

Enhancing interfacial properties of carbon fiber/polyamide 6 composites by *in-situ* growing polyphosphazene nanotubes

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Received 12 January 2021; accepted in revised form 13 March 2021

Abstract. We explored a simple approach to grow needle-like polyphosphazene nanotubes (PZSNT) on carbon fibers (CF-PZSNT) via *in-situ* polycondensation under mild reaction conditions, to form a PZSNT-based multiscale reinforcement. PZSNT with abundant free hydroxyl groups can significantly change the chemical surface and increase the specific surface area of carbon fibers. A significant improvement of interfacial shear strength was obtained from 39.7 MPa for the virgin CF/polyamide 6 composites to 69.6 MPa for the CF-PZSNT/polyamide 6 composites.

Keywords: polymer composites, carbon fiber, reinforcements, interface, polyphosphazene nanotubes

1. Introduction

Carbon fiber (CF) reinforced composites have been widely used as structural components due to their excellent mechanical properties, high specific strength and specific stiffness [1]. However, the overall performance of CF reinforced composites is largely controlled by the interfacial structure and interfacial properties between the carbon fiber and matrix. Therefore, many strategies to improve interfacial properties have been proposed [2, 3].

In recent years, it has been demonstrated that multiscale reinforcement, containing carbon fibers together with carbon-based nanofillers (*e.g.*, carbon nanotubes (CNTs)) on the surface of the fibers, can improve the interfacial properties of fiber reinforced composites [2, 4–7]. Chemical vapor deposition (CVD) is effective for directly growing CNTs onto carbon fibers (CFs) to form CNTs-based multiscale reinforcement. For example, Thostenson *et al.* [5] successfully prepared CNTs grown on CFs via CVD. It was demonstrated that the presence of CNTs at the carbon fiber/epoxy resins interface improved the

interfacial shear strength (IFSS) of the composites. A similar approach was described by Qian *et al.* [7] who synthesized CNTs onto CFs. The IFSS of the composites with CNTs exhibited around 60% improvement in comparison to that of the unmodified composites. However, growing CNTs onto CFs through CVD is usually accompanied by a significant decrease in the tensile strength of carbon fibers, which is attributed to the metal catalyst and high temperature deposition conditions in the CVD process [8, 9]. Alternatively, chemical bonding method is also proposed by many researchers for grafting CNTs onto CFs using different coupling agents [4, 10–12]. Zhao and Huang [13] grafted CNTs onto CFs using polyhedral oligomeric silsesquioxane (POSS) as coupling agent, and the IFSS was increased by 105%. Peng *et al.* [4] reported that using poly(amido) amine as coupling agent, CNTs grafted CFs reinforced epoxy composites exhibited the highest IFSS, with around 111% increase in comparison to that of acid-treated CFs reinforced composites. Nevertheless, before grafting CNTs, the carbon fibers must be oxidized to

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presence of benzophenone as indicator, and then distilled and stored in the presence of 4 Å molecular sieves. Other reagents were obtained from Tianjin Damao Co., Tianjin, China, and used as received.

2.2. In situ growth of polyphosphazene nanotubes on carbon fibers (CF-PZSNT)

As shown in Figure 1, the typical preparation process of CF-PZSNT is as follows: commercial carbon fiber was refluxed in acetone for 48 h to remove the sizing, and then oxidized in concentrated HNO₃ at 100 °C for 1 h to introduce oxygen-containing functional onto fiber surfaces (denoted as CF-O). HCCP grafted CF (CF-H) was prepared according to our previous study in [17]. 1.0 g of CF-H was firstly immersed to 60 ml of dry THF. Subsequently, 0.66 g of HCCP (1.9 mmol) and 1.40 g of BPS (6.0 mmol) were successively added, and the molar ratio of HCCP to BPS was set to 1.0:3.15. Next, an excess of TEA (4.0 ml) was added to the flask and reacted in an ultrasonic bath (480 W, 40 kHz) at –5 °C for 1 h. Finally, the modified carbon fiber was taken out and rinsed with THF and deionized water sequentially, to attain polyphosphazene nanotubes grown on CFs (CF-PZSNT).

2.3. Sample preparation for microbond test

In order to investigate the interfacial performance between CF-PZSNT and polyamide 6 (PA6), a microbond test was performed to investigate the interfacial shear strength (IFSS) of carbon fiber/PA6 composites. The preparation process of carbon fiber /PA6 microbond test specimen was shown in Figure 4a. A single carbon fiber was glued to a steel frame with dimension of 26 mm × 58 mm. The free fiber length in the frame was approximately 30 mm. Then, the PA6 monofilament was tied knot on the single carbon fiber. Next, the knotted PA6 monofilament was quickly heated to form small irregular PA6 bead using an electric soldering iron, which was tightly wrapped around the carbon fiber. Finally, the specimens were placed in an oven at a temperature of 230 °C, which was higher than the melting temperature of PA6. The time for specimens being retained in the oven was set to 4 min, to ensure that the PA6 was completely melted and symmetrical PA6 micro-droplets were formed. The specimens eventually cool down to ambient temperature. Each specimen contains about 10 PA6 micro-droplets. Only well-shaped symmetrical PA6 micro-droplets were selected for testing.

2.4. Characterization

The surface topography of carbon fiber was detected using Scanning electron microscope (SEM), which was performed on a Hitachi S-4800 field-emission SEM system (Hitachi Co., Japan). The TEM image of PZSNT was carried out on a Philips Tecnai F20 equipped with an accelerating voltage of 200 kV. The specific surface area was measured based on a Brunauer-Emmett-Teller (BET) adsorption isotherm (Micromeritics Instrument Corporation, ASAP 2020M analyzer, USA).

The surface composition analysis was performed on the AXIS UTLTRADLD electron spectrometer (Kratos, Japan) XPS. The wide scan spectrum was recorded for elemental quantification. Curve fitting was performed on the high-energy resolution spectrum from O_{1s} photoelectron region to resolve the overlapping peaks, and the data were corrected for the charging effect by referring to the graphitic carbon peak at 284.8 eV binding energy.

An interfacial micro-bond evaluation instrument (Model HM410, Tohei Sanyon Corporation of Japan) was used to investigate the interfacial shear strength (IFSS) of composites. The illustration of microbond test was shown in Figure 4a. The carbon fiber was loaded at a speed of 1 μm·s⁻¹ from the PA6 micro-droplet while the force was recorded against the displacement using a computer. The interfacial shear strength, *IFSS*, was determined using the Equation (1) [18]:

$$IFSS = \frac{F_{\max}}{\pi DL_e} \quad (1)$$

where F_{\max} is the force at the moment when interface debonding, D is the carbon fiber diameter, and L_e is the embedded length of carbon fiber in PA6 micro-droplet. The embedded length of the tested micro-droplet was approximately 90 μm. For each type of carbon fiber, about 30 valid data were collected and then averaged.

3. Results and discussion

Figure 1 shows a schematic diagram of the preparation process of CF-PZSNT. The carbon fibers was first oxidized and chemically grafted with HCCP to introduce reactive groups (P-Cl) onto the CFs, which will contribute to the formation of chemical bonds between CFs and polymer nanotubes. Subsequently, polyphosphazene nanotubes (PZSNT) grown on CFs was obtained through one-pot *in-situ* polycondensation

under ultrasonic irradiation at -5°C for 1 h. In the initial reaction period, a large number of polyphosphazene prepolymers and HCl were generated owing to the rapid polymerization of HCCP and BPS. It is noteworthy that the acid acceptor TEA can eliminate the HCl to afford triethylammonium chloride (TEACl) crystals in dry THF. Next, nanometer-sized polyphosphazene nanoparticles and rod-like TEACl crystals were both precipitated out. As shown in Figure 1, the precipitated TEACl crystals were deposited around the carbon fibers due to its high surface energy [19]. In the meantime, a large number of polyphosphazene (PZS) nanoparticles with low surface energy adhered onto the deposited TEACl crystals and CFs. The formation process of polyphosphazene nanotubes has been reported in detail by Zhu *et al.* [19]. PZS nanoparticles adhered onto TEACl crystals and spread over, and then further polymerized to form a stable core/shell structure even under ultrasonication. Finally, polyphosphazene nanotubes were attained by removing TEACl crystals with de-ionized water. In this current study, both the CFs and the deposited TEACl crystals were used as templates. Consequently, in the final reaction period, the PZS nanoparticles spread over the two templates, and the crosslinking reaction between the polyphosphazene prepolymers and PZS nanoparticles further carried out as the polymerization proceeded, resulting in a needle-like PZS nanotubes grown on CFs, as illustrated in Figure 1. SEM was first used to verify the surface topography changes of functionalized carbon fibers. For CF-O, a clean and smooth surface was observed (Figure 2a). By contrast, it can be seen that a large amount of PZSNT was universally distributed on the surface of CF-PZSNT, as shown in Figure 2b and 2c, forming a PZSNT-based multiscale reinforcement. More interestingly, Figure 2c shows that one end of PZSNT was obviously fixed on the surface of the fiber, just like the polymerized needle-like nanotubes with a length of 1–2 μm and an outer diameter of about 20–80 nm were directly grown on CFs. The hollow tubular structure of PZSNT was confirmed by transmission electron microscopy (TEM). Figure 2d and 2e show that the inner diameter of most of the nanotubes was about 5–10 nm, which was consistent with the value reported by Zhu *et al.* [19]. The specific surface area (SSA) of CF-O and CF-PZSNT was measured using Brunauer Emmett Teller (BET) adsorption method. Figure 3a shows that the SSA of CF-PZSNT increased from 0.72 to 1.38 m^2/g ,

which was approximately 92% higher than that of CF-O. In addition, the increased SSA implied that the interface contact area between CF-PZSNT and the polymer matrix could be greatly increased, which might be beneficial to enhance the interface interaction. The surface changes were also evaluated using XPS. Figure 3b shows the XPS wide-scan spectra of CF-PZSNT and CF-O. Table 1 lists the atom percent of the elements in detail. Compared with CF-O, three new elements $\text{P}_{2\text{p}}$, $\text{S}_{2\text{p}}$ and $\text{Cl}_{2\text{p}}$ were detected on the surface of CF-PZSNT, which were originated from HCCP and BPS that were used to prepare PZSNT. Additionally, the percentage of $\text{N}_{1\text{s}}$ slightly increased from 3.5 to 5.5%, while the percentage of $\text{O}_{1\text{s}}$ hardly changed (from 18.3 to 18.9%). To further analyze the surface chemistry of CF-O and CF-PZSNT, Figure 3c and 3d show the fitted curves of the high-resolution $\text{O}_{1\text{s}}$ spectra. In the case of CF-O, three component peaks were observed in the $\text{O}_{1\text{s}}$ spectrum, which were attributed to the C=O group (ketone, lactone, carbonyl group, ~ 531.4 eV), C–OH/C–O–C group (~ 532.8 eV) and chemisorbed oxygen or some adsorbed water [20], respectively. As we all know, XPS analysis can only obtain chemical information within 10 nm from the outermost surface of the fibers, whereas the diameter of polyphosphazene nanotubes grown on CF was much larger than the detected depth (Figure 2d and 2e). Consequently, the $\text{O}_{1\text{s}}$ spectrum of CF-PZSNT was fitted to three component peaks with binding energies at 531.5 eV for the O=S=O groups, at 532.7 eV for the phenolic hydroxyl groups (Ph–OH) and at 533.4 eV for the P–O–Ph groups, according to the reference measurement of Liua and Kim [21] and Dez and De Jaeger [22]. Furthermore, the relative content of the peak corresponding to the phenolic hydroxyl group (Ph–O–H) was 16.2% (Table 2), indicating that many free hydroxyl groups were generated on the outer surface of CF-PZSNT, which could effectively improve the wettability between CF and polar resin matrix, thereby enhancing the interfacial bonding of the composites. Figure 4 shows the IFSS results of PA6 composites reinforced with a series of carbon fibers. CF-PZSNT composites exhibited highest IFSS (69.6 MPa), which has an increase of 75.3% in comparison with CF composites (39.7 MPa) and about 32.8% in comparison with CF-O composites (52.4 MPa). It was clearly confirmed that the 75.3% increase in IFSS was owing to the multiscale structure of CF-PZSNT composites. As we all know, the phenolic hydroxyl

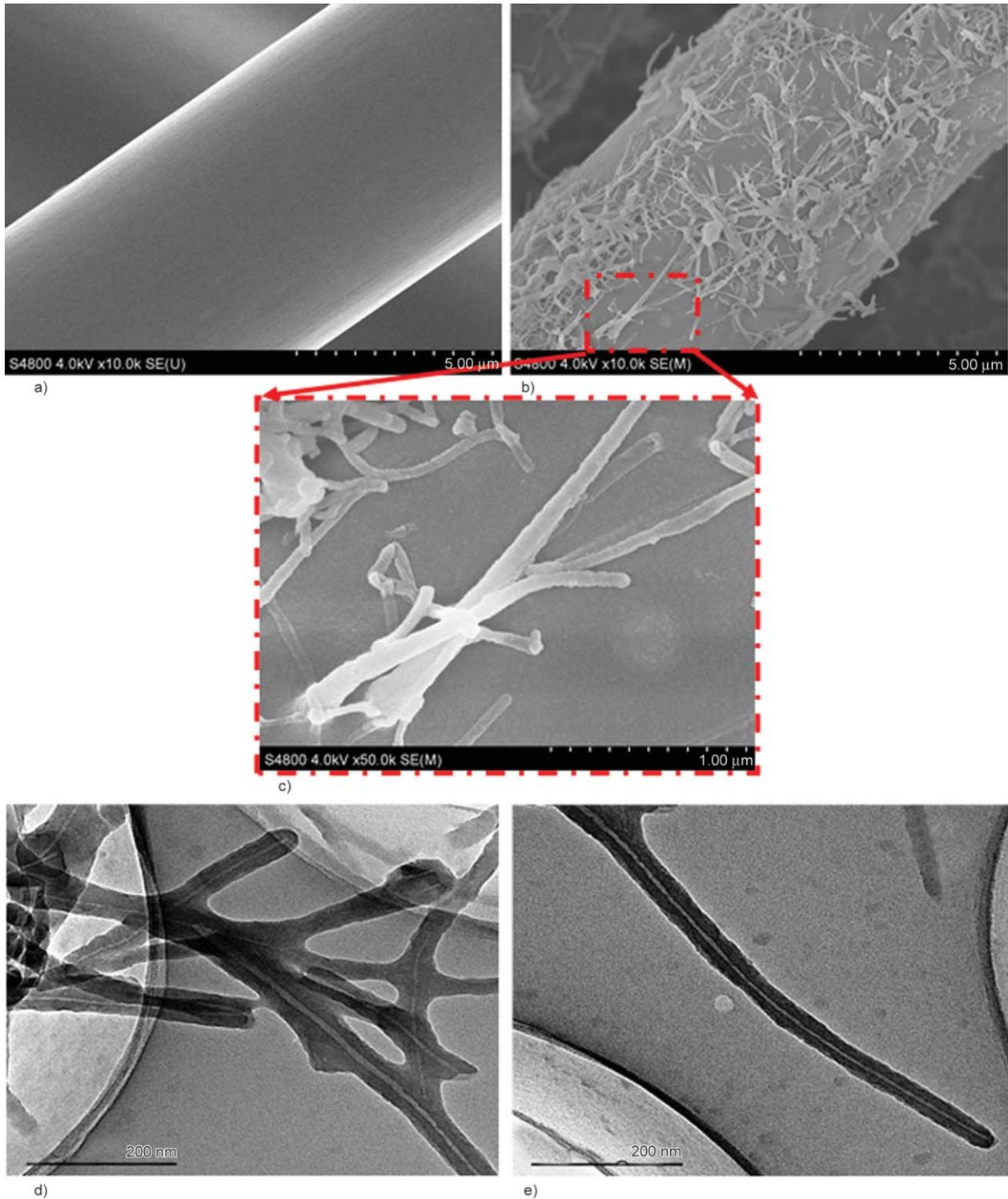


Figure 2. The SEM images of CF-O (a), CF-PZSNT (b) and the red dashed pane area in image (b) with higher magnification (c). The TEM images of polyphosphazenes nanotube (PZSNT) (d and e).

groups (Ph-OH) of PZSNT on CF could form hydrogen bonds with the amide groups (O=C-N-H) of PA6, thereby preventing PA6 chain from slipping. In addition, the polyphosphazene nanotubes can not only increase the surface area but also penetrate into the matrix, enhancing the mechanical interlocking with PA6. Therefore, the PZSNT-based multiscale

reinforcement with oxygen-containing functional groups contributed to enhance the interface interaction between CF and the polymer matrix. This was mainly owing to the potential hydrogen bonds as well as mechanical interlocking between PZSNT and PA6, thereby significantly improving the interface performances of the composites. In order to further

determine the reasons for such an improvement, the surface morphologies of CFs de-bonding from the PA6 matrix were analyzed using SEM, as shown in Figure 5. In the case of CF, the de-bonded CF surface

appeared smooth and almost no PA6 residue. This result suggested that the interface was easily de-bonded due to the weak van der Waals force interaction between CF and the PA6 matrix. Contrary to CF, in the case of CF-PZSNT, the de-bonded fiber shown a rough surface and was wrapped with a thin layer of PA6. It was noteworthy that polyphosphazene nanotubes (PZSNT) grown on CFs were broken and embedded in the residual PA6, as shown in Figure 5c and 5d, which was different from the results reported by Chen *et al.* [16]. This might be attributed to the

Table 1. Surface element content of CF-O and CF-PZSNT.

Sample	Element content [atom%]					
	C _{1s}	O _{1s}	N _{1s}	P _{2p}	S _{2p}	Cl _{2p}
CF-O	78.4	18.3	3.3	–	–	–
CF-PZSNT	65.7	18.9	5.5	4.6	4.2	1.1

Table 2. Relative content of oxygen-containing groups on CF and CF-PZSNT.

Sample	Binding energy ^a [eV]	Relative content [%]	Oxygen-containing groups
CF-O	531.4	21.8	C=O/O=C–OH
	532.8	71.6	C–O–C/C–OH
	534.5	6.6	O ₂ /H ₂ O
CF-PZSNT	531.5	44.9	O=S=O
	532.7	16.2	Ph–OH
	533.4	38.9	P–O–Ph

^aRelative content of oxygen-containing groups was calculated according to the fitted peak area, which was obtained from high-resolution O_{1s} spectrum.

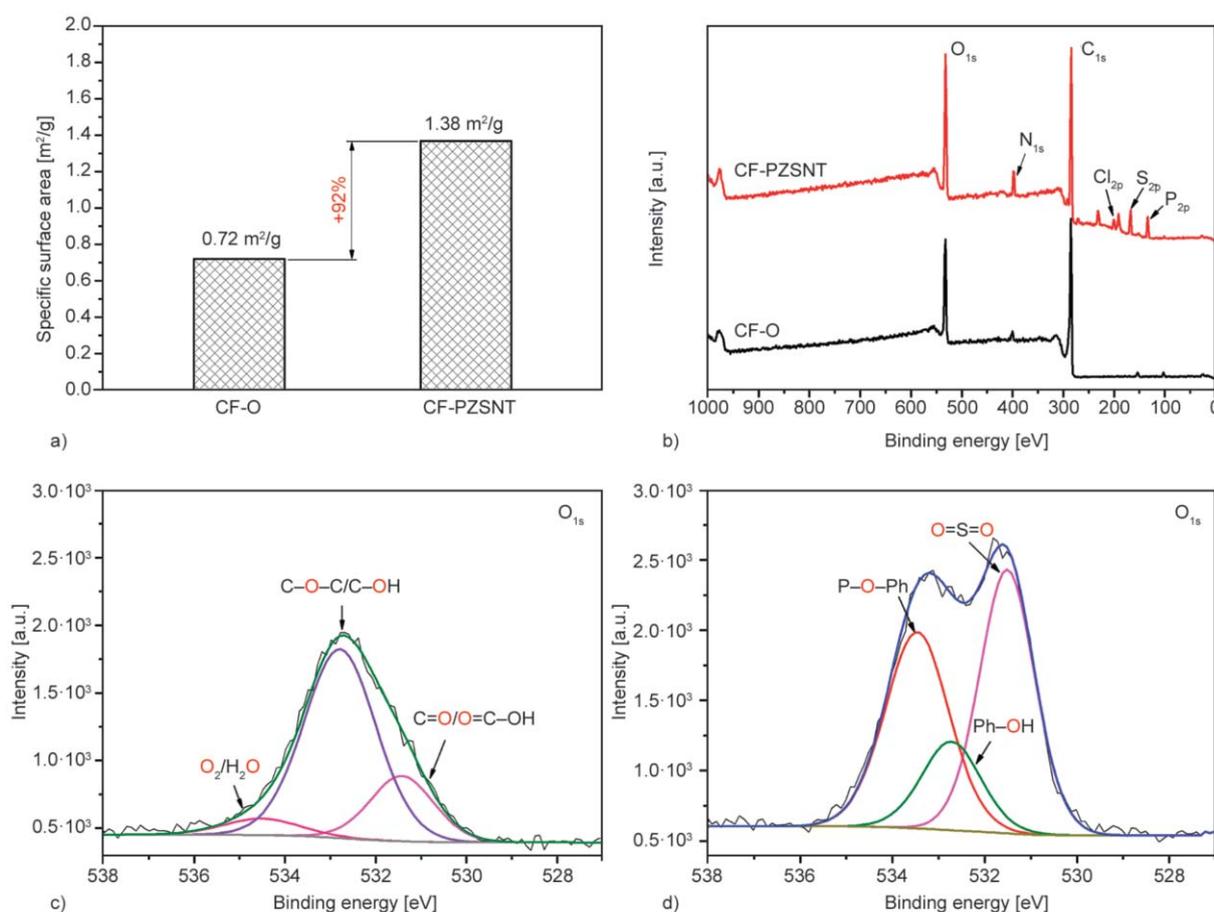


Figure 3. N₂ BET specific surface areas of CF-O and CF-PZSNT (a); The wide XPS spectra of CF-O and CF-PZSNT (b); High-resolution XPS O_{1s} spectra of CF-O (c) and CF-PZSNT (d).

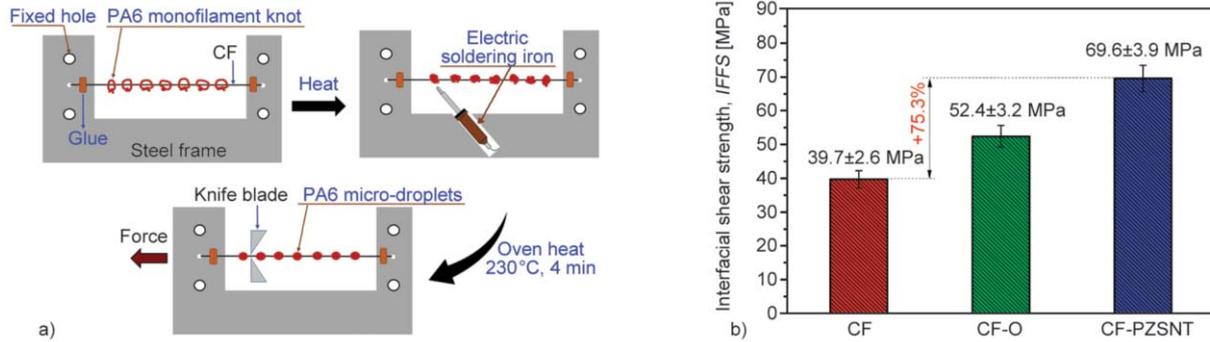


Figure 4. Schematic diagram of the preparation process of carbon fiber microbond test specimen, not to scale (a); IFSS results of PA6 composites reinforced with CF, CF-O and CF-PZSNT (b).

type of resin matrix. The embedded PZSNT indicated a strong bonding between PZSNT and CF, because it grown directly on CFs through *in-situ* polymerization (confirmed by SEM, see Figure 2c). Meanwhile, PZSNT enhanced the hydrogen bonds and mechanical interlocking between CF-PZSNT

and PA6 matrix, resulting in effectively transferring stress from matrix to the multiscale reinforcement (CF-PZSNT). These are the possible reasons why PZSNT-based multiscale reinforcement can significantly improve the interfacial performance of PA6 composites.

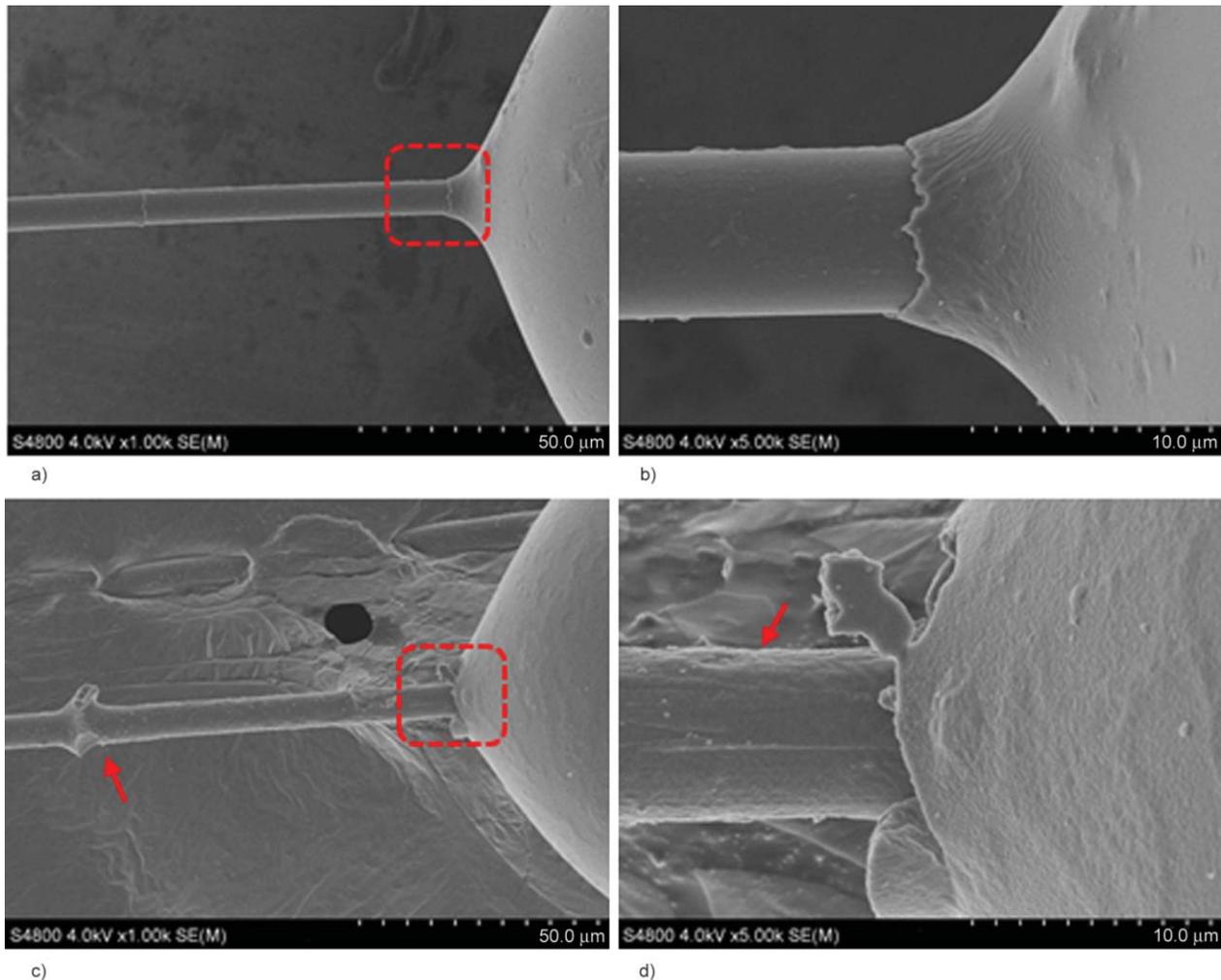


Figure 5. SEM images of the carbon fibers after de-bonding: (a) CF; (b) the red dashed pane area in image (a) with higher magnification; (c) CF-PZSNT; (d) the red dashed pane area in image (c) with higher magnification.

4. Conclusions

In this work, PZSNT-based multiscale reinforcement was prepared by in situ growth of polyphosphazene nanotubes on carbon fibers. Many PZSNTs with free phenolic hydroxyl groups were uniformly distributed on the carbon fiber surface, which might contribute to the formation of the hydrogen bonds and enhance the mechanical interlocking between the carbon fibers and PA6 matrix. The CF-PZSNT reinforced PA6 composites exhibited higher IFSS, with approximately a 75.3% increase in comparison to that of CF reinforced PA6 composites.

Acknowledgements

This study were financially supported by the Guangzhou Science and Technology Plan Project (No.20180410326), Guangdong Province Research and Development Plan of Key Areas (No.2019B010929001), Dongguan Innovative Research Team Program (No.2020607212008) and the Guangzhou Emerging Industry Development Fund Project of the Guangzhou Development and Reform Commission.

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