Thermally Conductive and Insulating Epoxy Composites by Synchronously Incorporating Si-sol Functionalized Glass Fibers and Boron Nitride Fillers

Rui-Han Zhang, Xue-Tao Shi, Lin Tang, Zheng Liu, Jun-Liang Zhang, Yong-Qiang Guo, and Jun-Wei Gu

Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi’an 710072, China

INTRODUCTION

Glass fibers (GFs)/epoxy laminated composites are one kind of light weight and outstanding design flexibility materials, which possess high specific stiffness and strength, excellent fatigue toughness, and low-cost, etc. [1–3] They are widely used in the fields of aerospace, automobile, wind turbine, and electronic packaging, etc. [4–6] However, low cross-plane thermal conductivity coefficient (λ┴) and poor interlaminar shear strength (ILSS) have seriously limited their broader application in thermal/structural integrated components fields. [6, 7]

As an important part of bearing strength inner polymer composites, GFs possess better processability, superior insulating properties, and excellent chemical stability, [8–9] in comparison with other commonly reinforced fibers (e.g., quartz, [10, 11] Kevlar, [12, 13] and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers). [14, 15] However, few active groups and poor wettability of GFs surface usually result in easy interlayer damage and brittle fractures of laminated composites. [16, 17] Besides, thermal interfacial resistance is the key barrier for effective thermal transport. Surface treatment of GFs could help to build the thermal bridge and reduce phonon scattering. Different functionalized methods have been developed to obtain better interfacial compatibility between GFs and epoxy resin, for instance, plasma, [18–19] coupling agent, [20–21] and grafting approach, etc. [22–23] Asadi et al. [24] prepared cellulose nanocrystals (CNC) coated chopped GFs/epoxy composites. Compared with pristine GFs/epoxy composites, the tensile and flexural strength values of the 0.17 wt% CNC coated GFs/epoxy composites were increased by 10% and 43%, respectively. In our previous work, [25] epichlorohydrin grafted GFs (f-GFs) were developed to prepare f-GFs/boron nitride (BN)/epoxy laminated composites. When the mass fraction of GBN-100 fillers was 20 wt%, the λ┴ and in-plane λ (λ//) values of the f-GFs/BN-GN-100/epoxy laminated composites reached the maximum of 1.21 and 3.55 W-m⁻¹-K⁻¹, respectively. Furthermore, the introduction of f-GFs could further enhance the mechanical properties of epoxy laminated composites. Nevertheless, the above approaches usually show complex process and uncontrollable grafting rate, and slight improvement in mechanical properties as well. The use of silica-sol...
can further simplify surface functionalization process, which can avoid using a lot of corrosive solvent and causing environmental pollution. In addition, compared with traditional coupling agent, the active groups on GFs surface can be further controlled by coating amount and concentration ratio of silica-sol.

There are two main methods for enhancing the λ values of epoxy resin and their composites. One is synthesizing intrinsic thermally conductive epoxy resin, the other is fabricating thermally conductive epoxy composites via introducing thermally conductive fillers.[26] However, the preparation of intrinsic thermally conductive epoxy resin is considerably cumbersome, difficult, and relatively expensive, which is applied only in laboratory stage.[27] Therefore, directly adding thermally conductive fillers can be regarded as the easiest and simplest method for improving the λ values of the epoxy composites.[28,29] Carbon-based fillers (CNTs,[30] graphite nanoplatelets (GNPs),[31] and graphene,[32] etc.) and ceramic fillers Al2O3,[33,34] BN,[35,36] aluminum nitride (AlN),[37,38] and SiC whisker (SiCw)[39] are the most common fillers to fabricate highly thermally conductive epoxy composites. Carbon-based fillers possess excellent electrical conductivity, and are therefore restricted in the electrical insulation field. BN fillers not only present higher λ value and high-temperature oxidation resistance, but possess ε value (about 4.0) that is the lowest among ceramic fillers.[40,41] Moreover, BN fillers are easier to connect with each other owing to their unique layered hexagonal structure, beneficial to forming more thermally conductive pathways inside epoxy resin. Hu et al.[42] obtained the epoxy/ordered 3D-BN composites via combing ice-templating self-assembly and infiltration method, which possessed high λ values up to 4.42 W·m⁻¹·K⁻¹ with 34 vol% BN fillers. Jiang et al.[43] prepared poly(glycidyl methacrylate) grafted h-BN particles (h-BN-PGMA)/epoxy composites which achieved λ value of 1.198 W·m⁻¹·K⁻¹ with 15 vol% h-BN-PGMA fillers, 5.05 times higher than that of pure epoxy resin. In our previous work,[44] thermally conductive and self-healable 60 wt% BN/thiol-epoxy elastomer composites presented the optimal λ value of 1.058 W·m⁻¹·K⁻¹, about 4 times that of pure epoxy resin.

In this work, silica-sol, synthesized from tetraethyl orthosilicate (TEOS) and γ-glycidoxypropyltrimethoxysilane (KH-560) via sol-gel method, was firstly developed to functionalize the surface of GFs (Si-GFs). And the thermally conductive BNN-30/Si-GFs/epoxy laminated composites were then fabricated via blending-impregnation followed by hot compresion, applying the micron boron nitride with particle size of 30 μm (BNN-30) as thermally conductive fillers and bisphenol A epoxy resin (E-44) as polymer matrix. Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were all performed to analyze and characterize the surface component and performance of the GFs and Si-GFs. Meantime, the effects of BNN-30 filler contents on the thermal conductivities, electrical insulation, and dielectric, mechanical and thermal properties of the BNN-30/Si-GFs/epoxy laminated composites were also investigated.

**EXPERIMENTAL**

**Surface Coating of GFs**

Glass fibers (GFs, 2.45 g·cm⁻³, Shanghai Jingtai Industrial Co. Ltd) were washed by absolute ethanol and deionized water successively. Silica-sol was then coated on the GFs surface and dried in the vaccum oven at 60 °C for 24 h, finally to obtain silica-sol coated GFs (Si-GFs).

**Fabrication of the Thermally Conductive BNN-30/Si-GFs/Epoxy Laminated Composites**

BNN-30 fillers (Y’an Baitu High-tech Materials Co., Ltd.) were firstly dispersed in epoxy resin and stirred uniformly. Curing agent of 3,3’-diaminodiphenyl sulfone (DDS) was then added into the above solution (epoxy:DDS = 3:1, W/W) and mixed at 110 °C for 2 h. Acetone was then added to obtain transparent BNN-30/epoxy prepreg glue, which was then coated on the surface of Si-GFs, followed by air-drying to obtain the BNN-30/Si-GFs/epoxy prepregs. The above BNN-30/Si-GFs/epoxy prepregs were then laid up and laminated under 5 MPa according to the following curing procedure: 110 °C/0.5 h + 170 °C/1 h. Si-GFs/epoxy laminated composites were also prepared by the same method. Schematic diagram for the preparation of thermally conductive BNN-30/Si-GFs/epoxy laminated composites is displayed in Fig. 1.

The information details of the “Main materials”, “Synthesis of silica-sol” and “Characterizations” are presented in the electronic supplementary information (ESI).

**RESULTS AND DISCUSSION**

**Structural Characterization on Silica-sol**

Fig. 2 shows FTIR spectra (Fig. 2a) and ¹H-NMR spectra (Fig. 2b) of silica-sol. In Fig. 2(a), the stretching vibration bands near 2930 cm⁻¹ (−CH2−), −CH3 and 1070 cm⁻¹ (Si−O) in TEOS are observed. For silica-sol, the characteristic band at 1060 cm⁻¹ is assigned to the Si−O−Si, ascribed to hydrolysis interaction between Si−OH. Furthermore, silica-sol shows not only the stretching vibration bands of −CH2−, −CH3, and Si−O−Si, but also the new characteristic absorption band near 908 cm⁻¹ (epoxy group). Meanwhile, in Fig. 2(b), the chemical shift at 1.26 ppm corresponds to the protons for −CH3 in TEOS alkyl chains.

Chemical shifts at 0.87 and 1.74 ppm are attributed to protons on the methylene group directly and indirectly connected to Si in the KH-560 alkyl chains. And the signals at 2.85 and 2.97 ppm are attributed to the two protons with different chemical environments in epoxy groups of silica-sol. In addition, a few more signals at 3.30−3.85 ppm appear, corresponding to protons for −O−CH2−, O−CH2, and CH2−O−CH3, respectively. Therefore, it can be deduced that the silica-sol has been synthesized successfully.

**Characterization on GFs and Si-GFs**

Fig. 3 shows FTIR spectra (Fig. 3a), XPS spectra (Fig. 3b), SEM morphologies, and EDS (Figs. 3c and 3d) of pristine GFs and Si-GFs. For pristine GFs, the band around 800−400 cm⁻¹ can be assigned to vibration band of Si−O. For Si-GFs, new characteristic stretching vibration bands of Si−OH and −CH3 appear near 3340 and 2930 cm⁻¹, respectively. Meantime, the characteristic band at 908 cm⁻¹ is assigned to epoxy groups. It
suggests that the silica-sol itself contains alkyl chains and epoxy groups. In addition, the characteristic peaks of O 1s, C 1s, Si 2s, and Si 2p are corresponding to 530.0, 285.0, 151.0, and 98.0 eV, respectively. Besides the original Si—O—Si (533.0 eV), O 1s peak of Si-GFs, new peaks of C—O—C (531.6 eV) and C—O—Si (532.4 eV) (Fig. 3b″) appear in comparison to that of O 1s peak for pristine GFs (Fig. 3b′), mainly attributed to new chemical bonds between epoxy groups and pristine GFs. In Table S1 (in ESI), pristine GFs mainly contains C, Si, and O elements, and the C/O and Si/O ratios reach 1.33 and 0.60, respectively. For Si-GFs, the relative contents of C and Si increase significantly, and the corresponding C/O and Si/O ratios reach 2.21 and 0.89, respectively, owing to lots of alkyl chains and Si—O bonds on the surface of Si-GFs. As observed, the surface of pristine GFs (Fig. 3c) is smooth. With the introduction of silica-sol, the surface of Si-GFs gets coarse (Fig. 3d). Figs. 3(c′)–3(c‴) further illustrate that the silica-sol is uniformly distributed on the surface of Si-GFs. The information of the density and gel content values of the epoxy laminated composites are presented in the Table S2 (in ESI).

Table S3 (in ESI) presents the data for thermal conductivities and mechanical properties of the pristine GFs/epoxy and Si-GFs/epoxy laminated composites. Compared with pristine GFs/epoxy laminated composites, the Si-GFs/epoxy laminated composites have better thermal conductivities and mechanical properties. In-plane λ (λ∥ = 0.96 W·m⁻¹·K⁻¹) and cross-plane λ (λ⊥ = 0.46 W·m⁻¹·K⁻¹) values of the Si-GFs/epoxy laminated composites are higher than those of pristine GFs/epoxy laminated composites (λ∥ = 0.76 W·m⁻¹·K⁻¹ and λ⊥ = 0.31 W·m⁻¹·K⁻¹). The addition of silica-sol can effectively im-

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prove the interfacial compatibility between Si-GFs and epoxy resin, beneficial to reducing phonon scattering and decreasing interface thermal barriers and defects, thereby improving the \( \lambda \) values of the Si-GFs/epoxy laminated composites.

Meantime, compared with pristine GFs/epoxy laminated composites (flexural strength of 467.1 MPa and ILSS of 27.9 MPa), flexural strength and ILSS values of the Si-GFs/epoxy laminated composites increase by 15.5% and 24.7% to 539.6 and 34.8 MPa, respectively. Pristine GFs present weaker interfacial bonding strength with epoxy resin. For Si-GFs/epoxy laminated composites, the enhancement of mechanical properties basically depends on physical and chemical interactions between Si-GFs and epoxy resin (Fig. 4b) in contrast to the pristine GFs/epoxy resin (Fig. 4a). On the one hand, silica-sol can adhere to GFs surface well by physical interaction. On the other hand, a large amount of polar groups on the sur-

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Fig. 3 (a) FTIR, (b) XPS spectra, and (b', b'') high-resolution O 1s. (c, d) SEM morphologies and (c′–c‴, d′–d‴) EDS of GFs and Si-GFs.

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face of Si-GFs can participate in co-cure reaction of epoxy resin with the help of DDS\(^{[46]}\) to form effective cross-linking networks, which not only possess better interfaces bonding strength but also can improve the mechanical properties.

**Thermal Conductivities of the BNN-30/Si-GFs/Epoxy Laminated Composites**

Figs. 5(a) and 5(a\(^{′}\)) show the \(\lambda_v\) and \(\lambda_L\) values of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites. Both \(\lambda_v\) and \(\lambda_L\) values are increased with increasing addition of BNN-30 fillers. Compared with Si-GFs/epoxy laminated composites (\(\lambda_v = 0.96 \text{ Wm}^{-1}\text{K}^{-1}\) and \(\lambda_L = 0.46 \text{ Wm}^{-1}\text{K}^{-1}\)), the \(\lambda_v\) and \(\lambda_L\) values of 15 wt\% BNN-30/Si-GFs/epoxy laminated composites are improved to 2.37 and 1.07 \(\text{Wm}^{-1}\text{K}^{-1}\), respectively, about 10.8 and 4.9 times those of the pristine epoxy resin (\(\lambda_v = \lambda_L = 0.22 \text{ Wm}^{-1}\text{K}^{-1}\)). According to EDS distribution of B, N, Si (Fig. 6), BNN-30 fillers can be evenly distributed on the surface of Si-GFs. BNN-30 fillers with the low content are randomly distributed inside the epoxy laminated composites, mostly isolated and difficult to connect with each other, and hardly to form effective thermally conductive channels. With the increasing addition of BNN-30 fillers, the forming probabilities of the (BNN-30)-(BNN-30) and (Si-GFs)-(BNN-30)-(Si-GFs) thermally conductive paths and/or networks are increased. Therefore, heat flow is easier to pass along the BNN-30 fillers, which would effectively enhance the \(\lambda_v\) and \(\lambda_L\) values of the BNN-30/Si-GFs/epoxy laminated composites.

In order to simulate the thermal conduction in practical application, we place the BNN-30/Si-GFs/epoxy laminated composites on a plate with 110 °C and record the surface temperature changes, and the obtained results are shown in Figs. 5(b)–5(d). Surface temperature of the Si-GFs/epoxy laminated composites in vertical direction reaches 75.2 °C after 30 s, while that of the 15 wt\% BNN-30/Si-GFs/epoxy laminated composites reaches 93.3 °C. In addition, surface temperature of the Si-GFs/epoxy laminated composites in flat direction reaches 80.6 °C after 30 s, and 95.0 °C for 15 wt\% BNN-30/Si-GFs/epoxy laminated composites. It further demonstrates that the thermal conductivities of the BNN-30/Si-GFs/epoxy laminated composites are improved with the increasing amount of BNN-30 fillers, consistent with the results from Figs. 5(a) and 5(a\(^{′}\)). Meantime, the uniform heat distribution (Fig. 5d) further presents the evidence of the relatively uniform dispersion of the BNN-30 fillers inside the BNN-30/Si-GFs/epoxy laminated composites.

In addition, thermal diffusion rate slows obviously and the heat flow is spread unevenly between interlayers for epoxy laminated composites. Si-GFs are beneficial to rapid diffusion of heat flow; only a small part of the heat is retained in epoxy resin, and phonons transport rapidly through Si-GFs as well. However, epoxy resin with low \(\lambda\) value is the main component at interlayers for BNN-30/Si-GFs/epoxy laminated composites. Phonons do random Brownian motion in epoxy resin, presenting longer mean free path and easy to be scattered.\(^{[46]}\) Meanwhile, the addition of silica-sol can improve the interfacial compatibility between Si-GFs and epoxy resin, which would be beneficial to the improvement of the heat propa-

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**Fig. 4** Illustration of interaction in (a) pristine GFs/epoxy and (b) Si-GFs/epoxy laminated composites.
Fig. 5  (a) $\lambda_{//}$ and (a') $\lambda_{\bot}$, (b, c) temperature versus heating time, (d) temperature distribution and heat transmitting pathway, and (e) schematic diagram for thermal transfer mechanism of the BNN-30/Si-GFs/epoxy laminated composites.
tion. Therefore, $\lambda_i$ values of the BNN-30/Si-GFs/epoxy laminated composites are higher than those of $\lambda_0$ values. The corresponding schematic diagram for thermal mechanism of the BNN-30/Si-GFs/epoxy laminated composites is shown in Fig. 5(e).

Electrical Insulation Properties of the BNN-30/Si-GFs/Epoxy Laminated Composites

Weibull cumulative distribution function is adopted to analyze the dielectric breakdown strength of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites using double parameters, defined as follows:

$$P = 1 - \exp \left( - \frac{E}{E_0} \right)^\beta$$

where $P$ is the cumulative probability of electric failure, $\beta$ is the shape parameter, $E$ is measured breakdown strength, and $E_0$ represents the breakdown strength at cumulative failure probability of 0.632 (i.e., $1 - 1/e$, where $e$ is the exponential constant), which is also regarded as the characteristic breakdown strength.

Distribution points are more evenly distributed on both sides of the fitted lines from Fig. 7(a). $\beta$ values, representing the Weibull modulus, are higher than 10, which indicates little dispersion in breakdown strength and provides high confidence degree. When the cumulative failure probability is 0.632, the characteristic breakdown strength ($E_0$) is shown in Fig. 7(b). With the increasing amount of BNN-30 fillers, the $E_0$ values of the BNN-30/Si-GFs/epoxy laminated composites increase firstly and then decrease. Compared with Si-GFs/epoxy laminated composites ($E_0 = 17.1$ kV·mm$^{-1}$), $E_0$ value of the 15 wt% BNN-30/Si-GFs/epoxy laminated composites is improved to 22.3 kV·mm$^{-1}$ and increased by 30.4%.

BNN-30 fillers with low content can reduce charge accumulation at surfaces and consume carriers energy effectively, which can increase the potential energy for the electronic transition, thereby enhancing the $E_p$. Nevertheless, with excessive addition of BNN-30 fillers, more reunions and inner defects are easily introduced inside the BNN-30/Si-GFs/epoxy laminated composites, and more and more charge accumulation promotes large-scale electric field distortion inside the BNN-30/Si-GFs/epoxy laminated composites, which will reduce the $E_p$. Besides, the carriers gain much more energy than their loss under high field. More electrons as the starting electrons collision, thus extremely increasing the concentration of carriers, which would reduce the dielectric breakdown strength of the BNN-30/Si-GFs/epoxy laminated composites.

In Figs. 7(c) and 7(d), both the surface resistivity ($\rho_s$) and volume resistivity ($\rho_v$) of the BNN-30/Si-GFs/epoxy laminated composites gradually decrease with increasing mass fraction of BNN-30 fillers. $\rho_s$ and $\rho_v$ values of the 15 wt% BNN-30/Si-GFs/epoxy laminated composites are reduced to $1.8 \times 10^{14} \Omega$ and $2.1 \times 10^{14} \Omega$·cm, respectively. The intrinsic electrical insulation of BNN-30 fillers is slightly poorer compared with epoxy resin and Si-GFs. The introduction of BNN-30 fillers leads to the improvement in space charge, which makes charge easier to achieve energy level transition, as well as to get rid of the nucleus, finally to reduce the $\rho_s$ and $\rho_v$ values. Notably, the obtained 15 wt% BNN-30/Si-GFs/epoxy laminated composites still preserve favorable electrical insulating properties, still far beyond the lower bound of electrical insulation ($\rho_s \geq 1 \times 10^{11} \Omega$, $\rho_v \geq 1 \times 10^9 \Omega$·cm). Meanwhile, both $\varepsilon$ and $\delta$ values of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites are improved with increasing the content of BNN-30 fillers as shown in Fig. S1 (in ESI).

Mechanical Properties of the BNN-30/Si-GFs/Epoxy Laminated Composites

Effects of the BNN-30 contents on the mechanical properties of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites are demonstrated in Fig. 8. Both the flexural

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strength and ILSS values increase firstly, and then decrease with increasing the mass fraction of BNN-30 fillers. Compared with Si-GFs/epoxy laminated composites (flexural strength of 539.6 MPa and ILSS of 34.8 MPa), the flexural strength and ILSS values of the 5 wt% BNN-30/Si-GFs/epoxy laminated composites are increased to the maximum value of 584.3 and 37.9 MPa, increased by 8.3% and 9.0%, respectively. Meantime, the flexural strength and ILSS values of the 15 wt% BNN-30/Si-GFs/epoxy laminated composites are decreased to 433.9 and 23.3 MPa, respectively. In the case of fewer loading of BNN-30 fillers, the relatively uniform dispersion of BNN-30 fillers inside the BNN-30/Si-GFs/epoxy laminated composites is conducive to transmitting stress and preventing the propagation of internal cracks effectively. However, the excessive BNN-30 fillers tend to agglomerate inside BNN-30/Si-GFs/epoxy laminated composites, which would generate more stress concentration points and defects and gaps. At the same time, the cracks are more easily expanded when subjected to external force, which could reduce the flexural strength and ILSS values of the BNN-30/Si-GFs/epoxy laminated composites.

CONCLUSIONS

Silica-sol was successfully synthesized for the surface functionalization of GFs. The introduced silica-sol on the Si-GFs surface is beneficial to the improvement of mechanical properties (especially for ILSS) and thermal conductivities for Si-GFs/epoxy laminated composites. In addition, as the amount of BNN-30 fillers increases, the $\lambda$ values, thermal stabilities, $\varepsilon$ and $\tan\delta$ values of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites are all increased gradually, while the dielectric breakdown strength and mechanical properties are both increased to the maximum and decreased afterwards.
The BNN30/Si-GFs/epoxy laminated composites with 15 wt% BNN30 fillers display the optimal comprehensive properties. $\lambda_1$ and $\lambda_2$ are the maximum of 2.37 and 1.07 W·m$^{-1}$·K$^{-1}$, 146.9% and 132.6% higher than those of Si-GFs/epoxy laminated composites ($\lambda_1 = 0.96$ W·m$^{-1}$·K$^{-1}$ and $\lambda_2 = 0.46$ W·m$^{-1}$·K$^{-1}$), respectively, also about 10.8 and 4.9 times than those of pure epoxy resin (0.22 W·m$^{-1}$·K$^{-1}$). And the heat-resistance index ($T_{HRI}$) and tan$\delta$, $E_{p}$, $\rho$, as well as $\rho_s$, are 197.3 °C, 4.95, 0.0046, 22.3 kV·mm$^{-1}$, $1.8 \times 10^{14}$ $\Omega$, and $2.1 \times 10^{14}$ $\Omega$·cm, respectively.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2391-0.

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REFERENCES

1. Yang X. L.; Li, K.; Xu, M. Z.; Liu, X. B. Designing a phthalonitrile/benzoxazine blend for the advanced GFRP composite material. Chinese J. Polym. Sci. 2018, 36, 106–112.
2. Xu, X.; Zhang, Y.; Jiang, J.; Wang, H.; Zhao, X.; Li, Q.; Lu, W. In-situ curing of glass fiber reinforced polymer composites via resistive heating of carbon nanotube films. Compos. Sci. Technol. 2017, 149, 20–27.
3. Agrawal, S.; Singh, K. K.; Sarkar, P. K. A comparative study of wear and friction characteristics of glass fibre reinforced epoxy resin, sliding under dry, oil-lubricated and inert gas environments. Tribol. Int. 2016, 96, 217–224.
4. Park, D. W.; Oh, G. H.; Kim, H. S. Predicting the stacking sequence of E-glass fiber reinforced polymer (GFRP) epoxy composite using terahertz time-domain spectroscopy (THz-TDS) system. Compos. Part B Eng. 2017, 177, 107385.
5. Shahkhosravi, N. A.; Yousefi, J.; Najafabadi, M. A.; Burvill, C.; Minak, G. Fatigue life reduction of GFRP composites due to delamination associated with the introduction of functional discontinuities. Compos. Part B Eng. 2019, 163, 536–547.
6. Rahmat, M.; Ashrafi, B.; Nafiel, A.; Djokic, D.; Martinez-Rubi, Y.; Jakubinek, M. B.; Simard, B. Enhanced shear performance of hybrid glass fiber-epoxy laminates modified with boron nitride nanotubes. ACS Appl. Nano Mater. 2018, 1, 2709–2717.
7. Gu, S. L.; Liu, H. H.; Cao, H.; Mercier, C.; Li, Y. J. Investigations on the interactions between Li-TFSI and glass fibers in the ternary PP/GF/Li-TFSI composites. Chinese J. Polym. Sci. 2018, 36, 113–118.
8. Halder, S.; Ahemad, S.; Das, S.; Wang, J. Epoxy/glass fiber laminated composites integrated with amino functionalized ZrO$_2$ for advanced structural applications. ACS Appl. Mater. Interfaces 2016, 8, 1695–1706.
9. Slobodian, P.; Loret, Pertegés S.; Riha, P.; Matyja, J.; Olejkni, R.; Schledzewski, R.; Kовар, M. Glass fiber/epoxy composites with integrated layer of carbon nanotubes for deformation detection. Compos. Sci. Technol. 2018, 156, 61–69.
10. Tang, Y.; Gu, J.; Yu, Y.; Kong, J. Preparation of POSS/quartz fibers/cyanate ester laminated composites. Polym. Compos. 2015, 36, 2017–2021.
11. Zhang, L. X.; Chang, Q.; Sun, Z.; Zhang, J. J.; Qi, J. L.; Feng, J. C. Wetting of AgCuTi alloys on quartz fiber reinforced composite modified by vertically aligned carbon nanotubes. Carbon 2019, 154, 375–383.
12. Alsadi, M.; Bulut, M.; Ekerli̇g; A.; Jabbar, A. Nano-silica inclusion effects on mechanical and dynamic behavior of fiber reinforced carbon/Kevlar with epoxy resin hybrid composites. Compos. Part B Eng. 2018, 152, 169–179.
13. Tang, L.; Dang, J.; He, M.; Li, J.; Kong, J.; Tang, Y.; Gu, J. Preparation and properties of cyanate-based wave-transparent laminated composites reinforced by dopamine/POSS functionalized Kevlar cloth. Compos. Sci. Technol. 2019, 169, 120–126.
14. 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(3-phenylene benzobisoxazole) fibers. ACS Appl. Mater. Interfaces 2019, 11, 39292–39303.
15. Liu, Z.; Zhang, J.; Tang, L.; Zhou, Y.; Lin, Y.; Wang, R.; Kong, J.; Tang, Y.; Gu, J. Improved wave-transparent performances and enhanced mechanical properties for fluoride-containing PBO precursor modified cyanate ester resins and their PBO fibers/cyanate ester composites. Compos. Part B Eng. 2019, 178, 107466.
16. Bhanuprakash, L.; Ali, A.; Mokkoth, R.; Varghese, S. Mode I and Mode II interlaminar fracture behavior of E-glass fiber reinforced epoxy composites modified with reduced exfoliated graphite oxide. Polym. Compos. 2018, 39, E2506–E2518.
17. Mahmood, H.; Vanzetti, L.; Bersani, M.; Pegoretti, A. Mechanical properties and strain monitoring of glass-epoxy composites with graphene-coated fibers. Compos. Part A-Appl. S. 2018, 107, 112–123.
18. Balkova, R.; Jancar, J.; Cech, V. Effect of RF-plasma deposition parameters on the composition and properties of organic layers deposited on glass fibers. Compos. Sci. Technol. 2009, 69, 2485–2490.
19. Cech, V.; Knob, A.; Hosein, H. A.; Babik, A.; Lepcio, P.; Ondreas, F.; Drzal, L. T. Enhanced interfacial adhesion of glass fibers by tetravinylsilane plasma modification. Compos. Part A-Appl. S. 2014, 58, 84–89.
20. Yang, W.; Zhang, Y. R.; Yuen, A. C. Y.; Chen, T. B. Y.; Chan, M. C.; Peng, L. Z.; Yang, W. J.; Zhu, S. E.; Yang, B. H.; Hu, K. H.; Yeoh, G. H.; Lu, H. D. Synthesis of phosphorus-containing silane coupling agent for surface modification of glass fibers: effective reinforcement and flame retardancy in poly(1,4-butyleneterephthalate). Chem. Eng. J. 2017, 321, 257–267.
21. Safi, S.; Zadhoshau, A.; Masoomi, M. Effects of chemical surface pretreatment on tensile properties of a single glass fiber and the glass fiber reinforced epoxy composite. Polym. Compos. 2016, 37, 91–100.
22. Li, S.; Lin, Q.; Zhu, H.; Hou, H.; Li, Y.; Wu, Q.; Cui, I. Improved mechanical properties of epoxy-based composites with hyperbranched polymer grafting glass-fiber. Polym. Adv. Technol. 2016, 27, 898–904.
23. Luo, N.; Zhong, H.; Yang, M.; Yuan, X.; Fan, Y. Modifying glass fiber surface with grafting acrylamide by UV-grafting copolymerization for preparation of glass fiber reinforced PVDF composite membrane. J. Environ. Sci. 2016, 39, 208–217.
24. Asadi, A.; Miller, M.; Moon, R. J.; Kalaitzidou, K. Improving the
interfacial and mechanical properties of short glass fiber/epoxy composites by coating the glass fibers with cellulose nanocrystals. *Express. Polym. Lett.* **2016**, *10*, 587–597.

25. Tang, L.; He, M.; Na, X.; Guan, X.; Zhang, R.; Zhang, J.; Gu, J. Functionalyzed glass fibers cloth/spherical BN fillers/epoxy laminated composites with excellent thermal conductivities and electrical insulation properties. *Compos. Commun.* **2019**, *16*, 5–10.

26. Yang, X.; Guo, Y.; Han, Y.; Li, Y.; Ma, T.; Chen, M.; Kong, J.; Gu, J. Significant improvement of thermal conductivities for BNNS/PVA composite films via electropinning followed by hot-pressing technology. *Compos. Part B Eng.* **2019**, *175*, 107070.

27. Yeo, H.; Islam, A. M.; You, N. H.; Ahn, S.; Goh, M.; Hahn, J. R.; Jang, S. G. Characteristic correlation between liquid crystalline epoxy and alumina filler on thermal conducting properties. *Compos. Sci. Technol.* **2017**, *141*, 99–105.

28. Zhang, G. D.; Fan, L.; Bai, L.; He, M. H.; Zhai, L.; Mo, S. Mesoscopic simulation assistant design of immiscible polyimide/BN blend films with enhanced thermal conductivity. *Chinese J. Polym. Sci.* **2018**, *36*, 1394–1402.

29. Yang, X.; Liang, C.; Ma, T.; Guo, Y.; Kong, J.; Gu, J.; Zhu, J. A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods. *Adv. Compos. Hybrid. Mater.* **2018**, *1*, 207–230.

30. Ji, C.; Yan, C.; Wang, Y.; Xiong, S.; Zhou, F.; Li, Y.; Sun, R.; Wong, C. P. Thermal conductivity enhancement of CNT/MoS2/graphene-epoxy nanocomposites based on structural synergistic effects and interpenetrating network. *Compos. Part B Eng.* **2019**, *163*, 363–370.

31. Owais, M.; Zhao, J.; Imani, A.; Wang, G.; Zhang, H.; Zhang, Z. Synergetic effect of hybrid fillers of boron nitride, graphene nanoplatelets, and short carbon fibers for enhanced thermal conductivity and electrical resistivity of epoxy nanocomposites. *Compos. Part A-App. S.* **2019**, *117*, 11–22.

32. Ruan, K.; Guo, Y.; Tang, Y.; Zhang, Y.; Zhang, J.; He, M.; Kong, J.; Gu, J. Improved thermal conductivities in polystyrene nanocomposites by incorporating thermal reduced graphene oxide via electropinning-hot press technique. *Compos. Commun.* **2018**, *10*, 68–72.

33. Huang, T.; Zhang, G.; Gao, Y. A novel silver nanoparticle-deposited aluminum oxide hybrids for epoxy composites with enhanced thermal conductivity and energy density. *Compos. interfaces* **2019**, *26*, 1001–1011.

34. Feng, Y.; He, C.; Wen, Y.; Zhou, X.; Xie, X.; Ye, Y.; Mai, Y. W. Multi-functional interface tailoring for enhancing thermal conductivity, flame retardancy and dynamic mechanical property of epoxy/Al2O3 composites. *Compos. Sci. Technol.* **2018**, *160*, 42–49.

35. Yu, C.; Zhang, J.; Li, Z.; Tian, W.; Wang, L.; Luo, J.; Li, Q.; Fan, X.; Yao, Y. Enhanced through-plane thermal conductivity of boron nitride/epoxy composite. *Compos. Part A-App. S.* **2017**, *98*, 25–31.

36. Han, J.; Du, G.; Gao, W.; Bai, H. An anisotropically high thermal conductive boron nitride/epoxy composite based on nacre-mimetic 3D network. *Adv. Funct. Mater.* **2019**, *29*, 1900412.

37. Huang, X.; Iizuka, T.; Jiang, P.; Ohki, Y.; Tanaka, T. Role of interface on the thermal conductivity of highly filled dielectric epoxy/AlN composites. *J. Phys. Chem. C* **2012**, *116*, 13629–13639.

38. Chung, S. L.; Lin, J. S. Thermal conductivity of epoxy resin composites filled with combustion-synthesized AlN powder. composites by coating the glass fibers. *Polym. Compos.* **2018**, *39*, E2125–E2133.

39. Xiao, C.; Chen, L.; Tang, Y.; Zhang, X.; Zheng, K.; Tian, X. Enhanced thermal conductivity of silicon carbide nanowires (SiCn)/epoxy resin composite with segregated structure. *Compos. Part A-App. S.* **2019**, *116*, 98–105.

40. Ma, T.; Zhao, Y.; Ruan, K.; Liu, Z.; Zhang, J.; Guo, Y.; Yang, X.; Kong, J.; Gu, J. Highly thermal conductivities, excellent mechanical robustness and flexibility, and outstanding thermal stabilities of aramid nanofiber composite papers with nacre-mimetic layered structures. *ACS Appl. Mater. Interfaces* **2020**, *12*, 1677–1686.

41. Han, Y.; Shi, X.; Yang, X.; Guo, Y.; Zhang, J.; Kong, J.; Gu, J. Enhanced thermal conductivities of epoxy nanocomposites via incorporating in-situ fabricated hetero-structured SiC-BNNS fillers. *Compos. Sci. Technol.* **2020**, *187*, 107944.

42. Hu, J.; Huang, Y.; Yao, Y.; Fan, G.; Sun, J.; Zeng, X.; Sun, R.; Xu, J. B.; Song, B.; Wong, C. P. Polymer composite with improved thermal conductivity by constructing a hierarchically ordered three-dimensional interconnected network of BN. *ACS Appl. Mater. Interfaces* **2017**, *9*, 13544–13553.

43. Jiang, Y.; Shi, X.; Feng, Y.; Li, S.; Zhou, X.; Xie, X. Enhanced thermal conductivity and ideal dielectric properties of epoxy composites containing polymer modified hexagonal boron nitride. *Compos. Part A-App. S.* **2018**, *107*, 657–661.

44. Yang, X.; Guo, Y.; Luo, X.; Zheng, N.; Ma, T.; Tan, J.; Li, C.; Zhang, Q.; Gu, J. Self-healing, recoverable epoxy elastomers and their composites with desirable thermal conductivities by incorporating BN fillers via in-situ polymerization. *Compos. Sci. Technol.* **2018**, *164*, 59–64.

45. Choi, S.; Yang, J.; Kim, Y.; Nam, J.; Kim, K.; Shim, S. E. Microwave-accelerated synthesis of silica nanoparticle-coated graphite platelets and properties of their epoxy composites. *Compos. Sci. Technol.* **2014**, *103*, 8–15.

46. Burger, N.; Laachachi, A.; Mortazavi, B.; Ferriol, M.; Lutz, M.; Toniazzo, V.; Ruch, D. Alignments and network of graphite fillers to improve thermal conductivity of epoxy-based composites. *Int. J. Heat Mass Trans.* **2015**, *89*, 505–513.

47. Luo, B.; Wang, X.; Wang, Y.; Li, L. Fabrication, characterization, properties and theoretical analysis of ceramic/PVDF composite flexible films with high dielectric constant and low dielectric loss. *J. Mater. Chem. A* **2014**, *2*, 510–519.

48. Xu, N.; Hu, L.; Zhang, Q.; Xiao, X.; Yang, H.; Yu, E. Significantly enhanced dielectric performance of polyvinylidene fluoride-co-hexafluoropropylene)-based composites filled with hierarchical flower-like TiO2 particles. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27373–27381.

49. Wang, Z.; Liu, J.; Cheng, Y.; Chen, S.; Yang, M.; Huang, J.; Wang, H.; Wu, G.; Wu, H. Alignment of boron nitride nanofibers in epoxy composite films for thermal conductivity and dielectric breakdown strength improvement. *Nanomaterials* **2018**, *8*, 242.

50. Chen, S.; Cheng, Y.; Xie, Q.; Xiao, B.; Wang, Z.; Liu, J.; Wu, G. Enhanced breakdown strength of aligned-sodium-titanate-nanowire/epoxy nanocomposites and their anisotropic dielectric properties. *Compos. Part A-App. S.* **2019**, *120*, 84–94.

51. Feng, C. P.; Wan, S. S.; Wu, W. C.; Bai, L.; Bao, R. Y.; Liu, Z. Y.; Yang, M. B.; Chen, J.; Yang, W. Electrically insulating, layer structured Si/GNPx/BN thermal management materials with enhanced thermal conductivity and breakdown voltage. *Compos. Sci. Technol.* **2018**, *167*, 456–462.

52. Yang, X.; Fan, S; Li, Y.; Guo, Y.; Li, Y.; Ruan, K.; Zhang, S.; Zhang, J.; Kong, J.; Gu, J. Synchronously improved electromagnetic interference shielding and thermal conductivity for epoxy nanocomposites by constructing 3D copper nanowires/thermally annealed graphene aerogel framework. *Compos. Part A-App. S.* **2020**, *128*, 105670.