A controllable interface in ZnO nanowires–hybridized carbon fiber composites: A numerical and experimental study

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Abstract
The Interfacial shear strength (IFSS) is a key parameter to determine the service performance of a carbon fiber (CF) reinforced composite. ZnO nanowires (ZWs) grow on the CF surface is a new method to reinforce the IFSS, where ZWs grow radially on carbon fibers to form a hybrid reinforcing phase. But the properties of ZWs are significantly different with varying ZW dimensions, in turn, causes a change in IFSS hence affecting the CFRP performance. To evaluate the optimal interfacial properties of CF composites, a micro-damage model was conducted to study the adhesive properties of a single ZW pullout from the matrix with varying dimensions of ZWs. The cohesive zone approach was used to model the interface between ZWs and the matrix. The simulation results showed that adhesive properties between ZWs and epoxy increase with the increase of ZWs' diameter and length. A pullout test was also conducted to determine the interfacial shear properties of the hybrid CF composites and verify the results of numerical values.

1. Introduction

The interface has a particularly role in fiber-reinforced composite material, which not only a bridge link the reinforce phase and the matrix phase, but also a carrier transfer the stress and other information. The Interfacial shear strength (IFSS) is a key parameter to determine the service performance of a carbon fiber (CF) reinforced composite. In order to improve the interfacial properties, nanofibers are grown on the surface of CF : like carbon nanotube and ZnO nanowires (ZWs). But the high temperature and catalysts required of carbon nanotube will cause the tensile strength of CF significantly decrease[1]. By contract, ZWs grow in a low temperature(<90˚) [2] which do not damage the CF.

ZnO nanowires (ZWs) are the strongest fibers with a nanoscale diameter can substantially improve the Interfacial shear strength (IFSS) of a carbon fiber (CF) reinforced composite. Ulises Galan et al.[3]analyzed the synthesis of ZWs on CF to obtain nanowires with controlled diameter and length and explore how these properties effect the IFSS. Kyungil Kong et al. [4] through the impact test indicated that ZWs grown on woven carbon fibers can improve the energy absorption, because of the cross-linked networks that distributed the energy over the interface area. However, there has been less research on the interfacial properties of ZWs embedded in composites.

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The purpose of this paper is to develop a numerical method to analysis the effect of the dimensions of ZWs on IFSS between fiber and EP. To evaluate adhesive properties between ZWs and EP with varying dimensions, a micro-damage model was conducted to study the adhesive properties of a single ZW pullout from the matrix with varying dimensions of ZWs. The cohesive zone approach was used to model the interface between ZWs and the matrix. In order to verify the results of numerical values, a pullout test was conducted to determine the interfacial shear properties of the hybrid CF composites.

2. Numerical simulations procedures and results

The mechanical properties of ZWs change with the size, and the size is significantly different with different Polyethylenimine (PEI) concentrations and growth time, even in the same growth time and same PEI concentration, there are still have subtle differences in the size of ZWs. To simple the simulation model, a few assumptions are used in this study:

It is assumed that the ZWs are uniformly grown on the carbon fiber, and they are ideally aligned in radial direction;

All the ZWs at each carbon fiber are assumed to have same radius and the length. Based on these assumption, an idealized hybrid fiber pullout problem is illustrate in figure.1
It is assumed that the ZWs are complete contact with EP.

2.1. 3D FEM FOR ZWS PULLOUT FROM EP

A 3D FEM was developed to simulate the single ZW pullout from EP. A pullout displacement was applied on the top of the ZW in the axial direction (Figure.1). In this study, the diameter of ZW was range from 50 to 200nm, the length of ZW was range from 1 to 5μm. The content of ZWs is 5%, and the content of EP is 30%. The matrix was modeled as an isotropic elastic material, and the mechanical properties were shown in Table 1. The ZW was modeled as an isotropic elastic material too, and the mechanical properties were estimated by the extending of core-shell composite nanowire model[5], this model is composed of a cylinder core and a surface shell. The Poisson ratio of ZWs calculated in this study is 0.3[6]. Because of the ultimate strength of the ZWs (about 7GPa)[7] is far greater than the strength of EP and interface, which is neglected in this numerical model.

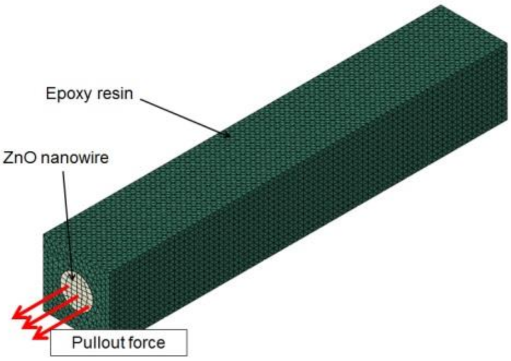

Figure 1. 3D FEM for ZWs pullout from EP.

The Young's modulus of ZnO nanowire is[8]:

$$E = E_0\left[1+8\left(\frac{E_S}{E_0}-1\right)\right]\left(\frac{r_s}{D}-3\frac{r_s^2}{D^2}+4\frac{r_s^3}{D^3}-2\frac{r_s^4}{D^4}\right) \tag{1}$$

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Where: E is the Young's modulus of ZWs; E_0 is the Young's modulus of cylinder core; E_S is the Young's modulus of surface shell; r_s is the depth of the shell; D is the diameter of ZWs;

Table 1. Matrix properties at room temperature used for the numerical simulations.

Elastic properties	*Epoxy TF1408*
Young's modulus (MPa)	2850
Poisson's ratio	0.37

2.2. The interface properties between ZW and EP

In this study, we used the commercial finite-element software Abaqus@ (version 6.10) to carry out the FE calculations. The fiber–matrix interphase is modeled using cohesive behavior with a mixed-mode traction–separation law[9].as illustrated in Figure. 2. The model uses a quadratic stress failure criterion[10] and a Benzeggagh-Kenane (BK) criterion[11] to evaluate the initial damage and crack propagation, respectively. The quadratic stress failure criterion is:

$$\left(\frac{\max\langle \sigma_n, 0\rangle}{N_{\max}}\right)^2 + \left(\frac{\sigma_t}{T_{\max}}\right)^2 + \left(\frac{\sigma_s}{S_{\max}}\right)^2 = 1 \tag{2}$$

Where σ_n , σ_s and σ_t are the stress components of pure normal direction, first shear direction and second shear direction, respectively; $N_{\max}$, $S_{\max}$ and $T_{\max}$ are the interfacial strength of pure normal direction, first shear direction and second shear direction, respectively.

The BK criterion for the crack propagation evaluation is:

$$G_{IC} + (G_{IIC} - G_{IC})\left\{\frac{G_{II} + G_{III}}{G_I + G_{II} + G_{III}}\right\}^{\eta} = G_C \tag{3}$$

Where G_i and G_{iC} ($i = I$, II , III) are corresponding strain energy release rates and fracture toughness under pure mode I, mode II and mode III loadings, respectively; and $G_C = G_I + G_{II} + G_{III}$; η is the BK exponent. And G_{iC} is the area under the traction-separation curve (Figure.2).

For obtaining a well converged simulation model, the interface stiffness in this study was set to 10^7 N/mm^3 [12]. And the σ_n , σ_s and σ_t was calculated by the following equation:

$$\sigma_n = \frac{\phi_n}{\delta_n}\exp\left(-\frac{\Delta_n}{\delta_n}\right)\left\{\frac{\Delta_n}{\delta_n}\exp\left(-\frac{\Delta_n^2}{\delta_n^2}\right) + \frac{1-q}{r-1}\left[1-\exp\left(-\frac{\Delta_n^2}{\delta_n^2}\right)\right]\left[r-\frac{\Delta_n}{\delta_n}\right]\right\} \tag{4}$$

$$\sigma_{t,s} = 2\left(\frac{\phi_n \Delta_{t,s}}{\delta_{t,s}^2}\right)\left\{q + \left(\frac{r-q}{r-1}\right)\frac{\Delta_n}{\delta_n}\right\}\exp\left(-\frac{\Delta_n}{\delta_n}\right)\exp\left(-\frac{\Delta_{t,s}^2}{\delta_{t,s}^2}\right) \tag{5}$$

Where ϕ_n is the interfacial potential of normal separation; δ_n , δ_t , δ_s are the characteristic lengths of cohesive law; Δ_n , Δ_t , Δ_s is the shear separation displacement; the values of parameter q and r are usually selected to reduce the computational efforts. $\sigma_n = \sigma_n^0$, at $\Delta_n = \delta_n$,When Δ_t =0; $\sigma_{t,s} = \sigma_{n,s}^0$, at $\Delta_{t,s} = \delta_{t,s} / \sqrt{2}$,When Δ_n =0.

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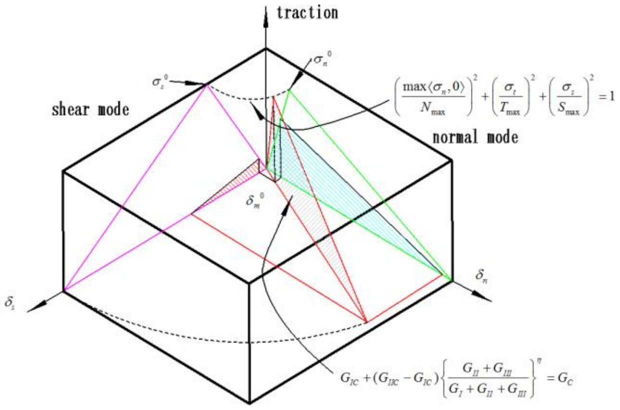

Figure 2. Mixed-mode traction–separation law

3. Micro-dropt debonding test

3.1. Materials

Carbon fibers used in the research were T300-B, which were purchased from Toray Industries, Inc. Analytical grade reagents of Zinc acetate 4ehydrate (99%), zinc nitrate hydrate, sodium hydroxide and hexamethylenetetramine (HMTA) were obtained from Sinopharm Chemical Reagent Co., A 20 wt.% methanol solution of PAMAM dendrimers (Generation 0 to 3) with ethylenediamine core and amino surface groups were obtained from Sigma-Aldrich Chemicals Co., Ltd.

ZWs grown on CF were prepared via a two-step process. First, the ZnO seed layer on the extracted fiber was prepared by the means of dip coating. The ethanol solution of dip coating was composed of zinc acetate 4ehydrate (0.002 M) and sodium hydroxide (0.005 M). After dip coating, the carbon fiber was annealed at 200°C for 15 mins to enhance the adhesion between the fiber and ZnO nanoparticles. Second, ZWs were grown on the carbon fiber using a hydrothermal method. Zinc nitrate hydrate (0.05M) and HMTA (0.05M, 99%) was used as the nutrient solution. The SEM imagines proved that ZWs successfully deposited on the carbon fiber surface (Figure.3).

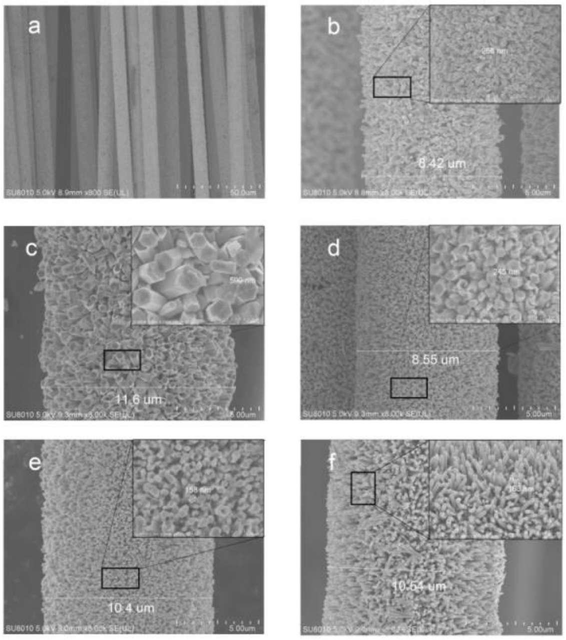

Figure 3. ZnO nanowires shows the uniform distribution on the carbon fiber surface in the large

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scale (a), and the morphology of ZnO nanowires was varied by the ultrasonic dispersion time, PEG concentration and reaction time ((b) 3h/0M/8h, (c) 3h/0M/13h, (d) 0h/0M/8h, € 0h/0.5M/8h, (f) 0h/1M/10h)

3.2. Test sample

The single ZW-CF was bonded on a thin stalloy, and adhered by micro-droplet uncured EP. And then the sample was cured in an oven under normal pressure (0.5MPa) at 120 °C keep 120min.

3.3.Microbond testing

In this section, the IFSS for ZW-CF pull out from EP was measured by HM410-microdroplet test equipment from TOHEI SANGYO, Japan. The force to pull the fiber out of the cured epoxy resin was measured for each specimen, and the interfacial shear strength (IFSS) τ_{IFSS} was calculated by the following equation 错误!未找到引用源。:

$$\tau_{IFSS} = \frac{F_{\max}}{\pi \cdot d_f \cdot l_e} \tag{6}$$

Where $F_{\max}$ is the maximum value of pull out force, d_f is the diameter of single fiber, and l_e is the embedded length of micro-droplet. For the comparable of test results, the embedded length of the EP micro-droplet was controlled in 70-90μm, and the contact angle was controlled in 40-45 ° C.

4. Results and discussion

The simulation results of pullout force versus ZWs diameter curves and pullout force versus ZWs length curves are presented in Figure.4 and Figure.5, respectively. It is can be clear seen in Figure.4 and Figure.5 that the pullout force increases significantly with the diameter and length of ZWs increasing.

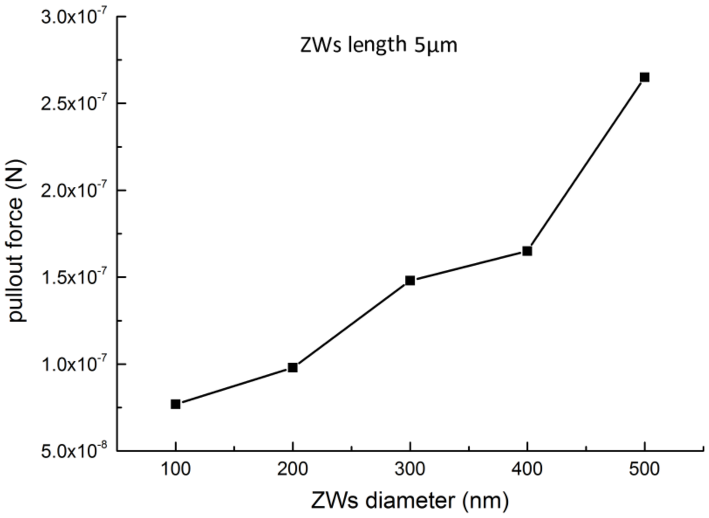

Figure 4. The simulation results of Pullout force versus ZWs diameter

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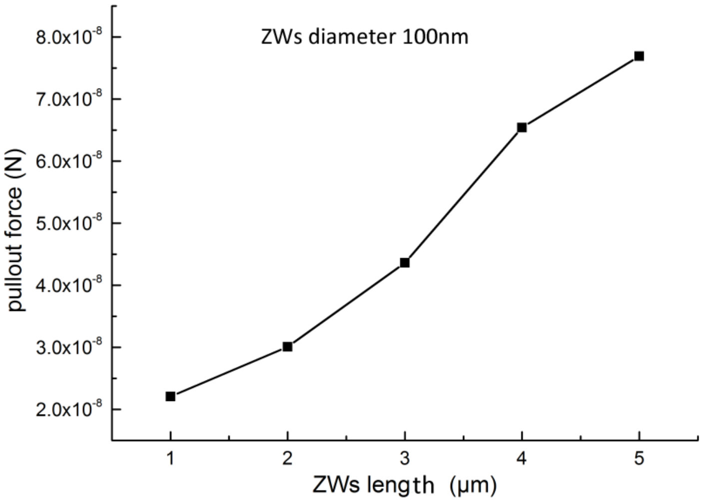

Figure 5. The simulation results of Pullout force versus ZWs length

The dimension of ZWs is influenced by varying the ultrasonic dispersion time, the reaction time and PEG concentration, for the difficult control of all the above factors, the size of ZWs will not create as the size in simulation used. Therefore, to analysis the relationship between IFSS and dimensions of ZWs–hybridized carbon fiber composites, the dimensions of the ZnO nanowires is quantified by the increased surface area of fiber. The surface area of ZWs grown on the carbon fiber used in this study were calculated from the averaged diameter and length measured by Figure. 3. The test results of IFSS versus surface areas of ZWs–hybridized carbon fiber composites are showed in Figure.6. It shows the value of IFSS is increased by surface areas, which means the increment of surface area with the resin matrix can increase proportionally interfacial adhesion, and verifies the results of numerical simulation values.

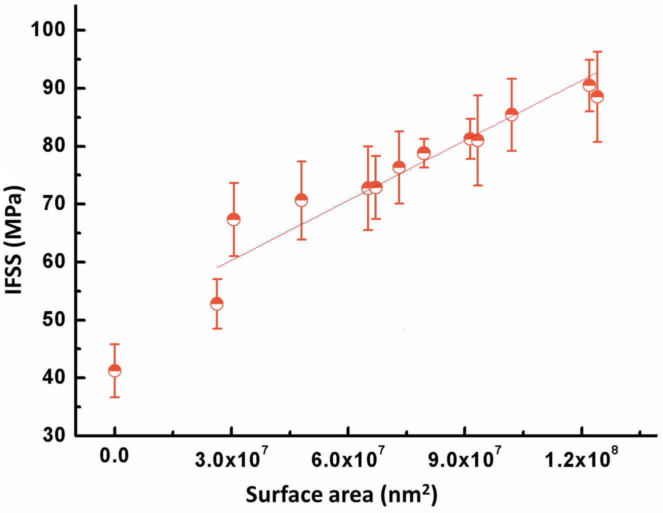

Figure 6. the test results of IFSS versus the surface area of ZWs

5. Conclusions

In this paper, the effects of varying ZW dimensions on the interfacial properties of CF/EP were investigated with a micro-damage model. The simulation results showed that adhesive properties

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between ZWs and epoxy increased significantly with the increase of ZWs' diameter and length. A pullout test was also conducted to determine the interfacial shear properties of the hybrid CF composites. The test results showed that ZnO nanowires (ZWs) grow on the CF surface can reinforce the IFSS of carbon and matrix, and verify the results of numerical values that with the increasing of ZW dimensions the IFSS will increase.

Acknowledgments

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