Thermal Cycling of Out-Of-Autoclave Thermosetting Composite Materials

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ABSTRACT

Carbon-fiber reinforced polymer material has been widely used in space/aerospace industries for manufacturing of spacecraft structures, satellite-panels and antennas. In space, composites can be subjected to the periodic thermal cycling (TC) in which temperature ranges from −196 to 180°C, depending on operational condition. Effect of thermal cycling on properties of flat laminates made of unidirectional (UD) and fabric out-of-autoclave (OOA) material will be presented. Flat laminates were made using recommended cure cycle by material supplier. Then the samples were cut and subjected to the thermal cycle. To do so, the samples were dipped into the liquid nitrogen (-196°C) and then transferred to the oven (140°C). After different number of cycles (10, 30, 60, 100, 150), inter laminar shear strength (ILSS) and dynamic mechanical properties were measured. Optical microscope was utilized to identify any damage within the resin. The results indicate that the ILSS of the UD composite will increase by about 7.3% after 150 cycles which might be due the post-curing during cycling. Conversely, the ILSS of fabric composite will reduce by about 9.7% which can be attributed to the creation of the defects (microcracks).

1 INTRODUCTION

In the past several years, structural parts manufactured by carbon/epoxy polymeric composite material have been widely used in space and aircraft industries [1–4]. This material has good mechanical properties which have led to numerous advanced applications ranging from space shuttle to military-civil aircraft structures [5–9]. It is lightweight, highly corrosion resistant and has high strength, stiffness and low thermal expansion that make it highly usable in different applications including space. Antennas for satellite are made using composite material which will be subjected to a big temperature variation from -196 to 180 °C in a relatively short period of time. This type of environment can cause thermal shocking which in turn can damage material and reduce its properties.

Thermal cycling/shocking can be define as a process of rapidly changes in the temperature of the specimen from low to high or vice versa [1-2, 10–12]. Thermal cycling can cause damages/cracks initiation in composite material. Different matrix and fiber coefficient of thermal expansion is the primary cause of damage in composite material due to the thermal cycling, thus contributing to deformation, stresses on interface, debonding and microcracks. The temperature changes in the specimen generate residual stresses and break the layers in the laminates. Experimental work have been conducted using thermal cycling facility to study the interlaminar shear strength and propagation of crack inside composite laminates[13-14].

Wilson [8] studied the thermal cycling of fabric samples 0/90 made of T300 carbon-fiber and high-temperature resin PMR15, cycled up to 1500 times between temperature range of -54 to 232°C. It was observed that there were increase in microcracking and weight loss of the samples. The authors suggested to control these effects by using higher strength resin and by small successive changes in ply orientation. Based on these suggestions, various specimens were prepared with different lay-up including (0/903)S, (02/902)S, (03/90)S, (90/03)S, (902/02) S and (903/0)S by Adams et al [9]. Samples were cycled up to 500 times with 5.6% increments in range of temperature from -157 to 121°C. During analysis of these samples, the transverse cracks were appeared at -46°C, which is a low temperature point. The cracks were located in low resin areas and delamination were perpendicular to fiber direction and propagated from the transverse direction (transverse crack). However, the sample with (903/0)S lay-up laminate was found thermally unstable and had uneven cracking in outer surface/layers.

Lord and Dutta et al [10] had manufactured carbon fiber specimens and cycled under the temperatures of - 195 to 22°C for determining their elastic properties. The result showed that not only moduli are significantly decreased but other mechanical properties like transverse tensile strength and interlaminar shear strength are reduced significantly. The results based on SEM (scanning electron microscopy test) examination showed that there was debonding between layers.

The purpose of this work is to study the behavior of out-of-autoclave material after thermal cycling by different means. Mechanical testing (Interlaminar Short Beam Shear test), DMA, and optical microscopic were used. As the number of thermal cycle increases the number of microcracks increases as well. To observe the cracks high magnified optical microscopic were used.

2 MATERIALS AND METHOD

2.1 Materials Selection and Manufacturing

The material used for this project was Cycom 5320-1 provided by Cytec Industries. It is a toughened carbon/epoxy prepreg system specifically designed for OOA manufacturing. Two laminates were made: (1) a UD laminate made of 24 layers of UD prepreg; and (2) a cross-ply laminate made of 8 layers of 5HS woven fabric (5-harness satin prepregs). The material was cured inside oven at 120°C for 3 hours and then post cured for 2 hours at 177 °C and the temperature was allowed to fall to room temperature afterwards. Figure 1 shows the cure cycle for the composite plate.

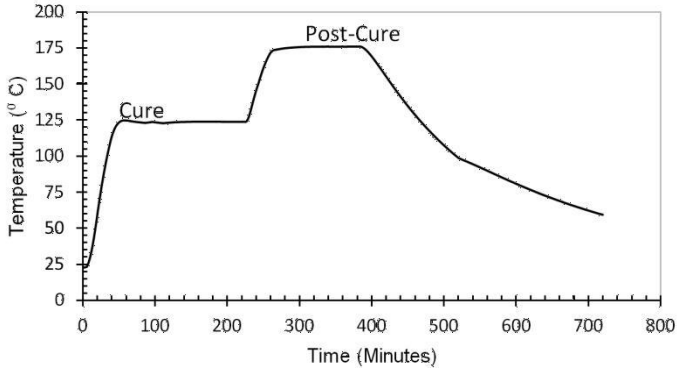

Figure 1. Cure cycle Cycom 5320-1.

2.2 Thermal Cycling Procedure

According to the requirements of coupon size for each standard test method (DMA, interlaminar shear) several specimens were cut out of the laminates. Five different set of samples were cycled at 10, 30, 60, 100 and 150 times, and compared with one unexposed sample set (non-cycled). One sample was cut with the thermocouple inside as the control sample during cycling. The time necessary for the center ply of this control specimen to reach the required hold temperatures (within 5°C) was recorded for each step of the thermal cycle. Based on these measurements, a cycle was defined as 2 minutes in the liquid nitrogen (LN), 5 minutes at room temperature (RT), 10 minutes in the oven, and 5 minutes again at RT. Thus, the total time for one cycle was 22 minutes. Cycling of the test samples was performed in a jar containing LN and a convection oven. The specimens were placed in a basket made of metal wire mesh having different shelves to minimize the contact between them and make the specimen temperature equilibrium faster. The basket was immersed in LN bath for cooling phase and put in the preheated oven for the heating phase of the cycle. After each cooling and heating phase, the basket containing the specimens was placed in RT to reach ambient temperature. Temperature cycle vs. time was recorded for several cycles using the control specimen. The temperature for the elevated temperature hold was 140°C for this cycle. Figure 2 shows the temperature cycle vs. time for 10 cycles.

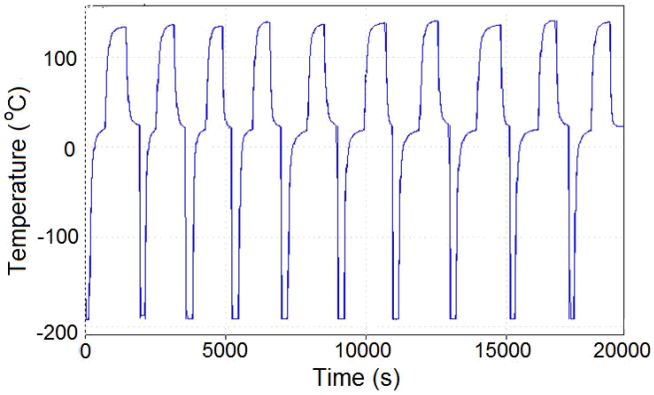

Figure 2. Temperature cycle vs. time for 10 thermal cycles.

2.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analyses were conducted using a TA instrument Q800, dynamic mechanical analyzer. The specimens with dimensions of 50 mm×15 mm×3 mm were used for the analysis. The analyses were done in three-point bending mode at a frequency of 1 Hz. The samples were heated from −150°C to 320°C at a heating rate of 5°C per minute, with 0.05 mm maximum displacement. The glass transition temperature (Tg) was determined from the peak of the tan delta curve.

2.4 Optical Microscopy

Optical microscope at 20X was utilized to observe the effect of thermal cycling on the ply-level crack propagation. To do so, one specimen from each laminate prior to cycling was cut and polished on one side of the cross section such that the fibers were perpendicular to the polished edge (perpendicular to view).

2.5 Mechanical Tests

The interlaminar shear strength (ILSS) tests were conducted using MTS 25KN load cell universal testing machine at 22°C and 50% relative humidity, in accordance with the ASTM D2344-13 standard test method. Each data point indicated in the results is an average of five

separate specimens with dimensions of 20 mm × 6.5 mm × 3 mm, all tested using a support span of 14 mm at a crosshead speed of 1 mm/min.

3 RESULTS AND DISCUSSION

3.1 Glass Transition Temperature and Damping Property

A common measurement on polymer composites is the glass transition temperature, Tg. It can be measured with various techniques, but DMA is by far the most sensitive one. To study the effects of thermal cycling on Tg and the damping parameter (tan δ) of the composites, DMA tests were run after specific number of thermal cycles. Figure 3 shows the tan δ (damping parameter) as a function of temperature for both unidirectional and cross-ply laminates. Consequently, Tg was determined from the peak of the tan δ curve.

Tan δ can be calculated from the ratio of the loss modulus to storage modulus, which represents the viscous and elastic portion of the material, respectively. Therefore, the damping properties of the material give the balance between the elastic phase and viscous phase in a polymeric structure and the Tg can be used to determine the crosslinking degree of the resin matrix. With a higher level of crosslinking in the resin matrix, a higher temperature is needed to pass the elastic region and reach the elastomeric state [18].

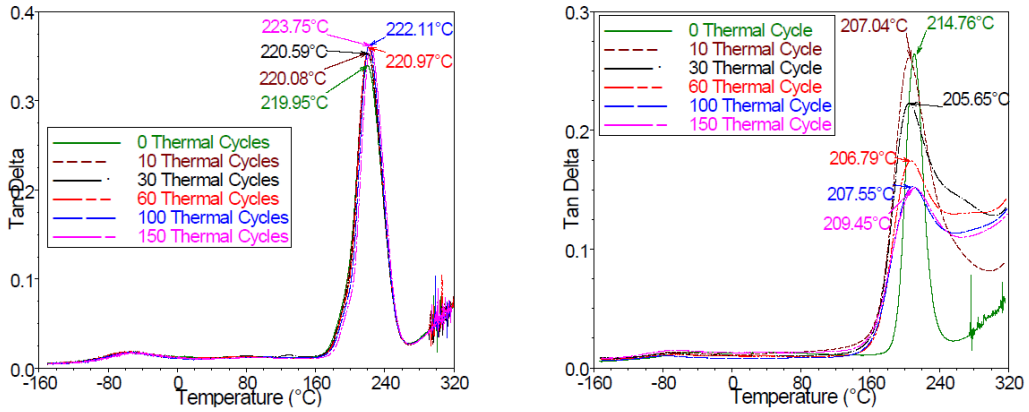

Figure 3. Tan δ of composites exposed to different thermal cycles: (a) UD; (b) Woven fabric.

No. of Thermal Cycles	Uni-directional		Woven Fabric	
	Tg°C	Tan δ_{max}	Tg°C	Tan δ_{max}
0	219.95	0.340	214.76	0.264
10	220.08	0.354	207.04	0.261
30	220.59	0.353	205.65	0.223
60	220.97	0.360	206.79	0.174
100	222.11	0.362	207.55	0.152
150	223.75	0.362	209.45	0.151

Table 1. Glass Transition Temperature (Tg) and maximum tan δ of composite laminates subjected to different thermal cycles.

Table 1 lists the values for Tg and the maximum tan δ of the present carbon/epoxy composite subjected to various thermal cycles. It can be seen that there is a slight increase in glass transition temperature of unidirectional laminates from 219.95°C to 223.75°C for non-cycled and 150-times-cycled samples, respectively. This indicates that during the thermal cycling, the temperature rising can cause more degree of crosslinking of the resin matrix which consequently induces post curing effect to some extent. Also, the maximum tan δ increases by 6.5% from 0.340 for unexposed samples to 0.362 for 150 times thermal cycled ones which indicates minor increase in viscosity of the material. However, the trend for the cross ply laminates is different; Tg decreases slightly from 214.76°C to 205.65°C up to 60 cycles and

increases again to 209.45°C as thermal cycles increase to 150 times while the magnitude of tan δ peak decreases by 57% from 0.264 to 0.151 and becomes squat as number of thermal cycles increase which means that material acts more elastic.

3.2 Microcrack Observation

Optical microscopy was used to observe the response of composite samples to thermal cycling. Both unidirectional and woven fabric composite samples were checked at 20x magnification prior to cycling to make sure that there is no microcrack in the surface, but there were voids present in samples as expected due to OOA curing of the materials and absence of pressure during cure. As can be seen in Figure 4, imaging after thermal cycles of UD samples showed no microcrack up to 150 thermal cycles. Conversely, imaging of cross ply specimen demonstrates the presence of microcracks in early cycles until 40 cycles. Figure 5 shows that the cracks start to grow in 90° plies around the voids and as the thermal cycles increases they propagate through the whole thickness of the ply and stop when reach 0° plies.

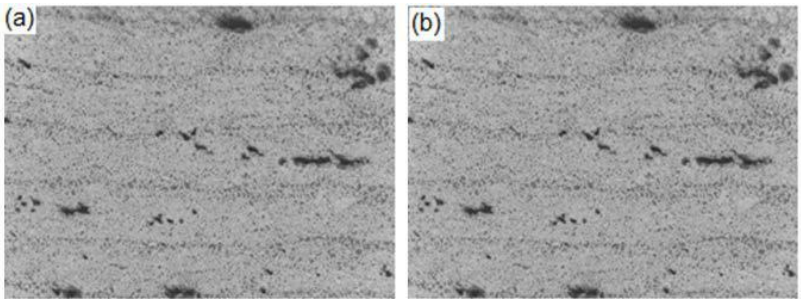

Figure 4. Microscopic images of UD composites exposed to different thermal cycles: (a) before exposure to thermal cycle; (b) after exposure to 150 cycles.

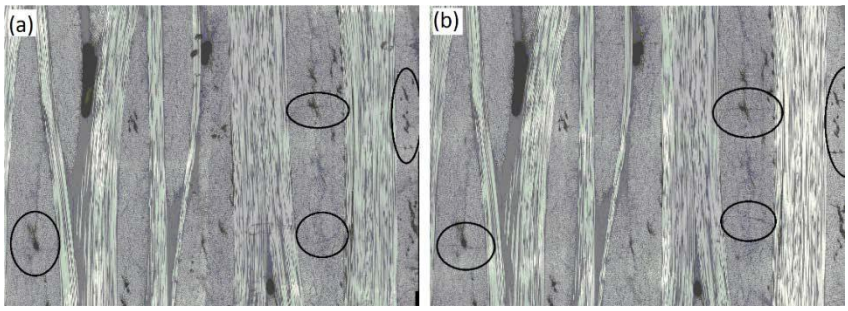

Figure 5. Microscopic images of woven fabric composites exposed to different thermal cycles (a) 10 cycles; (b) 40 cycles. Some of crack growths are circled for comparison.

3.3 Interlaminar Shear Strength (ILSS)

To evaluate the interfacial strength of polymer matrix composites, the ILSS test was conducted. Figure 6 shows the variation of the ILSS of the present carbon\epoxy composites versus different thermal cycles for both UD and fabric plates. The ILSS of the UD composite increased by 7.3% from 95.4 MPa for unexposed sample to 102.4 MPa for 150-times-cycled sample, even though there were some minor fluctuations of ILSS value in between. This could be due the fact that the cross-linking degree of the resin matrix increased due to thermal cycling. This is in accordance with the DMA results in which the Tg increased which is an indication of enhancement in the cross-linking degree of the resin. Moreover, ILSS of UD composite may also be affected by the interfacial bonding strength of fiber/matrix, as reported

by other [18-20]. It is worth mentioning again that for the UD sample no crack was initiated up to 150 cycles.
For composites made of woven fabric prepregs, as can be seen in Figure 6(b), with increasing the number of thermal cycles from 0 to 150, the ILSS of the composites gradually decreased by 9.8% from 63.4 MPa for unexposed sample to 57.2 MPa for 150-times-cycled sample. This different trend of ILSS for fabric and UD composite could be due to the fact that the absorbed heat in UD was mainly used for the post-curing; however, in the fabric composite, the thermal stresses due to the mismatch in the coefficient of thermal expansion (CTE) of fiber and matrix induced several cracks at fiber/matrix interface, as reported by Park and Gao [20-21].
Therefore, CTE mismatch was probably the dominant factor to decrease ILSS of the fabric composite, while post-curing was likely the main leading role for the UD composite.

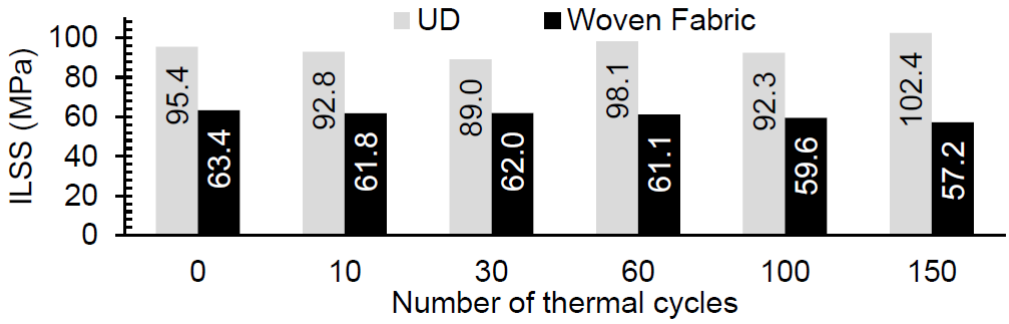

Figure 6. Interlaminar shear strength (ILSS) of composites subjected to different thermal cycles: (a) UD, (b) Woven fabric. The mean value of 5 specimens is displayed in column.

4 CONCLUSIONS

In this paper, the effect of thermal cycling on mechanical and physical properties of flat laminates made of carbon/epoxy prepregs manufactured OOA was examined. The study was conducted on both uni-directional (UD) and woven fabric laminates.

After 150 thermal cycles, Tg of UD laminate increased slightly which indicates uncompleted cure process of the matrix. During thermal cycling at high temperatures (close to curing temperature), the temperature rise can induce post curing effect to some extent and cause the improvement of crosslinking degree of the resin matrix [1]. Moreover, viscoelastic properties of the material were not notably affected by thermal cycling. No microcracks was observed after thermal cycling exposure, indicating no severe damage was introduced to the material. Even though there were some minor fluctuations of ILSS value at lower cycles, the ILSS of the 150-times-cycled UD composite sample increased by 7.3% compared with unexposed sample.

Cross ply laminates made of woven fabrics behaved differently form UD composite in terms of mechanical and physical properties. After 150 cycles, Tg decreased slightly, while tan δ decreased significantly which indicates the material behaves more elastic than viscose. Several microcracks were observed as a result of cycling. This can be due to a large mismatch in CTE of the resin and fiber. The temperature changes during cooling and heating phase of the cycle generate residual stresses and initiate cracks in composite plies especially around the voids. As a result, ILSS of fabric laminate gradually decreased by 9.8% after 150 cycles.

It can be concluded that during thermal cycling, CTE mismatch was the principal factor to decrease ILSS of fabric composites, while post-curing is the dominant factor to increase the ILSS of UD composite.

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