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CRYOGENIC AND ELEVATED TEMPERATURE CYCLING OF CARBON / POLYMER COMPOSITES FOR RESUABLE LAUNCH VEHICLE CRYOGENIC TANKS

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Key Words : Cryogenic Cycling, Carbon Fiber, Bismaleimides, Epoxy Resin

ABSTRACT

An apparatus was developed to repetitively apply a –196 °C thermal load to coupon-sized mechanical test specimens. Using this device, IM7/5250-4 (carbon / bismaleimide) cross-ply and quasi-isotropic laminates were submerged in liquid nitrogen (LN_2) 400 times. Ply-by-ply micro-crack density, laminate modulus, and laminate strength were measured as a function of thermal cycles. Quasi-isotropic samples of IM7/977-3 (carbon / epoxy) composite were also manually cycled between liquid nitrogen and an oven set at 120 °C for 130 cycles to determine whether including elevated temperature in the thermal cycle significantly altered the degree or location of micro-cracking. In response to thermal cycling, both materials micro-cracked extensively in the surface plies followed by sparse cracking of the inner plies. The tensile modulus of the IM7/5250-4 specimens was unaffected by thermal cycling, but the tensile strength of two of the lay-ups decreased by as much as 8.5 %.

1. INTRODUCTION

Polymer matrix / carbon fiber composites have been projected for application in launch vehicle cryogenic tanks to reduce vehicle weight and cost.[1] Reusable launch vehicles under development are expected to be launched repeatedly – requiring the fuel and oxidizer tanks to sustain hundreds of cycles at the temperature of liquid oxygen (-183 °C) and below. These tanks may also be allowed to reach more than 95 °C upon reentry to reduce the weight of thermal protection material necessary to shield the vehicle.

Researchers have cycled carbon / polymer composites at cryogenic temperature.[2-3] Timmerman, et al.[2] cycled model epoxy matrix composites with various carbon fibers in LN_2 to determine micro-cracking as a function of various fiber and matrix properties. Kessler, et al.[3] cycled an aerospace-grade toughened epoxy composite (IM7 / 977-2) with a combined cycle that consisted of cool down to –243 °C which is near the –253 °C temperature of liquid hydrogen, warm up to 127 °C, and back to room temperature. Quasi-isotropic laminates did not micro-crack after ten cycles, and their mechanical properties were not affected.

The response of IM7 / 5250-4 to a cryogenic environment has previously been studied. Pagano, et al.[4] did not conduct repeated thermal cycling but did submerge IM7 / 5250-4, in LN_2 and in liquid helium. Neither produced ply-level cracks. Pagano, et al.[4] also demonstrated that mechanically loaded cross-ply laminates of IM7 / 5250-4 micro-crack at decreasing ply-level stresses as the percentage of blocked plies increases. Donaldson, et al.[5] demonstrated that the strength of IM7 / 5250-4 decreased due to mechanical fatigue applied while the material was submerged in LN_2

The emphasis of this study was the effects of composite lay-up sequence on the amount and location of micro-cracks produced by hundreds of cryogenic or combined

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cryogenic and elevated temperature cycles. A description is provided of a relatively inexpensive machine that was developed and tested to cycle up to sixty-four specimens at once in liquid nitrogen. . This cycling device was demonstrated by cycling an advanced carbon / bismaleimide – IM7 / 5250-4 – composite 400 times between −196 °C and ambient temperature. Cross-ply laminates were tested to determine whether blocking plies affected thermal fatigue resistance. A quasi-isotropic laminate was also tested. Finally, another advanced composite that is valuable to the aerospace industry, IM7 / 977-3, was manually cycled between −196 °C and 120 °C to gain insight into the consequences of including elevated temperature in the thermal cycle.

2. EXPERIMENTAL

2.1 Apparatus

An image of the cycling apparatus is shown in Figure 1. The cycling apparatus consists of an aluminum frame 200 cm tall that is used to support and guide a sample container vertically. The sample container is attached to a hollow 19 mm square bar that can travel 100 cm and is actuated by a 24 VDC gear-head motor with a 150:1 gearbox. The sample container was fabricated from a minimum amount of 14 gage copper wire and galvanized steel mesh to maintain a relatively minor thermal mass. The mesh ensured that samples were not allowed to contact one another but could be spaced as close as 6.4 mm intervals allowing sixty-four 152 mm long by 15.2 mm wide samples to be placed in a 100 x 100 x 160 mm container. The sample container was submerged in a Pope Scientific 86 series vacuum-insulated glass dewar. The dewar was 56 cm tall (43 cm usable) with an inside diameter of 14 cm. As an example of nitrogen use, 24 samples cycled for 2 minutes in the LN_2 followed by a hold of 10 minutes outside the dewar consumed 60 liters of nitrogen in 90 cycles.

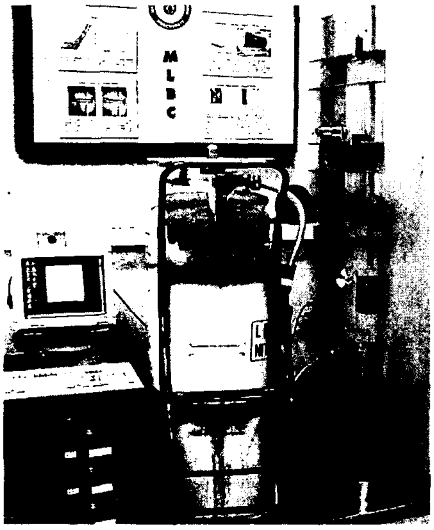

Figure 1. Device to automatically cycle coupons between −196 °C and ambient temperature

2.2 Materials

Cycling between −196 °C and ambient temperature was conducted on a composite consisting of medium stiffness IM7 carbon fibers from Hexcel and a high temperature bismaleimide matrix (5250-4 from Cytec-Fiberite). Lay-up 1, $[0/90]_{2S}$, was a cross-ply with two 90-degree plies adjacent ("blocked") at the center of the laminate. Lay-up 2, $[0/+45/-45/90]_S$, was a quasi-isotropic laminate that also had blocked 90 degree plies midway through the thickness. Lay-up 3, $[90/0/90/0/90/0/90/0/90]_T$, was a 9 ply, cross-ply laminate without blocked plies. Samples 152 mm long by 15.2 mm wide were cut with the 0-degree plies aligned parallel to the long side of the sample. With this choice of lay-ups, the effect of blocked lay-ups could be observed. A comparison could also be made between cracking in blocks of plies that were adjacent to plies with varying angles (45 and 90 degrees to the block).

Cycling between −196 °C and 120 °C was conducted on a composite consisting of the same IM7 fiber and a toughened epoxy matrix (977-3 from Cytec-Fiberite). Only one lay-up of this material was available, $[0_2/90_2]_S$, which will be referred to as "Lay-up 4." Lay-up 4 did not mimic any of the IM7 / 5250-4 lay-ups and therefore, did not allow a direct comparison between the two materials. It did, however, provide data on whether blocks of plies at the surface of the laminate crack completely through the block

2.3 Development of Cycle for Cryogenic Cycling

Tests were conducted to estimate the minimum hold times necessary to ensure that the plies on the inside of the laminate reached the desired temperatures (within 5 °C). A 0.102 mm thick k-type thermocouple was embedded between two 1.040 mm thick laminates of carbon / epoxy and attached to an Omega model CN77344-C2 thermocouple converter. The thermocouple tip was embedded 50 mm from the end of the 152 mm long sample. The center of the sample reached within 5 °C of −196 °C in less than 1.5 minutes. The inside of the laminate reached within 5 °C of ambient temperature (24 °C) in 6.0 minutes with the blowing fan off and in 2.5 minutes with the fan on. A conservative thermal cycle of 2 minutes in the LN_2 followed by 10 minutes exposed to ambient temperature was chosen.

2.4 Micro-crack Density

Each laminate was polished to a 0.2 μm finish on one of the lateral (152 mm long) sides prior to cycling. Ply-level cracks were observed at 100X in an optical microscope. A crack was included in the micro-crack density measurement if it extended vertically (through the ply thickness) more than three-fourths of the way through the ply. Cracks were counted after, 0, 1, 5, 30, 75, 125, 175, 250, 325, and 400 cycles in each non-zero degree ply along a 50 mm span centered lengthwise on each sample. The reported micro-crack density is the average of the micro-crack density over the 50 mm span on a minimum of 6 samples of each laminate.

The two-inch square IM7 / 977-3 samples manually cycled between –196 °C and 120 °C were polished on perpendicular sides. Crack density was not calculated. The full length of each polished side was observed at 100X in an optical microscope at intervals of 0, 1, 10, 30, 50, 70, 90, 110, 120, and 130 cycles to determine when the first crack appeared in the surface plies and when the first crack appeared in the inner 4 blocked plies.

2.5 Manual Combined Cryogenic and Thermal Cycling

Combined cryogenic and elevated temperature cycles were applied to two IM7 / 977-3 ($[0_2/90_2]_S$) samples by submersing them in LN_2 for 10 minutes followed immediately by being placing them in an oven at 120 °C for 10 minutes. No hold at ambient temperature was included.

An axial and transverse side of each of two samples were inspected for evidence of initiation of micro-cracking anywhere in the sample, initiation of micro-cracking of the inner block of plies, and a crack extending completely through the inner block of plies. The samples were scanned for cracks at intervals of 0, 1, 10, 30, 50, 70, 90, 110, 120, and 130 cycles. The number of micro-cracks was not recorded. A micro-crack first appeared in one of the outer blocks of zero-degree plies after 50 cycles were applied.

3. RESULTS AND DISCUSSION

3.1 Cryogenic Cycling of IM7 / 5250-4

In general, cracking initiated early and was significant on the outer plies while the inner plies experienced minimal cracking and resisted cracking until well over 100 cycles were complete. The measured micro-crack density as a function of cycles in LN_2 is shown in Figures 2-4 for Lay-ups 1-3.

3.1.1 Lay-up 1, $[0/90]_{2S}$ Referring to Figure 2, the maximum density of 0.062 micro-cracks / cm in Lay-up 1 was extremely low – representing approximately 1 crack per sample in each ply observed. Cracks did not form until between cycle 175 and cycle 250. When a crack formed in one of the inner 90-degree plies (ply 4 or 5) it grew completely through the block of plies as illustrated in the image in Figure 5 and arrested at the 0/90 interfaces with no delaminations along the 0/90 interfaces. A few cracks were also observed in the outer 90-degree plies (plies 2 and 7).

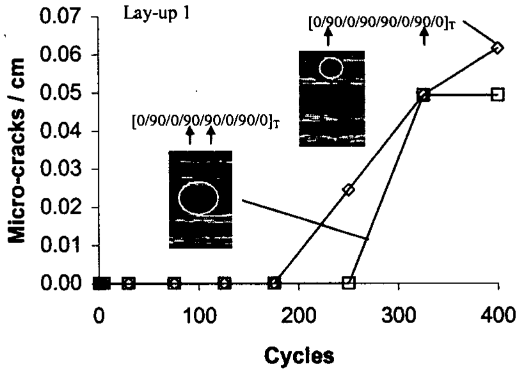

Figure 2. Micro-crack density in IM7 / 5250-4 blocked cross-ply laminate

3.1.2 Lay-up 2, $[0/+45/-45/90]_S$ The scanned plies (non-zero degree plies) in Lay-up 2 also did not crack until after cycle 175. Cracks were only observed in the block of 90-degree plies at the center of the samples. The micro-cracks initiated and grew completely through the block of 90-degree plies. Upon further cycling, some of these cracks continued to penetrate one-quarter of the way through the adjacent –45 degree plies. Minor delaminations (less than a ply thickness in length) at the 0/-45 interfaces were also observed at the tips of cracks running through the 90-degree plies

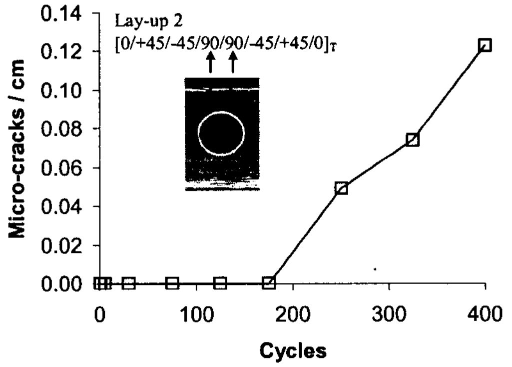

Figure 3. Center ply group micro-crack density in IM7 / 5250-4 quasi-isotropic laminate

3.1.3 Lay-up 3, $[90/0/90/0/90/0/90/0/90]_T$ The Lay-up 3 samples were the only ones oriented such that the surface plies could be inspected for micro-cracks. After 400 cycles the micro-crack density in the surface plies was very extensive, exceeding 5 cracks / cm (42 times greater than in the inner plies of Lay-ups 1 and 2). In fact, in some of the most heavily cracked regions more than one crack was present within a distance of 4 ply thicknesses.

While the large surface crack density is not desirable, no cracks were observed, even after 400 cycles, in any of the inner plies of the Lay-up 1 samples. This observation is consistent with Pagano *et al.'s*[4] demonstration of blocked plies being less resistant to mechanical loading. The inner plies of Lay-up 3 ($[90/0/90/0/90/0/90/0/90]_T$), which did not have blocked plies, were apparently more resistant to damage from thermal cycling than the inner plies of Lay-ups 1 ($[0/90]_{2S}$) and 2 ($[0/+45/-45/90]_S$ which did have blocked plies. In terms of using IM7 / 5250-4 as a material for cryogenic tanks, the ability to contain a fluid must be considered. Permeability with respect to LN_2 or liquid oxygen was not measured, however, a couple of observations can be made. The lack of cracks in any of the inner plies of Lay-up 3 is important because compared to the other lay-ups at least two additional plies are available to act as a barrier to fluid flow.

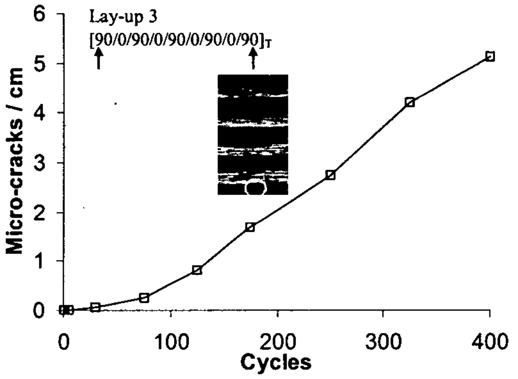

Figure 4. Surface ply micro-crack density in IM7 / 5250-4 cross-ply laminate

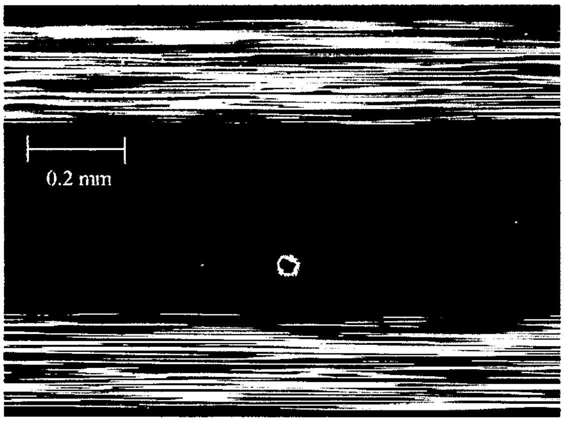

Figure 5. Micro-crack in 90-degree ply block of a $[0/90]_{2S}$ specimen

3.1.4 Mechanical Properties After 400 cycles the tensile modulus of the three IM7 / 5250-4 lay-ups was within 2.0 GPa of the tensile modulus measured prior to cycling. This variation is within the variation expected due to material non-uniformity. Tensile moduli of 81.6 GPa, 60.9 GPa, and 78.6 GPa were measured for Lay-ups 1, 2, and 3, respectively. Figure 6 shows a plot of the zero-degree tensile strength as a function of cycles in LN_2 for the three lay-ups tested. The general trend is a gradual decrease in strength with increasing number of cycles. The largest decrease in strength was measured for Lay-ups 1 ($[0/90]_{2S}$) and 2 ($[0/+45/-45/90]_S$) – approximately 8.5 % – while the strength of Lay-up 3 ($[90/0/90/0/90/0/90/0/90]_T$) decreased by only 4%. The decrease in strength of the quasi-isotropic Lay-up 2 may be due to cracks from the inner 90-degree plies penetrating partially into the 45-degree plies.

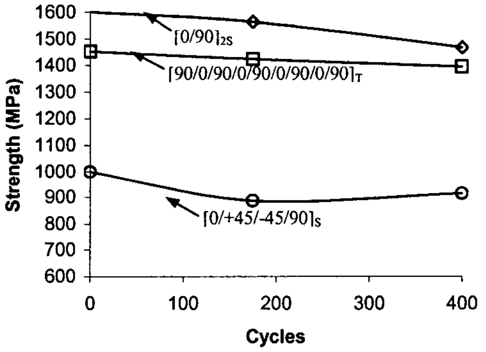

Figure 6. IM7 / 5250-4 zero-degree tensile strength as a function of LN_2 cycles

3.2 Combined Cycling of IM7 / 977-3

Combined cryogenic and elevated temperature cycles were applied to two IM7 / 977-3 ($[0_2/90_2]_S$) samples. The number of cracks in the outer plies increased as cycling continued, and the cracks in the surface block of plies extended through the two plies of the block. The first crack extending partially through the four plies of the inner block was present after 110 cycles. After 130 cycles, the partial crack in the inner plies of one of the samples had grown completely through the block.

The appearance of cracks in the outer plies significantly before formation of a crack in the inner plies (60 cycles prior) is consistent with the IM7 / 5250-4 tests in which surface ply cracks were present after 30 cycles but inner ply cracks did not form until after 175 cycles. The delay in the formation of inner ply cracks is also consistent with Timmerman *et al.'s*[2] observation that "the crack density in the inner plies was lower than the crack density in the outer plies" of the model carbon / epoxy laminates that were tested. However, the delay in formation of cracks in both IM7 / 5250-4 and IM7 / 977-3 as well as the continued increase in crack density in IM7 / 5250-4 is in contrast to Timmerman *et al.'s*[2] findings of cracks present after the first cycle and nearly constant crack density after 5 cycles. The number of applied cycles at which the first surface ply crack appeared was relatively consistent for the two materials – 30 cycles for IM7 / 5250-4 and 50 cycles for IM7 / 977-3 – despite the difference in their cycle profile.

4. CONCLUSIONS

This study examined the ply-level damage accumulated due to cycling polymer composite laminates in LN_2 (IM7 / 5250-4) and cycling in LN_2 followed by equilibration at 120 °C (IM7 / 977-3). Cross-ply lay-ups of both materials and a quasi-isotropic lay-up of IM7 / 5250-4 were studied. Micro-cracking was most severe in the surface plies where micro-cracks formed 60 to 100 cycles before micro-cracks were observed in the inner plies. The surface ply micro-crack density was also up to 42 times greater than observed for the inner plies. The micro-crack density in all lay-ups, except the central 90-degree block of one lay-up, did not appear to approach saturation even after 400 cycles. A relatively linear relationship between micro-crack density and the number of times submerged in LN_2 was apparent for the IM7 / 5250-4 samples once significant micro-crack density was established. A cross-ply lay-up with blocked plies ($[0/90]_{2S}$) was considerably less resistant to cracking of the inner plies than a non-blocked lay-up ($[90/0/90/0/90/0/90/0/90]_T$). The pattern of cracking, i.e. cracks first forming after 30 to 50 cycles in the surface plies followed by inner ply cracks forming after 110 to 175 cycles, was similar in both the material cycled in liquid nitrogen and the material subjected to a combined cycle. The tensile modulus of the IM7 / 5250-4 specimens was unaffected by thermal cycling, but the tensile strength of the $[0/90]_{2S}$ and $[0/+45/-45/90]_S$ lay-ups decreased by 8.5 %.

Future work will emphasize ply-level elastic analyses to study the stresses originating the micro-cracks and the possibility of predicting their initiation.

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