SAMPE Technical Conference, June 2-5, Seattle, WA 2014

Evaluation of RTM370 Polyimide Composites by Resin Film Infusion (RFI)

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ABSTRACT

RTM370 imide oligomer based on 2,3,3′,4′-biphenyl dianhydride (a-BPDA), 3,4′-oxydianiline (3,4′-ODA) and terminated with the 4-phenylethynylphthalic (PEPA) endcap has been shown to exhibit a low melt viscosity (10-30 poise) at 280°C with a pot-life of 1-2 h and a high cured glass-transition temperature (T_g) of 370°C. RTM370 resin has been successfully infused into fiberglass-stitched T650-35 carbon-fabric preforms (ranged from 3- to 6-mm thick) by resin film infusion (RFI). The resulting composite panels were inspected by ultrasonic C-scan and by photomicrographs before and after post-curing as a quality control. Mechanical tests such as un-notched compression (UNC), open-hole compression (OHC), and short-beam shear strength (SBS) at ambient and elevated temperatures were performed before and after isothermal aging at 288°C for 1000 h to assess high-temperature performance. Thermal cycling of RTM370 stitched composites was also conducted from -54°C to 288°C for up to 1600 cycles to evaluate the microcrack resistance of RTM370 polyimide composites fabricated by RFI.

1. INTRODUCTION

Resin film infusion (RFI), developed initially by Boeing [1], is a relative new technique to fabricate polymer-matrix composites without the use of carbon-fiber prepregs impregnated with resins and, often, with solvents. A resin as a film is placed on top or underneath a fibrous preform, tooling is located, and the assembly is enclosed with a vacuum bag through which the vacuum is applied. As the temperature rises in the autoclave, the resin film melts and infuses into the laminates beneath under the combined pressure gradient of the vacuum and autoclave pressure. The assembly is then cured into composites at elevated temperature. The advantages of RFI include: 1) Ability to produce composites with high fiber-to-resin ratio and low void content. 2) Environmental friendly without volatiles. 3) Capability to fabricate large components with minimum workforce. Numerous epoxies [2] and bismaleimides (BMI) resins [3] have been fabricated by RFI into high-quality composites and aircraft parts [4] in the aerospace field. However, the performance of epoxy and BMI are limited to 177 °C and 232 °C use temperatures [5], respectively. Boeing has conducted RFI using newly developed low-melt-viscosity, imidized oligomers, such as PETI-330 [6] or RTM370 [7], in order raise the higher temperature capability of composites for aircraft applications.

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RTM370 imide oligomers (Fig. 1) based on 2,3,3′,4′-biphenyl dianhydride (a-BPDA), 3,4′-oxydianiline (3,4′-ODA) and terminated with the 4-phenylethynylphthalic (PEPA) endcap has been shown to exhibit a low melt viscosity (10-30 Poise) at 280°C with a pot-life of 1-2 h and a high cured glass-transition temperature (T_g) of 370°C [8]. RTM370 polyimide/T650-35 carbon-fiber composites fabricated by resin transfer molding (RTM) have been shown to display outstanding mechanical-property retention after isothermal aging at 288 °C (550 °F) in an air-circulating oven [9]. RTM370 infused into triaxially braided T650-35 carbon-fiber preform afforded composites that exhibited 28-30% better impact resistance at 288°C (550°F) than at ambient temperature [10].

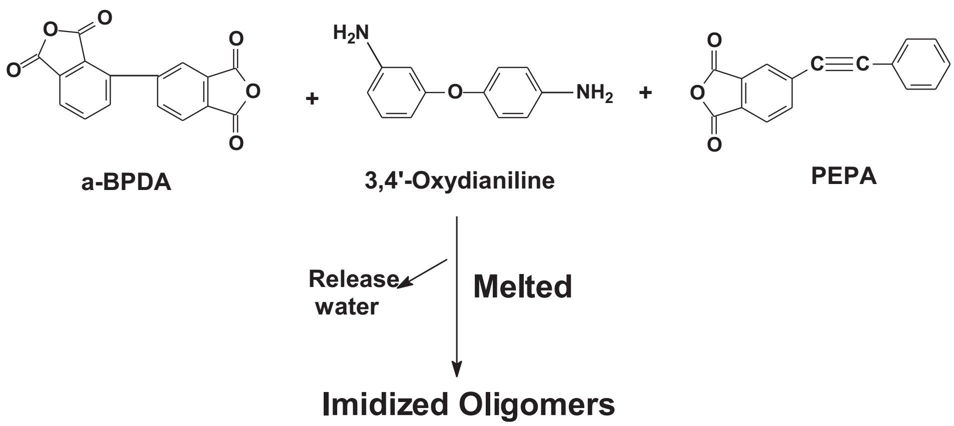


Figure 1. Solvent-Free Preparation of RTM370 Imide Oligomers

This paper presents an evaluation of RTM370 polyimide composites, fabricated with fiberglass stitched T650-35 fabric preforms (ranged from 3- to 6-mm thick) by resin film infusion (RFI), for potential airframe application. Mechanical properties were conducted from room temperature to 288°C (550°F). Additionally, mechanical properties after isothermal aging at 288°C for 1000 h and microcrack resistance after thermal cycling from -53°C to 288°C will be discussed.

2. Experimental

2.1 Preform Fabrication:

A) For initial mechanical evaluation for open-hole and un-notched compression and short beam shear strength, carbon-fiber preforms were constructed from 8 plies of T650-35 fabric with UC309 epoxy sizing in a quasi-isotropic layup and stitched with E-glass fiberglass thread at 1.24 stitches/cm^2 (8 stitches/in^2) density to create a preform with a thickness of 3 mm, and then were cut into 61 cm x 61 cm (24 in x 24 in) panel for infusion.

B) For compression-after-impact and thermal-cycling evaluation, two stacks of T650-35 preforms as described above were stitched together into a 6-mm-thick preform at 6.2 stitches/cm^2 (40 stitched/in^2) penetration, and then cut into 56 cm x 56 cm (22 in x 22 in) panels for infusion.

2.2 Resin Film Infusion

RTM370 Resin powder was degassed under vacuum at 288 °C, and made into resin plaques to be placed on top of the carbon-fabric preforms and then vacuum bagged. The bagged panels were put into an autoclave, then heated to 348°C (660°F) at ~3°C/min, and cured for 2 h. Some of the resulting panels were subjected to post-cure at 343°C (650°F) for 8 h to raise the T_g and achieve better mechanical strength for comparison purposes.

3. RESULTS AND DISCUSSION

3.1 Characterization of 3-mm RTM370 Thin Stitched composites

The glass-transition temperature (T_g) of the RTM370 composite as cured at 348°C (660°F) for 2 h is 304°C. However, additional post-curing at 357°C for 8 h and 16 h advanced the T_gs to 318°C and 344°C, respectively (Table 1). A cure temperature of 371°C for 2 h would be sufficient to provide higher T_g and afford better properties, but there is always a danger of delamination in polyimide processing by RFI at this temperature, based on Boeing's previous experience with similar polyimide resins.

Table 1. T_g of RTM370/T650-35 Stitched Composites

Post-Cure Condition	T_g (°C)
No post-cure	304
Post-cure 8 h @357 °C	318
Post-cure16 h @357 °C	344

An RTM370 stitched, carbon-fiber composite panel after fabrication (Fig. 1) was inspected using 5 MHz through-transmission ultrasonic C-scan and shown to be of high quality displaying no noticeable defects in the laminates (Fig. 2). The void content of the laminates was ~0.1% as measured by acid digestion. The analysis also indicated a resin content of 32.48% and a fiber volume fraction of 56.75%.

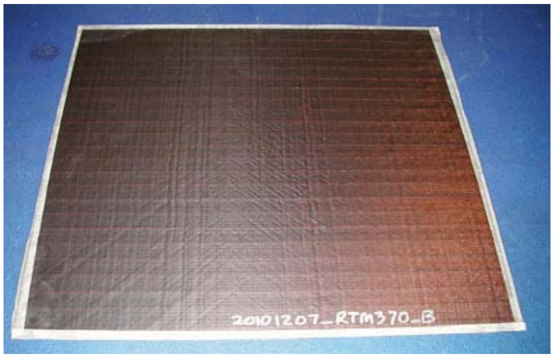
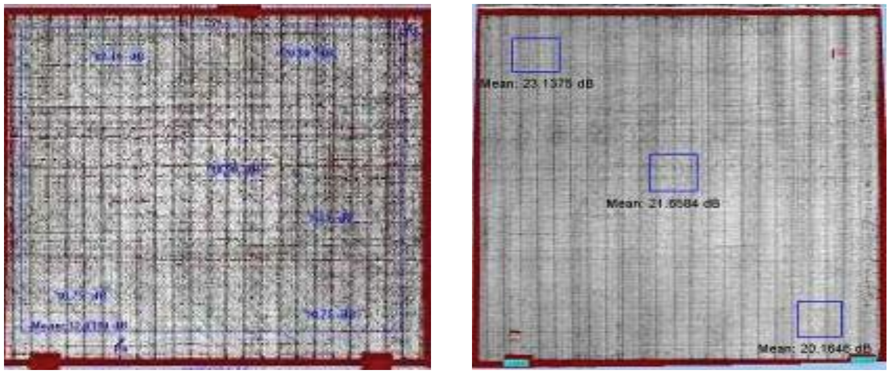


Figure 2. High quality of RTM370 stitched composite panel after cure and post-cure



Left: No post-cure Right: After post-cured

Figure 3. Ultrasonic C-scan of RTM370 polyimide composite panels (3-mm)

The quality of the laminates was also inspected by photomicrographs in cross-section at 50x magnifications to identify any microcracks, porosity or other internal anomalies. The specimens were cut and polished from various portions of the laminate to check consistency throughout the panel. The laminates showed evidence of high quality with no porosity or delamination throughout the cross section, as indicated by the photomicrographs with no post-cure (Fig. 4) and after post-cure (Fig. 5).

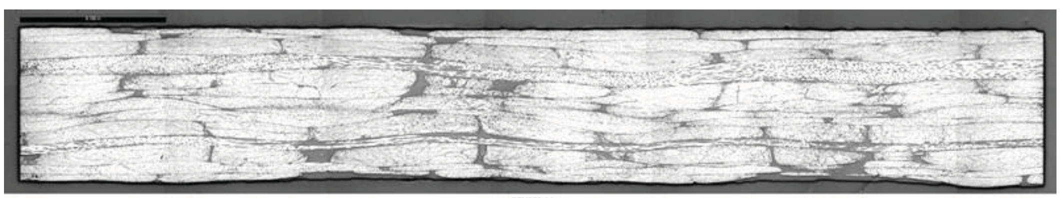


Figure 4. RTM370 No-Post Cure 50x Photomicrograph Shows No Flaws

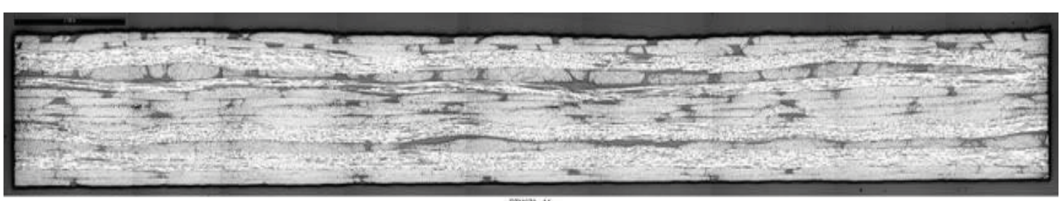


Figure 5. RTM370 Post Cured 50x Photomicrograph Shows No Flaws

3.2 <u>Mechanical Testing of 3-mm (Thin) RTM370 Stitched Composites</u>

To evaluate their thermo-oxidative stability, RTM370/T650-35 stitched composites were subjected to mechanical testing, including open-hole (OHC) and un-notched compression (UNC) as well as short beam shear tests (SBS) at 23 ºC, 288 ºC and 315 ºC with 3 specimens per test, before and after isothermal aging at 288°C (550°F) for 1000 h (Table 2). The specimens were subjected to 8 h of post-cure at 375°C (675°F), before testing to achieve a T_g of 318°C. After 500 h of aging at 288°C, some of the mechanical properties actually increased due to the post-cure effect of isothermal aging of RTM370 thermosetting polyimide, as the reactive PEPA endcap continued its crosslinking. In retrospect, a 16-h post-cure would raise the T_g to 344 °C as shown in Table 2, and would have provided better initial mechanical properties. However, as the isothermal aging proceeded to 500 h at 288°C, it had a similar effect to a post-cure and yield better mechanical properties before degradation occurred in the composites after 1000 h at 288 °C. As shown in Figs. 6-8, RTM370 stitched composites retained 60-65% of its initial mechanical properties after 1000 h of aging at 288 °C. Nevertheless, RTM370 stitched composites, processed by RFI at 348°C (660°F) for 2 h followed by 8 h of 357°C (675°F) post-cure, lost ~65% of their initial mechanical properties at 315°C. However, un-stitched RTM370/T650-35 composites with polyimide sizing (instead of UC309 epoxy sizing) processed by resin transfer molding (RTM) at 371°C (700 °F) for 2 h, followed by a 16-h post-cure at 343°C (650°F) exhibited better mechanical properties at 315°C (600°F) [9].

Table 2. Mechanical Properties of RTM370/T650-35 Stitched Composites (3-mm)

Tests	**Initial Property (MPa)**		**500 h@288°C (MPa)**		**1000 h@288°C (MPa)**	
Open-Hole Compression (OHC)	**RT**	203	**RT**	196	**RT**	241
	288°C	102	**288°C**	135	**288°C**	126
	315°C	58	**315°C**	73	**315°C**	50
Un-notched Compression (UNC)	**RT**	355	**RT**	355	**RT**	355
	288°C	160	**288°C**	226	**288°C**	199
	315°C	75	**315°C**	103	**315°C**	87
Short Beam Shear Strength (SBS)	**RT**	40	**RT**	46	**RT**	28
	288°C	16	**288°C**	24	**288°C**	23
	315°C	4	**315°C**	2	**315°C**	3

* The specimens were post-cured at 357°C (675 °F) for 8 h before testing

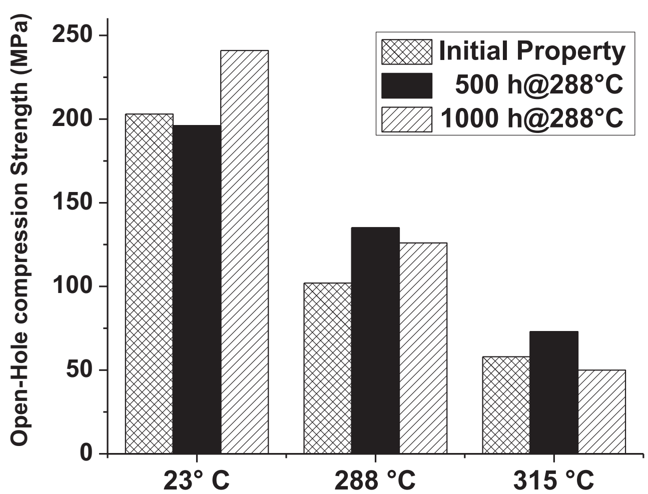


Figure 6. Open-hole Compression Strength of RTM370/T650-35 Stitched Composites Subjected to Isothermal Aging at 288°C (550°F) in Air for 1000 h

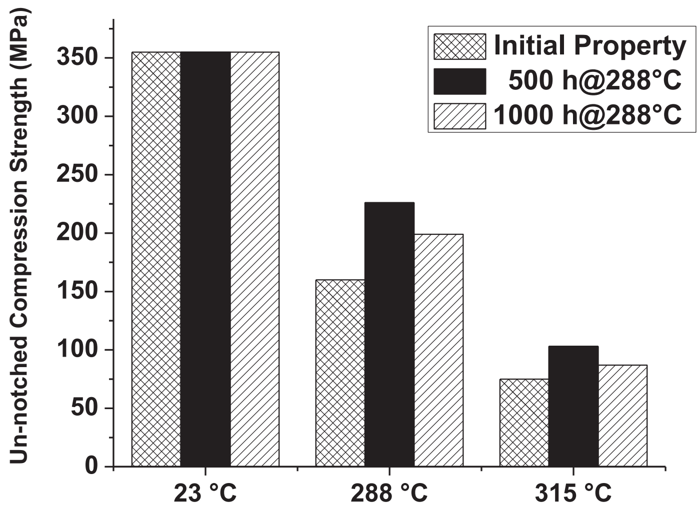


Figure 7. Un-notched Compression Strength of RTM370/T650-45 Stitched Composites Subjected to Isothermal Aging at 288°C (550°F) in Air for 1000 h

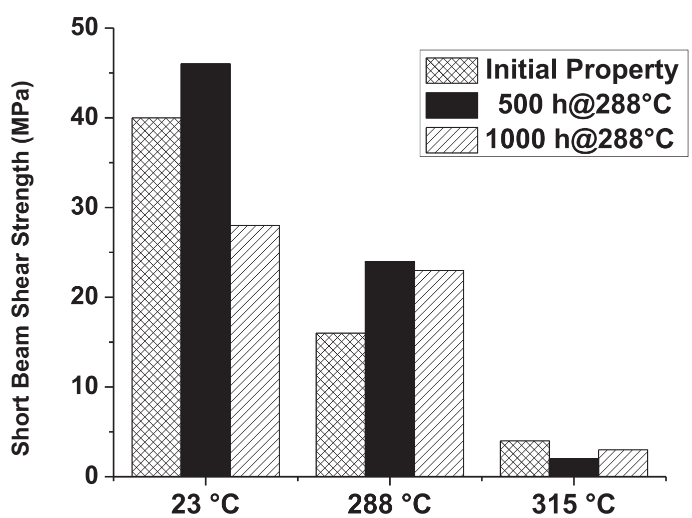


Figure 8. Short Beam Shear Strength of RTM370/T650-35 Stitched Composites Subjected to Isothermal Aging at 288°C (550°F) in Air for 1000 h

3.3 Characterization 6-mm (Thick) RTM370 Stitched Composites

To further investigate the processability of RTM370 imide resin, a thicker, 6-mm composite panel (56 cm × 56 cm) was made via RFI with 2 h cure at 348°C (660°F) and a post-cure at 357°C (675°F) for 16 h. The void contents of the laminates varied from 1.63-2.76%, and resin contents were between 31.67-33.88% whereas the fiber volumes ranged from 56.69 - 59.32%. These values are all within the acceptable range for typical RFI. Resin "toughness" of the resulting panel was evaluated by compression after impact (CAI) tests and examination of cross-sections after thermal cycling. The image of the 6-mm-thick RTM370 composites (Fig. 9) and the transmission ultrasound C-scans (Fig. 10) both show good-quality panels before and after post-cure; a representative photomicrograph shows no flaws after post-cure (Fig. 11).

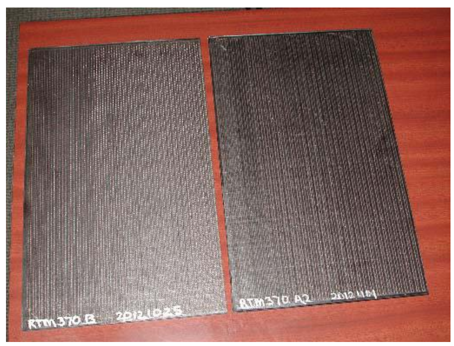
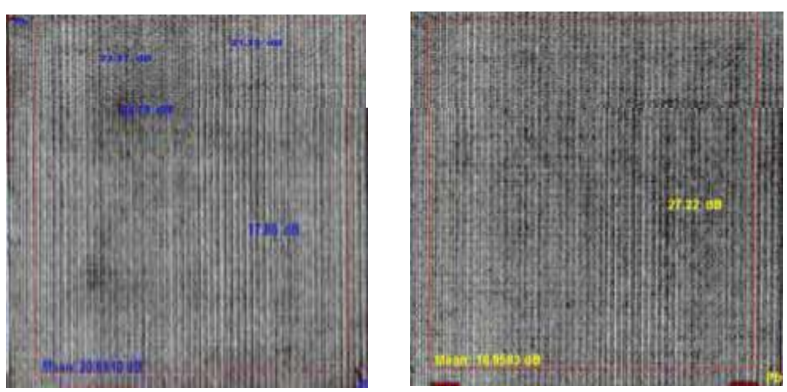


Figure 9. High quality of RTM370 stitched composite panel after cure and post-cure



a) No Post-Cure b) After Post-cure

Figure 10. Ultrasonic C-scan of RTM370 polyimide composite panels (6 mm thick)

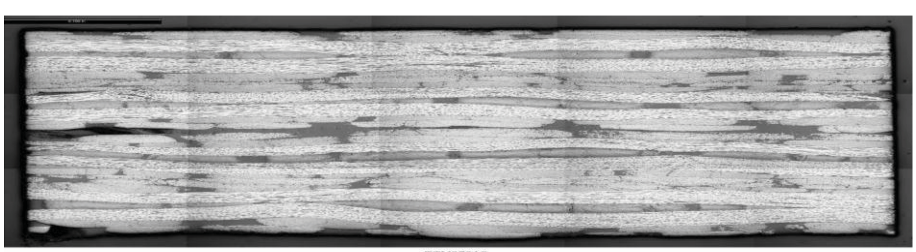


Figure 11. RTM370A2 Post-cured Photomicrograph Shows No Flaws

3.4 Mechanical Testing of 6-mm (Thick) RTM370 Stitched Composites

Both open-hole (OHC) and un-notched compression (UNC) tests were performed at 23ºC, 232°C and 288°C with 5 specimens to demonstrate the overall quality of the laminates. It is important to point out that the initial UNC and OHC properties listed in Table 3 at 23ºC and 288ºC are significantly higher than those recorded in Table 2 because the thick specimens were post-cured at 357°C (675°F) for 16 h before testing, instead of 8 h as for specimens shown in Table 2.

Table 3. **Compression Test Data for 6-mm (Thick) RTM-370/T650-35 Stitched Composites**

Mechanical Tests	Test Temperature	Compression Strength (MPa)
Open-Hole Compression OHC	**23°C (73ºF)**	278
	232°C (450°F)	226
	288°C (550°F)	177
Un-notched Compression UNC	**23°C (RT)**	437
	232°C (450°F)	299
	288°C (550°F)	274

* The specimens were post-cured at 357°C (675°F) for 16 h before testing

3.5 Compression-After-impact (CAI) Data

RTM370 stitched composite laminates were evaluated for CAI properties using 6-mm-thick specimens at CSULB test facilities in Long Beach, CA. Impact testing was performed on the Dynatup instrument per Boeing Specification BSS7260, Class II, Type 1. The impact energy for these tests was 275 in-lbs for each test. After impacting each panel with 373 J (275 in-lbs) impact energy, the typical panel looked as shown in Figure 12 on the top and bottom sides. In Figure 13 the individual NDE C-Scans of the impacted specimens show the extent of the damage from impact.

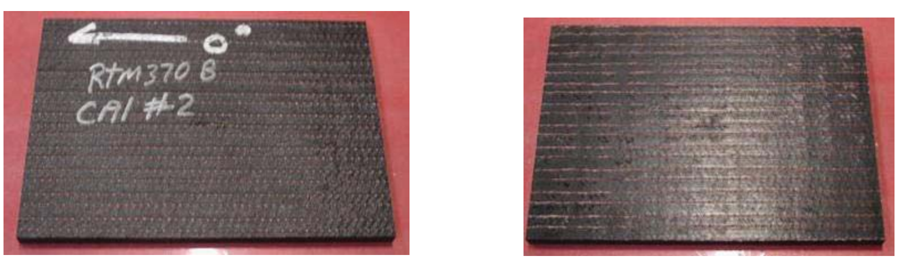


Figure 12. Impacted RTM370 Specimen, (Left) Top side, and (Right) Bottom side

Figure 13. NDE Images of Impacted RTM370 Stitched Composites

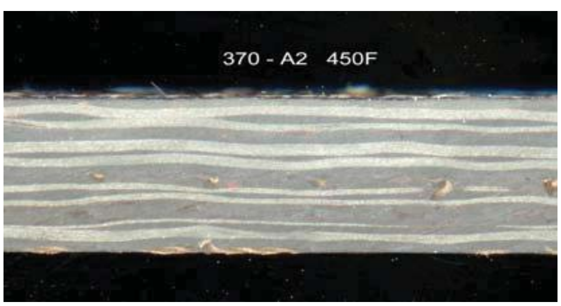
The compression-after-impact (CAI) tests were performed on three (3) specimens at room temperature with the above nominal 6-mm-thick specimens. The results were acceptable values that indicated good toughness of the RTM370 resin composite.

Table 2. Compression-After-Impact (CAI) Test Result

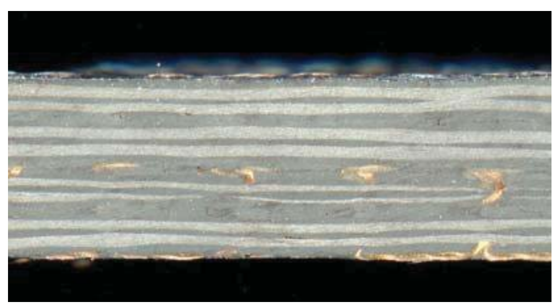
Composite Material	Average Failure Stress--CAI (MPa)
RTM370	266 ± 4

3.6 Thermal Cycling of RTM370 Stitched Composites (6 mm)

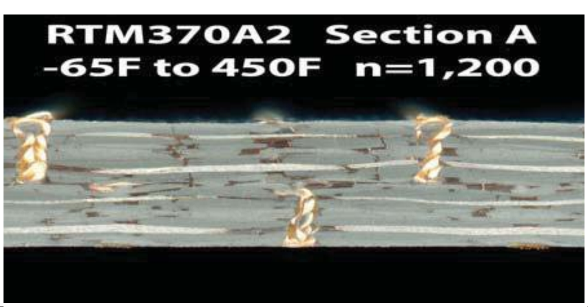
RTM370 stitched panels were subjected to thermal cycling over the range of -54°C to 232°C and another set of panels subjected to thermal cycling from -54°C to 288°C using the thermal-cycling chambers at Boeing. The results of these tests are shown in Figure 14 a-f. This evaluation tests microcrack resistance up to 2400 cycles at the selected temperature range. Each cycle from -54 °C to 232°C took 90 minutes, while the cycles for -54°C to 288°C took 120 minutes. Both thermal-cycling tests were terminated at 1600 cycles. The thermal-cycling tests to 232°C for RTM370 showed satisfactory photomicrographs up to 1200 cycles, but showed minor, but unacceptable, microcracks after 1600 cycles. The thermal-cycling tests to 288°C showed initial cracks at 1200 cycles, with serious damage seen after 1600 cycles. Figure 14 shows cross sections of thermally cycled specimens. Up to 800 cycles, there were no visually noticeable microcracks at 50× magnification. These results are encouraging when compared to competitive polyimide resins in similar tests. These data indicate that the use of RTM370 resin in long-term, high-temperature structures could require thermal-cycling tests applicable to the intended application to properly assess their durability.



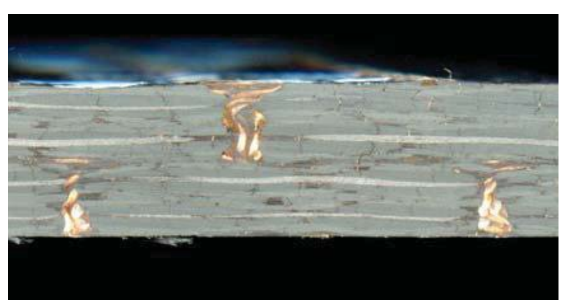
a) After 800 thermal cycles of -54°C to 232°C



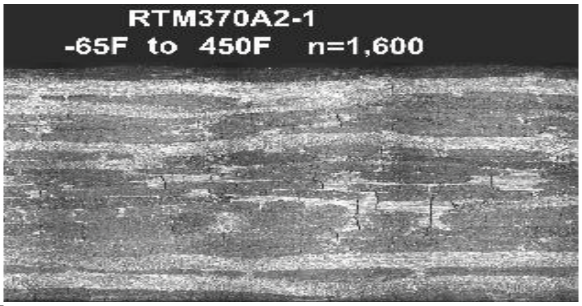
b) After 800 thermal cycles of -54°C to 288°C



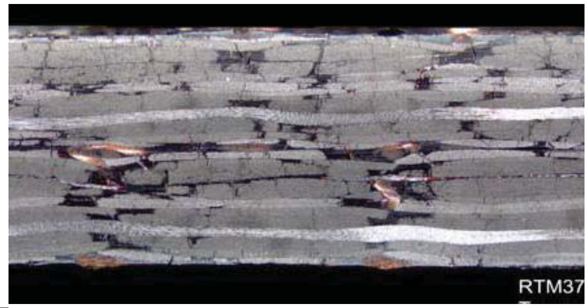
c) After 1200 thermal cycles of -54°C to 232°C



d) After 1200 thermal cycles of -54°C to 288°C



e) After 1600 thermal cycles of -54°C to 232°C



f) After 1600 thermal cycles of -54°C to 288°C

Figure 14. Cross sections of thermal-cycled RTM370 composite specimens.

4. Conclusions

In summary, RTM370 resin is a very promising polyimide resin and is relatively easy to process, especially into thicker, 6-mm laminates as shown by the processing of 56 cm × 56 cm panels. Many polyimide resins are not able to satisfactorily produce high-quality laminates at that thickness. Processing trials at the beginning of the program established usable cure/post-cure cycles and were verified by NDE. The mechanical properties of UNC and OHC were within the expected value range from RT to 288°C (550ºF). These data indicate that, while the 232°C (450ºF) and 288ºC (550°F) values were well within expected range, a longer-term application, especially at 288ºC (550°F), should be evaluated based on application time-at-temperature requirements. The compression-after-impact (CAI) tests also verified RTM370's toughness as evidenced by the very satisfactory value. The typical value at RT of ~270 MPa after a 373-J impact energy is very satisfactory compared to competing polyimide composites. The thermal cycling tests showed these materials to have above-average resistance to microcracking at both -54ºC to 232ºC and -54°C to 288°C up to 1200 thermal cycles, although they did not make it to the 2400-cycle target. Overall, RTM370 composites performed better than many competing polyimide resin composites.

Further characterization of these materials is recommended to determine the full spectrum of properties for targeted performance requirements tied to specific potential parts and platforms. Such characterizations should include a wider variety of mechanical tests, including notched properties, and the sensitivity of mechanical performance with sizing relating to elevated-temperature exposure, especially for extended periods of time. Future studies should also include processing trials to evaluate the feasibility of using RTM370 imide resin to produce larger, more complex parts, and manufacturability of representative structures. Such studies are essential if the material is to be used in any aerospace flight hardware.

5. ACKNOWLEDGEMENTS

This work was supported by NASA contracts NNC10AA03A and NNC12AA01A with Boeing under 50/50 cooperative agreement. Boeing Research & Technology at Huntington Beach, CA performed all the fabrication, quality and testing effort on the program with California State University, Long Beach (CSULB). The authors also like to thank Ohio Third Frontier for funding support through Maverick Corporation, and Akron Polymer Systems for producing and providing RTM370 resin for this study. In addition, funding support from NASA Supersonic program and NASA Glenn 2010 Tech Transfer Fund are greatly appreciated.

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