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FEASIBILITY OF KEVLAR 49/PMR-15 POLYIMIDE FOR HIGH TEMPERATURE APPLICATIONS

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FEASIBILITY OF KEVLAR 49/PMR-15 POLYIMIDE FOR HIGH TEMPERATURE APPLICATIONS

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Abstract

Kevlar 49 aramid organic fiber reinforced PMR-15 polyimide laminates were characterized to determine the applicability of the material to high temperature aerospace structures. Kevlar 49/3501-6 epoxy laminates were fabricated and characterized for comparison with the Kevlar 49/PMR-15 polyimide material. Flexural strengths and moduli and interlaminar shear strengths were determined from 75° to 600°F for the PMR-15 and from 75° to 450°F for the Kevlar 49/3501-6 epoxy material. The study also included the effects of hydrothermal and long-term elevated temperature exposures on the flexural strengths and moduli and the interlaminar shear strengths.

I. INTRODUCTION

Because of the limited thermo-oxidative stability of organic fibers and the possible degradation of the fiber properties at the high temperatures needed to process high temperature resins, organic fibers have found limited applications as a reinforcement for high temperature resins. However, DuPont's Kevlar 49 aramid organic fiber is unique in that it does not melt and has high short-term strength retention at temperatures approaching 500°F.(1) During long-term exposure in air at high temperatures, however, the bare fiber degrades.(1) Protection of the fiber with a thermo-oxidatively stable high temperature resin appears to be a viable means of retaining the inherent high strength properties of the fiber during extended exposure to high temperatures. The purpose of this investigation was to determine the feasibility of reinforcing PMR-15 polyimide resin matrix with Kevlar 49 fiber. The effects of thermo-oxidative and hydrothermal environments on the composite material properties were determined. The material was evaluated on the basis of flexural strength and modulus and short-beam interlaminar shear strength (ILSS) at room temperature and at elevated temperatures. The weight loss characteristics of bare Kevlar 49 and Kevlar 49/PMR-15 laminates were also determined. For comparative purposes, Kevlar 49/3501-6 epoxy laminates were also evaluated.

2. EXPERIMENTAL PROCEDURE

2.1 Fiber Reinforcement and Resins

The fiber reinforcement was DuPont 4560 denier Kevlar 49 aramid, zero twist roving (type 969) having a certified tensile strength of 534,000 psi, a tensile modulus of 18.5×10^6 and a density of 1.46 g/cc. The roving was supplied without a surface finish.

Two matrix resins were investigated. One was a high temperature polyimide resin designated PMR-15, and the other was Hercules 3501-6 epoxy resin. The PMR-15 solution was formulated from the methyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) at stoichiometric ratio of 2 NE/3.087MDA/2.087 BTDE. The BTDE was prepared as 50 weight percent solutions by refluxing a suspension of the corresponding dianhydride in anhydrous methanol for approximately 2.75 hours.

2.2 Composite Fabrication and Specimen Preparation

Prior to resin impregnation the roving was dried at 200°F for 16 hours in an air circulating oven. The roving was wound on a drum at 8 turns per inch to provide a cured ply thickness of approximately 7.5 mils. The fiber was impregnated with a predetermined quantity of resin to provide cured laminates having a fiber content of 55 to 60 volume percent. Prior to removing the prepregs from the drum, the prepregs were air dried to reduce the solvent content to approximately 10 percent. Unidirectional laminates were prepared by cutting 3 x 8 inch plies from the prepreg tape. In preparation for molding the Kevlar 49/PMR-15 laminates, a selected number of plies were stacked in a preform mold between porous Armalon fabric and imidized at 400°F for one hour under a pressure of approximately 0.1 psi. Molding was accomplished by placing the preform into a matched metal die that had been preheated to 450°F. Following a dwell time of 5 minutes at essentially 0 pressure, a mold pressure of 500 psi was applied and the mold temperature was increased to 550°F at the rate of 10°F per minute. Pressure and temperature were maintained for two hours followed by decreasing the temperature to 400°F before releasing the pressure and removing the laminate from the die. The cured laminates were postcured in an air circulating oven in which the temperature was raised from ambient temperature to 550°F at a rate of 4°F per minute and held at 550°F for 16 hours.

In preparing Kevlar 49/3501-6 laminates the 3 x 8 inch plies were placed in an air circulating oven at 235°F for 1 hour to volatilize the residual solvent. The plies were stacked in a cold matched metal die and then the die was placed into a press heated to 225°F. After a dwell of 30 minutes at zero pressure, the pressure was increased to 100 psi and the temperature raised to 350°F at a rate of 10°F per minute. These final conditions were maintained for 2 hours. The die was cooled to 150°F before pressure was released. Laminates were postcured 16 hours in a 400°F air circulating oven. The laminates were then inspected for possible defects, i.e. delaminations or voids, using "C" scan procedures.

2.3 Composite Environmental Exposure

Several 3 x 8 inch Kevlar 49 fiber reinforced laminates were fabricated with each resin system to provide sufficient materials for the study. Coupons (2-5/8 x 3 inches) were cut from a single 3 x 8 inch laminate and subjected to hydrothermal and thermo-oxidative exposure. All of the coupons were cut from essentially void free laminate as assessed by C-scan. The hydrothermal environment was accomplished by supporting the laminate coupons in a closed chamber above a 180°F water bath so that condensate formed on the laminate surfaces. The coupons were periodically removed from the chamber, blotted dry and then weighed. After saturation had been attained (no significant increase in coupon weight with increased exposure time) the coupons were removed from the chamber and sealed in a vapor proof container. The thermo-oxidative environments were provided by air circulating ovens. Bleed air was metered into the ovens at a rate of 6.1 inch^3 per minute. Coupons were periodically removed from the ovens and allowed to cool to room temperature in a desiccator before re-weighing to determine weight losses. The conditioned coupons were cut into flexural and short beam shear specimens using a diamond cutting blade. Flexural specimens were 1/4-inch wide by 2-5/8 inch long. The short beam shear specimens were 1/4 inch wide; the lengths of the specimens were selected so as to result in a shear test span-to-thickness ratio of 4.

2.4 Composite Testing

Flexural tests conformed essentially to the ASTM standard method D790. Tests were made on a 3-point loading fixture with a fixed span of 2 inches. The thicknesses of the various laminates ranged from 0.062 to 0.091 inches. The resultant span/thickness ratio ranged from 32 to 22. The rate of center loading for flexural testing was 0.05 inch/minute. Interlaminar shear strength tests were conducted in accordance to ASTM D 2344 using a constant span-to-thickness ratio of 4. The fiber content of the test specimens ranged from 53 to 60 percent by volume and was quantitatively determined from photomicrographs. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests the load was applied after the chamber had equilibrated at the test temperature.

3. RESULTS AND DISCUSSION

3.1 Fiber and Composite Thermo-oxidative Stability

It has been reported that bare Kevlar 49 aramid fiber shows no loss in room temperature tensile strength after being exposed to 302°F in air for seven days.(1) However, after exposure at 482°F for the same duration, the tensile strength was reduced by approximately 50 percent.(1) In the current investigation bare 4560 denier Kevlar 49 aramid roving was exposed in air at 500°F. The weight loss of the bare fiber as a function of exposure time is shown in figure 1. Also shown in the figure are the weight loss curves for Kevlar 49/PMR-15 laminates exposed in air at 500 and 550°F. Figure 2 shows a photomicrograph of a typical void free Kevlar 49/PMR-15 laminate. After 1000 hours of exposure the weight loss of the bare fiber was 2.9 percent. Strand tests of the exposed roving (impregnated with an epoxy resin) showed a reduction in tensile strength of about 65 percent compared to unexposed roving strength. It can be seen in figure 1 that the Kevlar 49/PMR-15 laminates underwent about one-third less weight loss after 1000 hours exposure at 500°F than did the bare Kevlar 49 fiber at 500°F. Even after 1500 hours at 550°F the laminate weight loss was only 2.3 percent. The results of these weight loss studies suggest that Kevlar 49/PMR-15 laminates have potential for use at temperatures up to 550°F.

3.2 Baseline Composite Properties

The room temperature and short-time elevated temperature flexural strenths and moduli and interlaminar shear strengths (ILSS) of the 3501-6 epoxy and PMR-15 laminates are shown in figure 3. The baseline curves shown in the figure are based on the results of three or more tests at various temperatures throughout the test temperature range. As it can be seen, the properties of both composite systems decreased with increasing test temperatures. However, at temperatures above 250°F the ILSS of the 3501-6 laminates decreased markedly. At temperatures above 350°F the laminate flexural properties exhibited a similar marked decrease and the failures were predominantly compressive. In contrast, the flexural properties of the PMR-15 laminates exhibited a gradual linear decrease to 600°F. The ILSS of the PMR-15 laminates did exhibit a more pronounced decrease above 500°F. The reduction in composite properties at elevated temperatures are attributable to lower matrix and fiber properties. Data in the literature show that both tensile strength and modulus of bare Kevlar 49 fiber are reduced by increased temperature.(2)

3.3 Effects of Long-Term Thermo-oxidative Exposure on Baseline Properties

Figure 4 shows the effects of long-term thermo-oxidative exposure on the properties of the Kevlar 49/PMR-15 and Kevlar 49/3501-6 composites. The data points shown in the figure were obtained by testing laminates that had been subjected to long-term exposure in air at various elevated temperatures and for various time periods. Each data point represents the average of three or more tests at the given test temperature. The data points are compared to the baseline composite properties. It is important to note that no degradation of the baseline flexural properties was observed for Kevlar 49/PMR-15 laminates (0.090 inches thick) that had been exposed in air for 1000 hours at 500°F or for 504 hours at 550°F. Significant degradation of baseline flexural properties was observed for room temperature, 300° and 400°F tests of laminates exposed in air for 1500 hours at 550°F. It should be noted that there appears to be a thickness effect in the extent of degradation. It can be seen that the flexural properties of 0.063 inch thick material are lower than for the flexural properties of the thicker (0.090 inch) laminates. This finding is in agreement with studies which showed that after extended elevated temperature exposure the tensile strength of Kevlar 49/epoxy composites decreased as the laminate thickness decreased.(3) Baseline flexural modulus was not found to be adversely affected by either extended high temperature exposure or laminate thickness. The baseline ILSS properties of the Kevlar 49/PMR-15 after 1000 hours at 500°F or 1500 hours at 550°F in air were degraded by extended exposure at the elevated temperatures. However, exposure at 550°F for 504 hours had a negligible effect on the ILSS. Note that a thickness effect on the ILSS was not observed. These results show that Kevlar 49 aramid fiber reinforcement in a high temperature resin matrix should be considered as a viable composite material for application for extended time at 500°F and for limited exposure at 550°F.

It also should be noted that the Kevlar 49/3501-6 laminate (0.071 inch thick) which had been exposed for 650 hours at 400°F exhibited no degradation of baseline properties. In fact, exposure at 400°F appeared to improve the laminate properties at the higher test temperatures.

It was reported that exposure of

bare Kevlar 49 roving at 392°F for 168 hours caused a 20 percent reduction of fiber tensile strength.(1) The Kevlar 49/epoxy results of this study indicate that 350°F epoxy resins, such as 3501-6, provide sufficient oxidative protection to the Kevlar 49 fiber to permit the application of Kevlar 49 reinforced epoxies at the maximum use temperature of the matrix (i.e. 350°F).

3.4 Hydrothermal Characteristics

Studies have shown that polymer matrices and Kevlar fiber absorb moisture and that the absorbed moisture affects their elastic and strength properties.(4,5,6) In the current investigation, both Kevlar 49/PMR-15 and Kevlar 49/3501-6 laminates were exposed to a wet environment until saturation had been achieved. Figure 5 shows the percent weight gain of the composites as a function of $(\text{time})^{1/2}$. It can be seen that both composite materials exhibited approximately the same rate of moisture absorption. It also can be seen that the Kevlar 49/PMR-15 material became saturated after a weight gain of approximately 2.2 percent while the Kevlar 49/3501-6 material became saturated after a weight gain of approximately 3.7 percent.

To assess the effect of moisture on the laminate properties, the flexural strengths and moduli and interlaminar shear strengths of the saturated materials were determined at various test temperatures. Figure 6 compares these properties to the baseline property curves. It can be seen that the Kevlar 49/3501-6 wet flexural strengths and moduli at temperatures above 200°F were significantly lower than the baseline properties of the 3501-6 laminates. In contrast, the Kevlar 49/PMR-15 wet flexural strengths and moduli did not differ significantly from the baseline properties of the PMR-15 laminates. However, there did appear to be a slight downward trend in flexural strength, particularly above 500°F. Associated with the lower flexural properties was a predominance of compression failures for laminates of both resin systems. All of the Kevlar 49/3501-6 specimens failed in compression at test temperatures at 300°F and above, whereas, all of the Kevlar 49/PMR-15 specimens failed in tension up to test temperatures of 400°F. Some of the Kevlar 49/PMR-15 specimens did exhibit a compression failure mode at 500°F and above.

The ILSS of both composite systems in the wet condition were found to be significantly lower than the baseline properties. It should be noted that for the 4:1 span-to-thickness ratio the Kevlar 49/3501-6 specimens exhibited thermoplastic behavior at 300°F and above; the Kevlar 49/PMR-15 specimens exhibited thermoplasticity at 400°F and above. This thermoplastic behavior made it difficult to interpret and determine the shear strengths at the higher temperatures.

An observation made from the flexural specimens was the presence of blisters on the surfaces of wet specimens after they had been tested at elevated temperatures. Blistering generally occurred in wet specimens of Kevlar 49/3501-6 tested above 350°F and in wet Kevlar 49/PMR-15 tested above 500°F. Figure 7 is a photomicrograph of a typical blister on a hydrothermally exposed Kevlar 49/3501-6 laminate which had been tested at 400°F. Fibers which had been forced out from the laminate surface and also subsurface cracks which had resulted from the rapid release of moisture can be seen. It is possible that the gross damage, or delamination, to the laminate structure contributed to the lower flexural properties observed at elevated temperature.

4. SUMMARY OF RESULTS

The following results were obtained from an investigation of Kevlar 49 aramid fiber reinforced PMR-15 polyimide and 3501-6 epoxy laminates exposed to thermal and hydrothermal environments:

1. Bare Kevlar 49 fiber exposed to air at 500°F for 1000 hours resulted in a weight loss of 2.9 percent as compared to 1.0 percent for a Kevlar 49/PMR-15 laminate with the same exposure.
2. No significant degradation of baseline flexural strength and modulus was observed for Kevlar 49/PMR-15 laminates exposed for 1000 hours in air at 500°F or for 504 hours at 550°F. However, reduction in baseline flexural properties were noted after 1500 hours at 550°F.
3. The baseline interlaminar shear strength (ILSS) properties of the Kevlar 49/PMR-15 after 1000 hours at 500°F or 1500 hours at 550°F in air were degraded by extended time exposure at temperature. However, exposure at 550°F for 504 hours had a negligible effect on the ILSS.
4. Kevlar 49/3501-6 laminates which had been exposed for 650 hours at 400°F exhibited no degradation of baseline properties.
5. Hydrothermally exposed laminates of Kevlar 49/PMR-15 showed no significant reduction of baseline flexural strength or modulus. However, hydrothermal exposure had a deleterious effect on the baseline flexural properties of Kevlar 49/3501-6.
6. Interlaminar shear strengths of both composite systems in the wet condition were found to be significantly lower than the baseline properties.

5. REFERENCES

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5. Augl, J. M., Moisture Sorption and Diffusion in Kevlar 49 Aramid Fiber. NSWC TR 79-51, March 30, 1979.

6. Browning, C. E., Husman, G. E., and Whitney, J. M., Moisture Effects in Epoxy Matrix Composite, Composite Materials: Testing and Design, ASTM STP617, 1976, p. 481.

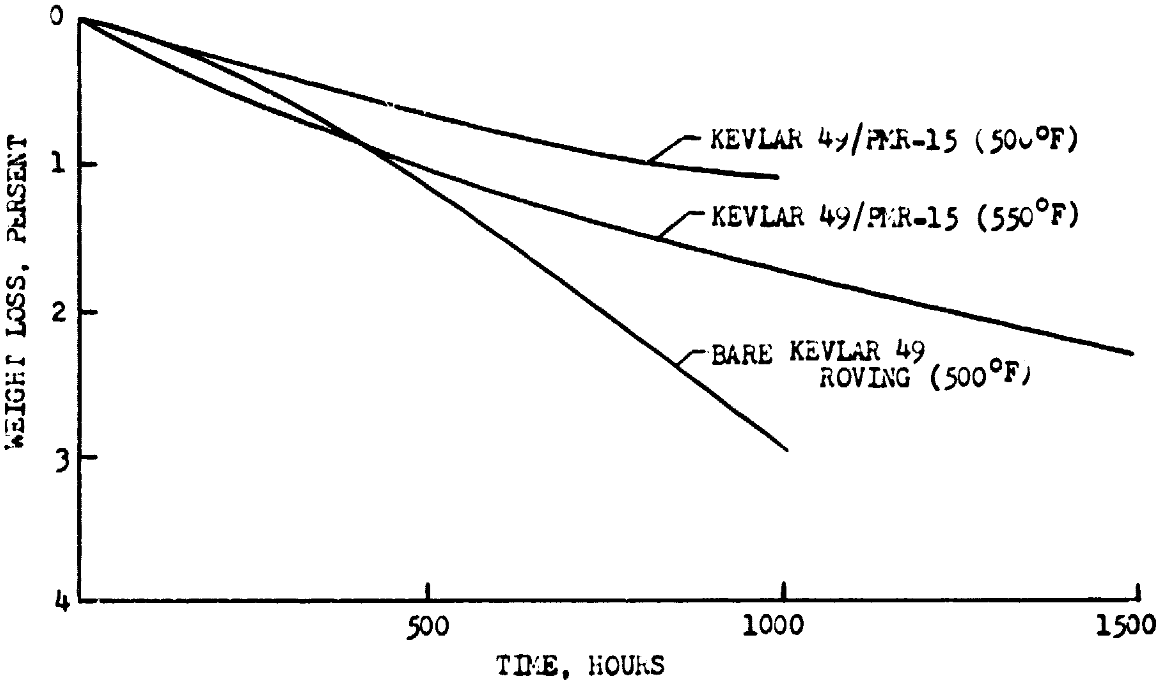

FIGURE 1.- WEIGHT LOSS OF KEVLAR 49 FIBER AND KEVLAR 49/PMR-15 COMPOSITE EXPOSED IN AIR AT ELEVATED TEMPERATURES.

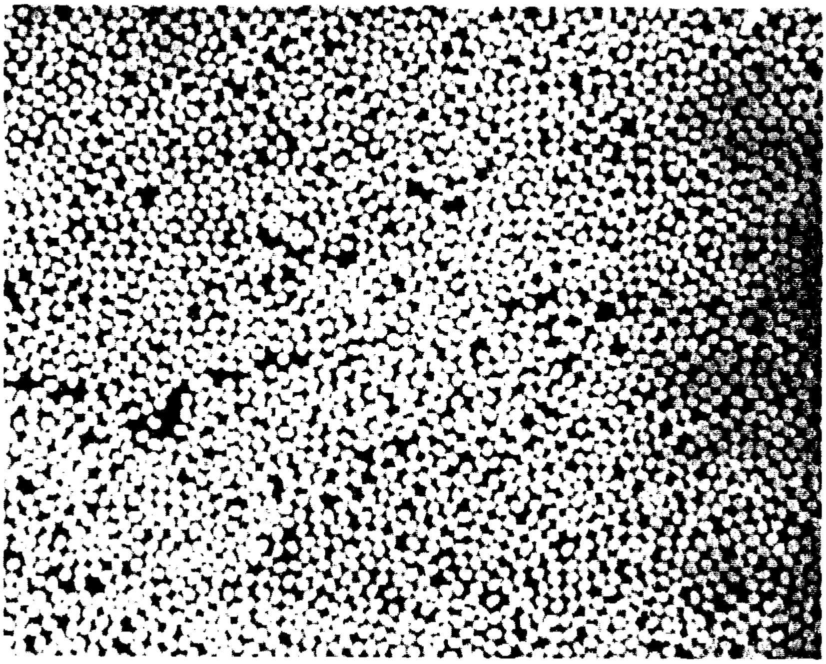

FIGURE 2.- PHOTOMICROGRAPH OF A TYPICAL KEVLAR 49/PMR-15 COMPOSITE. X250.

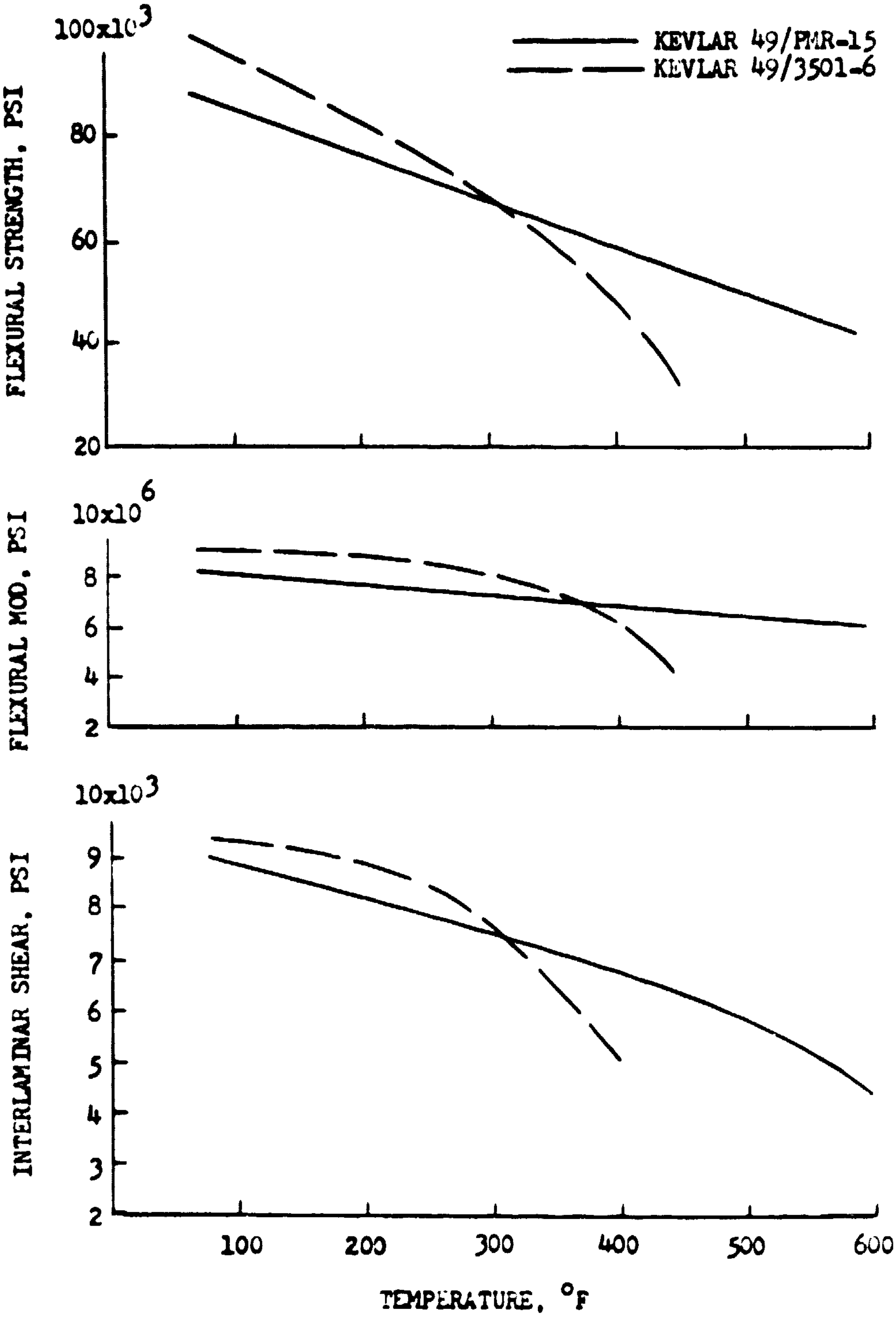

FIGURE 3.- BASELINE PROPERTIES OF POSTCURED UNIDIRECTIONAL KEVLAR 49/PMR-15 AND KEVLAR 49/3501-6 LAMINATES AS A FUNCTION OF TEMPERATURE.

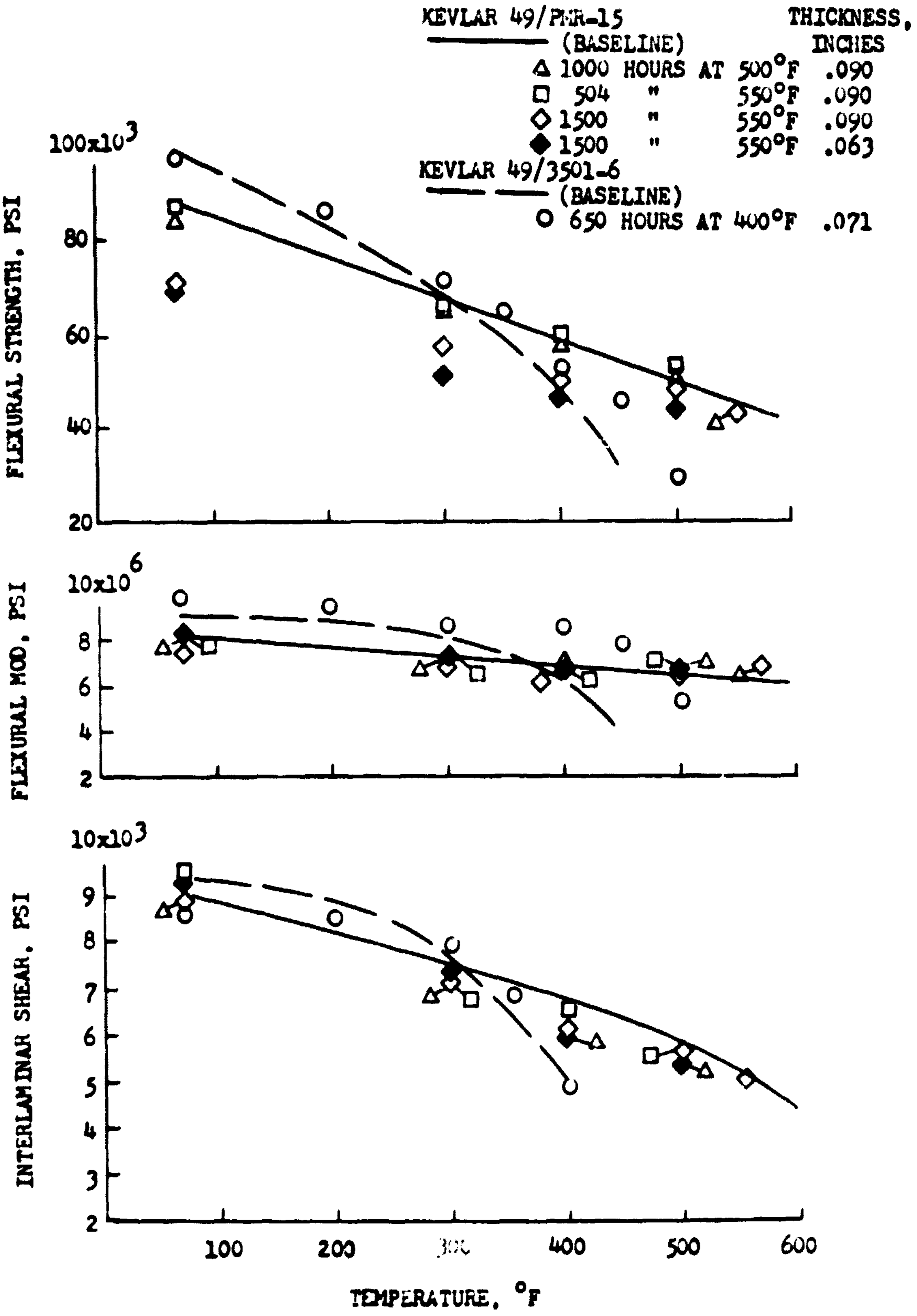

FIGURE 4.- COMPARISON OF THERMO-OXIDATIVELY EXPOSED KEVLAR 49/PMR-15 POLYIMIDE AND KEVLAR 49/3501-6 LAMINATE PROPERTIES TO BASELINE PROPERTIES AS A FUNCTION OF TEMPERATURE.

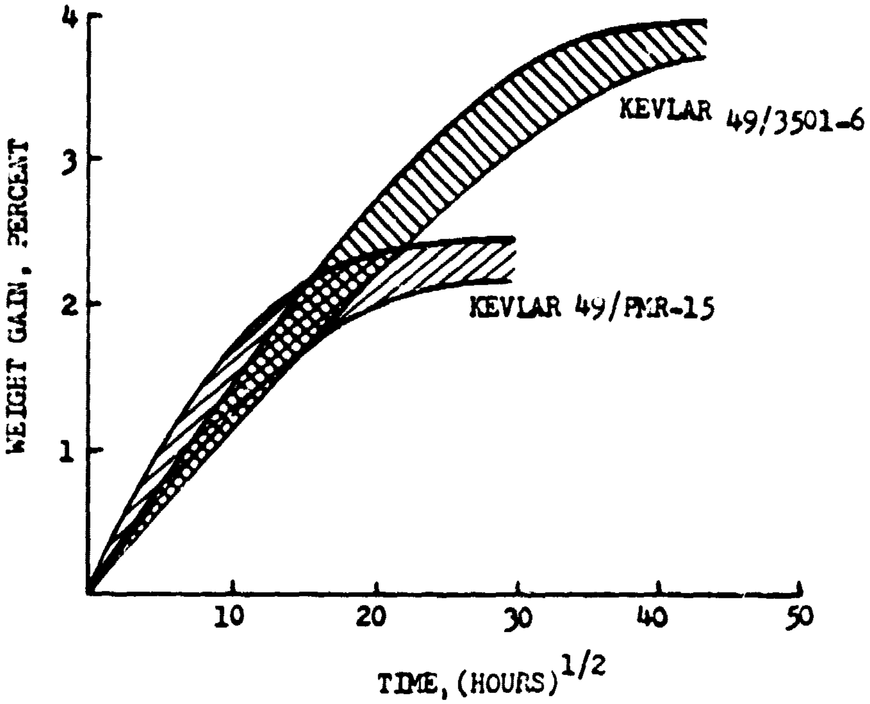

FIGURE 5.- WEIGHT GAIN OF COMPOSITE MATERIALS DUE TO ABSORBED MOISTURE AS A FUNCTION OF TIME.

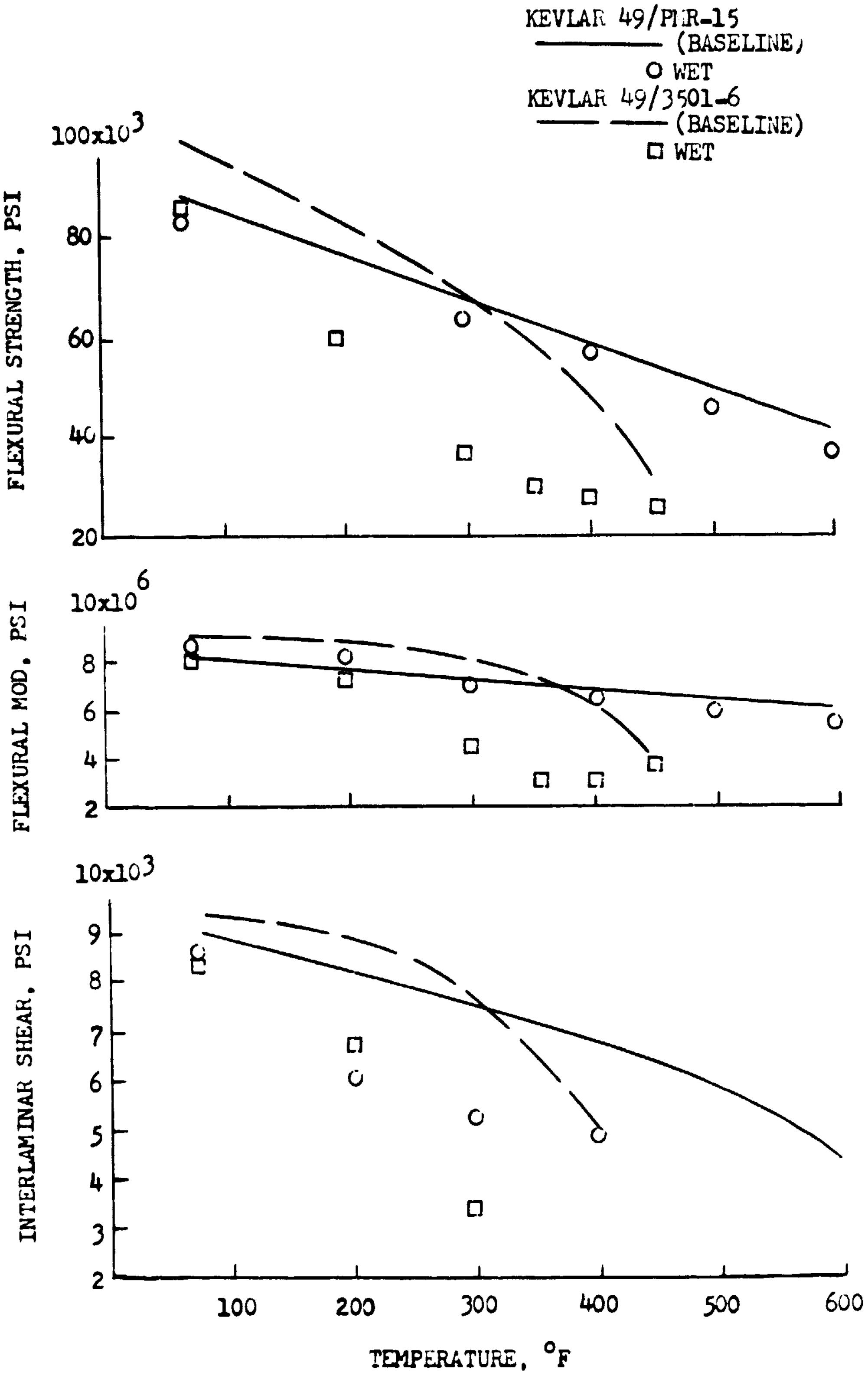

FIGURE 6.- COMPARISON OF HYDROTHERMALLY EXPOSED KEVLAR 49/PMR-15 POLYIMIDE AND KEVLAR 49/3501-6 LAMINATE PROPERTIES TO BASELINE PROPERTIES AS A FUNCTION OF TEMPERATURE.

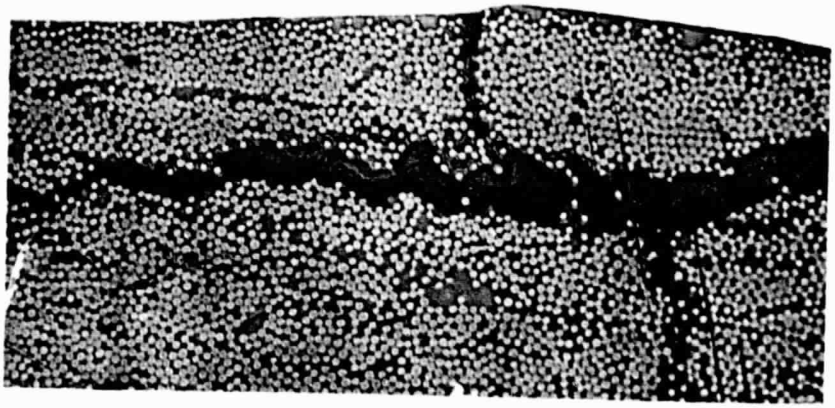

FIGURE 7.- PHOTOMICROGRAPH OF TYPICAL BLISTERING AS A RESULT OF TESTING A HYDROTHERMALLY EXPOSED KEVLAR 49/3501-6 LAMINATE AT 400°F. X100.