Flexible Towpreg Preparing Carbon Fiber-Reinforced Phenolic Resin Composites

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ABSTRACT: The current article describes a novel approach to produce the carbon fiber/phenolic matrix composites. The composites are focused on the carbon fibers and interfacial behavior. The washed, oxidized, and flexible towpreg-treated carbon fiber is investigated by tensile strength. To relate the interfacial behavior with the characteristics of the components, the surface free energy of the carbon fibers is carried out by capillarity. Thereafter, the tensile strength of carbon fiber strands, the interlaminar shear strength, and the flexure strength are measured. The results show that appropriate treatments could effectively improve the mechanical properties. Interfacial adhesion between the carbon fibers with phenolic resins being fractured under deformation and the dispersed resins on the flexible towpreg carbon fiber are, respectively, studied by scanning electron microscopy and optical microscope. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 577–583, 2008

Key words: matrix; coatings; surfaces; fibers; reinforcement

INTRODUCTION

Carbon fiber reinforced composites have become well established as structural materials and are valued particularly in aerospace applications because of their excellent thermal and electric properties, also have similar process to conventional polymer based composites.[1–4] In the open literature, much work is reported on the development of carbon/carbon composites with different matrix precursors. Phenolic resins are used as matrix precursors in carbon/carbon composites because they impregnate the fiber tows with ease and have a high carbon yield. When phenolic resins are heated, low molecular weight compounds, such as unreacted phenol, short-chain polymers, and water evolve generating condensation polymerization in the matrix, lead to shrinkage, pores, and weight loss.

On the other side, for taking advantage of the excellent mechanical properties of carbon fibers in composite materials an optimal interfacial adhesion between fibers with matrix is required.[5] During the process of the transfer from one fiber to another going through the matrix, the interface plays a main role in the overall mechanical performance of carbon fiber reinforced materials.[6] The interfacial behavior in a great extent depends on the surface of carbon fiber.[7] As the carbon fiber is extremely inert, usually untreated carbon fiber composites exhibit a weak bonding between fiber and matrix, giving as result composites with relatively low interlaminar shear strength. This problem has been overcome to a large extent by the development of fiber surface treatments,[8] e.g., oxidative etching, polymer coating, or plasma activation, which improve the bond strength between the carbon fiber and the polymeric matrix.

A flexible towpreg[9] consists essentially of the carbon fiber tows dispersed with the airflow spreader and fiber bundles which is coated with a discontinuous sheath of a matrix resin. The matrix resin thermally fuses to the bundle, which only the fibers on the exterior of the bundle disperse in a discontinuous manner, while fibers in the interior of the bundle remain substantially free of the matrix resin.

Preliminary process conditioning such as solvent and heating may either limit the materials which can be utilized, or adversely affect the desired properties of the ultimate composite application. Dry resin powders impregnation is likewise subject to difficulties.[10] Powdered resins and fibers may be mixed with a blender. However, in such measures the fibers tend to remain in discrete bundles resisting powdered resin penetration, and it results in a nonhomogenous mixture. Molding compositions prepared by such techniques are necessarily produced by batching operations rather than continuous production techniques. Application of dry resin to continuous fiber tows generally requires heating to assure coherence between the fiber and resin. However, heating may not be desirable or practical. Such techniques may not result in a uniform fiber–resin distribution.

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This method produces a very flexible multiply towpreg being suitable for weaving, braiding, and so on. As described above, although a number of different matrix precursors and interfacial adhesion have been reported, the effects of a flexible towpreg on preparation carbon fiber reinforced composites haven't been investigated in details.

The purpose of the present work is to analyze the influence of carbon fiber with different treatments on the interfacial behavior of the composites from two aspects: one is carbon fiber surface treatments and the other is the flexible towpreg process. The flexure strength by three point flexure measurements and the interlaminar shear strength (ILSS) by short beam-shear test are measured for evaluating the quality of the fiber/matrix interface. The interface bonding of the carbon fiber with the matrix is analyzed by SEM.

EXPERIMENTAL PROCEDURE

Materials and sample preparation

The carbon fibers used in our experiments were untreated and unsized 12 K polyacrylonitrile (PAN)-based high strength fibers, manufactured by Shanghai Carbon Factory, Jilin Carbon Group, China. The average diameter of these carbon fibers was $\sim$ 5 μm, and typical tensile modulus and strength were about 220 and 3.1 GPa, respectively. The used references for designating the carbon fibers with the different surface treatments were listed in Table I. Prior to use, the carbon fiber surfaces had been washed in a Soxhlet extractor with distilled tetrahydrofuran for 5 h. The washed carbon fibers had been oxidized by boiling concentrated nitric acid (HNO_3) for 1, 2, and 2.5 h respectively. Subsequently, it had been washed repeatedly with deionized water until the value of pH reached 7.0. Finally, the oxidized carbon fiber had been dried under vacuum at 110°C for 12 h.

Phenolic resins utilized in this study was FB resins (Bengbu High-Temperature Resistant Resin Factory, China), which was yellow powder with the size at the range of 3–20 μm and the gel time 70–100 s at 200°C.

The flexible towpreg processes which were illustrated in Figure 1 including dispersing carbon fiber tows and prepregging polymer powder. The dis-
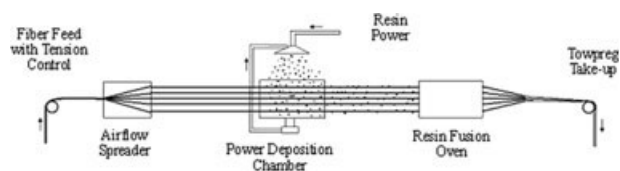
TABLE I
References for the Carbon Fibers with the Different Treatments

Carbon fiber treatment	Reference
Washed	CW
HNO_3 oxidized	CO
Flexible towpreg	CT
HNO_3 oxidized and flexible towpreg	COT

Figure 1 Schematic of power prepregging system.

posal carbon fiber was spread into the width of about 10 cm through the airflow spreader made by ourselves. Then phenolic resin powder was uniformly deposited on the carbon fibers tows at powder deposition chamber. Subsequently, dry flexible towpreg was obtained to assure the adhesion of fiber and resins steadily after impregnating carbon fibers with phenolic resin powder at 160°C through the resin fusion oven for 1 min.

Composites were prepared with different treated carbon fibers by subsequent hot pressing. The specimens were fabricated at 200°C with 20 Mpa hot-press for 15 min with a conventional composites mold process. These composites had been cured at 230°C for 10 h for the purpose that the condensation polymerization of phenolic resins was complete. The content of carbon fiber in the specimens was estimated at 1–10 vol %, and the composites were made by flexible towpreg and resin power being piled up alternately.

Measurements and analytical methods

Morphology and surface properties

An optical microscope was used to examine the distribution of resin powers on carbon fiber bundles, and the effect of surface treatment on the composites fracture morphology was observed by using scanning electron microscopy (SEM).

The dynamic contact angle method was applied to investigate the changes of the surface free energy on the carbon fibers.[11] Contact angle measurements of carbon fibers performed by using the experimental set-up was illustrated in Figure 2. In details, about 0.7 g of carbon fibers was packed into a plastic tube and then mounted indirectly on the measuring arm of the analytical balance with an accuracy of 0.1 mg. The packing factor of the fibers was measured for each continuous filament by measuring the increase in weight per unit time at the depth of zero in a complete immersing liquid. The test wetting liquids used for contact angle measurements were n-heptane and deionized water. The surface free energy of the fiber was calculated from the contact angles of water and n-heptane. Their polar and dispersive components of the total surface energy were known, as shown in Table II.
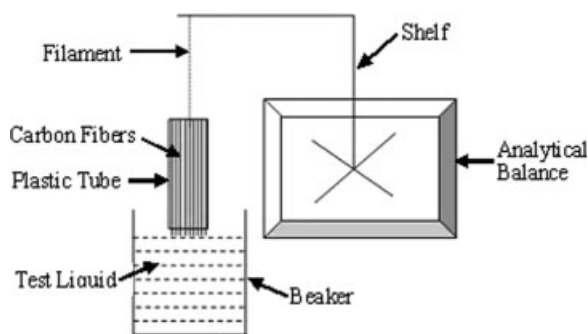
Figure 2 Schematic diagram of the principles of the capillary rise method.

Measurement of fiber volume fraction

Approximately 0.5 g of the specimen was cut from the laminated composites and weighed accurately. Then the sample was added into a conical flask containing about 30 mL of sulfuric acid (H_2SO_4) and reacted at 285°C for 1 h. The solution could be clarified while 30% hydrogen peroxide (H_2O_2) was dropped and all carbon fiber floated to the surface, the FB resins were completely oxidized in the acid. The quartz core funnel filtered out the carbon fiber, thereafter the carbon fiber had been washed by distilled water for several times, so that the H_2SO_4 could be completely removed from the carbon fibers. These fibers had been dried in vacuum at 150°C for 2 h and weighed to calculate the fraction of fibers. These fibers were checked in an SEM for traces of any matrix resin. The weight of the fiber left was measured and the fiber volume fraction was calculated by using the eq. (1):

$$V = (W_f/\rho_f)/(W_f/\rho_f + W_P/\rho_P) \qquad (1)$$

Where W_f and ρ_f were the weight fraction and density of carbon fiber, and W_P, ρ_P were those of matrix, respectively.

Mechanical properties

The tensile strength of carbon fiber strands were used to observe the change of oxidized, spread, and undisposal carbon fibers. The test of tensile strength was performed according to GB/T 3362-2005(crosshead speed of 2 mm/min). The carbon fibers were impregged with epoxy resin 6101 dissolved in acetone and cured at 120°C for more than 30 min. The gel content of carbon fiber strands was controlled at the range of 35–50%, the strands were cut into 210 mm and both ends were pinned up with scrip.

The three point flexure tests were carried out under a Computer Controlled Electronic Universal Testing Machine (WDW-100), which was used following GB3356-82 (crosshead speed of 2 mm/min, span-to-depth ratio of 32 : 1).

The apparent ILSS of unidirectional fiber reinforced composites was measured by using a short beam shear test. The phenolic resin cured composites were machined along the fiber direction into 10.00 × 4.90 mm short-beam shear specimens with 2 mm thickness. The test of interlaminar shear was performed according to GB-3357-82(cross-head speed of 2 mm/min, span-to-depth ratio of 5 : 1). More than seven specimens were tested for each ILSS of the composites. ILSS was determined by eq. (2).

$$ILSS = (3P_b)/(4b \cdot h)(MPa) \qquad (2)$$

Where ILSS was interlaminar shear strength (MPa), P_b was the critical load for crack propagation (N), b the specimen width (mm), h the specimen thickness (mm).

RESULTS AND DISCUSSION

Carbon fiber properties

To enhance the interface bonding of the carbon fiber with the matrix, concentrated nitric acid is used to promote the surface activation of carbon fiber. Figure 3 shows the tensile strength of carbon fiber strands washed by THF, the carbon fiber is oxidized in concentrated HNO_3 for different time and then spread by airflow. Comparing the tensile strength of carbon fiber strands washed with oxidized carbon fiber by concentrated nitric acid, it is clear that the tensile strength of oxidized carbon fiber is decreased, and a minimal strength emerges at the carbon fiber having been oxidized for 2.5 h, which implies the oxygen containing group increased on the surface of the oxidized carbon fiber. But the tensile strength is declined with the oxidized time being prolonged, which demonstrates the carbon fiber is destroyed by excessively oxidation. Manocha and Bahl[12] reported the similar phenomenon that carbon fiber composite treated with nitric acid solution had a lower strength than the untreated carbon fiber composite. However, the tensile strength of carbon fiber spread by airflow is clearly decreased; in our samples airflow results in stress concentration with the asymmetric carbon fiber. During the process of fiber forming, carbon elements on the surface have different attraction forces from the internal, well-structured carbon elements. Some carbons on the outside fiber surface have asymmetrical bonding and are called unbalanced car-

TABLE II
Surface-Free Energy Components of Reference Liquids Used for Fiber Surface Energy

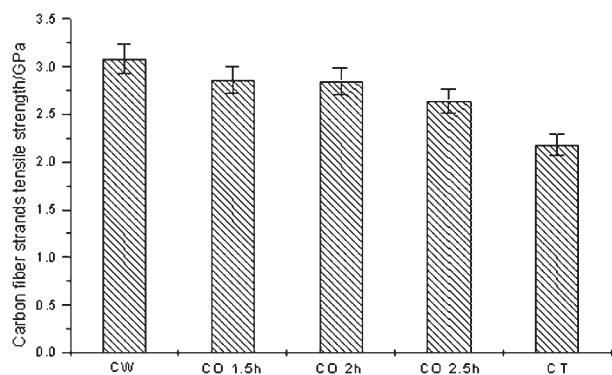| Liquid	γ_L (mJ/m^2)	γ_L^P (mJ/m^2)	γ_L^d (mJ/m^2)
Water	72.8	51.0	21.8
n-Heptane	19.7	0	19.7

Figure 3 Tensile strength of carbon fiber strands with CW, CO, and CT.

bon elements; they have higher reactivities. Hence, the surface reactivity of the carbon fiber depends on the number of unbalanced carbon elements.

Precise contact angle measurement of fibrous materials is a difficult and complex process; however, several methods for measuring the wettability of fibrous material have been proposed. In the early 1970s, Chwastiak[13] introduced a procedure for wicking rate measurement by enclosing a carbon fiber bundle in a glass tube so that the porosity was fixed for a given strand of carbon fibers. This procedure has been used successfully to evaluate the wettability of carbon yarn by water, glycol, heptane.[14] The contact angle used in this investigation is calculated by the eq. (3).

$$\frac{m^2}{t} = \frac{c \cdot \rho^2 \cdot \gamma_L \cdot \cos\theta}{\eta} \qquad (3)$$

Where m is the weight of the penetrating liquid, ρ the density of measuring liquid, c the packing factor, and γ_L, η are the liquid surface tension and viscosity, respectively.

Because we know ρ, η are the liquid characteristics of testing liquid, dm^2/dt and c are demonstrated by our experiment. And polar and dispersive com-

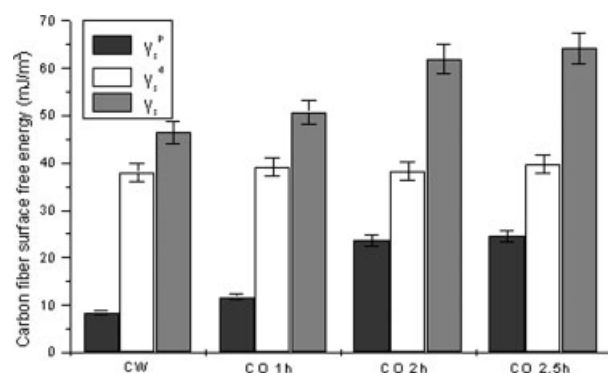ponents of surface free energy of carbon fibers are determined by measuring the contact angles of a variety of testing liquids with known polar and dispersive components and analyzing the results. The relationship is shown in the eqs. (4) and (5).

$$(1 + \cos\theta)\gamma_L = 2[(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}] \qquad (4)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad (5)$$

Where θ is the carbon fiber contact angle, γ_L the liquid surface tension, γ_s the carbon fiber surface free energy, γ_s^p, γ_s^d polar and dispersive components of the carbon fiber surface free energy, γ_L^p, γ_L^d polar and dispersive components of liquid surface tension.

The surface free energy is a strong gauge of solid surface, and adhesion strength between fibers with matrix is predominantly affected by the surface free energy of fibers. Wettability can be estimated by the surface free energy of the liquid on a fiber. Figure 4 shows the surface free energy of the oxidized carbon fibers. It indicates that the polar component of the fibers rise from 8.4 to 24.6 mJ m^{-2} by prolonging the process of oxidation. The polar component is related to the polar functional groups attached to the edges and corners of graphitic basal planes. However, the change of the dispersive component is negligible, which shows that the oxidation treatment on carbon fiber surface efficiently increases the surface free energy due to rising in the polar component.

Flexible towpreg processes

To produce a flexible towpreg being suitable for weaving, braiding, or knitting, the coating process must coat individual filaments in the tow, because coating the entire bundle encapsulates the tow, yielding a stiff prepreg. These stiff prepregs will prevent the fiber individual filaments dispersing in the matrix.
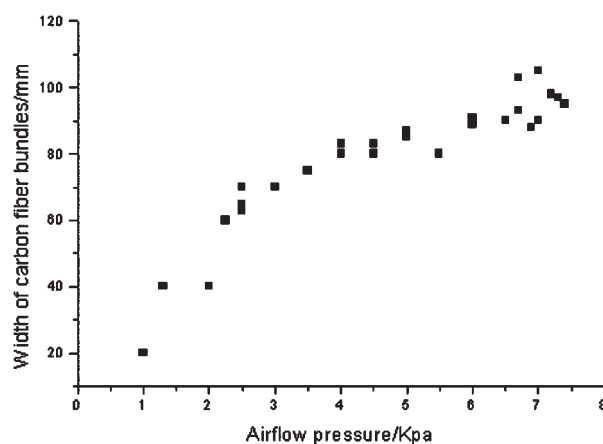

Figure 4 Surface free energy of concentrated nitric acid oxidized carbon fiber.

Figure 5 Width of carbon fiber bundles as the airflow pressure.

The airflow pressure is employed to disperse the width of carbon fiber bundles, as shown in Figure 5. With the airflow pressure ~ 8 Kpa, the carbon fiber is able to gently spread to a width of about 100 mm.

The airflow dispersing measurement provides an understanding of the microscopic structure of the flexible towpreg system, and the capability of towpreg impregnated with resin. Figure 6 is a microscopic of Olympus BX-POL towpreg surface magnified 100 times. As the image shows, the flexible towpreg is partially covered by resin. This irregular resin coverage is usually found in other prepreg system, but this irregularity should be reduced for dis-
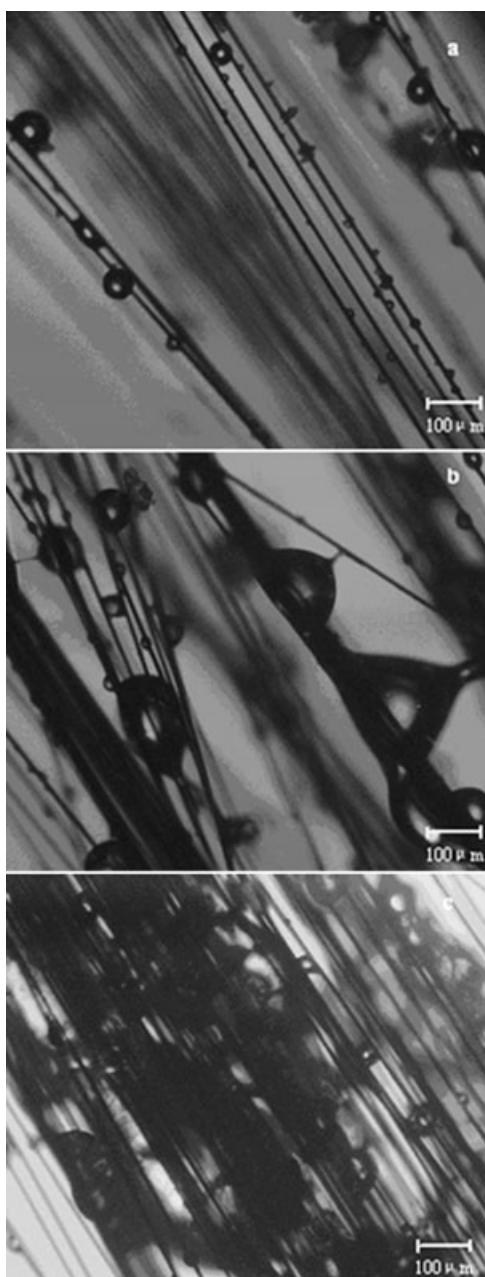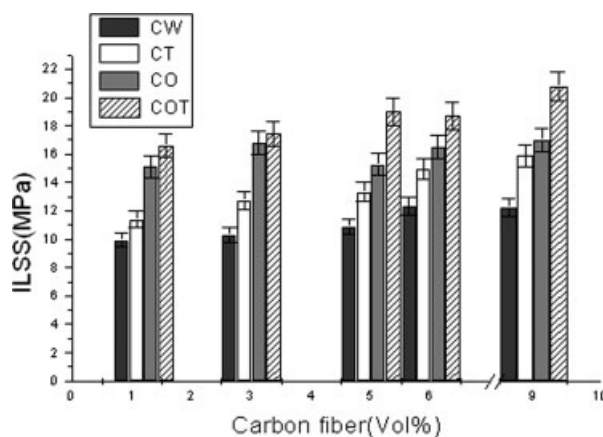

Figure 7 The ILSS of CW, CO, CT, and COT composites as V_f of carbon fiber.

continuous uniformity sheath of a matrix resin. During the process, the line speed of spread carbon fiber through the powder deposition chamber is very important. When a line speed of 2.4 m/min was used to the spread of carbon fiber, the process was stabilized and successfully generated the flexible towpreg with 46 wt % resins, as shown in Figure 6(a). But if the flexible towpreg passes the chamber very slowly, the carbon fiber would exhibit a stiff towpreg such as Figure 6(b,c). In the fusion oven providing adequate radiant heat, the 70% resin powers were fused on the fibers. Therefore on the exterior of the bundle the matrix resin thermally fuses in a discontinuous manner to the fibers, while fibers in the interior of the bundle remain substantially free of the matrix resin. That is significant to flexible towpreg and product a very flexible towpreg suitable for weaving, braiding, and so on.

Interfacial behavior analysis

The ILSS of composites is very important, and closely related to wetting of the fiber by the resin. The effect of V_f on the ILSS is controversial since
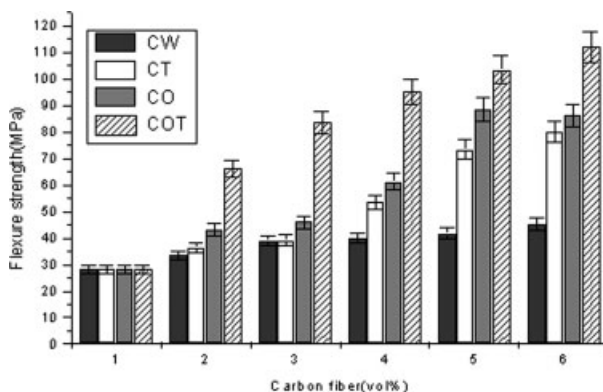

Figure 6 Optical microscope images of the flexible towpreg carbon fiber bundles (×100).

Figure 8 The flexural strength of CW, CO, CT, and COT composites as V_f of carbon fiber.
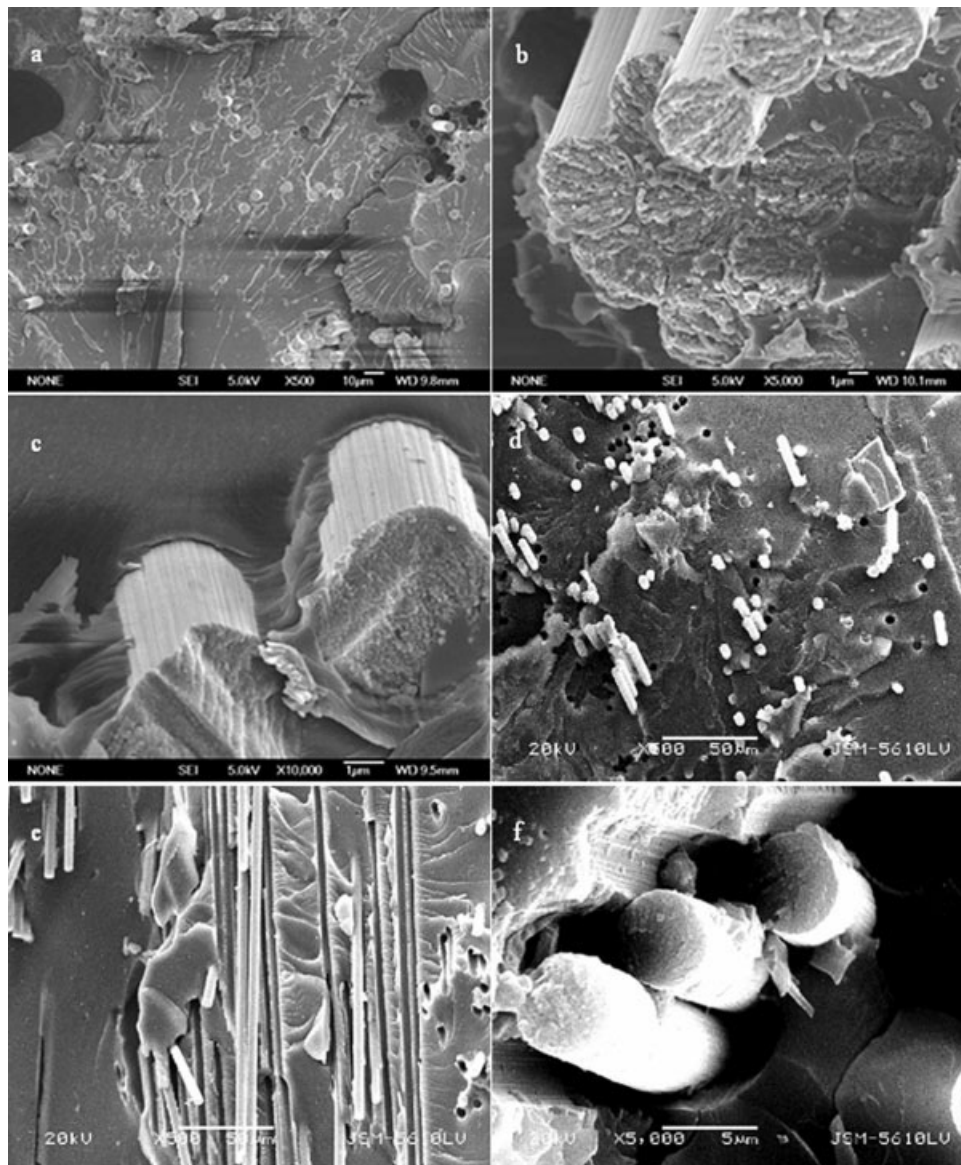
Figure 9   SEM images of the fractured surfaces of the composites with COT and CT.

there are data in the literature suggesting that it increases with an increase in V_f and others that suggest either that ILSS decreases or remains practically constant.[15] Figure 7 shows the ILSS values for all specimens tested. It appears that, in this case, when V_f is about 1 to 10% the ILSS remains constant to each type of composites with the different surface treatments of the carbon fiber. The values of apparent ILSS for the CT and CO composite are higher than the CW samples. These ILSS values for the CT and CO specimens are relatively low compared with the ILSS values of double treated COT for unidirectional carbon-fiber composites.

Figure 7 indicates that the flexible towpreg oxidized carbon fibers appears to affect significantly the ILSS of the composite. ILSS is improved by the process which the resin powers have been coated on the

fibers by means of flexible towpreg in composites. Namely, the flexible towpreg carbon fibers exhibit stronger fiber/matrix bonding than the untreated carbon fibers, because of enhancing the interface between the carbon fiber and matrix. Oxidized treatment can increase the polar functional groups on the carbon fibers and lead to adhesion improvement. The ILSS value of COT composite is higher than the CT and CO specimens at the same V_f as a result of the interface and polar functional groups being improved together.

The flexural strength of the composite regardless of the method of surface treatment increases with carbon fiber content in Figure 8. With the same carbon fiber content, the COT composite has higher flexural strength than the other composites, indicating that the spread of oxidized fibers improves the

interfacial strength between the carbon fiber with the phenolic resin. The flexural strength of COT composite is two to three times higher than CW composite. The flexural strength of the composite follows the order as CW, CO, CT, COT composites in the ILSS.

Surface morphology of the carbon fiber/phenolic resin composite is examined by SEM, Figure 9 shows the SEM images of the fractured surface of the composites. The carbon fibers are randomly dispersed in the matrix resin. There are some holes in the composite formed by pulling carbon fibers out of the matrix resin during the mechanical test as shown in Figure 9(d,e). It means that the adhesion between the carbon fiber and the phenolic resin is considerably weak. But it is not easy to find a hole in the COT/phenolic resin composite but to find some attached matrix resins on the surfaces of the carbon fibers in Figure 9(a). The treated carbon fiber attached phenolic resins very well at high magnify times in Figure 9(b,c). Thus, it reveals that the interfacial adhesion between carbon fiber and phenolic resin is improved by treating carbon fibers with oxidization. It has been shown that chemical bonging takes great importance in the increase of adhesion between the carbon fibers and the matrix resin.

CONCLUSIONS

In this work the effect of carbon fiber treatment method and flexible towpreg process, surface free energy of carbon fiber and interfacial behavior of carbon fiber/phenolic resin composite are investigated.

The surface energy of oxidized treated carbon fibers increased when they are contrasted to CW and CT. The surface energy of carbon fibers is critical properties in predicting the adhesion between fiber and matrix. Optical microscope images show the resins are discontinuous manner on the carbon fiber of the flexible towpreg. Flexural strength and ILSS of COT/phenolic resin composites increase. The SEM results indicate that the COT attached to matrix resins very firmly. These indicated to be an improvement of interfacial strength and fiber dispersing.

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