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Surface characterization and adhesion of carbon fibers to epoxy and polycarbonate

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Abstract

Surface characterization of the specially prepared Toray high-strength sample carbon fiber was undertaken with a view to evaluate and understand adhesion to polymer matrices. Surface chemical analysis by XPS, surface free energy determination from the dynamic contact angle, and microstructural characterization by STM was conducted and compared with before and after surface treatment of this fiber and with other PAN-based high-strength carbon fibers as well. It was found that the surface of Toray sample carbon fibers has higher O/C and N/C ratios than those of other PAN-based carbon fibers, such as the IM-7 and AS-4. The fiber surface free energy appears slightly lower than those of the IM7 and AS4. Adhesion of Toray Lab-carbon fibers measured by the single fiber fragmentation was determined to be in a similar level to AS-4 and IM-7 in various epoxy-amine thermoset systems and polycarbonate thermoplastic matrix.

Keywords: Carbon fibers; Carbon fiber surface characterization; Single fiber fragmentation test; Adhesion

1. Introduction

Carbon fibers have been widely used for reinforcement in structural composite materials not only due to their high specific strength and modulus, but also their decreasing cost [1]. The carbon fiber mechanical properties have been responsible for their use in demanding severe service environments. Accompanying their performance, a more comprehensive and intensive understanding of carbon fiber surface and adhesion is needed to utilize their superior properties.

In this research, we have conducted surface analysis of Toray Lab-sample carbon fibers in order to better understand adhesion to thermoset and thermoplastic matrix composites.

2. Experimental

2.1. Materials

2.1.1. Carbon fibers

The carbon fiber for this study was supplied by Toray Industries Inc. with non-surface treated (UT) and surface treated (ST). The fiber surface treatment applied is the electrochemical oxidation process, but a detailed description cannot be mentioned in this paper because this is a proprietary of the manufacturer. The fiber has similar properties to the commercial Torayca T-700G® carbon fiber, and its typical properties are a tensile strength of 4.9 GPa, modulus of 240 GPa and an elongation of 2.0%.

2.1.2. Matrices

Two different kinds of epoxy resins, diglycidyl ether of Bisphenol A-based EPON 828® and novolac EPON 160® (Shell Chemical Co.), were used for thermoset matrix composites. Three different amine curing agents,

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Table 1
Composition and processing conditions of epoxy matrix single fiber fragmentation coupon

Matrix	Curing agent (phr)[a]	Curing Cycle
EPON 828	m-PDA (14.5)	@75 °C(2 h) → @125 °C(2 h)
	T-403 (45.0)	@85 °C(2 h) → @150 °C(2 h)
	D-230 (35.0)	@80 °C(2 h) → @125 °C(3 h)
EPON 160	m-PDA (16.5)	@75 °C(2 h) → @125 °C(2 h)
	D-230 (37.5)	@80 °C(2 h) → @125 °C(3 h)

[a] Stoichiometric amount of amine curing agents.

m-PDA (Aldrich Chemical), Jeffamine D-230® and Jeffamine T-403® (Huntsman Corporation) with stochiometric amounts for epoxy matrix were employed. Table 1 shows the matrix combination of epoxy and curing agent with different curing cycles.

In order to evaluate adhesion of the fiber to thermoplastic matrix and investigate the effects of the molecular weight on the adhesion, two different molecular weight types of Bisphenol A-based pure polycarbonate (PC), Lexan 8040® (GE Plastics, MW 24,894) and Polysciences polycarbonate (MW 32,000–36,000) were used. Also, the different consolidation time and temperatures, which were decided based upon the previous work done with similar composites system in our composites center [2], were applied to investigate the effects of processing parameters.

2.2. *Fiber surface analysis*

The fiber surface chemistry was determined by X-ray photoelectron spectroscopy (Perkin-Elmer Physical Electronics PHI5400 spectrometer) with a monochromatic Mg X-ray source operated at 30 kV and 300 W with an emission current of 20 mA.

Advancing contact angles between test liquids (water, formamide and diiodomethane) and single fibers were measured using a Dynamic Contact Analyzer (DCA 322, Cahn), so-called micro-Wilhelmy technique. Surface tensions of the testing liquids were not measured for this study, and used the reference values [3]. All of the contact angles were obtained at an immersion speed of 20 μm/s, by removing the initial 1.0 mm fiber immersion data, which can have fiber end effects and not true surface property. The fiber diameters used for the contact angle computation were determined with non-polar hexane with at least 20 samples, and measured average fiber diameters were 6.83 μm for UT and 7.04 μm for ST fiber. Owens–Wendt equation obtained from the contact angles, which is a linear equation in the form of $y = mx + b$ with the slope "m" and intercept "b" given by the square root of the polar and dispersive components, was used for the free energy computation. The Owens–Wendt equation is described in detail in the Refs. [4–6].

The topography of the fibers was evaluated by a scanning tunneling microscope (Nanoscope III, Digital Instruments) with a type E piezo scan head and a commercial Pt–Ir tip (Nanotips®). To measure the topology of the fibers in the height data mode, scans were conducted keeping a constant tunneling current. Bias voltages and setpoint currents were varied with a range of 50–150 mV and 0.7–8.0 nA, respectively. Five images with magnifications of 300 nm $(X) \times 300$ nm $(Y) \times 20$ nm (Z) for the UT and ST fiber were collected to compute the surface roughness parameter R_a and the surface area of fibers.

2.3. *Adhesion strength*

To quantify the level of adhesion of the fibers to thermoset and thermoplastic matrix, the single fiber fragmentation was employed. Epoxy matrix sample preparation and the single fiber fragmentation procedure are described well elsewhere [7]. The interpretation of the test results was based on the Kelly-Tyson approach $\tau = \sigma_f d/2l_c$ [8] (τ*: interfacial shear strength,* σ_f*: fiber tensile strength at the critical fiber fragmentation length, d: fiber diameter,* l_c*: critical fiber fragmentation length*). The single fiber fragmentation test process is shown in Fig. 1 and tensile test coupon in Fig. 2.

Thermoplastic matrix specimens were fabricated by melt-processing thin sheets of PC matrix with carbon fibers sandwiched in the middle. Pre-form sheets with one-half of the thickness of the final specimens were first produced by hot-pressing dried PC granules between Al foil sheets with the thickness controlled by Al mold thickness. Single separated carbon fibers were then draped across the matrix sheet and held in place using a high-temperature adhesive tape. Another matrix sheet was then carefully placed over this assembly followed by a thin Al sheet. Melt-processing consolidation was conducted by a hot-pressing with predetermined temperatures, time and pressure, after drying the assembly at 125 °C for 60 min to remove moisture. Cooling was accomplished by a standard platen water cooling system at approximately 1 °C/min. The final dogbone-shaped specimens with straight carbon fiber were obtained using a die-punch. A more detailed procedure is given in Ref. [2].

3. Results

3.1. *Surface chemical analysis*

XPS atomic ratios of the carbon fibers are shown in Table 2. As shown in the table, O/C and N/C ratios increased by 120% and 190%, respectively, after surface treatment. These O/C and N/C atomic ratios in the ST

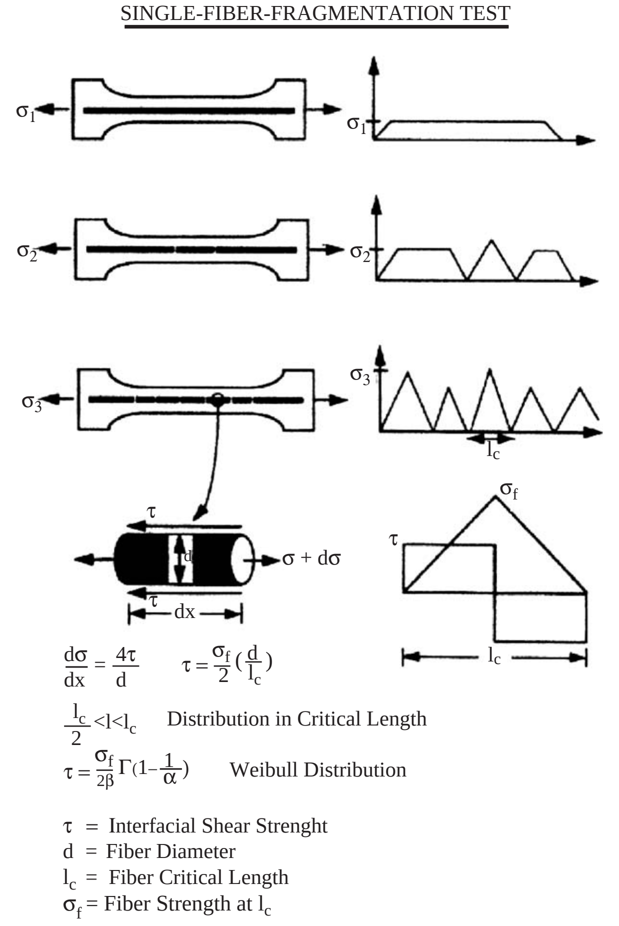

Fig. 1. Schematic representation of the single fiber fragmentation process.

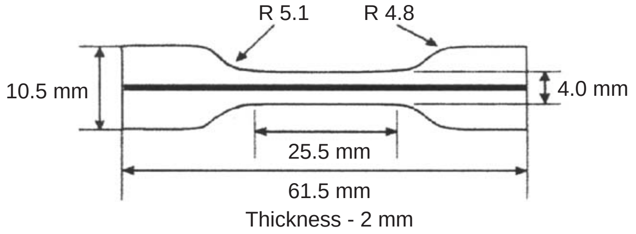

Fig. 2. Dimensional details of the single fiber fragmentation coupon.

carbon fiber seem to be relatively higher than those of IM-7®, PANEX-33® [9] and AS-4® carbon fiber [10,11], which have been used frequently as model fibers for adhesion with polymer matrix. In order to investigate the change of carbon fiber surface chemistry with fiber aging in the ambient environment, the fiber surface chemistry were observed as shown in Table 2. As the fibers were aged in the ambient condition, a marginal oxygen concentration increase occurred in both carbon fibers. However, nitrogen concentration was not changed.

3.2. Surface free energy

The advanced dynamic contact angle and fiber surface free energy obtained from Owens–Wendt plot based on the contact angle are shown in Table 3. The standard errors associated by determining the contact angle are also given in Table 3. As shown in Table 3, the polar component (γ^p) shows increase of about 200% after the fiber surface treatment. This is assumed to be due to the increases in surface oxygen and nitrogen as shown in Table 2, which would result from introduction of carboxyl, hydroxyl and amine groups, etc. during the surface treatment. On the other hand, it is clear from Table 3 that the dispersive component (γ^d) of the free energy does not vary significantly between untreated and treated samples. From the data in Tables 2 and 4, it is assumed that the dispersive component of carbon fiber surface free energy is not affected by the increases of chemical functional groups and specific surface area of fiber, which are provided by the fiber surface treatment.

3.3. Fiber topography

Fig. 3 shows STM images obtained at 300 × 300 nm scanning scale with 20 nm vertical range value for the UT and ST fibers. Both of the fibers have rippled surfaces consisting of oval-shaped grains which form ribbon-like structure extending along the fiber axis in twisting each other. The oval-shaped grains in the ST

Table 2
Surface chemical analysis results of the Toray Lab-carbon fibers

Fibers	Date	C	O	N	Others	O/C	N/C
UT carbon fiber	12/17/01	86.5	9.0	2.4	2.1	.104	.028
	03/25/02	87.2	7.6	2.5	2.7	.087	.029
	09/09/02	88.4	6.7	2.6	2.3	.076	.030
ST carbon fiber	12/17/01	75.7	17.4	6.2	0.7	.230	.082
	03/25/02	76.3	15.6	7.4	0.7	.204	.097
	09/09/02	77.3	14.9	7.0	0.8	.193	.091
IM-7 (ST) [9]	—	84.4	12.2	3.2	0.2	.145	.038
AS-4 [10,11]	—	86.9–88.0	7.2–10.3	2.8–4.2	0.6	.082–.119	.032–.048

Table 3
Contact angles and surface free energies (mJ/m^2) of the Toray Lab-carbon fibers determined from the advanced dynamic contact angle measurement

Fibers	Contact angle			Surface free energy		
	H_2O	CH_2I_2	$HCONH_2$	Dispersive	Polar	Total
UT carbon fiber	80 (±0.9)	42 (±1.2)	58 (±1.2)	36.3	3.9	40.2
ST carbon fiber	61 (±1.9)	38 (±1.0)	38 (±1.8)	38.9	11.7	50.6

Table 4
Average surface roughness and surface area obtained from STM images

Fiber	R_a (nm)	Area (nm^2) (300 × 300 nm area)
UT carbon fiber	1.2	100,734
ST carbon fiber	1.8	140,501

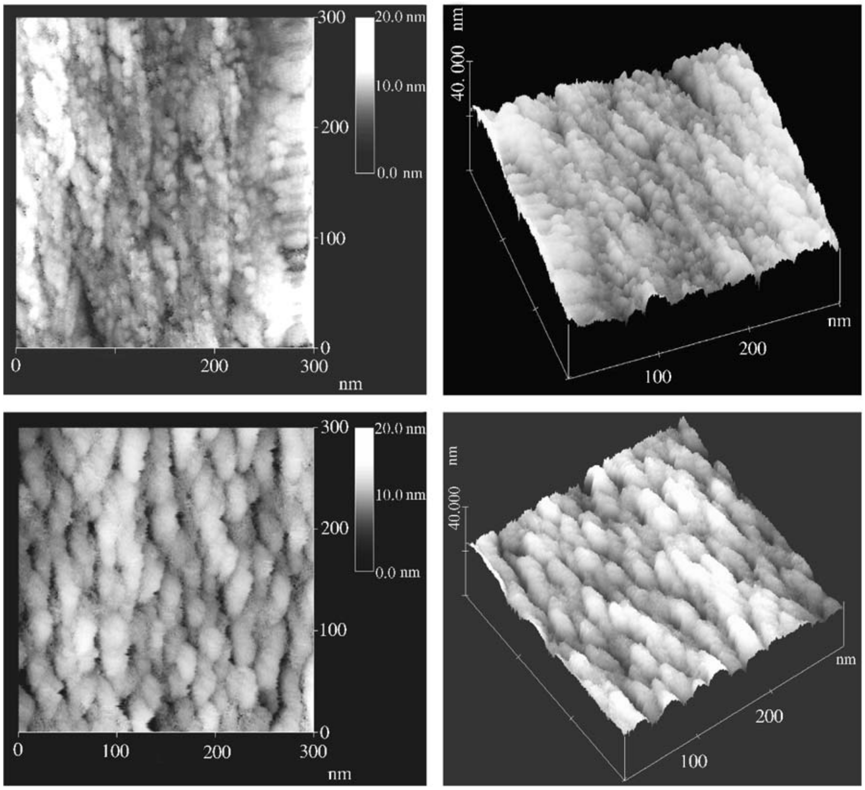

Fig. 3. STM top view (left) and tilted view (right) image of the UT and ST Toray Lab-carbon fibers.

fiber were measured by STM with an average size of about 20 nm in the longer and 11 nm in the shorter direction. After surface treatment, the fiber surface structure was seen to have rougher and clearer grain structures, which results in about 1.5 and 1.4 times increases of the surface roughness and specific surface area, respectively, as shown in Table 4.

3.4. *Adhesion: epoxy matrix composites*

Carbon fiber tensile strengths used for the computation of the IFSS using the Kelly-Tyson equation were determined from the extrapolation of the fiber tensile strength by the single fiber tensile test, as shown in Fig. 4. The test was conducted by Toray Industries Inc. in accordance with ASTM C 1557-03 [12] with the gage lengths of 5, 10, 25, and 50 mm at a cross-head speed of 0.5 mm/min.

IFSS of Toray Lab-sample carbon fibers to epoxy matrix are shown in Fig. 5. In the UT fiber, the IFSS are in the range of 35–42 MPa with a marginal change depending on the epoxy-amine matrix systems. On the other hand, the ST fiber demonstrates 44–62 MPa which gives an increase of 18–48% after surface treatment.

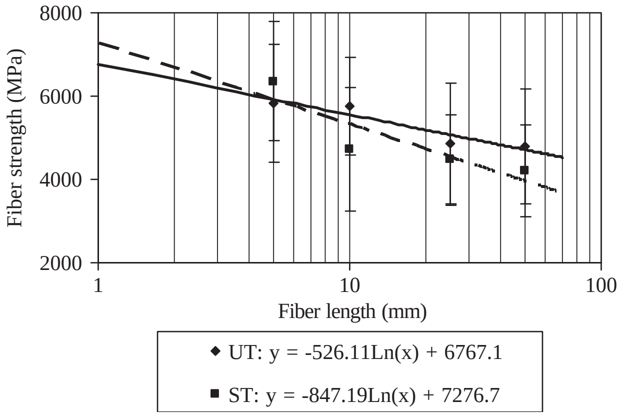

Fig. 4. Tensile strength of the Toray Lab-carbon fibers with different gage lengths.

Among the epoxy-amine curing systems, EPON 160/m-PDA matrix seems to have higher level of adhesion to the ST fiber than any other epoxy systems. One of the reasons for the adhesion increment can be ascribed to the matrix shear modulus increase [13–15]. In this experiment, matrix flexural modulus measurements were conducted with the dynamic mechanical analyzer (DMA 2980, TA Instruments), and the adhesion increase was seen to be proportional to the matrix modulus with the relation of $(E_{\text{fiber}}/E_{\text{matrix}})^{0.7}$ and $(E_{\text{fiber}}/E_{\text{matrix}})^{0.5}$ for the UT and ST fibers, respectively. In comparing with Hercules AS-4 and IM-6 carbon fibers in EPON 828/m-PDA matrix system [16,17], Toray ST fiber was determined to have a similar level of adhesion as shown in Table 5. Contrary to the ST fiber, the Toray UT fiber demonstrated higher adhesion than those of AU-4 and IM-6 UT fiber.

3.5. Adhesion: polycarbonate matrix composites

The IFSS of the carbon fibers to PC matrix is shown in Figs. 6 and 7. As shown, the consolidation temperature is found to have a significant influence on the adhesion, especially more significant in lower molecular weight PC (Lexan 8040). The adhesion was increased by 30–36% for the Lexan 8040, and 13–15% for the Polysciences PC, respectively, as the consolidation temperature increases from 230 to 310 °C. T_g values of PC by differential scanning calorimetry (DSC 2950, TA Instruments) were not to change significantly with processing temperatures and were 152 °C. This indicates that there is no crystallization in PC matrix. And if there would be any crystallization during the processing, which is known to increase the adhesion, it would be small and only confined to the interface as found by Kardos et al. [18–20]. As the consolidation time was increased at 230 °C, IFSS was increased and approaches 55 MPa after 50 min, as shown in Fig. 8. From these

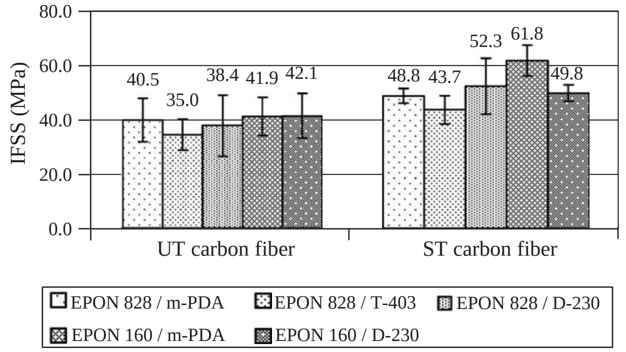

Fig. 5. IFSS of the Toray Lab-carbon fibers in epoxy matrix by the single fiber fragmentation test.

Table 5
Comparison of IFSS, l_c/d and fiber tensile strength at l_c of the Toray Lab-carbon fibers with AS-4 and IM-6 carbon fibers in EPON 828/m-PDA matrix

Carbon fibers		IFSS (MPa)	l_c/d	Tensile strength @ l_c/d (MPa)
Toray	UT	40.5	90.3	7002
	ST	48.7	79.6	7753
AS-4 [16]	UT	28.8	99.5	5723
	ST	50.9	57.2	5826
IM-6 [17]	UT	29.2	132.3	7700
	ST	53.9	77.2	8300

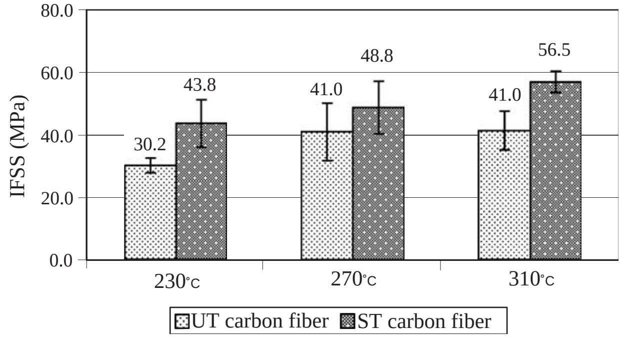

Fig. 6. IFSS of the Toray Lab-carbon fibers in Lexan 8040 polycarbonate (consolidation at 0.083 MPa for 20 min).

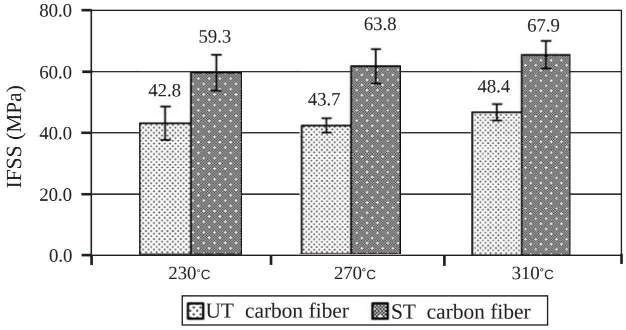

Fig. 7. IFSS of the Toray Lab-carbon fibers in Polysciences polycarbonate (consolidation at 0.083 MPa for 20 min).

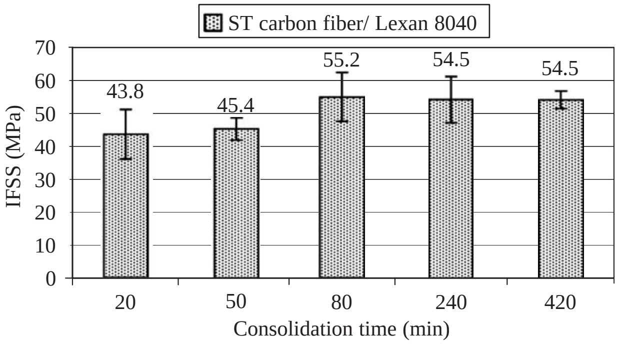

Fig. 8. IFSS variation with the consolidation time of the Toray ST Lab-carbon fiber prepared at 230 °C and 0.083 MPa.

results, it can be concluded that the mechanism of IFSS improvement in PC matrix is the enhanced adsorption of matrix polymer at higher processing temperature and time. Also, it is seen that the adhesion increase was achieved by 7–42% in the UT fiber and 20–35% in the ST fiber, respectively, with increasing molecular weight of PC. This can be explained by more contact points between polymer molecules and the fiber surface in higher molecular weight PC. And these contact points increase polar and hydrogen bond interactions by carbonyl groups which exist in bisphenol-A PC, result in adhesion improvement [2]. Toray ST fiber was seen to have a similar level of IFSS to AS-4 carbon fiber [17].

4. Conclusions

Surface characterization and adhesion performance of Toray Lab-carbon fibers to polymer matrices have been conducted, and the following conclusions are made.

The carbon fibers studied have higher O/C and N/C ratios compared to those of other high-strength PAN-based carbon fibers, and the surface treatment increased about 200% of the polar surface free energy.

The topography of the carbon fibers determined by STM appears to consist of ribbon-like structures extending along the fiber axis in twisting each other, similar to the surface microstructures of other PAN-based carbon fibers.

IFSS of Toray Lab-carbon fibers to epoxy matrix is in the range of 35–42 and 44–62 MPa for UT and ST fibers by the single fiber fragmentation test.

IFSS of Toray ST Lab-carbon fibers to polycarbonate is at a similar level of AS-4 fibers, and increased as processing temperatures, time and molecular weight of PC are increased.

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