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The Effects of Moisture on the Material Properties and Behavior of Thermoplastic Polyimide Composites

ABSTRACT: Thermoplastic polyimides are a relatively new class of polymers that exhibit high-temperature stability and are useful in composite applications. One such material is Avimid® K3B reinforced with Magnamite® IM7 graphite fibers. This composite system exhibits excellent strength and toughness, retains its strength and toughness after prolonged exposure to elevated temperatures, and resists microcracking at extremely low (liquid nitrogen) temperatures. Further characterization of IM7/K3B thermoplastic composites is focused on evaluating hygrothermal effects on the material properties and behavior. The environmental conditioning test matrix includes three temperatures (20, 40, and 80°C) and four relative humidity levels (75, 85, 97, and 100%). Observations and conclusions from these studies include the following: (1) the moisture diffusivity of IM7/K3B has a classic Arrhenius dependence on temperature; (2) the moisture saturation level depends on the relative humidity level to the power of 1.34 with a maximum value of 0.55% by weight; (3) the glass transition temperature T_g is lowered with moisture absorption but is recovered when the sample is redried; (4) the intralaminar fracture toughness G_{Ic} remains constant after extensive hygrothermal conditioning; (5) the diffusion kinetics are Fickian in general, except for a few non-Fickian anomalies that are related to development of transverse microcracks.

KEY WORDS: polymer matrix composites, polyimide matrix, graphite fibers, moisture, hygrothermal effects, glass transition temperature, fracture toughness, diffusion, transverse microcracking

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Nomenclature

D Transverse diffusivity of the composite laminate (cm^2/s)
M_{sat} Moisture saturation level, weight %
G_{Ic} Intralaminar fracture toughness, J/m^2
a Notch length of the fracture toughness test specimen, mm
δ Notch width of the fracture toughness test specimen, mm
T_g Glass transition temperature, °C
E'' Loss modulus, MPa
% RH   Percent relative humidity of the conditioning environment
wt%   Weight % or % by weight
v_f Fiber volume fraction

Over the past 20 years, the effects of moisture on fiber-reinforced polymeric composite materials have been studied extensively [1-9]. In many of these studies, significant changes in the mechanical properties and various forms of moisture-induced damage have been reported [4-8]. For example, absorbed moisture has been shown to reduce the glass transition temperature T_g of the resin [4,5] reduce matrix-dominated properties of the composite such as transverse tensile strength and intralaminar shear strength [4-6], and cause swelling of the resin that induces residual stresses and causes the formation of microcracks [5,7-10]. These deleterious effects of absorbed moisture have been attributed to plasticization and degradation of the resin matrix and degradation of the fiber-matrix interface [5-10]. To date, most moisture studies have been concerned with thermosetting matrix composites (for example, graphite/epoxy) that absorb as much as 1.2 to 2% moisture by weight in 95 to 100% relative humidity environments (for fiber volume fractions v_f between 60 and 68%) [1,2,5-7]. Recently, thermoplastic (semicrystalline and amorphous) matrix composites have been developed that absorb very little moisture compared to their thermosetting matrix counterparts [3,4]. An example of such a system is a thermoplastic matrix composite composed of an amorphous polyimide matrix, Avimid®[4] K3B, reinforced with Magnamite®[5] IM7 graphite fibers ($v_f = 62\%$) [11], that absorbs up to 0.55% moisture by weight during water immersion. In this study, extensive hygrothermal characterization of the IM7/K3B system is conducted to determine moisture-induced degradation, predict moisture contents in service environments, and develop accelerated environmental conditioning methods.

Experimental

Materials

The particular thermoplastic matrix composite used in this study employed an amorphous polyimide matrix, Avimid® K3B, reinforced with Magnamite® IM7 graphite fibers ($v_f = 62\%$) [11]. Laminates were laid up in house and then processed by The DuPont Co. under optimized processing conditions [12]. Laminate configurations included the following: $[90]_{10}$, or unidirectional laminates; $[0_2/90]_s$, or thin cross-ply laminates; $[0_2/90_2/0_2]_s$, or thick cross-ply laminates; and $[45/0/-45/90]_s$, or quasi-isotropic laminates. After processing and prior to any testing or conditioning, ultrasonic c-scanning (transducer frequency = 15 MHz) was

used to inspect laminate quality. No defects were detected in any of the panels. Also, baseline (dry) longitudinal and transverse tensile testing of unidirectional specimens was performed in accordance with Test Method for Tensile Properties of Fiber-Resin Composites (ASTM D 3039). The average strengths and moduli measured were within 5% of reported values [11,13].

Hygrothermal Conditioning

The hygrothermal conditioning test matrix consisted of three temperatures, 20, 40, and 80°C, and four relative humidity (RH) levels—75, 85, 97, and 100% RH. For 100% RH conditioning, samples were immersed directly in water contained in stainless steel tanks that were roughly 0.003 m^3 in volume. The remaining humidity conditions for 20 and 40°C environments were created within desiccators in accordance with Practices for Maintaining Constant Relative Humidity by Means of Aqueous Solutions (ASTM E 104). For the 40°C conditioning environments, the desiccators were then placed in the water baths used for the immersion studies, while the 20°C desiccators sat out in a controlled room-temperature environment. An environmental chamber was used to create 80°C humidity environments (except for 100% RH). The temperatures of the 40 and 80°C water baths were maintained by a temperature feedback controller, that employed J-type thermocouples (wrapped in a polyimide tape to limit galvanic corrosion) and flexible heating blankets as heating elements. Distilled, deionized water was used in all of the aqueous solutions and in the 100% RH baths. To date, conditioning times of the various specimens range from 1000 to 4400 h. (See the following subsections and the Results section for more specific information on conditioning times.)

During preliminary studies of moisture diffusion in the IM7/K3B system, the weights of specimens taken from each type of laminate reached equilibrium (dry) values after 2 to 3 days under vacuum at 120°C. Also, in an unpublished study,[6] IM7/K3B specimens were conditioned in 95% RH environments and then dried under vacuum at several elevated temperatures (>100°C). No significant degradation was observed after drying at 120°C. Therefore, all specimens were initially dried for 4 days under vacuum at 120°C prior to hygrothermal conditioning. Limited hygrothermal cycling studies were also performed which included 1200 to 1800 h of conditioning in the environments described previously, followed by desorption for 4 days under vacuum at 120°C, and finally reimmersion of the specimens into their original environments.

Weight Measurements

Square specimens with length dimensions of about 5 cm were cut with a diamond saw from each of the four types of laminates and used to measure moisture uptake during hygrothermal conditioning. At least three samples were conditioned in each constant-temperature, constant-humidity environment for 1200 to 4400 h. A few samples were used for limited hygrothermal cycling studies described in the previous subsection. Prior to conditioning, cross-ply and quasi-isotropic samples were polished on one edge to a 5-μm finish. This extra step allowed for the nondestructive detection of microcrack initiation by simply observing the polished edge of a sample under an optical microscope each time it was removed for weighing. Weight measurements were taken periodically during both absorption and desorption using a digital balance accurate to ± 1 mg. The surfaces of samples immersed

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[6] Personal communication with Dick Cornelia, The DuPont Co., Wilmington, DE, 1994.

in water baths were blotted dry with a cloth before they were weighed. Specimens were removed from their environments for weighing and microcrack inspection for no longer than 30 min (typically 15 to 20 min). Moisture loss during these removal periods was calculated to be insignificant.

Mode I Intralaminar Fracture Toughness

Intralaminar fracture toughness G_{Ic} was measured using a double edge notch (DEN) test [14]. Unidirectional panels with dimensions of 20.3 by 13 cm were end-tabbed and cut into four 20.3 by 2.5 cm samples using a slot grinder. Samples taken from conditioned panels were cut at least 1 cm from the panel's edges to eliminate any edge effects from the moisture absorption process. Notches were cut with a 0.5-mm diamond blade to approximately 6.9 mm in length on each side at the center of the sample. Notch lengths a and notch widths δ were measured to an accuracy of ± 0.01 mm using a microscope equipped with a micrometer-driven stage. In Ref 14, notches were cut with a thinner 0.3-mm diamond blade. However, the thinner blade is less rigid and, due to out-of-plane vibration, yields equivalent notch widths to the thicker blade ($\delta \sim 0.7$ mm). Sample geometry is illustrated in Fig. 1.

Baseline (dry) panels were cut and notched and then dried for four days under vacuum at 120°C prior to testing. Samples taken from conditioned panels were cut and notched 2 to 3 days prior to testing. These samples were then placed back into their original environments until they were tested. Total exposure times ranged from 1200 to 3600 h (see Results section), and one panel (four specimens) was conditioned in each environment for each chosen exposure time. All specimens were pulled in tension until failure occurred using a mechanical load frame. All testing was performed at room temperature, and G_{Ic} values were calculated as specified in Ref 14. After testing, the fracture surfaces of the G_{Ic} samples were observed under a scanning electron microscope (SEM) at magnifications up to 5000X at 30 kV.
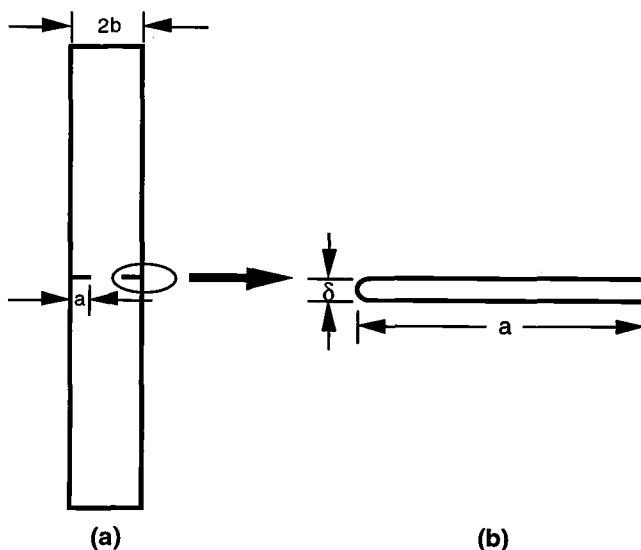

(a)   (b)

FIG. 1—(a) Double edge notch (DEN) test geometry as described in Ref 14 and (b) illustration of actual notch geometry observed in this study.

Glass Transition Temperature

Glass transition temperature T_g was measured by dynamic mechanical analysis (DMA). Samples were cut from conditioned and unconditioned unidirectional panels to roughly 6 by 1.25 cm using a diamond saw, and samples were taken at least 1 cm from the edge of a conditioned panel to avoid edge effects. Conditioned samples were tested after reaching moisture saturation levels in 20 and 80°C water baths and in the 20°C 75% RH environment, with the goal of producing bounds on the observed T_g reductions. DMA testing involved dynamic loading of samples in flexure (3-point bend) with a frequency of 1 Hz as the temperature was increased at a rate of 2°C/min. T_g values were measured with fibers oriented transversely and longitudinally to the neutral axis of the specimen. T_g is reported as the peak in the loss modulus, E''.

Damage Development

Ultrasonic c-scans were made of cross-ply panels immersed in 20, 40, and 80°C water for at least 1300 h. The scans included normal incidence and 30° polar backscattering, which enables determinations of transverse cracks [13]. After observing the onset of microcracking in the edge-polished samples under an optical microscope, moisture weight gain specimens were removed periodically from their conditioning environments, sectioned with a diamond saw, mounted in epoxy, ground and polished to a 5-μm finish. These polished cross-sectional surfaces of conditioned (and also unconditioned) samples were then observed using an optical microscope (magnifications up to 1000X). Damage was characterized as the number of transverse microcracks per ply per centimeter of cross-sectional material. Thus, a microcrack was counted only if it extended through the thickness of at least one ply.

Results

Characterization of Moisture Diffusion

Absorption and desorption of moisture for the IM7/K3B composite system can be characterized, in general, by Fick's second law [2]. In Figs. 2 and 3, average moisture uptake data are shown for 20°C conditioning of unidirectional specimens and 40°C conditioning of thick cross-ply specimens, respectively. The fitted curves were generated using an approximate solution to Fick's second law [1]. Generally, the standard deviation for each data point and the scatter of the data points about the curves are within the experimental accuracy of the balance used to weigh the samples, for example, ±1 mg corresponds to ±0.017 and ±0.015 wt%, respectively, for unidirectional and thick cross-ply specimens near saturation levels. However, a significant increase in the saturation levels of thick cross-ply specimens conditioned in 97 and 100% RH environments was observed after 4400 h (see Fig. 3). To date, moisture diffusion into unidirectional laminates has not deviated from Fickian behavior in any of the environments. (Conditioning in 40°C 75% RH and in 80°C 85 and 95% RH has not yet been completed.) Deviations from Fickian behavior, consisting of increases in saturation level after long times, have been observed during elevated-temperature conditioning of some cross-ply and quasi-isotropic specimens (see Discussion section).

Moisture saturation levels M_{sat} for the four laminate types increased with increasing humidity level, as shown in Fig. 4. This dependence was fitted with a power law function of the form [1,2]
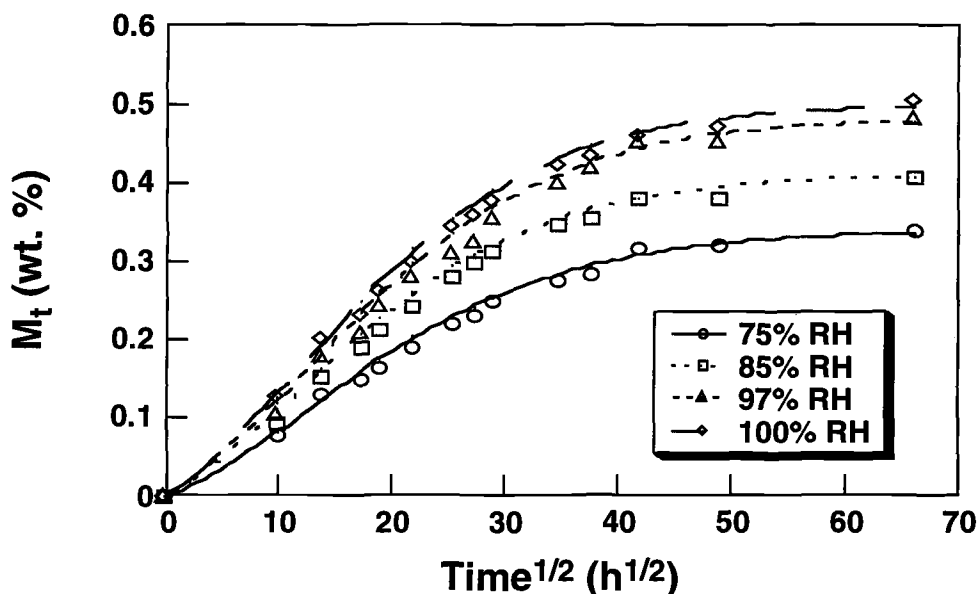
$$M_{sat} = c(\% \text{ RH})^n \qquad (1)$$

FIG. 2—*Moisture absorption curves for unidirectional IM7/K3B specimens conditioned in 20°C environments. Each data point is an average of 4 to 7 specimens. The curves shown approximate Fickian Behavior.*
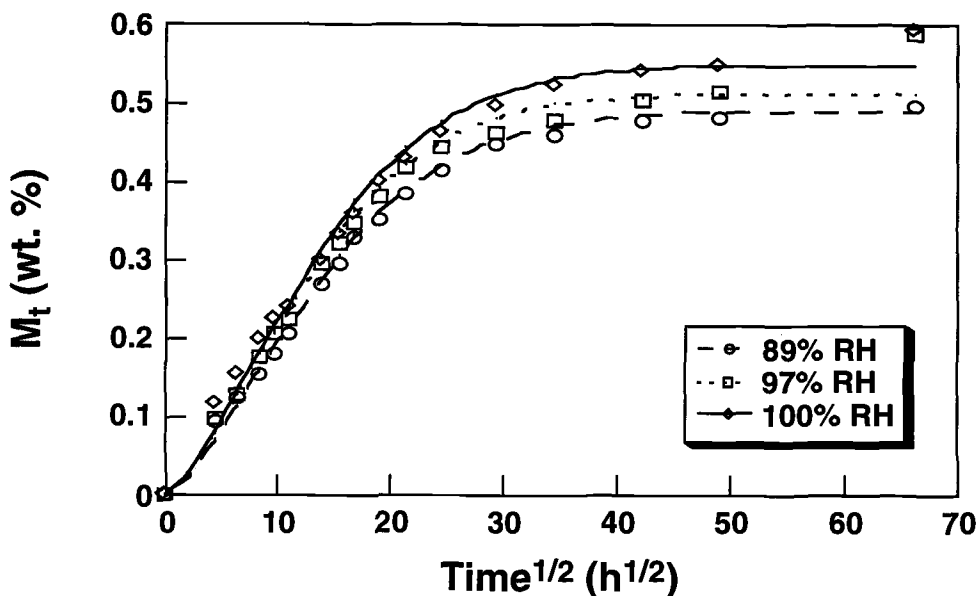

FIG. 3—*Moisture absorption curves for thick cross-ply IM7/K3B specimens conditioned in 40°C environments. Each data point is an average of 9 specimens. The curves shown approximate Fickian behavior.*
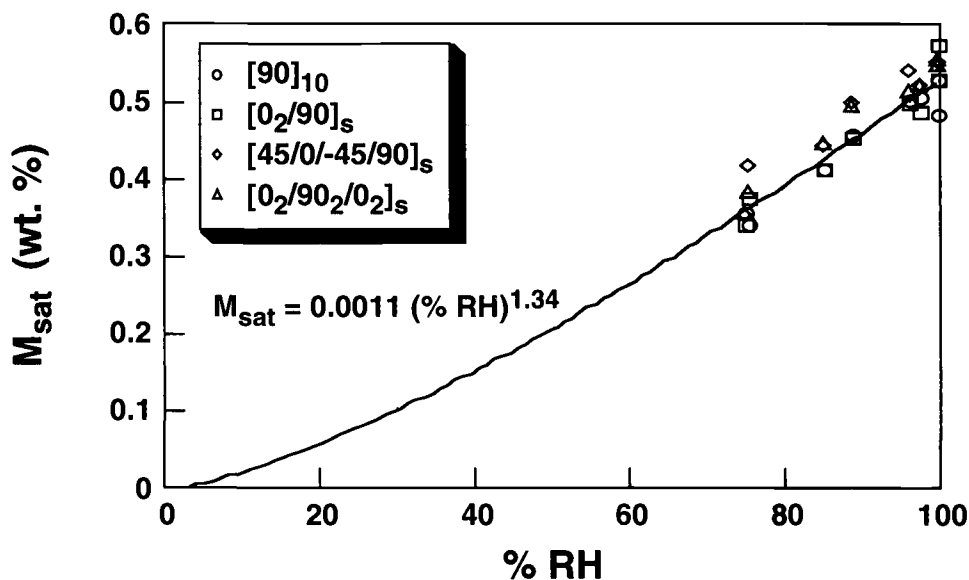
FIG. 4—*Moisture saturation levels plotted as a function of relative humidity for IM7/K3B laminates. Each data point is an average of 3 to 9 specimens.*

where $c = 0.0011$ and $n = 1.34$ are empirical parameters. No dependence of the saturation level on temperature has been observed over the investigated temperature range. Diffusivities were calculated for absorption in 20, 40, and 80°C environments and for desorption at 120°C using the solution for Fick's second law at short times [1,2]. A plot of diffusivity D as a function of inverse temperature is shown in Fig. 5. The diffusivity can be characterized by classical Arrhenius behavior and is given as a function of temperature, T (K), by

$$D = 0.01 \exp [-4750/T] \tag{2}$$

Deviations from this diffusion behavior occurred during the desorption and re-absorption of moisture in cross-ply specimens. Desorption diffusivities of cross-ply specimens conditioned for 2400 h in 20°C environments and for 1200 to 1800 h in 40°C environments were 20 to 50% higher than those of unidirectional specimens that had received the same conditioning. Upon reabsorption of cross-ply specimens conditioned at 40°C, absorption diffusivities increased 30 to 65% above their initial values. Thin cross-ply specimens conditioned for 2400 h in 20°C environments showed similar increases in absorption diffusivities, but the diffusivities of thick cross-ply specimens that had received the same conditioning remained relatively constant. Moisture cycling seems to also have a moderate effect on the diffusion behavior of unidirectional laminates conditioned for 1800 at 40°C, as diffusivities increased between 15 and 25% above initial values. In several cases, slight increases (5 to 10%) in moisture saturation levels were also observed for both unidirectional and cross-ply specimens during re-absorption. A comparison of diffusivities and saturation levels between the first and second absorption cycles is shown in Table 1.
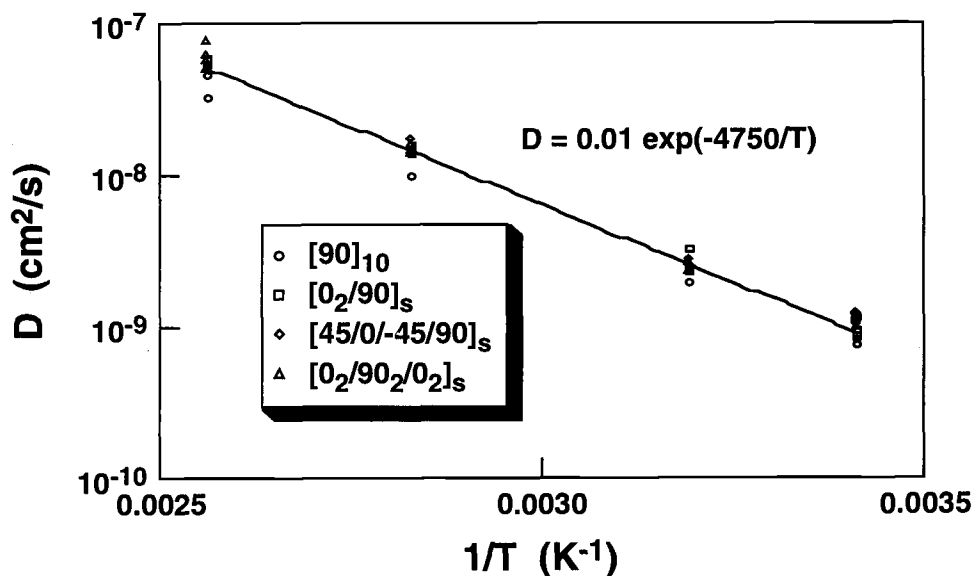
FIG. 5—*Arrhenius plot of diffusivity D (cm²/s) as a function of inverse temperature for IM7/K3B laminates. Each data point is an average of 3 to 9 specimens.*

Mode I Intralaminar Fracture Toughness

The results of fracture toughness testing of samples conditioned at 20 and 40°C are shown in Figs. 6 and 7, respectively. Unidirectional specimens conditioned in room-temperature, high-humidity environments for up to 3600 h have exhibited no measurable toughness loss. Similarly, fracture toughness values have remained constant for specimens conditioned in 40°C environments for up to 3000 h. Also, no toughness loss has been observed for specimens conditioned in 80°C 75% RH for up to 1500 h. Specimens conditioned to saturation (300 h) in 80°C 100% RH did exhibit a moderate loss in toughness of 30 to 40%. However, the degradation mechanism (unknown at this time) responsible for this toughness loss might be active only during elevated-temperature water immersion and may not be representative of an "accelerated" conditioning effect.

Glass Transition Temperature

To date, only limited glass transition temperature T_g testing has been performed, the results of which are shown in Table 2. Standard deviations of the given values are of the order of 0.5°C. T_g values for dry specimens are similar to a T_g value of 255°C reported by Cornelia [4] for the same composite system. T_g values for moisture-saturated specimens were as much as 11% lower than the baseline value for a sample conditioned in the 80°C 100% RH environment. However, this effect was reversible, as T_g returned to its baseline value when the specimen was redried. These results indicate that moisture acts as a plasticizer to the polymer matrix. Similar results have been obtained by Cornelia [4] for several polyimide composite systems. More extensive characterization of T_g as a function of the conditioning time, temperature, and humidity level is currently under evaluation (see Discussion section).

TABLE 1—*Comparison of diffusivities* D *and moisture saturation levels* M$_{sat}$ *for IM7/K3B specimens selected for limited cycling studies.*

Laminate/Conditioning Environment	Conditioning Time, h	D, cm²/s, Cycle 1	M$_{sat}$, wt %, Cycle 1	D, cm²/s, Cycle 2	M$_{sat}$, wt %, Cycle 2
[90]$_{10}$ 40°C, 89% RH	1200	2.05×10^{-9}	0.430	2.36×10^{-9}	0.460
[90]$_{10}$ 40°C, 89% RH	1800	1.81×10^{-9}	0.445	2.25×10^{-9}	0.465
[90]$_{10}$ 40°C, 97% RH	1200	2.90×10^{-9}	0.470	2.80×10^{-9}	0.490
[90]$_{10}$ 40°C, 97% RH	1800	2.50×10^{-9}	0.465	3.20×10^{-9}	0.510
[90]$_{10}$ 40°C, 100% RH	1800	2.40×10^{-9}	0.510	2.80×10^{-9}	0.540
[0$_2$/90]s 40°C, 89% RH	1800	2.80×10^{-9}	0.470	2.82×10^{-9}	0.470
[0$_2$/90]s 40°C, 97% RH	1800	2.60×10^{-9}	0.500	3.50×10^{-9}	0.540
[0$_2$/90]s 40°C, 100% RH	1800	3.20×10^{-9}	0.510	4.06×10^{-9}	0.540
[0$_2$/90$_2$/0$_2$]s 40°C, 89% RH	1200	1.96×10^{-9}	0.450	2.60×10^{-9}	0.450
[0$_2$/90$_2$/0$_2$]s 40°C, 89% RH	1800	2.80×10^{-9}	0.470	2.82×10^{-9}	0.470
[0$_2$/90$_2$/0$_2$]s 40°C, 97% RH	1200	2.59×10^{-9}	0.480	3.89×10^{-9}	0.530
[0$_2$/90$_2$/0$_2$]s 40°C, 97% RH	1800	2.60×10^{-9}	0.500	3.50×10^{-9}	0.540
[0$_2$/90$_2$/0$_2$]s 40°C, 100% RH	1800	3.20×10^{-9}	0.510	4.06×10^{-9}	0.540
[90]$_{10}$ 20°C, 75% RH	2400	0.85×10^{-9}	0.345	0.86×10^{-9}	...
[90]$_{10}$ 20°C, 85% RH	2400	0.94×10^{-9}	0.420	1.15×10^{-9}	...
[90]$_{10}$ 20°C, 97% RH	2400	0.86×10^{-9}	0.495	0.91×10^{-9}	...
[0$_2$/90]s 20°C, 75% RH	2400	1.31×10^{-9}	0.380	1.63×10^{-9}	0.410
[0$_2$/90]s 20°C, 85% RH	2400	0.83×10^{-9}	0.425	1.25×10^{-9}	0.440
[0$_2$/90]s 20°C, 97% RH	2400	0.97×10^{-9}	0.470	1.08×10^{-9}	0.500
[0$_2$/90$_2$/0$_2$]s 20°C, 75% RH	2400	1.17×10^{-9}	0.400	1.15×10^{-9}	...
[0$_2$/90$_2$/0$_2$]s 20°C, 85% RH	2400	1.24×10^{-9}	0.470	1.18×10^{-9}	...
[0$_2$/90$_2$/0$_2$]s 20°C, 97% RH	2400	0.95×10^{-9}	0.520	1.02×10^{-9}	...

Damage Development

Preliminary moisture studies included conditioning of cross-ply laminates in 80°C 100% RH for 1300 to 1500 h. During conditioning, moisture absorption was characterized by Fickian behavior up to saturation followed by a second stage uptake to a new saturation level, as reported in a previous section. After conditioning, both thin and thick cross-ply

FIG. 6—*Intralaminar fracture toughness* G_{Ic} *(J/m^2) of unidirectional IM7/K3B specimens conditioned in 20°C environments for up to 3600 h. Each data point is an average of 4 specimens. No toughness loss was observed.*
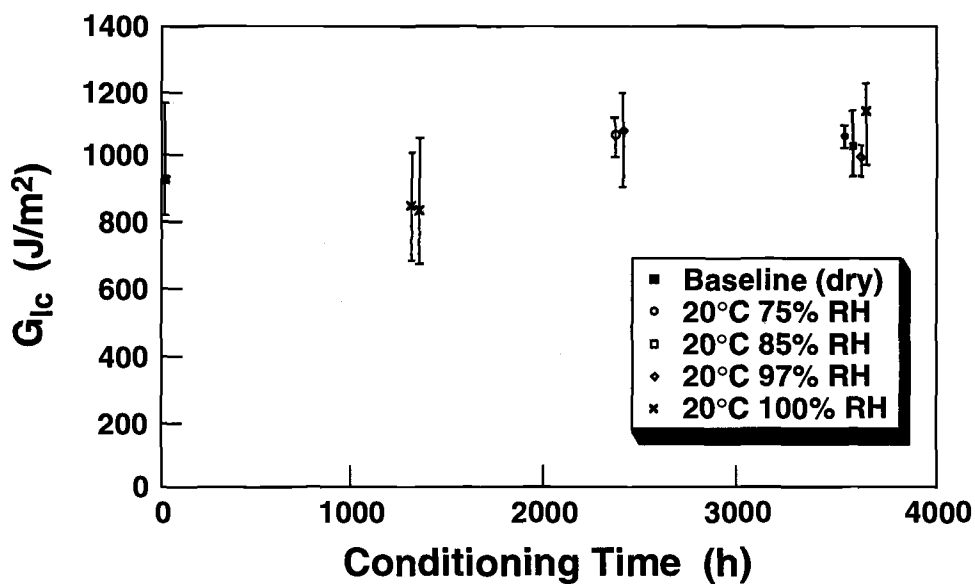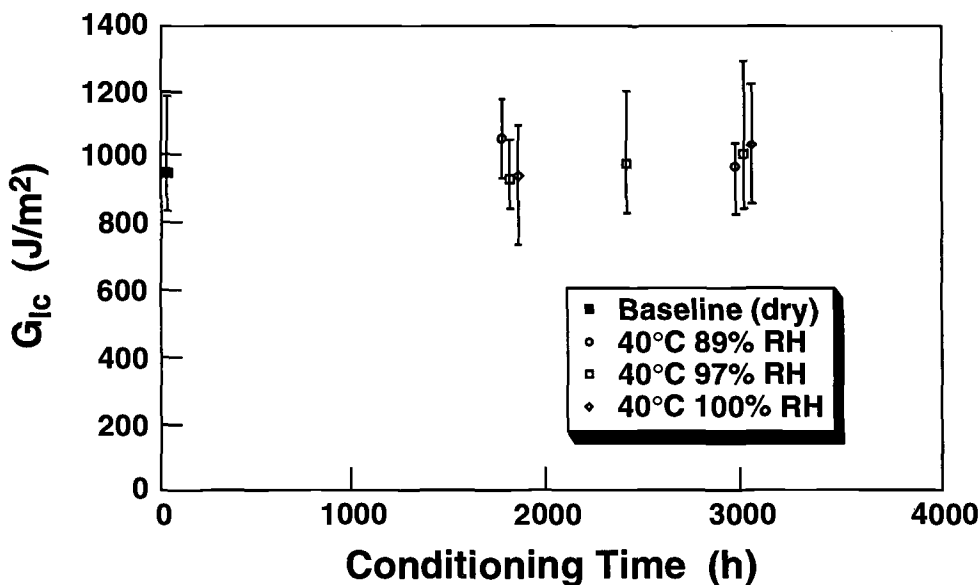
FIG. 7—*Intralaminar fracture toughness* G_{Ic} *(J/m^2) of unidirectional IM7/K3B specimens conditioned in 40°C environments. Each data point is an average of 4 specimens. No toughness loss was observed.*

TABLE 2—T_g *measured after conditioning unidirectional IM7/K3B samples in various environments to saturation, and then again after redrying the samples.*

Conditioning	T_g Longitudinal Specimen, °C	T_g, Transverse Specimen, °C
Baseline, dry	262°	252°
20°C, 75% RH	245°	247°
→ Redried	260°	251°
20°C, 100% RH	236°	246°
→ Redried	260°	252°
80°C, 100% RH	233°	245°
→ Redried	262°	252°

laminates were sectioned, mounted in epoxy, and polished to reveal microcrack densities of 6 cracks/ply/cm or more. Subsequent conditioning studies have included periodic checks for microcracks. Except for a few anomalous specimens (see Discussion section), no significant microcracking (<1 crack/ply/cm) has developed in any laminates conditioned for up to 4400 h in 20 and 40°C environments, or in samples conditioned for up to 1500 h in the 80°C 75% RH environment.

Discussion

Moisture diffusion in IM7/K3B laminates is generally Fickian in nature. In a few cross-ply and quasi-isotropic specimens conditioned in 40°C 97% RH and 80°C 100% RH environments, some deviations from Fickian behavior were observed. After reaching saturation, these specimens would begin to take up more moisture and reach a new saturation level. This anomalous behavior was correlated to the microcrack density. For example, the second uptake of moisture for a thin cross-ply specimen conditioned in the 40°C 97% RH environment for 1200 h corresponded to a microcrack density of 3 to 4 cracks/ply/cm. However, these high crack densities and the non-Fickian diffusion was only observed for a few specimens, and was not representative of the overall sample population. Microcrack densities of only 1 crack/ply/cm or less have been observed in specimens that have not shown second uptakes in moisture. Thus, a large number of microcracks must form before any significant increases in moisture absorption can be measured. However, even low crack densities allow for increases in diffusivities during desorption and re-absorption. This observation is consistent with other moisture studies that have shown increasing deviations from Fickian behavior in graphite/epoxy composites during moisture cycling [8].

Generally, conditioning of polymer composites in high humidity environments has a significant effect on the macroscopic properties of the composite system, particularly at high temperatures due to a reduction in the glass transition temperature T_g [5,6]. For amorphous, uncrosslinked polymers such as Avimid® K3B, T_g represents a characteristic softening of the resin, reducing the ability of the matrix to transfer load to the fibers and thus reducing the elevated-temperature properties of the composite [5,15]. Our results indicated that T_g for unidirectional IM7/K3B specimens was reduced due to moisture saturation but recovered when the composite was redried. The magnitude of this reduction in T_g, however, was dependent on the fiber direction of the DMA specimen. In fact, the T_g was lowered only 2 to 3% for transverse specimens compared to a 6 to 11% reduction for longitudinal specimens. Also, the baseline T_g values differ by 10°C between the two specimen types. Further, Wedgewood [11] has reported a dry resin T_g of 237°C using dynamic scanning calorimetry, and a moisture-saturated T_g value for unidirectional composite of around 200°C based on a drop

in flexure strength at elevated temperatures. These differences in reported T_g values might be due to the interaction between the mechanics of flexure loading and specimen anisotropy and can lead to discrepancies in the magnitude of the effect of moisture. Because the glass transition occurs over a range of temperature and can depend on test parameters such as heating rate, the choice of T_g could be another source of differences between reported values. Further characterization of the effects of moisture on T_g will include testing isolated polymer and unidirectional composite specimens using several different loading configurations.

Intralaminar fracture toughness G_{Ic} remained unchanged after four to five months of both room temperature and 40°C conditioning. Microscopic observation of conditioned unidirectional specimens revealed no microcracks or fiber-matrix debonding, which is consistent with no observed toughness loss. A moderate reduction in G_{Ic} was found for specimens conditioned for 300 h in 80°C 100% RH. The fracture surfaces of these specimens (observed using SEM) were characterized by a reduced amount of plastic flow of resin over the fibers, as compared to specimens that showed no toughness loss. Thus, some degradation of the fiber-matrix interphase region might have occurred, possibly resulting in the observed toughness loss. However, this degradation occurred after a limited amount of conditioning in an elevated-temperature water bath that may not be representative of a possible service environment. Other studies involving the conditioning of carbon- and glass-reinforced epoxies in environments with similar temperatures and humidity ranges as this study have observed anomalous behavior during elevated-temperature water immersion that was not observed in other environments [2,16]. Therefore, the toughness loss might not be an accelerated effect of the elevated-temperature, high-humidity conditioning.

Some moisture-induced degradation has been observed in the form of transverse microcracking in cross-ply and quasi-isotropic laminates. Microcracking in thin cross-ply specimens (6-ply) and quasi-isotropic specimens (8-ply) usually begins in the surface plies on the rough "bag" side of the specimen. A density of 2 to 3 cracks/cm develops in the bag-side plies before microcracking is seen in the surface plies on the smooth "tool" side. (Here, the side of the laminate laid down on the autoclave tool and the opposite side which faces up during autoclave processing are referred to as the tool side and bag side, respectively.) This effect could be due to resin bleeding from the bag side during processing, which could reduce the local toughness and cause locally high residual stresses. The thick cross-ply specimens (12-ply) do not show the same microcracking tendencies, indicating that the microcracking behavior may depend somewhat on thickness. In general, microcracks appear in the surface plies before any interior microcracking is observed. This behavior does not seem to be caused by moisture gradients, however, as microcracking occurs after saturation levels have been reached.

The formation of transverse microcracks in the absence of an externally applied load is puzzling, especially considering no toughness loss has been measured in panels conditioned for much longer periods of time than is required for microcrack initiation. Using the effective-flaw model developed by Wang [13] and assuming no swelling of the polyimide matrix as reported in Ref 4, a fracture toughness of between 10 and 100 J/m^2 can be estimated for a thin cross-ply laminate that microcracks without applied load. This value is one to two orders of magnitude below the measured G_{Ic} values. This finding is consistent with Tsotsis and Weitsman [17], who reported a difference of three orders of magnitude between measured interlaminar G_{Ic} values and predicted G_{Ic} values for interfacial debonding and microcracking in moisture-saturated graphite/epoxy laminates. Other reasons for the formation of moisture-induced transverse microcracks include the constraint imposed by large fiber volume fractions on resin swelling [18], the ability of moisture to break chemical bonds and alter the surface-free energy at the fiber-matrix interface [8], and the attraction of moisture to the fiber-matrix interphase region due to stoichiometric or molecular weight gradient [19,20].

However, the latter two possibilities would result in a loss in fracture toughness during hygrothermal conditioning, which is not observed. The former explanation would result in local residual stresses that could be significant enough to cause microcrack initiation. Further study of possible effects is needed, including studies of moisture-induced swelling and of the effect of moisture on the fiber-matrix interface.

Conclusions

Hygrothermal conditioning of IM7/K3B thermoplastic composite laminates in several high-humidity environments has been performed. The moisture diffusion process was shown to be characterized by Fickian behavior, except in a few cases where moisture-induced degradation was significant. The moisture saturation level was shown to have a power law dependence on relative humidity but was not significantly affected by temperature. Also, a classical Arrhenius dependence of diffusivity on inverse temperature was observed. Moisture absorption induced the development of microcracks in the absence of an applied stress in quasi-isotropic and cross-ply laminates. Generally, microcracks were observed only in the surface plies and the microcrack densities were small. Observations from limited moisture cycling studies indicated that even small microcrack densities might be important during desorption and reabsorption of moisture. In a few cases involving cross-ply specimens, microcrack densities reached significant levels and caused non-Fickian, second-stage moisture absorption. However, these few cases may have been affected by other factors, such as resin bleed during processing. Further, these cases occurred in elevated-temperature (40 and 80°C) 97% and 100% relative humidity environments that might introduce degradation mechanisms that are not active in more realistic (lower humidity) environments.

Intralaminar fracture toughness values remained unchanged after 3000 to 3600 h of conditioning, and only a small reduction in glass transition temperature was observed in moisture-saturated specimens, which was recovered upon redrying the specimens. Also, moisture-induced degradation has not been observed in unidirectional laminates. Therefore, the macroscopic properties and behavior of unidirectional laminates seem relatively unaffected by steady-state hygrothermal conditioning.

Future Work

Continuation of this research includes further conditioning of composite laminates in various environments and further characterization of T_g, G_{Ic}, and microcrack resistance as a function of conditioning time, temperature, and humidity level. Also, the effects of combined moisture and temperature cycling need to be addressed, as well as the effect of applied stress on the moisture diffusion process. Microscopic studies, including fragmentation testing of hygrothermally conditioned single fiber test specimens, will also be performed. Finally, efforts will be made to develop test methodology that can evaluate the long-term durability of polymeric composite systems.

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