Kevlar-29 섬유강화 복합재료의 기계적 계면 특성 연구

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Studies on Mechanical Interfacial Properties of Kevlar-29 Fibers Reinforced Composites

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KEY WORDS : chemical treatment, mechanical interfacial properties, interlaminar shear strength, critical stress intensity factor, impact properties, ductile index

ABSTRACT

The effects of chemical treatment on Kevlar-29 fibers have been studied in a composite system. The surface characteristics of the Kevlar-29 fibers were characterized by pH, acid-base value, and X-ray photoelectron spectroscopy (XPS). The mechanical interfacial properties of final composites were studied by interlaminar shear strength (ILSS) and critical stress intensity factor (K_{IC}). Also, the impact properties of the composites were investigated in the differentiating studies between initiation and propagation energies, and ductile index (DI) along with maximum force and total energy. It was found that the chemical treatment with phosphoric acid (H_3PO_4) solution significantly affected the degree of adhesion at interfaces between fibers and resin matrix, resulting in improving the mechanical interfacial strength of the composites. This was probably due to the presence of chemical polar groups on Kevlar surfaces, leading to an increment of interfacial binding force in a composite system.

1. INTRODUCTION

Since it was launched in the market in 1972, Kevlar fibers have been adapted to a variety of applications. Especially, they are well suited to high-performance composite applications, because they combine a high specific strength and modulus with a high thermal resistance, chemical inertness, and moreover, they exhibit low electrical conductivity as compared with metallic or carbon fibers. Therefore, a number of research contributions have been made on Kevlar fibers and its composites.[1,2]

However, the Kevlar fibers-reinforced composites show poor interfacial adhesion between the Kevlar fiber and the matrix resin, due to the low surface energy and chemically inert surface of the fiber. In order to improve the interfacial adhesion of the Kevlar fibers-reinforced composites, extensive studied have been performed.[3,4] Among the various methods, chemical treatment is known to be a very efficient method for improving the interfacial adhesion of the Kevlar fibers-reinforced composites.[5]

Kevlar fibers-reinforced composites are mainly used as impact-resistant materials and the most important mechanical properties of the composites is impact resistance, especially energy-absorbing capacity during the impact process. It is therefore very important research subject to obtain the Kevlar fibers-reinforced composites having high impact resistance and strong interfacial adhesion at the same time. Although, some studies have dealt with this subject, the relationship between the interfacial adhesion and the impact resistance are not well understood.[6,7]

In this work, we execute the chemical treatment on

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Kevlar fibers in order to obtain the Kevlar fibers-reinforced epoxy composites showing high impact resistance and strong interfacial adhesion. And, the effects of the chemical treatment on the relationship between the interfacial adhesion and the impact resistance are investigated and the important factors affecting interfacial adhesion and impact properties are also discussed.

2. EXPERIMENTAL

Materials and Sample Preparation

The aramid fibers used in this study were Kevlar-29 (Type 964, density: 1.44 g/cm^3, diameter: 14 μm, manufactured by Du Pont Co.) Epoxy resins were diglycidylether of bisphenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co.), which had an epoxide equivalent weight of 190-210 g.eq^{-1} and a viscosity of about 5000 cps at 25℃. Diamino-diphenylmethane (DDM, purchased from Aldrich Chem. Co.) was selected as a hardener and methylethylketone (MEK) was used to reduce a high viscosity of DGEBA.

Chemical treatments of Kevlar fibers were conducted by the laboratory pilot scale apparatus to improve the degree of adhesion at interfaces between fibers and matrix. The chemical treatment used was 0, 10, 35 wt% phosphoric acid (H_3PO_4) solution.

Unidirectional composite laminates were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepregs with subsequent hot pressing. Laminates made with 30 plies of prepregs were fabricated in a hot-press at 7.4 MPa at 150℃ for 150 min with a vacuum bagging method. The fiber volume fraction of bulk specimens was about 50% (±0.2%) for all composites.

Measurements

The surface pH of Kevlar fibers was measured according to the ASTM D 3838 and the acid and base values on surface were determined by Boehm's titration technique.[8] The X-ray photoelectron spectroscopy (XPS or ESCA) experiment was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg-K α X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} torr.

Interlaminar shear strength (ILSS, the distance between supports divided by the thickness of specimens, L/d=5; cross-head speed, 2.0 mm/min) was conducted by three-point short-beam bending test method to estimate the interfacial adhesion strength of the composites, according to the ASTM D 2344.

An analytical expression for critical stress intensity factor (K_{IC}) may be characterized by single edge notched (SEN) tested in three-point flexure. The three-point bending test having notch was conducted using an Instron Model 1125 mechanical tester according to the ASTM E-399. A span-to-depth ratio of 4:1 and cross-head speed of 1 mm/min were used.

The low-velocity impact test was performed with a drop-weight impact tester (ROSAND Instrumented Falling Weight Impact Tester, Type 4). The maximum drop height was 1 m and a maximum velocity of 1.8 m/sec was reached.

The surface conditions of the Kevlar fibers with anodic oxidation treatment were observed using a scanning electron microscopy (SEM, Model JEOL JSM-840A).

3. RESULTS AND DISCUSSION

Surface properties

Table 1 shows the experimental surface properties of the Kevlar fibers treated by chemical treatment in aqueous phosphoric acid (H_3PO_4) solution. The results of pH show that the surface properties of untreated Kevlar fibers are a slight excess of basic properties. This is probably due to the existence of basic groups on the fiber surface. Both the pH and the acid values of Kevlar fibers treated with H_3PO_4 acidify to those of the untreated fibers, and indicate that the concentration of 10 wt% H_3PO_4 provides an optimum condition to the surface acidity.

It is well known that XPS has been used as a powerful analytical technique to evaluate the surface compositions of the Kevlar fibers.[9] The surface compositions of the fibers for current concentration of H_3PO_4 are summarized in Table 1. As a result, the amounts of surface oxygen are increased with increasing the concentration of H_3PO_4 up to 35 wt%, whereas nitrogen are not largely influenced on the current concentration of H_3PO_4. This result suggests that the oxidation of Kevlar fiber surfaces occurred in phosphoric acid solution with

Table 1. pH, acid value, and chemical compositions of the anodic oxidation treated Kevlar fibers

Concentration of H_3PO_4 (wt%)	pH	Acid value (mequiv./g)	C_{1s}	O_{1s}	N_{1s}	O_{1s}/C_{1s}
Untreated	7.01	15.9	73.3	24.5	1.3	0.334
1	6.97	30.0	72.5	25.1	1.5	0.346
10	6.95	65.7	70.8	32.4	1.1	0.457
35	6.78	72.5	72.6	32.9	1.6	0.453

optimum concentrations. It is then resulted in increasing the surface acidity or hydroxyl and carboxyl functional groups on the chemical treated Kevlar fibers. From the result of Tables 1, the chemical treatment in phosphoric acid solution makes an important role in increasing the acidic properties of Kevlar fibers. Moreover, the increasing of acidic groups on the surface may expect to promote the surface energy of the fibers as well as the interfacial bonding by establishing secondary or van der Waals forces at the interfaces between fibers and matrix.[10]

Consequently, from the results of surface analyses, we can confirm that the surface properties of Kevlar fibers are changed to acidic in nature, resulting in increasing the interfacial binding force with matrix resins.

Mechanical Interfacial Properties

It is generally accepted that the mechanical properties of composites depend strongly on the degree of adhesion at interfaces between fibers and matrix.[11] For the interfacial mechanical properties of composites, ILSS was calculated by the following Eq. (1).

$$ILSS = \frac{3P}{4bd} \tag{1}$$

where, P is the load at moment of break, b the width of the specimen, and d the thickness of the specimen.

Also, the critical stress intensity factor (K_{IC}) is one of the fracture toughness parameters, which describes the state of stress in the vicinity of the tip of a crack as a function of the specimen geometry, the crack geometry and the applied load on the basis of linear elastic fracture mechanics.[12] For the SEN bending specimens, the value of K_{IC} was calculated using the Eq. (2).

$$K_{1C} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \tag{2}$$

where, P is the load obtained from the load-deflection curve, L the span between the supports, Y the geometric factor described in ASTM E 399, and b and d the specimen width and thickness, respectively.

Figs. 1 and 2 show the results for ILSS and K_{IC} of the composites according to the concentration of phosphoric acid solution. As a result, the effect of fiber surface treatment conditions and the resulting fiber-matrix adhesion on mechanical properties of composite show remarkable relationships. Thus, K_{IC} value is to increase with increasing the ILSS value for the degree of adhesion at interfaces. The maximum strength values of ILSS and K_{IC} are obtained at the chemical treatment of 10 wt% phosphoric acid solution. Therefore, we suggest that additional energy is needed to extend the interfacial crack at this condition, which is attributed to the increasing the interfacial adhesion between fiber and matrix.[11]

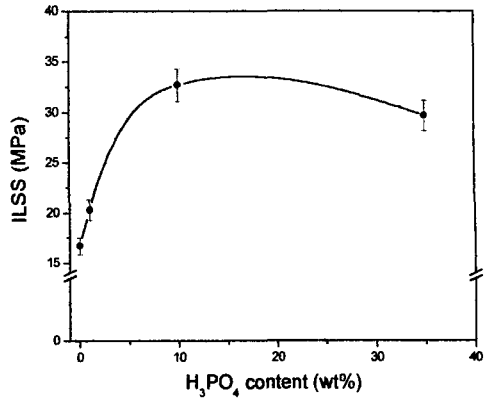

Fig. 1. ILSS for H_3PO_4 treated-Kevlar fibers-reinforced composites as a function of H_3PO_4 content.

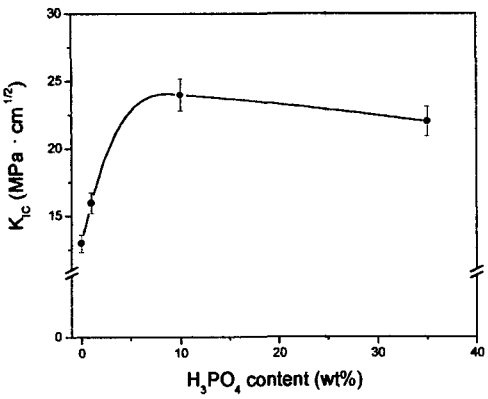

Fig. 2. K_{IC} for H_3PO_4 treated-Kevlar fibers-reinforced composites as a function of H_3PO_4 content.

The impact behavior is major mechanical properties in order to evaluate the degree of toughness of composite materials. When the materials are impacted, transferring load absorbs into the materials and it affects the residual mechanical properties.[13]

Fig. 3 shows a schematic representation of the load history in an impact test. There is a region of fracture initiation followed by a region of fracture propagation. The total impact energy measured during the test, E_t, is the sum of the initiation energy, E_i, and the propagation energy, E_p. If the material behavior is elastic to failure and the stress in the specimen is adequately described by simple beam theory, then the initiation energy in a unidirectional composite reinforced with one type of fiber is given by Eq. (3).[14]

$$E_i = \frac{Lwt}{18} \cdot v_f \cdot \frac{\sigma_f^2}{E_f} \tag{3}$$

where, L is the span length, w the specimen width, t the specimen thickness, v_f the fiber volume fraction, σ_f the fiber stress at failure (tension or compression, which

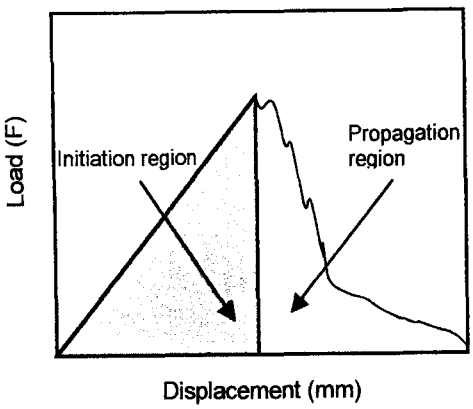

Fig. 3. Schematic presentation of the load history in an impact test.

ever is smaller), and E_f the fiber modulus.

The second portion of the impact energy, E_p, is more complex way since E_p is dependent on material fracture mechanisms that, in turn, are influenced by specimen geometry as well as by material properties. For specimens having a similar geometry, the relative percentage of energy absorbed in fracture initiation and propagation provides an indication of the ductility of materials. The ductility index (*DI*) can be defined as the ratio of propagation energy to initiation energy.[6,15]

$$DI = \frac{E_p}{E_i} \tag{4}$$

Therefore, brittle materials have low E_p and, as a result, low *DI*, as deduced in Eq. (4). The results of the E_p, E_i, and *DI* of the composites are shown in Fig. 4. As a result, the total energy absorbed during the impact test, i.e., impact properties of H_3PO_4 treated Kevlar fibers-reinforced composites are decreased with increasing the

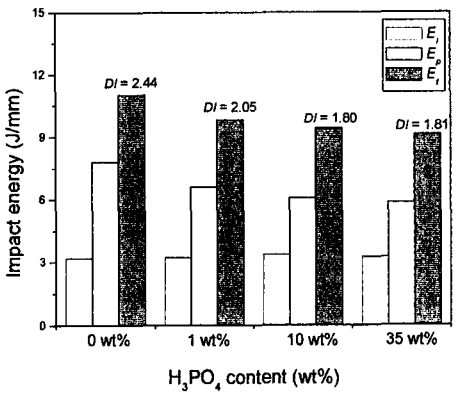

Fig. 4. Initiation (E_i), propagation energies (E_p), and ductile index (*DI*) for H_3PO_4 treated-Kevlar fibers-reinforced composites.

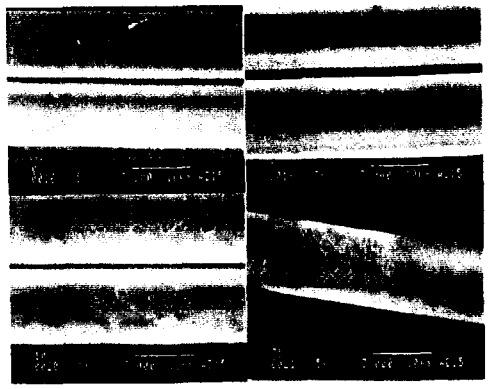

Fig. 5. SEM photographs on surface conditions of H_3PO_4 treated-Kevlar fibers as a function of H_3PO_4 content.

concentration of H_3PO_4. This is probably due to the increase of higher impact stiffness, resulting in increasing the brittle behavior of the composites, owing to the increase of interfacial adhesion.[16]

Fig. 5 shows the SEM photographs of the Kevlar fibers with and without chemical surface treatment with H_3PO_4. It can be seen that the chemical surface treatment does lead to a significant change in surface morphology at the microscopic scale. Also, the photographs of Fig. 5 illustrate how the toughening of the surface occurs in the case of fibers etched in phosphoric acidic solution. This is probably due to the result of the attack of oxygen in Kevlar fibers. Therefore, we can be expected that the chemical treatment with acidic solution may lead to the micro-etch formation on surface of Kevlar fibers.

4. CONCLUSION

In this study, we investigate the effect of chemical treatment on mechanical interfacial and impact properties of Kevlar fibers-reinforced epoxy composites. As a result, the chemical treatment with phosphoric acid (H_3PO_4) solution significantly affects the degree of adhesion at interfaces between fibers and resin matrix, resulting in improving the mechanical interfacial strength. This is probably due to the presence of chemical polar groups on Kevlar surfaces, leading to an increase of interfacial binding force between fibers and matrix in a composite system.

REFERENCES

(1) Yue, C. Y., Sui, G. X., and Looi, H. C. *Compos. Sci. Technol.*, Vol. 60, 2000, pp. 421.
(2) De Lange, P. J., Mader, E., Mai, K., Young, R. J., and Ahmad, I., *Composites*, Vol. 32, 2001, pp. 331.
(3) Sheu, G. S., and Shyu, S. S., *J. Adhesion Sci.*

Technol., Vol. 8, 1994, pp. 1027.
(4) Bennett, J. A., and Young, R. J., *Compos. Sci. Technol.*, Vol. 57, 1997, pp. 945.
(5) Park, S. J., and Park, B. J., *J. Mater. Sci. Lett.*, Vol. 18, 1999, pp. 47.
(6) Park, S. J., Park, W. B., and Lee, J. R., *J. Mater. Sci.*, Vol. 35, 2000, pp. 6151.
(7) Lawcock, G. D., Ye, L., Mai, Y. W., and Sun, C. T., *Compos. Sci. Technol.*, Vol. 57, 1998, pp. 1621.
(8) Park, S. J., and Kim, K. D., *Carbon*, Vol. 39, 2001, pp. 1741.
(9) Rooke, M. A., and Sherwood, P. M. A., *Carbon*, Vol. 33, 1995, pp. 375.
(10) Park, S. J., *Long-range Force Contributions to Surface Dynamics, Interfacial Forces and Field: Theory and Application*, Hsu, J. P. ed., Marcel Dekker, New York, 1999, pp. 385.
(11) Varelidis, P. C., Papakostopoulos, D. G., Pandazis, C. I., and Papaspyrides, C. D., *Composites Part A: Appl. Sci. Manuf.*, Vol. 31, 2000, pp. 549.
(12) Xian, X. J., Poon, Y. M., and Choy, C. L., *J. Thermo. Compos. Mater.*, Vol. 10, 1997, pp. 151.
(13) Richardson, M. O. W., and Wisheart, M. J., *Composites Part A: Appl. Sci. Manuf.*, Vol. 27, 1996, pp. 1123.
(14) Lee, W. L., and Lin, C. F., *Mater. Sci. Eng. A*, Vol. 308, 2001, pp. 124.
(15) Sakai, M., *J. Mater. Res.*, Vol. 14, 1999, pp. 3630.
(16) Park, S. J., and Cho, M. S., *Carbon*, Vol. 38, 2000, pp. 1053.