The Effect of Hygrothermal Aging on the Microcracking Properties of of Some Carbon Fiber/Polyimide Laminates

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Hygrothermal aging in the absence of external loads can lead to spontaneous formation of matrix microcracks in carbon fiber laminates made with Avimid® K polymer. The microcracks are caused by a water-induced decrease in the laminate microcracking toughness. A parallel decrease in neat K polymer toughness suggests that changes in the matrix play a role in water-induced microcracks.

Introduction

When dry, quasi-isotropic, Avimid® 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 despite the absence of externally applied load. The time to initiate water-induced microcracks, t_m (in minutes), was

$$\log t_m = \frac{3423}{T} + 1.35 \tag{1}$$

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.

For interpretation of this phenomenon, we assume that microcracks form in the 90° plies when the energy release rate for formation of a complete microcrack, G_m, exceeds the microcracking toughness of the material, G_{mc} [1–8]. An *exact* result for the relevant energy release rate is [8]:

$$G_m = \frac{(1+\lambda)}{2D} \frac{E_c^2}{E_T^2} \sigma_{x0}^2 \Delta \left(\frac{1}{E_A^*} \right) \tag{2}$$

where λ is the ratio of the number of supporting plies to the number of 90° plies, D is the current crack density, E_c is the composite axial modulus in the absence of any cracking, E_T is the transverse modulus of the ply material (*i.e.*, the loading-direction modulus of the 90° plies), σ_{x0} is the loading-direction stress in the 90° plies in the absence of any microcracks, and E_A^* is the effective axial modulus of the cracked laminate [8]. Residual stresses are included through the term σ_{x0} which is a sum of mechanical loads and residual stresses:

$$\sigma_{x0} = \frac{E_T}{E_c}\sigma_0 + \sigma_{res} \tag{3}$$

where σ_0 is the applied stress and σ_{res} is the residual stress in the 90° plies before any microcracking.

In the absence of applied loads, the *residual* energy release rate for *initiation* of microcracking is $G_{m,res} = G_m(\sigma_0 = 0, D = 0)$ (note: although it is not apparent by Eq. (2), the $\lim_{D \to 0} G_m$ is a well-defined quantity [6]). If the material toughness, G_{mc}, is less than $G_{m,res}$ then microcracks will form due to residual stresses alone; if $G_{mc} > G_{m,res}$ then no microcracks will form until there is an additional applied mechanical load. Water-induced microcracking occurs either when G_{mc} decreases to $G_{m,res}$ or when $G_{m,res}$ increases to G_{mc}. Because microcracks are within the matrix or at the fiber/matrix interface, a decrease in G_{mc} can be caused either by a decrease in the

matrix toughness or by a decrease in the fiber/matrix interface toughness. An increase in $G_{m,res}$ can be caused by an increase in residual stresses. Normally water absorption counteracts thermal residual stresses and leads to a *decrease* in σ_{res}; thus it is unlikely that changes in residual stresses are causing the microcracking.

This paper describes some the hygrothermal aging experiments on Avimid® K polymer laminates. We measured the laminate G_{mc}; it decreased with immersion time. We measured the neat K polymer toughness; it also decreased with immersion time suggesting that changes in matrix toughness play a role in water-induced microcracking. Finally, we confirmed that changes in residual stresses play no role in water-induced microcracking.

Materials and Methods

Both Avimid® K polymer laminates and neat Avimid® K polymer were molded and cut by McDonnell Douglas. Laminate specimens were 12.7 mm wide and 125 mm long. The $[45/0/-45/90]_s$ laminates had thicknesses of about 1 mm. The neat resin samples were 12.7 mm wide, 125 mm long, and 6.35 mm thick. Before use, all samples were dried at 120°C until all water was removed. After drying, samples were immersed in water maintained at 80°C and allowed to soak for various amounts of time. Before any mechanical testing, the samples were again dried at 120°C until all water was removed. Thus all mechanical tests were performed on dry samples.

To determine laminate toughness, 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. [7] to determine G_{mc}. In brief, the analysis method uses Eq. (2) and a two-dimensional variational mechanics analysis to find E_A^*. The properties assumed for the K polymer laminates are given in Ref. [5]. The microcracks occurred only in the 90° plies. The required properties of the supporting plies were determined using laminated plate theory on a symmetric $[45/0/-45]$ sublaminate [4]. The neat resin fracture toughness was measured using standard fracture mechanics methods on a notched, three-point-bending specimen [9]. All results were verified to be valid plane-strain measurements.

Results and Discussion

A series of K polymer laminates were immersed in water at 80°C for times ranging from zero to 100 hours. The water uptake obeyed Fickian behavior with a diffusion constant of $D = 8.1 \times 10^{-13}$ m²/s. The equilibrium water content after 100 hours was 0.42% by weight. The microcracking fracture toughness as a function of immersion time is given in Fig. 1A. There was no change in the first 10 hours, but there was a steady decrease for longer times. After only 30 hours there was a 5% decrease in G_{mc}; after 100 hours there was a 28% decrease in G_{mc}. In water-induced microcracking experiments, microcracks spontaneously formed in about 1000 hours when immersed at 80°C. Although we have not done G_{mc} experiments for longer aging times, we assume that water-induced microcracks form because G_{mc} continues to decrease until it becomes equal to $G_{m,res}$ after 1000 hours of immersion.

To explore the cause of the decrease in laminate G_{mc} during hygrothermal aging, we did aging experiments on neat K polymer. We immersed neat K polymer specimens in water at 80°C for times ranging from zero to 500 hours (note: longer times were required because the neat resin specimens were thicker). The water uptake obeyed Fickian behavior with a diffusion constant of $D = 10.2 \times 10^{-11}$ m²/s. The equilibrium water content after 500 hours was 1.56% by weight.
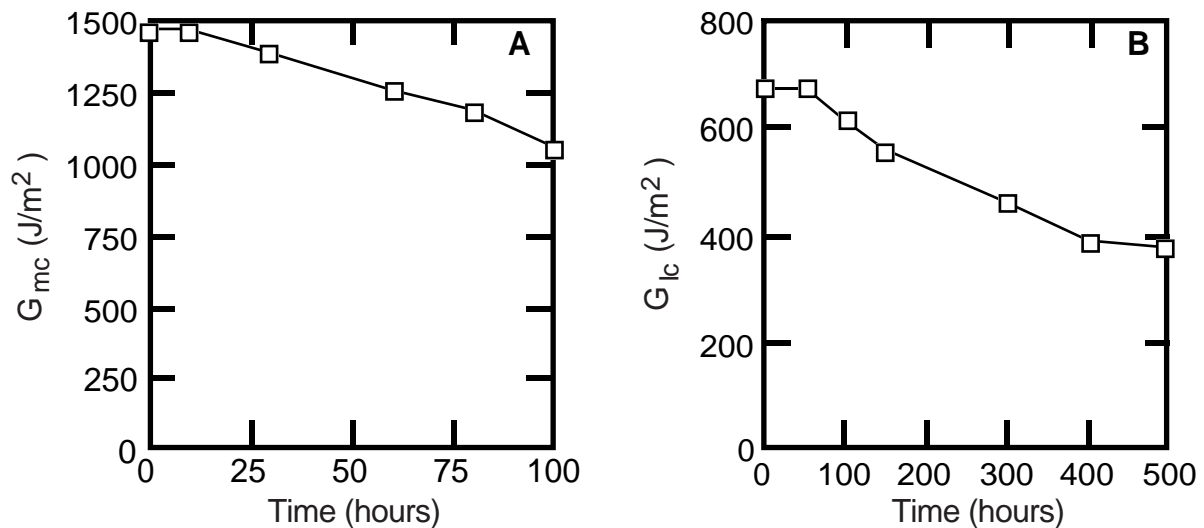
Figure 1. The microcracking fracture toughness, G_{mc}, of Avimid$^{®}$ K polymer laminates (A) and plane-strain fracture toughness, G_{Ic}, of neat K polymer (B) as a function of immersion time in water at 80°C.

As predicted by theory, the neat resin diffusion constant is larger than the laminate diffusion constant [10]. The toughness as a function of aging time is given in Fig. 1B. There was no change at early times (the first 50 hours), but there was a steady decrease for longer times. After 100 hours there was an 11% decrease in G_{Ic}; after 500 hours there was a 43% decrease in G_{Ic}. Comparing Figs. 1A and 1B, the decrease in neat resin toughness parallels the decrease in laminate toughness. We suggest the matrix toughness plays a role in the decrease in laminate G_{mc}. Because we have not yet studied the effect of aging on the fiber/matrix interface, we cannot be certain whether the decrease in matrix toughness is the sole factor in the decrease in G_{mc} or whether there is additional effect due to a decrease in interface toughness.

One possible cause for the decrease in G_{Ic} of the neat resin could be a decrease in molecular weight, perhaps caused by hydrolysis. To check for obvious decreases in molecular weight, we looked for changes in the glass-transition temperature as a function of immersion time in water at 80°C. With zero immersion time the T_g of K polymer, as measured by DSC, was found to be 238°C. We found no change in T_g (±2°C) for immersion times up to 500 hours. We conclude that either there was no change in molecular weight, or any changes in molecular weight were too small to have an influence on T_g.

Finally, we checked for possible changes in residual stresses. Unbalanced [0/90] laminates were immersed in 80°C water for various amounts of time [11]. As expected, water uptake caused the residual stresses and therefore the curvature or the unbalanced laminates to decrease. Water uptake swells the matrix relative to the fibers and partially cancels thermal residual stresses that resulted from differential shrinkage of the matrix relative to the fibers. To look for changes in the original level of residual stress we dried the samples after water immersion and compared final laminate curvature to initial curvature. As back calculated by laminated plate theory, the average residual stress in the 90° plies before aging was 61 ± 3 MPa. After water exposure, the residual stress increased an average of 1.9 ± 0.3 MPa or about a 3%. The increase in residual stress is small and therefore plays only a minor role in determining $G_{m,res}$.

Conclusions

Immersion of Avimid$^{®}$ K polymer laminates in 80°C water causes a decrease in microcracking toughness, G_{mc}. We claim that water-induced microcracks occur when the decrease in G_{mc}

is large enough that the residual stresses alone can cause microcracking. An advantage of measuring G_{mc} as opposed to waiting for water-induced microcracks is that we can see the deleterious effect of water immersion much sooner. At 80°C, we already noticed a 5% decrease in G_{mc} after only 30 hours of immersion while the first water-induced microcracks did not form until after 1000 hours of immersion. We claim that microcracking toughness experiments can be used to screen a variety of resins with the purpose of quickly determining which ones are most susceptible to water-induced microcracks.

We observed a parallel decrease in the toughness of neat K polymer as a function of water immersion time. We claim this decrease plays a role in water-induced microcracking. We have not been able to measure the fiber/matrix interface toughness as a function of immersion time. Thus we do not know whether the decrease in matrix toughness is the dominant factor or only one of the factors. The mechanism for the decrease in neat K polymer toughness is also not known. As evidenced by the T_g results, there was no obvious decrease in molecular weight. Two possible non-chemical mechanisms are physical aging and damage induced by heterogeneous swelling. For physical aging we speculate that water could plasticize K polymer thus promoting aging even well below the glass-transition temperature. Perhaps the aging leads to embrittlement of the matrix. By heterogeneous swelling we mean that the water uptake could be nonuniform. It is possible that gradients in stress caused by a nonuniform distribution of water could cause microscopic damage that provides a nucleus for the formation of microcracks.

Acknowledgements

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