Processing and Properties of Vacuum Assisted Resin Transfer Molded Phenylethynyl Terminated Imide Composites*

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ABSTRACT

Polyimide composites are very attractive for applications that require a high strength to weight ratio and thermal stability. Recent work at NASA Langley Research Center (LaRC) has concentrated on developing new polyimide resin systems that can be processed without the use of an autoclave for advanced aerospace applications. Due to their low melt viscosities and long melt stability, certain phenylethynyl terminated imides (PETI) can be processed into composites using high temperature vacuum assisted resin transfer molding (HT-VARTM). VARTM has shown the potential to reduce the manufacturing cost of composite structures. In the current study, two PETI resins, LARC™ PETI-330 and LARC™ PETI-9, were infused into carbon fiber preforms at 260 ºC and cured at temperatures up to 371 ºC. Photomicrographs of polished cross sections were taken and void contents, determined by acid digestion, were below 4.5%. Mechanical properties including short block compression (SBC), compression after impact (CAI), and open hole compression (OHC) were determined at room temperature, 177 °C, and 288 °C. Both PETI-9 and PETI-330 composites demonstrated very good retention of mechanical properties at elevated temperatures. SBC and OHC properties after aging for 1000 hours at temperatures up to 288 °C were also determined.

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1.0 INTRODUCTION

Due to their combination of processability and mechanical properties, aromatic polyimides are finding increased use in aerospace applications. Polyimide composites are very attractive for applications that require a high strength to weight ratio and performance at use temperatures above 177 °C. 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 (OOA). Controlled molecular weight imide oligomers containing phenylethynyl endcaps, the phenylethynyl terminated imides (PETI) are readily processed into neat resin moldings, bonded panels and composites. LaRC™ PETI-330 is a low molecular weight imide oligomer (number average molecular weight (M_n) ~1250 g/mole) with a low melt viscosity and a post cure glass transition temperature (T_g) of 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 designed specifically for making composites using resin transfer molding (RTM) and resin infusion (RI) processing. PETI-330 laminates exhibit good mechanical properties up to 288 °C [1,2] and have retained almost 98% of room temperature open hole compression strength after aging 500 h at 288°C [3]. A new PETI resin based on LaRC™ PETI-8 has been synthesized at LaRC and given the designation LaRC™ PETI-9. This resin system 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. PETI-9 has a cured T_g of around 265 °C as determined from DSC.

The vacuum assisted resin transfer molding (VARTM) process was developed as a variation of RTM over twenty years ago to make commercial and military ground-based and marine composite structures [4,5]. It has shown potential to reduce the manufacturing cost of these structures. The Seemans Composite Resin Infusion Molding Process (SCRIMP) [6] is a vacuum infusion process using a high-permeability layer to rapidly distribute the resin on the part surface and allows through-thickness penetration. The Controlled Atmospheric Resin Infusion Process (CAPRI) patented by The Boeing Company [7], is a SCRIMP variation where vacuum debulking and a reduced pressure difference is used to minimize thickness gradients and resin bleeding. Studies using epoxy resin systems have demonstrated that the VARTM process can make void free structures with fiber volume fractions approaching 60% [8]. VARTM using vinyl ester resins has traditionally yielded composites with low void contents as well; these have found applications in the marine industry [9, 10]. It should be noted that the focus so far has been on room temperature VARTM.

The CAPRI VARTM process has been extended to the fabrication of composite panels from polyimide systems developed at NASA LaRC. Various LaRC polyimides (i.e. PETI-330, PETI-8, PETI-9) were infused by VARTM at high temperatures, a process referred to as HT-VARTM. In HT-VARTM, resin flow lines, tools, sealants and bagging materials must be able to tolerate the high temperature processing cycle. Although the evaluation of these resins has shown that they exhibit the necessary melt flow characteristics for HT-VARTM processing, the resulting laminates had void contents greater than 7% by volume [11,12]. It was determined that the voids resulted from degradation of some of the phenylethynyl groups to form volatile by-products at the low consolidation pressure. Recently, researchers at NASA LaRC have been successful at reducing the void content to <3% by adjusting the processing cycle, while still achieving sufficient fiber volume (>58%) [13,14].

This paper focuses on the HT-VARTM processing of quasi-isotropic laminates based on simulations performed at the University of Delaware [15]. Work was carried out to generate an extensive database of mechanical properties. These properties include short block compression (SBC), compression after impact (CAI), and open hole compression (OHC) at room temperature, 177 °C, and 288 °C. SBC and OHC properties were also determined after aging for 1000 h at temperatures up to 288 °C.

2.0 EXPERIMENTAL

2.1 Materials

Two PETI resins were used for the HT-VARTM processing trials. PETI-330 was purchased from Ube Chemicals Ltd, Japan and PETI-9 from Imitec Inc., Schenectady, NY, USA. 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., Anahiem, CA, USA.

2.2 High Temperature VARTM

The HT-VARTM setup utilized in this work is shown in Figure 1. A 1.27 cm thick steel plate was used as the 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 (Thermalimide™, Airtech) and high temperature sealant were used to seal an inner bag that contained the appropriate number of layers of carbon fiber perform, five layers of Al screen flow media, Release Ease™ fabric, and a breather material. An additional outer bag provided redundancy against leaks in the inner bag after infiltration. For SBC and CAI panels, a quasi isotropic lay-up of 16 plies with $[\pm45/(0/90)/\pm45/(0/90)]_{2s}$ orientation was used for IM7-6K 5-harness and the T650-35-3K 8-harness carbon fiber fabrics. For OHC panels, a quasi isotropic lay-up of 8 plies with $[\pm45/(0/90)/\pm45/(0/90)]_{s}$ orientation was used for IM7-6K 5-harness and the T650-35-3K 8-harness carbon fiber fabrics. In the case of the uniweave fabric, a quasi isotropic lay-up of 16 plies with $[-45/0/45/90]_{2s}$ was used. Each type of carbon fabric was heat treated with a 1 h hold at 400 °C, prior to infusion, to remove sizing.

Prior experience demonstrated [13] that a setup where two ovens were connected to each other by a heated tube worked best. For this work, a larger connecting tube comprising of a 1.27 cm (½”) diameter stainless steel tube encased in a 1.91 cm (¾”) diameter tube (around which a heating coil was wrapped) was used which improved the temperature control and the flow of resin into the tool. Both resins, PETI-330 and PETI-9, were used to make quasi-isotropic panels. Each resin was heated to the infusion temperature of 260 ºC under vacuum and further degassed at that temperature for 5 minutes. Vacuum on the resin pot was then reduced to 50.8 kPa and the connecting valve between the pot and heated tube was opened to allow the resin to flow until infusion was complete. The infusion time varied depending on the type of carbon fabric and resin used but all samples were allowed to infuse for 2 h or longer to ensure that the resin had flowed through the thickness of the panel. Conditions were guided by simulations performed at the University of Delaware [15]. For PETI-330, the cure cycle involved taking the panel to 310 ºC and holding for 8 h, then to 371 ºC and held for another 1 h before being cooled down to room temperature. In the case of PETI-9, the samples underwent a 2 h hold at 290 °C and another 2 h hold at 300 °C, followed by an 8 h hold at 316 °C.

2.3 Composite characterization

C-scan inspections of the composite panels were carried out using a 3 axis (x, y and z) Ultrasonic Scanner from SONIX Advanced Acoustic Solutions with WIN IC (C-Scan) Version 4.1.0k software. A conventional ultrasonic pulse-echo C-scan method with a gain set to about 54 dB was used for detecting and characterizing defects in composites. 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 [13].

2.4 Composite Mechanical Properties

Compressive mechanical properties of the composites were determined by SBC according to the NASA standard [16], OHC according to ASTM D6484 and CAI according ASTM D7137. CAI specimens were impacted with a dropped weight of 5.369 kg (11.837 lb); the indenter had a 1.59 cm (0.625 in.) diameter hemi-spherical tip. SBC, CAI and OHC tests were carried out with an Instron test stand with an 88.96 kN (20 kip) load cell. The speed of testing was 0.127 cm (0.05")/min. Elevated temperature (ET) coupons where heated to either 177 °C or 288 °C and held at the test temperature for 10 minutes in the environmental chamber prior to testing. Some SBC and OHC specimens were aged in an air circulating oven for 1000 h at either 177 °C or 288 °C prior to testing at room temperatures (RT).

3.0 RESULTS AND DISCUSSION

3.1 HT-VARTM

For the two biaxial fabrics, IM7 and T650, panel fabrication did not provide any issues. However, with the PETI-330 and IM7-uni fabric, there was incomplete infusion with 16 plies. Hence, for this particular OHC sample, it was decided to infuse 8 plies. A staged curing cycle, as described in previous papers [14], was also used. Figure 2 shows photomicrographs of polished cross-sections of typical HT-VARTM panels. Table 1 shows the fiber volume fractions and void contents of the panels fabricated for this work. In general, the void contents averaged ~3.5% for the 8 ply OHC panels and around 4% for the 16 ply SBC and CAI panels.

3.2 Mechanical properties

A database of mechanical properties at RT, ET and after aging at ET for 1000 h was determined to demonstrate the potential of HT-VARTM as a viable OOA process for the manufacture of high-temperature resistant composites. It should be noted that the different fabrics utilized in this work should result in different properties due not only to differences in their fibers, tow sizes and weaves but also due to differences in their permeabilites [15]. Permeability may affect panel quality and characteristics as shown in Table 1.

Figures 3 and 4 summarize the SBC data. At RT, the PETI-9 resin demonstrated similar RT SBC properties of 426 MPa for the IM7 5HS fabric and 410 MPa for the T650 8HS fabric. The PETI-330 with the IM7 5HS fabric gave a RT compression strength of 400 MPa; the strength was just slightly less on the T650 8HS fabric. As seen in Figure 3, PETI-330 retained 68-71% of its RT properties at 288 °C. The ET strength was virtually unchanged even after 1000 h aging at 288 °C in air. After aging, the RT strengths were 77% (T650) to 85% (IM7) of the initial RT values. PETI-9 has a lower T_g and use temperature, so elevated temperature testing and aging were conducted at 177 °C. PETI-9 retained 81-82% of its RT compression values at 177 °C and aging for 1000 h at 177°C reduced the RT compression strength by only 3-6%.

The OHC strengths of the HT-VARTM samples at various temperatures and aging conditions are presented in Figures 5 and 6. For comparison, OHC data for PETI-8 composites, from Reference 16, are also included in Figure 5. The PETI-330 demonstrated higher OHC values with the T650 fabric compared to the IM7 fabrics. At RT, the T650 fabric resulted in the highest OHC strength of the three fabrics (250 MPa compared to 218 MPa and 216 MPa for the IM7 5HS and IM7 uniweave, respectively). This result may be due to high fiber volume fractions for the T650 series (~62% versus ~55% for the other fabrics as shown in Table 1).

At RT, the PETI-9 resin system demonstrated similar OHC values for all three fabric types of between 251 MPa and 267 MPa. The PETI-9 OHC data is also very comparable to previous PETI-8 data. In general, the PETI-9 resin system resulted in higher OHC values at RT than the PETI-330 resin system. This observed property difference is an example of the trade-offs generally observed in PETI-type resins. The PETI-9 and PETI-8 resins have greater concentrations of flexible ether groups, leading to higher toughness, lower T_g's and lower use temperatures. PETI-330, with a lesser amount of ether linkages, exhibits a higher T_g and use temperature but a reduced damage resistance/ damage tolerance.

As shown in Figure 5, PETI-330 retained 75-80% of its RT OHC values at 288 °C for all three fabric types. Due to its high T_g of around 330 °C, PETI-330 was able to maintain OHC values of 187 MPa for the T650 8HS fabric, 177 MPa for the IM7 uniweave fabric, and 167 MPa for the IM7 5HS fabric at this elevated temperature.

As also shown in Figure 5, PETI-9, with a T_g of around 265 °C, retained 80-82% of its RT OHC values at 177 °C for the T650 fabric (212 MPa) and IM7 uniweave (215 MPa) and 92% for the IM7 5HS fabric (231 MPa). After aging at 177 °C for 1000 h, all the PETI-9 materials retained 100% of their initial RT strengths (Figure 6). These results demonstrate the potential use of this OOA processed HT-VARTM material for extended use at 177 °C.

CAI data for composites from both PETI-330 and PETI-9 resins are shown in Figure 7. Impact parameters created from the drop weight impact and resultant approximated damage areas (obtained from C-scan images) are presented in Table 2. The PETI-330/IM7 5HS composites resulted in slightly higher CAI values compared to the T650 samples, 188 MPa versus 159 MPa. As shown in Table 2, the damage areas produced by the impact for the T650 8HS CAI samples were around the twice those generated for the IM7 5HS samples. The larger damaged area would result in a lower CAI strength. The differences in weave, fiber, and panel quality (Table 1) all play in a role in affecting these results.

The PETI-330 composites with both the IM7 5HS and the T650 8HS fabric retained 83-85% of their RT CAI properties at 288 °C. The PETI-330/IM7 5HS material demonstrated an OHC strength at 288°C of 157 MPa while the T650 8HS material gave 135 MPa. It is interesting to note that the IM7 5HS samples had a CAI strength at 288°C equal to that of the T650 8HS samples at RT.

Overall, the PETI-9 resin resulted in better RT CAI values for both fabric types compared to PETI-330. The PETI-9/IM7 5HS composites demonstrated a very good RT CAI strength of 263 MPa. As with the PETI-330, the PETI-9 CAI samples with the IM7 5HS fabric resulted is less damage compared to the T650 8HS fabric and thus better CAI strengths. As shown in Table 2, the approximated damage areas of the PETI-9 composites were about half the size of those for the PETI-330 composites for each carbon fabric. Since PETI-9 is a tougher resin system, this result as well as the better CAI results would be expected. However, it should be noted that the higher T_g of the PETI-330 affords it a higher use temperature.

As shown in Figure 7, the PETI-9/ IM7 5HS material retained 77% of its RT strength at 177 °C (202 MPa). Although not as good as the IM7 5HS fabric samples, the PETI-9/ T650 material retained 90% of its RT CAI values at 177 °C.

4.0 CONCLUSIONS

The NASA LaRC HT-VARTM process could be used to fabricate quasi-isotropic composite panels from two PETI resin systems. The process gives void contents of around 2-3.5% for 8 ply and around 4% for 16 ply panels, slightly higher than for previous smaller, thinner test panels. Fiber manufacturer and weave affected the results, but both PETI-9 and PETI-330 HT-VARTM composites demonstrated very good retention of properties at elevated temperature (177 °C for PETI-9 and 288 °C for PETI-330) as well as after aging for 1000 h at those same temperatures.

5.0 ACKNOWLEDGEMENTS

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6.0 FIGURES AND TABLES

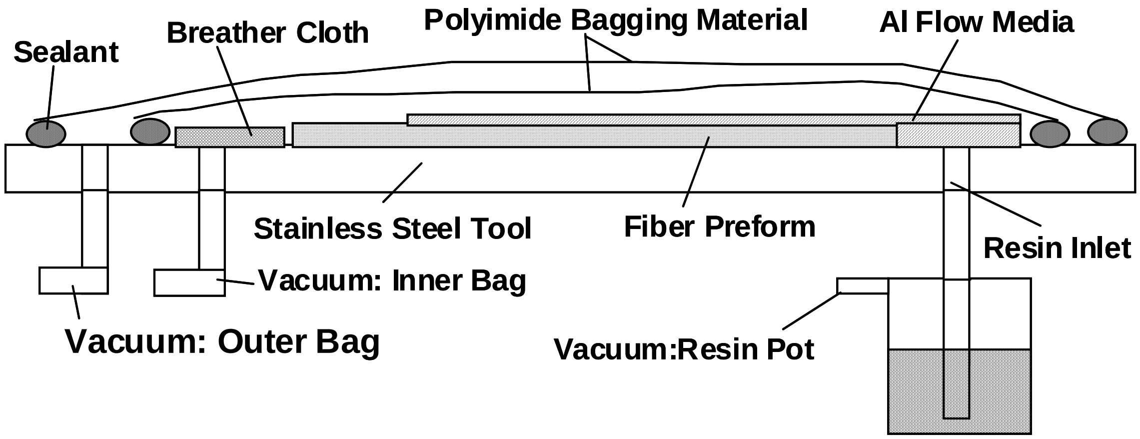

Figure 1: Schematic of HT-VARTM set up.

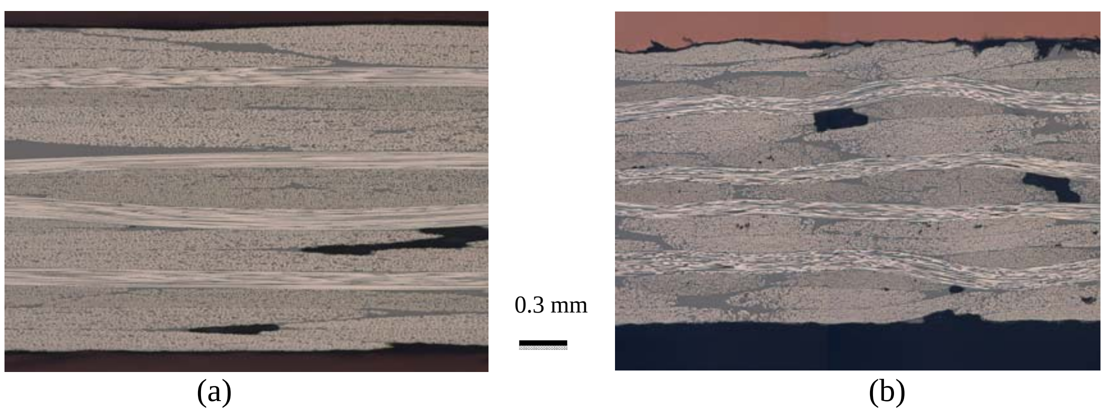

Figure 2: Photomicrographs of PETI-9 (a) and PETI-330 (b).

Table 1. Average physical properties of tested coupons.
[Fiber Volume Fraction (%) / Void Volume Fraction (%)]

	Material: Fabric / Resin					
Test Coupons	**IM7-5HS/ PETI-9**	**T650-8HS/ PETI-9**	**IM7-Uni/ PETI-9**	**IM7-5HS/ PETI-330**	**T650-8HS/ PETI-330**	**IM7-Uni/ PETI-330**
SBC RT	57.2 / 3.9	59.6 / 4.4	N/A	53.4 / 3.9	58.3 / 4.5	N/A
SBC ET	57.2 / 3.9	59.6 / 4.4	N/A	53.4 / 3.9	58.3 / 4.5	N/A
SBC Aged	57.2 / 3.9	59.6 / 4.4	N/A	53.4 / 3.9	58.3 / 4.5	N/A
OHC RT	58.7 / 2.7	63.7 / 3.6	57.4 / 2.7	57.5 / 2.9	62.4 / 3.2	56.5 / 1.7
OHC ET	57.6 / 2.4	60.0 / 3.7	57.5 / 3.1	53.5 / 4.2	63.1 / 3.4	53.5 / 3.8
OHC Aged	58.2 / 2.6	57.5 / 2.9	61.9 / 3.7	55.7 / 3.6	62.4 / 3.2	55.7 / 1.7
CAI RT	56.8 / 2.9	61.7 / 4.2	N/A	55.9 / 2.9	60.1 /3.8	N/A
CAI ET	56.8 / 2.9	60.8 / 4.2	N/A	55.9 / 2.9	60.1 /3.8	N/A

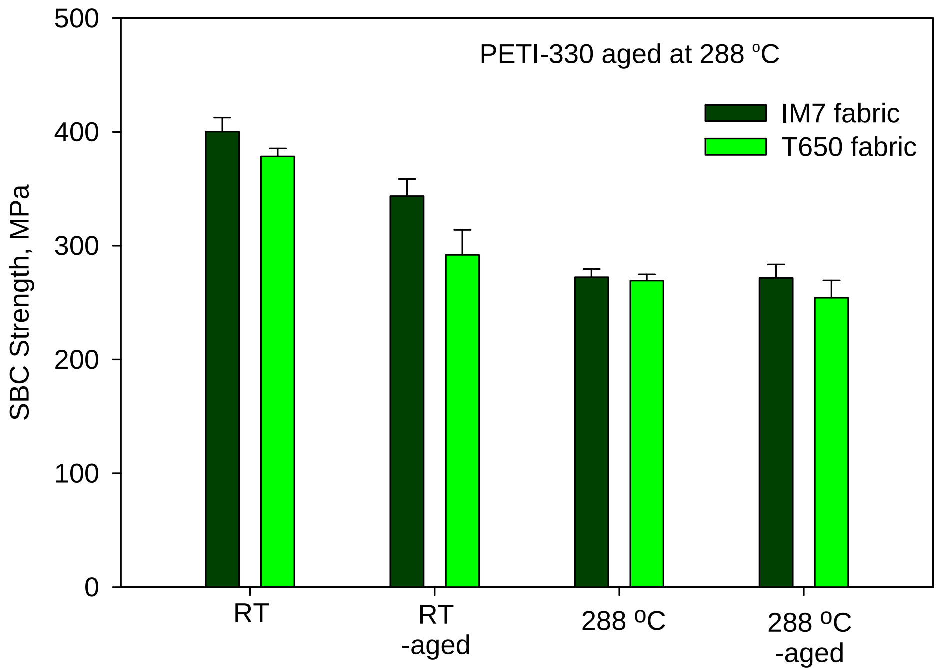

Figure 3: SBC strength of PETI-330; unaged and aged samples measured at RT and ET.

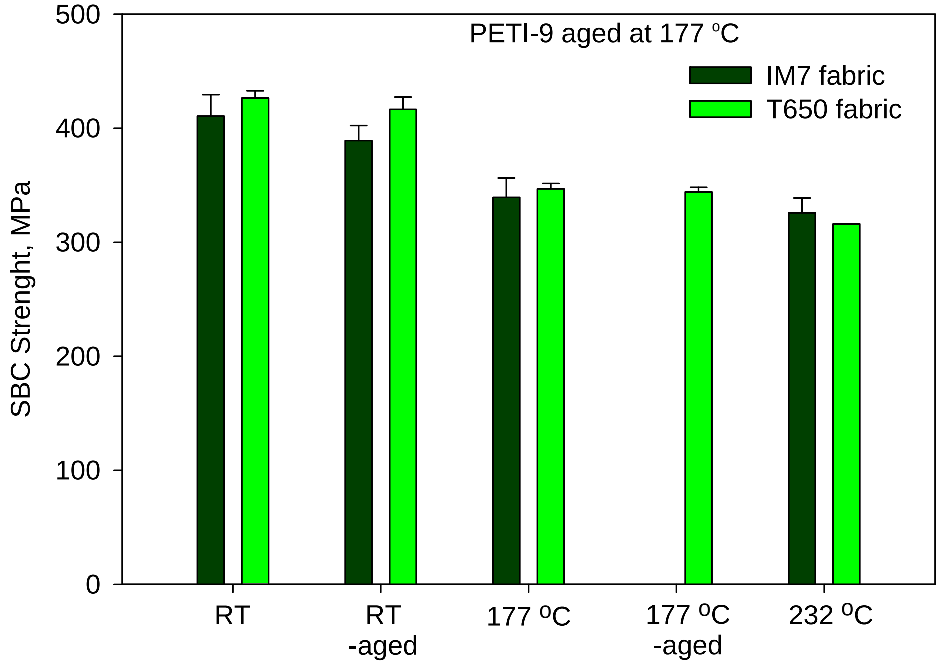

Figure 4: SBC strength of PETI-9; unaged and aged samples measured at RT and ET.

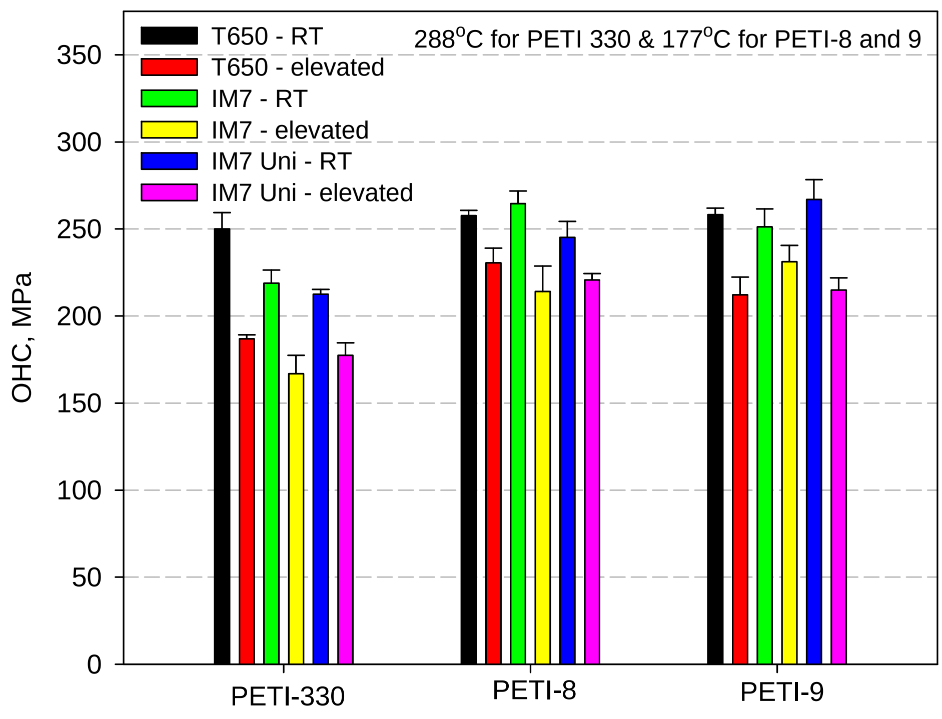

Figure 5: OHC strengths of PETI-8, PETI-9 and PETI-330 measured at RT and ET.

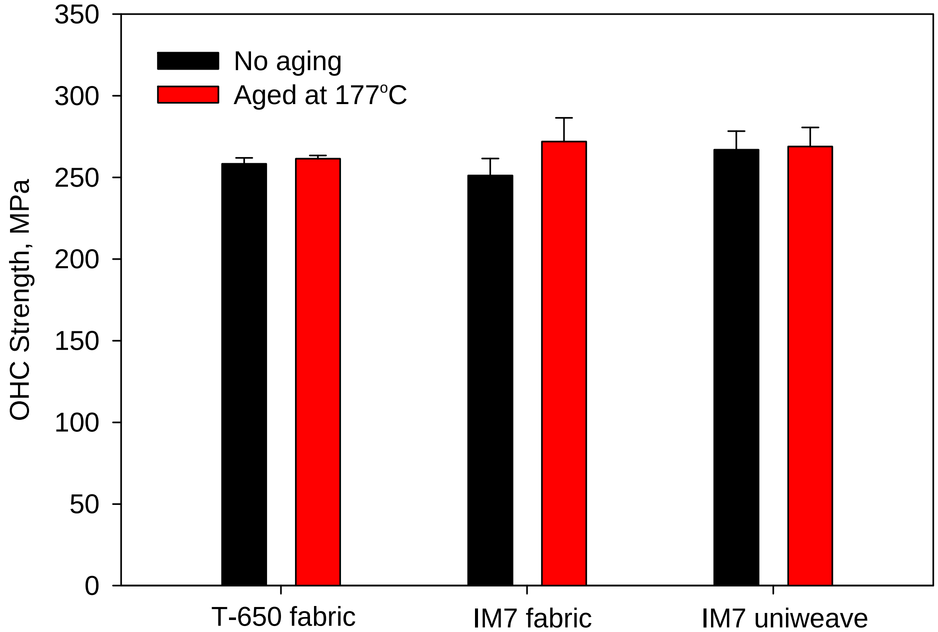

Figure 6: OHC strengths of PETI-9 measured at RT before and after 1000 h aging at 177°C.

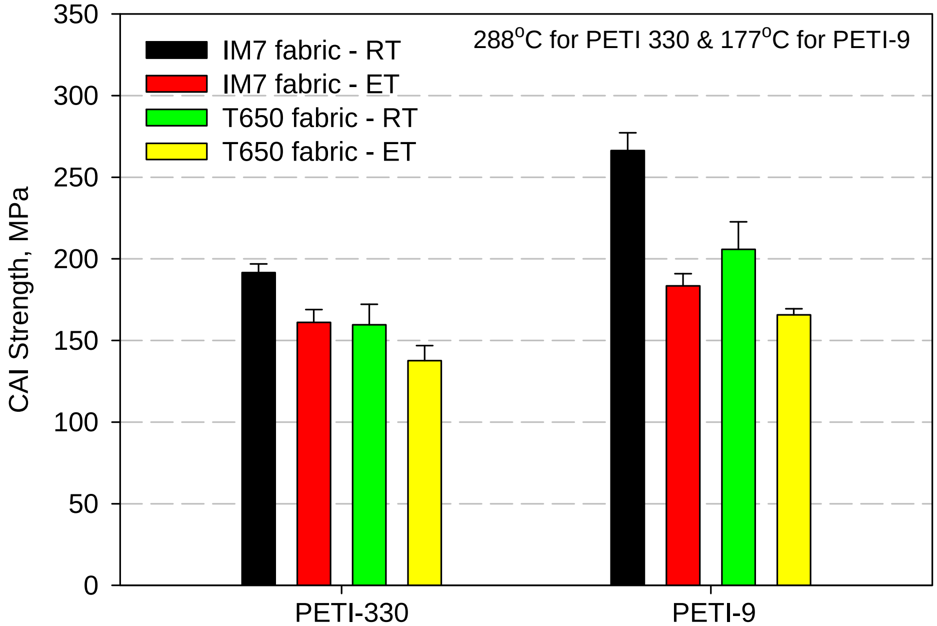

Figure 7: CAI strengths of PETI-330 and PETI-9 composites.

Table 2. Average CAI panel parameters (dropped weight of 5.3691 kg and an indenter with a 1.59 cm diameter hemi-spherical tip).

Material	CAI Test Temp., °C	Impact Energy, J	Drop Height, cm	Max. Force, N	Dent Depth, mm	Damage Area*, cm^2
PETI-330 / IM7 5HS	RT	399.54	63.24	25.41	0.62	3.16
PETI-330 / IM7 5HS	288°	385.97	61.09	25.20	0.51	4.23
PETI-330 / T650 8HS	RT	448.04	70.91	28.26	0.96	8.70
PETI-330 / T650 8HS	288°	460.61	72.90	27.51	0.45	8.56
PETI-9 / IM7 5HS	RT	375.98	59.51	25.38	0.45	1.92
PETI-9 / IM7 5HS	177°	384.04	60.78	25.20	0.58	2.38
PETI-9 / T650 8HS	RT	447.82	70.88	27.63	1.05	3.90
PETI-9 / T650 8HS	177°	451.00	71.38	25.94	1.06	3.14

*approximated from C-scan images post impact

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