INTERFACIAL STUDIES OF CARBON FIBER/EPOXY COMPOSITES USING SINGLE FIBER FRAGMENTATION TEST

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Abstract
Single fiber fragmentation tests were carried out to measure the properties of the fiber-matrix interface in several carbon fiber/epoxy composite systems. Four kinds of carbon fibers (CFs) were studied: 1. primary CFs (used as received); 2. desized CFs (sizing removed through thermal treatment); 3. resized CFs (deposited with epoxy sizing by solution); 4. Carbon nanotube (CNT)-grafted CFs (grown with CNTs using a chemical vapour deposition method). The interfacial shear strength decreased by around 30% for the desized CFs and the CNT-grafted CFs compared with the primary CFs. The value of interfacial shear strength for the resized CFs was 20% larger than that of the desized CFs. There is a good agreement between the results of single fiber fragmentation tests and that of contact angle tests.

1 Introduction

Fiber-reinforced polymer composites (FRPC) are of great interest and make a huge impact in various industrial fields such as aerospace, automotive, construction sport and oil/gas industries due to their potential for superior mechanical properties [1]. It is well known that the mechanical behavior of composites depends not only on the properties of the constituent materials, but also on the nature of fiber/matrix interface [2]. For CFs, various surface treatments such as electrochemical oxidation [3], wet chemical oxidation [4], gas phase oxidation in ozone or oxygen mixtures [5], plasma [6] and sizing treatment [7], have been applied to improve the fiber/matrix adhesion. After these surface treatments of CFs, interfacial strength is typically promoted by enhancing the chemical adhesion of the fibers with the matrix or by increasing the fiber surface area [8].

The application of a thin polymer coating, defined as sizing, on the surface of fibers is an efficient treatment in promoting adhesion with the matrix and improving handling and processing of fibers [2]. When dealing with CFs reinforcing epoxy matrices, most of the commercial sizings are also epoxy based. This is because a higher elastic modulus and lower fracture toughness interface region could be produced after the sizing process [9].
Another ideal approach for the reinforcement of composite materials is introducing carbon nanotubes (CNTs) into conventional fiber-reinforced composites due to the outstanding

mechanical, thermal and electrical properties of CNTs [10].Chemical vapor deposition(CVD) provides an efficient way to grow CNTs directly onto CFs, which can be then used in traditional FRPC [11]. There have been some positive results [12] reported on the improvement of critical mechanical properties of multifunctional composites with CNT-grown fibers, including the increase of hardness and interlaminar shear strength of the composites.

To characterize the interface property of fibers and matrix in the composites, single fiber fragmentation test provides a popular and feasible method. It can be used to assess the ability of the interface to transfer the stresses from the matrix to the fiber [13]. The fiber stress state in the fiber fragmentation test specimen is somewhat similar to that in the real composite [14].

In the present study, CFs are treated in two different ways: grafted with CNTs by using CVD method and deposited with epoxy sizing by solution. The surface properties of the crude CF and modified CFs are characterized by scanning electron microscopy and contact angle measurements. The effect of surface modification on the interfacial shear strength is studied using the single fiber fragmentation test and the interfacial shear strength is calculated using the Kelly–Tyson method [15].

2 Experimental

2.1 Materials

Sized, polyacrylonitrile (PAN)-based T700GC CFs (defined as as-received CFs) provided by Torayca Inc. (Tokyo, Japan) have been used in this study. The as-received CFs have been treated in two different ways: one with sizing removed (defined as desized CFs) through the thermal treatment at 700^{o}C for 10 minutes and the other grown with CNTs (defined as CNT-grafted CFs) through CVD method. The desized CFs have been then coated with a thin layer of epoxy sizing (defined as resized CFs). All other chemicals have been used as received.

2.2 Resizing of the desized CFs

For the sizing, a solution of epoxy resin in acetone at 1 wt% was prepared. Subsequently, the desized CFs were soaked in the solution for several minutes. Finally, the CFs were dried in a oven at 60 ^{o}C for 15 hours.

2.3 Grafing CNTs onto CFs

The graft of CNTs onto CFs has been conducted using CVD method [16]. The reactions were performed in a tubular quartz reactor (around 10 cm in diameter) equipped with an electrical furnace. Ferrocene catalyst was injected into the reaction tube by fluidized floating catalyst method using argon as the carrier gas. Acetylene (C_2H_2) was used as the hydrocarbon source and a mixture of H_2/Ar was used as the carrier gas. The reactions were performed at 750 ^{o}C for about 10 minutes in dynamic mode using a 1:11.5 flow ratio of C_2H_2 to carrier gas. Before the sample was removed, the furnace was cooled down to room temperature under the protection of argon gas.

2.4 Characterization of CFs' surface properties

The surface morphologies of CFs were studied by means of a LEO Gemini 1530 scanning electron microscope (SEM). The contact angles between the epoxy (WWA, RESOLTECH) and the surface of CFs were quantified by the low-bond axisymmetric drop shape analysis (LBADSA) [17]. The single CFs were dipped into the epoxy to have the epoxy droplets formed on the surface of the CFs. The images of the droplets were captured using a contact angle meter SURFTENS (OEG, German). The contact angles were determined from 30 droplets, on three fibers, for each type of CFs, to obtain statistically significant averages.

2.5 Single fiber fragmentation tests

Stoichiometric proportions of epoxy (diglycil ether bisphenol A based, EP-502, Polymer Gvulot) and hardener (diethylene tetramine based, EPC-9, Polymer Gvulot) were mixed and degassed in a vacuum cell at room temperature. A single fiber was carefully separated from a yarn and aligned on a polycarbonate plate (35×70×2 mm^3). Fiber straightening was achieved by gluing one end of the fiber, fastening with light weight at the other end and then gluing. A spacer was aligned in the middle of the plate. Fibers were aligned on both sides. Liquid epoxy resin was spread on the plate, covered and a load of about 1kg was applied carefully on the top of the plate. The sample was cured for 5h at 80°C and then allowed to cool slowly to room temperature. After curing, the epoxy film was cut to size using a specially designed cutter. The gauge length of all samples was about 15mm. The fragmentation tests were performed by using a minimat 2000 (Rheometric Scientific) tensile testing apparatus equipped with a load cell of 200N under a microscope with crossed polarized light, fitted with a video camera. The samples were tested at a rate of 0.05mm/min, the fracture events were recorded as a function of applied load. When a break occurred, the corresponding stress was recorded and the mean length of the fragments present was calculated by dividing the initial gauge length of the specimen by the number of breaks (plus one) present at that stress.

2.6 Evaluation of interfacial properties

Fragmentation test of a single fiber composite sample can be viewed as a multiple "in-series" tensile test of single fibers (fragments, in fact) of varying lengths, for which the Weibull/weakest link model is valid [18]. The mean tensile strength $\overline{\sigma}$ of fibers having an average length L is given by:

$$\overline{\sigma} = \alpha L^{-1/\beta} \Gamma\left(1+\tfrac{1}{\beta}\right) \tag{1}$$

where α and β are the scale and shape parameters of the Weibull distribution for strength, respectively, and Γ is the gamma function. For the fragmentation test, the relationship between the average fragment length $\bar{s}$ and the fiber stress σ_f is given by inverting Eq (1):

$$\bar{s} = \alpha^{\beta} \sigma_f^{-\beta} \left\{ \Gamma\left(1+\frac{1}{\beta}\right) \right\}^{\beta} \tag{2}$$

$$\text{or,} \quad \ln \bar{s} = -\beta \ln \sigma_f + \beta \ln \left\{ \alpha \Gamma\left(1+\frac{1}{\beta}\right) \right\} \tag{3}$$

σ_f, may be obtained from the stress applied to the composite:

$$\bar{\sigma} = \sigma_{appl}\left(\frac{E_f}{E_m}\right) \tag{4}$$

where E_f and E_m are the fiber and matrix module, respectively.

The values of α and β can easily be obtained from a plot of ln ($\bar{s}$) against ln (σ_f).
The interfacial shear strength τ can be estimated from the Kelly-Tyson model [15]:

$$\tau = K\frac{d_f\sigma_f(\bar{l})}{2\bar{l}} \tag{5}$$

where K adopts a mean value of 0.75, d_f is the fiber diameter, $\sigma_f(\bar{l})$ is the fiber strength at the sauturation length $\bar{l}$.

3. Results and discussion

3.1 Surface properties of CFs

The surface morphologies of the CFs have been studied using SEM and the characteristic micrographs of the CFs are given in Figure 1.

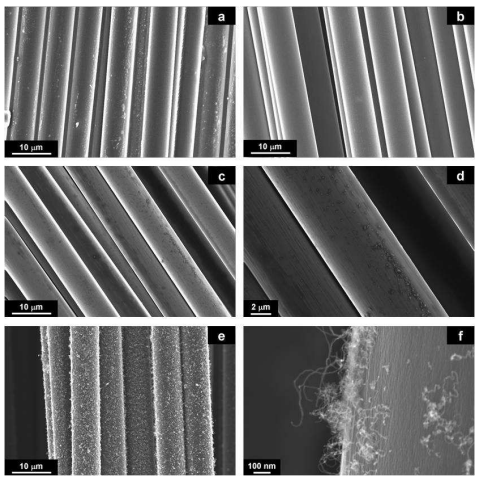

Figure. 1 SEM micrographs of: (a) as-received CFs, (b) desized CFs, (c)-(d) resized CFs and (e)-(f) CNT-grafted CFs**.**

From these images, it can be clearly seen that the desized CFs (Figure 1 (b)) has no matrix adhered to fibers showing that the fiber surfaces are cleaner than other modified fibers. The resized CFs (Figure 1 (c) and (d)) show less amount of epoxy adhering to the fibers compared with the commercial as-received CFs (Figure 1 (a)), which may be because the sizing epoxy used here is not as suitable to be adhered to the fibers as the commercial sizing epoxy. The CNT-grafted CFs (Figures 1 (e) and (f)) exhibit that CFs are covered with CNTs possessing the diameter around 10 nm.

Typical images of WWA epoxy droplets formed on the surfaces of different CFs are shown in Figure 2. The contact angles were quantified by the LBADSA method [17]. By removing the

sizing from the commercial as-received CFs, the contact angle increases from 29.2 ± 1.5° (as-received CFs) to 33.5 ± 2.2° (desized CFs), which could be attributed to a decrease in the roughness of desized CFs. The contact angle of resized CFs is 30.6 ± 1.5° after resized with WWA epoxy and lower than that of as-received CFs. This may be because the surface roughness of the resized CFs is smaller than that of as-received CFs, which is in agreement with the SEM results. After grafted with CNTs, the contact angle increases slightly from 33.5 ± 2.2° (desized CFs) to 34.4 ± 0.6° (CNT-grafted CFs). This phenomenon might be attributed to the fact that the CNTs are more hydrophobic than the CFs surface, resulting in the deterioration in wetting [10].

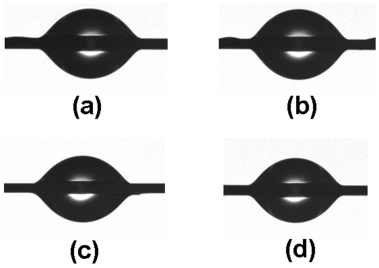

Figure 2. Typical images of WWA epoxy droplets formed on the surfaces of (a) as-received CFs, (b) desized CFs, (c) resized CFs and (d) CNT-grafted CFs.

3.2 Single fiber fragmentation tests

3.2.1 Photoelastic features

Polarized light was used to observe in-situ fragmentation of the fibers. The use of polarizers enables the observation of the stress state near fiber breaks and the interface between the fibers and the matrix. As the fiber break, the specimen exhibits birefringence colors around the fiber-matrix interface. The birefringence effect provides a useful tool for observing stress patterns and the fracture of the opaque CFs [19]. When a tensile loading is applied to the specimen, the load is transferred from matrix to fiber through the interface and stress will build along the fiber, creating a birefringent effect. When the fiber fails, the stress drops to zero in the break gap between fiber fragments, creating an area of no birefringence. Figure 3 shows the changes of the pattern in the interfacial stress for different single fiber composites. The as-received CFs exhibit the most concentrated birefringent pattern which is associated with high levels of adhesion. For the desized CFs, there are large break gaps and long debonded interfaces. Some debond zones even become connected, producing “chain-like” breaks. This could result from loosely bonded or weak interfaces. Once the desized CFs are resized with epoxy sizing, the break gaps become smaller and the stress pattern is less dispersive. As to the CNTs-grafted CFs, a diffuse birefringent pattern is found.

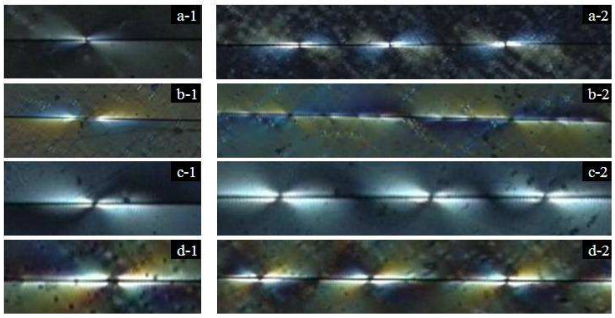

Figure 3. Birefringent stress pattern in single fiber composites reinforced by: (a) as-received CFs, (b) desized CFs, (c) resized CFs and (d) CNT-grafted CFs.

3.2.2 Interfacial shear strength

In the single fiber fragmentation tests, real-time fragmentation data (number and length of fragments) were obtained at increasing level of stress. The relation between the average fragment length and the fiber stress can be created, as shown in Figure 4. The continuously monitored fragmentation procedure provides a simple way to measure the shape parameter for strength from a single fragmentation test rather than extensive measurements of single fibers at different gauge length [20].

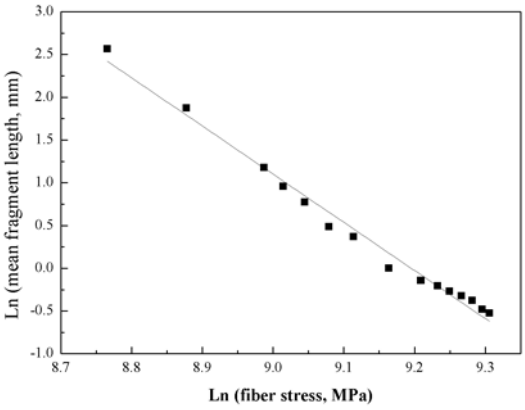

Figure 4. Typical ln-ln plot of the mean fragment length against fiber stress. The shape parameter for strength is the opposite of the slope.

Calculation of interfacial shear strength was carried out for those specimens that reached a saturation state using Eq (5). The results listed in Table 1 indicate that the interfacial shear strength of the as-received CFs is the strongest.

Fiber	As-received	Desized	Resized	CNT-grafted
Fiber diameter [μm]	7.2	7.1	6.9	7.0
Weibull shape parameter	4.7	9.5	7.2	4.9
Weibull scale parameter [GPa]	11.2	10.8	10.2	10.4
Rang of fiber stress [GPa]	6.5-11.5	6.0-10.0	6.0-12.0	4.0-11.0
Average fiber fragment length at sauturation [mm]	0.71	0.95	0.71	0.90
Fiber strength at average saturation length [GPa]	11.0	10.3	9.8	10.1
Interfacial shear strength [MPa]	56.3	39.9	49.6	35.5

Table 1. Interfacial shear strengths obtained from single fiber fragmentation tests

This may result not only from the strong adhesion formed between the fiber and the matrix, but also from the non-stoichiometric interface produced by the sizing. The main effect of a sizing is to produce a brittle interface region surrounding the fiber [21]. In a formulation of epoxy based sizing, a lower amount of curing agent is used compared to the stoichiometric quantity, creating a layer having a higher modulus along with lower fracture toughness. The higher modulus makes the shear stress transfer to the fiber more efficient. Meanwhile, the failure is directed into the matrix because of the decreased fracture toughness. The removal of sizing yields a significant decrease in interfacial shear strength (about 29%). When the desized CFs were resized with epoxy sizing, the interfacial shear strength increased from 39.9 MPa to 49.6 MPa. The increase of interfacial shear strength correlated well with the reduction in contact angles (Figure 5). This indicates that the sizing formulation used here is quite efficient to promote the interfacial properties. For the CNT-grafted CFs, the value of

interfacial shear strength is lowest among all the samples studied in the manuscript. Lv et al. [22] demonstrated that the graft of CNTs onto the CFs can improve the interfacial shear strength between the CNT-carbon fiber hybrids and the epoxy resin. But in our case, opposite results were obtained. The possible reason is that as the CNTs grown here are much smaller and the density is lower, the presence of CNTs did not contribute much to the increase of fiber surface roughness. On the other hand, the CNTs are more hydrophobic than the unmodified CFs, resulting in a poorer wettability with the epoxy resin [23].

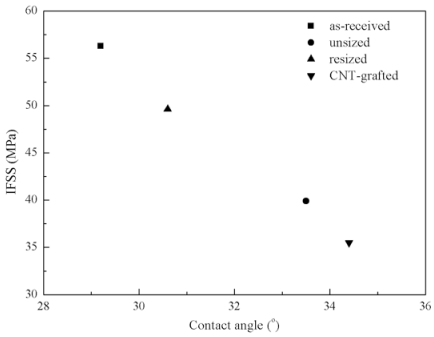

Figure 5. Interfacial shear strength plotted as a function of contact angle.

4. Conclusion

Commercially sized T700GC CFs were desized and then resized with epoxy or grafted with CNTs, to get resized CFs or CNT-grafted CFs. The surface morphologies of the CFs were studied using SEM and the results indicate that resized CFs show lower amount of epoxy adhering to the fibers compared with the commercial as-received CFs, and the CNT-grafted CFs exhibited that CFs are covered with CNTs possessing a diameter around 10 nm. Contact angles between WWA epoxy and CFs were quantified by the LBADSA method and demonstrated that the sizing CFs (as received CFs and resized CFs) possess better wettability (smaller contact angles) than the desized CFs, but it is opposite to the CNT-grafted CFs. Single fiber fragmentation tests were conducted to study the interfacial properties of CFs/epoxy composites. The results showed that the sizing formulation used in this study is quite efficient to improve the interfacial properties, but the CNT-grafting does not have positive effect for the improvement of relative properties.

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