

Environmentally Friendly Sizing Strategy for PBO Fiber-reinforced Composites through Building Carbon Nanosphere Coatings

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Electronic Supplementary Information

Abstract Sizing treatment has shown great potential in improving the interfacial properties of poly(*p*-phenylene benzodioxazole) (PBO) fiber-reinforced composites, but is severely limited due to the use of flammable and explosive organic solvents. Herein, a new high-efficiency waterborne sizing agent has been developed by using functionalized carbon nanospheres (CNSs) as a nano-reinforcement. Due to abundant oxygen-containing groups, the CNSs greatly improves the surface activity, wettability, and roughness of the PBO fibers. As a result, the interfacial shear strength of the CNSs sized fiber-reinforced composite increases by 79.6% compared with that of the pristine fiber-reinforced composite. Moreover, the excellent mechanical and thermal properties of the PBO fibers remain almost unchanged after sizing treatment. Thus, this work provides an environmentally friendly and scalable method for constructing a strong interface between the PBO fibers and the matrix resins, which makes sense in promoting the application of PBO fiber-reinforced composites in aerospace and military industries.

Keywords Carbon nanospheres; Sizing treatment; PBO fiber-reinforced composites; Environmentally friendly; Scalable methods

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INTRODUCTION

Poly(*p*-phenylene benzodioxazole) (PBO) fibers have been considered as one of the most promising reinforcements for resin matrix composites due to their ultra-high strength and modulus, as well as excellent heat resistance, chemical resistance, and flame retardancy.^[1–4] However, the surface of PBO fibers is very smooth and chemically inert, resulting in weak interfacial bonding with the resin matrix, which severely impairs the mechanical strength of their composites.^[5,6] Therefore, the surface modification of PBO fibers becomes a research topic of great scientific significance and practical value.

Various techniques, including plasma modification, coupling agent treatment, oxidative fluorination modification, chemical grafting, etc.,^[7–10] have been developed to enhance the surface activity of PBO fibers. Among these, the grafting of carbon nanomaterials, such as carbon nanotubes and graphene oxide, onto the surface of PBO fibers to fabricate micro/nano multiscale reinforcements has been proven to be an effective method to improve the interfacial properties.^[11–17] However, the reaction conditions of chemical grafting are relatively harsh, requiring the use of strong

acids or bases, and multi-step reactions, which will inevitably reduce the intrinsic mechanical properties or heat resistance of PBO fibers.^[18,19]

Sizing treatment is an important pre-processing step in the industrial preparation of prepregs, which is characterized by simplicity, mildness, and scalability.^[20–23] Recently, the introduction of nanoparticles into sizing agents to improve their interfacial enhancement efficiency has become a research hotspot. Our group previously reported an efficient sizing agent for PBO fibers by incorporating amino-functionalized nanosilica and benzoxazole compatibilizers.^[24] Tang *et al.* coated calcia-doped ceria nanoparticles on PBO fibers by sizing treatment, which considerably improved their interfacial bonding strength with cyanate resins.^[25] However, most sizing agents developed for PBO fibers need to be prepared with dimethyl sulfoxide, acetone, ethyl acetate, etc., as solvents. These organic solvents are flammable and explosive, which will seriously pollute the environment and threaten the safety of operators.^[26–28] Therefore, there is an urgent need to develop a high-efficiency waterborne sizing agent to meet the development concept of green and sustainable chemistry.

Carbon nanospheres (CNSs) are a kind of spherical carbon nanomaterials, which have large specific surface area, high conductivity, excellent mechanical, and thermal stability, and have been widely used in the preparation of various function-

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al materials.^[29,30] Moreover, compared with other carbon nanomaterials, CNSs are inexpensive, readily available, and rich in active groups (such as carboxyl, hydroxyl, and epoxy groups) without further treatment. Herein, CNSs were used for the first time to prepare a novel high-efficiency waterborne sizing agent for PBO fibers (Scheme 1). Epoxy resins, as one of the thermosetting resins that have been widely studied and applied, were selected as the matrix resins here due to the advantages of low cost, good process performance and high interfacial bonding strength.^[31,32] The excellent reinforcement effect of CNSs on the interface of PBO fiber-reinforced composites was deeply studied. This simple, efficient, and pollution-free route enables it to be scaled up from laboratory to industrial production, which is of great significance for promoting the application of PBO fiber-reinforced composites.

EXPERIMENTAL

Materials

High modulus PBO fibers, with an average diameter of 17.5 μm , were obtained from Zhongke Jin Qi Co., Ltd. CNS water dispersion was purchased from Beijing Deke Daojin Science and Technology Co., Ltd. E-51 epoxy resin and 4,4'-methylene-bis(2-ethylaniline) (H-256) were received from Wuxi Bluestar Epoxy Co. (China) and Hubei Jusheng Technology Co. (China), respectively. All chemicals and solvents were used as received.

Preparation of CNS Sizing Agent

CNSs were added to deionized water at controlled concentrations of 0.5 wt%, 1 wt%, 2.5 wt% and 5 wt%, respectively. The mixture was sonicated at a frequency of 40 kHz for 1 h to form a well-dispersed sizing agent.

Fiber Treatment

PBO fibers were first ultrasonically washed with acetone for

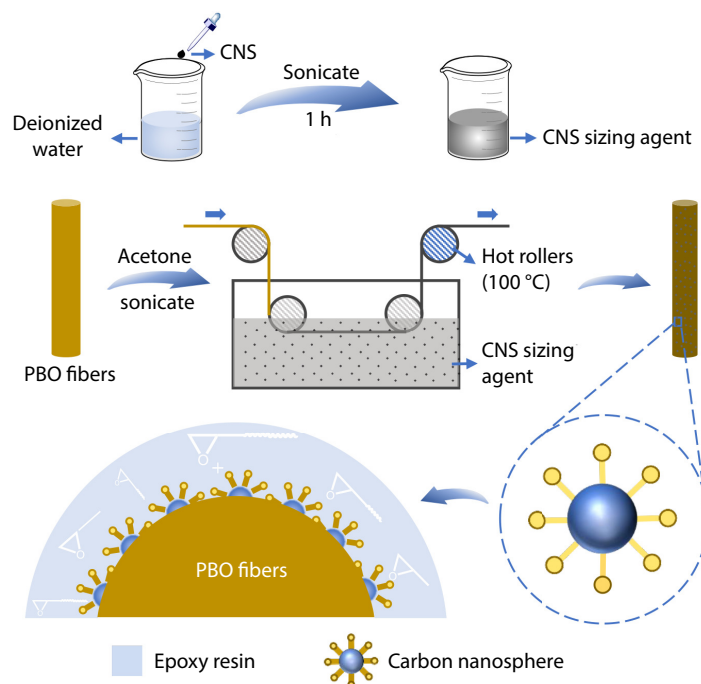
three times, and then dried at 100 °C for 2 h to remove the original sizing agent and contamination prior to use. Then, the CNS sizing agent was introduced onto the PBO fibers by a laboratory-made sizing device, as shown in Scheme 1. In brief, the pristine PBO fibers were pulled through the CNS sizing agent and dried on hot rollers at 100 °C. The pulling speed was kept slow enough to achieve good wetting of the fibers and prevent any possible damage. The PBO fibers coated with different CNS contents were named as PBO-C0.5, PBO-C1, PBO-C2.5, and PBO-C5, respectively.

Preparation of PBO Fiber-Reinforced Composites

The PBO fiber-reinforced composites were prepared by a hot-pressing process. In a typical experiment, the epoxy resin (GT-807A-1) containing the curing agent (GT-807B-1) was evenly brushed on the surface of the satin-wave PBO fabrics. Subsequently, the obtained prepregs were neatly stacked in a mold and hot-pressed at 90 °C and 5 MPa for 3 h. The content of PBO fabrics in the composites was controlled at about 70 wt%.

Characterizations

The particle size and zeta potential of CNSs in aqueous solution were tested on a dynamic light scattering instrument (Zetasizer Nano-ZS, Malvern). A He-Ne laser, which has a wavelength of 633 nm and a fixed detector angle of 90°, was adopted in the tests. The X-ray photoelectron spectra of the samples were recorded using a ESCALab 250Xi (Thermo Scientific) equipped with a 200 W monochromatic Al K α radiation source. A 500 μm X-ray beam spot was used, and the ultimate pressure of the analysis chamber was approximately 5×10^{-8} Pa. Thermogravimetric analysis (TGA) was performed on a TGA 8000 (PerkinEmler) in a nitrogen atmosphere. The surface micromorphology of modified PBO fibers was observed by a field emission scanning electron microscope (SEM, JSM-6700F,



Scheme 1 Progress of sizing treatment.

JEOL). The tensile strength of PBO single fiber was measured by a universal tensile machine (Instron series 3365) with a load cell of 100 N. The gauge length was 20 mm, and the strain rate was $1 \text{ mm} \cdot \text{min}^{-1}$. The average of 20 test results was taken. The relative weight content of CNSs coated on PBO fibers, designated as C_s (wt%), was evaluated by weighing method using the Eq. (1). Five samples were tested for each system.

$$C_s = \frac{W_s - W_o}{W_s} \times 100\% \quad (1)$$

where W_o and W_s are the weights of the PBO fibers before and after sizing, respectively.

The interfacial shear strength (IFSS) can reflect the transfer efficiency of stress between fibers and resins, and is widely used in the evaluation of interfacial properties of composites. The IFSS of PBO fibers was measured by the microdroplet debonding method on an interfacial performance evaluation device (HM410, MODEL, Japan). E-51 and H-256 were mixed in a weight ratio of 100/32 and dropped on the monofilament to form resin droplets. These droplets were cured at 90, 120 and 150 °C for 2, 2 and 3 h, respectively, resulting in PBO single-fiber composites. For debonding testing, the droplets were blocked with a blade, then the fiber was moved to pull it out of the resin, and the force required was recorded in real time. The IFSS could be calculated by Eq. (2):

$$\text{IFSS} = \frac{F_{\max}}{\pi dl} \quad (2)$$

where IFSS (MPa), $F_{\max}$ (N), l (mm) and d (mm) represent the interfacial shear strength, the maximum pull-out force, embedded length of resin droplet and the diameter of PBO fibers, respectively. The average of 30 IFSS measurement results was taken.

The interlaminar shear strength (ILSS) of the PBO fiber-reinforced composites was determined by the three-point short beam shear test according to ASTM D-2344. The samples were cut by water jet and the size was 30 mm × 6.5 mm × 2 mm. Tests were performed on the Instron 3365 using a 5000 N load cell with a crosshead speed of $1 \text{ mm} \cdot \text{min}^{-1}$.

RESULTS AND DISCUSSION

Characterization and Analysis of CNS

The structure and performance of CNSs are the key factors affecting the effect of interface modifications. Fig. 1(a) is the TEM image of CNSs. The statistics of the particle size and distribution are presented in Fig. S1 (in the electronic supplementary information, ESI). It can be seen that the CNSs are approximately spherical with an average diameter of 40 nm and a narrow size distribution.

The dynamic light scattering was used to investigate the particle size and distribution of CNSs in aqueous solution. As shown in Fig. 1(b), the hydrated particle size of CNSs is about 58 nm, which is larger than the dry particle size measured by TEM, indicating that CNSs have strong hydrophilicity and obvious swelling behavior in water. A zeta potential test was carried out to analyze the surface charging properties of CNSs. As shown in Fig. 1(c), the zeta potential of CNSs is -50 mV , which may be caused by the abundant oxygen-containing functional groups on their surface. Thus, the strong electrostatic repulsion between CNS particles enables them to be stably dispersed in aqueous solution.

XPS analysis was performed to further analyze the types of oxygen-containing functional groups. It can be seen from the wide-scan spectra of Fig. 1(d) that the surface of CNSs only contains two elements, C and O, and the content of oxygen is as high as 20.2%. Figs. 1(e)–1(f) further show the C1s and O1s curve fittings, and the detailed contents of the correlative functional groups are listed in Table 1. As shown in Fig. 1(e), five identical peaks occur at 284.4, 285.4, 286.5, 287.4 and 289 eV, which are corresponded to $\text{C}=\text{C}/\text{C}-\text{H}/\text{C}-\text{C}$, $\text{C}-\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{O}$ functional groups, respectively. On the other hand, as Fig. 1(f) shows, the O1s peak consists of two characteristic peaks with binding energies of 532.9 and 533.4 eV, corresponding to $\text{O}=\text{C}$ and $\text{C}-\text{O}/\text{C}-\text{O}-\text{C}$ groups, respectively. Based on these results, it can be inferred that there may be four oxygen-containing groups on the surface of CNSs: hydroxyl, epoxy, carbonyl, and carboxyl groups.

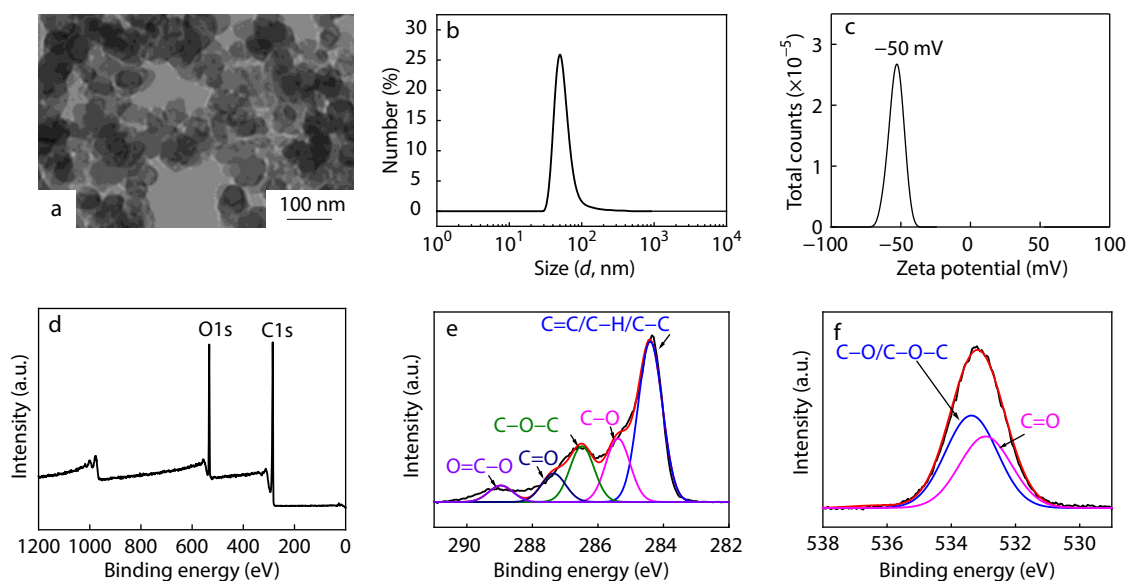


Fig. 1 (a) TEM image, (b) particle size distribution, (c) zeta potential, (d) wide-scan XPS spectrum, (e) C1s and (f) O1s spectra of CNSs.

Table 1 Contents of functional groups on the CNS surface.

Sample	C=C/C—H/C—C (%)	C—O (%)	C—O—C (%)	C=O (%)	O=C—O (%)
CNS	49.5	19.6	17.2	8.7	5

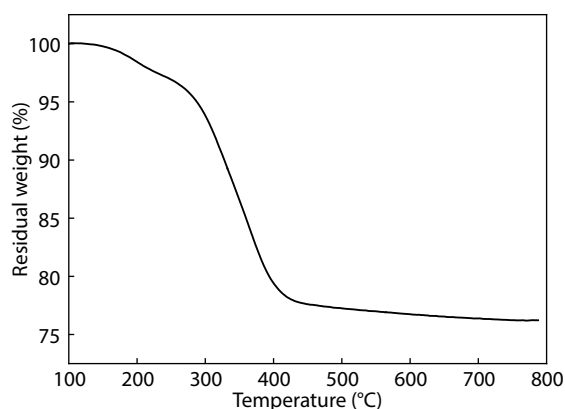
Combined with the previous test results of zeta potential, it can be further speculated that the oxygen-containing functional groups are likely to be carboxyl groups, which can endow the surface of CNSs with abundant negative charges due to their strong ionization ability in water.

TGA was conducted to investigate the thermal stability of CNSs. As can be seen from Fig. 2, the thermal weight loss of CNSs can be divided into two stages: (1) the weight loss below 200 °C is mainly caused by the removal of adsorbed water, which is about 1.7%; (2) the weight loss above 200 °C is mainly due to the decomposition of oxygen-containing functional groups, which is about 23.7%. The TGA result is consistent with the zeta potential and XPS results, both indicating the existence of plentiful oxygen-containing functional groups on the CNS surface.

The environmentally friendly waterborne sizing agent was prepared by using CNSs as the nano-reinforcement. The dispersion stability of CNSs in deionized water directly determines the microstructure of the coating on the sized PBO fibers. It can be seen from Fig. 3 that CNSs can be well dispersed in deionized water to form a uniform and stable system. Even after standing for three days, no obvious aggregation or precipitation can be observed in the dispersion with a high CNS concentration of 5 wt%. This indicates that CNSs have excellent compatibility with deionized water, which creates favorable conditions for sizing treatment.

Physicochemical Characterizations of PBO Fibers

XPS was conducted to analyze the surface elements and

**Fig. 2** TGA curve of CNSs.**Fig. 3** Dispersion stability of CNSs in deionized water.

chemical composition of the PBO fibers. The pristine PBO fibers (Fig. 4a) exhibit four typical peaks at binding energies of 284.8, 285.7, 286.9 and 288.7 eV, corresponding to C—C, C—N, C—O, and N=C—O, respectively. After sizing treatment (Fig. 4b), a new peak appears at the binding energy of 289 eV, which can be attributed to the O=C—O group. The percentage of each carbon-containing functional group can also be calculated accordingly as listed in Table 2. It shows that the C—C and C—O functional groups on the surface of the pristine PBO fibers are 69.3% and 9.8%, respectively. After sizing treatment, the C—C content decreases to 61.1%, while the C—O content increases to 16.6%. At the same time, O=C—O group appears with a content of 2%. The XPS results confirm that oxygen-containing functional groups such as carboxyl groups have been successfully introduced onto PBO fibers by sizing treatment, which is conducive to the formation of strong chemical bonds with the matrix resin.

The CNS concentration in the sizing agents determines the content of CNSs (C_s) on the surface of sized PBO fibers, which in turn shows a great impact on the surface morphology of the PBO fibers. As shown in Table 3, the C_s increases step by step with the increase of CNS concentration in the sizing agents. Figs. 4(c)–4(f) and Fig. S2 (in ESI) present SEM images of various PBO fibers under 3000 magnification. Obviously, the surface of the unmodified PBO fibers is rather smooth and free of attachments, so it is difficult to form an effective mechanical interlock with the matrix resin. With the introduction of CNSs, the surface of the PBO fibers gradually becomes rougher. When the CNS concentration is 0.5 wt%, it is difficult to observe clear CNS particles. This may be because the CNS particles are rather small and coated uniformly. In addition, part of the surface may not be covered by the CNS particles due to the low concentration. With the increase of the CNS concentration, the protrusions on the surface increase, which can provide more attachment sites for the matrix resin and thus improve the interfacial properties of the composites. When the CNS concentration reaches 5 wt%, the excessive CNS particles aggregate to form clusters, which makes the fibers rougher. Disadvantageously, however, the clusters tend to be sites of stress concentration that degrade the interfacial performance.

The mechanical properties of PBO fibers before and after sizing treatment were evaluated by single fiber tensile strength tests as shown in Fig. 4(g). The single fiber tensile strength of PBO-C0, PBO-C0.5, PBO-C1, PBO-C2.5 and PBO-C5 fibers are 4.2, 4.36, 4.88, 4.67 and 4.59 GPa, respectively. Clearly, the simple and gentle treatment process creates favorable conditions for PBO fibers to maintain their original excellent properties. The sized fibers even show slightly better tensile strength than the pristine one, which could be attributed to the repair of defects on the fiber surface by the CNS coating via π - π interaction.

The thermal stability of various PBO fibers was investigated by TGA tests. It can be seen from Fig. 4(h) that the thermal decomposition temperatures of the sized fibers are slightly re-

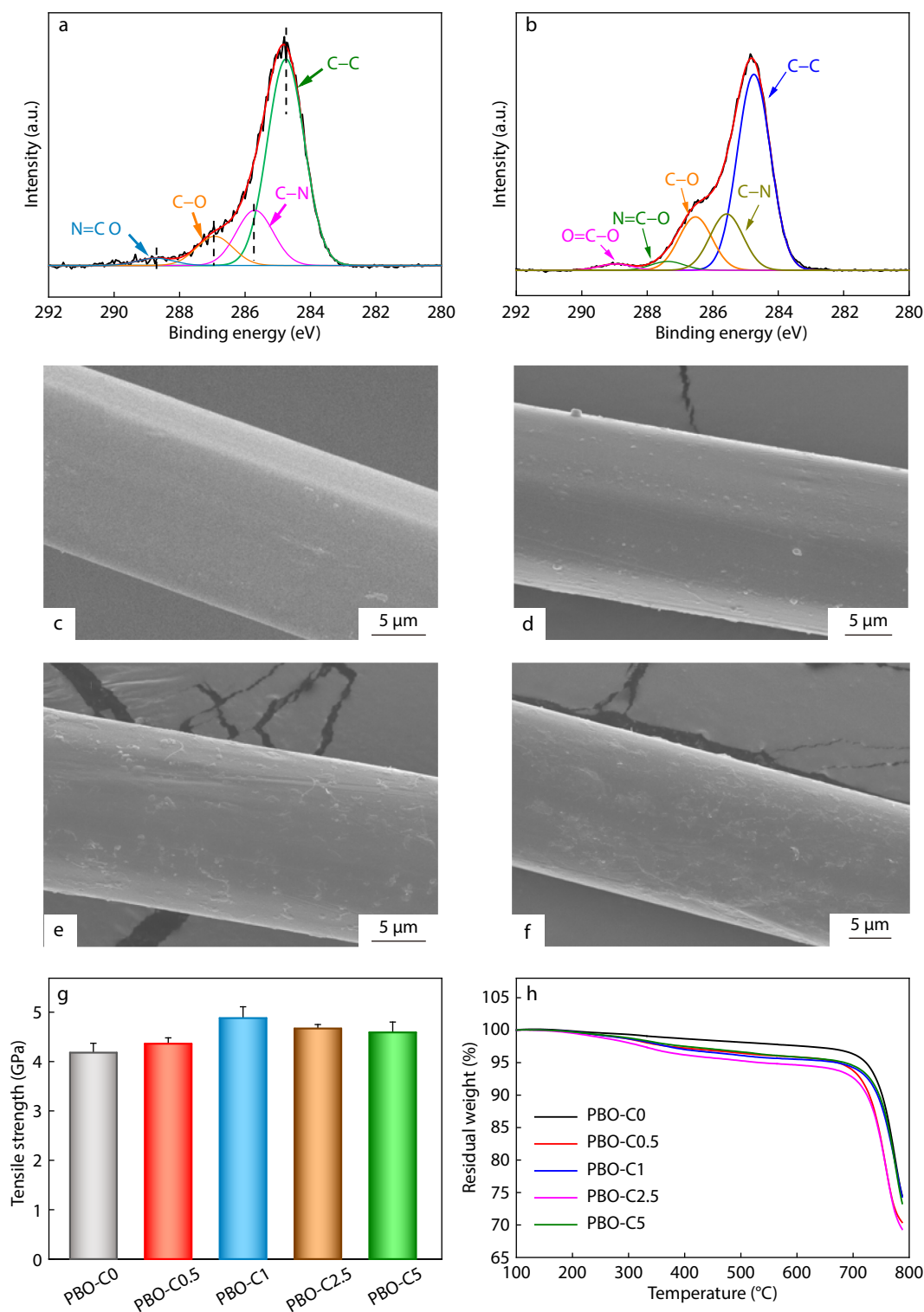


Fig. 4 C1s XPS spectra of (a) PBO-C0 and (b) PBO-C2.5; SEM images of (c) PBO-C0, (d) PBO-C1, (e) PBO-C2.5 and (f) PBO-C5; (g) Tensile strength and (h) TGA curves of PBO fibers before and after sizing treatment.

duced. Undoubtedly, the weight loss before 600 $^{\circ}\text{C}$ is caused by the removal of absorbed water and the decomposition of the functional groups on the CNSs. However, it should be noted that this part of the weight loss only accounts for about 4%, which has little effect on the overall thermal stability of

the modified fibers.

Interfacial Properties of PBO/Epoxy Composites

IFSS is an important indicator to measure the interfacial properties of composites. The micro-debonding method was used to test the IFSS of the PBO fiber-reinforced composites

Table 2 Contents of surface functional groups on PBO-C0 and PBO-C2.5 fibers.

Sample	C—C (%)	C—N (%)	C—O (%)	N=C—O (%)	O=C—O (%)
PBO-C0	69.3	18.5	9.8	2.4	0
PBO-C2.5	61.1	17.5	16.6	2.7	2

Table 3 C_s of the fibers treated with different concentrations of sizing agents.

Sample	Concentration of sizing agents (wt%)	C_s (wt%)
PBO-C0	0	0
PBO-C0.5	0.5	2.1
PBO-C1	1	2.4
PBO-C2.5	2.5	3.2
PBO-C5	5	4.2

before and after sizing treatment and the results are shown in Fig. 5(a). The IFSS of the pristine PBO fiber-reinforced composites was only 22.6 MPa. This is due to the smooth surface and low surface energy of the untreated PBO fibers, which have poor interface bonding with the matrix resin. After the CNS sizing treatment, the wettability of the resins toward the PBO fibers is enhanced, and the IFSS of the composites is significantly improved. The IFSS values of PBO-C0.5, PBO-C1, PBO-C2.5 and PBO-C5 reinforced composites are 31.6, 38.1, 38.9 and 40.6 MPa, respectively. Obviously, the PBO-C1 reinforced composites shows a drastic increase of 68.6% compared with the unmodified one. Subsequently, the growth of the IFSS slows down when the CNS concentration exceeded 1 wt%. As shown, the IFSS of the PBO-C5 reinforced composite is 79.6% higher than that of the PBO-C0 reinforced composite, but only 6.6% higher than that of the PBO-C1 reinforced composite. This could be attributed to two opposing effects of the CNSs at high concentrations. On the one hand, the CNSs increase the surface

activity and roughness of the fibers, which will improve the IFSS of the composites. On the other hand, the excess CNSs can aggregate at the surface to form defects, thereby reducing the stress transfer efficiency at the interface. As a result, the improvement of the IFSS is limited.

To visualize the effect of interfacial reinforcement, a simple model was created as shown in Fig. 5(d). In detail, one end of a single fiber was fixed with a resin pellet, and the other end was pulled by a tensile machine to simulate a hanging weight. The loading force increased gradually over time and was recorded by a computer. The length of fiber embedded in the resin was kept as consistent as possible for different samples. PBO-C0 and PBO-C1 were selected as representatives to compare the force required to completely pull the fiber out of the resin, and photos of the samples at different loading periods were taken. The results are shown in Fig. 5(e). For PBO-C0 fiber, when the loading force increases to 169.1 mN, the fiber is completely pulled out, leaving a hollow resin pellet. But in sharp contrast, the sample of PBO-C1 remains intact when the force also reaches 169.1 mN, and no sign of pulling out can be found. This comparison visually demonstrates the interfacial enhancement capabilities of CNS sizing agents. The force required to pull PBO-C1 out of the resin is 270.6 mN, 60% higher than that of PBO-C0, which is basically consistent with the IFSS results.

To vividly illustrate the advantages of this rather mild and simple sizing method, we carefully compared the tensile

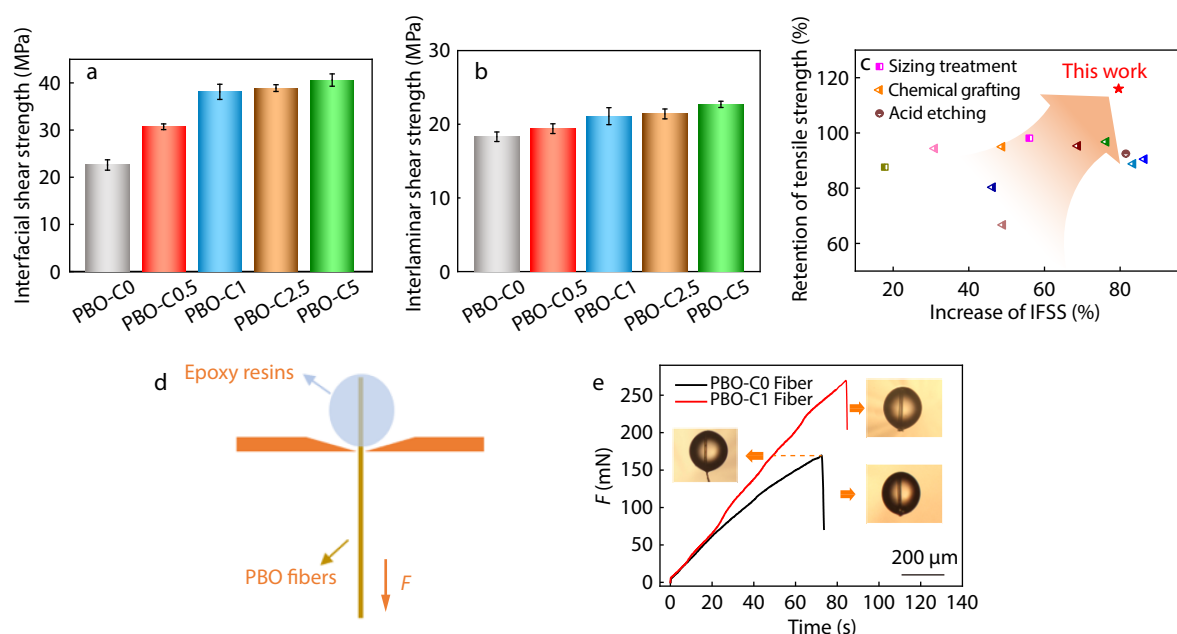


Fig. 5 (a) IFSS results of PBO/epoxy composites before and after sizing treatment; (b) ILSS results of PBO/epoxy composites before and after sizing treatment; (c) Comparison of the increase of IFSS and the retention of tensile strength among this work and previously reported surface modified PBO fibers; (d) Simple model for intuitive demonstration of interface enhancements; (e) Loading force as a function of time.

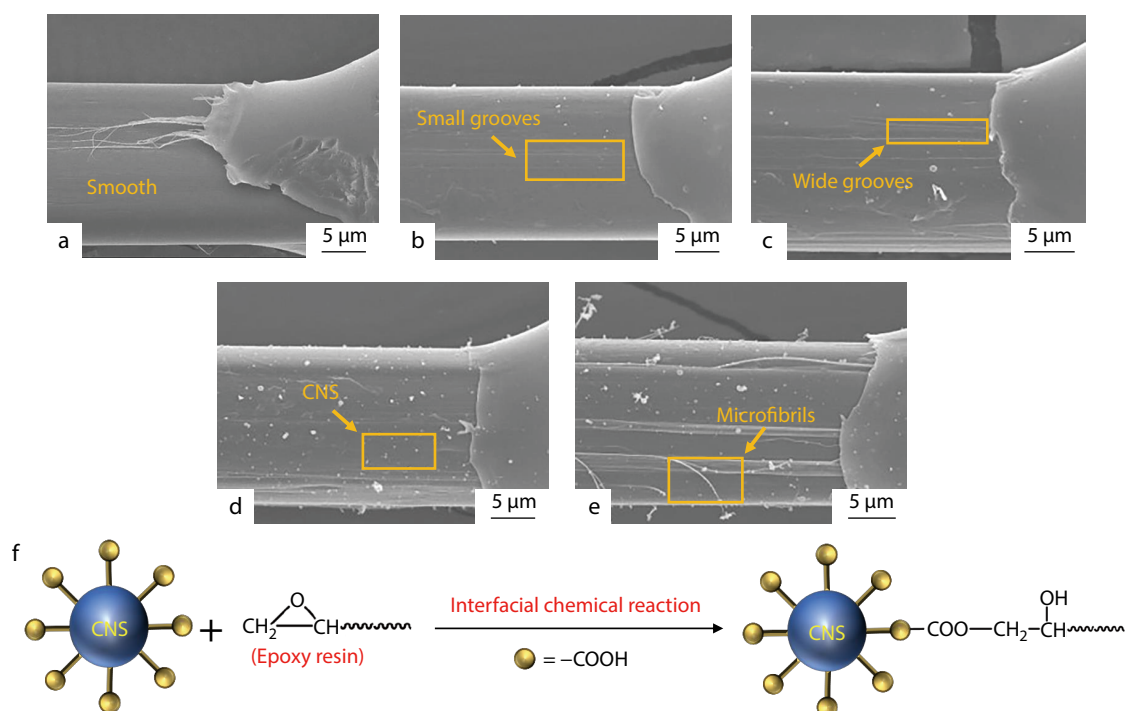


Fig. 6 SEM images of fracture surfaces: (a) PBO-C0, (b) PBO-C0.5, (c) PBO-C1, (d) PBO-C2.5, (e) PBO-C5; (f) Interfacial chemical reaction between CNSs and epoxy resins.

strength retention and the IFSS increase of the modified fibers in this work with those reported in the literature, as shown in the Fig. 5(c). Obviously, it can be seen that CNS sized PBO fibers not only show significantly improved interfacial properties, but also retain the excellent mechanical properties.

The macroscopic mechanical properties of the composites, the interlaminar shear strength (ILSS), were further tested to demonstrate the interfacial enhancement effect of CNSs. As shown in Fig. 5(b), the ILSS of the composites presents a variation trend similar to that of the IFSS, that is, it gradually improves with the increase of the CNS contents. Finally, the ILSS of the PBO-C5 reinforced composite is improved by 24% compared with that of the PBO-C0 reinforced composite. The results of ILSS and IFSS firmly support the critical role of CNSs in the construction of mechanically robust interfaces.

Furthermore, the interfacial failure mechanism of the composites is revealed by observing the surface microstructure of the PBO fibers after debonding. As shown in Fig. 6(a), the fracture surface of the pristine PBO fibers is still quite smooth, indicating that the interaction between the fibers and the matrix resins is extremely weak. In contrast, the surface morphologies of the sized fibers are changed significantly after debonding. The active interfacial layer introduced by sizing treatment is destroyed during the debonding process. For PBO-C0.5 (Fig. 6b), some fine and shallow grooves can be found on the fracture surface. A few resin-embedded CNSs are also exposed at the same time. As the CNS concentration increases, the grooves become deeper and wider, and the CNSs observed also increase significantly. When the CNS concentration increases to 5 wt% (Fig. 6e), many microfibrils are stripped off from the fiber surface. The severe damage of the

interfacial layer results in a hierarchical morphology. The destruction of the interface and the peeling of the microfibrils can dissipate a large amount of energy, thereby greatly improving the IFSS of the composites. Therefore, the PBO-C5 possesses the strongest interface among all the samples.

According to the above research results, the interface enhancement mechanism can be summarized. Good wetting of the fibers by the resin is a prerequisite for obtaining a mechanically strong interface. The oxygen-containing functional groups carried by the CNSs enhance the surface activity of the PBO fibers, which facilitates the wetting and spreading of the epoxy resins, resulting in an interface with fewer defects such as bubbles and voids. Meanwhile, the high specific area of the CNSs increases the contact area between the PBO fibers and the resins, thus promoting the mechanical interlock between them. What's more, the carboxyl groups of the CNSs chemically react with the epoxy resins (Fig. 6f), which can further strengthen the bonding force between the resins and the PBO fibers. Under the synergistic effect of these aspects, the interfacial adhesion properties of the PBO fiber-reinforced composites have been greatly improved.

CONCLUSIONS

In this work, we developed a green and environmentally friendly sizing agent for PBO fibers using only water as the solvent. The functionalized CNSs with excellent water dispersibility was used as the nano-reinforcement and introduced onto the PBO fibers by sizing treatment. XPS and SEM results show that the CNSs disperse well on the PBO fibers, which helps to improve the surface activity, roughness, and wettability. On this basis, the IFSS of the sized PBO fiber-

reinforced composites increases significantly. When the CNS concentration is 5 wt%, the IFSS of the composites reaches its maximum, which is 79.6% higher than that of the pristine one. Moreover, the sized PBO fibers possess excellent mechanical properties and heat resistance. In all, this new type of sizing agent can effectively overcome the serious environmental pollution of traditional solvent-based sizing agents and provide strong interfacial adhesion between the PBO fibers and the epoxy resins.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2834-x>.

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REFERENCES

- Chen, L.; Du, Y.; Huang, Y.; Ng, P. F.; Fei, B. Facile fabrication of hierarchically structured PBO-Ni(OH)₂/NiOOH fibers for enhancing interfacial strength in PBO fiber/epoxy resin composites. *Compos. Sci. Technol.* **2016**, 129, 86–92.
- Hao, X.; Zhu, J.; Jiang, X.; Wu, H.; Qiao, J.; Sun, W.; Wang, Z.; Sun, K. Ultrastrong polyoxazole nanofiber membranes for dendrite-proof and heat-resistant battery separators. *Nano Lett.* **2016**, 16, 2981–2987.
- Luo, L.; Hong, D.; Zhang, L.; Cheng, Z.; Liu, X. Surface modification of PBO fibers by direct fluorination and corresponding chemical reaction mechanism. *Compos. Sci. Technol.* **2018**, 165, 106–114.
- Yu, Z.; Wu, S.; Li, C.; Xiao, Y.; Zheng, L.; Liu, J.; Zhang, B. Ultra-low dielectric constant fluorinated graphene/polybenzoxazole composite films with excellent thermal stabilities and mechanical properties. *Compos. Part A-Appl. Sci. Manuf.* **2021**, 145, 106387.
- Lu, K.; Ge, X.; Wei, Z.; Li, G.; Yang, X.; Liu, H. Synergistically enhanced ultraviolet aging resistance and interfacial adhesion of poly(*p*-phenylene benzobisoxazole) fiber with soluble naphthalimide sizing. *Polym. Compos.* **2021**, 42, 2122–2134.
- Liu, Z.; Zhang, J.; Tang, Y.; Xu, J.; Ma, J.; Kong, J.; Gu, J. Optimization of PBO fibers/cyanate ester wave-transparent laminated composites via incorporation of a fluoride-containing linear interfacial compatibilizer. *Compos. Sci. Technol.* **2021**, 210, 108838.
- Chen, L.; Hu, Z.; Wu, Z.; Wu, G.; Ma, L.; Zhang, C.; Huang, Y. POSS-bound ZnO nanowires as interphase for enhancing interfacial strength and hydrothermal aging resistance of PBO fiber/epoxy resin composites. *Compos. Part A-Appl. Sci. Manuf.* **2017**, 96, 1–8.
- Tang, L.; Zhang, J.; Wu, C.; Tang, Y.; Ma, H.; Kong, J.; Gu, J. UV etched random copolymer membrane coated PBO fibers/cyanate ester wave-transparent laminated composites. *Compos. Part B-Eng.* **2021**, 212, 108680.
- Song, B.; Liu, Z.; Pan, D.; Wang, T.; Wang, L.; Dong, B.; Guo, Z. Layer-by-layer constructing interface with rigid-flexible transition structure for improving interfacial adhesion of PBO fiber composites. *Compos. Commun.* **2020**, 22, 100466.
- Liu, Z.; Fan, X.; Cheng, L.; Zhang, J.; Tang, L.; Tang, Y.; Kong, J.; Gu, J. Hybrid polymer membrane functionalized PBO fibers/cyanate esters wave-transparent laminated composites. *Adv. Fiber Mater.* **2022**, 4, 520–531.
- Chen, L.; Du, Y.; Huang, Y.; Wu, F.; Cheng, H. M.; Fei, B.; Xin, J. H. Hierarchical poly(*p*-phenylene benzobisoxazole)/graphene oxide reinforcement with multifunctional and biomimic middle layer. *Compos. Part A-Appl. Sci. Manuf.* **2016**, 88, 123–130.
- Chen, Y.; Zhang, S.; Liu, X.; Pei, Q.; Qian, J.; Zhuang, Q.; Han, Z. Preparation of solution-processable reduced graphene oxide/polybenzoxazole nanocomposites with improved dielectric properties. *Macromolecules* **2015**, 48, 365–372.
- Li, Y. W.; Zhao, F.; Song, Y. J.; Li, J.; Hu, Z.; Huang, Y. D. Interfacial microstructure and properties of poly(phenylene benzobisoxazole) fiber grafted with graphene oxide via solvothermal method. *Appl. Surf. Sci.* **2013**, 266, 306–312.
- Song, B.; Liu, Z.; Chen, L.; Ma, L.; Huang, Y. Poly(*p*-phenylene benzobisoxazole) fiber/epoxy composites reinforced with carbon nanotubes and graphene oxide for enhanced interfacial adhesion and mechanical strength. *ACS Appl. Nano Mater.* **2021**, 4, 12158–12169.
- Wang, M.; Wang, C.; Song, Y.; Zhang, C.; Shao, L.; Jiang, Z.; Huang, Y. Facile method to functionalize graphene oxide nanoribbons and its application to poly(*p*-phenylene benzobisoxazole) composite. *Compos. Sci. Technol.* **2018**, 165, 124–130.
- Song, B.; Liu, Z.; Wang, T.; Wang, L. Grafting of CNTs onto the surface of PBO fibers at high-density for enhancing interfacial adhesion, mechanical properties and stability of composites. *J. Colloid Interface Sci.* **2021**, 598, 113–125.
- Guo, J.; Mao, B.; Li, J.; Wang, X.; Yang, X. Rethinking the reaction pathways of chemical reduction of graphene oxide. *Carbon* **2021**, 171, 963–967.
- Hu, Z.; Lu, F.; Liu, Y.; Zhao, L.; Yu, L.; Xu, X.; Yuan, W.; Zhang, Q.; Huang, Y. Construction of anti-ultraviolet "shielding clothes" on poly(*p*-phenylene benzobisoxazole) fibers: metal organic framework-mediated absorption strategy. *ACS Appl. Mater. Interfaces* **2018**, 10, 43262–43274.
- Liu, Z.; Song, B.; Wang, T.; Wang, L. Significant improved interfacial properties of PBO fibers composites by *in-situ* constructing rigid dendritic polymers on fiber surface. *Appl. Surf. Sci.* **2020**, 512, 145719.
- Liu, R.; Han, Z.; Li, W.; Li, X.; Zhuang, Q. Improvement of the interfacial shear strength of poly(*p*-phenylene benzobisoxazole) fiber/epoxy resin composite via a novel surface coating agent. *Polym. Compos.* **2016**, 37, 1198–1205.
- Tang, L.; Yang, Z.; Tang, Y.; Zhang, J.; Kong, J.; Gu, J. Facile functionalization strategy of PBO fibres for synchronous improving the mechanical and wave-transparent properties of the PBO fibres/cyanate ester laminated composites. *Compos. Part A-Appl. Sci. Manuf.* **2021**, 150, 106622.
- Tang, Y.; Dong, W.; Tang, L.; Zhang, Y.; Kong, J.; Gu, J. Fabrication and investigations on the polydopamine/KH-560 functionalized PBO fibers/cyanate ester wave-transparent composites. *Compos. Commun.* **2018**, 8, 36–41.
- Yu, L.; Lu, F.; Huang, X.; Liu, Y.; Li, M.; Pan, H.; Wu, L.; Huang, Y.; Hu, Z. Facile interface design strategy for improving the uvioresistant and self-healing properties of poly(*p*-phenylene benzobisoxazole) fibers. *ACS Appl. Mater. Interfaces* **2019**, 11, 39292–39303.
- Wu, S.; Li, C.; Yu, Z.; Ling, R.; Xiao, Y.; Zheng, L.; Liu, J.; Zhang, B. Nondestructive strategy to effectively enhance the interfacial

- adhesion of PBO/epoxy composites. *ACS Appl. Mater. Interfaces* **2020**, *12*, 45383–45393.
- 25 Tang, L.; Fan, X.; Tang, Y.; Zhang, J.; Kong, J.; Gu, J. Calcia-doped ceria hybrid coating functionalized PBO fibers with excellent UV resistance and improved interfacial compatibility with cyanate ester resins. *Appl. Surf. Sci.* **2021**, *569*, 151124.
- 26 Liu, J.; Liu, X.; Wang, D.; Wang, H. An important factor affecting the UV aging resistance of PBO fiber foped with nano-TiO₂: the number of amorphous regions. *Polymers* **2019**, *11*, 869.
- 27 Steinke, K.; Sodano, H. A. Enhanced interfacial shear strength in ultra-high molecular weight polyethylene epoxy composites through a zinc oxide nanowire interphase. *Compos. Sci. Technol.* **2022**, *219*, 109218.
- 28 Zhu, P.; Liu, B.; Bao, L. Preparation of a sub-100 nm-thick polyetherimide coating layer with nano-TiO₂ particles on poly(*p*-phenylene benzobisoxazole) fiber surface. *J. Appl. Polym. Sci.* **2018**, *135*, 46852.
- 29 Liu, X.; Vadiyar, M. M.; Oh, J. K.; Ye, Z. Designing ultrasmall carbon nanospheres with tailored sizes and textural properties for high-rate high-energy supercapacitors. *ACS Appl. Mater. Interfaces* **2021**, *13*, 32916–32929.
- 30 Zhu, R.; Li, L.; Wang, Z.; Zhang, S.; Dang, J.; Liu, X.; Wang, H. Adjustable dimensionality of microaggregates of silicon in hollow carbon nanospheres: an efficient pathway for high-performance lithium-ion batteries. *ACS Nano* **2022**, *16*, 1119–1133.
- 31 Zhang, R.; Shi, X.; Tang, L.; Liu, Z.; Zhang, J.; Guo, Y.; Gu, J. Thermally conductive and insulating epoxy composites by synchronously incorporating Si-sol functionalized glass fibers and boron nitride fillers. *Chinese J. Polym. Sci.* **2020**, *38*, 730–739.
- 32 Gu, J.; Xu, S.; Zhuang, Q.; Tang, Y.; Kong, J. Hyperbranched polyborosilazane and boron nitride modified cyanate ester composite with low dielectric loss and desirable thermal conductivity. *IEEE T. Dielect. El. In.* **2017**, *24*, 784–790.