

# HYGROTHERMAL AGING OF POLYIMIDE MATRIX COMPOSITE LAMINATES

John A. Nairn and Man-Hee Han

*Materials Science and Engineering, University of Utah  
122 S Central Campus Dr Rm 304, Salt Lake City, UT, 84121-0560, USA*

**SUMMARY:** Two polyimide-matrix systems were subjected to a series of hygrothermal aging experiments at various temperatures and relative humidities. For each aging condition, we measured the microcracking fracture toughness as a function of aging time. The toughness decreased with time. The rate of decrease increased with temperature and relative humidity. All experimental results could be fit to a simple first-order kinetics analysis where the degradation rate was assumed to be proportional to the total exposure to water above a threshold level below which no degradation occurs. The kinetics analysis was used to construct a hygrothermal aging master plot that can be used to make predictions of toughness degradation due to arbitrary hygrothermal environments. The master plot can be constructed from a few experiments on specimens immersed in water and thus is a potential accelerated test method for characterizing hygrothermal stability.

**KEYWORDS:** Microcracking, hygrothermal aging, durability, environmental effects, hydrolysis, accelerated test methods, polyimide matrix, fracture toughness

## INTRODUCTION

Various types of polyimide-matrix composites are being considered for use in high-temperature applications such as for supersonic aircraft. It was previously observed, however, that some polyimide laminates can spontaneously microcrack when exposed to hot and wet environments [1]. For example, when quasi-isotropic, Avimid<sup>®</sup> K polymer laminates were immersed in water at temperatures ranging from 35°C to 95°C, the water uptake initially had Fickian behavior, but later, after apparently reaching an equilibrium level of water saturation, showed a non-Fickian jump in uptake rate. Microscopy results showed that the secondary uptake process was caused by spontaneous formation of matrix microcracks in the 90° plies despite the absence of any externally applied load. The time to initiate water-induced microcracks,  $t_m$ , (in minutes), was

$$\log t_m = \frac{3423}{T} + 1.35 \quad (1)$$

which translates to an apparent activation energy of 28 kJ/mol. For example, when immersed in 80°C, water-induced microcracks initiated in about 1000 hours [1].

Spontaneous microcracking is caused by water-induced degradation of the toughness of the polyimide composite material [1]. Eventually, the toughness drops enough that microcracks can form due to residual stresses alone. In this paper we report results of monitoring the degradation in toughness properties prior to and after the onset of spontaneous microcrack formation. The experiments include results for two different polyimide materials. For one material, experiments were done for water immersion, for exposure to various levels of humidity, and for various temperatures. All results can be interpreted with a simple kinetics analysis in which degradation rate depends on the integrated exposure to water. The kinetics scheme was used to derive an effective water-exposure time that was then used to generate a master-plot for hygrothermal stability. The master plot can be used to predict toughness degradation rates for any hygrothermal conditions.

## MATERIALS AND METHODS

### Laminate Materials and Microcracking Experiments

The two laminate materials used were DuPont Avimid® K3B Polymer/IM7 carbon fiber and PETI5/IM7 carbon fiber composites. Each of these materials was laminated into  $[0/90_2]_s$  cross-ply laminates and supplied to us by the Boeing Company. For hygrothermal aging experiments, a series of laminates 12.7 mm wide, 150 mm long, and 0.76 mm thick were dried at 120°C to remove moisture and then placed in a test tube either immersed in water or suspended over a salt solution [2,3] to provide a constant relative humidity environment. While aging, the moisture content was periodically recorded. After selected aging times, specimens were removed, redried at 120°C, and subjected to microcracking experiments, described below, to measure the microcracking toughness as a function of aging time. For Avimid® K3B Polymer/IM7 laminates, experiments at 80°C were done for immersed samples and for samples at 76%, 50%, and 26% relative humidities. Additional experiments were done for immersed samples at 60°C and 43°C. For PETI5/IM7, the only experiments were for samples immersed in water at 80°C.

### Microcracking Experiments and Analysis

To determine the toughness as a function of aging time, we measured the density of microcracks as a function of applied load. For each aging condition, three separate specimens were end-tabbed with aluminum end tabs and loaded at 0.01 mm/sec in a 25 kN MTS servohydraulic frame. The loading was periodically interrupted and the specimens were removed and observed on edge by optical microscopy to record the density of microcracks in the 90° plies. The resulting data was analyzed using the methods described in Ref. [4] to determine microcracking fracture toughness denoted as  $G_{mc}$ . In brief, the analysis assumes the next microcrack forms when the energy released by that crack exceeds the critical energy release rate or toughness,  $G_{mc}$ , of the material [4,5]. At later aging times, many laminates had spontaneously microcracked to some extent. These cracks were caused by residual stress and the analysis methods [4] can account for such initial cracks and still determine  $G_{mc}$ .

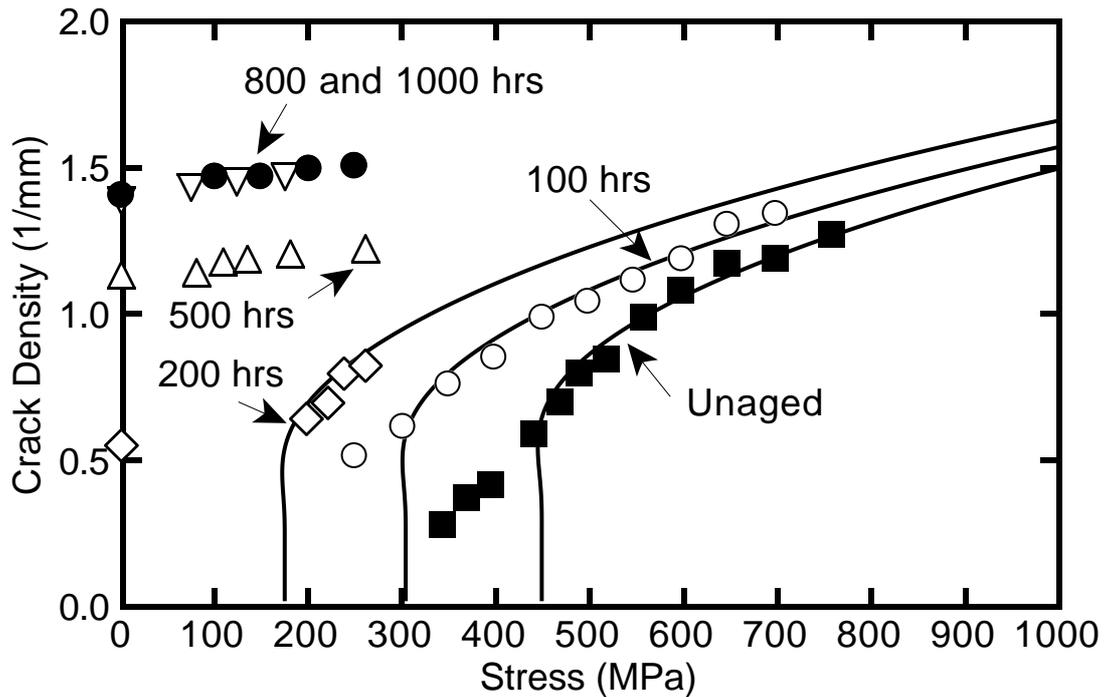


Fig. 1: Microcrack density as a function of applied load for Avimid® K polymer laminates after immersion in water at 80°C for various amounts of time.

## RESULTS

Some raw microcracking results from Avimid® K polymer laminates for microcrack density as a function of applied load following immersion in water at 80°C for various amounts of time are plotted in Fig. 1. The raw data clearly shifts to the left with aging time indicating a significant drop in toughness with exposure time. After 200 hours of aging there were some initial microcracks, but additional microcracks formed during subsequent loading. Samples with 500, 800, and 1000 were nearly saturated in microcracks before mechanical testing. Subsequent loading caused very few additional microcracks.

The smooth lines in Fig. 1 are the fracture mechanics analyses used to determine  $G_{mc}$  as a function of aging time [4]. The unaged laminates had a toughness of  $G_{mc} = 960 \text{ J/m}^2$ ; this toughness rapidly dropped with aging time. The specimens with aging times greater than 500 hours have no smooth lines. It is difficult to unambiguously fit these flat results to find  $G_{mc}$ , but it is possible to determine that the toughness must be very low ( $< 50 \text{ J/m}^2$ ); for plotting purposes, the toughness of laminates saturated with microcracks prior to testing was assumed to be zero.

Figure 2 plots  $G_{mc}$  as a function of aging time for the water-immersion results in Fig. 1 and for similar experiments where the laminates were exposed to various levels of relative humidity. The drop in toughness gets lower as the humidity drops. At the lowest humidity of 26%, there was no sign of toughness drop in the first 1000 hours. Figure 3 plots  $G_{mc}$  as a function of aging time for Avimid® K polymer laminates immersed in water, but at various temperatures. The degradation rate gets slower at lower temperature.

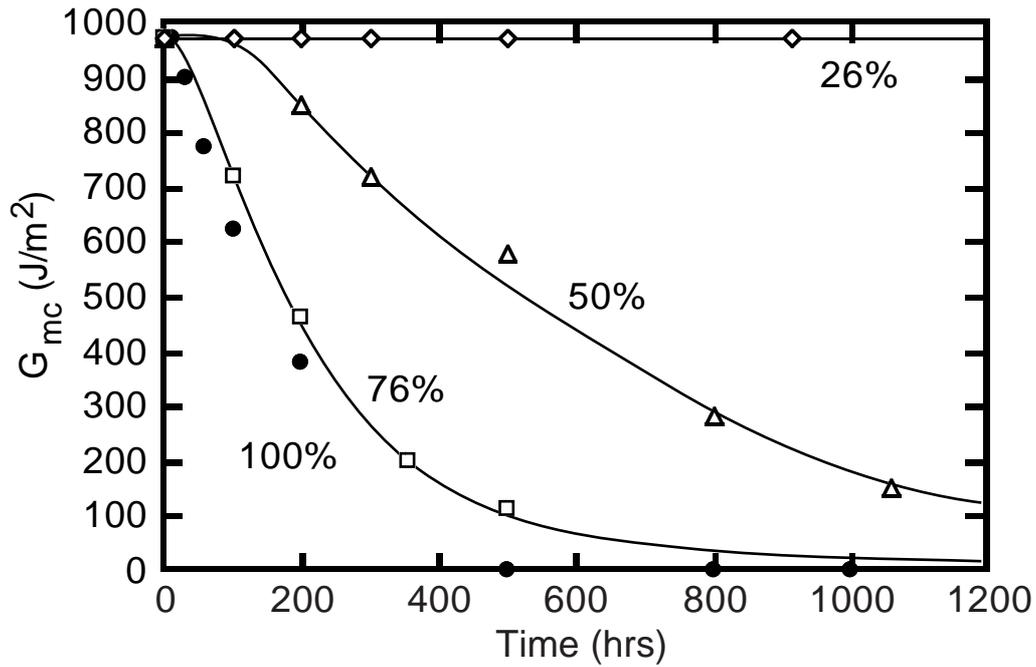


Fig. 2: Microcracking fracture toughness,  $G_{mc}$ , as a function of time for Avimid<sup>®</sup> K polymer laminates aged at 80°C while immersed in water (100%) or exposed to relative humidities of 76%, 50%, and 26%.

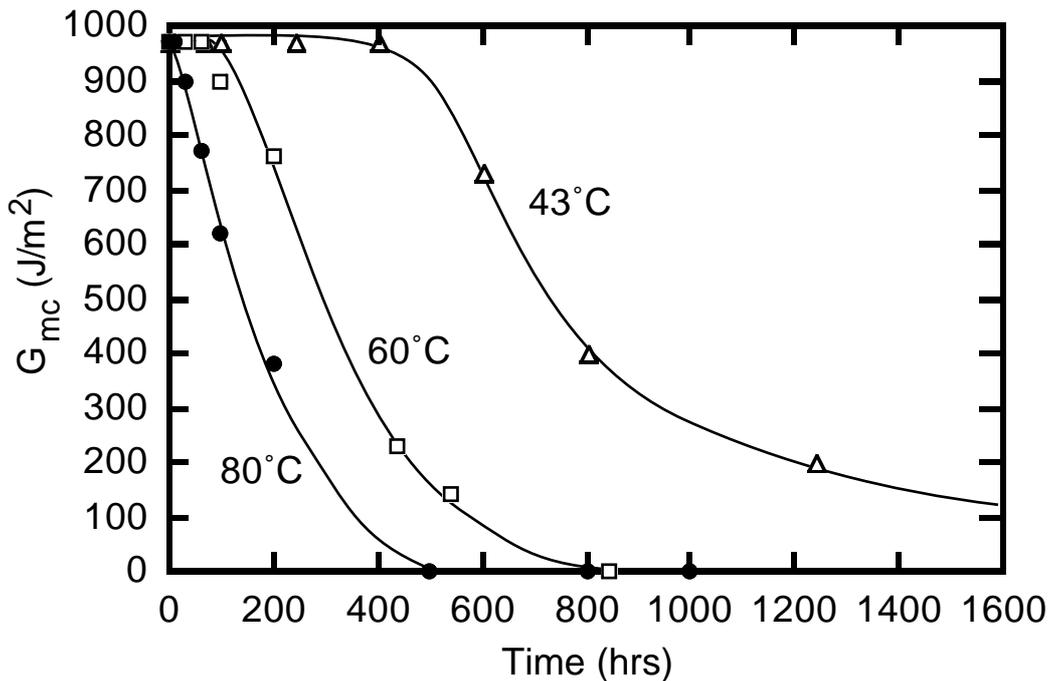


Fig. 3: Microcracking fracture toughness,  $G_{mc}$ , as a function of time for Avimid<sup>®</sup> K polymer laminates immersed in water but aged at 80°C, 60°C, and 43°C.

Some similar experiments were done for PETI5 laminates, but the degradation rate was much slower. Figure 4 plots  $G_{mc}$  as a function of aging time for the water-immersion results at 80°C. The toughness did not start to drop until after 2000 hours. By 3500 hours, it had only dropped 30%. We did not do experiments for PETI5 at other humidities or other temperatures.

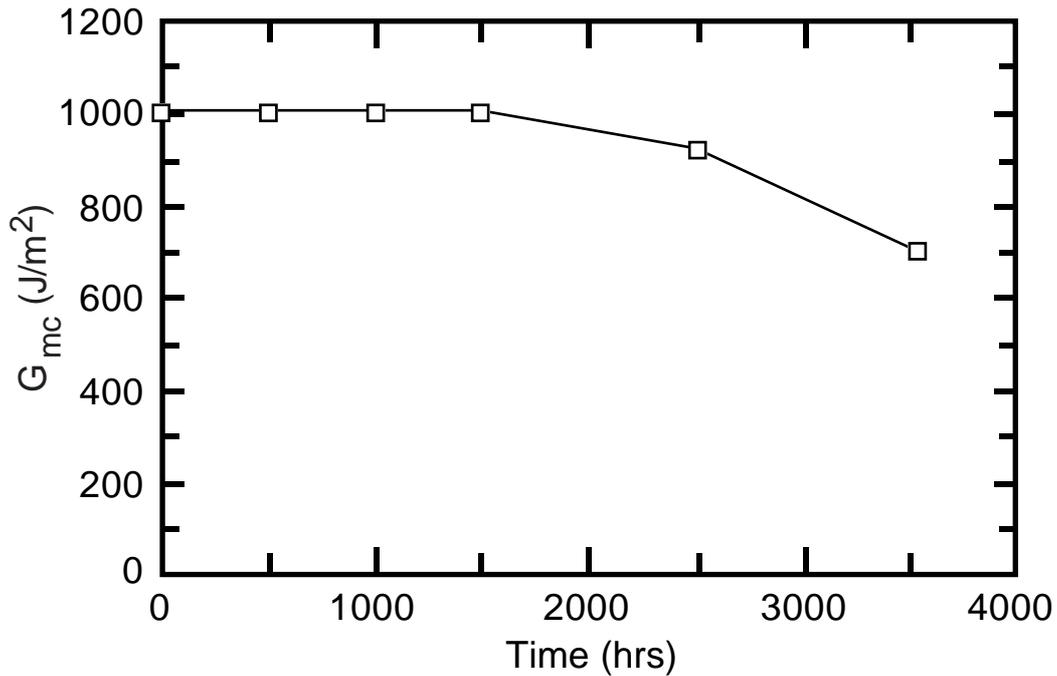


Fig. 4: Microcracking fracture toughness,  $G_{mc}$ , as a function of time for PETI5 laminates aged at 80°C while immersed in water.

While samples were aged under various conditions, we periodically weighed the specimens and recorded the amount of water uptake as a function of time. Such data can be used to calculate effective diffusion constants for water absorption in these laminates. Table 1 summarizes the water uptake results for the saturation level of water absorption and for the time to reach 90% of the saturation level. The total weight gain when immersed is nearly independent of temperature, although the absorption time scales get slower at lower temperature as the water diffusion rate gets lower. At 80°C, the total weight gain scales approximately with the relative humidity. Note that the relative humidities listed in Fig. 2 were not measured but rather were the documented humidities for various salt solutions [2,3]. Because we did experiments at temperatures outside the range of the document salt-solution humidities, our actual humidities may be different. Perhaps that ratio of the saturation water level at humidity to the saturation water level under reduced humidity is a better measure of the actual relative humidity. This ratio is given in Table 1 as the *Effective RH*. Also listed in the table is the time to reach 90% of toughness degradation; this time is much longer than the time to reach saturation. In other words, most degradation occurs after reaching saturation water levels.

Table 1: Summary of water uptake results for Avimid® K polymer laminates and a comparison to the rate of degradation in toughness

Conditions	Weight Gain (%)	Effective RH (%)	Hrs to 90% Weight Gain	Hrs to 90% Decrease in $G_{mc}$
80°C, Immersed	0.432	100	40	390
80°C, 76% RH	0.376	87	40	550
80°C, 50% RH	0.280	74	40	>1200
80°C, 26% RH	0.121	28	40	>>1200
60°C, Immersed	0.440	100	80	600
43°C, Immersed	0.420	100	170	>1400

## DISCUSSION

For all hygrothermal conditions and for both polyimide systems, the microcracking toughness decreased with time. The decrease was probably caused by hydrolysis of the polyimide resins [6]. There appears, however, to be a threshold effect. The toughness remained constant a short amount of time and then decreased. In this section, we suggest a simple first order kinetics analysis for the degradation process. We assume the rate of degradation is proportional to the water content. To account for the threshold effect, we assume that the first water goes into sites that do not cause damage and only the later water causes hydrolysis. Thus, the first order degradation is first order in water concentration (% weight gain) above some threshold concentration.

By the first order kinetics with a threshold effect, the rate in decrease in toughness is

$$\frac{dG_{mc}}{dt} = \begin{cases} 0 & \text{for } t < t_{thres} \\ k([H_2O(t)] - [H_2O]_{thres}) & \text{for } t > t_{thres} \end{cases} \quad (2)$$

which integrates to

$$G_{mc} = \begin{cases} G_{mc}^0 & \text{for } t < t_{thres} \\ G_{mc}^0 \exp\left(-k \int_{t_{thres}}^t ([H_2O(t)] - [H_2O]_{thres}) dt\right) & \text{for } t > t_{thres} \end{cases} \quad (3)$$

where  $k$  is a rate constant,  $[H_2O(t)]$  is the water weight gain as a function of time,  $[H_2O]_{thres}$  is the threshold concentration below which no degradation occurs,  $t_{thres}$  is the time for the water weight gain to reach  $[H_2O]_{thres}$ , and  $G_{mc}^0$  is the toughness before aging. For a given set of hygrothermal aging conditions, the two parameters for fitting experimental results are  $k$  and  $[H_2O]_{thres}$ . We were able to fit all experimental results to Eqn (4). Furthermore, the results for all humidities at a single temperature could be fit with the same values for  $k$  and  $[H_2O]_{thres}$ . At 80°C, the threshold water weight gain was determined to be 0.23%. This result predicts that for effective RH below 53%, there should be no degradation in toughness. This prediction agrees with the results at RH 26% (which had an effective RH of 28%); at least for the first 1000 hours, the results at low humidity showed no degradation in toughness.

By the form of Eqn (3), any two samples that have experienced the same integrated exposure to water should have the same degradation in toughness. Thus, it should be possible to derive a master plot for hygrothermal degradation where results at any temperature and humidity are shifted to some reference temperature and humidity. The effective time under the standard conditions is calculated by solving the numerical equation

$$\int_{t_{thres}^{ref}}^{t_{eff}} k^*(t, T_{ref}, RH_{ref}) dt = \int_{t_{thres}}^t k^*(t, T, RH) dt \quad (4)$$

for  $t_{eff}$  or the effective time at the reference temperature,  $T_{ref}$ , and reference humidity,  $RH_{ref}$ . Here  $t$  is the actual time at temperature  $T$  and relative humidity  $RH$ ,  $t_{thres}^{ref}$  and  $t_{thres}$  are the times to reach the threshold water concentration at  $T_{ref}$  and  $T$ , respectively, and

$$k^*(t, T, RH) = k(T)([H_2O(t, T)] - [H_2O(T)]_{thres}) \quad (5)$$

is an effective rate constant. Within  $k^*(t, T, RH)$ , the constants  $k(T)$  and  $[H_2O(T)]_{thres}$  depend only on temperature while the experimental data for  $[H_2O(t, T)]$  depend on temperature and humidity.

Give a set of experimental results for water uptake at various temperatures and humidities, the results can substituted into Eqn (4) and numerically integrated to construct a master plot for hygrothermal aging. By the results in Table 1, however, it is noted that the time for significant toughness degradation is much greater than the time to reach saturation water uptake. With this observation, it is possible to approximately solve Eqn (4) by ignoring the rising portion of the water uptake curves and assuming all degradation occurs at saturation water content. In other words, we assume  $k^*(t, T, RH)$  is a constant or independent of time and equal to  $k^*(\infty, T, RH)$  or its value at saturation water level. Eqn (4) then integrates to

$$t_{eff} = t_{thres}^{ref} + \frac{k^*(\infty, T, RH)}{k^*(\infty, T_{ref}, RH_{ref})} (t - t_{thres}) \quad (6)$$

Figure 5 gives a master plot for all our results on Avimid<sup>®</sup> K polymer laminates using reference conditions of water immersion at 80°C. Shifting by Eqn (6) requires knowledge of the temperature and humidity dependence of  $k^*(\infty, T, RH)$ . The temperature dependence for saturation conditions from our limited experiments can be described by an apparent activation energy of 26 kJ/mol which is very close to the apparent activation energy from spontaneous microcracking formation experiments [1]. Because  $k(T)$  and  $[H_2O(T)]_{thres}$  appear to be independent of humidity and  $[H_2O(t, T)]$  scales with humidity,  $k^*(\infty, T, RH)$  at any humidity can be calculated from the immersed result (RH=100%) using

$$\frac{k^*(\infty, T, RH)}{k^*(\infty, T, 100\%)} = \frac{RH - F}{1 - F} \quad (7)$$

where F is the ratio of the threshold water concentration,  $[H_2O(T)]_{thres}$ , to the saturation water weight gain when immersed in water.

## CONCLUSIONS

Polyimide-matrix composites show degradation in toughness when exposed to water and high temperature. All experimental results can be fit to simple first-order kinetics by assuming there is some threshold water concentration below which no degradation occurs. The rate constants calculated from these fits can be used to shift all results to a master plot for hygrothermal aging. By extrapolating rate constants to other temperatures it is possible to use the master plot to predict hygrothermal degradation at any temperature and humidity. By calculating the integrated exposure to water under any hygrothermal conditions, such as hygrothermal cycling conditions, it should similarly be possible to use the master plot to predict the extent of toughness degradation caused by those conditions.

Construction of hygrothermal aging master plots for other matrix systems is a potential accelerated test method for characterizing the hygrothermal stability of matrix resins. The

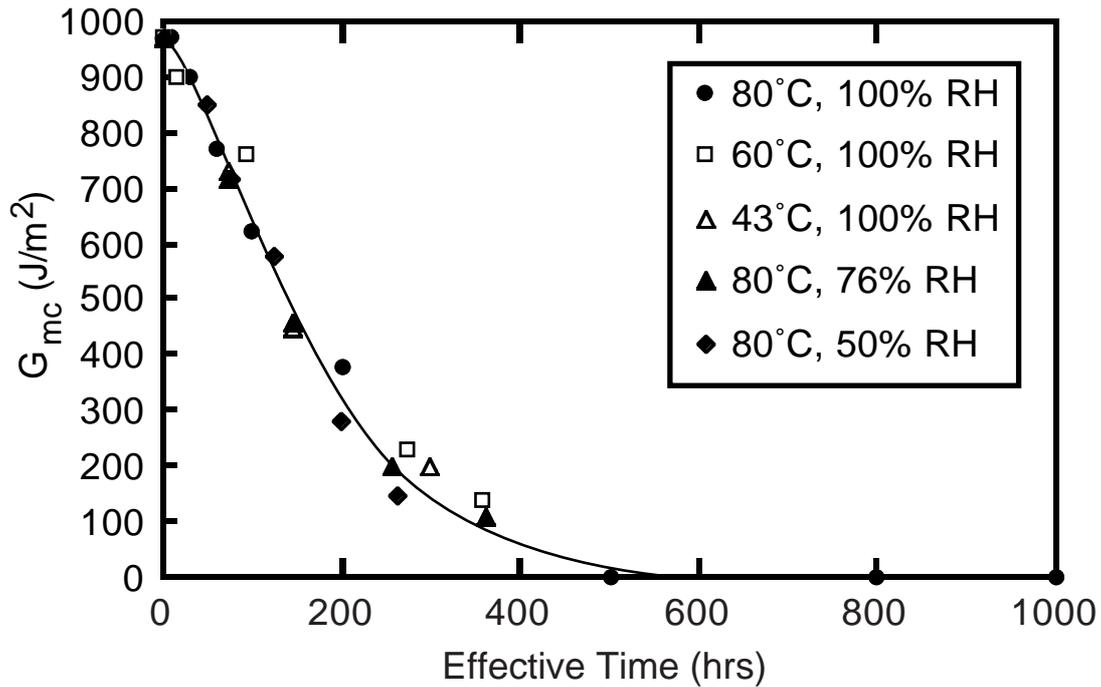


Fig. 5: Master plot for hygrothermal aging of Avimid® K polymer laminates for reference conditions of immersion in water at 80°C.

minimal experiments are to measure toughness degradation at the reference temperature while immersed in water and at several other temperatures while immersed in water. Such results at several temperatures can be used to give the temperature dependence of  $k^*(\infty, T, 100\%)$ . The humidity dependence can be extrapolated from  $k^*(\infty, T, 100\%)$  using Eqn (7) without the need for additional experiments at reduced levels of humidity.

### Acknowledgments

This work was supported, in part, by a grant from the Mechanics of Materials program of the National Science Foundation (CMS-9713356), and , in part, under a Boeing contract NAMP-1294-1544.

### REFERENCES

1. Kim, H. W., Grayson, M. A. and Nairn, J. A., "The Effect of Hygrothermal Aging on the Microcracking Properties of Some Carbon Fiber/Polyimide Laminates," *Advanced Composite Letters*, Vol. 4, 1995, pp. 185-188.
2. Greenspan, L., "Humidity Fixed Points of Binary Saturated Aqueous Solutions," *Journal of Research of the National Bureau of Standards - A. Physics and Chemistry*, Vol. 81A, 1977, pp. 89-96.
3. Wexler, A. and Hasegawa, S., "Relative Humidity-Temperature Relationships of Some Saturated Salt Solutions in the Temperature Range 0° to 50°C," *Journal of Research of the National Bureau of Standards*, Vol. 53, 1954, pp. 19-26.

4. J. A. Nairn, S. Hu, and J. S. Bark, "A Critical Evaluation of Theories for Predicting Microcracking in Composite Laminates," *Journal of Material Science*, Vol. 28, 1993, pp. 5099-5111.
5. J. A. Nairn, "Exact and Variational Theorems for Fracture Mechanics of Composites with Residual Stresses, Traction-Loaded Cracks, and Imperfect Interfaces," *International Journal of Fracture*, submitted, 1999.
6. R. DeIasi and J. Russell, "Aqueous Degradation of Polyimides," *Journal of Applied Polymer Science*, Vol. 15, 1971, pp. 2965-2974.