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EFFECT OF HIGH–TEMPERATURE LOADING ON MECHANICAL PROPERTIES OF NICALON FIBERS AND NICALON FIBER/SiC MATRIX COMPOSITES*

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Strength distributions of Nicalon fibers in Nicalon fiber–reinforced silicon carbide (SiC) matrix composite specimens, before and after exposure to elevated temperature (1300 °C) were obtained from fracture mirror size evaluations, while strength of as–fabricated Nicalon fibers were obtained from bundle tests. Mechanical properties such as ultimate strength of Nicalon/SiC composites exposed to elevated temperatures (800°C ~ 1300°C) were compared with those of as–fabricated composites at room temperature. Effects of long term exposure at elevated temperatures (1200°C) on the composite mechanical properties was also investigated. Results are interpreted on the basis of thermal degradation of reinforcing Nicalon fibers.

Introduction

Continuous–fiber–reinforced ceramic composites (CFCC's) are candidate materials for elevated temperature structural applications because of their improved flaw tolerance, large work of fracture, and noncatastrophic mode of failure.[1–4] High strength of reinforcing fibers is an important parameter which controls fracture behavior of CFCC's. Strength of reinforcing fibers is critical because once a matrix crack is initiated and extended, load is transferred from the matrix to the fibers in the wake of the crack. Weak fibers fracture and lead to catastrophic failure of the composite, whereas strong fibers accommodate the stresses. It has been shown by theoretical analysis and experimental observation that the amount of fiber pullout, which contributes to the toughening of a composite, is strongly influenced by the mean strength and the variability in strength of the reinforcing fibers.[5] Also, the ultimate load–bearing capacity of the composite is determined by fiber strength characteristics.[6] Therefore, it is clear that the strength of fibers and their strength retention at elevated temperatures are important for the design and development of CFCC's with superior mechanical properties.

Results of an investigation into the effect of elevated temperature exposure on the strength distribution of Nicalon fibers as well on mechanical properties of Nicalon/SiC composites are reported in this paper. Single–fiber strength distribution of as–fabricated Nicalon fibers was obtained from bundle tests. Strength distributions of fractured fibers in as–fabricated Nicalon/SiC composites and after elevated temperature exposure of composites were assessed from measurements of fracture mirror radii. Variations in the mechanical properties of composites evaluated as a function of test temperatures are compared with those evaluated at room temperature and are correlated to the fiber strength characteristics. . Limited tests were also conducted to investigate the effect of long term exposure at elevated temperatures on composite ultimate strength.

Experimental Procedure

Material

Carbon–coated ceramic–grade Nicalon fibers were used to study the effect of high temperature exposure on fiber strength distribution. SiC fibers were chosen for this study because of their high temperature stability and successful incorporation as reinforcements in composites for commercial applications.[7–9] Tows of Nicalon fibers were used to determine single–fiber strength distribution from bundle tests. Nicalon fiber tows of various lengths were carefully extracted from Nicalon fiber mats.¶ Typically, each tow consisted of 500 individual fibers with nominal diameters of 10–15 μm. Polymer–derived Nicalon fibers consist primarily of β–SiC crystallites with an average size of 1.7 nm, along with excess carbon and SiO.[10,11] The reported[12] density and elastic modulus (E_f) of Nicalon fibers are 2.55 g/cm^3 and 210 GPa, respectively.

Nicalon–fiber–reinforced SiC matrix composites were used to evaluate the strength distribution of fibers in the composites, which were fabricated at Oak Ridge National Laboratory by densifying multiple layers of Nicalon mats stacked in a graphite die. Chemical vapor infiltration (CVI), under forced conditions of thermal and pressure gradients, was used to densify the preforms with SiC. Details of specimen fabrication of the composite are described elsewhere.[7,13] The resulting composites were ≈90% dense.

¶ Distributed by Dow Corning Corp., Midland, MI.

Bundle and Flexure Tests

The fiber bundle test, originally developed by Manders and Chou,[14] was employed to determine the single–fiber strength distribution of as–fabricated Nicalon fibers. Weibull parameters, needed to describe the strength distribution of fibers, were estimated from load–strain plots of a fiber bundle loaded in uniaxial tension.[15] Bundle tests were conducted on a universal testing system† using the experimental set–up shown schematically in Fig. 1. Tests were conducted on fiber tows with gage lengths ranging from 27 to 100 mm under ambient conditions and at a loading rate of 0.5 mm/min.

Flexural tests for continuous Nicalon–fiber–reinforced SiC composites bars (2.9 x 4.2 x 25.4 mm) were conducted in four–point–bend mode at room and elevated temperatures on the universal testing system. For room temperature tests, loading and support spans were 9.53 and 19.05 mm, respectively, and tests were conducted at a loading rate of 1.27 mm/min at ambient conditions..

Composite bars (2.9 x 4.2 x 28.0 mm) tested at elevated temperatures were coated with SiC (35 μm thick) to prevent oxidation of exposed carbon coating on the fiber surface caused by cutting of composite specimens. For elevated temperature tests, SiC fixtures with loading and support spans of 12.7 mm and 25.4 mm, respectively were used. The loading rate for these tests was 1 mm/min. The composite bars were exposed to the test temperature for 15 minutes or as specified in air prior to fracturing them in vaccum. All specimens were loaded perpendicular to the layers of mats. Fractured composite specimens were examined on a scanning electron microscope§ (SEM) to

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† Model 4505, Instron Corp., Canton, MA.

§ Model JXA-840A, JEOL Co., Ltd., Tokyo, Japan.

locate the failure origin and establish the associated characteristic fracture surface morphology of the fibers.

Results and Discussion

Strength Distribution of As–Fabricated Nicalon Fibers

In the present study, distribution function used to describe Nicalon fiber strength is given in Eqn. 1.[16] This formulation was used because strength distribution of fibers were obtained from fibers having various gage lengths and it was appropriate to account for the size effect and represent the Weibull strength distribution at a standard gage length, L, taken to be 10 mm.

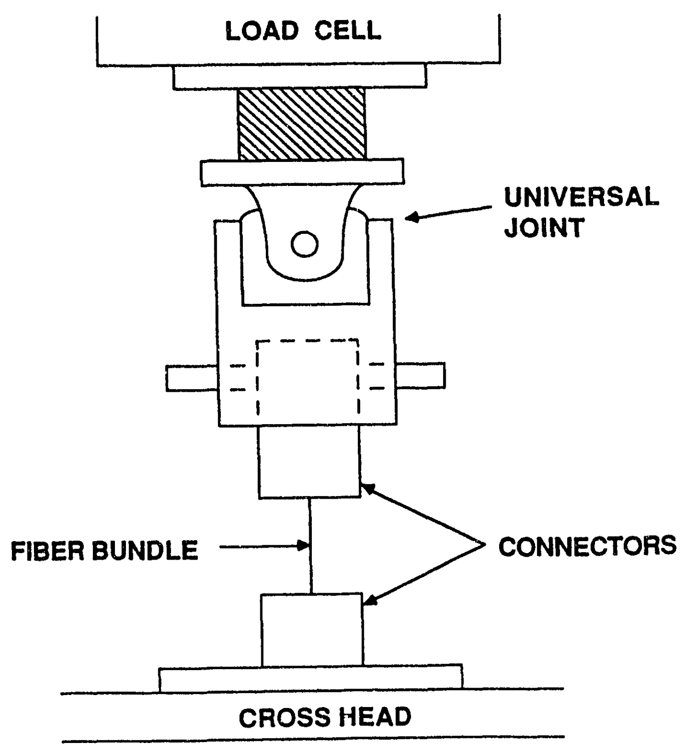

Figure 1. Schematic Representation of Experimental Set–Up Used for Bundle Tests.

$$F(\sigma) = 1 - \exp\left[-\frac{L}{L_o}\left(\frac{\sigma}{\sigma_o}\right)^m \right] \quad (1)$$

In Eq. 1, $F(\sigma)$ is the cumulative failure probability at an applied stress σ, σ_o is the scale parameter signifying a characteristic strength of the distribution, and m is the Weibull modulus that characterizes flaw distribution in the material, and L_o is the fiber gage length at which the Weibull parameters are determined. Thus, by using the Weibull distribution function as given by Eq. 1, it is possible to compare scale parameters at equivalent fiber gage lengths assuming the strength controlling flaws are independent of the fiber gagelength.

Figure 2 shows a typical load–strain plot obtained from a bundle test. Strain or displacement in the fiber bundle at a particular load was determined by subtracting the system (grips, connectors, etc.) displacement from the absolute displacement of the crosshead of the testing machine. Displacement due to system accessories was obtained by estimating system compliance following the procedure described in ASTM D 3379–75.[17]

Weibull parameters (σ_o or in terms of strain, ε_o, and m) of the as–fabricated Nicalon fibers were obtained from the maximum load P_{max}, slope of the linear portion of the load–strain behavior, S_o, slope of the line joining the maximum load to the origin, S_A, (as indicated on Fig. 2) and the specimen gage length, L_o, by solving the following equations:[15]

$$m = \frac{1}{\ln\left[\frac{S_o}{S_A}\right]} \tag{2}$$

$$P_{max} = S_o \varepsilon_o \left(\frac{1}{2.718 L_o m}\right)^{1/m} \tag{3}$$

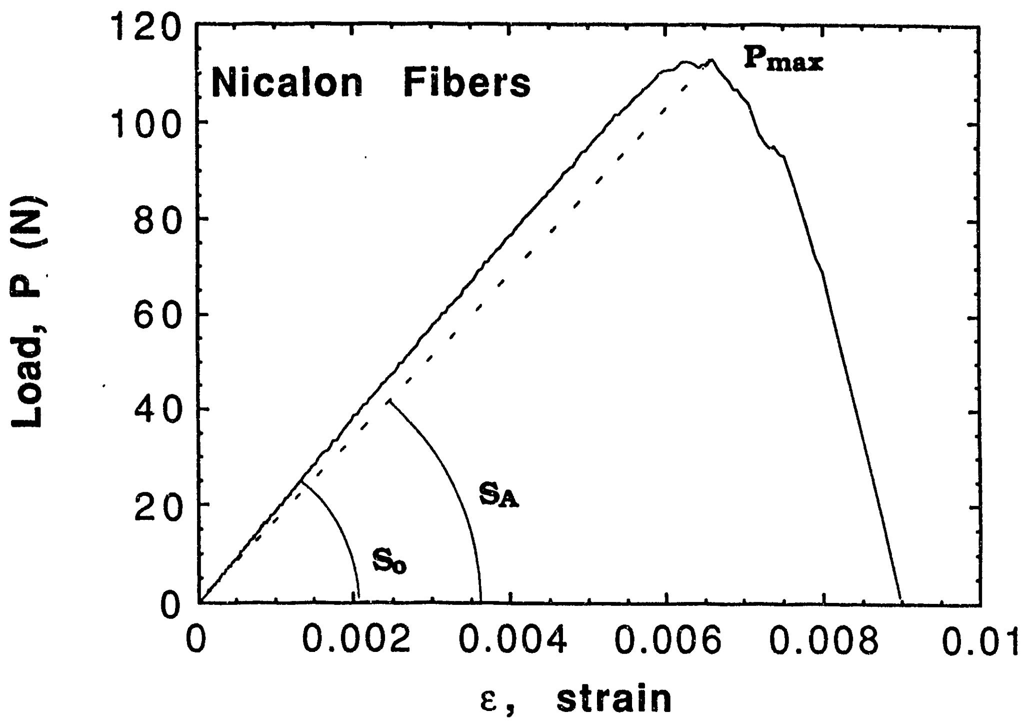

Fig. 2. Typical Load–Strain Variation Obtained from a Bundle Test of Nicalon Fibers.

$$\sigma_o = E_f \varepsilon_o \tag{4}$$

Results of seven tests conducted on fiber bundles with various gage lengths gave an average value for the Weibull modulus as 7.1. The average value for the scale parameter, after correcting it for a gage length of 10 mm using Eq. 1, was 3.45 GPa. These results are in accordance with reported values in the literature for Nicalon fiber strength distribution. Goda and Fukunaga[16] obtained strength distribution for Nicalon fibers by single–fiber testing on fibers with a gage length of 10 mm. Their reported values for the Weibull modulus and scale parameter are 4.7 and 4.24 GPa, respectively.

Strength Distribution of Nicalon Fibers in Composites After Processing

The strength distribution parameters of fibers in the composite were evaluated from characteristic features on the fractured surfaces in composites tested in four-point-bend mode. Typical surface morphology of a fractured fiber in Nicalon fiber–reinforced SiC composite, tested at room temperature in four–point–bend mode, is shown in Fig. 3. Characteristic features associated with brittle failure, such as mirror (smooth region around the fracture origin) and hackle (region of multiple fracture planes) are clearly observable on the surface of fractured fibers. SEM investigation of the fibers showed that most failed from defects or flaws located at the fiber surface.

For glasses and ceramics, such fracture surface features as mirror radii can be correlated to tensile strength through the empirical relationship:[18,19]

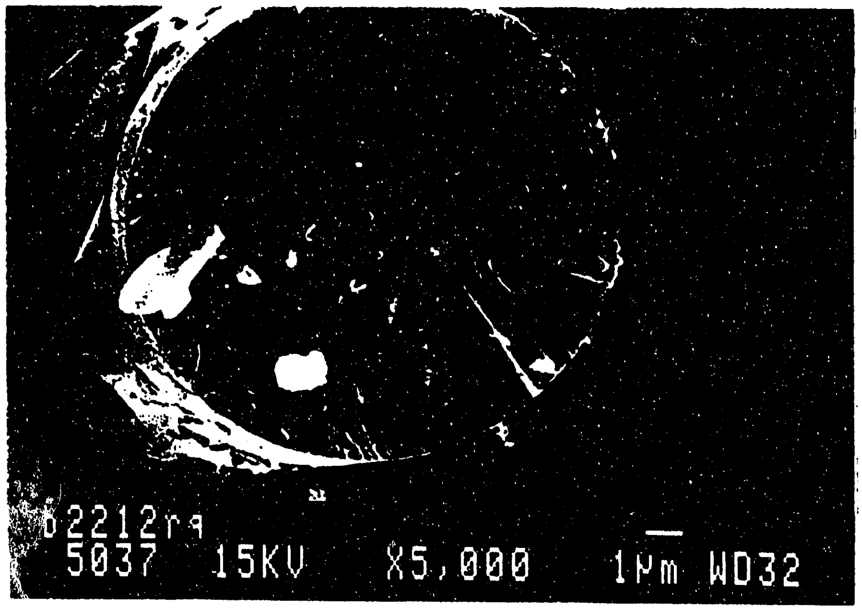

Fig. 3. Micrograph Showing the Surface Morphology of a Fractured Fiber in a Nicalon Fiber–Reinforced SiC Composite.

$$\sigma_f r_m^{1/2} = A_m \quad (5)$$

where r_m represents the mirror radii, σ_f is the tensile strength, and A_m is the mirror constant, which is related to the fracture toughness of the material and taken to be 3.5 MPa$\sqrt{m}$.[5] Strengths of more than 30 Nicalon fibers from five different fractured composite specimens were determined by measuring their fracture mirror radii and using Eq. 5. It should be noted that the fiber gagelength, L_o, over which uniform stress acts in composites is expected to be of the order of the fiber pullout lengths as shown in Fig. 4. Therefore, for accurate estimation of scale parameter, fiber gagelength was taken to be twice the average of the pullout length and was found to be 340 μm.[20] Thus, using Eq. 1 Weibull modulus and scale parameters of Nicalon fibers in composites at a gagelength of L=10 mm were obtained as 6.0 and 1.31 GPa, respectively.

Strength Distribution of Nicalon Fibers in Composites After High Temperature Exposure

The procedure followed for the determination of strength distribution parameters of fibers in composite specimens exposed to 1300°C for 15 min and fractured in four–point–bend mode was similar to that as described in the previous section. Weibull modulus and scale parameters of these Nicalon fibers at a gagelength of 10 mm were obtained as 7.8 and 1.24 GPa, respectively. Here it was assumed that mirror constant, A_m, is 3.5 MPa$\sqrt{m}$ and fiber gagelength in composite is 340 μm.

Comparison of Fiber Strength Distributions

Figure 5 compares the strength distribution of as–fabricated Nicalon fibers with those incorporated in the composite and after exposure at 1300°C for 15 minutes. Also shown in Fig. 5, for comparison purposes, is the strength distribution obtained from single–fiber tests of Nicalon fibers.[16] This figure shows two significant results: first, as–fabricated fibers exhibit an average strength of more than 50% greater than that of fibers incorporated in composites. Second, after high temperature exposure, there is further reduction in the Nicalon fiber strength compared to the fibers in as–fabricated composite. However, the Weibull moduli remains almost same in all three cases.

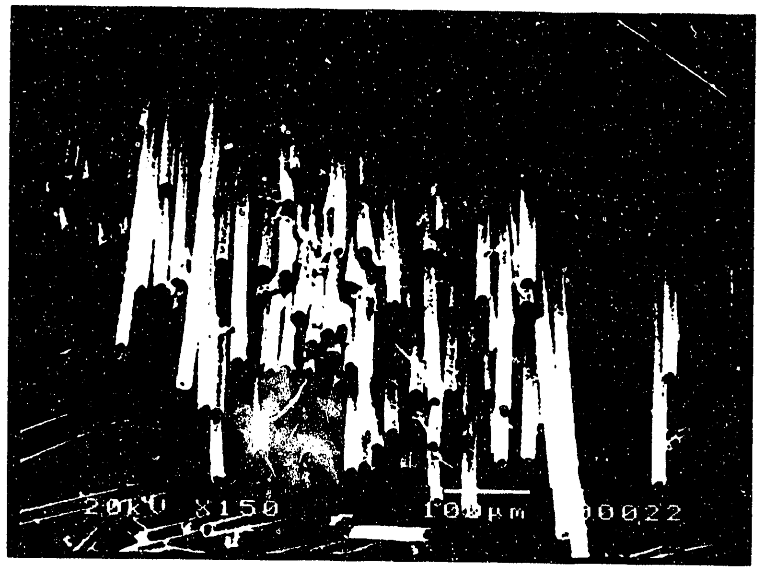

Figure 4. Fracture Surface of Nicalon/SiC Composite Showing Fiber Pullout.

Reduction of fiber strength suggests that during processing, either new flaws are generated or preexisting flaws become more severe. Figure 6 shows SEM photomicrograph of fractured fibers with distinct surface flaws, which are believed to have been introduced by mechanical and thermal damage to the fibers. The damage may have occurred during the handling of fiber mats and processing of composites.

Strength degradation of Nicalon fibers due to exposure to high temperatures is well documented in the literature. Loss of tensile strength of more than 30 and 70% has been reported for ceramic–grade Nicalon fibers by exposure at temperatures 1000 and 1200 °C, respectively, for 12 h in a wet–air atmosphere.[21] This loss of tensile strength is attributed to microstructural and stochiometric changes that occur in the fibers at elevated temperatures. Similar changes, although not as severe, are expected for the carbon–coated Nicalon fibers investigated in this study. Higher processing temperatures (in the range of 1200 °C) and longer exposure times (over 24 h) used in the fabrication of the composites make it difficult to prevent fiber degradation. Okamura et al.[22] have shown that formation of an SiO_2 film can also contribute to the reduction of both the tensile strength and the Young's modulus of the fibers. Also, the failure to observe a significant change in the Weibull modulus implies that the flaw distribution remains similar but the flaws become more severe due to degradation of inherent material properties. This again may be related to thermal degradation of the fiber material.

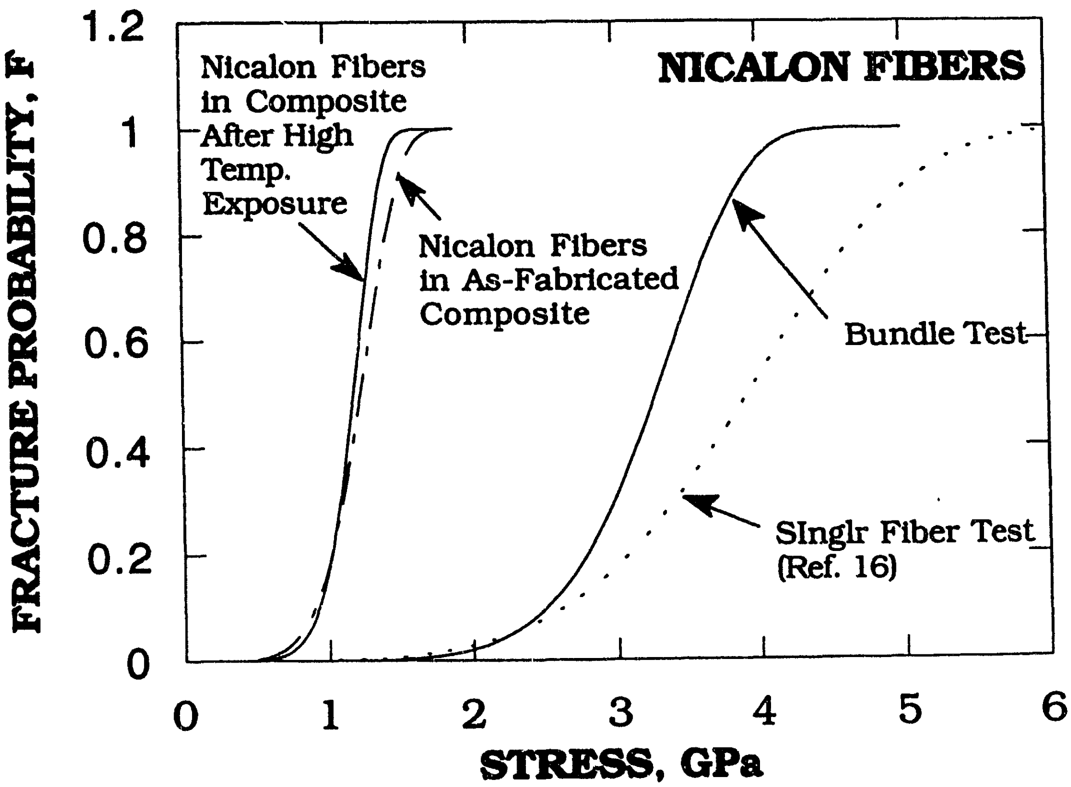

Figure 5. Weibull Strength Distribution of Nicalon Fibers in As–Fabricated State (Bundle Test), After Processing, and After Exposure to 1300°C for 15 min.

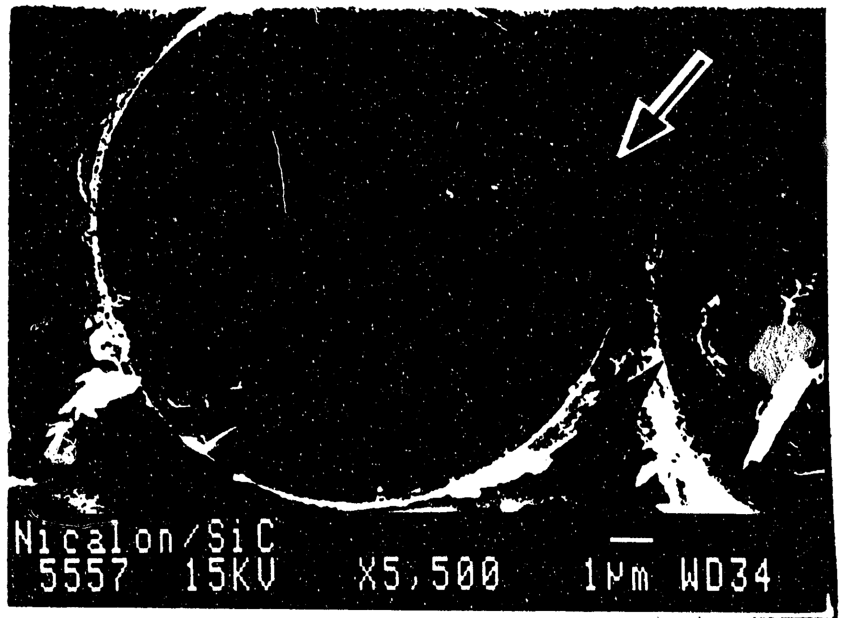

Figure 6. Micrograph of Fractured Nicalon Fibers in SiC Matrix Composite Showing Surface Defects as the Failure Origins.

Mechanical Properties Evaluations

Flexural tests were conducted to establish changes in the mechanical properties of the composites caused by the variations in the fiber strength characteristics as discussed above. Figure 7 shows the typical load–displacement plot obtained during flexural tests conducted at room temperature. Characteristic features associated with CFCC's such as matrix cracking (deviation from linearity) and extensive fiber pullout signified by the large area under load–displacement plot are observed in these composites.

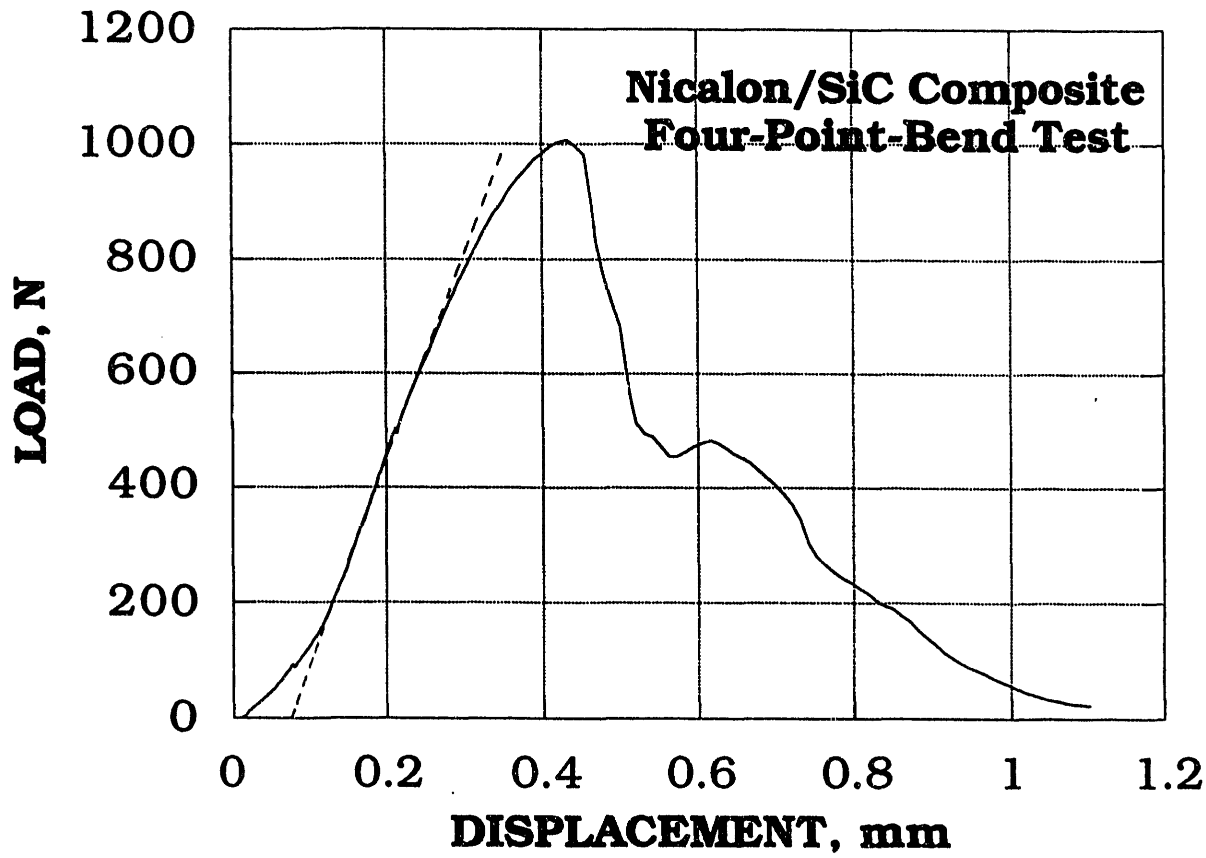

Figure 7. Typical Load–Displacement Variation for Nicalon/SiC Composite Obtained in Flexural Tests

Strength was determined from the peak load reached during the flexural tests. At this point applied stress is supported primarily by the fibers.[4] Therefore, any changes in fiber strength characteristics caused by elevated temperature exposure will reflect on the flexural strength. As shown in Fig. 8 flexural strength increases with the test temperature from a room temperature value of ≈400 MPa to ≈532 MPa at 800°C. Thereafter, strength decreases to ≈270 MPa at 1300°C.

Gradual failure as shown in Fig. 7 was observed for all tests. Initial increase in strength with temperature is similar to that observed in SiC/SiC composites and may be related to matrix softening effects.[13,23] The decrease in flexural strength at 1300°C is attributed to fiber degradation as observed from quantitative fiber strength evaluations discussed earlier. However, as shown in Fig. 5 the strength of fibers in composites exposed to 1300°C is not significantly lower as compared to fibers in as–fabricated composites. This is at odds with the large difference in flexural strength of composite tested at room temperature and at 1300°C. It is believed that overestimation of fiber strength is because of unavailability of data for mirror constant value and pullout lengths for Nicalon fibers in the composites at 1300°C. These properties at elevated temperatures can be significantly different from the room temperature data as used in this study.

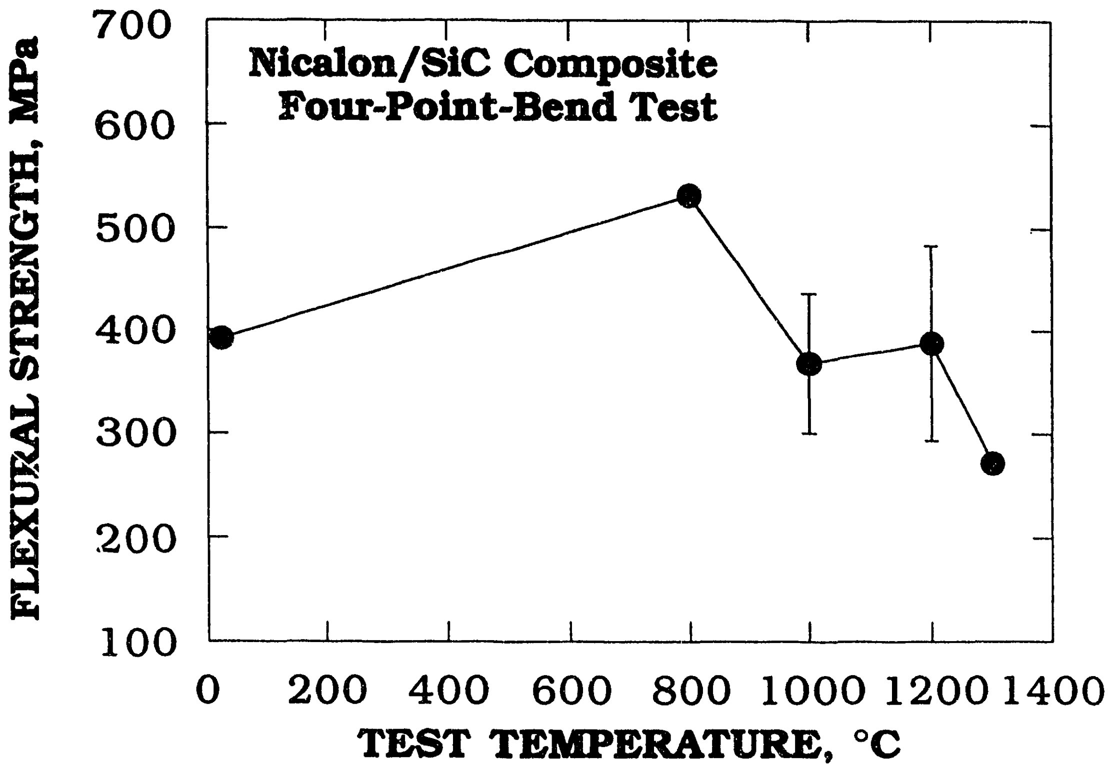

Figure 8. Variation of Flexural Strength of Nicalon/SiC Composites With Test Temperature.

Figure 9 shows the effect of exposure time at 1200 °C on the flexural strength of Nicalon/SiC composites. Composite bars were exposed at 1200°C in air for various periods of time: 15 minutes, 24 h, and 96 h. After exposure, specimens were cooled to room temperature and then again heated to 1200°C for testing. Strength drops by about 100 MPa as composite is held for a period of 24 h. However, with longer exposure of 96 h strength remains constant. The initial drop in strength may be due to fiber degradation by oxygen diffusing through cracks (channels) in the protective coating or at any exposed fiber surface. Over a period of time these channels may become blocked thereby preventing further fiber damage and strength degradation. Currently, additional tests are being conducted to establish these effects and quantitatively compare the fiber strength characteristics in composites as a function of exposure time.

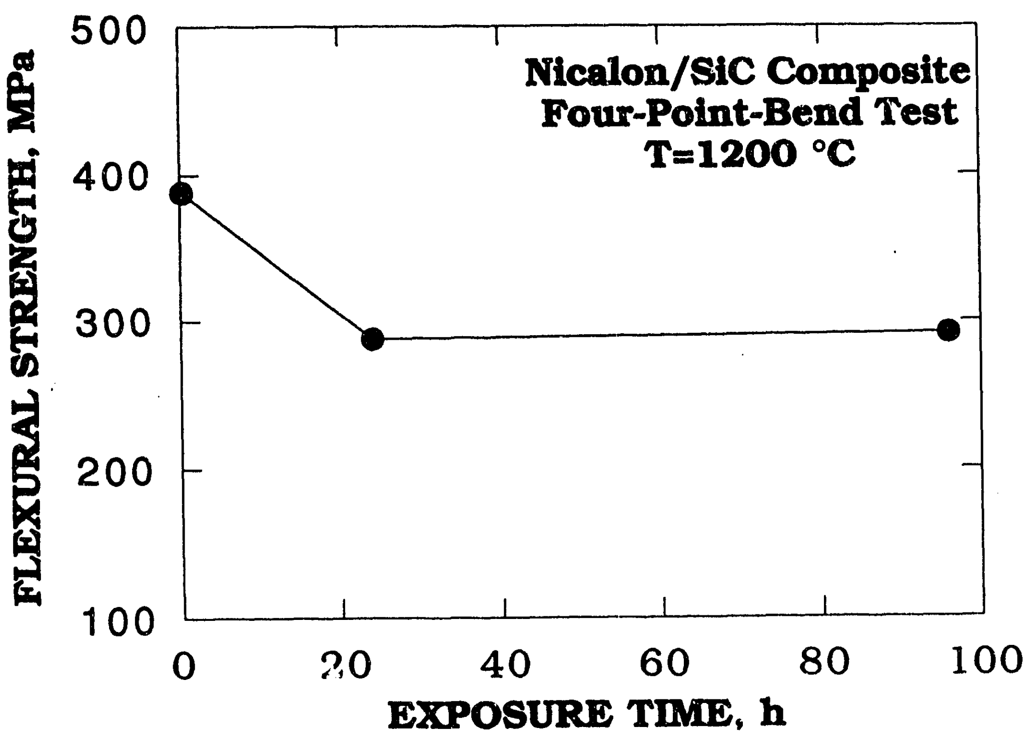

Figure 9. Effect of Long Term Exposure of Flexural Strength on Nicalon/SiC Composites at 1200°C.

Conclusions

1. Strength distribution of as–fabricated Nicalon fibers was obtained from the bundle test procedure, whereas fracture mirror radii measurements were made to estimate strengths of fibers in composites both after fabrication and after elevated temperature exposure.

2. Results indicate a decrease in the strength of Nicalon fibers in composites compared to as–fabricated fibers. Moreover, there is a further decrease in strength of fibers after 1300°C exposure of the composites. However, the Weibull moduli for the three cases were similar.

3. Decrease in the average strengths of Nicalon fibers after incorporation into composites is attributed to thermal and mechanical degradation of fibers during processing.

4. Flexural strength of Nicalon/SiC composites was found to decrease with test temperature. At 1200°C, exposure time of 24 h significantly reduced the strength. These variations in strength were correlated to fibers strength characteristics and its degradation with temperature and time.

Acknowledgments

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