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Effect of kidney-type and circular cross sections on carbon fiber surface and composite interface

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Abstract

A comprehensive experimental study was conducted to identify the differences of the kidney-type section carbon fibers and circular section carbon fibers in the surface characteristics of fibers and interfacial properties of composites. It was revealed that the kidney-type fibers with larger specific surface area had a better adsorption characteristic and higher surface free energy compared with the circular fibers. Mechanical tests under interfacial shear and interlaminar shear loads have shown that the kidney-type fiber/epoxy composites outperformed the circular fiber/epoxy composites by a significant margin of 23.5% and 12.7%, respectively. The matrix was engulfed by the hollowed-out area of the kidney-type fiber, which allowed the matrix to secure more bonds, resulting in the effective transfer of the load applied to the fiber-reinforced composite system. Many kidney-type fibers overlapped and embraced with each other. Thus the large contact areas between fibers became strong bonding places and interface between fibers and matrix was not damaged easily.

Keywords: A. Carbon fiber; A. Polymer-matrix composites; B. Fibre/matrix bond; D. Surface analysis; Cross section shape

1. Introduction

Carbon fibers are extensively used as reinforcements in composites such as carbon fiber-reinforced plastics, carbon–carbon composite and carbon fiber-reinforced cement. The interface between carbon fibers and matrix plays a critical role in controlling the overall properties of composites, such as mechanical performance, fracture toughness and environment stabilities. Interfacial characteristics determine the way loads can be transferred from the polymer to the fiber. The sensitivity of the overall behavior of composites to fiber/matrix adhesion has also long been realized [1–4]. Fiber/matrix adhesion involves very complex physical and chemical mechanisms. The majority of previous efforts were concentrated on the chemical aspects of fiber/matrix adhesion through the use of plasma treatment [5–7], oxidation [8,9], electrochemical treatment [10] and coatings [1,11]. However, not much attention has been paid to the physical aspects of fiber/matrix interaction. One of the most important physical aspects is the geometry of reinforcing fibers, which influences the adhesion between fiber and matrix, stress transfer and local mechanisms of failure [12,13]. In addition to chemical bonding, the fiber/matrix bond strength in shear is largely dependent on the roughness of the fiber surface and the fiber/matrix contact area. Recently carbon fibers with deformed cross-sectional shapes have been developed. In structural mechanics, as the optimization of the stress distribution of materials, some design engineers proved that hollow or noncircular-type fibers were better than circular ones in mechanical properties and that they have been applied in many structural materials, such as I-beam train road, construction support pipe/pile rod, etc. Especially, C-type carbon fiber has a curved area in the surface contacting with matrices that can improve interfacial bonding force. The phenomenon result

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may solve a delamination, playing a great part in the overall properties of carbon fiber-reinforced composites [14,15].

In this work, the surface characteristics of circular and kidney-type fibers are investigated by the BET adsorption and fiber surface free energy. And the interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) are applied to identify the influence of fiber cross-sectional shapes on interfacial properties of composites. The fracture mechanisms of fiber/epoxy interface are analyzed by scanning electron microscopy (SEM) micrographs.

2. Experimental

2.1. Materials

Two types of polyacrylonitrile based carbon fibers used were produced by Institute of Coal Chemistry, Chinese Academy of Sciences in the same manufacturing conditions such as spinning, holding time of stabilization and carbonization. The average diameter of carbon fiber with circular cross-sectional shape is 7 μm. The average cross section width and thickness of kidney-type fiber are 9 μm and 3 μm, respectively (Fig. 1a). The physical properties of kidney-type and circular section carbon fibers are shown in Table 1. The kidney-type and circular section fibers are both sized and the weight ratio of sizing materials is both about 4%.

The matrix system used was E-618 epoxy resin system consisting of diglycidyl-ether of bisphenol-A (supplied from Yue-Yang Chem. Co. of China), curing agent: phthalic-anhydride and benzyl-dimethylamine at 100, 70 and 1 parts by weight, respectively.

Using the carbon fibers and epoxy resin system, the prepreg was laid unidirectionally into a mold to manufacture composites. The prepreg was pressed and cured under

Table 1
Physical properties of carbon fibers

	Density ($g\,cm^{-3}$)	Tensile strength (GPa)	Tensile modulus (GPa)	Cracking specific elongation (%)
Kidney-type	1.766	3.68	203	1.83
Circular	1.764	3.64	205	1.81

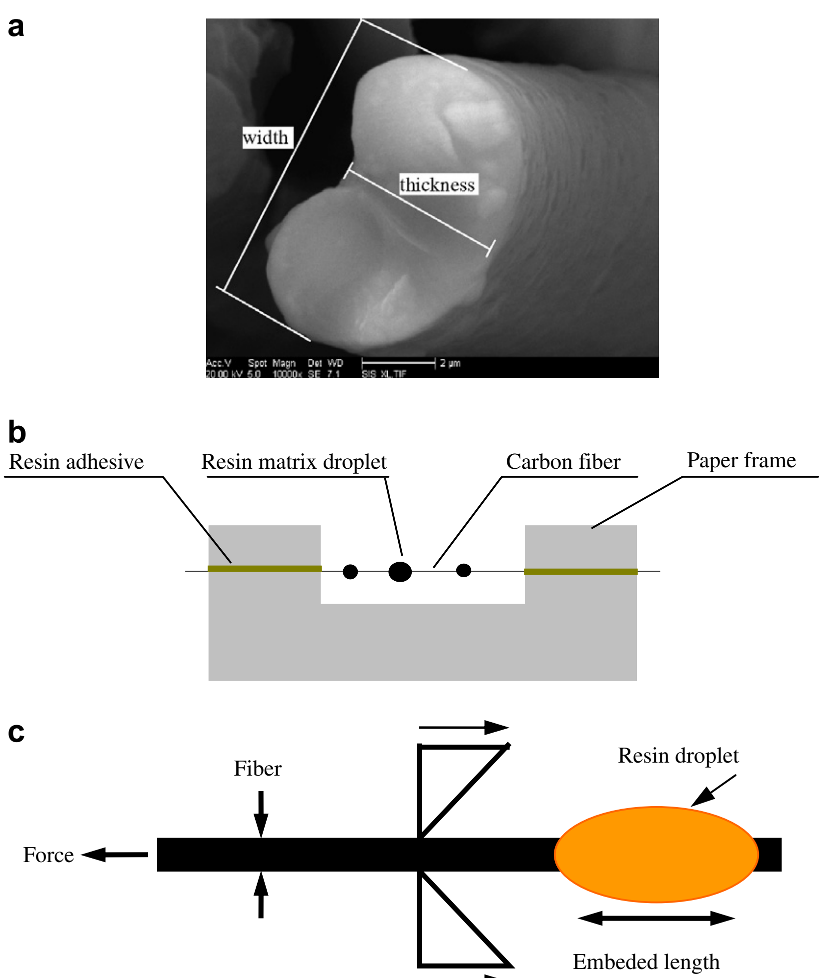

Fig. 1. Schematic diagrams of kidney-type fiber section and micro-composite test. (a) Width and thickness of kidney-type section; (b) single fiber pull-out specimen; (c) schematic drawing of IFSS test.

5 MPa pressure for 2 h at 90 °C, then under 10 Mpa pressure for 2 h at 120 °C and last under 10 MPa pressure for 4 h at 160 °C by hot-press machine and we could obtain specimens with fiber mass fraction of 64 (±1%).

2.2. Measurements

Failure of fiber-reinforced composites was inspected by SEM (FEI SIRION 200). The adsorption characteristics of fibers were determined by generating N_2 adsorption isotherms at −196 °C using ASAP2405 apparatus. BET specific surface area, pore volume, and pore average diameter of fibers were obtained from the nitrogen adsorption isotherms.

Carbon fiber surface energy (γ_f^T), its dispersive component (γ_f^d) and polar component (γ_f^p) were determined by dynamic contact angle analysis (DCAA). All the measurements were carried out by a capillary method in an impregnating apparatus SB-312 made in China. In the experiment, some bundles of fiber were aligned and inserted into a polyethylene tube with diameter 2 mm and length 40 mm. The fiber bundles protruded 2 mm outside the tube. The ends of the bundles were impregnated by water and normal octane, respectively. The fiber samples were extracted in acetone before the measurement of adsorption characteristics and surface energy, to remove the impurities and sizing material.

For the investigation of interfacial properties, a micro-composite (single fiber composite) test was performed to determine IFSS of the kidney-type and circular section carbon fiber/epoxy resin composites. The micro-composite specimens were prepared in paper frames with dimensions of 20×100 mm^2. The free fiber length was approximately 30 mm. Some resin droplets were placed against a monofilament and cured (Fig. 1b). A single fiber pull-out test was carried out using an interfacial micro-bond evaluation instrument made by Tohei Sanyon Corporation of Japan (Fig. 1c).

ILSS of the composites was measured by short-beam bending test according to ASTM D-2344 using an Instron 1125. A span-to-depth ratio of 5:1, cross-head speed of 2 mm min^{-1}, and sample thickness of 2 mm were used. Tensile tests were carried out, following ASTM standard D3039-94 at a cross-head speed 2 mm min^{-1}. More than eight specimens were tested for each of composites studied and the average value was taken in the present work studied.

3. Results and discussion

3.1. Adsorption characteristic of fibers

Carbon fibers which are used as reinforced materials should possess a reasonably large specific surface area, which allows the exposure of active phase to the matrix. Fig. 2 shows N_2 adsorption–desorption isotherms of the kidney-type and circular fibers. The isotherms of both groups (kidney-type and circular) resembled each other and were classified as type I in the IUPA classification [16]. At any relative pressure, the kidney-type fibers adsorbed noticeably more N_2 than the circular fiber. This indicates that the kidney-type fibers contained an appreciable amount of mesopores and macropores, in addition to micropores.

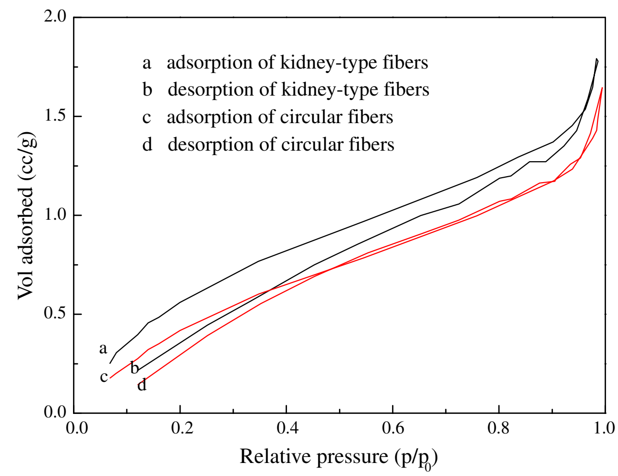

Fig. 2. Nitrogen adsorption–desorption isotherms for kidney-type and circular section carbon fibers.

Table 2
Pore structure characteristics of carbon fibers

	Pore volume (ml g^{-1})	Specific area (m^2 g^{-1})	Average diameter (nm)
Kidney-type section	0.003	3.03	3.7
Circular section	0.002	2.64	3.5

As previously mentioned, nitrogen isotherms were analyzed by the BET method to obtain the specific surface area, pore volume and average pore diameter of carbon fibers studied. Typical results are shown in Table 2. It should be noted that the specific surface area, pore volume and average pore diameter of kidney-type fibers with equivalent production conditions were larger than those of circular fibers, respectively. It indicates that the adsorption characteristic of kidney-type fibers was better than that of circular fibers with similar manufacturing conditions [17].

3.2. Surface energy of fibers

In the surface energy analysis, the contact angle between wetting liquid and carbon fiber can be calculated using the following equations [18]:

$$\Delta\gamma = \frac{0.064\, H^2 \rho_f \eta (1-\varepsilon)^2 m^2}{d_f k^2 w_f \rho_l^2 \varepsilon^3 v_T t} \tag{1}$$

$$\cos\theta = \frac{\Delta\gamma}{\gamma_l} \tag{2}$$

Table 3
Contact angle and surface free energy of carbon fibers

	Water contact angle (°)	Octane contact angle (°)	γ^{d} (mJ m^{-2})	γ^{p} (mJ m^{-2})	γ^{T} (mJ m^{-2})
Vaporized water	–	–	21.6	51.0	72.6
Normal octane	–	–	21.3	0	21.3
Kidney-type fibers	50.6 ± 2.1	78.1 ± 2.2	53.1 ± 1.6	2.7 ± 0.3	55.8 ± 1.4
Circular fibers	53.6 ± 1.8	81.0 ± 2.0	48.9 ± 1.1	2.8 ± 0.2	51.7 ± 1.2

where $\Delta\gamma$ is the change in fiber surface free energy; γ_l is the surface tension of immersion liquid; ε is the volume percent of fibers in tube (ε is in the range 48–52%); H is the length of fiber bundle (40 mm); ρ_f and ρ_l are the densities of fiber and immersion liquid, respectively; η is the viscosity of immersion liquid; k is the hydraulic constant; v_T is the total volume of system; w_f is the weight of fiber bundle; d_f is the diameter of a single fiber; t is the time of immersion equilibrium; θ is the dynamic contact angle; m is the amount of adsorption at immersion equilibrium.

The dynamic contact angle (shown in Table 3) is used to calculate the fiber surface free energy according to Kealble equation [19–21,7]

$$\gamma_l^T(1+\cos\theta) = 2(\gamma_l^d\gamma_f^d)^{1/2} + 2(\gamma_l^p\gamma_f^p)^{1/2} \tag{3}$$

$$\gamma_f^T = \gamma_f^d + \gamma_f^p \tag{4}$$

where γ_f^T, γ_f^d and γ_f^p are the total surface free energy, dispersive component energy and polar component energy of the carbon fiber, respectively. γ_l^T, γ_l^d and γ_l^p are the surface tension of immersion liquid, its dispersive and polar component, respectively. The surface free energy values for the liquids used and carbon fibers measured in experiments are presented in Table 3.

It was clear from the table that the kidney-type fibers had a dispersive component of 34.1 mJ m^{-2}, compared with 28.9 mJ m^{-2} for the circular fibers, a difference of 18.0%. However, the non-dispersive (polar) component remained considerably constant for the carbon fibers studied, showing no appreciable variation between kidney-type and circular fibers. This may be due to the same content of surface polar groups on fibers. Thus, the kidney-type fibers performed marginally (16.1%) better than those with circular section in surface free energy. The surface free energy of carbon fibers are certainly related to the wettability of the fiber surface by the resin matrix. The high surface free energy is beneficial to the well wettability of fibers, resulting in the high composite shear strength [22,23].

3.3. Interfacial properties of composites

For the fibers with irregular cross sections such as kidney-type section fibers, the original shear lag model would not provide accurate calculations for IFSS, because it

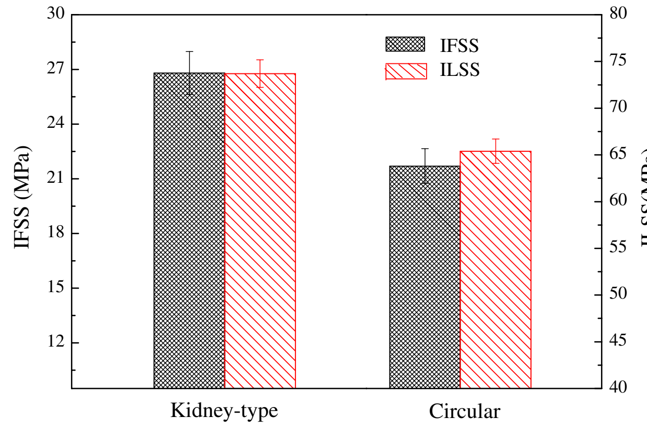

Fig. 3. IFSS and ILSS of kidney-type and circular section carbon fiber composites.

assumes a circular fiber cross section. In this paper, a modified shear lag model [24] is employed to calculate the interfacial shear strength by the following equations:

$$\tau_f^* = \frac{\sigma_p n^* \pi d^*}{S_f}\coth(n^* L/d^*) - \tau_{rf} \tag{5}$$

$$n^* = \left[\frac{E_m}{E_f(1+v_m)\ln[S_R/S_f]}\right]^{1/2} \tag{6}$$

where τ_f^* is the fiber/matrix interfacial shear strength; σ_p is the maximum fiber tensile stress during pull-out test; n^* is the dimensionless shear lag constant; d^* is the equivalent diameter of fiber deduced from fiber cross-sectional area; L is the embedded length of fiber; τ_{rf} is the residual shear stress at the fiber surface or at an annulus; E_f or E_m is the tensile modulus of fiber or that of matrix; v_m is the Poisson's ratio of matrix; S_f or S_R is the circumference length of fiber cross-sectional area or that of an annulus in matrix.

IFSS, τ_f^*, values were calculated using Eq. (5) for the modified shear lag models, assuming the residual stress was zero and the results are shown in Fig. 3. It was noted that the IFSS for kidney-type fiber composites was 23.5% greater than the IFSS for circular fiber composites. These results are likely due to the fact that the basic properties of kidney-type fibers widen specific surface area, improve the wetting ability and enhance the contact area with matrix, resulting in effectively transferring the applied stress.

As part of a separate investigation into improving the through-thickness performance of composite materials, interlaminar shear strength testing was undertaken on both kidney-type fiber composites and circular fiber composites with approximately the same fiber volume fraction. The results in Fig. 3 indicated that the ILSS of kidney-type carbon fiber-reinforced composites was improved by 12.7%, compared with that of circular carbon fiber-reinforced ones. This is probably attributed to the curved section of kidney-type carbon fiber and the effective stress interaction between fiber and matrix. The contact area with matrix is wider, leading to the greater friction force and the effective load transfer. In addition, the tensile strength and modulus of kidney-type fiber/epoxy composites were improved due to the increased interfacial properties. The average tensile strength and modulus of kidney-type carbon fiber-reinforced composites were 1657.6 MPa and 134.4 GPa, and the average tensile strength and modulus of circular carbon

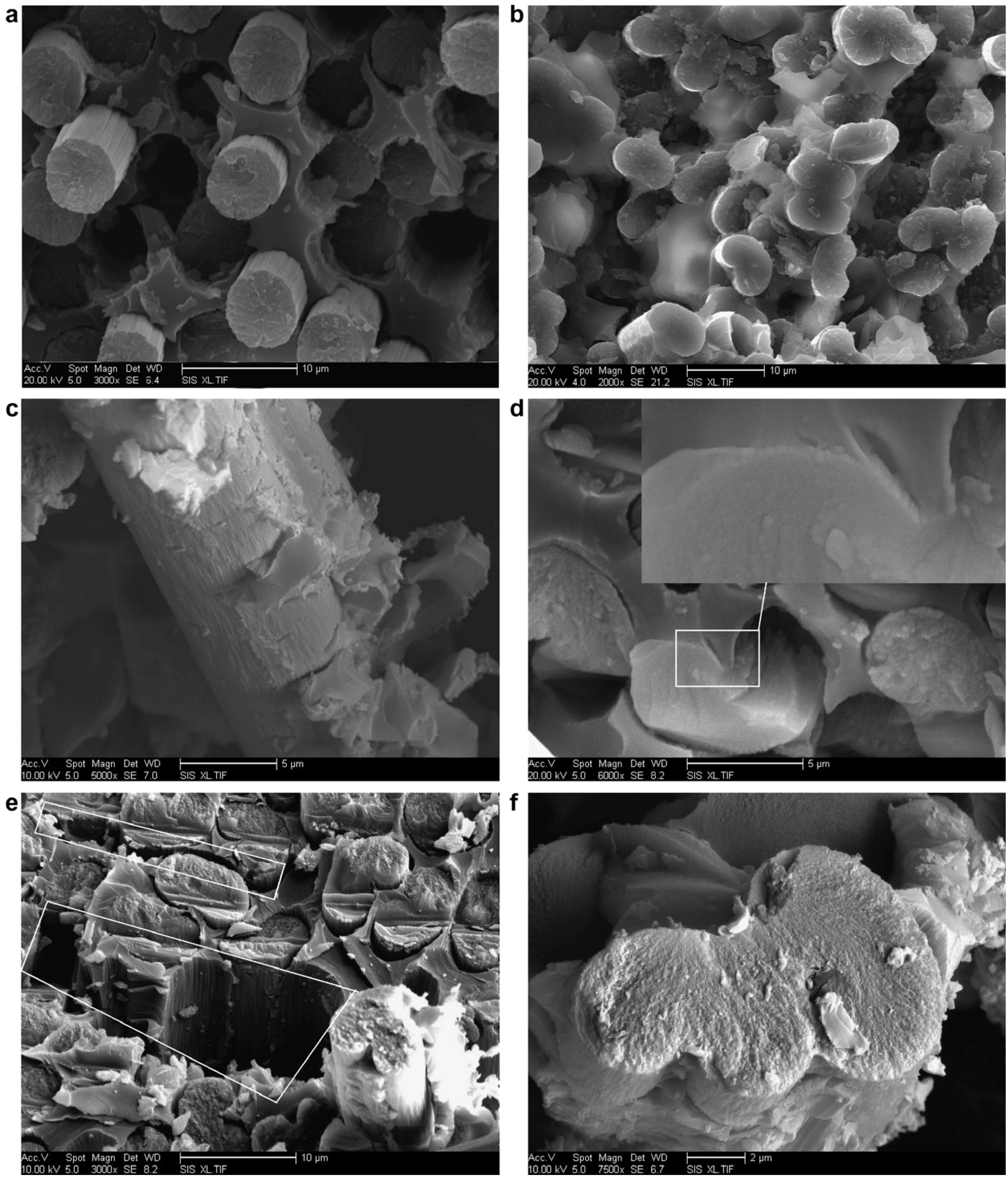

Fig. 4. SEM photographs of carbon fiber/epoxy composite fracture. (a) Section of circular fiber composites; (b) section of kidney-type fiber composites; (c) filament surface of kidney-type fiber composites; (d) interface between matrix and concave of kidney-type fiber; (e) deformation of the composite specimen; (f) interface between concave and convex of fibers.

fiber-reinforced composites were 1542.3 MPa and 128.9 GPa, respectively.

3.4. Morphologies of composite interface fracture

Fig. 4 shows the SEM micrographs of interlaminar shear fracture surfaces of the two composite systems. The fracture surfaces of circular fiber/epoxy showed few matrix materials sticking on fibers, designating the occurrence of interface failure (Fig. 4a). For the kidney-type fiber/epoxy composites, the matrix materials sticking on the concave surfaces of fibers indicated breakage of matrix failure and the fracture convex surfaces were of the same character as the fracture surfaces of circular fiber composites, except that the split was much more pronounced in the former case (Fig. 4b and c).

The kidney-type fiber was hollowed-out along the fiber axis, making it expected to greater interface. Up to the curved area of the fibers, matrix was impartially contributed and had a good bonding on the concave surface of fibers, which was demonstrated by the failure mode of fiber side and matrix side, as shown in Fig. 4d. This picture represents that the matrix was engulfed by the hollowed-out area of the kidney-type fiber, which allowed the matrix to secure more bonds and intimated the better adhesive force between two phases, resulting in the effective transfer of the load applied to the fiber-reinforced composite system [14]. However, the typical longitudinal splitting interface between convex surface of kidney-type fibers and matrix can be seen in Fig. 4d, indicating the extensive longitudinal cracking along the contact area between convex surface of fibers and matrix.

When shear stress is continuously applied to the specimens of composite to some stage, fiber breakage will happen progressively at random places, which induces tiny transverse cracks in the matrix. Some of these cracks will change path when they confront the fibers and then easily propagate along the contact area between fibers to cause longitudinal fiber/matrix splitting through the formation and propagation of longitudinal cracks, resulting in a large deformation of the specimen [2] shown in Fig. 4e. It can be observed that the delamination along the fiber axis and longitudinal fiber/matrix splitting marked by trapezium frames in Fig. 4e occur when composite breakage happens.

The failure behavior of kidney-type fiber/epoxy specimens was different from that of circular fiber/epoxy specimens. For the circular fiber/epoxy system, when the applied stress reaches the maximum, the breakage of interface between fiber convex surface and matrix appears and the failure of the specimen happens suddenly, followed by the stress decrease abruptly to zero. However, for the kidney-type fiber/epoxy specimens, when the breakage of interface between the convex surface and matrix occurs, the concave surface still withstand some load, followed by subsequent breakage of concave surface of some fibers.

Since the fiber cross-sectional shape is round, the epoxy resin can easily impregnate the fibers and the fibers in the composite have less contact areas with each other (Fig. 4a). However, for kidney-type fiber/epoxy, the fibers have the preferred alignment because of the fiber rotation during fabrication of the prepreg and composite laminates. In the process of making prepreg and curing composites, the pressure is applied perpendicularly onto the plane of prepreg or laminates, and the fibers in the prepreg or laminates will rotate in the liquid resin to some extent due to the resin transverse flow, so that the long axis of the fiber cross section tends to be perpendicular to the direction of the applied pressure [2]. As a result, many fibers overlapped and embraced with each other, as shown in Fig. 4b and f. In such areas the contact area is very large and the strength transferred by stress decreases, so that these areas become strong bonding places and interface between fibers and matrix is not damaged easily (Fig. 4f).

4. Conclusions

The adsorption characteristic of kidney-type fibers was found to be better than that of circular fibers. Between the two types of fibers, kidney-type fibers showed the higher surface free energy. These results can be explained by fact that the specific surface area of kidney-type fibers is larger than that of circular fibers.

IFSS test has indicated that the kidney-type fiber composites performed marginally (23.5%) better than those manufactured using circular fibers. Similarly, under interlaminar shear load the kidney-type fiber composites offered a performance advantage of approximately 12.7%. These results are probably due to the fact that the hollowed-out area of the kidney-type fiber can engulf the matrix and many kidney-type fibers are overlapped and embraced with each other. Therefore, the mechanical interlocking forces are improved and the interfacial contact areas between reinforcement and matrix are widened, resulting in effectively transferring the applied stress.

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