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

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 Electronic Supplementary Information

Abstract Glass fibers (GFs)/epoxy laminated composites always present weak interlaminar shear strength (ILSS) and low cross-plane thermal conductivity coefficient ($\lambda_{\perp}$). In this work, silica-sol, synthesized from tetraethyl orthosilicate (TEOS) and KH-560 via sol-gel method, was employed to functionalize the surface of GFs (Si-GFs). Together with a spherical boron nitride (BNN-30), the thermally conductive BNN-30/Si-GFs/epoxy laminated composites were then fabricated. Results demonstrate that Si-sol is beneficial to the improvement of mechanical properties for epoxy laminated composites (especially for ILSS). The BNN-30/Si-GFs/epoxy laminated composites with 15 wt% BNN-30 fillers display the optimal comprehensive properties. In-plane λ ($\lambda_{//}$) and $\lambda_{\perp}$ reach 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 ($\lambda_{//}$ = 0.96 W·m⁻¹·K⁻¹ and $\lambda_{\perp}$ = 0.46 W·m⁻¹·K⁻¹), respectively, and also about 10.8 and 4.9 times those of pure epoxy resin ($\lambda_{//}$ = $\lambda_{\perp}$, 0.22 W·m⁻¹·K⁻¹). And the heat-resistance index (T_{HRI}), dielectric constant (ϵ), dielectric loss ($\tan\delta$), breakdown strength (E_0), surface resistivity (ρ_s) as well as volume resistivity (ρ_v) are 197.3 °C, 4.95, 0.0046, 22.3 kV·mm⁻¹, 1.8×10^{14} Ω, and 2.1×10^{14} Ω·cm, respectively.

Keywords Thermally conductive composites; Glass fibers; Epoxy resin; Silica-sol; Surface functionalization

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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.^[4,5] However, low cross-plane thermal conductivity coefficient ($\lambda_{\perp}$) 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 easy 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,^[22,23] etc. 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 $\lambda_{\perp}$ and in-plane λ ($\lambda_{//}$) values of the *f*-GFs/GBN-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

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can further simplify surface functionalization process, which can avoid using 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 Al_2O_3 ,^[33,34] BN,^[35,36] aluminum nitride (AlN),^[37,38] and SiC whisker (SiC_w),^[39] etc.) 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* combining ice-templating self-assembly and infiltration method, which possessed high λ values up to $4.42 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 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 $1.198 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 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 $1.058 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, about 4 times that of pure epoxy resin.

In this work, silica-sol, synthesized from tetraethyl orthosilicate (TEOS) and γ -glycidoxypolytrimethoxysilane (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 compression, applying the micron boron nitride with particle size of $30 \mu\text{m}$ (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, $2.45 \text{ g}\cdot\text{cm}^{-3}$, 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 vacuum 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 (Ya'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: $110^\circ\text{C}/0.5 \text{ h} + 170^\circ\text{C}/1 \text{ h}$. 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} ($-\text{CH}_2-$, $-\text{CH}_3$) and 1070 cm^{-1} ($\text{Si}-\text{O}$) in TEOS are observed. For silica-sol, the characteristic band at 1060 cm^{-1} is assigned to the $\text{Si}-\text{O}-\text{Si}$, ascribed to hydrolysis interaction between $\text{Si}-\text{OH}$. Furthermore, silica-sol shows not only the stretching vibration bands of $-\text{CH}_2-$, $-\text{CH}_3$, and $\text{Si}-\text{O}-\text{Si}$, 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 $-\text{CH}_3$ 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 $-\text{O}-\text{CH}_2-$, $\text{O}-\text{CH}_3$, and $\text{CH}_2-\text{O}-\text{CH}_2$, 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 $800\text{--}400 \text{ cm}^{-1}$ can be assigned to vibration band of $\text{Si}-\text{O}$. For Si-GFs, new characteristic stretching vibration bands of $\text{Si}-\text{OH}$ and $-\text{CH}_3$ appear near 3340 and 2930 cm^{-1} , respectively. Meantime, the characteristic band at 908 cm^{-1} is assigned to epoxy groups. It

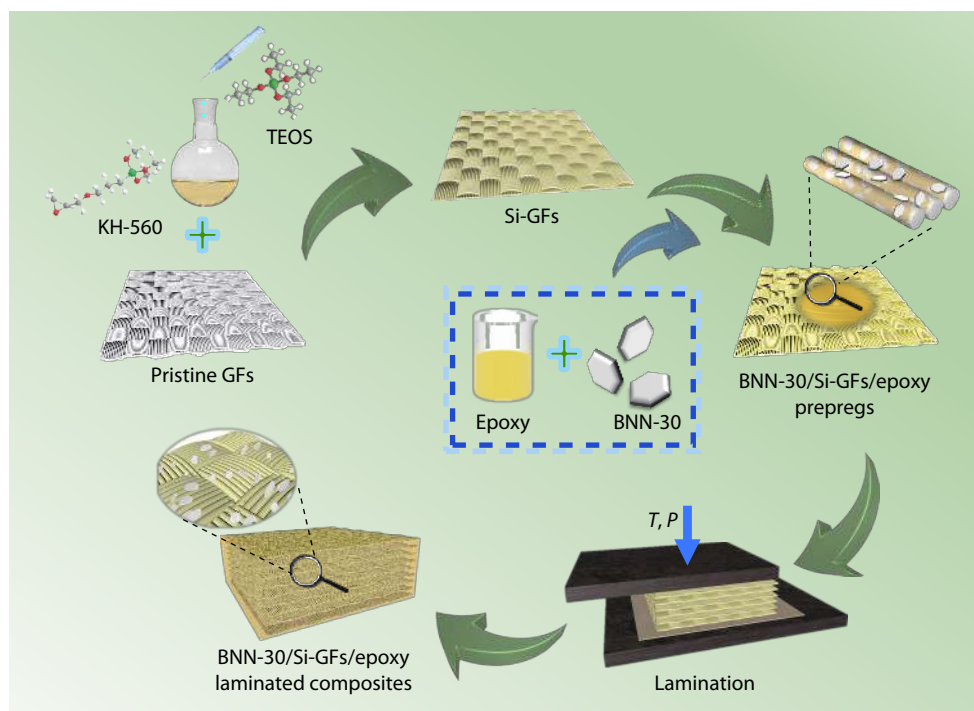


Fig. 1 Schematic diagram for the preparation of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites.

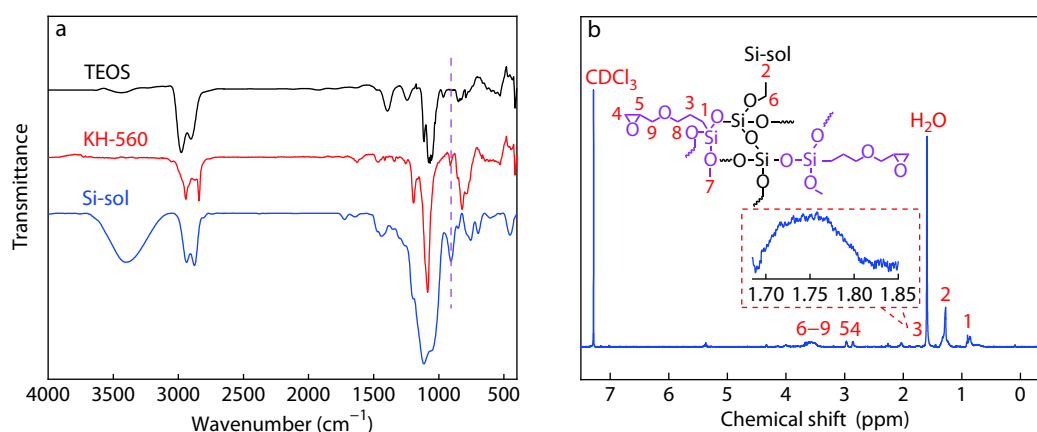


Fig. 2 (a) FTIR and (b) ^1H -NMR spectra of silica-sol.

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 sur-

face of Si-GFs gets coarse (Fig. 3d). Figs. 3(c')–3(c'') and Figs. 3(d')–3(d'') 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 ($\lambda_{//} = 0.96 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and cross-plane λ ($\lambda_{\perp} = 0.46 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) values of the Si-GFs/epoxy laminated composites are higher than those of pristine GFs/epoxy laminated composites ($\lambda_{//} = 0.76 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $\lambda_{\perp} = 0.31 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). The addition of silica-sol can effectively im-

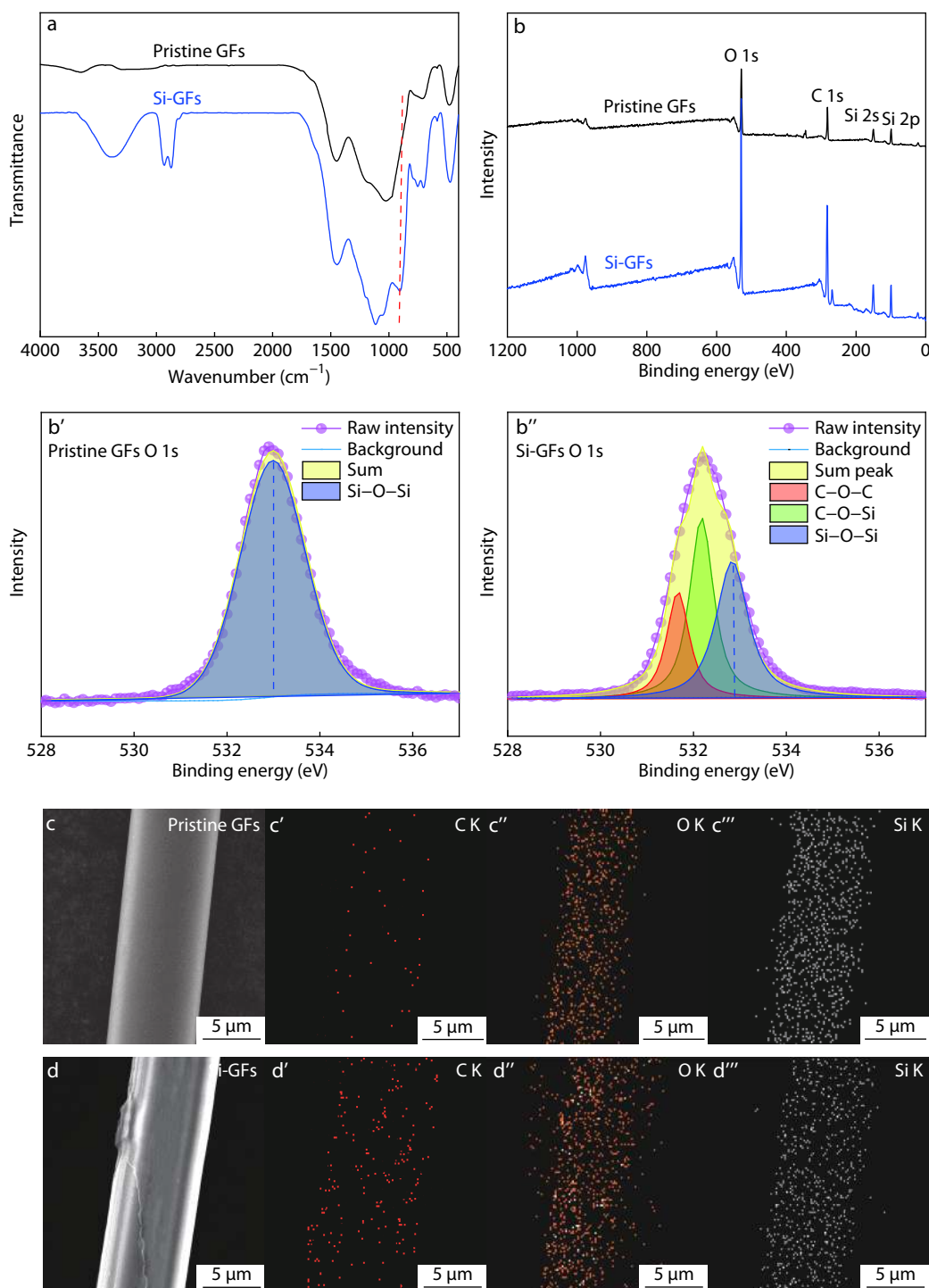


Fig. 3 (a) FTIR, (b) XPS spectra, and (b', b'') high-resolution O 1s. (c, d) SEM morphologies and (c'–c''', d'–d''') EDS of GFs and Si-GFs.

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 λ 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, silicasol can adhere to GFs surface well by physical interaction. On the other hand, a large amount of polar groups on the sur-

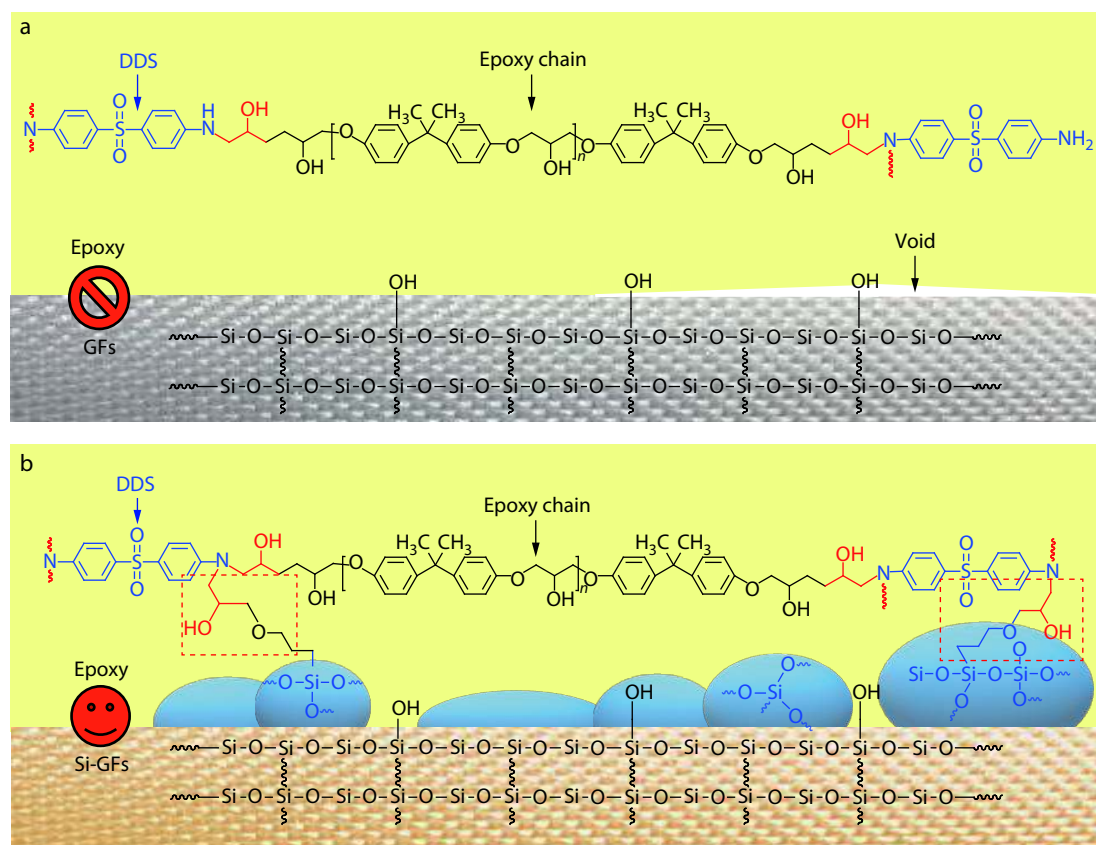


Fig. 4 Illustration of interaction in (a) pristine GFs/epoxy and (b) Si-GFs/epoxy laminated composites.

face of Si-GFs can participate in co-cure reaction of epoxy resin with the help of DDS^[45] 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 $\lambda_{//}$ and $\lambda_{\perp}$ values of the thermally conductive BNN-30/Si-GFs/epoxy laminated composites. Both $\lambda_{//}$ and $\lambda_{\perp}$ values are increased with increasing addition of BNN-30 fillers. Compared with Si-GFs/epoxy laminated composites ($\lambda_{//} = 0.96 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $\lambda_{\perp} = 0.46 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), the $\lambda_{//}$ and $\lambda_{\perp}$ values of 15 wt% BNN-30/Si-GFs/epoxy laminated composites are improved to 2.37 and $1.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, increased by 146.9% and 132.6%, respectively, also about 10.8 and 4.9 times those of the pristine epoxy resin ($\lambda_{//} = \lambda_{\perp} = 0.22 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). 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 $\lambda_{//}$ and $\lambda_{\perp}$ 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 λ 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 propaga-

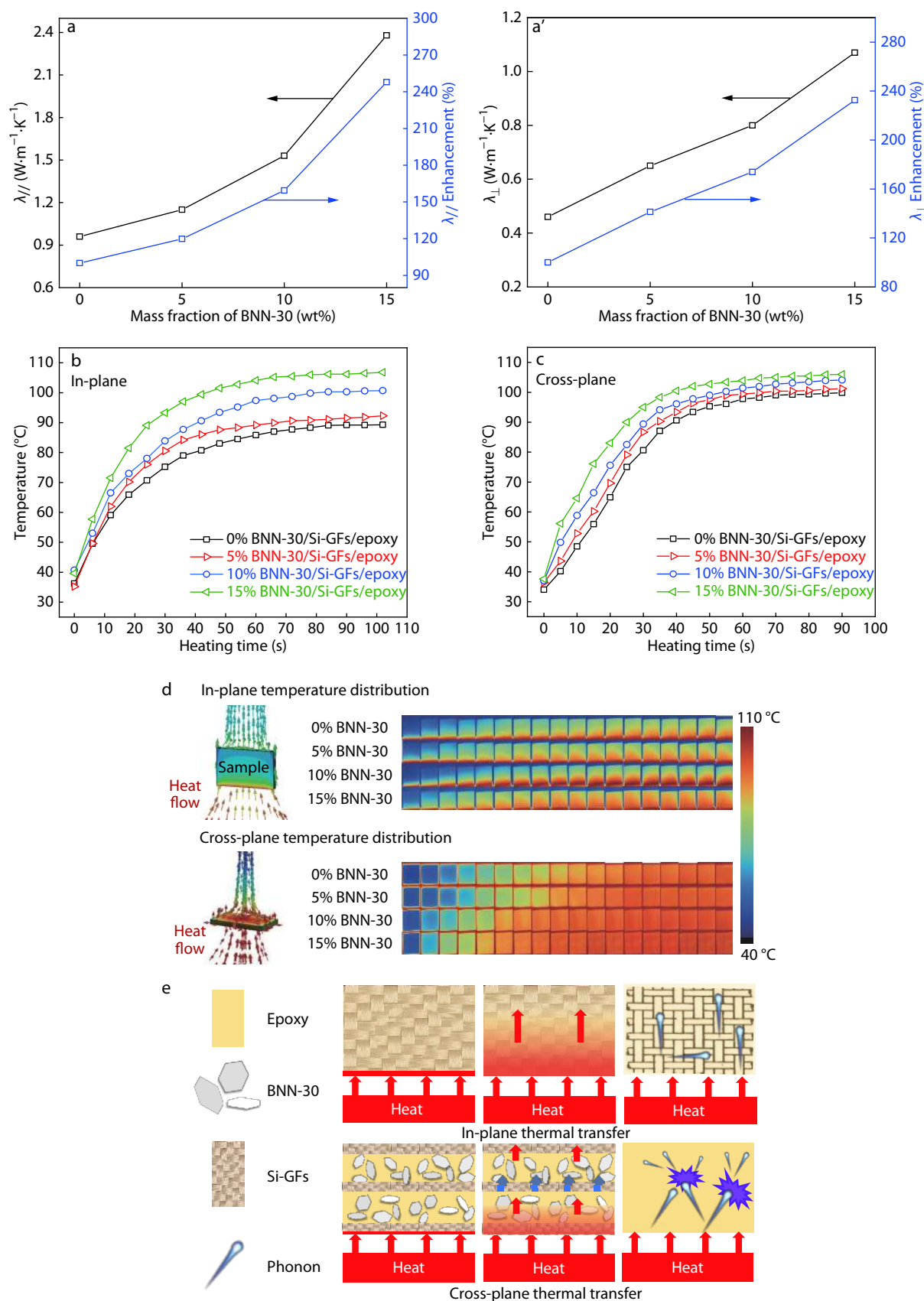


Fig. 5 (a) $\lambda_{//}$ and (a') $\lambda_{\perp}$, (b, c) temperature versus heating time, (d) temperature distribution and heat transmitting pathway, and (e) schematic diagram for thermal transfer mechanism of the BNN-30/Si-GFs/epoxy laminated composites.

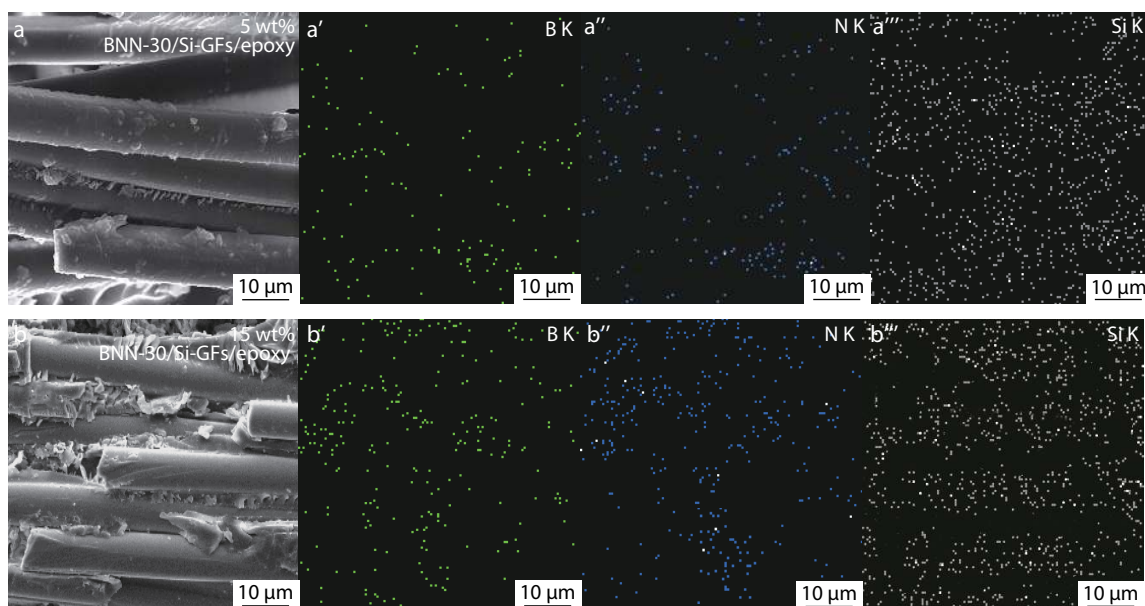


Fig. 6 (a, b) SEM and (a'–a''', b'–b''') EDS images of the fracture surfaces for BNN-30/Si-GFs/epoxy laminated composites with (a'–a''') 5 wt% and (b'–b''') 15 wt% BNN-30 fillers.

tion. Therefore, $\lambda_{//}$ values of the BNN-30/Si-GFs/epoxy laminated composites are higher than those of $\lambda_{\perp}$ 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/Epoxylaminated 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:

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

where P is the cumulative probability of electric failure, β 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).^[47,48] β 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 ($E_0 = 17.1 \text{ kV}\cdot\text{mm}^{-1}$), E_0 value of the 15 wt% BNN-30/Si-GFs/epoxy laminated composites is improved to $22.3 \text{ kV}\cdot\text{mm}^{-1}$ 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_0 . 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_0 . 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.^[49,50]

In Figs. 7(c) and 7(d), both the surface resistivity (ρ_s) and volume resistivity (ρ_v) of the BNN-30/Si-GFs/epoxy laminated composites gradually decrease with increasing mass fraction of BNN-30 fillers. ρ_s and ρ_v values of the 15 wt% BNN-30/Si-GFs/epoxy laminated composites are reduced to $1.8 \times 10^{14} \Omega$ and $2.1 \times 10^{14} \Omega\cdot\text{cm}$, 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 ρ_s and ρ_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 ($\rho_s \geq 1 \times 10^{11} \Omega$, $\rho_v \geq 1 \times 10^9 \Omega\cdot\text{cm}$).^[51] Meanwhile, both ϵ and $\tan\delta$ 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/Epoxylaminated 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

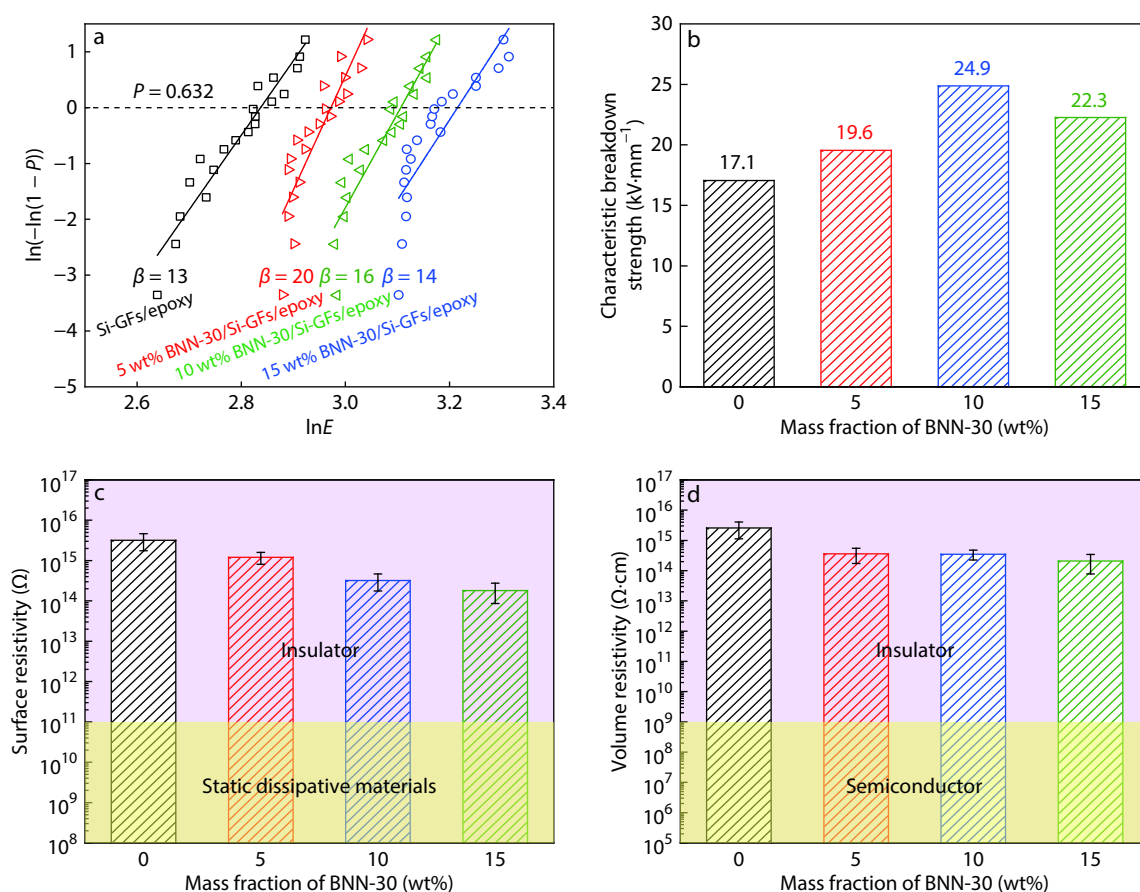


Fig. 7 (a) Weibull plots of E distribution, (b) breakdown strength, (c) surface electrical resistivity, and (d) volume electrical resistivity of the BNN-30/Si-GFs/epoxy laminated composites.

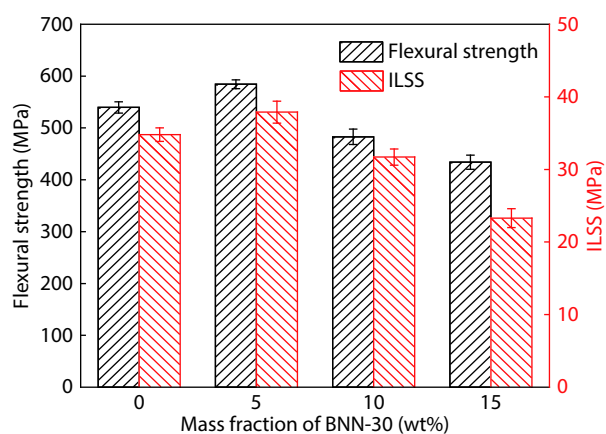


Fig. 8 Effects of BNN-30 contents on the mechanical properties of the BNN-30/Si-GFs/epoxy laminated composites.

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 λ values, thermal stabilities, ϵ 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 BNN-30/Si-GFs/epoxy laminated composites with 15 wt% BNN-30 fillers display the optimal comprehensive properties. $\lambda_{//}$ and $\lambda_{\perp}$ 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 ($\lambda_{//} = 0.96$ W·m⁻¹·K⁻¹ and $\lambda_{\perp} = 0.46$ W·m⁻¹·K⁻¹), respectively, also about 10.8 and 4.9 times than those of pure epoxy resin ($\lambda_{//} = \lambda_{\perp} = 0.22$ W·m⁻¹·K⁻¹). And the heat-resistance index (T_{HRI}), ε and $\tan\delta$, E_0 , ρ_s as well as ρ_v are 197.3 °C, 4.95, 0.0046, 22.3 kV·mm⁻¹, 1.8×10^{14} Ω, and 2.1×10^{14} Ω·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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