Avimid® K3B/IM7 복합재료의 80°C 물에서의 노화현상

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The Aging Effect of Avimid® K3B/IM7 Laminates in 80°C Water

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ABSTRACT

The Hygrothermal aging of the laminates of Avimid® K3B/IM7 in 80°C water was studied as a function of immersion time prior to forming microcracks. The factors causing the 80°C water to degradation of the laminates could be the degradation of the matrix toughness, the change in residual stresses or the interfacial damage between the fiber and the matrix. The times to saturation in 80°C water for the laminates and for the neat resin were 100 hours and 500 hours. After 500 hours aging of the neat resin, the glass transition temperature was changed less than 1% by DSC test, and the weight gain was 1.55% increase with the diffusion coefficient $7x10^{-6}$ m/s^2 and the fracture toughness was decreased about 41%. After 100 hours fully saturated aging of the $[+45/0/-45/90]_s$ K3B/IM7 laminates in 80°C water, the weight gain was 0.41% increase with the diffusion coefficient $1x10^{-6}$ m/s^2. In 100 hours, the loss of the fracture toughness of the laminates was 43.8% of the original toughness by the microcracking fracture toughness criterion. Therefore, the main factor to degrade the microcracking toughness of the laminates could be the degradation of the matrix fracture toughness.

초 록

미세균열이 생기기 전 80°C 물속에서 침수시간에 따른 Avimid® K3B/IM7 복합재의 습기노화 현상에 관하여 연구하였다. 80°C 물속에서 복합재의 파괴인성을 저하시키는 요인으로는 수지 파괴인성의 저하나 잔류응력의 변화 그리고 섬유와 수지 사이의 계면 손상이다. 80°C 물속에서 수지에 습기가 포화되는 시간은 500 시간이며 K3B/IM7 복합재에 습기가 포화되는 시간은 100 시간이다. 수지가 500 시간 가속노화한 후 DSC 시험을 한 결과 T_g는 1% 이내 증가하였으며, 무게는 $7x10^{-6}$ m/s^2 확산속도로 1.55% 증가하였다. K3B/IM7복합재에 관하여 물속에서 100시간 지난 후 무게는 $1x10^{-6}$ m/s^2 확산속도로 0.41% 증가했다. 500 시간 노화한 후 수지의 파괴인성은 41% 저하하였으며 100 시간 노화한 후 $[+45/0/-45/90]_s$ K3B/IM7 복합재의 미세균열 파괴인성은 43.8% 감소하였다. 그러므로 80°C 수분노화 시험에서 복합재 적층의 파괴인성을 감소시키는 주요 원인은 수지 파괴인성의 저하라고 할 수 있다.

Key Words: Hygrothermal Aging(수분노화), Micracracking Fracture Toughness(미세균열 파괴인성강도), Diffusion(확산)

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1. Introduction

McDonnell Douglas did the experiments to measure the time to form water induced microcracks as a function of temperature in the laminates of Avimid K3b/IM7. Our experiments were to measure how the hygrothermal aging affected the microcracking toughness of the laminates as a function of immersion time prior to forming microcracks. McDonnel Douglas gave the data that the times to saturation in 80°C water for Avimid® K3B/IM7 laminates and the neat resin were 100 hours and 500 hours. Avimid® K3B neat resin samples were placed in 80°C water from 50 hours to 500 hours.

How the weight gained and how the aging affected the samples were studied. The factors to degrade the toughness of the laminates could be the degradation of the matrix toughness, the change in residual stresses or the interfacial damage between the fiber and the matrix. The first way to study hygrothermal aging was to study the aging of the neat resin. The neat resin samples were characterized by the three-point bending tests under the plane-strain conditions. The 80°C water aging had an effect on the neat resin K3B. Therefore, the failure analysis dominated by matrix was chosen. The laminates layup was [+45/0/-45/90]s. During the experiments to microcrack the 90° ply in the middle of the laminates, there were no microcracks in +45 or -45 plies. The microcracks in the 90° plies were found sufficient to yield good results. To get the microcracking fracture toughness of the composite materials, the energy release rate by the variational analysis was used in this thesis [1, 2].

2. Experiment

2.1 The Aging of Neat Resin Avimid® K3B in 80°C Water

2.1.1 Materials and Methods

The K3B samples were 6.5 mm thick, 12.6 mm wide and 101.6 mm long. The samples were put in the container which contained 80°C water from 50 hours through 500 hours. The samples were taken out of the oven periodically and the weight gain was measured.

Before the three point bending tests, the samples were dried out in 60°C oven for two hours to return to the initial weight. The single edge crack of each sample was made with a band saw first, and then sharped with a fresh razor blade. The cracks were longer than the half of the specimen width. The samples were then loaded on a three point bending fixture in an MTS frame using a cross head rate of 0.01 mm/sec until the sample broke. A critical intensity factor K_{IC} was determined by means of Eq. (1).

$$K_{IC} = y\left(\frac{6}{BW^2} * \frac{PS}{4}\sqrt{a}\right) \tag{1}$$

where,

$y = 1.93 - 3.07r + 14.53r^2 - 25.11r^3 + 25.8r^4$,

S ; the length of the sample,

$S > 4W$,

P ; applied maximum load to fracture,

$r = \frac{a}{W}$.

Next, the determined K value was plugged into the following plane strain behavior ASTM requirements, and all the dimensions were checked to see whether the requirements were satisfied.

a ; crack length > $2.5(\frac{K_{IC}}{\sigma_y})^2$, (2)

B ; sample thickness > $2.5(\frac{K_{IC}}{\sigma_y})^2$,

W ; specimen width > $6.27(\frac{K_{IC}}{\sigma_y})^2$,

where, K_{IC} was the plane-strain toughness and σ_y was the yield stress.

Under the plane strain conditions, K_{IC} could be converted to the G_{IC} (E=3,760 Mpa, ν =0.365).

2.1.2 Results and Discussion

To understand the water diffusion into the neat resin K3B, the diffusion coefficient D, whose magnitude was the indicative of the rate at which atoms diffuse, was introduced. Fick's second law was as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad (3)$$

where, C was the concentration in terms of weight % or mass of diffusing species per unit volume (kg/m^3). D was called the diffusion coefficient which was expressed in square meters per second (m^2/s). t was time (sec).

Let us consider the model as the slab whose boundary conditions were :

for t=0, C=0 at $0 \leq x \leq B$,

for t>0, $C=C_{sat}$ (saturated concent.) at x=0

$C=C_{sat}$ at x=B (thickness).

Applying these boundary conditions to Fick's second law yielded the following solution Eq. (4) :

$$C(x,t) = C_{sat} + \frac{2}{B}\sum_{m=1}^{\infty} e^{-D\beta_m^2 t}\frac{1}{\beta_m} sin\beta_m x \quad (4)$$
$$(C_{sat} cos m\pi - C_{sat})$$

where, $C(x,t)$ represented the concentration at length x after time t, and $\beta_m = \frac{m\pi}{B}$.

Taking a few terms in Eq. (4) and calculating the average value of the diffusion coefficients inside the body, the results were obtained (refer to Table 1).

Table 1. The Theoretical Percent of Weight Gain for Avimid K3B Neat Resin as a Function of Immersion Time in 80°C Water

immersion time (hrs)	50	100	150	300	500
weight gain(%)	0.70	0.93	1.09	1.36	1.50

Table 2. The Experimental Percent of Weight Gain for Avimid K3B Neat Resin as a Function of Immersion Time in 80°C Water

immersion time (hrs)	50	100	150	300	500
weight gain(%)	0.97	1.06	1.22	1.25	1.56

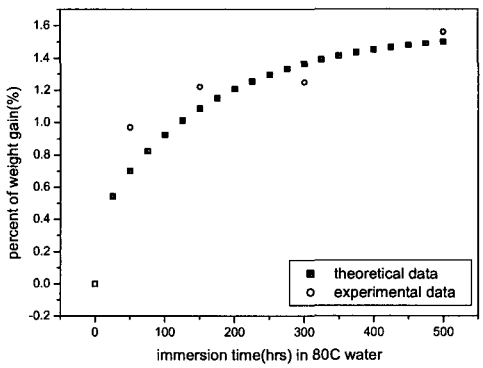

Fig. 1 The Percent of Weight Gain as a Function of Immersion Time at 80°C Water for Neat Resin K3B

Figure 1 showed how much weight the

samples gained. The average original weight for two samples was 16.78 g. After 500 hours, the weight went up to 17.04 g which was 1.56% increase. The weight gain in 100 hours was 1.06% increase. The detail data were in Table 2. The red circle shape data were the experimental data and the black square data were the theoretical data with the diffusion coefficient $7.0x10^{-6}$ m^2/s.

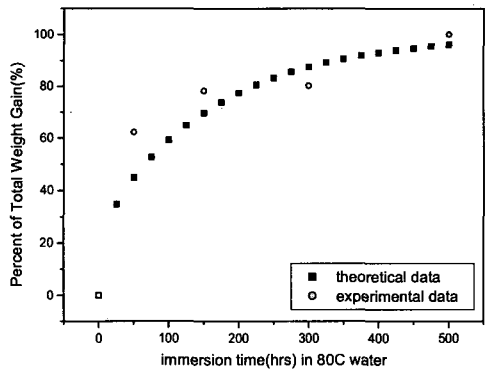

Fig. 2 The Percent of Total Weight Gain as a Function of Immersion Time at 80C Water for Neat Resin K3B With the Diffusion Coefficient $7.0x10^{-6}$ m^2/s

In Figure 2, the percent of total weight gain was estimated from each percent of the weight gain divided by percent of weight gain of 500 hours. The percent of total weight gain of 500 hours was 100% which meaned saturation. In only 50 hours, the percent of total weight gain increased to 62.20%, and then increased slowly. After 500 hours, the percent of total weight gain no longer increased or the sample was almost saturated.

Figure 3 showed the changes in fracture toughness as a function of immersion time. The results presented the average fracture toughness for two replicate experiments. The error of two samples was about ±6%. The toughness showed a gradual loss as the aging time increased. The unaged fracture toughness was 670 J/m^2. The 100 hours aging changed the microcracking toughness to 610 J/m^2 which corresponded to the 9% decrease of the original toughness. In 500 hours, the loss of the microcracking toughness was 41% of the original toughness.

Table 3. The Fracture Toughness for Avimid K3B Neat Resin as a Function of Immersion Time in 80°C Water. The Data Presented the Average Values of Two Experiments

immersion time (hrs)	0	50	100	150	300	400	500
fracture toughness(J/m^2)	670	670	610	560	455	400	395

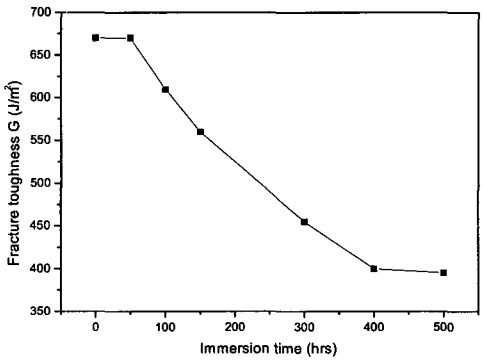

Fig. 3 The Fracture Toughness as a Function of Aging Time in 80C Water for Neat Resin K3B

The glass transition temperature was measured using differential scanning calorimetry (DSC) in which the difference in energy inputs into a substance and a reference material was measured as a function of

temperature, and the substance and the reference material were subjected to the controlled-temperature program. The original glass transition temperature of K3B was 238°C. After 500 hours aging, the glass transition temperature was 240°C. Therefore, the change of the glass transition temperature T_g was 0.8%.

Table 4. The Glass Transition Temperature for Avimid K3B Neat Resin as a Function of Immersion Time in 80°C Water

immersion time (hrs)	0	300	500
Tg for the first sample	238°C	240°C	240°C
Tg for the second sample	238°C	239°C	240°C

2.2 The Aging of Avimid® K3B/IM7 in 80°C Water

2.2.1 Materials and Methods

The layup of Avimid® K3B/IM7 laminates was [+45/0/-45/90]s. The sample dimensions were 12.6 mm wide, 100 mm long and had the thickness determined by the stacking sequence. Before the samples were put in the water, the weight of the samples was measured. The samples then were placed in a container which contained 80°C water from 10 hours to 100 hours. The warm water evaporated quickly, so the same temperature water was poured into the container regularly. Two samples were taken out periodically from the sealed oven holding the container, and the weight gain was measured. Before the static tensile tests, the samples were dried out in 60°C hot oven for two hours to the constant weight. The samples were then loaded on the MTS frame using a cross head rate of 0.01 mm/sec until the samples were broken or the end tabs failed.

2.2.2 Results and Discussion

Figure 4 describe how much weight the samples gained. The average weight gain for two samples in 100 hours was 0.01 g which corresponded to a 0.42% increase of the original weight.

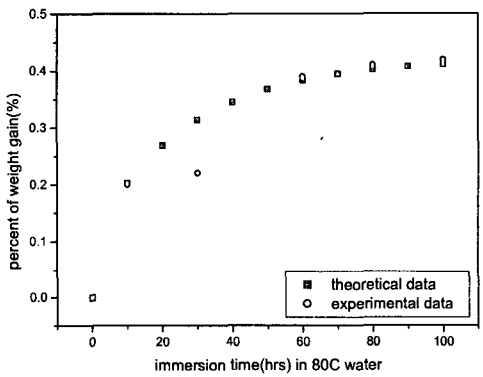

Fig. 4 The Percent of Weight Gain for Avimid K3B/IM7 [+45/0/-45/90]s Laminates

In Figure 4, the red color data were the result from the experimental data and the black color data were the result from the theoretical data. These data were in Table 5.

Table 5. The Percent of Weight Gain for Avimid K3B/IM7 as a Function of Immersion Time in 80°C Water

immersion time (hrs)	10	30	60	80	100
the first sample weight gain(%)	0.18	0.20	0.40	0.43	0.43
the second sample weight gain(%)	0.22	0.24	0.38	0.40	0.41
average(%)	0.20	0.22	0.39	0.41	0.42

Figure 5 described the percent of total weight gain as a function of immersion time at 80°C water for Avimid® K3B/IM7. The percent of total weight gain was calculated from the percent of weight gain divided by the percent of weight gain of 100 hours. In 60 hours, the percent of total weight gain increased to about 95%, and then increased slowly.

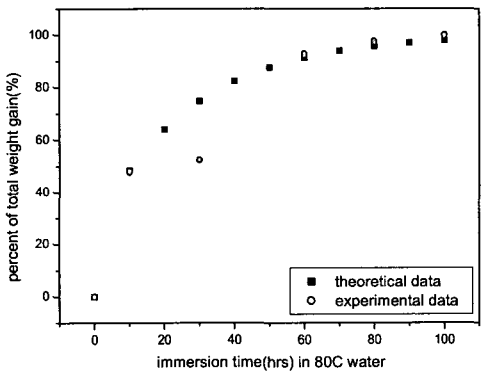

Fig. 5 The Percent of Total Weight Gain for Avimid K3B/IM7 [+45/0/-45/90]s Laminates as a Function of Immersion Time at 80°C Water with the Diffusion Coefficient $1.0x10^{-6}m^2/s$

The red circle data were the experimental data and the black square data were the theoretical data with diffusion coefficient $1.0x10^{-6}$ m^2/s.

To get the microcracking fracture toughness of the composite materials, the energy release rate by the variational analysis was used in this thesis [2]. The method was summarized as follows.

In Figure 6, the laminates was under an axial stress, σ_0, in the x direction. Under most experimental conditions, the microcracks formed in the 90° plies spaning the entire cross-section of those plies. The variational mechanics analysis determined all components of the stress tensor in the x-z plane. In this paper, one only required the tensile stress in the 90° plies.

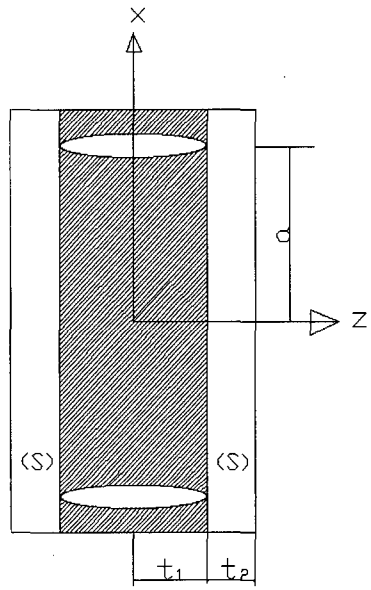

Fig. 6 Edge View of Microcracks in the 90° plies of $[(S)/90_n]_s$ Laminates. ((s) is sublaminates)

The result was

$$\sigma_0 = \frac{1}{k_m^{(1)}}\left(\sqrt{\frac{G_{mc}}{C_3 t_1 Y(D)}} - k_{th}^{(1)}T\right) \qquad (5)$$

where, the terms $k_m^{(1)}$ and $k_{th}^{(1)}$ were the effective mechanical and thermal stiffnesses of the 90° plies.

$$k_m^{(1)} = \frac{E_x^{(1)}}{E_x^0} \text{ and } k_{th}^{(1)} = -\frac{\Delta\alpha}{C_1} \qquad (6)$$

Here E_c^0 was the x-direction modulus of the laminate, $E_Z^{(1)}$ was the x-direction modulus of the 90° plies, $\Delta\alpha = \alpha_x^{(1)} - \alpha_x^{(2)}$ was the difference between the x-direction thermal expansion coefficients of the 90° plies and the (S) sublaminate, and C_1, C_3 were the constants defined in the Ref(3). Microcrack density ($D = \frac{N}{L}$) was the average crack density, N was the number of cracks and L was the sample length and Y was a function defined in Ref. (3). In Eq. (5), there were two unknowns G_{mc} (microcracking fracture toughness), T(the temperature difference that determined the level of residual stresses). T could be measured by various means. Therefore if one had an unknown G_{mc} , we could predict the experimental results (stress (σ_0) vs microcrack density(D)). The unknown G_{mc} could be obtained from the comparison between the experimental data and the theoretical line drawn from Eq. (5) using a single value of G_{mc} .

Figure 7 showed in detail how the 80°C water affected the aging of K3B/IM7 laminates. As the immersion time increased, the higher microcrack density was found at a lower stress. The experimental data (symbols in Fig. 7) were matched with the solid lines drown by the values in Table 6. The material constants was referred in [4].

Figure 8 showed how the 80°C water changed the microcracking toughness of K3B/IM7 laminates as a function of aging time. The unaged microcracking toughtness was 1.6 J/m^2. The 30 hours aging changed the microcracking toughness to 1.5 J/m^2 which corresponded to 6.3% decrease of the original toughness.

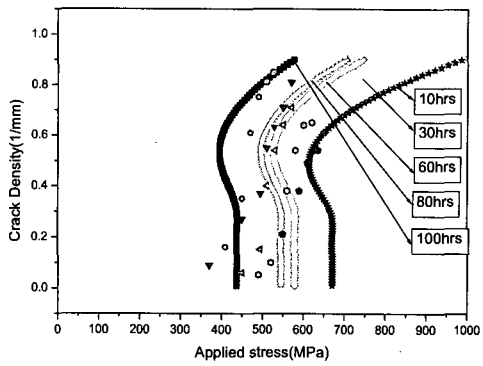

Fig. 7 The Microcrack Density as a Function of the Applied Load in Avimid K3B/IM7 [+45/0/-45/90]s Laminates

Table 6. Microcracking Toughness for Avimid K3B/IM7 as a Function of Immersion Time in 80°C Water

immersion time(hrs)	0	10	30	60	80	100
Microcracking Fracture Toughness(J/m^2)	1.6	1.6	1.5	1.3	1.2	0.9

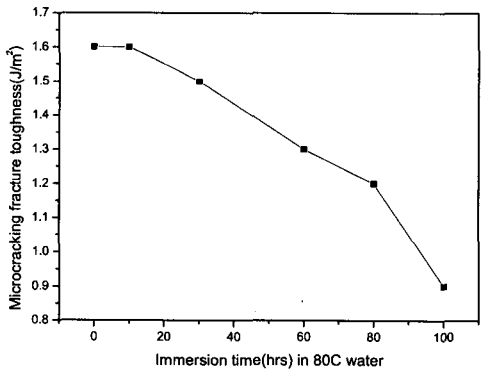

Fig. 8 The Microcracking Fracture Toughness as a Function of Immersion Time in Avimid K3B/IM7 [+45/0/-45/90]s Laminates in 80°C Water

In 100 hours, the loss of the microcracking toughness was 43.8% of the original toughness. Therefore, the microcracking toughness of the saturated laminates in 80°C water was degraded almost half.

The factors causing the 80°C water to degrade the microcracking toughness of the laminates could be the degradation of the matrix fracture toughness, the change in residual stresses or the interfacial damage between the fiber and the matrix. Referring to Fig. 3, the 500 hours aging changed 41% of the original toughness of the neat resin K3B. Therefore, the main factor to degrade the microcracking toughness of the laminates could be the degradation of the matrix fracture toughness.

3. Conclusions

In the present work, the hygrothermal aging of the laminates of Avimid® K3B/IM7 in 80°C water was studied. The times to saturation in 80°C water for the laminates and for the neat resin were 100 hours and 500 hours. After 500 hours aging of the neat resin, the weight gain was 1.55% increase with the diffusion coefficient $7x10^{-6}$ m/s^2. The fracture toughness was decreased about 41% by three point bending test.

After 100 hours fully saturated aging of the $[+45/0/-45/90]_s$ K3B/IM7 laminates in 80°C water, the weight gain was 0.41% increase with the diffusion coefficient $1x10^{-6}$ m/s^2. In 100 hours, the loss of the fracture toughness of the laminates was 43.8% of the original toughness by the microcracking fracture toughness criterion. Therefore, the main factor to degrade the microcracking toughness of the laminates could be the degradation of the matrix fracture toughness.

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