Effect of Electrochemical Treatment on Pull-Out Properties of 73/27 HBA/HNA Copolyester Fibers in Thermosetting Matrix

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ABSTRACT: The surface of high-strength 73/27 HBA/HNA fibers was electrochemically modified in aqueous sodium hydroxide solution (10 wt %) with the change of the applied current to improve the interfacial shear strength (IFSS) of the fiber in the thermosetting matrix. A sodium component was identified on the surface of the treated fibers by scanning electron microscopy (SEM). The detection of sodium is best interpreted as the existence of a negative charged functional group ($-COO^-Na^+$) on the surface of the treated fibers. A pull-out test was used to measure the IFSS of the HBA/HNA fibers and epoxy/amine cure system. According to the calculating value from Greszczuk's geometrical model, the IFSS increased with the applied current in the range of 50–450 mA. However, no further increase in the IFSS was observed for strong treatment (1500 mA). There was an optimum by applied current to obtain maximum IFSS. The electrochemical treatment of the 73/27 HBA/HNA copolyester fibers was effective in altering their surface chemistry and improving the interfacial adhesion at the moderate treating conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 15–21, 1999

Key words: pull-out properties; interfacial shear strength; electrochemical treatment; TLC polyester; thermosetting matrix

INTRODUCTION

Interest in thermotropic liquid crystalline polymers (TLCPs) has grown in recent years due to their inherently high stiffness and strength, highuse temperatures, excellent chemical resistance, and low and adjustable coefficient of thermal expansion.¹⁻⁶ However, despite extensive research and development, as well as several recent commercialization, TLCPs currently have relatively few established commercial markets. The materials tend to be expensive, primarily due to high monomer costs. Blending TLCPs with other, less

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expensive, thermoplastics offers the possibility for exploiting many of their desirable characteristics, but at a reduced material cost. So, blending of TLCPs, in particular with low-cost thermoplastics, is a useful way to upgrade the properties of thermoplastics, and can offer both price and property advantages. Besides their good properties, one major problem that limits commercial interest of TLCP blend with thermoplastics is the poor impact strength, which is mainly due to the lack of interaction and of interfacial adhesion between the blend components.

To enhance the interaction and adhesion between the blend components in incompatible blend systems, there were several studies on the interface science and the modification of materials.⁷⁻¹⁰ Of these studies, work in interface science

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Figure 1 Schematic representation of the continuous anodic oxidation process: 1, fiber tow; 2, treatment bath; 3, washing bath; 4, water inlet; 5, water outlet; 6, hot air drying; 7, motor.

has concentrated on the alteration of the material surface characteristics or on the study of the effect of specific fiber treatments on the composite properties. Fiber surface modifications that have been examined include the physical roughening and chemical modification of the fiber surface.⁸ The chemical treatments have been preferred, because they afford improvement without the potential for degradation of the fiber properties that are inherent in surface roughening.

Electrochemical techniques have been developed and are conventionally used in the treatment of fiber surfaces such as carbon fiber, glass fiber, and LCP fiber.^{7,11–13} The interfacial adhesion of the blend system largely depends on the physical or long-range force between the blend components, and it affects the final mechanical properties of the composites.^{14,15} Pull-out testing has long been considered a desirable way of investigating basic characteristics of the single-fiber/matrix interface or having a rapid assessment of this interface quality with new surface treatments.^{16,17} Therefore, the results for pull-out tests in a single fiber/thermosetting matrix are able to give useful information for the interfacial properties in TLCP blend systems.

The work described here is a systematic study of the relative influence of surface modifications of the 73/27 HBA/HNA copolyester fiber on the properties of epoxy matrix composites using a pull-out test.

EXPERIMENTAL

Materials and Sample Preparation

The thermotropic liquid crystalline polymer was Vectra A 900 produced by Hoechst Celanese. This is totally aromatic copolyester-type LCP based on 6-hydroxy naphtoic acid (HNA, 27 mol %) and 4-hydroxy benzoic acid (HBA, 73 mol %). It has a melting temperature of 282°C, and density of 1.40 $g \cdot cm^{-1}$.

The epoxy resin used in this study was a diglycidylether of bisphenol A (DGEBA, YD 114 supplied from Kukdo Chem. Co. of Korea) and a triethylene tetramine hardener (13 phr on the basis of epoxy adduct). Epoxide equivalent weight of the YD 114 was 190–210 g \cdot Eq⁻¹. and the density was 1.14 g \cdot cm⁻³ at 25°C.

Fiber Preparation

The fibers were prepared by spinning the polymer through a capillary rheometer (Instron Model 3211, L/D = 40, D = 0.1235 cm) at 300°C. The apparent shear rate was fixed at 0.6 cm \cdot min⁻¹. The diameter of fiber was 0.25 mm.

Electrochemical Treatment of 73/27 HBA/HNA Copolyester Fibers

The surface modifications examined were applied using an electrochemical technique in 10 wt % aqueous sodium hydroxide solution. The continuous process was used in this study to treat 73/27 HBA/HNA fibers. Electrochemical treatments were conducted in a vessel containing an aqueous sodium solution with a 0.475 m-length treatment chamber, as shown in Figure 1. The take-up speed was 30 cm \cdot min⁻¹. The applied currents were 50, 150, 450, and 1500 mA.

Sample Preparation for the Pull-Out Test

The specimens were cured at 50°C for 4 h, 100°C for 4 h, and 120°C for 4 h. The cured specimens were carefully polished on both sides to aid in the observation of the embedded length using a polarized optical microscope, as seen in Figure 2.



Figure 2 Schematic representation of a pull-out test.



Figure 3 Photos of the fiber sample embedded in the matrix.

Optical Measurement

The observation of the embedded length of the fibers was carried out by using a crosspolarized light microscope (Carl Zeiss Laborrux 12 Pols) with an automatic camera. A photo with an HBA/ HNA fiber embedded in the matrix is given in Figure 3.

Scanning Electron Microscopy (SEM)

The morphology of the fibers was analyzed by using SEM (SEM 515, Philips Co.). Measured surfaces were coated with gold for the microscopy.

Pull-Out Test

A small single fiber is embedded in a resin and the debonding load for the pull-out of the fiber from the resin is measured and calculated for the interfacial shear strength (IFSS, τ) using the following equation:

$$\tau = \frac{F}{2\pi \cdot r_f \cdot L} \tag{1}$$

where *F* is the debonding load, r_f the fiber radius, and *L* the embedded length.

This technique has been successfully studied in carbon and boron fibers in an epoxy resin.^{17,18} According to Desarmot's proposition¹⁷ on the basis of Greszczuk's geometrical model,¹⁸ IFSS measured from the pull-out tests may allow for the determination of the maximum interfacial shear strength, τ_m , derived from the maximum debonding load, F_m , at L = 0, using the following equation:

$$\begin{aligned} \pi_i &= \left(\frac{F_i}{2\pi \cdot r_f}\right) \times \alpha \\ &\times \left[\coth(\alpha \cdot L) \times \cosh(\alpha \cdot L) - \sinh(\alpha \cdot L)\right] \end{aligned} (2)$$

where

$$lpha = \left(rac{2G_m}{b_i \cdot r_f \cdot E_f}
ight)^{1/2} ext{ in } b_i = r_f \ imes \ln\!\left(rac{R}{2r_f}
ight)$$

with b_i is defined by Greszczuk, as the effective thickness of the interface, and R is the radius of the matrix involved by the shear stress according to Cox.¹⁹ The parameters E_f , G_m , and r_f are the Young's modulus of the fiber, the shear modulus of the matrix in Greszczuk experiments, and the fiber radius. Therefore, α is a constant, depending on the nature of fiber and matrix used. These values obtained in our experimental conditions are noted in Table I.

RESULTS AND DISCUSSION

Fiber Surface Treatments

EDS X-ray spectra was used to measure the qualitative results of inorganic materials of the samples before and after electrochemical treatment with 450 mA in an NaOH aqueous solution. Sodium ion was observed only on the treated samples, as shown in Figure 4, and it is likely an indication of the sodium was chemically bonded on the surface of 73/27 HBA/HNA copolyester fibers. Chen and McCarthy²⁰ reported that after treatment of polyethylene terephthalate (PET) in a 1*M* NaOH aqueous solution for 16 min at 60°C, the contact angle reached a minimum value. The lower contact angle at higher pH values indicates the presence of carbonyl ester functional groups that ionizes to —COO⁻Na⁺ groups. For the

Table IAverage Parameters Used in ThisExperimental Condition

Items	Values
$\begin{array}{l} G_m \; ({\rm GPa}) \\ E_f \; \; ({\rm GPa}) \\ r_f \; \; ({\rm mm}) \\ R \; \; ({\rm mm}) \\ b_i \; \; ({\rm mm}) \\ \alpha \; \; ({\rm mm}^{-1}) \end{array}$	$1.3 \\ 10.35 \\ 0.275 \\ 4.25 \\ 0.562 \\ 1.275$



Figure 4 EDS X-ray spectra of the samples before and after anodic treatments.

treated PET, peel tests indicated that the multilayer assemblies show good mechanical integrity; no failure was observed in the multilayers. The surface of the HBA/HNA copolyester fibers contains carbonyl ester functional groups, which can ionize as a negative charge at sufficiently high pH. Therefore, the detection of sodium ion for the treated fiber suggests that the carbonyl functional groups on the fiber surface ionized as a negative charge under high pH circumstance.

Elemental analysis results normalized to 100% C, O, and H are given in Table II. Results show that the electrochemical treatment of 73/27 HBA/ HNA fibers results in the increase of oxygen content and the decrease of hydrogen content even though the change is not large. The decrease of hydrogen content can be interpreted as additional evidence of the formation of a negative charge $(-COO^-Na^+)$ in carbonyl groups on the fiber surface at high pH. Park et al.¹³ and Ehrburger and Donnet²¹ proposed the following mechanism for the formation of a negative charge on the carbon fiber surfaces.

$$C_x + H_2O + e^- \rightarrow C_x - H + OH^-$$

$$C_xOOH + OH^- \rightarrow C_xOO^- + H_2O$$

 $C_xOO^- + Na^+ \rightarrow C_xOO^-Na^+$

For the HBA/HNA copolyester, the formation of a negative charge might be explained by a similar mechanism with that obtained from carbon fiber surfaces.

Single-Fiber Pull-Out Test

It is well known that the stress transfer from the matrix polymer to the reinforcing fiber depends on the interfacial adhesion between the reinforcing fibers and the matrix polymer, and it affects the mechanical properties of composite materials. One of the important factors influenced on the interfacial adhesion is the physical bond (e.g., van der Waals force and hydrogen bond) between reinforcing fibers and the matrix polymer. The physical bond can usually be controlled by the surface modification of reinforcing fibers. To investigate the effect of surface modification by an anodic treatment of 73/27 HBA/HNA fibers on the interfacial adhesion, the pull-out test on the single fiber is used to measure IFSS of the HBA/ HNA fibers and epoxy/amine system.

Figure 5 shows the debonding load of the samples after curing as a function of the applied current. The increase in the applied current results in the increase of the debonding load of 73/27HBA/HNA fibers and the epoxy cure system up to 450 mA. However, a further increase of the applied current (1500 mA) took place in the decrease in debonding load. In a reinforcing fiber and epoxy composite system, the debonding load depends on several factors such as physical bonding between reinforcing fibers and epoxy, fiber roughness, and the degradation of the reinforced fiber by chemical treatment. The increase of the applied current increases the amount of negative functional groups, which can easily react with the functional group of the epoxy resin, and it can

Table II E	Elemental	Analysis	Data d	of 73/27	HBA/HNA	Fibers
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Element	Current (mA)				
	0	50	150	450	1500
C (wt %)	70.96	70.85	70.52	70.51	70.01
H (wt %)	3.38	3.39	3.33	3.29	3.31
O (wt %)	25.66	25.76	26.15	26.20	26.68



Figure 5 Debonding load of an HBA/HNA fiber in an epoxy cure system.

simultaneously degrade the HBA/HNA copolyester by hydrolyzing the carbonyl groups.

Hydrolytic degradation of the fully aromatic copolyester was investigated to reduce the ecolog-

ical problems related to plastic recycling by Jin et al.²² They reported that a strong hydrolysis condition, such as a higher pH and temperature, accelerates the hydrolysis degradation of the aromatic copolyester. The decrease in the debonding load of the sample after treating at 1500 mA can be explained by the fact that the electrochemical treatment at high current results in the hydrolysis degradation of the HBA/HNA fiber in an NaOH aqueous solution. That is, the hydrolysis degradation of the HBA/HNA copolyester fibers can influence their interfacial adhesion properties. Figure 6 shows the surface morphology of the HBA/HNA fibers. For the sample treated at 1500 mA, SEM reveals that the electrochemical treatment resulted in some mechanical cracks due to the hydrolysis degradation on fiber surfaces.

To determine the IFSS based on the geometrical model, the debonding load data and the average parameters, as listed in Table II, were used to calculate the IFSS according to eq. (2). Figure 7 shows the dependence of IFSS on the imbedded length of fiber in a matrix, and the maximum



Fiber-untreated

Fiber-treated by 150mA





Amplification of A





 $\label{eq:Figure 7} \begin{array}{l} \mbox{Figure 7} & \mbox{Dependence of IFSS on the embedded length of the fiber in an epoxy cure} \\ \mbox{system.} \end{array}$

Current (mA)	Maximum IFSS (MPa)		
0	600		
50	820		
150	870		
450	1530		
1500	1400		

Table IIIMaximum IFSS of 73/27 HBA/HNAFibers and Epoxy/Amine Cure System

IFSS data derived from Figure 7 are summarized in Table III. The IFSS increased with the applied current in the range of 50–450 mA. However, no significant change in the IFSS is observed for the strong treatment (1500 mA) in the system studied. These results indicate the existence of optimum current for improving interfacial adhesion for HBA/HNA copolyester and epoxy/amine cure systems, and provide the possibility of enhancing the lack of interaction and of interfacial adhesion between the blend component in the TLCP blend with thermoplastics.

CONCLUSIONS

A pull-out test on the single fiber of the 73/27 HBA/HNA copolyester treated by an electrochemical method conclusively shows that the improvement of IFSS occurred. IFSS of the sample treated at 450 mA showed an optimum value, and increased above two times as high as that of the sample untreated. The increase in IFSS could be explained by the improvement of a physical bond between 73/27 HBA/HNA fibers, which introduced the negative functional groups (—COO⁻Na⁺) and epoxy resin. However, there was no significant change in the IFSS for the sample treated over 450 mA. This result could be interpreted as the effect of hydrolysis degradation of 73/27 HBA/

HNA copolyester fibers on the interfacial adhesion properties.

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