論文

PSF/AS4 복합재료의 가속노화가 피로강도에 미치는 영향

김형원*

The Effects of Physical Aging of PSF/AS4 Laminate on Fatigue

Hyung-Won Kim*

ABSTRACT

The effects of aging on fatigue of PSF/AS4 laminates was studied using the new energy release rate analysis. The analysis by the variational mechanics has been useful in providing fracture mechanics interpretation of matrix microcracking in cross-ply laminates. This paper describes the changes of the critical energy release rate ΔGmc (microcracking toughness) about the variation of the aging period during fatigue loading. The master plot by modified Paris-law gives a characterization of a material system's resistance to microcrack formation. PSF/AS4 [0/902]$_s$ laminates were aged at four different temperatures based on the glass transition temperature for 60 days. At all temperatures, the toughness decreased with aging time. The decrease of the toughness at higher temperature was faster than at lower temperature. To assess the effects of aging on fatigue, the unaged laminates were compared with the laminates which were aged for 60 days at 170°C near 180°C T_g. The slope of dD/dN versus ΔG_m of the aged laminates was lower than that of the unaged laminates. There was a significant shift of the aged data to formation of microcracks at the lower values of ΔG_m.

초 록

PSF/AS4 복합재 적층구조의 가속노화가 피로강도에 미치는 영향을 변분이론을 이용한 에너지 발산율(energy release rate) 분석을 이용하여 연구하였다. 변분이론 분석은 수지미소균열에 대한 파괴역학을 해석하는데 사용되어 왔으며 이 논문에서는 피로하중 하에서 가속노화 시간에 따르는 파괴인성이 어떻게 변하는가를 설명하였다. 수정된 Paris 법칙에 의한 선도는 각 재료마다 미소균열이 형성되는 특성을 나타낸다. PSF/AS4 [0/902]$_s$ 적층구조가 60일 동안 유리천이온도에 근거를 두고 세분한 4개의 각기 다른 온도로 가속노화를 하였다. 모든 온도에서 파괴인성은 가속노화 시간에 따라 감소하였다. 높은 온도에서의 파괴인성의 감소는 낮은 온도에서의 감소보다 빠르게 진전되었다. 가속노화가 피로강도에 미치는 영향을 파악하기 위해 유리천이온도인 섭씨 180도에 가까운 170도에서 60일 동안 노화한 것과 노화하지 않은 것을 비교하였다. 노화된 시편에 대하여 파괴인성의 변화(ΔG_m)가 낮은 값에서 미소균열이 형성되는 것을 알 수 있었다.

Key Words : Aging effect(노화효과), Fracture toughness(파괴인성), Neat resin(순수수지), Static tensile(정적인장), Microcracking(미세균열), Fatigue(피로)

Nomenclature

G_m : energy lease rate
k_m, k_{th} : effective mechanical and thermal stiffness of the 90° plies
σ_0 : total applied axial stress
T : effective residual stress temperature
D : microcracking density
Y(D) : calibration function of crack density(D)

---

* 국방과학연구소(Agency for Defence Development), 교신저자(E-mail:hwk4539@hanmail.net)

1. Introduction

When composites are used at the elevated temperatures for long times, the issue of aging becomes important. Aging is defined as time-dependant changes in the composite. The changes can be due to physical aging or chemical aging. This thesis focuses mostly on physical aging. Physical aging is associated with rearrangement of the polymeric matrix that normally leads to densification. In evaluating composite materials, the importance of aging is the effect on the laminate properties. Some properties that might change are *toughness, stiffness, weight, and glass transition temperature.* In this paper, the effect of aging on microcracking toughness was the main concern. PSF/AS4 laminates were chosen as a test material, because the glass transition temperature of PSF/AS4 prepregs was relatively so low that the aging tests were simplified. The most direct way to study aging is to study the neat resin [1]. Three point bending tests were performed for single-edge notched neat resin samples of PSF by a fracture mechanics analysis. The toughness as a function of aging temperature for different periods was obtained. To get the effect on composite toughness, microcracking experiments on $[0/90_2]_s$ laminates of PSF/AS4 were performed. The aging process was periodically interrupted and the microcracking data of the laminates were collected. Having microcracking toughness data of PSF/AS4 laminates, a master curve was drawn by using time-temperature superposition. An alternative method for assessing the effect of aging on microcracking properties is to observe the development of microcracks during fatigue loading. The microcracking fatigue properties were measured for unaged laminates and for laminates that had been aged for 60 days at 170°C. The results of fatigue test were presented.

2. Experiment

2.1 Neat resin PSF 3-point bending tests

2.2.1 Materials and Methods

Polysulfone, an amorphous thermoplastic matrix, is tougher than most thermoset matrix resins. and its Tg is 180°C. The neat resin samples that were 3.5 mm thick, 12.6 mm wide, and 50.0 mm long were cut to be the single-edge crack with a saw first, and sharped with a fresh razor blade. All cracks were longer than 0.5W. The samples were aged at either 175°C or 180°C with aging period varying from 0 day to 60 days. During the aging process, the aging was interrupted and neat resin specimens were tested for fracture toughness. Each sample was loaded on a 3-point bending fixture in an MTS frame using a cross head rate of 0.01 mm/sec until fracture. By three point bending test, a critical intensity factor K_{Ic} was determined by means of Eq. (1).

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

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 [2, 3] requirements, and all the dimensions were checked to see whether the requirements were satisfied.

$$\begin{aligned} &a \text{ ; crack length} > 2.5\left(\frac{K_{Ic}}{\sigma_y}\right)^2, \\ &B \text{ ; sample thickness} > 2.5\left(\frac{K_{Ic}}{\sigma_y}\right)^2, \qquad (2) \\ &W \text{ ; specimen width} > 6.27\left(\frac{K_{Ic}}{\sigma_y}\right)^2, \end{aligned}$$

where K_{Ic} is the plane-strain toughness and σ_y is the yield stress.

Under the plane-strain conditions, K_{Ic} can be converted to the G_{Ic} (E=2,480 MPa, ν=0.3).

2.2.2 Results and discussion

The most direct way to study aging of PSF/AS4 laminates is to study the neat resin.

The toughness as a function of aging period at either 175°C or 180°C is plotted in Fig. 1. The results present the average fracture toughness for two replicate experiments (the error of two samples is about 4.5%). The toughnesses are higher than expected but show a significant toughness loss as aging time increases. The reason that the toughnesses are higher compared to the conventional results is probably the sharpness of the original notch formed in the specimen. For brittle materials, it is often possible to propagate a stable crack at the tip of the notch by razor blade method, but for

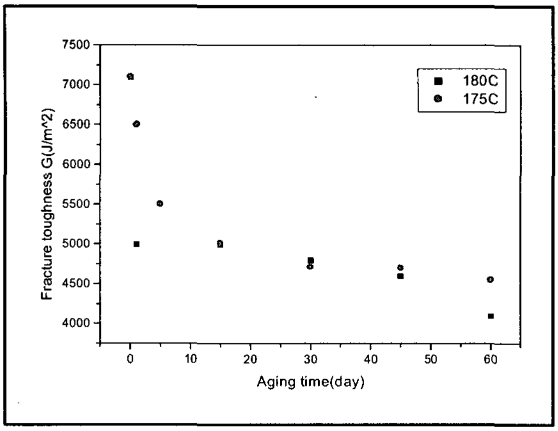

Fig. 1 The toughness as a function of aging time for neat resin PSF specimens. The circle data are from 175°C and the square data are from 180°C. The error of the two samples is about 4.5%.

the tougher materials such cracks do not form easily. The toughness decrease was faster and further for aging at 180°C than for aging at 175°C.

2.2 The PSF/AS4 laminates

2.2.1 The unaged PSF/AS4 laminates

Neat resin results are significant, but the most important result is the effect on composite toughness. The most likely effect of aging is on the matrix and thus the characterization of composite toughness should concentrate on matrix-dominated failure modes such as microcracking. The first microcracking experiments are to measure the microcrack density in the 90° plies which is the number of microcrack divided by the length of the specimen as a function of applied load for the unaged material. The stacking sequence of the laminates is $[0/90_2]_s$. Once the microcrack density is obtained, a microcracking toughness could be determined by the variational analysis.

The variational mechanics analysis determines all components of the stress tensor in the x-z plane. In this paper, the tensile stress in the 90° plies is only required. The result is [4].

$$\sigma_{u} = \frac{1}{k_m^{(1)}}\left(\sqrt{\frac{G_{mc}}{C_3 t_1 Y(D)}} - k_{th}^{(1)} T\right) \tag{3}$$

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

$$k_m^{(1)} = \frac{E_x^{(1)}}{E_c^0} \text{ and } k_{th}^{(1)} = -\frac{\Delta\alpha}{C_1} \tag{4}$$

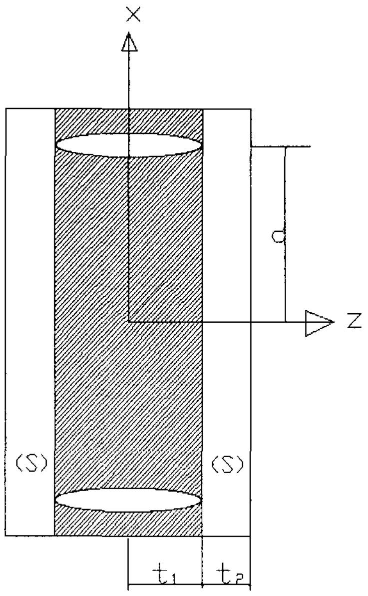

Fig. 2 Edge view of microcracks in the 90° plies of $[(S)/90_n]_s$ laminates. ((s) is sublaminates)

Table 1 The mechanical properties for PSF/AS4 unidirectional laminate

E_A (GPa)	E_T (GPa)	G_A (GPa)	G_T (GPa)	ν_A	ν_T	α_A $(ppm/^\circ C)$	α_T $(ppm/^\circ C)$	T_{eff}
134	9.8	5.5	3.6	0.3	0.5	-0.09	28.8	-225

here E_c^0 is the x-direction modulus of the laminate, $E_Z^{(1)}$ is the x-direction modulus of the 90° plies, $\Delta\alpha = \alpha_x^{(1)} - \alpha_x^{(2)}$ is the difference between the x-direction thermal expansion coefficients of the 90° plies and the (S) sublaminate, and C_1, C_3 are the constants defined in the Ref (4). $D = \frac{N}{L}$ is the average crack density, N is the number of cracks and L is the sample length and Y is a function defined in Ref. (4).

In eq. (3), there are two unknowns G_{mc} (microcracking fracture toughness), T(the temperature difference that determines the level of residual stresses). T can be measured by various means. Therefore if an unknown G_{mc} is found, the experimental results (stress(σ_0) vs microcrack density(D)) could be predicted. The unknown G_{mc} can be obtained from the comparison the experimental data with the theoretical line drawn from eq. (3) using a single value of G_{mc} using the mechanical properties in Table 1.

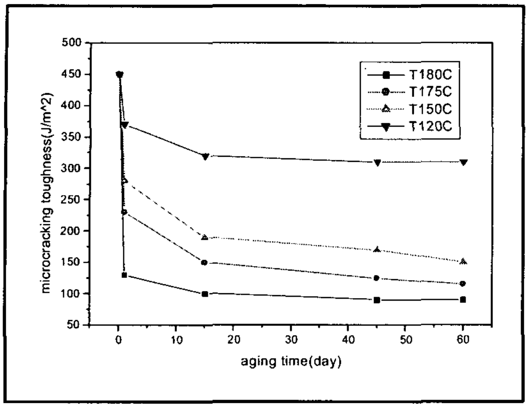

Fig. 3 The microcracking toughness as a function of aging time for $[0/90_2]_s$ PSF/AS4 laminates.

The sample dimensions were nominally 12mm wide and 150 mm long and the thicknesses were determined by the stacking sequence.

The result of the microcracking toughness of the unaged Psf/As4 laminates was 450 J/m^2 and the thermal load term ΔT was -150°C.

2.2.2 The aged Psf/As4 laminates

PSF/AS4 $[0/90_2]_s$ laminates were aged at four different temperatures for 0 to 60 days (0 to 1440 hours). Even before any load was applied to the laminate, some microcracks were found in the laminate. These microcracks were assumed to be caused by residual thermal stresses. The observation of microcracks before loading is an indication that G_{mc} is low. The microcracking toughness (G_{ms}) as a function of aging time is plotted in Fig. 3. At all temperatures, the toughness dropped with time (refer to Table 2). The decrease in toughness was faster at higher temperatures than at lower temperatures. At all temperature, there was already a significant drop after only one day of aging. The G_{mc} values were indeed low ranging from a low of 370 J/m^2 to a high of 90 J/m^2. The laminate toughness decreased with aging and, on a percentage basis, decreased more than the neat resin fracture toughness. In other words, the ratio of the 60 day aged toughness to the unaged toughness was lower in the composite than in the neat resin. There was also more than an order of magnitude difference between the neat resin toughness and the laminate toughness. The usual explanation for the low laminate toughness is that in the composite the plastic zone size is restricted by the fibers. As a result, the energy dissipation that occurs in the neat resin does not occur in the composite and the toughness is lower.

Table 2 The microcracking toughness of $[0/90_2]_s$ PSF/AS4 laminates as a function of aging time

aging days	G_{mc}(J/m^2) at T=180°C	G_{mc}(J/m^2) at T=175°C	G_{mc}(J/m^2) at T=150°C	G_{mc}(J/m^2) at T=120°C
0	450	450	450	450
1	130	230	280	370
15	100	150	190	320
45	90	125	170	310
60	90	115	150	310

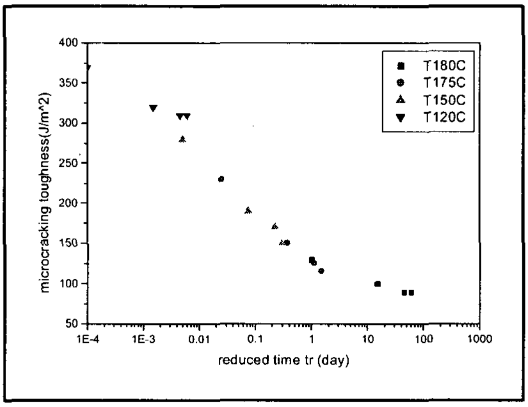

Fig. 4 Microcracking toughness of PSF/AS4 laminates as a function of reduced aging time at a reference temperature of 180°C.

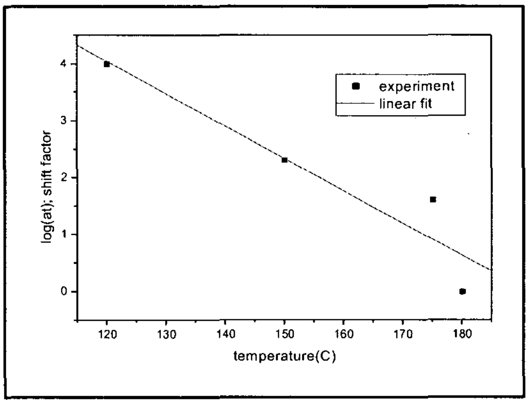

Fig. 5 The shift factor for microcracking toughness of PSF/AS4 laminates as a function of aging temperature.

Having mechanical property data of PSF/AS4 as a function of time and temperature, a master curve can be drawn by using time-temperature superposition. The microcracking toughness thus was plotted as a function of reduced time, t_r defined as the following equation.

$$\log t_r = \log \frac{t}{a_T} = \log t - \log a_T \tag{5}$$

where t is actual time and $\log a_T$ is the temperature-dependant shift factor. The test temperature of 180°C arbitrarily was selected to be the reference temperature and the data at other temperatures were shifted to achieve the maximum overlap between experimental results on a reduced time plot. The master plot is given in Fig. 4. The master plot defines a smooth curve. In principle, this plot could be used to predict the microcracking toughness after any amount of time at any aging temperature. For some conditions, there was only slight overlap between experiments at two adjacent temperatures. It would be more confident in the master curve if the data at various temperatures had been extended to longer times resulting in more overlap on the reduced time plot.

The shift factor as a function of temperature required to produce the master plot is given in Fig. 5. The qualitative result from Fig. 4 and Fig. 5 is that degradation in microcracking toughness due to physical aging can be observed in reasonably short time scales even well below the glass transition temperature.

2.2.3 Effect of aging on fatigue of PSF/AS4 laminates

An alternative method for accessing the effect of aging on microcracking properties is to study the development of microcracks during the fatigue loading. A fracture mechanics interpretation of the propagation of microcracks during fatigue testing is based on a modified Paris-law approach. To apply Eq. (3) to the analysis of fatigue experiments, a modified Paris-law approach was used in which the rate of increase in microcrack density per cycle, dD/dN, during fatigue loading could be predicted using a modified Paris law as the following equation.

$$\frac{dD}{dN} = A\Delta G_m^n \qquad (6)$$

where ΔG_m is the range in G_m for the maximum and minimum loads in the fatigue cycle and A and n are material properties that describe the resistance of the material to fatigue-induced microcracks. Eq. (6) used the range in energy release rate, ΔG_m, instead of the range in stress-intensity factor, ΔK. This substitution is made because an expression for G_m is obtained and the stress intensity factor has no physical meaning for formation of a complete microcrack.

The fatigue tests were run on an MTS 25KN hydraulic testing frame using load control. The load span was set to cycle between a maximum stress, σ_{max}, and the stress span, $\Delta\sigma_o$. The cycling rate was usually 5 Hz. During the fatigue test, the load cycling was periodically stopped and the microcrack density was measured by examining the sample edges under an optical microscope and counting the cracks. The fatigue experiment is to vary σ_{max} and σ_{min}. For each $\Delta\sigma$, ΔG_m was calculated for low microcrack density and the microcrack density was measured as a function of cycle number. A linear fit to the microcrack density data gives the rate of increase in microcrack density as a function of ΔG_m. Finally, a log-log plot of dD/dN as a function of ΔG_m should be linear with intercept log a and slope n.

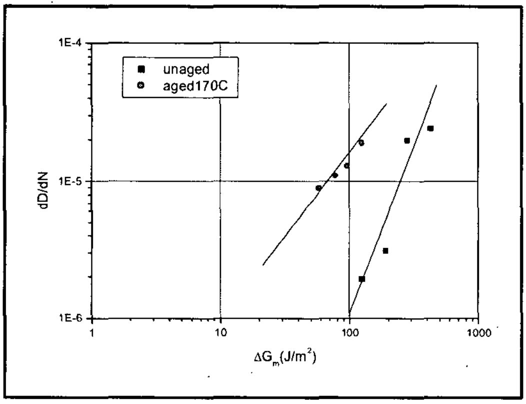

Fig. 6 Microcracking fatigue properties of PSF/AS4 $[0/90_2]_s$ laminates before and after aging.

To assess the effect of aging on the microcracking properties of PSF/AS4 laminates, the microcracking fatigue properties were measured for unaged laminates and for laminates that had been aged for 60 days at 170°C. From the aging data Fig. 3, the static toughness of the aged laminates for 60 days at 170°C should be about 125 J/m^2. The fatigue data showed that aging had a significant effect on the fatigue properties of the laminates. The slopes of aged (n=0.816) and unaged (n=2.04) laminates were different, and there was a significant shift of the aged data to formation of microcracks at lower values of ΔG_m. Therefore as an alternative way to see aging, the fatigue test had a good results.

3. Summary

As a simple model system for aging of thermoplastic matrix composites, $[0/90_2]_s$ PSF/AS4 laminates were studied.

The main concern in this paper was the effect of aging on microcracking toughness. A series of aging experiments at four different temperatures from 0 to 60 days have been expressed as a master plot at a single reference temperature by using time-temperature superposition. At all temperature, there was already a significant decrease after only on day of aging. The laminate toughness decreased with aging and, on a percentage basis, decreased more than the neat resin toughness. In other words, the ratio of the 60 day aged toughness to the unaged toughness was lower in the composite than in the neat resin. The energy release rate analysis has been successful in predicting the experiments of fatigue test using a modified Paris-law approach. The rate of increase in microcrack density per cycle during fatigue loading, dD/dN, could be predicted. The microcracking fatigue properties were measured for unaged laminates and for laminates that had been aged for 60 days at 170°C. The aging had a significant effect on the fatigue properties of the laminates. There was a significant shift of the aged data to formation of microcracks under fatigue loading.

References

1) Highsmith, A. L. and Reifsnider, K. L., "Stiffness Reduction Mechanism in Composite Laminates," *ASTM STP 775,* 1982, pp. 103.
2) ASTM E399-78a.
3) Hashemi, s. and J. G. Williams, *J. Mat. Sci. 19,* 1984, pp. 1261.
4) J. A. Nairn, "The strain energy release rate of composite microcracking: A variational approach," *J. Comp. Mat. 23,* 1989, pp. 1106.
5) S. Liu, and J. A. Nairn, "Fracture mechanics analysis of composite microcracking: Experimental results in fatigue," *Proc. of the Amer. Soc. of Comp., 5th Tech. Conf..,* 1990, pp. 287.
6) Struick L. C. E., *Physical aging in amorphous polymers and other materials,* Elsevier, Amsterdam, 1978.
7) G. Williams, *Fracture Mechanics of Polymer,* Ellis Horwood. Chichester. 1984.