fully suppress evolution and volatilization of these low molecular species, resulting in panels with higher void contents.

3.5 Short Beam Shear Strength Properties

Specimens used for mechanical testing were prepared following the standards mentioned in Section 2.6. The SBS tests were carried out over several temperatures. Figure 5 shows the SBS data for the PETI-8 specimens. As evident from the figure, the strength values of the HT-RTM samples are higher than the HT-VARTM samples at all temperatures for T650 and IM7-uni fibers. However, the HT-VARTM specimens have better strength retention at ET. The HT-VARTM IM7-uni sample had 68% retention of strength at 177 °C compared to 62% for HT-RTM and 89% for T650 compared to 76% for HT-RTM. For the IM7-6K samples, the strength values are comparable at all temperatures even though the HT-RTM had significantly lower void content.

Figure 6 shows the SBS data for the PETI-330 samples prepared by HT-RTM and HT-VARTM. Once again, at room temperature, the HT-RTM specimens had higher strength values compared to the HT-VARTM specimens. However, at higher temperatures, the PETI-330 processed by VARTM showed a very good retention of properties and at 288 °C, the HT-VARTM specimens showed higher strength values compared to HT-RTM. It has been seen in a previous study with PETI-298 and AS 4 fibers [10] that SBS strength values of the samples at RT and at elevated temperatures are similar when processed by RTM or by VARTM even though the VARTM sample has a higher void content and a lower fiber volume.

4. Summary

As the need to focus on out-of-autoclave processes increases, processes like RTM and VARTM are becoming increasingly popular in the aerospace industry. At the same time, polyimide composites are gaining attention for applications that require a high strength to weight ratio and excellent thermal stability. Two high temperature resistant polyimide resins developed at the NASA Langley Research Center, PETI-330 and PETI-8, were successfully processed by RTM or and VARTM resulting in composites with high retention of strength at elevated temperatures. Although the HT-RTM panels processed in this work had dry spots, the well wet-out portions

had very low (<1%) void contents but the process is limited in size. The HT-VARTM processed PETI resins, on the other hand, have essentially no size limitation but resulted in laminates with void contents around 2.5%. Both the PETI-330 and PETI-8 resins were demonstrated to be processable by the infusion processes RTM and VARTM with various carbon fiber fabric preforms. However, more work is required to optimize the processes and the resin systems.

5. Acknowledgements

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6. Figures and Tables

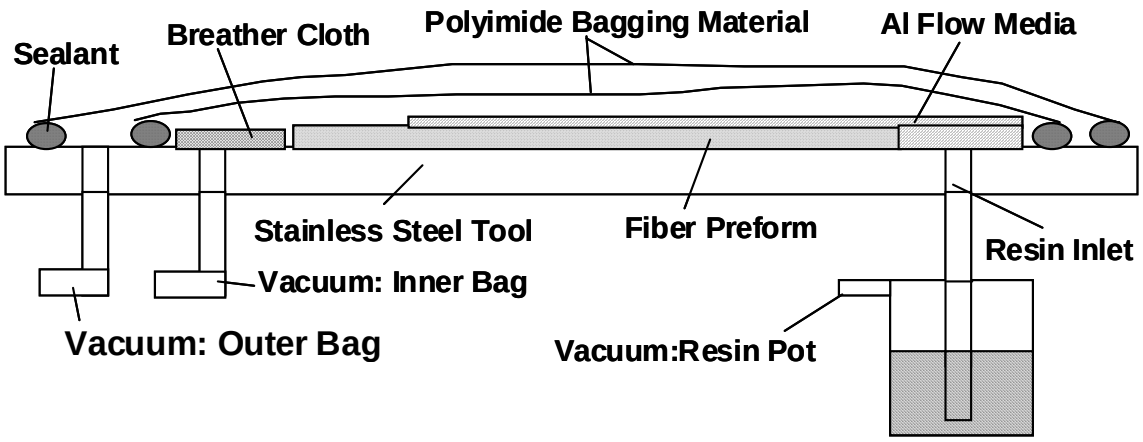


Figure 1: Schematic of HT-VARTM set up

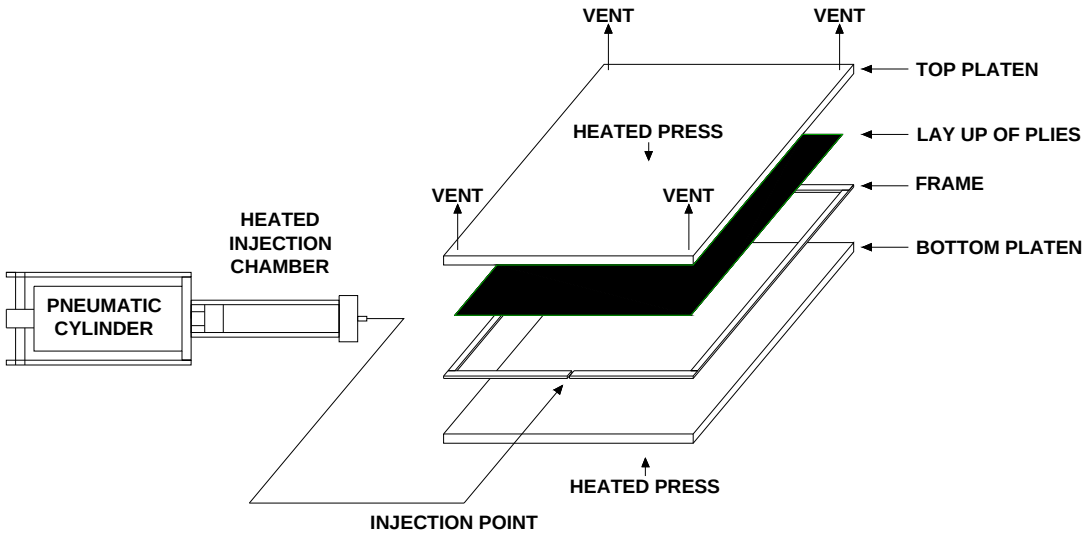
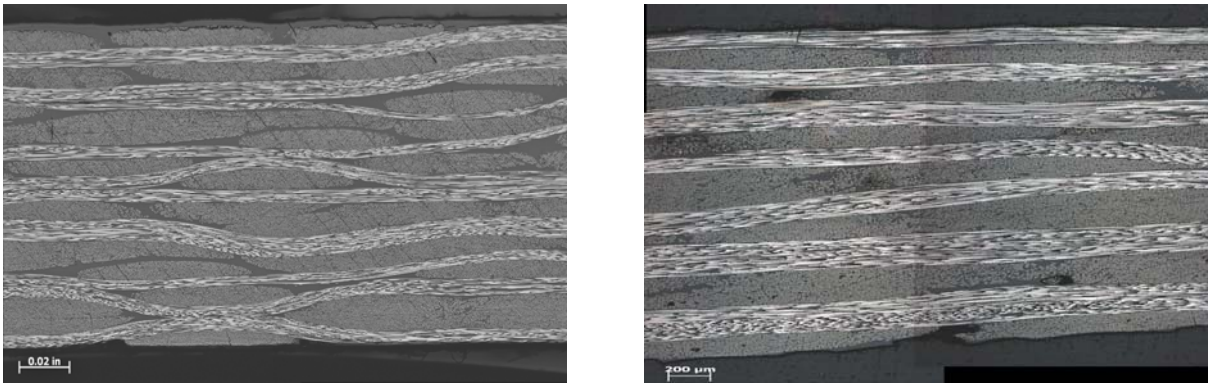
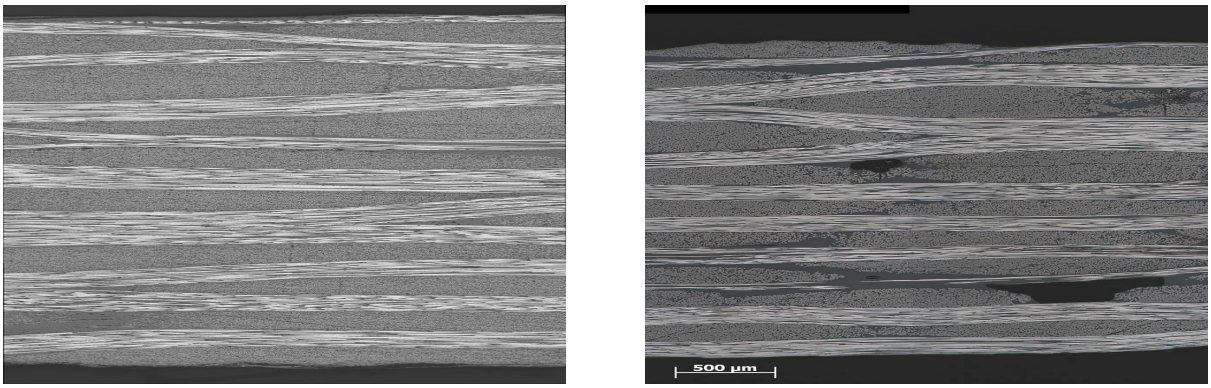


Figure 2: Schematic of HT-RTM set up



(a) (b)

Figure 3: Laminates of PETI-330/IM7-6K made by (a) HT-RTM and (b) HT-VARTM



(a) (b)

Figure 4: Laminates of PETI-8/IM7-6K made by (a) HT-RTM and (b) HT-VARTM

Table 1: Void content and fiber volume content of PETI laminates

Resin	C-fabric	Process	Void Volume, %	Fiber Volume, %
PETI-8	T650-3K	HT-RTM, #3	2.1	64.9
		HT-VARTM	3.2	62.8
	IM7-6K	HT-RTM, #1	0.7	59.3
		HT-VARTM	2.6	55.4
	IM7-uni	HT-RTM, #4	0.6	61.3
		HT-VARTM	1.4	59.1
PETI-330	T650-3K	HT-RTM [14]	0.9	59.6
		HT-VARTM	3.3	62.3
	IM7-6K	HT-RTM, #2	0.9	60.2
		HT-VARTM	2.5	57.3

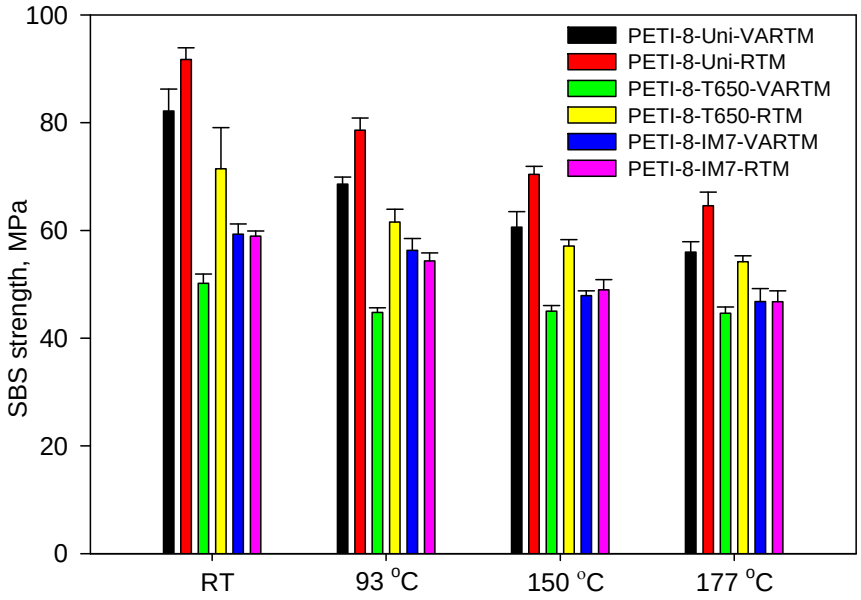


Figure 5: Short beam shear strength of PETI-8 with different C-fabrics

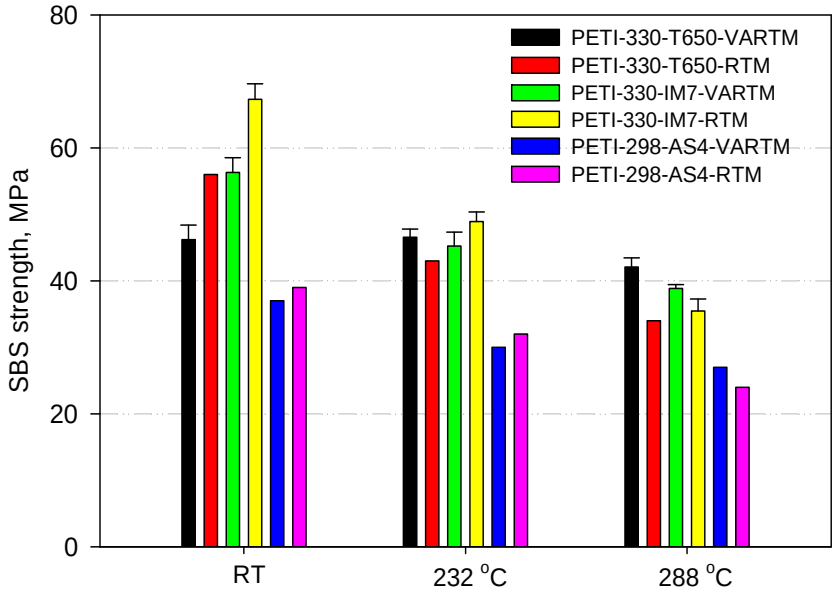


Figure 6: Short beam shear strength of PETI-330 with different C-fabrics (present study) and PETI-298 with AS 4 fibers of previous study [10]

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