

Composite Properties of RTM370 Polyimide Fabricated by Vacuum Assisted Resin Transfer Molding (VARTM)

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ABSTRACT

RTM370 imide resin based on 2,3,3',4'-biphenyl dianhydride (a-BPDA), 3,4'-oxydianiline (3,4'-ODA) with the 4-phenylethynylphthalic (PEPA) endcap has been shown to exhibit a high cured T_g (370 °C) and low melt viscosity (10-30 poise) at 280 °C with a pot-life of 1-2 h. Previously, RTM370 resin has been successfully fabricated into composites reinforced with T650-35 carbon fabrics by resin transfer molding (RTM). RTM370 composites exhibit excellent mechanical properties up to 327°C (620°F), and outstanding property retention after aging at 288°C (550°F) for 1000 h. In this work, RTM370 composites were fabricated by vacuum assisted resin transfer molding (VARTM), using vacuum bags on a steel plate. The mechanical properties of RTM370 composites fabricated by VARTM are compared to those prepared by RTM.

KEY WORDS: Polyimide, Resin Transfer Molding (RTM), VARTM, Advanced Composites

1. INTRODUCTION

Traditionally polyimide composites have been fabricated into laminates from unidirectional prepregs or fabrics impregnated with resins. Most notably, PMR-15 composites [1] were fabricated from prepregs containing the monomer reactants in methanol, and Avimid N[®] [2] and PETI-5 [3] composites were processed from prepregs containing polyamic acid resins dissolve in high boiling N-methyl-2-pyrrolidinone (NMP). To fabricate complex shaped components, the aerospace industry often relies on costly hand lay-up or towpreg placement. In addition, the NMP or alcohol contained in the prepregs must be removed during processing, which is difficult for thick parts, and could lead to undesirable high void content in the composites or a high scrap rate for production. Therefore, it would produce significant cost savings (~30%), if the polyimide could be adapted to low-cost manufacturing processes, such as resin transfer molding (RTM) or vacuum assisted resin transfer molding (VARTM), similar to what is commonly used for epoxy and bismaleimide (BMI) composite fabrication in the aerospace industry.

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The major obstacle to fabricating polyimide composites by RTM or VARTM, via the injection of imide resins into carbon fiber preforms with desirable shapes under pressure or vacuum, is the high melt viscosities commonly associated with polyimides. Over the past 10 years, significant advances have been made to lower the melt viscosities of polyimides by making lower molecular weight imide oligomers terminated with 4-phenylethynylphthalic anhydride (PEPA), which exhibited a wide processing window between the melt and the crosslinking of the PEPA endcap. PETI-298 (cured $T_g = 298$ °C) derived from 3,3',4,4'-biphenyl dianhydride (s-BPDA), a mixture of 3,4'-oxydianiline (3,4'-ODA) and 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) with the PEPA endcap, displayed a low melt viscosity (complex viscosity, $\eta^* = 6-10$ poise at 280 °C) adaptable to RTM processing [4].

The real breakthrough in the development of low melt viscosity imide oligomers hinges upon the discovery that 2,3,3',4'-biphenyl dianhydride (a-BPDA) produces lower melt viscosity imide oligomers with higher glass transition temperature (T_g) than the corresponding s-BPDA. NASA Langley's PETI-330 [5] formulated from a-BPDA, 1,3-bis(4-aminophenoxy)-benzene (1,3,4-APB) and 1,3-phenylenediamine with the PEPA endcap exhibited a low complex melt viscosity (η^*) of 18-30 poise at 280 °C and a cured T_g of 330 °C. Furthermore, PETI-375, derived from a-BPDA, 1,3,4-APB and 2,2'-bis(trifluoromethyl)benzidine and terminated with PEPA endcap, showed a higher T_g of 375 °C and improved thermo-oxidative stability [6]. PETI-330 and PETI-375 have been successfully fabricated into composites with low-void content by RTM.

Previously we have reported an alternative approach to prepare low melt-viscosity imide oligomers by a solvent-free melt process using a-BPDA and kinked diamines, such as 3,4'-oxydianiline (3,4'-ODA), 3,4'-methylene dianiline (3,4'-MDA) and 3,3'-methylenedianiline (3,3'-MDA), along with the PEPA endcap [7]. Other asymmetric dianhydrides, such as 3,4'-oxydiphthalic anhydride (a-ODPA) [8] and 2,3,3',4'-benzophenone dianhydride (a-BTDA) [9], have also been successfully used to make low melt-viscosity imide resins in combination with kinked diamines and the PEPA endcap [10].

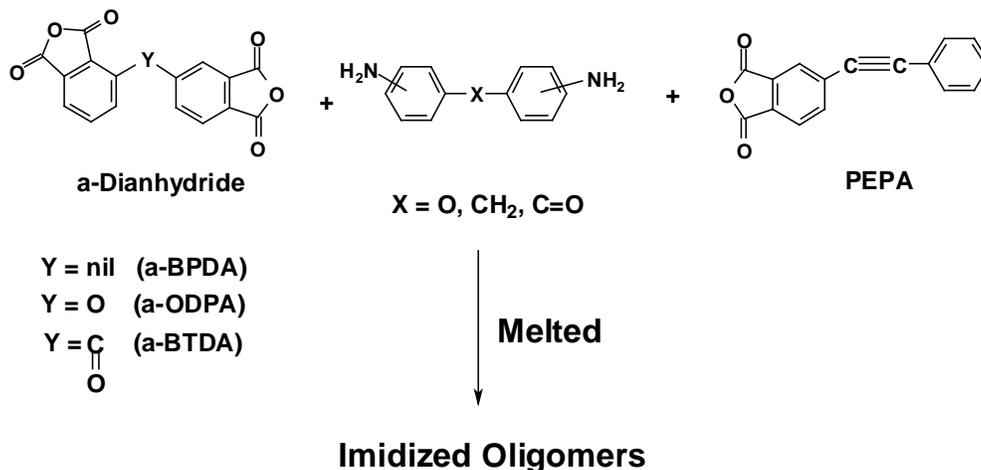


Figure 1. Preparation of low-melt viscosity imide resins by a solvent-free process.

RTM370 resin formulated from a-BPDA, 3,4'-Oxydianiline (3,4'-ODA) and PEPA endcap displays high cured T_g of 370 °C and low melt-viscosity (10-30 poise) and a long pot-life (1-2 h). RTM370 composites fabricated by RTM also exhibit excellent mechanical properties at 315 °C and outstanding strength retention after isothermal aging at 288 °C for 1000 h in air [9].

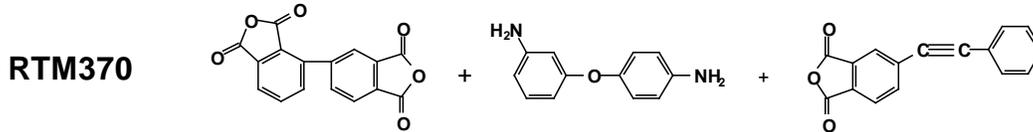


Figure 2. Composition of RTM370 imide resin.

The objective of this work was to fabricate RTM370 composites by VARTM, and compare the physical and mechanical properties of VARTM panels with those made by RTM. Both RTM and VARTM use net shape fiber preforms to meet requirements for complex parts, instead of relying on prepreg hand lay-up or towpreg placement [11]. However, RTM requires molds which can be expensive for large or complex structures, whereas VARTM [12] can simply use vacuum bags and a single tool. RTM uses positive pressure to push the resin into preforms in a closed mold, which is a faster process than VARTM, where resin is drawn into the preform by vacuum and the speed to fill the preform is dependent primarily on the resin viscosity. A contrast between VARTM and RTM processing conditions are summarized in Table 1 [13].

Table 1 Comparison of VARTM vs RTM Processes

Parameter	VARTM	RTM
Mold	Use vacuum bags	Need a mold
Resin infusion by	Vacuum pump	Injector equipment
Injection /vent pressure	0 Pa / 0.1 MPa	0.6-1.5 MPa / 0.1 MPa
Compaction Pressure	0.1 MPa	1-100 MPa
Fiber volume fraction	0.5-0.6, Typically lower	0.5-0.6
Part size	Large Scale	Small to medium scale
Part Production	Low volume	Low to medium volume

2. EXPERIMENTAL

2.1 Resin Preparation and Characterization

The RTM 370 imide resin used in this VARTM study was supplied by Akron Polymer Systems in Akron, Ohio. A mixture of 2,3,3',4'-biphenyl dianhydride (a-BTDA), 3,4'-oxydianiline (3,4'-ODA), 4-phenylethynylphthalic anhydride (PEPA) and the respective diamine was melted

above 200 °C for 1 h to form the corresponding phenylethynyl terminated imide oligomers. The resulting solids were then ground into powders. The rheology was measured by a Ares Rheometer manufactured by TA Instruments, using the parallel plate geometry with 1 g of imidized powder at a ramp rate of 4 °C/min and frequency at 10 rad/sec.

2.2 Composite Fabrication

The preforms were constructed from 8 harness satin weave (8HS) carbon fabrics with a polyimide high temperature size (HTS), using an 8-ply quasi-isotropic lay-up [+45/0/90/-45]_s. The composite panels were fabricated using a high temperature VARTM process [14]. VARTM processing was conducted by laying the release plys, fabric and flow medium on top of a stainless steel tool, using Kapton to construct an inner bag and an outer bag sealed with high temperature bagging putty. The tool and the vacuum bags were preheated to 288 °C for 1 h under vacuum, while 600g of resin was also heated from ambient to 288 °C to achieve a melt state and degassed under vacuum. The melted resin was then drawn from a reservoir heated at 288° C to wet out the preforms under 0.1 MPa of vacuum, in contrast to 1.38 MPa pressure used in RTM. The composites were cured at 371 °C (700 °F) for 2 h and then further post-cured in an oven at 343 °C (650 °F) for 8 h to enhance the mechanical properties of the composites at elevated temperatures.

3. RESULTS AND DISCUSSION

3.1 Physical properties and viscosity profiles of neat resins

RTM370 imide resin, formulated with a-BPDA, 3,4'-oxydianiline (3,4'-ODA) and 4-phenylethynylphthalic anhydride, exhibited a high glass transition temperature (T_g = of 370 °C), after postcure at 371 °C (700 °F) for 16 h (Table 2). RTM370 resin displayed a low melt-viscosity of 6.6-35 poise for the first hour of the hold at 280 °C, and viscosity increased to 85 poise during the second hour of the hold (Figure 3).

Table 2. Physical Properties of RTM370 Imide Resin

Resin	Dianhydride	Diamine	Cured Resin T_g /NPC ¹ By TMA ³	Cured Resin T_g /PC by TMA ³
RTM370	a-BPDA	3,4'-ODA	342 °C	370 °C ²
RTM370 Composite ⁴			338 °C ⁵ by DMA ⁶	350° C ⁵ by DMA ⁶

¹ NPC = No Post-cure

² PC = Post-cured at 371°C (700°F) for 16 h.

³ TMA = Thermal mechanical analysis heated at 10°C/min, using expansion mode.

⁴ The composite specimens were post-cured at 343°C (650°F) for 8 h.

⁵ T_g based on the onset of decline of storage modulus G' .

⁶ DMA = Dynamic mechanical analysis were performed at 5 °C/min heating rate, using a single cantilever.

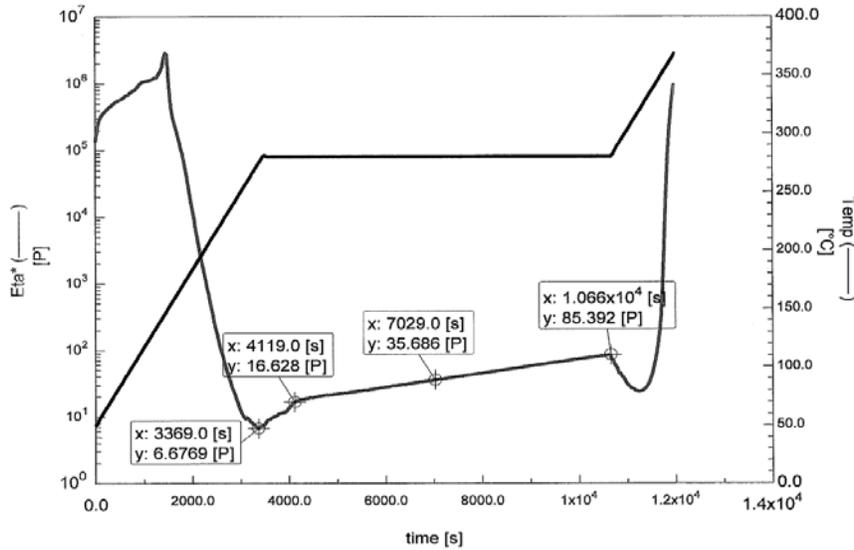
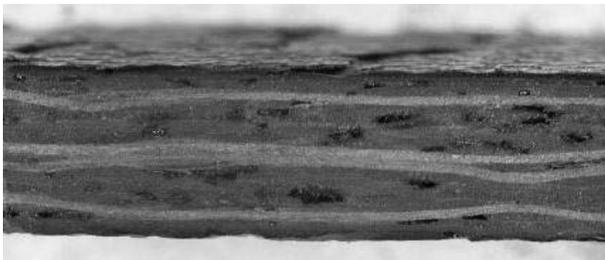


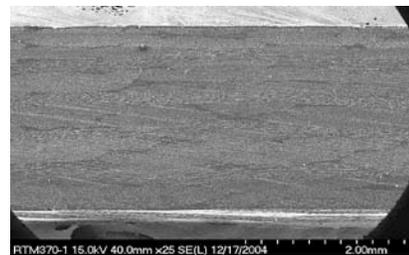
Figure 3. Rheology of RTM370 made by Akron Polymer Systems.

3.2 Characterization and mechanical properties of RTM370 T650-35 polyimide composites

T650-35 carbon fabric reinforced RTM370 composites exhibit T_g 's of 338 °C by DMA before post-cure, and 350 °C after post-cure at 343 °C (650 °F) for 8 h (Table 1). RTM370 VARTM composites display non-uniformity as shown by scanning electron micrograph (Fig. 4a) with ~6.5% void content, whereas the corresponding RTM panels show very uniform resin distribution (Fig. 4b) with 1% void content. The use of external pressure (1.38 MPa) during the RTM process leads to a lower void content than VARTM that uses only 0.1 MPa. The resin content for VARTM panels ranged from 35-38 wt% while the RTM panels had 35-36 wt% resin content. The fiber volume for the RTM370 VARTM and RTM panels are 49-53% and 53-56% , respectively, which are lower than the conventional prepreg composite with 65% fiber volume, but in line with conventional VARTM's fiber volume of 50-60% as listed in Table 1. It took approximately 1.5 h to infuse the RTM370 panels by VARTM compared to 20-30 min for injection by RTM.



a) RTM370 composite made by VARTM



b) RTM370 composite by RTM

Figure 4. Scanning electron micrographs of RTM370 composites fabricated by VARTM vs RTM.

All RTM370 composites were post-cured at 343 °C (650 °F) for 8 h before testing to advance the crosslinking of PEPA to achieve optimal mechanical properties. Isothermal aging was also conducted on RTM370 VARTM composites at 288 °C (550 °F) for 1000 h in an air circulating oven. Mechanical properties of RTM370 composites fabricated by VARTM are compared to those processed by RTM (Table 3).

Table 3 Mechanical Properties and Thermal Stability of RTM370/T650-35/8HS/HTS Polyimide Composites (VARTM vs RTM)

RTM370 Composite	Test Temp. (°C)	OHC Strength (MPa)			OHC Modulus (GPa)			SBS Strength (MPa)		
		Initial @288°C	500 h @288°C	1000h @288°C	Initial @288°C	500 h @288°C	1000h @288°C	Initial @288°C	500 h @288°C	1000h @288°C
VARTM	RT	233	194	120	37	38	33	43	37	22
	288	186	197	135	40	42	38	31	27	17
	315	182	---	118	42	---	38	29	26	15
	327	184	---	---	41	---	---	30	26	16
RTM	RT	269	287	230	44	47	46	51	54	43
	288	241	244	184	48	44	45	41	41	41
	315	231	---	---	46	---	---	31	---	---
	32	241	---	---	48	---	---	30	---	---

Figure 5 shows that the open-hole compression strength (OHC) of RTM370 VARTM composites possess about 77-78% of OHC property of RTM panels (Fig. 5). The VARTM and RTM composites have comparable OHC modulus (Fig. 6). RTM370 VARTM composites have lower initial short-beam shear strength (SBS) at room temperature and at 288 °C but comparable SBS at 315-327 °C, relative to RTM panels (Fig.7). The lower mechanical strength of composites fabricated by VARTM could be attributed to their higher void contents and lower fiber volume, relative to those manufactured by RTM. However, RTM370 exhibits higher temperature performance up to 327 °C (620 °F), exceeding the use temperature of BMI-5270-1.

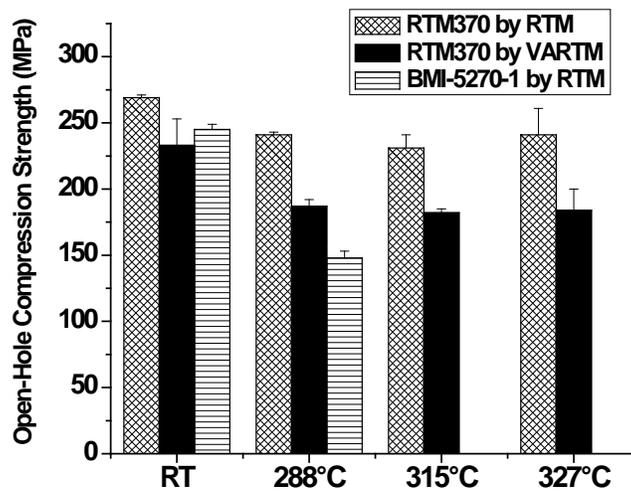


Figure 5. Comparison of open-hole compression strength of RTM370 composites fabricated by VARTM vs RTM.

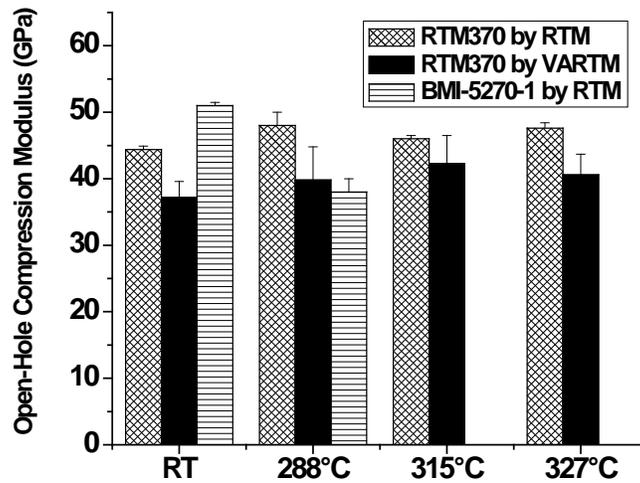


Figure 6. Comparison of open-hole compression modulus of RTM370 composites fabricated by VARTM vs RTM.

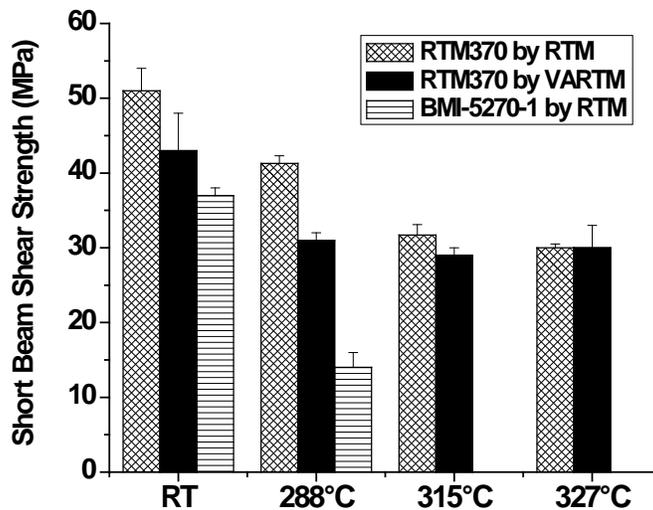


Figure 7. Comparison of short-beam shear strength of RTM370 composites fabricated by VARTM vs RTM.

Isothermal aging conducted at 288 °C (550° F) for 1000 h indicates that RTM370 composites processed by RTM consistently display better property retention than the corresponding VARTM panels. RTM panels were processed under 1.38 MPa of external pressure with ~1% voids whereas VARTM panels were infused only under 0.1 MPa of vacuum with ~6.5% voids. The higher void content in VARTM composite specimens would be expected to expose more of the internal surface area of the composites to air, leading to more thermo-oxidative degradation than the lower void content composites prepared by RTM. However, the higher void content of composites fabricated by VARTM should more readily allow out-gassing during heating, avoiding composite damage and delamination. The SBS property lost during isothermal aging is

particularly evident, compared to OHC (Fig. 8 and Fig. 9). However, the modulus does not seem to be affected as much by aging (Fig. 10). To lower the void contents of RTM370 VARTM composites, it is suggested to inject RTM370 at 260 °C rather than 280 °C to slow down the curing of the PEPA endcap. Additionally, adding a hold at ~300 °C for several hours to help the consolidation of resin, instead of ramping directly to the final cure at 371 °C, might help lower the voids, as it has been determined to lower the void content to ~3% in PETI-330 composites made by VARTM [15].

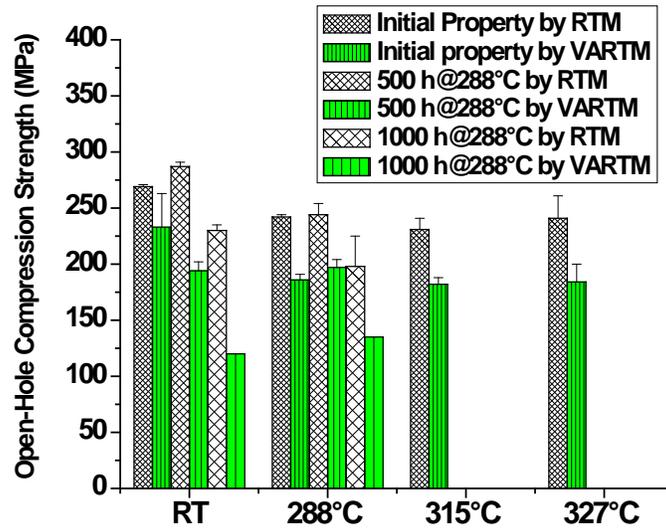


Figure 8. Open-hole compression strength of RTM370 composites subjected to isothermal aging at 288 °C (550 °F) for 1000 h in circulating air.

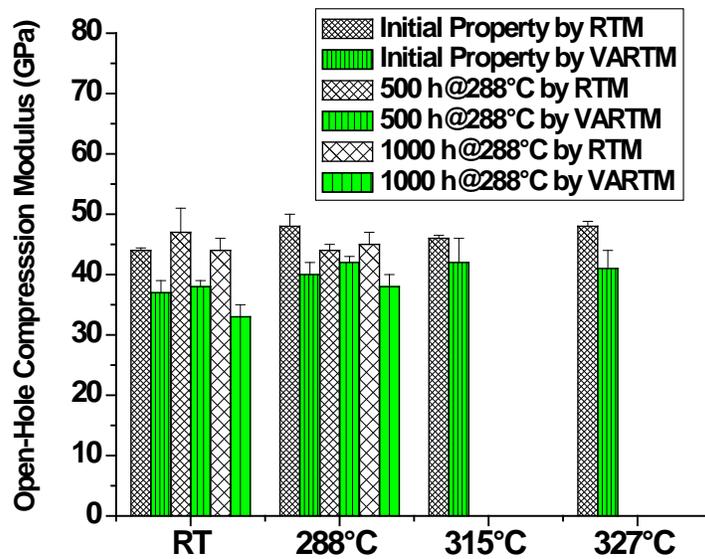


Figure 9. Open-hole compression modulus of RTM370 composites subjected to isothermal aging at 288 °C (550 °F) for 1000 h in circulating air.

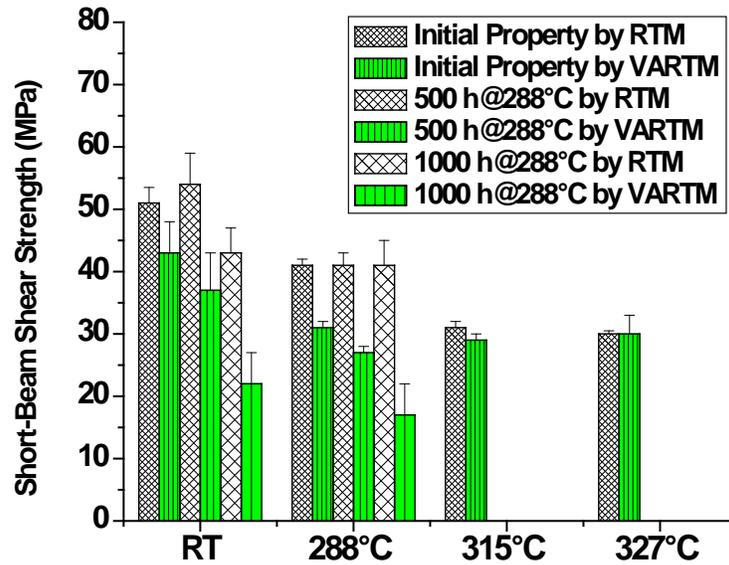


Figure 10. Short-beam shear strength of RTM370 composites subjected to isothermal aging at 288 °C (550 °F) for 1000 h in circulating air.

4. CONCLUSION

RTM370 imide resin composed of 2,3,3',4'-biphenylphthalic anhydride (a-BPDA), 3,4'-oxydianiline (3,4'-ODA) and terminated with 4-phenylethynylphthalic anhydride (PEPA) has been successfully fabricated into carbon fabric reinforced composites by an out-of-autoclave VARTM process, using vacuum bags. The mechanical properties of RTM370 VARTM panels are slightly lower than those of RTM processed panels, due to its higher void contents (~6.5%) than RTM panels (~1% void). Nevertheless, RTM370 VARTM composites exhibit outstanding mechanical properties up to 327 °C (620 °F), and display good thermo-oxidative stability after 1000 h of isothermal aging in air at 288 °C (550 °F). In summary, RTM370 imide resin can be fabricated into high quality composites by RTM under 1.38 MPa of external pressure, but further VARTM process development is still needed to reduce the void content to meet the industry standard (<2%). However, the fact that a high T_g polyimide resin with 315 °C (600 °F) performance capability can now be processed by VARTM is a significant advance for aerospace applications.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- 1) Serafini, Tito T., Delvigs, P. and Lightsey, George R. "Thermally Stable Polyimides from Solutions of Monomer Reactants." *J. Applied Polym. Sci.*, 16 (4) (1972): 905-915.
- 2) Gibb, Hugh. H. "Processing of Composites Based on NR-150B2." *SAMPE Tech Conf.* 10 (1978): 211-226.
- 3) Hergenrother, P. M. "Development of Composites, Adhesives and Sealants for High-Speed Commercial Airplanes." *SAMPE J.*, 36(1) (2000): 30-41
- 4) Smith, Joseph G. Jr., Connell, John W., Hergenrother, Paul. M., Criss Jim M. "High Temperature Transfer Molding Resins." *SAMPE Intl. Sym.* 45 (2000): 1584-1597.
- 5) Connell, John W., Smith, Joseph G., Jr.; Hergenrother, Paul M. & Criss, Jim M." High Temperature Transfer Molding Resins: Composite Properties of PETI-330." *SAMPE Intl. Sym.* 48(2) (2003):1076-1086.
- 6) Connell, John W., Smith Joseph G. Jr., Hergenrother, Paul M. & Criss, Jim M. "High Temperature Transfer Molding Resins: Preliminary Composite Properties of PETI-375." *Proc. of 49th SAMPE Intl. Sym.* May 16-20, Long Beach, CA (2004), CD version
- 7) Chuang, Kathy C., Criss, Jim M. Jr., Mintz, Eric A. Shonkwiler Brian, Scheiman, Daniel A., Nguyen Baochau N., McCorkle Linda S. "Low-Melt Viscosity Polyimide Resins for Resin Transfer Molding (RTM) II." *Proc. of 52th Intl. SAMPE Sym.* June 3-7, Baltimore, MD (2007), CD version
- 8) Chuang, Kathy C., Criss, Jim M. Jr., Mintz Eric A. "Polyimide Composites Based on Asymmetric Dianhydride (a-ODPA vs a-BPDA)." *Proc. of 54th Intl. SAMPE Sym.* May 18-21, Baltimore, MD (2009), CD version
- 9) Chuang, Kathy C., Criss, Jim M. Jr., Mintz Eric A. "Polyimide Composites Based on Asymmetric Dianhydride (a-BPDA vs a-BTDA) for Resin Transfer Molding (RTM)." *Proc. of 55th Intl. SAMPE Sym.*, May 17-20, Seattle, WA (2010), CD version
- 10) Chuang, Kathy C. "Low Melt Viscosity Imide Resins for Resin Transfer Molding" in "Innovations in Materials Manufacturing, Fabrication, and Environmental Safety" Mel Schwartz Ed., CRC Press, New York, Chapter 21, (2010): 629-658.
- 11) Schwartz Mel "Resin Transfer Molding and Associated Closed Molding and Infusion" in "Innovations in Materials Manufacturing, Fabrication, and Environmental Safety" Mel Schwartz Ed., CRC Press, New York, Chapter 17, (2010): 503-529.
- 12) Glancey, James L. "Vacuum Assisted Resin Transfer Molding" in "Innovations in Materials Manufacturing, Fabrication, and Environmental Safety" Mel Schwartz Ed., CRC Press, New York, Chapter 18, (2010): 531-544.
- 13) Yoon, Myung-Keun "VARTM Processing" in "Innovations in Materials Manufacturing, Fabrication, and Environmental Safety" Mel Schwartz Ed., CRC Press, New York, Chapter 19, (2010): 545-574.
- 14) Criss, Jim M., Koon, Robert. W., Hergenrother, Paul M. Connell, John W., Smith, Joseph G. "High Temperature VARTM of Phenylethynyl Terminated Imide Composites." *Intl. SAMPE Tech. Conf.* 33 (2001): 1009-1021.
- 15) Ghose Sayata, Cano, Roberto J., Watson Kent A., Britton Sean M., Jensen Brian J., Connell John W., Herring, Helen M., Linberry, Quentin J. "High Temperature VARTM of Phenylethynyl Terminated Imides." *High Performance Polymers*, 21(5) (2009): 653-672