



Polyphosphazene nanotubes/carbon fibers hierarchical hybrid reinforcement for improving interfacial adhesion of polyamide 6 composites

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Abstract

Continuous carbon fibers (CFs) reinforced thermoplastic composites have been gradually used as lightweight structural components for their excellent mechanical performances. However, the interface debonding and earlier damage of the composites tend to occur under external loading due to the inherently poor interfacial bonding between CFs and thermoplastic matrix. Herein, a layer of hierarchical poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) coating combining with nanotubes (PZSNTs) was assembled uniformly surrounding CFs surfaces to enhance the interface adhesion of the CF-reinforced polyamide 6 (CF/PA6) composites. Atomic force microscopy (AFM) and dynamic contact angle (DCA) measurement demonstrated that the PZSNTs coating significantly improved the surface roughness, wettability and surface energy of the modified CFs. An evident enhancement of interfacial shear strength (IFSS) was obtained from 37.68 to 52.32 MPa for CF-PZSNTs reinforced PA6 composites, showing an increase of 38.8% in comparison with that of the bare CF/PA6 composites. The fracture surface morphologies of CFs showed that there was more fragmented resin residue adhering to the fibers surfaces. It means that the transition of the PZSNTs coating not only significantly enhanced the interfacial wettability and mechanical interlocking between the fibers and PA6 matrix but also provided a loading absorption/transfer layer that could efficiently transfer stress and assist in holding back excessive stress spreading in the flaw and improve overall mechanical properties. The construction of PZSNTs layer could improve the surface roughness, wettability and polarity of the CF-PZSNTs, thus bring the IFSS enhancement of the fiber-reinforced thermoplastic PA6 composites.

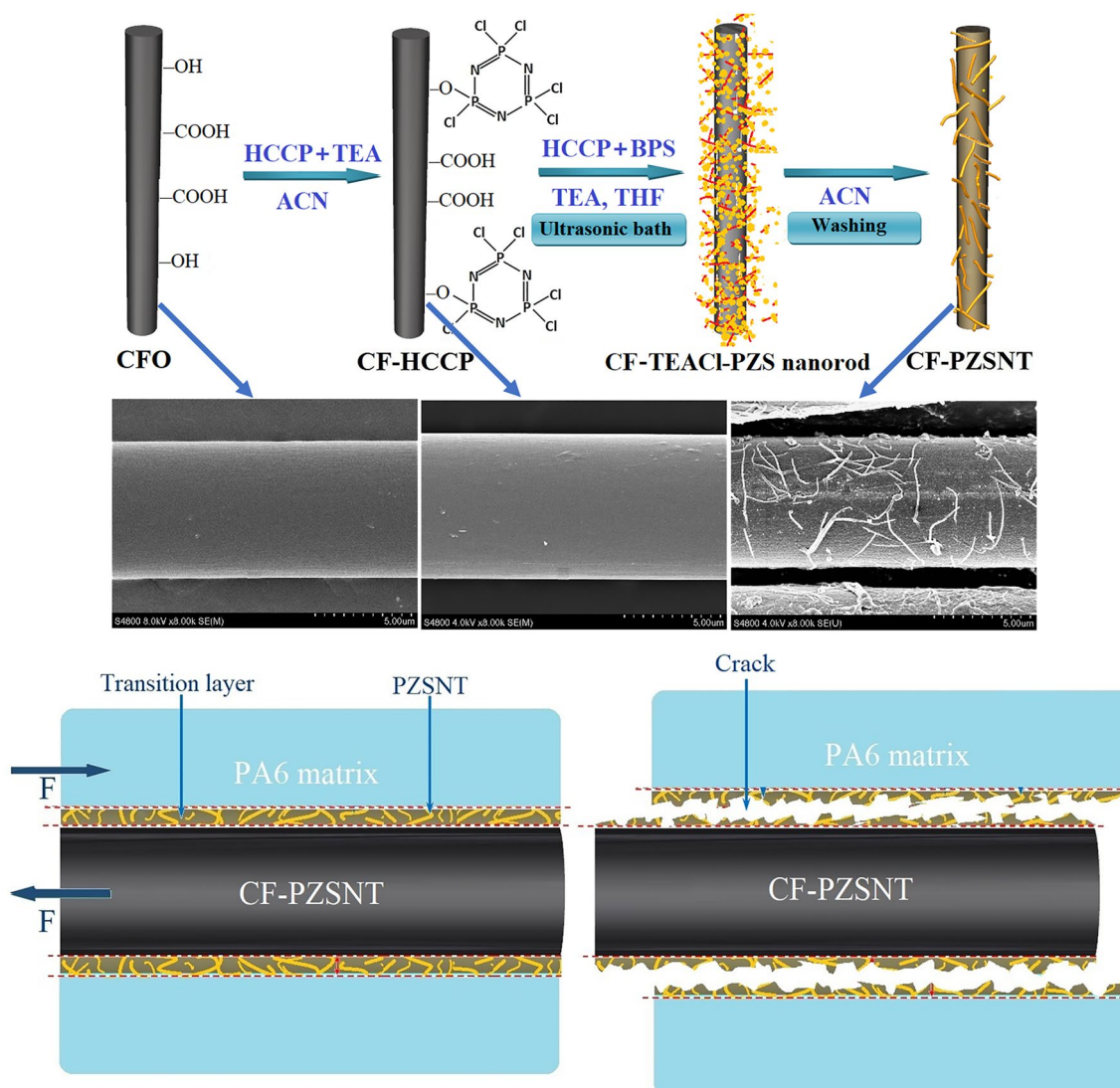
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Graphical abstract



Keywords Carbon fiber · Interfacial property · Polyamide · Composites · Nanotube

Introduction

Continuous carbon fibers (CFs) reinforced polymer composites have been widely used as lightweight, high-performance structural materials for their excellent mechanical properties [1–3]. However, the interfacial adhesion of carbon fibers composites tends to be weak for suffering from poor adhesion to matrix polymers [4, 5], especially for thermoplastic composites. The weak interface adhesion severely limited the reinforcing efficiency of CFs-reinforced thermoplastic composites and further restricted its engineering application on sophisticated occasions [6].

Hence, considerable efforts such as electrochemical oxidation [7, 8], plasma treatment [9, 10], surface sizing or coatings [11], chemical grafting [12, 13], electrophoresis deposited [14, 15], and other hierarchical modification methods [16] have been made on the surfaces of the CFs to enhance the mechanical interlocking, wettability and molecular binding of the fiber reinforced composites.

It is also speculated that the introduction of hierarchical reinforcements at the interface between CFs and thermoplastic matrix has become a promising strategy to achieve more excellent interfacial properties because of the synergistic effects of nanoparticles, such as graphene, carbon nanotubes or nanoclay [17–19]. Nevertheless, the treatment

processes are so complicated that it only can be carried out in the laboratory and even inevitably damage the body of fibers, due to the high temperature with metal catalysts, vigorous pre-oxidation and a long reaction time [20]. In addition, the overlapping of agglomerated nanoparticles in the matrix may lead to earlier initiation of the debonding process.

In our previous work, we have found that poly(cyclotriphosphazene-*co*-4,4'-sulfonyldiphenol) (PZS) nanotubes (PZSNTs) grown on carbon fibers by a surprisingly simple polycondensation can improve interfacial adhesion of CF/EP composites effectively [21]. In this latest research, we prepared PZSNTs/CF hierarchical hybrid enhancements with the optimization parameters and studied the influence of CFs modification on the interfacial interaction of CFs/PA6 composites. The results showed that the interface adhesion between CF-PZSNTs and PA6 is significantly improved compared with bare CFs, which was proved by the interfacial shear strength (IFSS) test of CFs/PA6 composites. It has potential application in improving interfacial properties during the surface modification production line for the manufacturing process of fiber-reinforced high-temperature thermoplastic prepregs or composites [22, 23].

The purpose of introducing a hierarchical PZSNTs layer on the fibers surfaces was to improve overall mechanical properties and, most of all, to enhance the interfacial adhesion of CFs/PA6 composites. The surface morphology, roughness, chemical composition, wettability of CFs, interfacial properties and failure mode of these composites were also explored.

Experimental

Materials

Commercially available T700S CFs (Toray, Japan) with a diameter of 7 μm were used in this study. Polyamide 6 (PA6, 1.13–1.15 g cm^{-3} , 210–220 $^{\circ}\text{C}$) is an injection molding grade resin, bought from Nanjing Hongrui Plastic Products Co., Ltd., Nanjing, China. Hexachlorocyclotriphosphazene (HCCP, $\text{N}_3\text{P}_3\text{Cl}_6$, 1.98 g cm^{-3}) was obtained from Zibo Lanyin Chemical Co., Ltd., China. Bis(4-hydroxyphenyl) sulfone (BPS, $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}$, 1.366 g cm^{-3}), tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$, 0.89 g cm^{-3}) and triethylamine (TEA, $\text{C}_6\text{H}_{15}\text{N}$, 0.728 g cm^{-3}) (AR, 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Anhydrous acetonitrile (ACN, $\text{C}_2\text{H}_3\text{N}$, 0.78 g cm^{-3}) was bought from Shanghai Aladdin Industrial Co., Ltd. The other chemicals (concentrated nitric acid and anhydrous alcohol) were obtained from Sinopharm Chemical Reagent Co., Ltd. Anhydrous THF was prepared by refluxing in the presence of benzophenone and sodium under nitrogen protection. PA6

must be dried under vacuum at 100 $^{\circ}\text{C}$ for 8–12 h before using it.

Surface modification of carbon fibers

The preparation processes of poly(cyclotriphosphazene-*co*-4,4'-sulfonyldiphenol) nanotubes/CFs (CF-PZSNTs) hierarchical hybrid reinforcements have schemed in Fig. 1. First, the T700 CF were washed in acetone by Soxhlet apparatus at 90 $^{\circ}\text{C}$ for 36 h to get rid of polymer sizing and contaminants (registered as bare CF), and then the bare CFs were oxidized in concentrated nitric acid (HNO_3) at 100 $^{\circ}\text{C}$ for 2 h introduce some oxygen-containing functional groups (denoted as CFO).

Secondly, HCCP grafted CFO as the intermediate product of hierarchical carbon fiber reinforcement was prepared according to our previous work [21]. The CFO was functionalized with HCCP and TEA in anhydrous acetonitrile to yield HCCP-modified fibers (registered as CF-HCCP). Thirdly, HCCP (0.30 g) and BPS (0.50 g) were put into the round-bottom flasks with dry THF (15 mL and 60 mL, respectively) and underwent ultrasonic-assisted dissolution. Then immediately, the CF-HCCP was immersed into the flask with a mixture solution of HCCP/THF and BPS/THF. Subsequently, the TEA (3 mL) was rapidly dripped into the above reaction mixture and the modification was carried out in an ultrasonic bath (100 W, 40 kHz) at 40 $^{\circ}\text{C}$ for 0.5–2 h to obtain cross-linked polyphosphazene-modified carbon fibers.

Finally, the modified CF was cleaned with anhydrous alcohol 2–3 times and then extracted with anhydrous acetonitrile for 8 h, to clear out by-product (triethylamine hydrochloride and oligomers) and unreacted monomers completely, followed by vacuum drying at 60 $^{\circ}\text{C}$ for 6 h to obtain micro-nano hierarchical hybrid carbon fiber reinforcements, named CF-PZSNTs.

Characterization

The microscopic and interface morphologies of CFs before and after modification were analyzed with a scanning electron microscope (SEM) (S-4800, Hitachi, Japan). The microstructure of PZSNTs was also investigated by transmission electron microscopy (TEM) (JEM-2100, Hitachi, Japan) operated at 200 kV. PZSNTs were scattered in ethanol by ultrasonic bath for 0.5 h, subsequently, dropped onto the copper grids for observation.

The surface morphology and roughness of PZSNTs hybrid coating were obtained by atomic force microscope (AFM) (Dimension 3100V Veeco, USA) in tapping mode. An area of 5 $\mu\text{m} \times 5 \mu\text{m}$ was scanned and evaluated by R_a , which represents the average roughness in the measuring range.

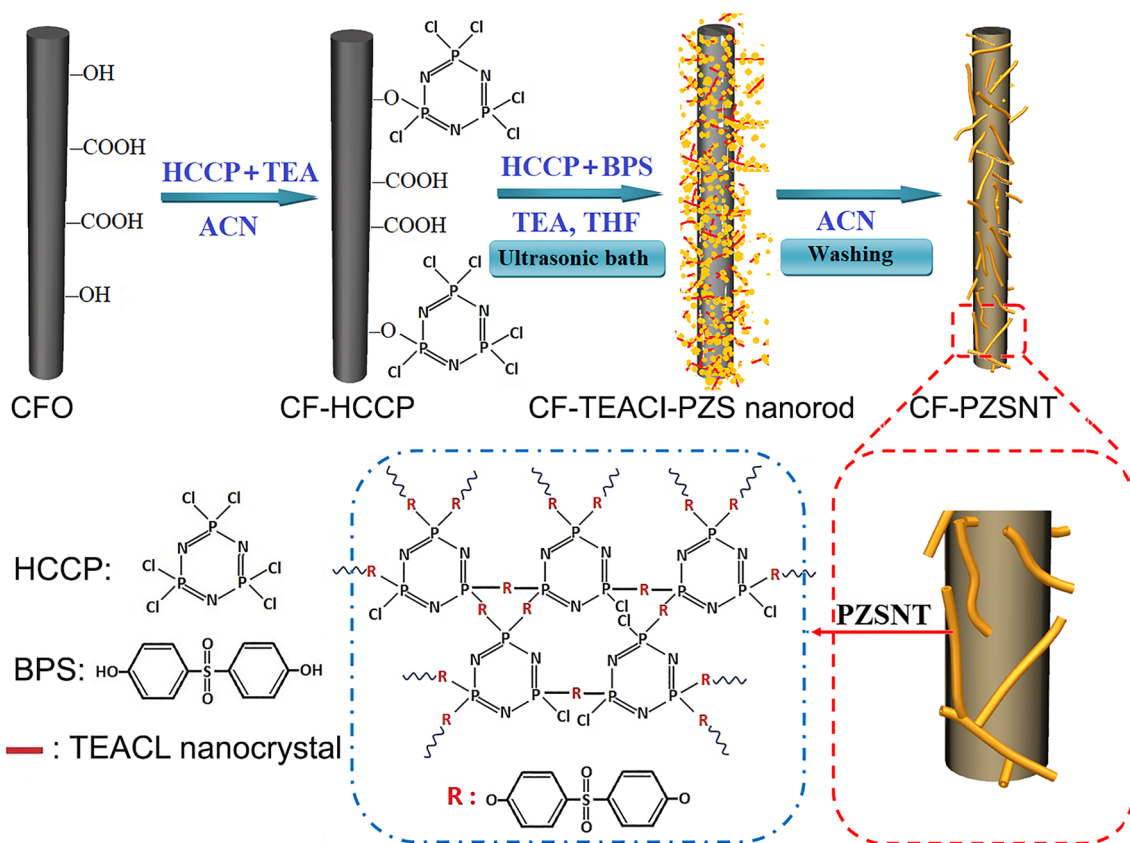


Fig. 1 The schematic preparation of PZS coating and PZSNTs on carbon fiber

The surface chemical structures of fibers were detected by a fourier transform infrared spectroscopy (FTIR) (Nicolet, Nexus-6700, USA) using pressed KBr powder tablets, the preparation process of KBr tablets with carbon fibers is given in Supplementary Materials S1. The FTIR measurements were conducted via scanning the samples 32 times in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution ratio of 2 cm^{-1} .

The surface chemical compositions of carbon fibers before and after modification were analyzed by means of X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Shimadzu, Japan) to evaluate the typical element's chemical status of CF-PZSNTs coating and study the modifying reaction process at a base pressure of 2×10^{-9} mbar with Al K α excitation radiation (1486.6 eV).

Dynamic contact angle tests were operated to evaluate the surface energy of fibers with a dynamic contact angle meter and tensiometer (DCAT21, Germany) according to our previous works [24, 25]. The details of the calculation of the dynamic contact angle and surface energy of carbon fibers are given in Supplementary Material S2.

The debonding experiments of single fiber microdroplet composite were examined to estimate interface bonding performance between CFs and PA6 matrix using the interfacial

evaluation equipment (HM410, Japan). CFs/PA6 monofilament composites were prepared by a melt-impregnating technique based on a delicate heating device equipped with inert gas system which is specially embed in the interfacial evaluation equipment for the preparation of the thermoplastic samples and examined by the micro-droplet debonding test method [25]. The sample preparation diagram of the monofilament CFs/PA6 micro-droplet composite was shown in Fig. 2a. All samples were stored in a desiccator at room temperature for 36 h before the debonding test. The schematic of the single fiber microbond test was presented in Fig. 2b, and the details of the calculation of IFSS are presented in Supplementary Material S3.

Results and discussion

Surface morphology analysis

The surface morphologies of CFs before and after modification were observed by SEM, as shown in Fig. 3. Apparent morphologic variation can be detected between the bare and modified fibers. The results showed that the surface of the received CF may appear to be uneven, and there are

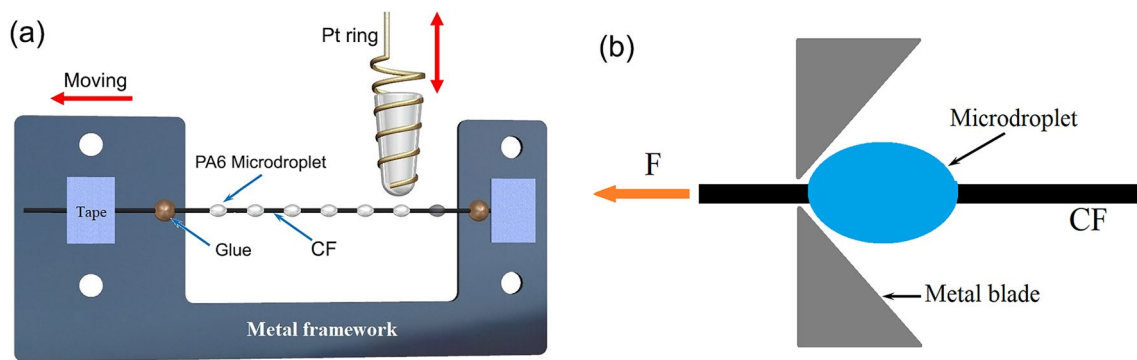
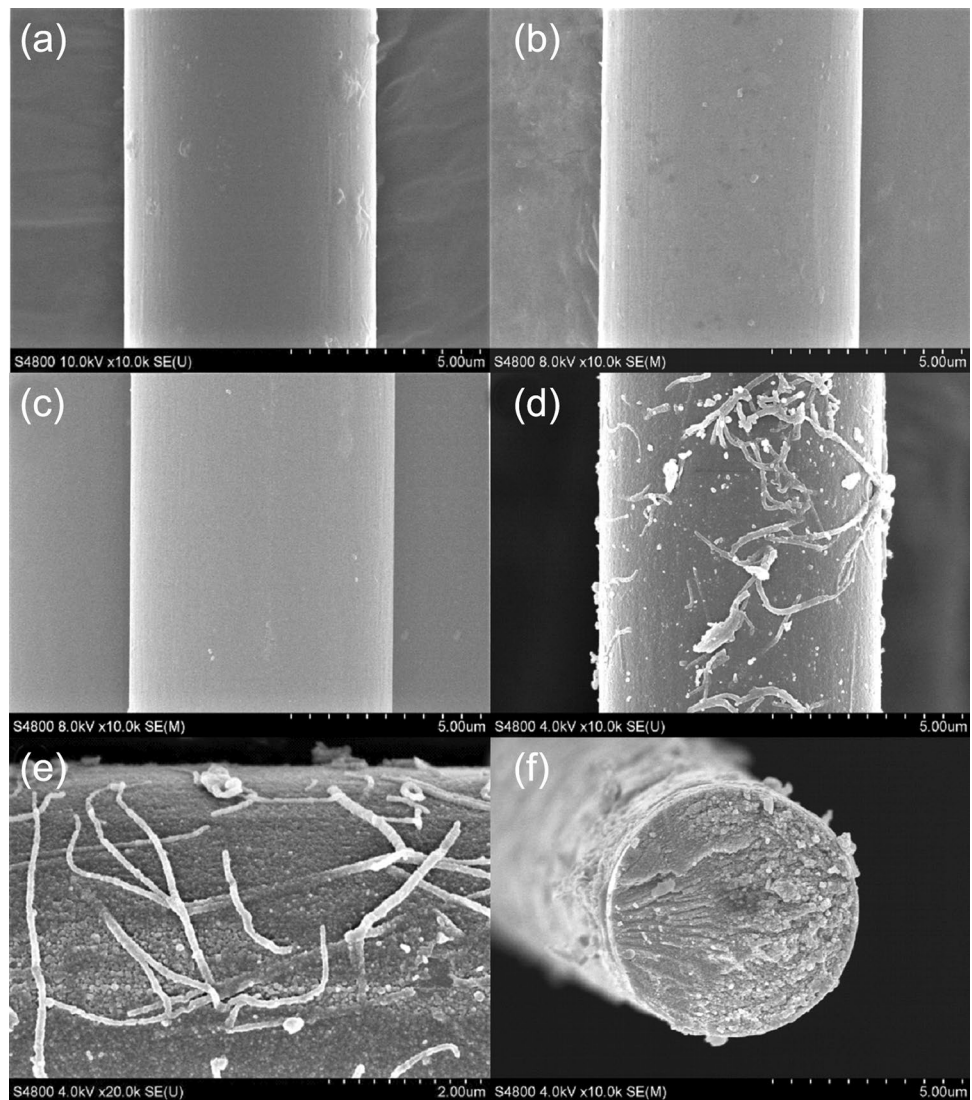


Fig. 2 Schematic diagram for CFs/PA6 micro-debonding test: **a** specimen preparation, and **b** single fiber micro-bond test

Fig. 3 SEM micrographs of fiber surface: **a** received CF; **b** bare CF; **c** CFO; **d** and **e** CF-PZSNTs; **f** CF-PZSNTs transverse cross section



commercial sizing coatings and small bumps on the fiber surface (Fig. 3a). From Fig. 3b and c, it can be seen that both bare CF and CFO show a similarly clean and smooth surface

alongside a little residue sizing, and there are some subtle microgrooves distributed along the longitudinal direction of the fibers.

Fig. 4 TEM images of PZSNTs (Scale bar: **a** 500 nm and **b** 100 nm)

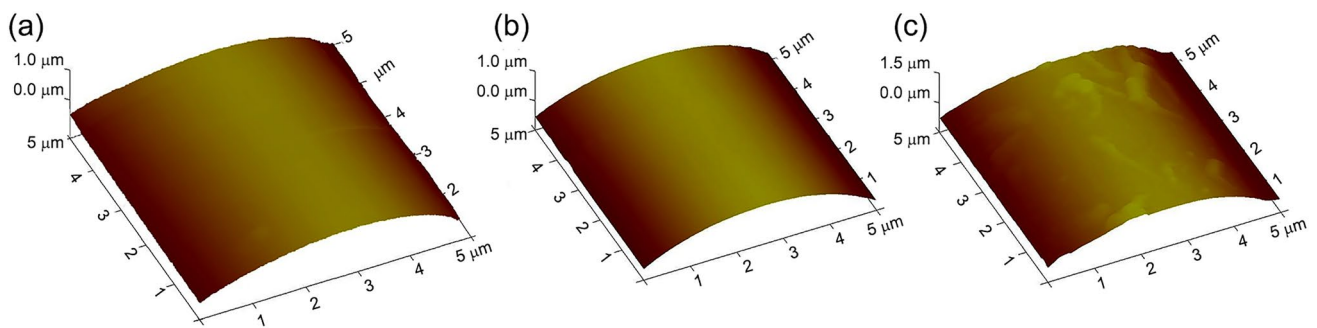
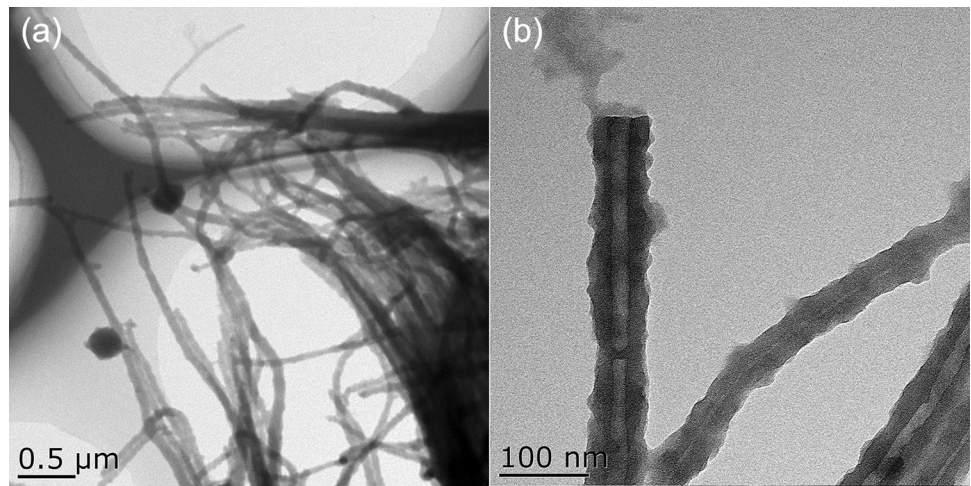


Fig. 5 The AFM images of: **a** bare CF, **b** CFO and **c** CF-PZSNTs

The typical SEM micrographs of the PZSNTs-deposited carbon fibers are shown in Fig. 2d and e, a new hierarchical structure consisting of polymer coating and nanotubes on the fiber surface was achieved, and the formation mechanism and core/shell structures of PZSNTs have been revealed in detail elsewhere [21]. Cross-linked PZSNTs distribute with random orientation and uniform dispersion on the fiber surface, which formed an interconnected or decentralized hierarchical network with only a few agglomerates.

The typical SEM morphology of the CF-PZSNTs transverse cross section is shown in Fig. 3f. It is obvious that a layer of coating with a thickness of 50–80 nm compactly deposited on the fiber surface, and lots of PZS nanoparticles were attached to the coating surface, the nanotube on the fiber surface were even buried partly by these nanoparticles. It was also beneficial to fix the PZSNTs on the surface of fiber tightly.

The TEM images of PZSNTs are displayed in Fig. 4a and b. The clusters of PZSNTs look like flexible noodles with hollow tubular structures and rough walls. A type of the tube is a few micros in length, with an inner diameter of about 10–20 nm and a shell thickness of about 20–40 nm (Fig. 4b). In a word, SEM and TEM images showed that the inner

Table 1 Surface roughness of fibers

Sample code	CF	CFO	CF-PZSNTs
R_a (nm)	20.94 ± 2.72	15.08 ± 3.21	43.44 ± 4.15

and outer surfaces of the nanotubes were rough and made of closely arranged nanoparticles, which can further prove that these polymer nanotubes were assembled by active nano poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) particles.

Furthermore, the surface topographies and properties of CFs were examined by AFM. As shown in Fig. 5, the surface of bare CF and CFO looks clean and smooth with a roughness (R_a) of 20.94 and 15.08 nm, respectively (Fig. 5a and b in that order). After modification, the surface roughness increased owing to the formation of a hybrid PZS coating with a lot of PZSNTs on the fiber surface. The R_a value of CF-PZSNTs (Fig. 5c) was reached 43.44 nm and the average R_a of different fibers are listed in Table 1.

The AFM analysis was consistent with the aforementioned SEM results, that is to say, the increased R_a can provide multiplied contact area and nano-scale mechanical

interlock between carbon fibers and matrix, thus enhancing the composite's interfacial bonding strength [26, 27].

Surface chemical composition

Wide-scan XPS spectroscopy was used to appraise the surface chemical compositions of CFs. The elemental compositions of CF-PZSNTs and CFO are displayed in Fig. 6 and listed in Table 2. As one can see, three new elements of P2p, S2p and Cl2p were detected in the CF-PZSNTs spectrum besides the elements of O1s, N1s and C1s in CFO, due to the introduction of the hybrid PZS coating which contain phosphorus, sulphur and residue of chlorine [25]. In addition, according to our previous work [21], the percentage of N1s and O1s slightly increased from 1.66% and 17.73% to 4.69% and 19.09%, respectively. Moreover, the O/C ratio increased from 0.22 to 0.28, all indicating that the PZS coating and nanotubes have been successfully assembled on the carbon fiber surface by an in-situ polymerization process. In addition, the C 1s spectra were further fitted to estimate the functional groups on fiber surfaces before and after modification, and found that many polar groups were introduced onto the fiber surface. The details are shown in Supplementary Material S4.

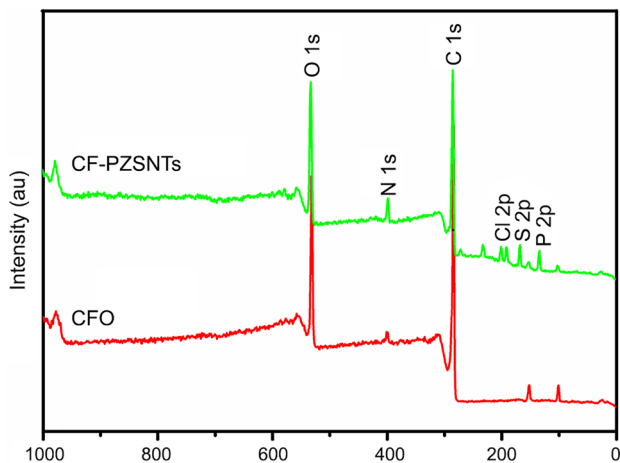


Fig. 6 Wide-scan XPS spectroscopy of CFO and CF-PZSNTs

Table 2 Surface element analysis of carbon fibers [21]

Sample code	Element content (atomic %)							
	C	O	N	Cl	S	P	O/C	S/P
CFO	80.61	17.73	1.66	–	–	–	0.22	–
CF-PZSNTs	67.46	19.09	4.69	1.43	3.41	3.92	0.28	0.87

Surface wettability analysis

The higher surface energy of the fibers is beneficial to the wettability and permeability between CFs and PA6 matrix, thus improving the interfacial adhesion strength of CF/PA6 composite. As shown in Table 3, the contact angle ($^\circ$), the surface energy (γ) including the dispersion component (γ^d) and polar component (γ^p) of the CFs before and after modification are listed in detail. It is clear that a declining trend in contact angles of bare CF, CFO and CF-PZSNTs was observed from 71.8 to 44.3 (Min) for polar water and from 63.5 to 51.2 (Min) for non-polar diiodomethane (DIM), correspondingly. Besides that, for bare CF, CFO and CF-PZSNTs, surface energy and its components increased from 37.5 to 57.8 (Max) mJ/m^2 , 11.0 to 24.9 (Max) mJ/m^2 and 26.5 to 32.9 mJ/m^2 , respectively.

The improvement of polar components could be interpreted by the creation of numerous polar PZS functional groups on CFs surfaces. The increase in dispersive components may be attributed to the improvement of surface roughness arising from PZSNTs and other nanoparticles on the modified fibers surfaces and the difference in surface chemical structure between cyclomatic-type polyphosphazene coating and carbon fibers (CF and CFO) [21, 28]. Therefore, both the γ^p and γ^d helped to make CFs have higher surface energy for plenty of polar groups and increased surface roughness, which is beneficial to the subsequent formation of the infiltration performance of molten PA6 and the mechanical interlock with polymer matrix, thus to improve interfacial properties of the resulting CFs reinforced composites [29].

Table 3 Contact angles and surface energies of CFs

Sample code	Contact angle ($^\circ$)		Surface energy (mJ/m^2)		
	Water	DIM	γ^p	γ^d	Γ
CF [21]	71.8 ± 4.3	63.5 ± 4.8	11.0	26.5	37.5
CFO [21]	62.1 ± 5.1	61.4 ± 0.7	16.3	27.7	44.0
CF-PZSNTs-0.5 h	55.5 ± 5.1	56.6 ± 3.3	19.1	30.5	49.6
CF-PZSNTs-1 h [21]	44.3 ± 1.9	52.4 ± 4.1	24.9	32.9	57.8
CF-PZSNTs-2 h	50.2 ± 3.1	51.2 ± 4.6	20.9	33.6	54.5

Interfacial property of composites

The IFSS results of CFs/PA6 composites are displayed in Fig. 7, at first a mild decrease in the IFSS value (37.68 MPa) with a decrement of 3.83% compared with that of the received CFs/PA6 was obtained owing to the removal of the commercial sizing. For the introduction of PZS coating with nanotubes on CFs via in-situ template polymerization, the IFSS of CF-PZSNTs/PA6 composites was 52.32 MPa, which was an evident improvement of 38.9% and 23.7% in comparison with bare CF/PA6 and CFO/PA6 composites (42.28 MPa), respectively. It is confirmed that introductions of PZS coating and PZSNTs on the CFs surfaces were contributed to enhance significantly the interface strength of the resulting composites.

The improvement of the interface strength may be mainly related to the enhanced surface energy, better wettability and permeability, and potent mechanical interlocking between the hierarchical CFs and PA6 matrix caused by the introduction of PZSNTs surrounding the fibers in composites, which was similar to those of CF/PA6 composites modified with CNTs [27]. Furthermore, better dispersion of PZSNTs on the CFs surfaces was also contributed to the good interfacial performance of composites, and PZSNTs embedded on the CFs surfaces not only expanded the effective contact area but also could penetrate into the polymer matrix to increase more anchor points with PA6. Thus, it can be concluded that the potential loading transition layer as well as mechanical interlocking microstructure between hierarchical modified carbon fibers and PA6 matrix mainly helped to the obvious improvement of the interfacial and mechanical performances of CF-PZSNTs/PA6 composites.

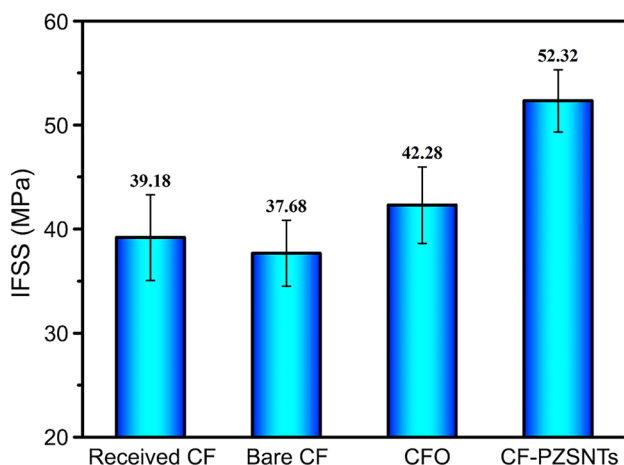


Fig. 7 IFSS test of received CF, bare CF, CFO and CF-PZSNTs

Interfacial microstructure analysis

To further dissect the interface behavior and the improvement mechanisms of interfacial adhesion after modification, the fracture surface morphologies of the different fibers debonding from the PA6 matrix were observed by SEM and the results are shown in Fig. 8. These SEM micrographs of fracture surfaces can help us to understand the reinforcing mechanisms of hierarchical hybrid coating together with PZSNTs functionalized carbon fiber.

For bare CFs/PA6 composites (Fig. 8a and b), the fracture surface is clean, this indicates that the interfacial bonding between bare CFs and PA6 matrix was held together by relatively weak bonds, and appearing a typical feature of interface failure.

As for CFO, the debonding CF surface (Fig. 8c and d) looks quite smooth. There was almost no PA6 residue on the fiber surface after de-bonding. This means that the interface was easily damaged due to the weak interaction between CFO and PA6, and showing the common interface failure mode [29].

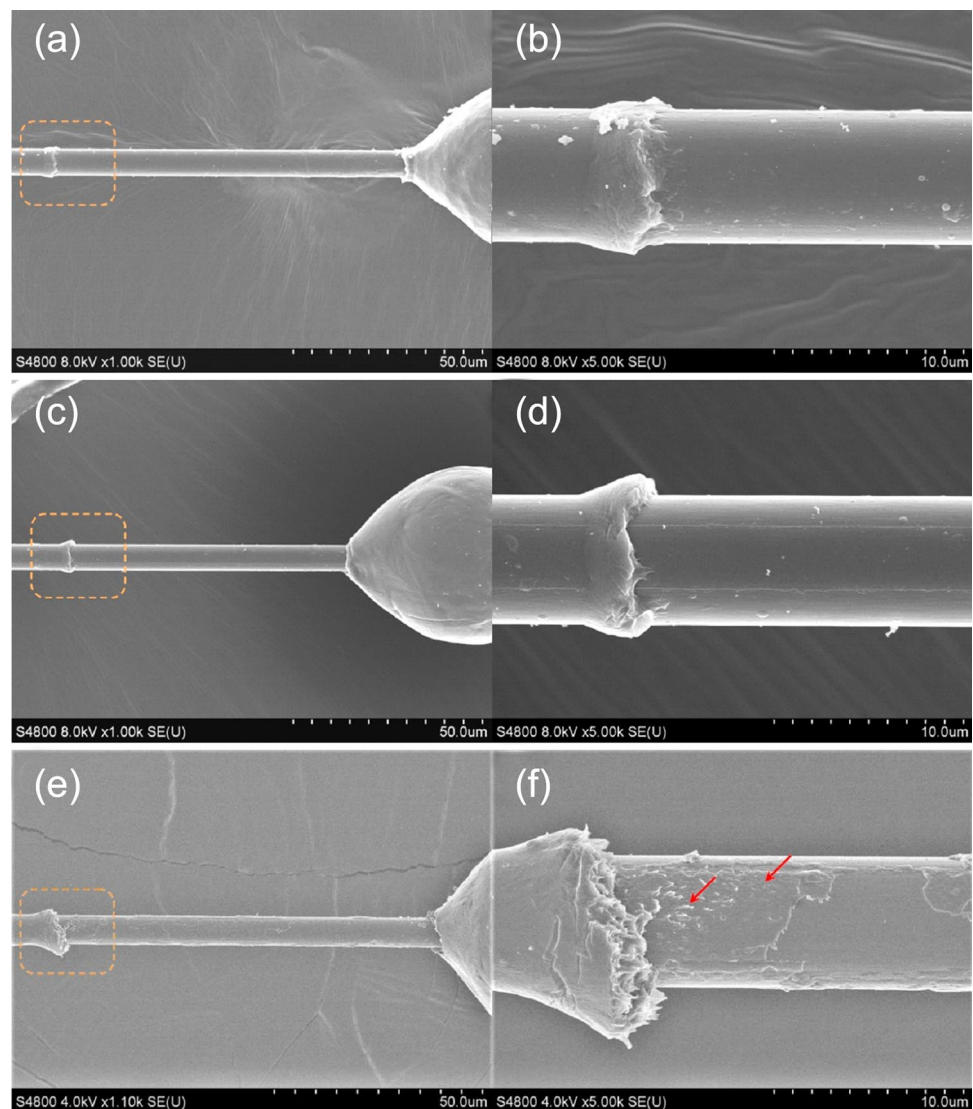
While, for CF-PZSNTs/PA6 (Fig. 8e and f), we can notice that there was obvious fragmented resin adhering to the fiber surface and an amount of PZS coating or resin (marked in red arrows in Fig. 8f) existed on the fractured interface region, indicated that the interface between CF-PZSNTs and PA6 was so strong that debonding failure was not confined to the interface region only, mainly presenting a cohesive failure mode. That is, the interfacial interaction between fiber and matrix has been obviously improved after modification with PZS coating and PZSNTs. These observations were consistent with the IFSS results, the stronger the interfacial adhesion, the more remaining resin on the fiber surface.

From the analytical comparison of the debonding CFs surfaces, we can deduce that these PZSNTs and PZS coating acted as a bridge to connect CF-PZSNTs and PA6 resin. By inserting it to the hierarchical composite interface region they can obviously improve the interfacial adhesion of composites. They enhanced the wettability, permeability and the effective contact area of fibers and strengthened mechanical interlocking between fibers and matrix, which is believed will enhance the IFSS of the CFs composites.

In addition, when stress was imposed on the modified CFs/PA6 composites, for one thing, the load transferred from the matrix to fibers through the hierarchical composite interface, and the cracking initiation was restricted. On the other hand, the PZSNTs coating can prompt crack diversion and refrain crack propagation at the interfacial region. In other words, the interfacial adhesion of CF-PZSNTs/PA6 was better than those of the unmodified CF/PA6.

As stated in the preceding, the significant improvements in surface roughness, wettability and interfacial properties for CF-PZSNTs/PA6 were achieved compared to CF/PA6

Fig. 8 SEM micrographs of debonding fibers in micro-bond test: **a, b** CF, **c, d** CFO and **e, f** CF-PZSNTs



and CFO/PA6 composites. In that way, the transition effect of the hierarchical PZS layer can provide a positive contribution to improve the interfacial adhesion performances of the CFs composites and offer valuable guidance for enhancing the interface bonding strength of other carbon fiber reinforced thermoplastic composites.

To further understand the probable mechanisms of hierarchical PZS coating at the interface region for the improvement of interfacial adhesion, a set of intuitive illustrations of the interface region of CFs/PA6 composites is shown in Fig. 9. For bare CF and CFO, there is almost no PA6 matrix remains on the fiber surface after interface debonding because of adhesion failure (Fig. 9a and b). The interface failure may occur on the fiber surface due to the weak interfacial interactions, thus the interface debonding occurs easily. For CF-PZSNTs, there are many PA6 resin residues and PZS coating fragments on the debonding surface (Fig. 9c), so the interface failure may transfer to dominant cohesive

mode, which is confirmed by the remaining PA6 resin on fiber surface (Fig. 8e and f).

The construction of PZSNTs on the carbon fiber surface, endows fiber composites with a hierarchical composite interface (Fig. 9c), which can augment fracture area and play an anchoring role to improve the interfacial interaction (Fig. 10). Moreover, the PZSNTs interphase at the interface region of CF-PZSNTs/PA6 composites worked as a physical force absorption layer, which could transfer and disperse the stress evenly and help to restrain excessive propagation of cracks and change the paths of crack tips in the flaw, to improve overall mechanical properties [29, 30]. This made clear that the interface adhesion of CF-PZSNTs/PA6 composite was much stronger than that of the unmodified CF/PA6 composites. The observations are consistent with the IFSS testing results, which indicated that the stronger interface strength leads to increased residual PA6 resin on the debonding fiber surface. In a word, the improvement of

Fig. 9 Proposed failure mechanism of CFs/PA6 composites: **a** bare CF, **b** CFO and **c** CF-PZSNTs

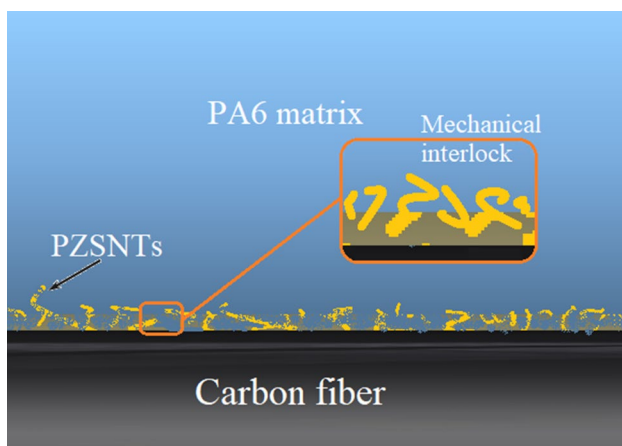
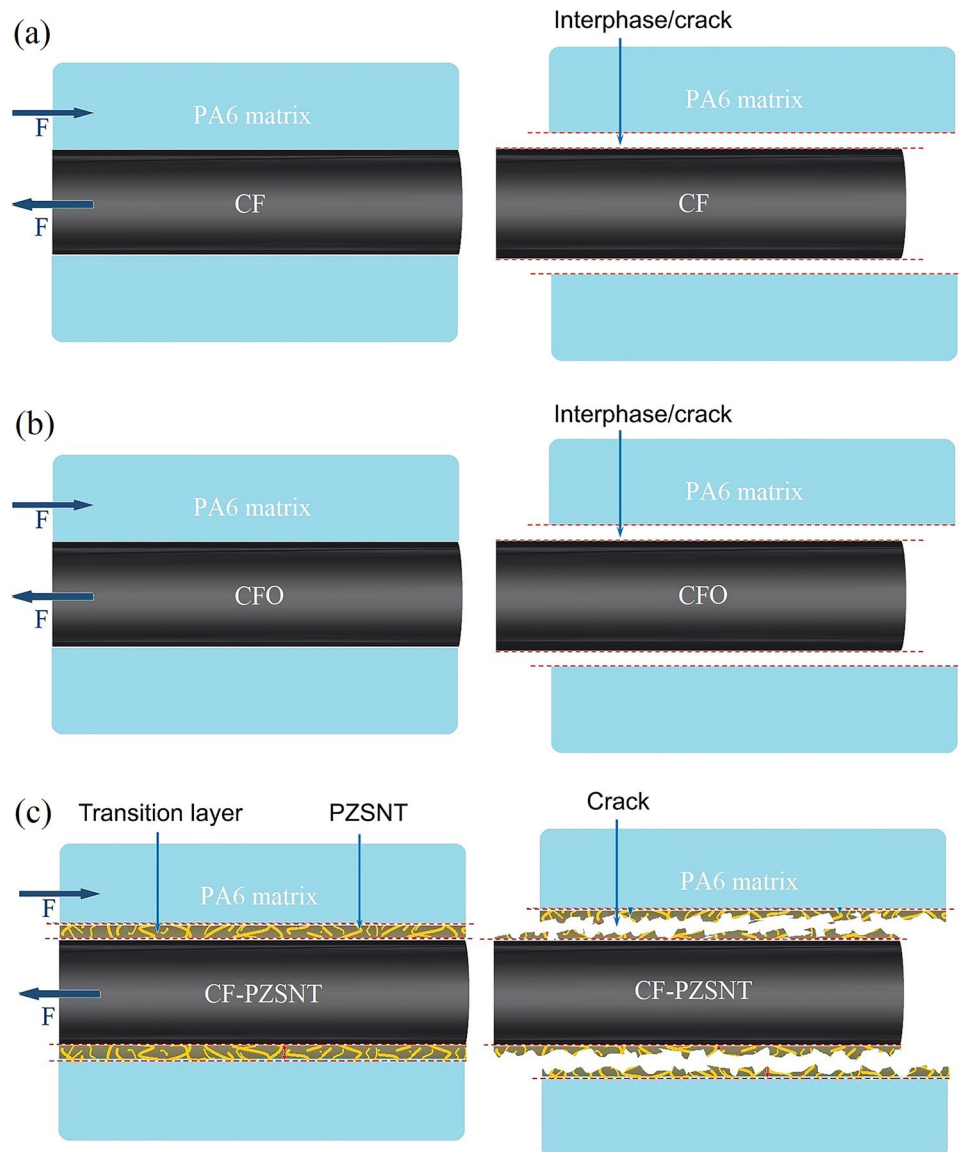


Fig. 10 The schematic diagrams of microscopic mechanical interlocking

interfacial adhesion properties can be attributed to the fact that higher surface energy, better wettability and reasonable mechanical interlocking were borne between carbon fibers and the PA6 matrix under processing conditions.

Conclusion

In this work, the surface functionalization of carbon fibers was successfully prepared with a hybrid poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) coating combining with nanotubes via a facile in-situ template polymerization. A large number of PZSNTs were deposited onto the CFs surfaces with random orientation, which markedly enhanced the surface wettability, compatibility and roughness of fibers to improve the interface interactions and

bonding of CFs/PA6 composites. The results showed that the interfacial bonding strength of CF-PZSNTs/PA6 composites was improved significantly. The presence of PZSNTs can provide the CFs with higher surface energy, better wettability and permeability, proper surface roughness and a loading transition layer, which were responsible for the IFSS enhancement of the composites. The interface enhancement mechanisms of CFs/PA6 composites and failure mode were also studied in detail. This facile interface modification method can be used for versatile and expandable fabrication of high-performance carbon fibers reinforced thermoplastic composites.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13726-023-01180-x>.

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Data availability The data underlying the manuscript are available within the manuscript and its online supplementary materials.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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