

**Out of the Autoclave Fabrication
of LaRC™ PETI-9 Polyimide Laminates***

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ABSTRACT

The NASA Langley Research Center developed polyimide system, LaRC™ PETI-9, has successfully been processed into composites by high temperature vacuum assisted resin transfer molding (HT-VARTM). To extend the application of this high use temperature material to other out-of-autoclave (OOA) processing techniques, the fabrication of PETI-9 laminates was evaluated using only a vacuum bag and oven cure. A LaRC™ PETI-9 polyimide solution in NMP was prepared and successfully utilized to fabricate unidirectional IM7 carbon fiber prepreg that was subsequently processed into composites with a vacuum bag and oven cure OOA process. Composite panels of good quality were successfully fabricated and mechanically tested. Processing characteristics, composite panel quality and mechanical properties are presented in this work. The resultant properties are compared to previously developed LaRC material systems processed by both autoclave and OOA techniques including the well characterized, autoclave processed LaRC™ PETI-5.

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1.0 INTRODUCTION

Due to their combination of high thermal stability and mechanical properties with improved processability, 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-9 resin system has been synthesized (Figure 1) at LaRC and is a phenylethynyl endcapped aromatic polyimide ($M_n \sim 1125$ 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, which is similar to the autoclave processable PETI-5 resin ($T_g \sim 270^\circ\text{C}$) previously developed at LaRC.

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 [1,2]. It has demonstrated the ability to significantly reduce the manufacturing cost of these structures. Studies using epoxy resin systems have demonstrated that the VARTM process can make void free structures with fiber volume fractions approaching 60% [3]. Recently, the VARTM process has been extended to the fabrication of composite panels from polyimide systems developed at NASA LaRC. Various LaRC polyimides (i.e. PETI-8, PETI-9, PETI-330) 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. The evaluation of these resins has shown that they exhibit the necessary melt flow characteristics for HT-VARTM processing. 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%) [4-6].

Recently, industry has developed VBO versions of toughened epoxies that are resulting in strength properties and specific stiffness equivalent to polymer matrix composites (PMC) structure cured in an autoclave. These results promise to lower the cost and thereby further increase the use of PMC as primary structure on aerospace vehicles. During the past five years, CYTEC Engineered Materials has developed an OOA prepreg material to significantly lower the manufacturing costs associated with large-scale carbon fiber reinforced polymer (CFRP) structure. This OOA prepreg composite material, CYCOM® IM7/5320-1, has been shown to provide equivalent or better properties than the autoclave epoxy prepreg system, CYCOM® IM7/977-3. After lay-up, the part is vacuum-bagged and cured in an oven at $\sim 176^\circ\text{C}$ ($\sim 350^\circ\text{F}$) using atmospheric pressure only (101 KPa, 14.7 psi), resulting in aerospace quality CFRP parts with fiber volume fraction (FVF) exceeding 60% and void content of less than 2% [7].

Since PETI-9 has a very low melt viscosity at elevated temperature and remains soluble after imidization, it is an ideal candidate for a VBO prepreg. Solution prepregging utilizing polyimides as fully imidized polymers in solvents such as N-methylpyrrolidinone (NMP) is a viable technique for producing unidirectional prepreg tape. The low viscosity PETI resins can be processed by VBO cure by tailoring the pre-impregnated carbon fiber tape and carefully controlling the process cycle.

In order to further the state-of-the-art in lightweight structure and increase their operational temperature regime, the NASA LaRC PETI-9 resin system has been developed for application in OOA-VBO processing. This effort utilized the existing NASA LaRC multipurpose tape machine to develop out-of-autoclave, vacuum bag oven (VBO) processable pre-impregnated tape to fabricate high-performance, fiber-reinforced composite primary structure with increased temperature resistance for future aerospace vehicles.

2.0 EXPERIMENTAL

2.1 Materials

A 30 wt% solids solution of LaRC PETI-9 polyimide resin in NMP which had a Brookfield viscosity of 5500 cP at 52°C (125°F) was obtained from Imitec Inc., Schenectady, NY, USA. Hexcel IM7 12k unsized carbon fiber was exclusively in the current work.

2.2 VBO Tape Fabrication

The NASA LaRC prepregger [10-12] shown schematically in Figures 2 and 3 has the capability of prepregging uni-tape from resin solution, films and powders. Utilizing the LaRC prepregger, the PETI-9 imide solution was used to coat unsized IM7 fiber to fabricate unidirectional tape of various widths. The properties of the resultant prepreps are presented in Table 1.

Table 1. IM7/ PETI-9 VBO prepreg characteristics.

Prepreg Run	Fiber Areal Weight, g/m ²	Volatiles, wt% (wet)	Resin, wt% (dry)	Length, m	Width, cm
TM343	142	13	40-43	8.6	8.9
TM344	130-145	11-13	42-46	17	8.9
TM346	145	13-15.5	50	42	21.6

2.3 Composite Characterization

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 [4].

2.4 Composite Mechanical Properties

Mechanical properties, including flexural, short beam shear (SBS), short block compression (SBC) and open hole compression (OHC) strengths, of the cured composite panels were determined at NASA LaRC. Flexural and SBS properties were determined following ASTM C790 and ASM D2344, respectively, utilizing a Sintech 2W mechanical testing machine with a 4.4 kN (1000 lb) load cell. The specimens were tested at a displacement rate 1.27 mm/min. SBC testing was performed according to the NASA standard [13] and OHC testing was performed following the Northrop OHC test [14]. Both tests were done using an Instron test stand with an 88.96 kN (20 kip) load cell.

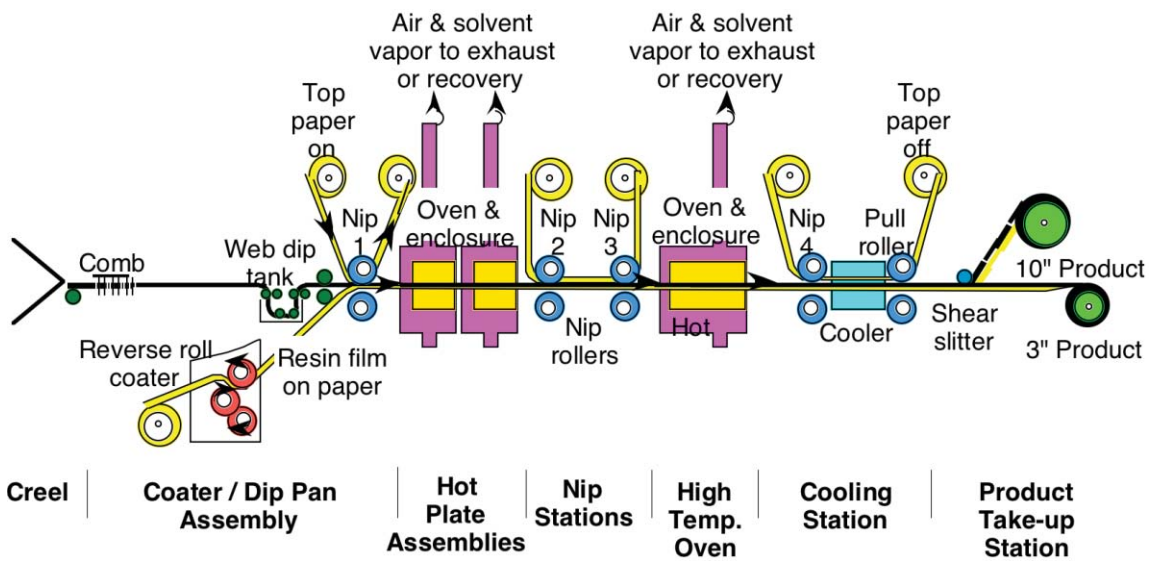


Figure 2. Schematic of LaRC multipurpose prepreg machine.

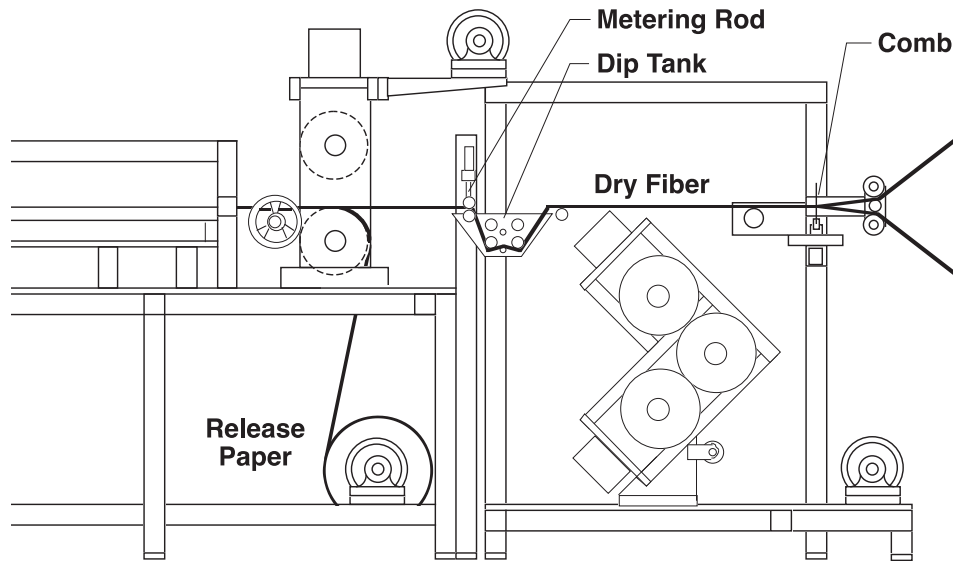


Figure 3. Schematic of solution coating.

3.0 RESULTS AND DISCUSSION

3.1 VBO Prepreg

The NASA LaRC prepregger [10-12] (Figures 2 and 3) was successfully utilized to fabricate PETI-9 imide resin/ unsized IM7 fiber unidirectional tape of various widths. The PETI-9 solution was placed into the dip tank which was heated to approximately 52°C where the IM7 fiber passed through going over and under a set of bars which worked the solution into the fiber tows. The wetted fibers were pulled through a set of metering rods set to a specified gap to control the resin content of the material. The impregnated fibers were then passed through a series of ovens and nip rollers to de-volatize and shape the material to the proper dimensions and uniformity across the width. Despite being fully imidized, the PETI-9 imide solution behaved similarly to previous PETI amid acid solutions resulting in good quality prepreg with few splits and gaps. During the third prepregging run for scale up, the resin content (Table 1) was increased since the initial processing trials demonstrated excessive resin bleed during the composite processing.

3.2 VBO Composites

Composite panels were fabricated utilizing a vacuum bag oven cure process. PETI-9 prepreg was cut and laid up onto a tool with bleeder and breather cloth top and bottom. The panel was vacuum bagged and processed with the same staged cure cycle developed for HT-VARTM PETI-9 panels. This cure cycle had been demonstrated to result in low void content HT-VARTM PETI-9 panels [4-6]. Initial processing trials resulted in a wavy surface finish. The addition of a top caul plate eliminated this issue. Both

unidirectional and quasi-isotropic panels were fabricated. The resulting characteristics of the panels are presented in Table 2. Typical photomicrographs of the panels are presented in Figures 4 and 5. As shown in the table, the unidirectional panels resulted in very high fiber volume fractions and void volume in the 2-3% range. These panels were fabricated from the initial narrow prepreg runs TM 343 and TM 344. The quasi-isotropic panels resulted in a fiber volume fraction of 62% and void volume of 3.4%. Quasi-isotropic panels were fabricated with the wider prepreg which had a higher resin content. As seen in Figure 4, the voids found in these panels tended to be large in size. Figure 5 shows the high fiber packing and typical void formation for unidirectional panels. These types of voids appear to be similar in type to those observed for HT-VARTM panels. [4-6]

Table 2. VBO composite panel characteristics.

Material	Composite Lay-up	Fiber Volume, %	Void Volume, %	Prepreg Run	Test
IM7/ PETI-9	[0] ₂₀	70.5	2.1	343	SBS
IM7/ PETI-9	[0] ₁₂	70.4	2.99	344	Flex
IM7/ PETI-9	[-45/0/45/90] _{4s}	62.9	3.43	346	SBC
IM7/ PETI-9	[±45/90/0/0/±45/0/0/±45/0] _s	n/a	n/a	346	OHC

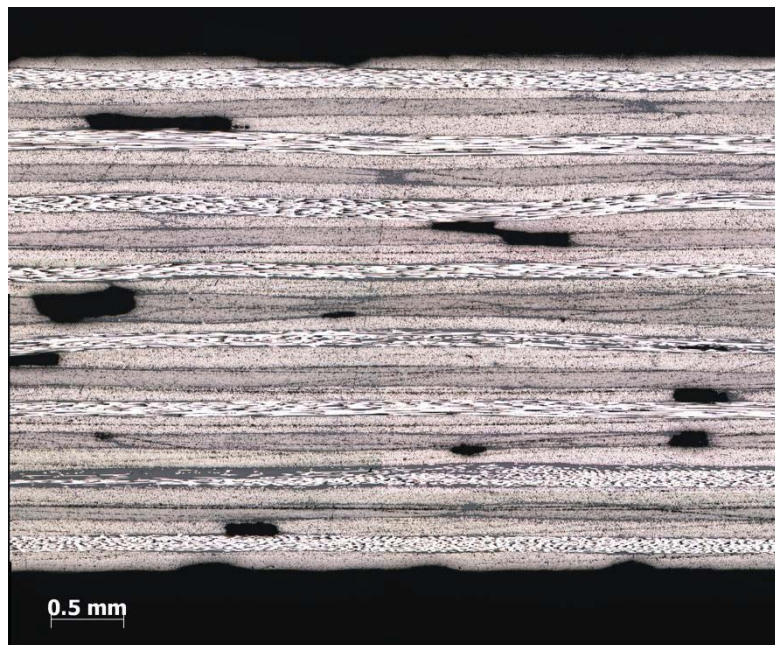


Figure 4. Photomicrographs of quasi-isotropic 32 ply IM7/ PETI-9 VBO panel. [3.43 % voids, 63% fiber by volume]

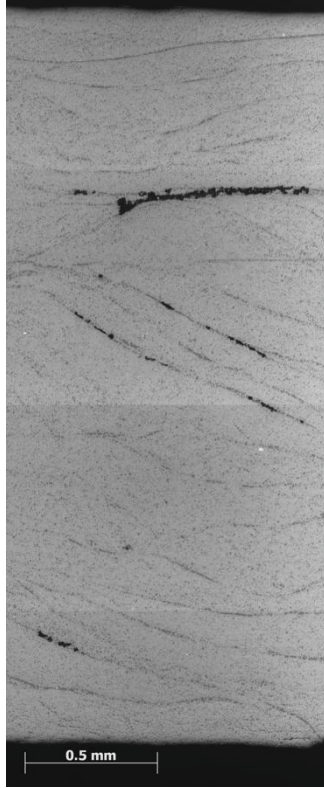


Figure 5. Photomicrographs of unidirectional IM7/ PETI-9 VBO panel.
[2 % voids, 70% fiber by volume]

3.3 Mechanical properties

The mechanical properties obtained in this work are compared to data from Reference 6 and are shown in Figures 6, 7, and 8. For comparison, data from panels that were processed as described in Section 3.2, but were cured with the addition of a consolidation pressure of 586 kPa (85 psi) in an autoclave are also presented. As shown in Figures 6 and 7, the PETI-9 VBO SBS and flexural properties compare quite well to those of the same material that was autoclaved, as well as to those of PETI-5 processed in an autoclave. These properties were better than those of PETI-8 and PETI-9 panels when processed by HT-VARTM. SBS strength properties at elevated temperatures were higher than the other materials as well.

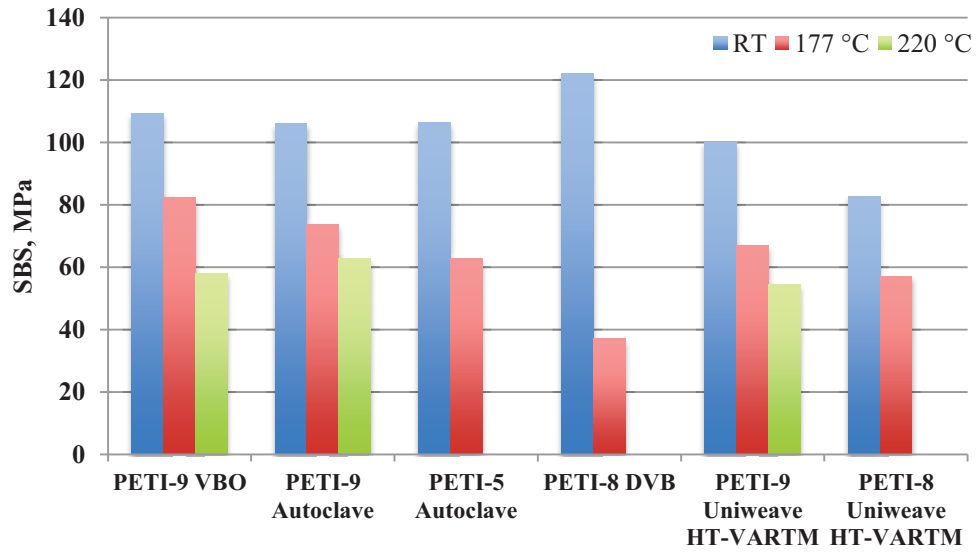


Figure 6. Short beam shear data of various PETI composites.

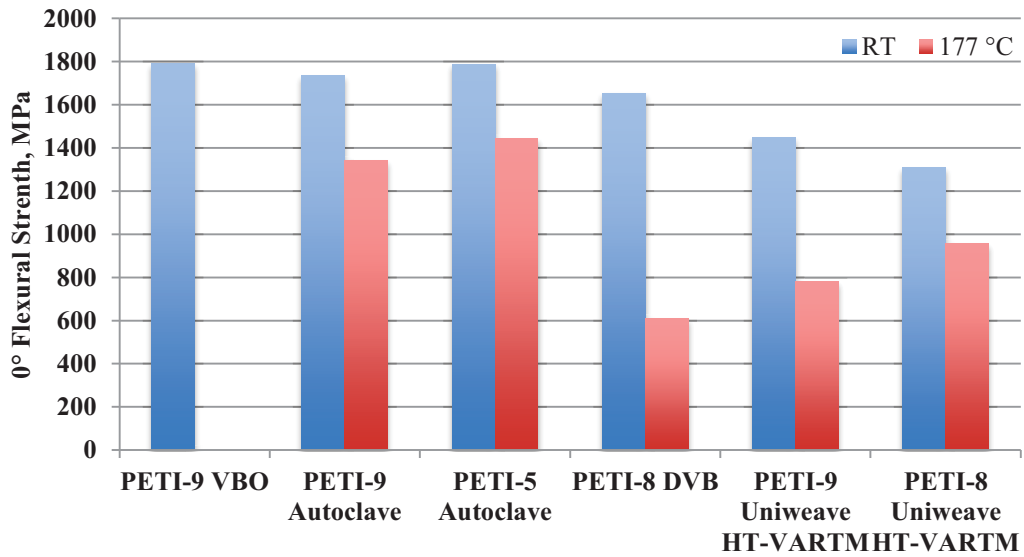


Figure 7. Flexural data of various PETI composites.

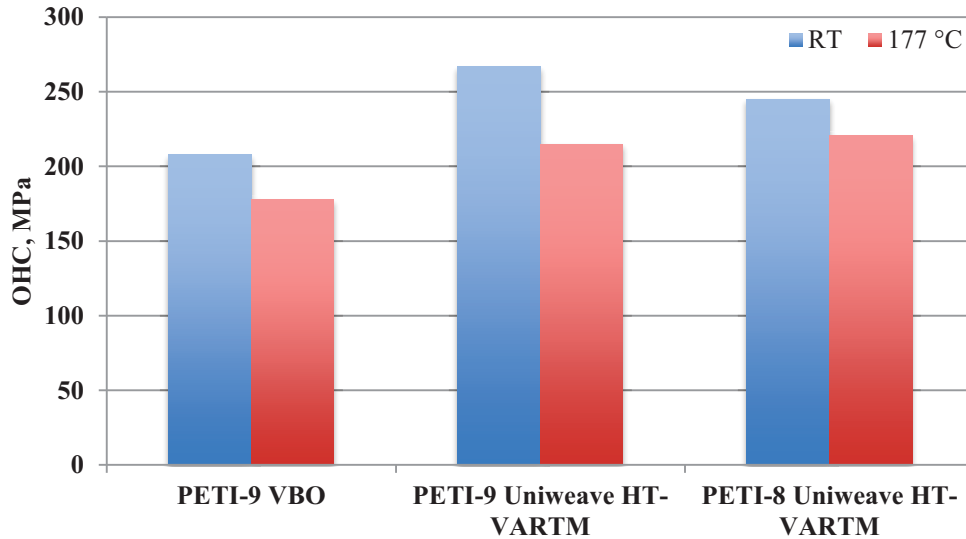


Figure 8. OHC data of various PETI composites.

As shown in Figure 8, the OHC results were lower than those obtained for both PETI-9 and PETI-8 HT-VARTM panels from previous work. However, it is important to note that the data generated in this work used the Northrop OHC test while the HT-VARTM data is based on the ASTM D6484 OHC standard. The smaller Northrop OHC specimen was chosen for this work because of a limited amount of prepreg. The Northrop OHC uses a 7.62 by 2.54 cm specimen with a $[\pm 45/90/0/0/\pm 45/0/0/\pm 45/0]_s$ layup while the ASTM OHC test used a 30.48 by 3.81 cm specimen with a $[-45/0/45/90]_{4s}$ layup. Both specimen types have a 0.635 cm hole centered on the test coupon. The retention of properties at 177°C was very good as it retained 86% of its RT OHC strength. The IM7/PETI-9 baseline compression results based on the NASA SBC test resulted in a value of 409 ± 31 MPa, which is quite similar to the SBC value of 426 MPa obtained for IM7 5-harness satin weave/ PETI-9 HT-VARTM panels. [6]

4.0 CONCLUSIONS

The NASA LaRC developed PETI-9 resin system, was successfully processed into composite panels with void volume contents of 2-3% utilizing a VBO process. The fully imidized solution was successfully used to make high quality prepreg that lends itself to VBO processing. These preliminary SBS and flexural properties of the resultant composites were very similar to previous LaRC materials processed by both HT-VARTM (101.4 kPa) and autoclave (586 kPa-1.4 MPa). The OHC compression data determined with the Northrop OHC test demonstrated lower properties when compared to previous materials fabricated by other processes and tested by the ASTM OHC test. Overall, the initial results indicate that PETI-9 could be a viable high temperature resistant resin system that can be processed without an autoclave by a VBO process. Further optimization of the process could further improve panel quality and mechanical

properties. The excess resin bleed during processing can be reduced by either lower compaction pressures during processing, or by a small increase in the molecular weight during the polyimide synthesis.

5.0 ACKNOWLEDGEMENTS

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