Thermal and Mechanical Durability of Graphite-Fiber-Reinforced PMR–15 Composites

Kenneth J. Bowles
Lewis Research Center
Cleveland, Ohio

National Aeronautics and
Space Administration

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K.J. Bowles
Polymers Branch, Materials Division, NASA Lewis Research Center, Cleveland, Ohio 44135 USA

ABSTRACT: Earlier work, which reported relationships between compression properties and elevated temperature aging times and weight losses, also pointed out the apparent influence of surface layer formation and growth on the retention of compression properties during extended aging times. Since that time, studies have been directed toward evaluating the growth of the surface layer. This layer was found to change in its composition and features as the aging temperature changed. Microcracks and small voids initiated and advanced inward at all temperatures. Visible oxidation at the surface occurred only at temperatures above 260 °C. Relationships between layer thickness and aging time and temperature were evaluated and empirically formulated. Then, the compression properties were graphically related to the surface layer thickness with excellent correlation. The surface layer was observed to influence the compression strength of thin samples only.

1 INTRODUCTION

Programs are under way at the NASA Lewis Research Center to develop advanced propulsion systems for 21st century aircraft. To do this, it is necessary to develop predictive models that describe the durability of polymer matrix composite structural propulsion components under extreme ambient conditions. This paper is aimed toward developing an engineering-based description of the thermal and mechanical durability of graphite-fabric-reinforced, polyimide, PMR–15 composites at temperatures ranging from 204 to 343 °C. Aging times reached 26,300 h for specimens aged at 204 °C. Particular attention was given to those chemically induced physical changes that have the most influence on the degradation of compression properties. Results were evaluated by the (1) thermal oxidative stability (TOS) of the composite, (2) composite compression properties, and (3) microstructural changes.

2 MATERIALS

The material that was studied was PMR–15 reinforced with T650–35, 24 by 23, 8 harness satin-weave graphite fiber fabric. The aged specimens measured about 11- by 9-cm in length and width and were either 4, 8, or 20 plies thick. These dimensions were chosen to provide nominal cut-edge to total-surface-area percentages of 3, 5, and 12 percent, where the total surface area consisted of both cut and molded surfaces. The molded surfaces were those that were in contact with the metal mold or vacuum bag during the curing process. The materials were processed at GE Aircraft Engines, Inc., in Evendale, Ohio.

3 TESTING

The composite materials used were aged in air-circulating ovens at temperatures of 204, 260, 288, 316, and 343 °C, and an air flow maintained at 100 cm^3/min. The laminates were removed periodically, allowed to cool in a desiccator, weighed, and either returned to the oven or permanently removed for testing. The aging time was considered to be complete when the weight loss exceeded 10 percent.

All specimens were conditioned at 125 °C for 16 h before compression tests were conducted. The compression tests were performed as specified in *Test Method for Compressive Properties of Rigid Plastics* (ASTM D–695M), with a cross-head speed of 1.2 mm/min, a temperature of 23.3 °C, and a relative humidity of 50 percent. No end tabs were used. Strain was measured with an extensometer, and moduli were measured using strains and loads at 500 and 1500 microstrain. Surface layer thicknesses were measured from photomicrographs of sectioned specimens.
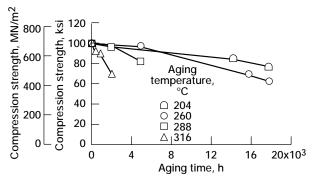
Figure 1. Compression strength of T650–35/PMR–15 composite specimens as a function of aging time at various temperatures. Number of plies, 20.
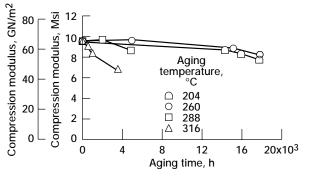

Figure 2. Compression modulus of T650–35/PMR–15 composite specimens as a function of aging time at various temperatures. Number of plies, 20.
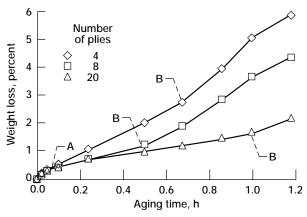

Figure 3. Weight loss of T650–35/PMR–15 composites as a function of aging time at 316 °C.

Figure 4. Microcrack and oxidation layer growth during isothermal aging

4 RESULTS

Selected specimens were removed from the aging ovens for compression testing at different times during the aging periods. Figures 1–2 (from Bowles et al. 1995) show strengths and moduli, respectively, of the 20-ply specimens plotted against aging time. When the ordinate variable is aging time, the relationships all appear to be separate linear curves with a different slope for each temperature. However, the data from the 204 and 260 °C tests appear to be identical. When percent weight loss is the independent variable, all the data except that of the specimens aged at 204 °C appear to collapse onto a single curve with the relationship $\ln S_C = 4.614 - 10.259 \times 10^{-2}\, w$, where S_C is the compression strength in MN/m^2 and w is the percent weight loss. Neither of these two relationships, percent weight loss or aging time, produce one weight loss curve that accommodates the data at all the temperatures that were studied. The data from Figure 1 indicate that the PMR–15 composite material will not retain its strength very long at temperatures over 260 °C. The initial moduli values appear to be retained for longer periods at the lower temperatures (Fig. 2).

As mentioned in the MATERIALS section, the fabric-reinforced composites had two types of surfaces. For these tests, the majority of surface area was composed of a resin-rich molded surface that was in contact with the autoclave bagging material during the processing phase. The cut edges, which contained fiber ends and axial fiber surfaces, comprised the second type of surface. Previous studies showed that weight loss rates are different for these two types of surfaces (Bowles & Meyers 1986). This can be illustrated by the typical weight-loss versus aging-time plot (at 316 °C) shown in Figure 3. The plot can be broken into three distinct sections:

(1) The origin to point A shows a rapid weight loss that is proportional to the specimen volume.

(2) Point A to B shows a linear weight loss rate.

(3) After point B, the weight loss rate is accelerated because of cracking and exposed fiber oxidation, mainly along cut surfaces.

Figure 4 shows a schematic of the surface damage growth during this period. The depth of cut surface damage increased with increasing specimen thickness. Because of this, weight loss data cannot be compared for specimens of different thicknesses. Also, weight losses from cut surfaces exceed those from molded surfaces (Bowles & Kamvouris 1995).

Two different types of surface degradation occur in these composites. Aging at the higher temperatures (288 to 316 °C) produces a light-colored surface layer that grows inward and causes voids and microcracks to initiate and grow within the layer, as in Figure 5a. The light color is attributed to the formation of solid oxidation products at the higher temperatures. At the lower temperatures (Fig. 5b), specimens show the same advance of voids and microcracks into the surface, but
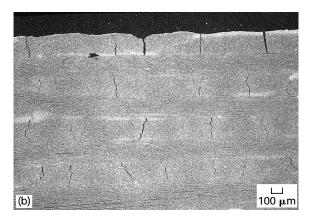
Figure 5. Surface oxidation of T650–35/PMR–15 composite specimens aged in air. (a) Aged 1000 h at 316 °C. (b) Aged 10,000 h at 204 °C.
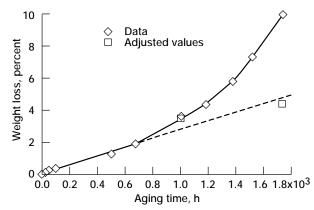

Figure 6. Adjusted weight loss of composites at 316 °C. Number of plies, 8.

Figure 7. Surface layer thickness as a function of aging time at various temperatures.

the oxidized light band of matrix material is not visible. The two degradation mechanisms that are operating during isothermal aging are surface oxidation and bulk thermal degradation. Results of compression testing of composite layers that were machined parallel to the molded surface layer show that after aging was completed at 204 °C for 26,300 h the compression strength of the visibly damaged layer was one half that of the apparently less damaged central core material. This leads one to believe that the growth of the cracked surface layer contributes to the degradation of the mechanical properties of PMR–15 composite material.

Because the measured weight loss includes the cut-edge weight loss, it does not represent the material that was machined into the compression test specimens. Consequently, an estimate of the cut-edge weight loss was determined. Cut edges were trimmed off some of the aged 11- by 9-cm panels. These pieces were dried and weighed, and their dimensions were measured with calipers. The density of the central piece and each edge piece was calculated and compared with the calculated densities of the pristine laminate, and new (adjusted) percent weight loss values were calculated from the changes in densities. A sample of the results are shown in Figure 6. These data appear to lie on or near an extrapolated extension of the AB section of the weight loss curve, showing that the actual weight loss is much less than that measured during the isothermal oven tests. It is obvious that another means of evaluating composite damage should be investigated.

The thickness of the surface layer grows during the isothermal aging time. Figure 7 shows the relationship between the thickness of the resin-rich surface damage layer and the aging time at all temperatures. The relationships appear to be linear at all five temperatures, with slower growth rates at the lower temperatures. The data from the two lower temperature tests indicate what may be an initial fast rate of growth and then a slower steady rate after 1000 h of aging. This may be normal scatter, however. One item of interest is that these linear curves appear similar to the compression strength curves in Figure 1.

Figures 8–10 present compression strength, plotted as a function of the layer thickness of the composite at various temperatures. Each figure contains data for one specimen thickness: 1.50, 2.77, or 6.78 mm (4, 8, or 20 plies). All the data for the two thicker specimens (Figs 9–10) fall on one curve. The calculated, "best fit" set of data included in Figures 9–10 is consistently close to the measured values. For specimens machined parallel to the molded surfaces of large specimens, the
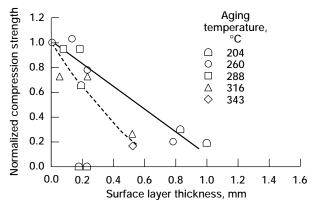
Figure 8. Composite compression strength as a function of surface layer thickness at various temperatures. Number of plies, 4.
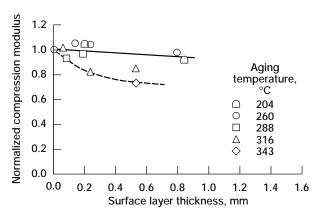

Figure 11. Compression modulus as a function of surface layer thickness at various temperatures. Number of plies, 4.
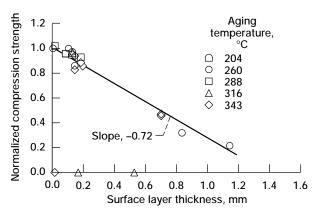

Figure 9. Composite compression strength as a function of surface layer thickness at various temperatures. Number of plies, 8.
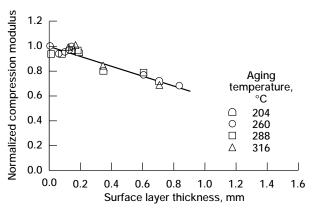

Figure 12. Compression modulus of composites as a function of surface layer thickness at various temperatures. Number of plies, 8.
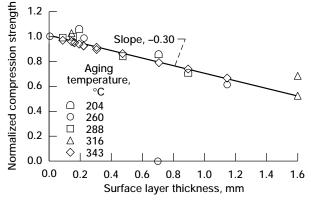

Figure 10. Composite compression strength as a function of surface layer thickness at various temperatures. Number of plies, 20.
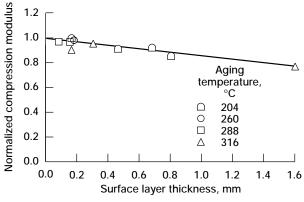

Figure 13. Composite compression modulus as a function of surface layer thickness at various temperatures. Number of plies, 20.

inner, crack-free material decreased in strength by a considerable amount (as much as 50 percent). The measured strength of the core material was close to that of an aged specimen with surface degradation and the same thickness. These data indicate that the formation and growth of the surface layer does not significantly reduce the compression properties of 8- and 12-ply fabric-reinforced composites. This was not so for the thinnest specimens. It is evident in Figure 8 that the 316 °C data fell below those of lower temperature compression strengths. This is due to the larger percentage of the weaker oxidation layers at the outer surfaces. Figures 11–13 show the moduli as a function of the layer thickness. In Figures 12–13, the modulus data collapsed onto one linear curve.

The relationship between specimen thickness and the retention of compression properties is evident in these figures. The 8- and 20-ply specimens retained their moduli considerably longer than the 4-ply composite. One other fact to acknowledge is that the moduli of the 8-ply composite material did not decrease by more than 30 percent over the time studied for aging at temperatures below 288 °C. Structures that are stiffness dependent should be useable for tens of thousands of hours.

5 SUMMARY AND CONCLUSIONS

The results of this study indicate that simple, linear relationships exist between the compression properties of graphite-fiber-fabric/PMR–15 composites and the depth of the surface layer that develops and grows during periods of aging at elevated temperatures. The buildup of the surface layer is indicative of the physical condition of the fabric-reinforced PMR–15 composites at all temperatures that were studied. However, although the surface layer is indicative of the decrease in strength, the central core volume is the main contributor.

Specimen thickness is a significant factor in the deterioration of compression properties during such periods of exposure. It is apparent from Figures 8–10 that the influence of the surface layer diminishes as the composite thickness increases. This is especially apparent in Figure 8. The strength data from the 4-ply specimens aged at 316 °C are below those measured at the other three temperatures. As noted earlier, the surface layer for a specimen aged at 316 °C had a compression strength about half that of the core material after aging at 204 °C for 26,300 h. Thus, for specimens that had a significant amount of oxidative attack in the surface layer, thinner specimens should show lower strengths than those aged at lower temperatures. That is what we see in Figure 8. Two deleterious mechanisms are observed within the specimens: surface oxidation and core reactions.

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Kenneth J. Bowles
NASA Lewis Research Center
Cleveland, Ohio 44135 USA

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