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The overall technical objective of the Phase I effort was to extend and advance the state the-art in high temperature composite fabrication techniques by developing a High Tempera Vacuum Assisted Resin Transfer Molding (VARTM) process for polyimide resins. This was accomplished by drawing on M&P Technologies' past "small-scale" fabrication successes, do selecting the best practices/methods, and ultimately demonstrating equivalent properties Resin Transfer Molded Polymer Matrix Composites (PMCs). Specific objectives included 1) develop optimized process parameters for VARTM with scalability in mind, 2) down select t best candidate resins and determine equivalency to RTM panels, and 3) determine applicati for Phase II sub-component demonstrations.

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VARTM PROCESSING OF HIGH TEMPERATURE POLYMER MATRIX COMPOSITES

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1. PROJECT OBJECTIVES

The overall technical objective of the Phase I effort was to extend and advance the state-of-the-art in high temperature composite fabrication techniques by developing a High Temperature Vacuum Assisted Resin Transfer Molding (VARTM) process for polyimide resins. This was accomplished by drawing on M&P Technologies' past "small-scale" fabrication successes, down selecting the best practices/methods, and ultimately demonstrating equivalent properties to Resin Transfer Molded Polymer Matrix Composites (PMCs). Specific objectives included 1) develop optimized process parameters for VARTM with scalability in mind, 2) down select the best candidate resins and determine equivalency to RTM panels, and 3) determine applications for Phase II sub-component demonstrations.

2. WORK PERFORMED

2.1. Resin Characterization. Rheological measurements were conducted using circular parallel aluminum plates (diameter = 25 mm) on a T.A. Instruments AR G2 rheometer at a heating rate of 3°C/min. Specimen disks (2.54 cm in diameter and 1.0 mm thick) were prepared by compression molding imide powder under 13,000 psi for 2 min at room temperature. The compacted resin disk was subsequently loaded into the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a variable strain and a fixed angular frequency of 100 rad/sec while the lower plate was attached to a transducer, which recorded the resultant torque. Storage (G') and loss (G") moduli and complex melt viscosity (η^*) as a function of time (t) were measured at several temperatures. Thermogravimetric analysis (TGA) was performed on a Seiko 200/220 instrument on powder samples at a heating rate of 3°C/min in nitrogen. The samples were heated from room temperature to 800°C.

2.2. Processing Trials. The PETI-330 resin was dried by heating under vacuum to 230-260°C for 30-60 minutes. The J1 polyimide was used "as-received", after degassing for 30 minutes at 260°C, and 5 hours at 260°C. The VARTM trials were conducted using a stainless steel tool and T650-35 carbon fabric. The release plies, fabric, and flow medium were laid up on the tool and bagged using Kapton™ and high temperature bagging putty. The laminate was approximately 254 mm by 305 mm and an eight ply quasi-isotropic lay-up was used. An outer bag was then placed over the inner bag. The tool was then preheated to 288°C with both bags under vacuum. The resin was simultaneously heated from room temperature to 288°C and allowed to melt. The resin was then transferred to a container in the oven and allowed to reach to 288°C. Prior to infusion, the laminate was held at approximately 315°C for 30 minutes to burn off the epoxy size on the T650-35. The inlet valve was then opened and the resin was allowed to infuse into the fabric. Once fully wet-out the laminate was heated to 371°C and allowed to cure for 1 hour for PETI-330 and 3 hours for J1-polyimide. The laminate was then cooled to room temperature at a rate of 3-5°C/min. Figure 1 shows the general VARTM set-up.

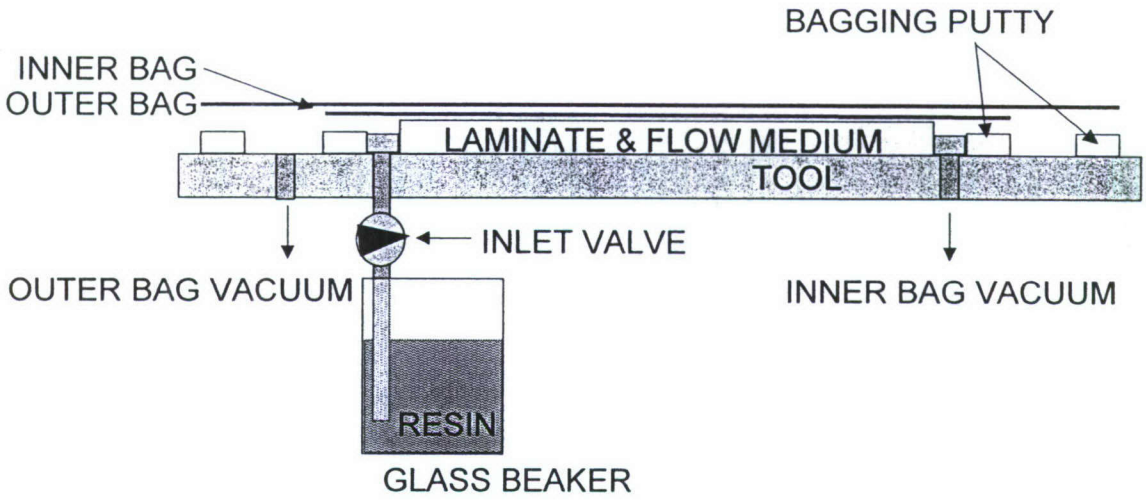


Figure 1. Schematic diagram of VARTM set-up.

2.3. Laminate Characterization. The quality of the laminates was determined using ultrasonic inspection, thickness measurements, acid digestion, dynamic mechanical thermal analysis (DMTA) and photomicrographic analysis. The best and worst areas were then sectioned and photographed. DMTA was performed for determination of the Tg using a Seiko 200/220 instrument on composite samples that were approximately 20 mm x 3.5 mm x 0.5 mm. The DMTA was performed at 1, 10 and 20 Hz. The samples were heated from room temperature to 440°C at a heat rate of 10°C/min in tension mode and 20 micron amplitude. The 10 Hz traces were graphed and the Tg was determined from the slope intercept of the loss modulus curve. Thickness measurements were taken using a micrometer with accuracy to 0.00005 inch. Acid digestion measurements were performed according to the ASTM D2734 method.

In addition to determining the quality of the laminates, Short Beam Shear (SBS) testing was conducted on PETI-330 and J1 polyimide VARTM laminates and Open Hole Compression testing was conducted on the down-selected J1 polyimide composite. Both tests were conducted at room temperature and 288°C (550°F) using ASTM test methods.

3. RESULTS AND DISCUSSION

3.1. Thermal Gravimetric Analysis (TGA) Results. The TGA of the as-received PETI-330 and the de-gassed or dried PETI-330 were very similar showing no volatiles or reduction in weight up to approximately 400°C. The as-received J1 polyimide had over 3 percent reduction in weight at 288°C and approximately 6 percent reduction in weight at 371°C (refer to Figure 2). Therefore, it was decided to degas the J1 polyimide at 260°C for 5 hours per recommendations

from the literature [30] in order to remove the volatiles. A TGA was then redone carried out on the dried or degassed samples and showed no significant weight loss up to approximately 400°C.

3.2. Dynamic and Isothermal Rheology of the Resins. The rheology was determined before and after de-gassing for both resins. The dynamic rheology trace of PETI-330 before and after drying is given in Figure 3. From the curves little difference is seen in the viscosity behavior for the "as-received" versus the dried or de-gassed PETI-330. An isothermal trace of the PETI-330 after drying is given in Figure 4 and shows the resin to have a low enough viscosity (1-3 Pa*s) for infusion for approximately 90 minutes.

The dynamic rheology trace of J1 polyimide is given in Figure 5 for the as-received and the resin that was degassed for 5 hours at 260°C. From the traces it is seen that the degassing step decreased the resin pot life while increasing the resin minimum viscosity, as is shown in Figure 6. It was therefore decided to degas the last batch of resin for only 30 minutes at 260°C.

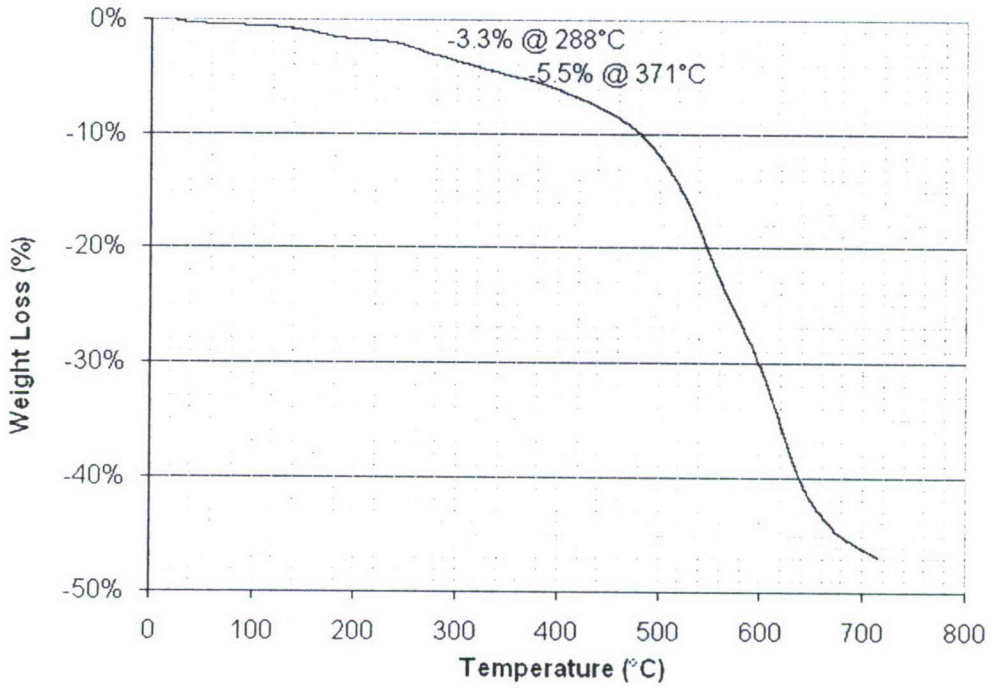


Figure 2. TGA Trace for J1-Polyimide (as-received).

3.3 PETI-330 VARTM Results. Three PETI-330 panels were VARTM'ed and the resultant laminate quality was determined. The first panel (AF-03-1) was VARTM'ed using as-received resin while the second panel (AF-03-2) was VARTM'ed using resin that had been previously de-gassed. During the last VARTM trial (trial 3) the gas-trap broke and therefore the results of the

last run are not given. The acid digestion results of the panels are given in Table 1. From these results it is seen that the PETI-330 VARTM

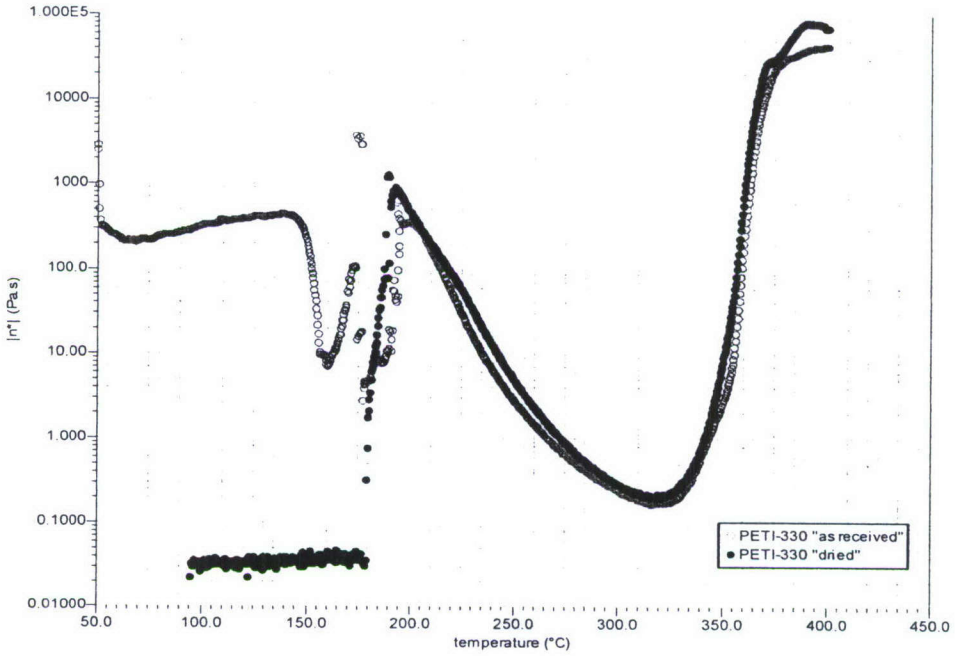


Figure 3. Dynamic Rheology of PETI-330 before and after drying.

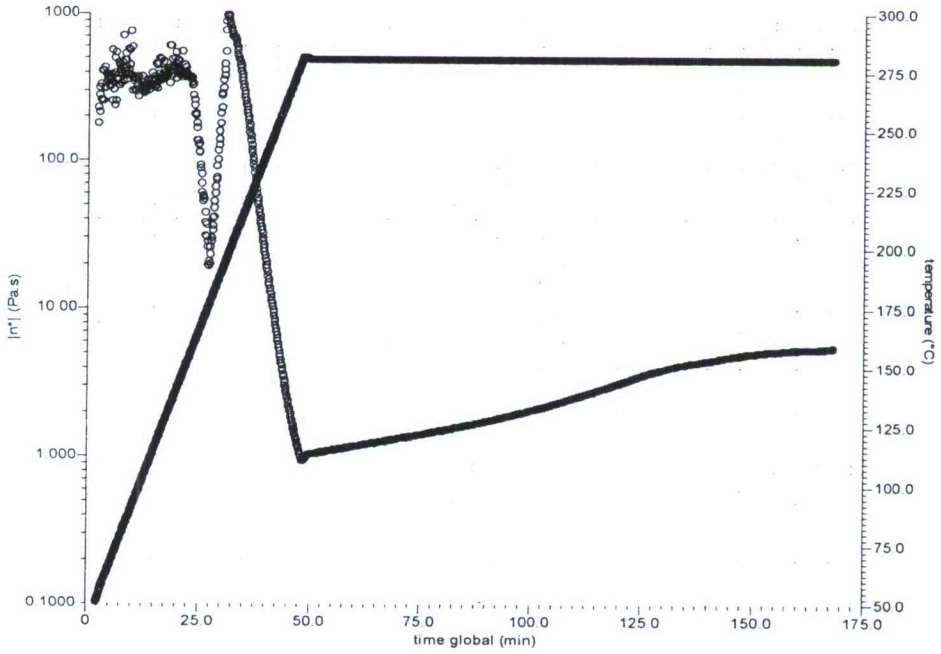


Figure 4. Isothermal viscosity of dried PETI-330 at 288°C (550°F).

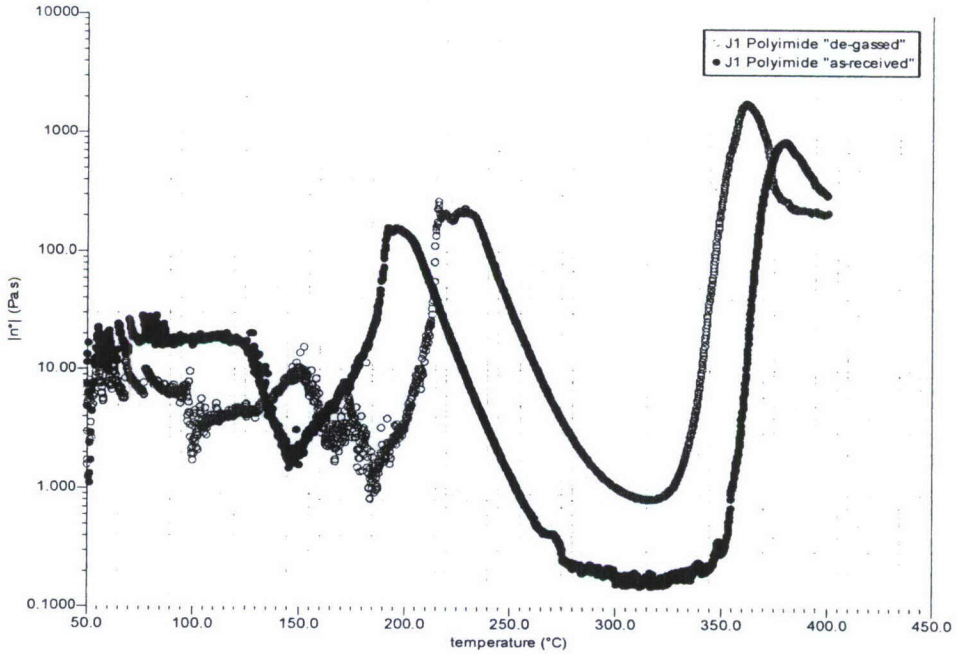


Figure 5. Dynamic Rheology of J1 Polyimide before and after drying.

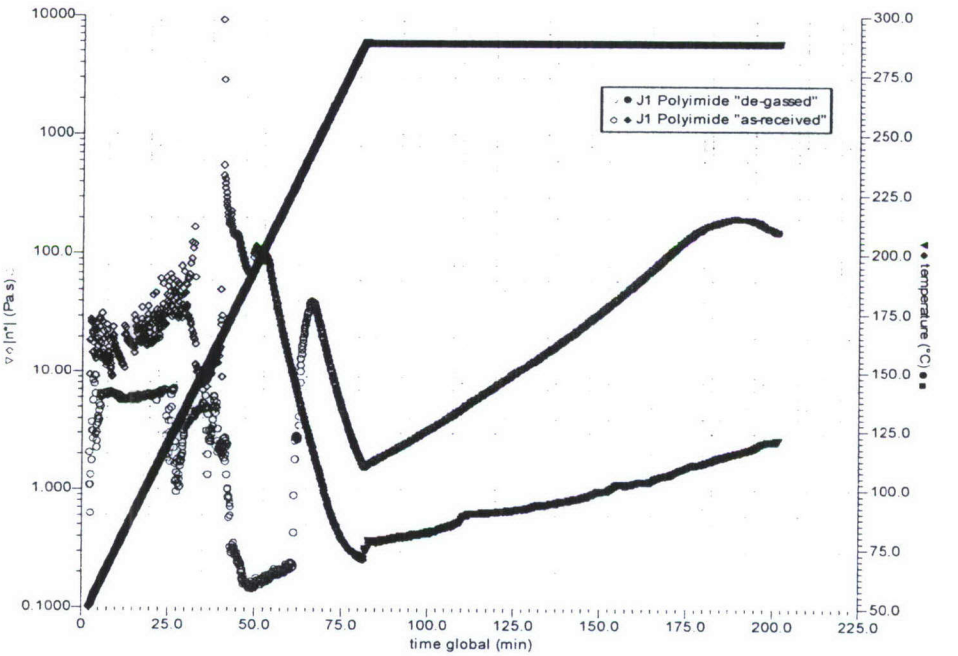
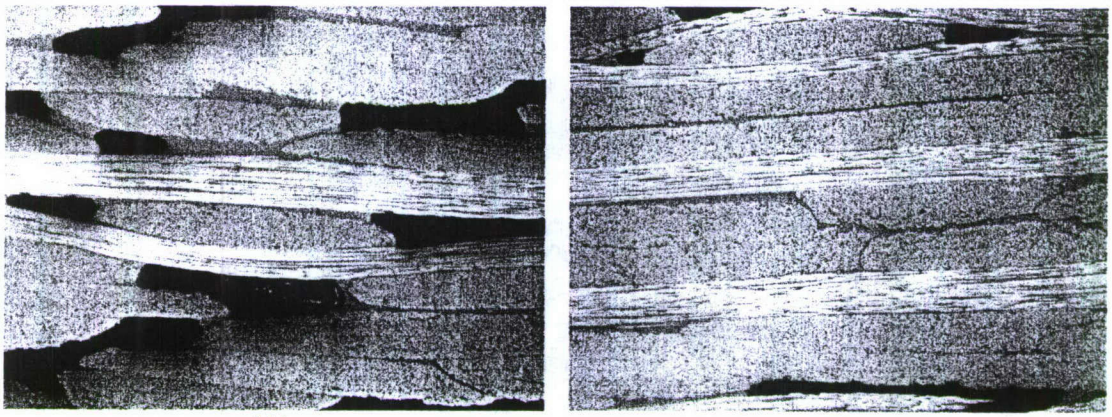


Figure 6. Isothermal traces of J1 Polyimide before and after drying.

trials were able to improve the laminate quality by increasing the fiber volume and decreasing the porosity from trial 1 to 2. Photomicrographs of the panels are given in Figures 7 and 8 and confirm the quality improvement from panel AF-03-1 to AF-03-2. These results show the feasibility of processing PETI-330 laminates using the VARTM process and infer that further processing refinements and optimization will results in high quality laminates.

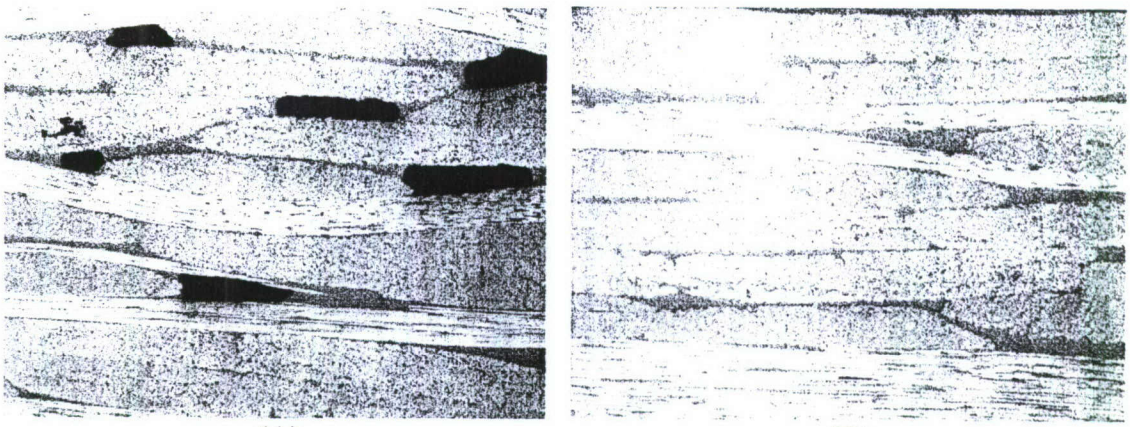
Table 1. Acid Digestion Results for PETI-330 VARTM Panels.

Panel ID	Density (g/cc)	Resin Wt (%)	Fiber Volume (%)	Resin Volume (%)	Voids (%)	Note
AF-03-1	1.49	31.9	57.2	36.0	6.8	Trail 1
AF-03-2	1.53	27.6	62.6	32.0	5.3	Trial 2
AF-03-3	N/A	N/A	N/A	N/A	N/A	Gas-Trap Broke



(A) (B)

Figure 7. Photomicrographs of AF-03-1 panel showing (A) worst and (B) best areas.



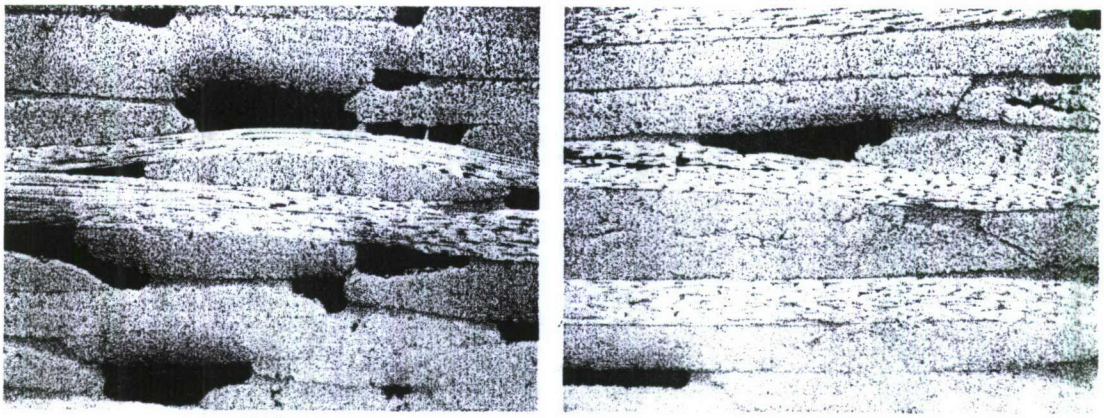
(A) (B)

Figure 8. Photomicrographs of AF-03-2 panel showing (A) worst and (B) best areas.

3.4 J1 Polyimide VARTM Results. Three J1 polyimide panels were VARTM'ed and the resultant laminate quality determined. The first panel (AF-03-4) was VARTM'ed using as-received resin. This panel fully wet-out and had a porosity of approximately 9 percent. It was noticed that the resin appeared to boil and smoke upon heating to 260°C (500°F) and therefore, for the second trial the resin was degassed per the recommended cycle presented in the literature, 5 hours at 260°C [30]. This panel did not fully wet-out presumably because of the reduced processing window and increased viscosity (refer to Figure 5) but did have lower porosity and a higher fiber volume. It was therefore decided to degas the last of the J1 polyimide resin for only 30 minutes at 500°F in an attempt to increase the pot life and reduce the minimum viscosity over the 5 hour degassed sample. This panel did fully wet-out and had a reduced porosity over the first panel and approximately 57 percent fiber volume. The acid digestion results of the three J1 polyimide VARTM trials are given in Table 2. Photomicrographs from the 3 panels are given in Figures 9 to 11 for the 1st VARTM panel to the 3rd VARTM panel, respectively. The photomicrographs visually confirm the acid digestion results. These results show the feasibility of VARTM of J1 polyimide and of improving the current process to achieve high quality composites with low porosity. This is inferred from the steady improvement in panel quality for each successive trial and the ability to achieve 4 percent porosity in only 3 trials.

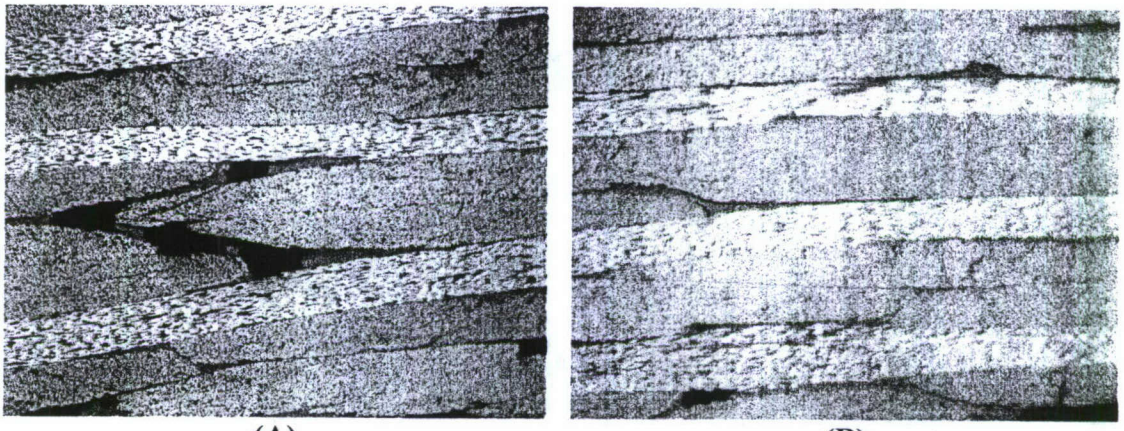
Table 2. Acid Digestion Results for J1 Polyimide VARTM Panels.

Panel ID	Density (g/cc)	Resin Wt (%)	Fiber Volume (%)	Resin Volume (%)	Voids (%)	Note
AF-03-4	1.46	31.7	56.3	35.1	8.6	as received
AF-03-5	1.53	31.5	59.2	36.5	4.3	Degassed 5 hrs/500°F - short shot
AF-03-6	1.48	32.2	56.6	36.1	7.3	Degassed 30 min/500°F



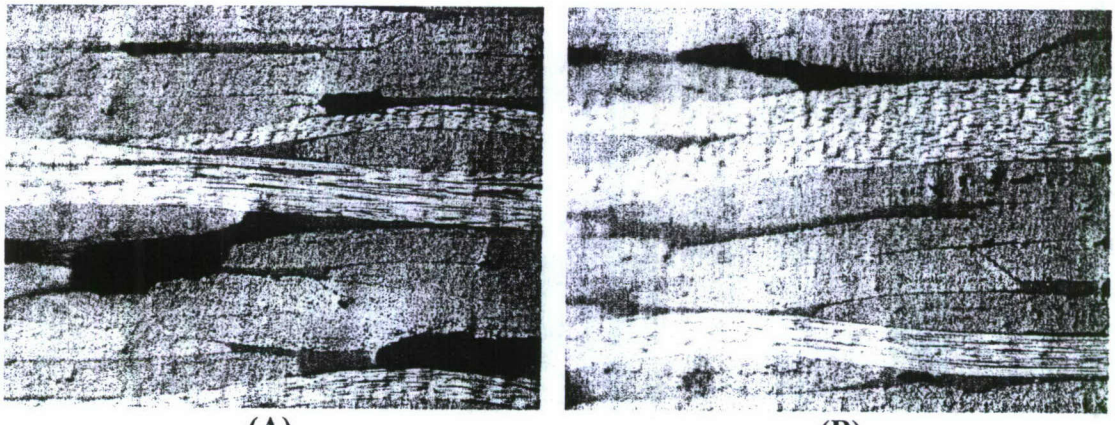
(A) (B)

Figure 9. Photomicrographs of AF-03-4 panel showing (A) worst and (B) best areas.



(A) (B)

Figure 10. Photomicrographs of AF-03-5 panel showing (A) worst and (B) best areas.



(A) (B)

Figure 11. Photomicrographs of AF-03-6 panel showing (A) worst and (B) best areas.

3.5 Thermal and Dimensional Analysis Results. The thickness measurements of the VARTM panels are given in Table 3 along with the per ply thickness (ppt) and fiber volume as determined from thickness and fiber areal weight (FAW). The fiber volumes in the Table are similar to those determined from acid digestion but are slightly lower in general. The PETI-330 laminates were found to have an average Tg of 343 ± 3°C prior to post cure. The panels had not been post cured at the time of submission of this paper. The J1 polyimide had a Tg of 386 ± 8°C.

Table 3. Thickness Measurements on VARTM Panels with ppt and Fiber Volume.

Measurement (inch)	AF-03-1	AF-03-2	AF-03-3	AF-03-4	AF-03-5	AF-03-6
1	0.12440	0.10900	0.13290	0.12435	0.11210	0.12345
2	0.12705	0.11400	0.12855	0.12640	0.11640	0.12610
3	0.12505	0.11105	0.12785	0.12365	0.11585	0.12240
4	0.12410	0.11045	0.13045	0.11785	0.11525	0.12900
5	0.12775	0.11530	0.13400	0.11770	0.11195	0.12375
6	0.13025	0.11705	0.13605	0.12400		0.13500
7	0.12615	0.11755	0.13105	0.11935		0.12200
8	0.12285	0.11035	0.13210	0.11915		0.12770
Average	0.12595	0.11309	0.13162	0.12156	0.11431	0.12618
Stan. Dev.	0.00237	0.00331	0.00274	0.00340	0.00213	0.00436
ppt	0.01574	0.01414	0.01645	0.01519	0.01429	0.01577
*Fiber Volume	53%	59%	51%	55%	58%	53%

*As determined from FAW

3.6 Mechanical Testing Results. Short Beam Shear testing was performed on both PETI-330 and J1-polyimide laminates and the results are given in Figures 12 and 13, respectively. Figure 14 shows comparison of VARMT and RTM laminates and shows that the VARTM laminates have equivalent or better SBS Strength than RTM laminates at 288°C (550°F). OHC testing was only performed on the down-selected J1 polyimide and summary and comparative data is given in Table 4. Figure 15 gives the OHC Strength and Figure 16 gives the OHC Modulus for J1 polyimide VARTM laminates and for PETI-330 and RTM330 RTM laminates. From the data it is seen that the J1 polyimide / T650-35 VARTM laminates have equivalent or better than OHC properties than comparable polyimide/T650 RTM laminates. The OHC specimens were made from an additional VARTM panel that was made after the J1 polyimide down-select. The panel had a fiver volume of 60 percent, a resin weight of 30.2 percent, and a void volume of 5 percent.

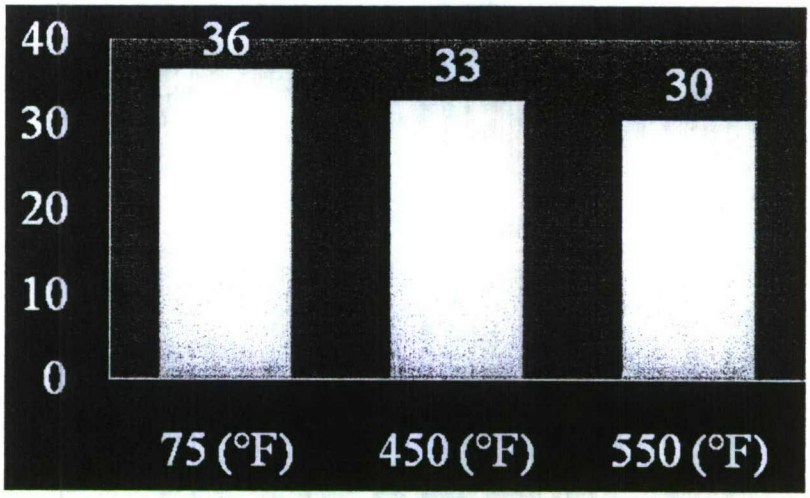


Figure 12. Short Beam Shear Strength (MPa) of PETI-330/T650-35 VARTM Laminates.

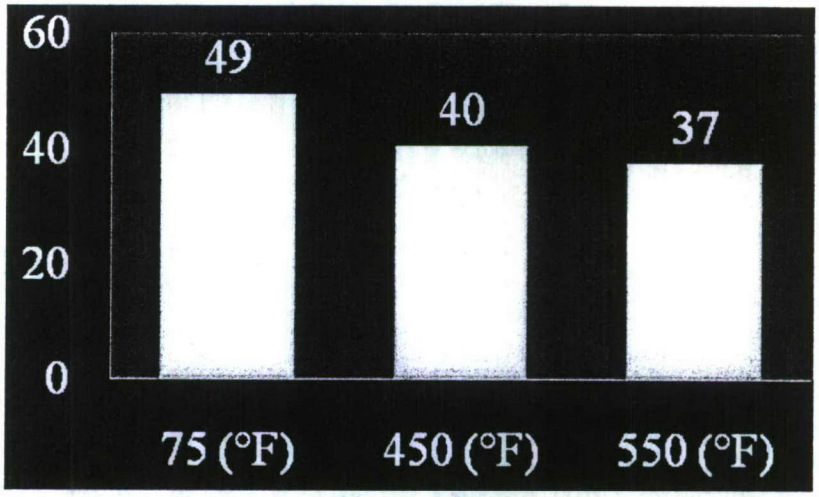


Figure 13. Short Beam Shear Strength (MPa) of J1 Polyimide/T650-35 VARTM Laminates.

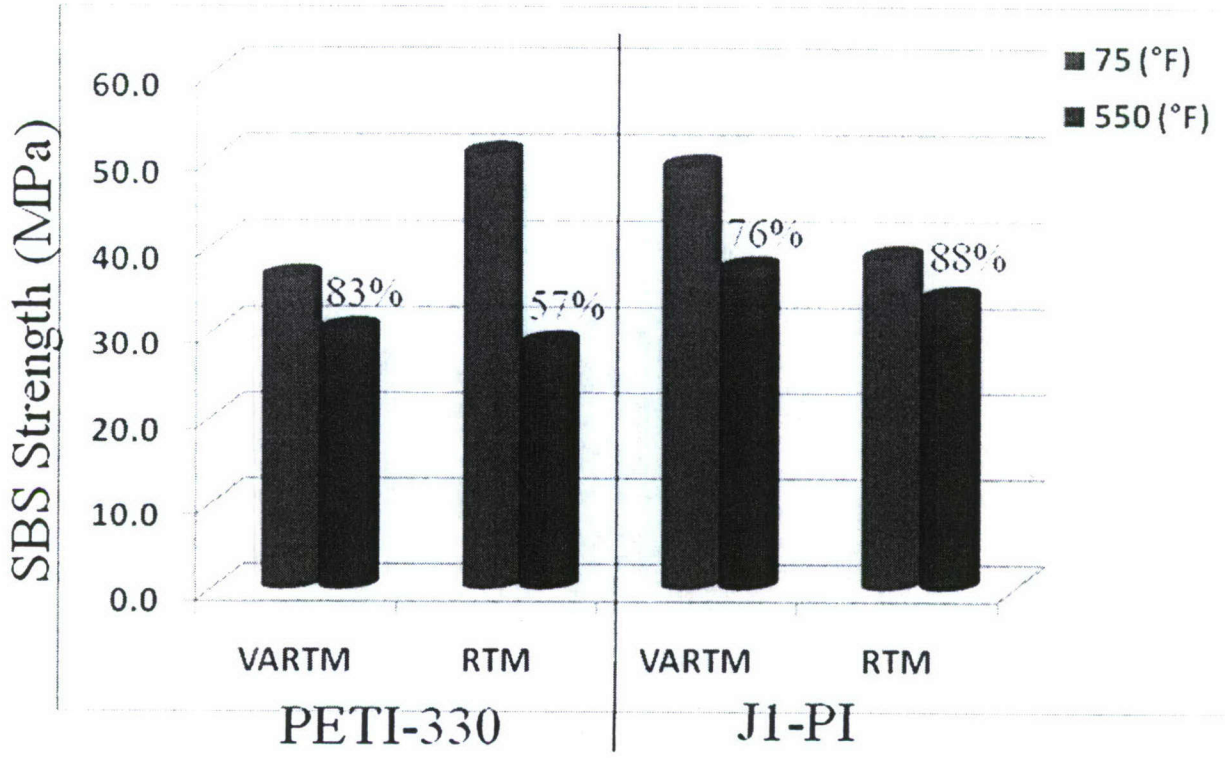


Figure 14. SBS Strength Comparison PETI-330 & J1-PI / T650-35 PMCs showing VARTM laminates to have better than or equivalent properties to RTM.

Table 4. OHC Summary and Comparative Data.

Material	RT Compressive Strength (MPa)	550F Compressive Strength (MPa)	RT Compressive Modulus (GPa)	550F Compressive Modulus (GPa)
*J1 Polyimide / T650-35	255	248	45.0	44.8
**PETI-330 / T650-35	270	200	47.2	45.0
**RTM330 / T650-35	252	220	43.0	45.0

* From VARTM laminate, ** From RTM laminate data obtained from High Temple Website

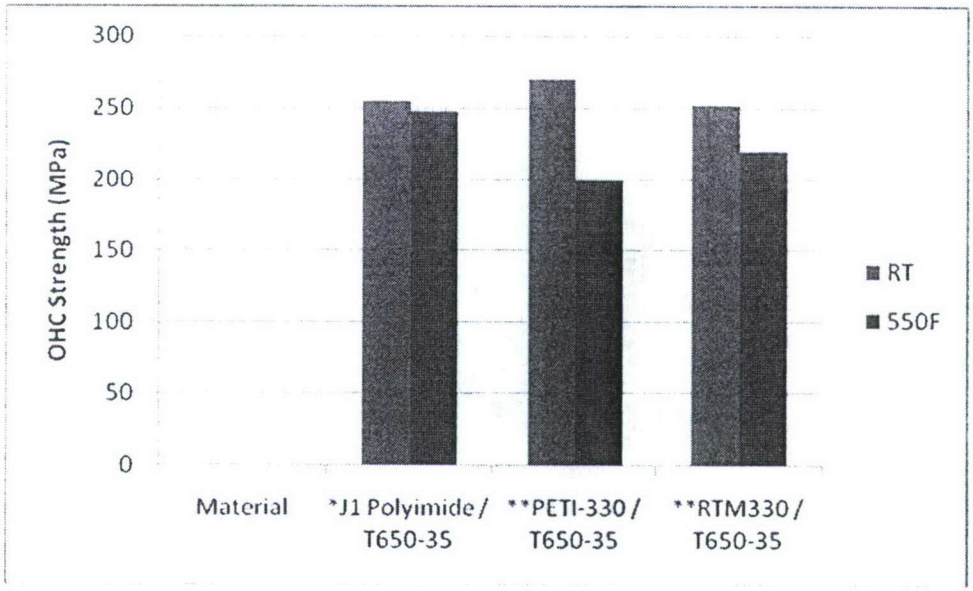


Figure 15. OHC Strength of J1 Polyimide (* = VARTM) at RT and 288°C (550°F) compared to PETI-330 and RTM330 (= RTM) laminates.**

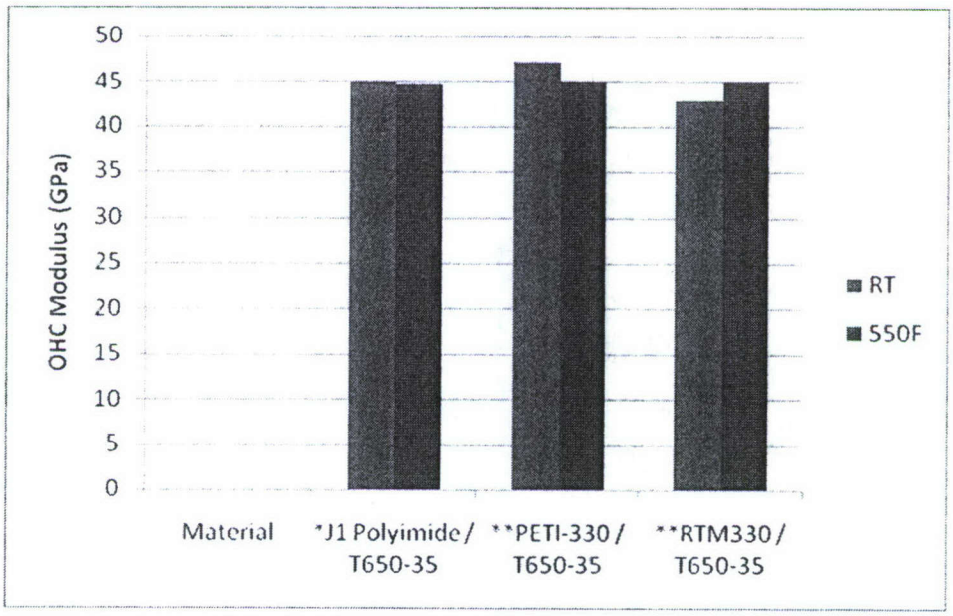


Figure 15. OHC Modulus of J1 Polyimide (* = VARTM) at RT and 288°C (550°F) compared to PETI-330 and RTM330 (= RTM) laminates.**

4. APPLICATIONS

Hypersonic vehicles, including manned systems under development by industry, the Air Force, NASA and DARPA, as well as missile systems will require the high temperature and potential

weight savings characteristics of polyimide composite materials. Unlike RTM materials, which require high production volumes to offset high upfront tooling costs, VARTM polyimide resins are more ideally suited to prototype and limited production runs where reduced tooling costs help retain affordability on low volume applications. Near term examples of potential components from VARTM using polyimide resins include secondary and tertiary structures such as engine cowlings and fairings.

5. CONCLUSIONS, RECOMMENDATIONS & FEASIBILITY

Polyimide resins capable of VARTM processing were developed and processed into high quality composites. These polyimide resins promise to extend both the temperature capability and the lifetime over resins currently available and will be an important technology in the manufacture of affordable supersonic aircraft and reusable launch vehicles. The ability to VARTM these materials will facilitate their use in prototype and limited volume applications. This work has demonstrated the ability to VARTM flat panels having approximately 4 percent porosity for both PETI-330 and J1 polyimide resins with fiber volumes in the upper 50s to 60 percent. This was accomplished in 2-3 trials which infer that further process refinement and optimization will result in even higher quality composites. The composites had Tg's up to 386°C (727°F) which indicates that they have potential use temperatures at approximately 600°F. The PETI-330 and J1 polyimide VARTM panels gave equivalent or better than SBS strength than RTM laminates. The J1 polyimide VARTM panels gave equivalent or better than OHC strength and modulus than RTM laminates. Therefore this work developed a VARTM process for these materials that gives equivalent or better than properties to RTM. This work demonstrated the feasibility to VARTM these new polyimide materials and offers promising technology for the affordable processing of secondary, tertiary, and prototype structures.

Future work would focus on obtaining more complete mechanical properties, on refinement of processing conditions to reduce porosity and improve properties, on scale-up of the process, on determining equivalency and advantages relative to other processes, and on demonstrating the VARTM process on real aircraft components.

6. ACKNOWLEDGMENTS

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8. PUBLICATIONS STEMMING FROM RESEARCH EFFORT

A paper entitled "VARTM OF POLYIMIDE COMPOSITES" was submitted and excepted for publication in the upcoming SAMPE Technical Conference this May.

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