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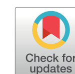
A 3D interconnected Cu network supported by carbon felt skeleton for highly thermally conductive epoxy composites



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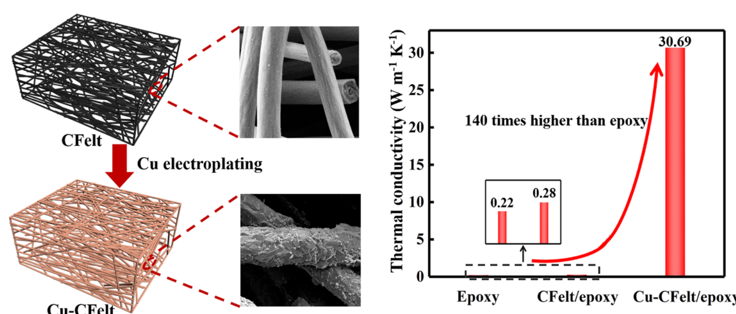
HIGHLIGHTS

- Carbon felt was used as skeleton to support the 3D interconnected Cu network.
- The 3D interconnected Cu network acts as thermal conductive channel in epoxy composite.
- The obtained composite achieves an ultrahigh thermal conductivity of 30.69 W m^{-1} K^{-1}.
- The Cu-CFelt/epoxy composite maintains good mechanical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective heat removal through polymer composites has become a crucial issue in thermal management. Constructing a 3D interconnected filler network in polymer matrix is generally considered to be one of the most effective strategies for enhancing thermal conductivity of polymer-based composites. Herein, a unique 3D interconnected Cu network was successfully fabricated to enhance the thermal transfer properties of epoxy composites. We used Carbon felt (CFelt) as 3D skeleton to electroplate Cu on the CFelt surface for constructing the 3D Cu film network, which can serve as continuous heat conductive highways. The highly thermally conductive epoxy composites were then prepared by impregnating epoxy resin into the 3D Cu-plated CFelt (Cu-CFelt) network. Taking advantage of the 3D interconnected Cu heat transfer channel, an ultrahigh thermal conductivity of 30.69 W m^{-1} K^{-1} was achieved, which exhibited nearly 140 times higher than that of pure epoxy (0.22 W m^{-1} K^{-1}) and 110 times higher than that of CFelt/epoxy composite (0.28 W m^{-1} K^{-1}). And our composite exhibited outstanding thermal behaviors during heating and cooling processes. Additionally, the obtained composite maintained good mechanical properties and presented superior electrical conductivity of 7.49×10^4 S cm^{-1}. Our work reveals that the novel 3D Cu-CFelt/epoxy composites have strong application prospects in thermal management materials.

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1. Introduction

The development of miniaturization and integration of electronic devices and electrical equipment inevitably leads to excessive heat generation and accumulation, which will affect normal operation and damage these devices [1–4]. Therefore, seeking highly efficient thermal management materials to dissipate the generated heat is critical to the performance, lifetime and reliability of these devices. Typically, polymer materials with light weight, low cost, corrosion resistance and easy processing have been widely used to prepare thermally conductive composite materials [5]. Unfortunately, common polymers exhibit very low thermal conductivity in the range of 0.1–0.6 W m^{-1} K^{-1} due to phonon scattering from numerous structural defects, such as disordered structure and various entanglements within polymer [6]. To tackle this problem, thermally conductive fillers, including metals (Ag [7], Cu [8,9]), inorganic particles (BN [10], SiC [11], Al_2O_3 [12], AlN [13], SiO_2 [14]) and carbonaceous materials (carbon nanotubes (CNTs) [15], graphene [16], carbon fibers [17]) have been added into polymer matrix to enhance the thermal conductivity of polymer-based composites. However, due to the difficulty in forming an effective heat conduction network, conventional methods such as simple blending are difficult to achieve high thermal conductivity at low fillers loadings [18], while high fillers loadings not only deteriorate the mechanical properties but also make processing difficult and greatly increase the cost [19].

With the deepening of research, it has been found that the formation of 3D thermal conductive network in polymer matrix is one of the most effective and promising methods to achieve high thermal conductivity [20,21]. In this case, most heat can transfer along the 3D heat conduction channel. To date, many efforts have been attempted to prepare the 3D filler network, including chemical vapor deposition (CVD) [22], freeze-drying [20], ice-template [23], self-assembly [24], etc. After the 3D structure was introduced into the polymer matrix, the thermal conductivity of the composites was enhanced effectively. For example, Li et al. prepared a 3D filler network by in-situ growth of CNTs on the surface of BNNS via CVD. The obtained BNNS/CNT/epoxy composites showed a significant cross-plane thermal conductivity enhancement of 615% compared with the pure epoxy at a low CNTs loading [22]. Although the composites filled with 3D structure prepared by these methods can achieve high thermal conductivity, the unavoidable thermal resistance at filler-filler interfaces has negative impacts on the thermal conductivity of composites [25], and some fabricating methods are relatively complex and difficult to scale up [26].

Carbon felt (CFelt), which has a good 3D cross-linked structure weaved by carbon fibers, has wide application prospects owing to its high mechanical strength, conductivity, light weight, high porosity and low cost [27]. However, CFelt exhibits a low thermal conductivity [28] mainly due to its fibrous porous structure and high thermal resistance at the fiber-fiber interfaces resulted from the obvious gaps between the adjacent fibers. Cu has been widely used as filler to improve the thermal conductivity of composites since the cost of it is significantly less than Ag and Au and it has a comparable thermal conductivity which is in the range of 350–400 W m^{-1} K^{-1} [29]. Moreover, Cu can be deposited on another conductive filler surface easily by electroplating, which has multiple advantages such as the effortless control of film thickness, high deposition rates, simple operation and the ability to produce uniform coating on non-flat materials surface. Yu et al. prepared continuous heat conduction pathways of Cu via electroplating Cu onto carbon fibers, and the obtained epoxy composites exhibited high thermal conductivity in parallel direction [30].

In this work, taking the 3D structure and good electrical conductivity of CFelt into consideration, we chose CFelt as the skeleton to support the 3D filler network and the continuous 3D Cu network was fabricated by electroplating Cu on the CFelt surface. The generated Cu not only coated CFelt skeleton uniformly, but also acted as bridges to link the adjacent carbon fibers. After the infiltration and curing of epoxy resin, we prepared highly thermally conductive composites. Benefiting from the continuous 3D Cu heat conduction pathway, the composite presented outstanding thermal conductivity as high as 30.69 W m^{-1} K^{-1}. In addition, the thermal conductivity could be adjusted easily by changing the electroplating time. Moreover, the composites exhibited good mechanical strength and electric conduction. These attractive properties demonstrate that our composites have broad potentials for the application of heat dissipation and thermal interface materials.

2. Experimental section

2.1. Materials

CFelt was bought from Beihai Carbon Co., Ltd. (China). Sulfuric acid (H_2SO_4) and acetone were purchased from Tianjin Yuanli Chemical Co., Ltd. (China). Sodium chloride (NaCl) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) were obtained from Tianjin Komi Chemical Reagent Co., Ltd. (China). Nitric acid (HNO_3) was provided by Aladdin. Bisphenol A epoxy resin (E-51) was bought from Jining Huakai Resin Co., Ltd. (Jining, China). D-230 curing agent was purchased from Chuzhou Huisheng Electronic Materials Co., Ltd. (Chuzhou, China). All reagents were analytically pure.

2.2. Surface treatment of CFelt

The surface treatment of CFelt included three steps. Firstly, CFelt was treated at 400 °C for 60 min in muffle oven. Secondly, the after-heated CFelt was immersed in acetone for 40 min at ambient temperature, then washed several times with deionized water and dried in an oven at 80 °C. Finally, the dried CFelt was immersed in a concentrated nitric acid solution (65 wt%) with water bath under 95 °C for 40 min. After being washed with deionized water to neutrality and drying at 80 °C, the CFelt was successfully modified.

2.3. Preparation of 3D Cu-plated CFelt (Cu-CFelt) structure

Electrodeposition was used for plating Cu on CFelt skeleton which was conducted in an electroplating bath including parallel CFelt cathode and Cu anode separated by the distance of 15 mm. The electroplating solution consisted of 150 g/L $CuSO_4 \cdot 5H_2O$, 140 mg/L NaCl and 260 g/L H_2SO_4. Electroplating was performed at a constant current density of 75 mA/cm^2 for different time (1–10 h) at ambient temperature to achieve the desired Cu content. The fabricated Cu-CFelt samples were rinsed several times with deionized water and then dried in a vacuum oven at 70 °C to prevent oxidation of the Cu layer.

2.4. Preparation of the 3D Cu-CFelt/epoxy composites

The Cu-CFelt/epoxy composites were prepared by pouring the resin into the Cu-CFelt framework. Specifically, the epoxy resin (E-51) and curing agent (D-230) were first mixed with a weight ratio of epoxy to D-230 of 3:1 and stirred in the Automatic Rev-Rot Gravity Vacuum Mixer to obtain a homogeneous solution. Then, the mixture of epoxy resin and curing agent was poured into the Cu-CFelt framework in the mold. After curing at 90 °C for 120 min and 120 °C for 120 min, the Cu-CFelt/epoxy composites were successfully prepared. The corresponding Cu-CFelt/epoxy composites were designated as Cu-$CFelt_x$/epoxy, where x represented the electroplating time. For example, the Cu-$CFelt_1$/epoxy denotes that the CFelt was electroplated Cu for 1 h. And the Cu loading in Cu-$CFelt_1$/epoxy composite is 3.59 vol%.

2.5. Characterization

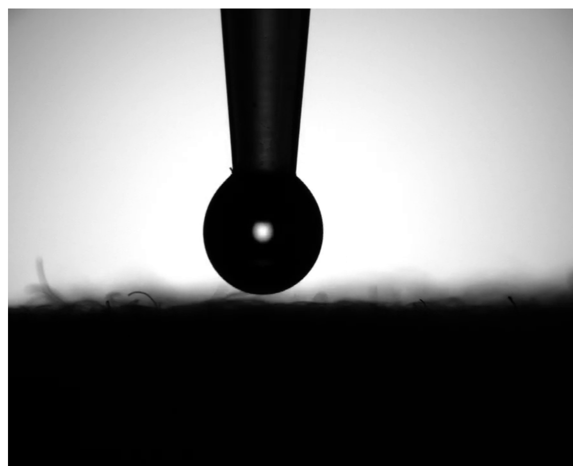
The micromorphology of the CFelt, Cu-Felt and Cu-Felt/epoxy composites were characterized using scanning electron microscope

(SEM, Quanta 200). The elemental analysis of Cu-CFelt was taken by X-ray energy dispersive spectrometer (EDS) detector. Measurements of water contact angles (WCAs) about CFelt were tested by a Contact Angle System Theta lite (Biolin, Sweden) with 10 μL deionized water droplets. The functional groups on the surface of CFelt before and after modification were examined using Fourier transform infrared (FT-IR) spectrometer (Perkin Elmer). The crystallographic properties of CFelt and Cu-CFelt were investigated by X-ray diffraction (XRD, Rigaku Ultima IV using Cu Kα radiation, λ = 1.5406 Å, 40 kV and 40 mA). Thermal conductivity of the composites was measured using the Thermal Conductivity Meter (SETARAM, France) based on the transient plane source method (TPS). The measurements were performed on two-side parallel samples by putting the sensor between two slab shape samples. For each sample, the measurement was repeated several times and the average value was taken to be the thermal conductivity of the composites. The surface temperature of the composites during heating and cooling processes was recorded by infrared thermograph (Ti480 Pro, Fluke). The standard four-point probe technique (RTS-9, Guangzhou Four Probe Technology Co., Ltd. (Guangzhou, China)) was used to measure the electrical conductivity of Cu-CFelt/epoxy composites. The flexural strength of the composites was tested using Electromechanical Universal Testing Machine (CMT8502, MTS SYSTEMS (CHINA) CO., LTD.) at a loading rate of 2 mm/min.

3. Results and discussion

3.1. Preparation and characterization of Cu-CFelt

Fig. 1 presents the synthesis route of the Cu heat conduction network supported by CFelt skeleton and its epoxy composites. The specific preparation process can be seen in experimental part. Firstly, we chose CFelt as the 3D skeleton for deposition of highly thermally conductive Cu. As shown in Fig. S1, the carbon fibers of CFelt are tangled and lapped by each other to form a 3D network. And CFelt provides a large internal free room to accommodate particles deposition due to the high porosity and large specific surface area of it. Sizing agents are widely used on CFelt surface to protect it from fluffing and wearing during post-processing, which are not conducive to the immersion of CFelt in electroplating bath and make it difficult for Cu to deposit on CFelt surface uniformly [31]. Therefore, CFelt needs to be modified in order to remove surface impurities and enhance the surface activity. The morphologies of CFelt before and after treatment are shown in Fig. 2a–d. Fig. 2a and b show that some obvious spotted impurities are adhered to original CFelt surface. After modification, the impurities almost disappear and surface roughness of CFelt increases with the narrow grooves deepening (Fig. 2c and d). The FT-IR spectra of pristine and modified CFelt are shown in Fig. 2e. In the spectrum of pristine CFelt (Fig. 2e(i)), the characteristic peaks at 3448 cm^{-1} and 1622 cm^{-1} correspond to the O–H vibration [32] and H–O–H bending [33], respectively. After the modification of CFelt, the intensity of O–H band and H–O–H band increased (Fig. 2e(ii)). In addition, the characteristic peaks around 2932 cm^{-1}(v (COOH)), 1391 cm^{-1}(v (COO)) [1] and 1097 cm^{-1}(v (C–O)) [34] can also be observed, which reveals that more oxygen-containing functional groups exist on the modified CFelt surface. The insets in Fig. 2a and c show the WCAs of CFelt before and after modification. The WCA is 141.4 ± 0.3° for pristine CFelt, which is not conducive to the subsequent experimental process. In contrast, we can see a 10 μL water droplet is absorbed by the treated CFelt (Movie S1). The change of WCA further indicates that the modified CFelt has outstanding hydrophilicity. The results clearly clarify that the surface roughness and surface activity of CFelt are enhanced remarkably and more hydrophilic groups are introduced to CFelt surface after surface treatment. Moreover, the electrochemical activity of CFelt is also increased after modification [27]. In this way, CFelt is easier to immerse in plating solution. Besides, the adhesion and uniformity of Cu layer on CFelt skeleton are improved.



Movie S1.

After the CFelt was modified, Cu was deposited on the CFelt skeleton by electroplating to form the 3D interconnected Cu network. The SEM images in Fig. 3a1–d2 show the micromorphology of CFelt and Cu-CFelt. The cross-sectional images of samples reveal that the thickness of Cu layer continuously increases with the increasing plating time (insets in Fig. 3a2, b2, c2 and d2). To analyze this change more accurately, we separately counted 100 carbon fibers and Cu-plated carbon fibers with different plating time to analyze the variations of average thickness of the Cu layer at different plating time (Fig. S2a–d). Statistical results indicate that the average thickness of the Cu layer increases almost linearly with the increasing plating time (Fig. S3). Such relation of the thickness of Cu layer with plating time indicates that the thickness of Cu layer can be well controlled in a simple way, which is helpful to control

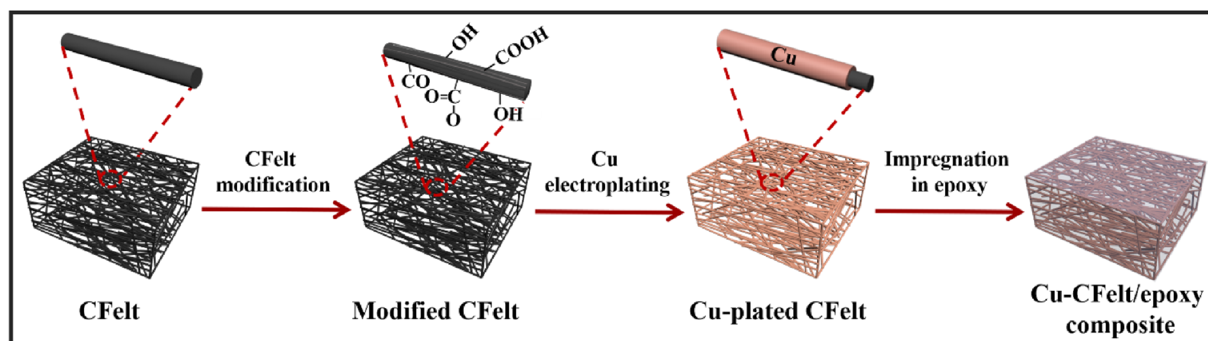


Fig. 1. Schematic of fabrication process of the Cu-CFelt/epoxy composites.

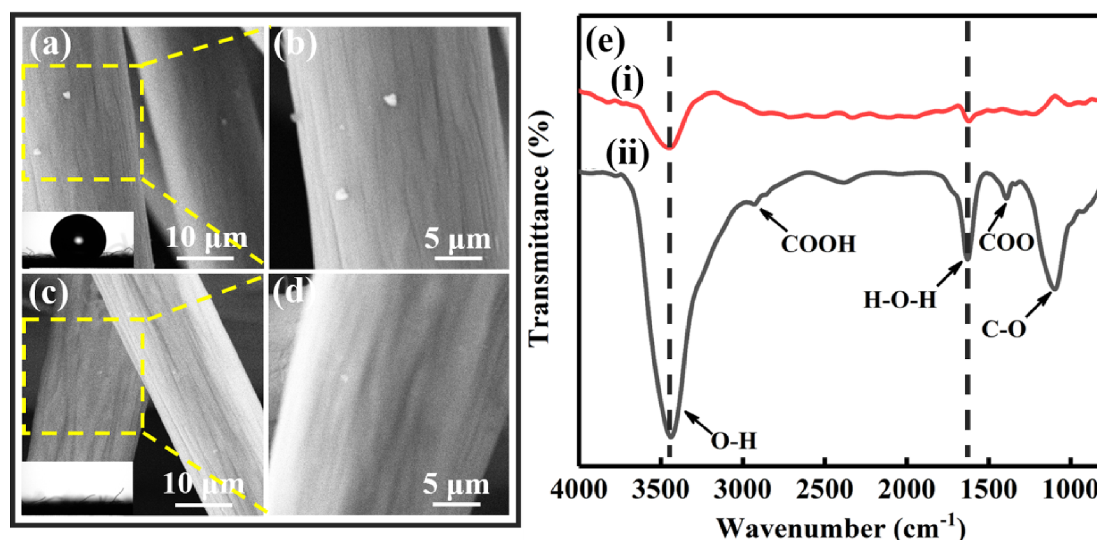


Fig. 2. SEM images of (a, b) pristine CFelt and (c, d) CFelt after modification. The insets in (a) and (c) are the WCAs of pristine CFelt and modified CFelt, respectively. (e) FTIR spectra of (i) pristine CFelt and (ii) CFelt after modification.

the thermal conductivity of our Cu-CFelt/epoxy composites. For CFelt without Cu coating in Fig. 3a1 and a2, we find that the adjacent carbon fibers are simply lapped by each other with obvious gaps between them. As for Cu-CFelt$_4$ in Fig. 3b1 and b2, the 3D CFelt skeleton is coated by Cu thoroughly and uniformly, so the 3D Cu network was formed on CFelt skeleton. Furthermore, the electroplated Cu can serve as bridges to connect the adjacent Cu-plated carbon fibers to enhance the cross-linking degree and continuity of the 3D Cu network. As the plating time increased (Fig. 3c1–d2), the thickness of Cu layer gradually increases. The thicker Cu layer make more adjacent Cu-plated carbon fibers connect to each other and decrease the porosity of CFelt.

The EDS scanning test of carbon, oxygen and copper was carried to investigate the composition at the cross section of Cu-CFelt (Fig. 4a). The presence of a large amount of Cu element proves that Cu was successfully deposited on CFelt surface. The crystallographic properties of CFelt before and after electroplating were analyzed by XRD (Fig. 4b). The XRD pattern of modified CFelt shows the typical broad peak of carbon material located between 18° and 30°, which is related to the C (0 0 2) plane of CFelt [31]. After electroplating, the XRD patterns of Cu-CFelt$_4$ and Cu-CFelt$_{10}$ show three obvious diffraction peaks which correspond to characteristic reflection peaks of (1 1 1), (2 0 0), and (2 2 0) plane of Cu, respectively, indicating the typical face-centered cubic (fcc) crystal structure of Cu [35]. And we do not observe the characteristic peaks of oxidation state of Cu on the XRD patterns of Cu-CFelt$_4$ and Cu-CFelt$_{10}$, revealing that Cu particles in metallic form are coated on CFelt skeleton. In addition, the XRD patterns of Cu-CFelt$_4$ and Cu-CFelt$_{10}$ both show a decrescent C (0 0 2) peak. This phenomenon can be regarded as a favorable evidence for the formation of compact and uniform Cu layer on CFelt surface since the XRD characteristic signal belonging to CFelt was obscured or absorbed by Cu layer.

3.2. Morphology of the Cu-CFelt/epoxy composites

After Cu-CFelt skeleton was fully impregnated with epoxy resin and the mixture was cured, the Cu-CFelt/epoxy composites were prepared. It is believed that the network-morphology and the filler-matrix interface connection play the necessary roles in determining the thermal conductivity of polymer composites [25,36]. Fig. 5 shows the

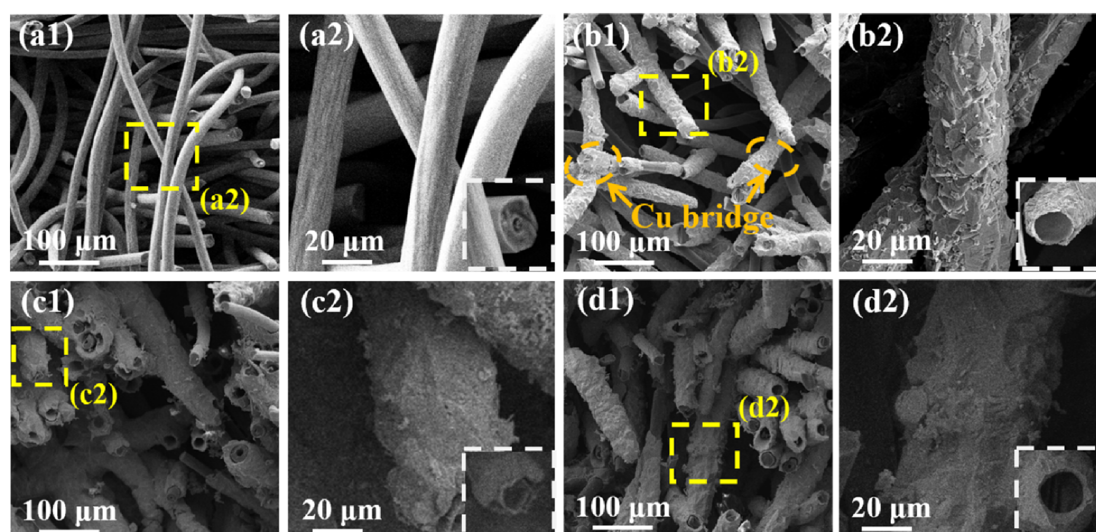


Fig. 3. SEM images of CFelt: (a1) and (a2), Cu-CFelt$_4$: (b1) and (b2), Cu-CFelt$_8$: (c1) and (c2) and Cu-CFelt$_{10}$: (d1) and (d2), respectively. The insets show the cross-sectional views of CFelt, Cu-CFelt$_4$, Cu-CFelt$_8$ and Cu-CFelt$_{10}$, respectively.

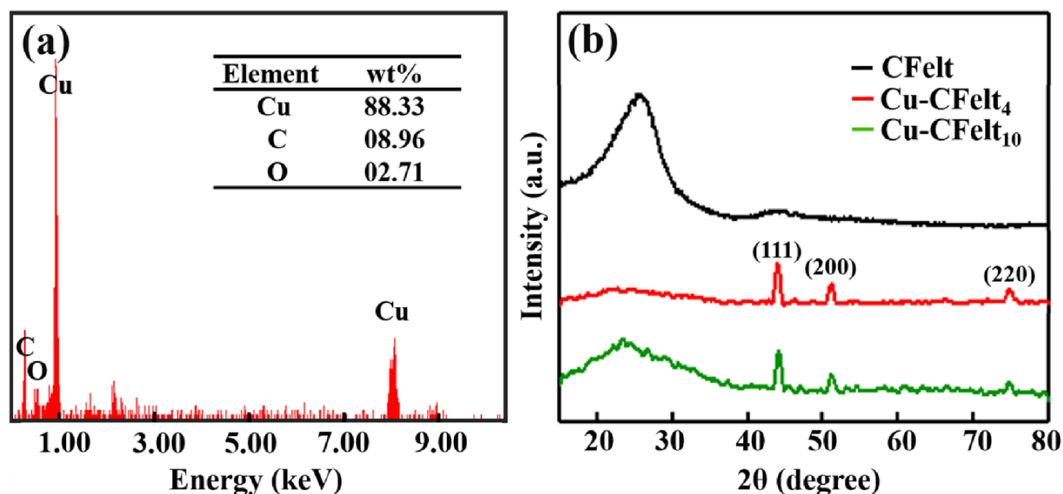


Fig. 4. (a) EDS spectrum of Cu-CFelt and (b) XRD patterns of CFelt, Cu-CFelt$_4$ and Cu-CFelt$_{10}$.

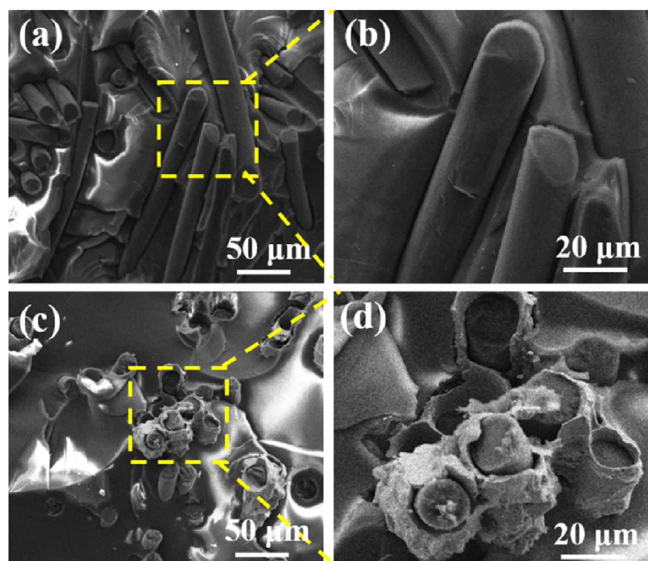


Fig. 5. SEM images of (a, b) CFelt/epoxy and (c, d) Cu-CFelt/epoxy composites.

morphologies of the fractured surfaces of CFelt/epoxy and Cu-CFelt/epoxy composites. CFelt shows favorable compatibility with epoxy matrix (Fig. 5a and b), which can be explained by the increased roughness and functional groups on the modified CFelt surface [34]. The functional groups on the surface of CFelt can react with those functional groups of epoxy resin to form covalent bonds which lead to robust interfacial adhesion between CFelt and epoxy matrix. As shown in Fig. 5c and d, after impregnation with epoxy resin, the 3D Cu-CFelt structure maintains well. Meanwhile, the interspace in the 3D Cu-CFelt skeleton is fully filled with epoxy resin and no obvious voids between Cu-CFelt and epoxy are observed, revealing the good interfacial compatibility between the Cu-CFelt and epoxy.

3.3. Thermal properties of the Cu-CFelt/epoxy composites

We measured the thermal conductivity of epoxy, CFelt/epoxy and Cu-CFelt/epoxy composites with different Cu loadings at room temperature. The thermal conductivity of pure epoxy is 0.22 W m^{-1} K^{-1}, which agrees well with previous report [37]. Fig. 6a shows that the thermal conductivity of Cu-CFelt/epoxy composites increases nonlinearly with the increasing of Cu loading. The maximum thermal conductivity of 30.69 W m^{-1} K^{-1} is obtained by the Cu-CFelt$_9$/epoxy composite with Cu loading of 29.34 vol%, revealing nearly 140 times higher than that of pure epoxy (0.22 W m^{-1} K^{-1}) and 110 times higher than that of CFelt/epoxy composite (0.28 W m^{-1} K^{-1}). After that, the thermal conductivity slightly decreases. The main reason is that excessive electroplating time causes massive Cu to enrich on the Cu-CFelt surface and decreases the porosity of Cu-CFelt, so epoxy resin cannot fully impregnate into the voids of the 3D structure. Additionally, we notice that even after 1 h electroplating, the thermal conductivity of Cu-CFelt$_1$/epoxy composite with a low Cu loading of 3.59 vol% is 1.61 W m^{-1} K^{-1}, which still increases by 6 times than that of pure epoxy and 5 times than that of CFelt/epoxy composite, respectively.

The dramatic enhancement of the thermal conductivity of the Cu-CFelt/epoxy composites is ascribed to the existence of the 3D interconnected Cu network in the composites. To better understand the enhancing mechanism, a schematic of thermal conduction is illustrated in Fig. 7. As for CFelt/epoxy composite, heat transfers slowly in CFelt framework and polymer matrix (Fig. 7a). The main reason is the high thermal resistance at the interfaces between the fibers resulted from the obvious gaps between the adjacent carbon fibers. As a result, the heat transport performance of the CFelt/epoxy composite is not improved significantly than that of pure epoxy. On the contrary, as for Cu-CFelt/epoxy composites (Fig. 7b), a uniform and dense Cu layer is deposited on the 3D CFelt skeleton. And some electroplated Cu bridges the adjacent Cu-plated fibers, which not only greatly reduces the thermal resistance between the carbon fibers, but also strengths the 3D network. Therefore, most heat transfers along the 3D Cu thermal conductive channel by the fast motion of electrons. Meanwhile, the phonon transmission by CFelt also leads to moderate enhancement of the thermal conductivity of Cu-CFelt/epoxy composites. Consequently, the thermal conductivity of Cu-CFelt/epoxy composites is enhanced remarkably. As the time of electroplating increases, the Cu layer on CFelt skeleton becomes thicker and more Cu-plated carbon fibers connect to each other by electroplated Cu, resulting in a faster heat conduction through the enhanced 3D Cu network. Obviously, the attractive thermally conductive performance of the Cu-CFelt/epoxy composites results from the continuous 3D Cu heat conduction highway and the given Cu volume fraction.

Table 1 shows a comparison of the thermal conductivity of our Cu-CFelt/epoxy composites with those reported previously Cu-filled composites. Among these, the thermal conductivity enhancement (TCE) is calculated by:

$$TCE = \frac{k_c - k_m}{k_m}$$

Where k_c and k_m are the thermal conductivity of the composites and

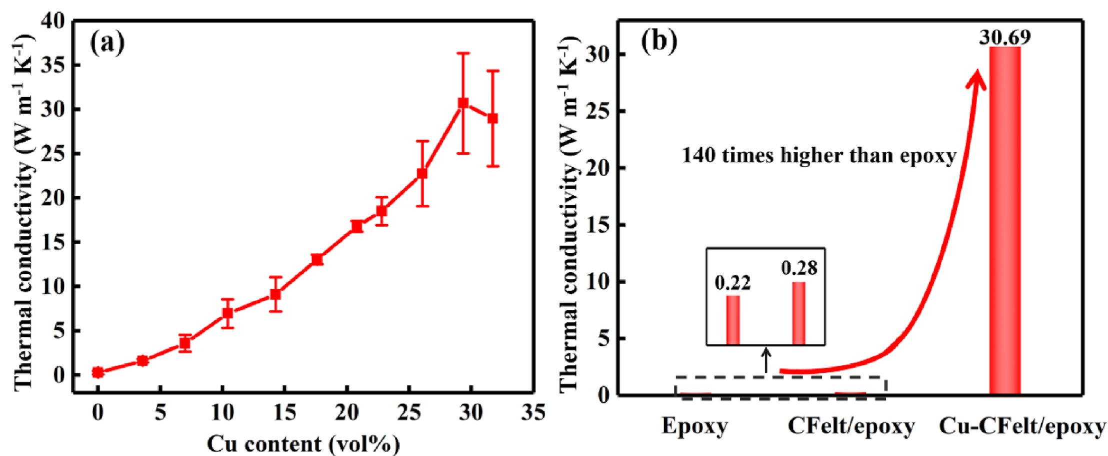


Fig. 6. (a) Thermal conductivity of the Cu-CFelt/epoxy composites as a function of the loading fraction of Cu and (b) comparison of the thermal conductivity of epoxy, CFelt/epoxy and Cu-$CFelt_9$/epoxy composites.

polymer matrix, respectively. As seen in Table 1, the Cu-CFelt/epoxy composite in our work exhibits an excellent thermal conductivity, which is comparable or superior to that of most other previous reported thermally conductive composites filled with Cu in different morphologies, such as spherical Cu particles, Cu nanowires and Cu flakes. For example, Xu et al. prepared Cu flakes by simple ball milling Cu micro sphere, and by simple incorporating 70 wt% Cu flakes into epoxy matrix, the thermal conductivity of epoxy composites was increased to 2.05 W m^{-1} K^{-1} [38]. Our results reveal that the continuous 3D Cu network in our work tremendously enhances the thermal transport performance of composites.

To study the stability of the thermal conductivity of our composites, we measured the thermal conductivity of Cu-CFelt/epoxy composites after being exposed at ambient environment for 30 days. As shown in Fig. S4, the thermal conductivity of the composites barely change compared with the pristine thermal conductivity. The results reveal that the obtained Cu-CFelt/epoxy composites show a long longevity.

In order to visually demonstrate the thermal management

Table 1
Comparison of thermal conductivity of our Cu-CFelt/epoxy composites with other Cu-filled composites reported in previous work.

Fillers	Loading	Matrix	TC (W m^{-1} K^{-1})	TCE (%)	Reference
CuNWs	4.1 vol%	PU	0.62	226	[39]
Cu NP/PMMA bead	30 wt%	Epoxy	1.05	518	[29]
Cu flakes	70 wt%	Epoxy	2.05	–	[38]
MPTS-Cu-CF	10 wt%	SR	2.23	1073	[31]
$Cu@SiO_2$	25 vol%	Epoxy	2.9	1833	[40]
Cu@rGO	80 wt%	Epoxy	7	3082	[33]
Cu-CFelt	29.34 vol%	Epoxy	30.69	13,850	This work

Abbreviations: CuNWs, copper nanowires; PU, polyurethane; Cu NP, Cu nanoparticle; PMMA, polymethylmethacrylate; MPTS, (3-mercaptopropyl) trimethoxysilane; CF, carbon fibers; SR, silicone rubber; rGO, reduced graphene oxide.

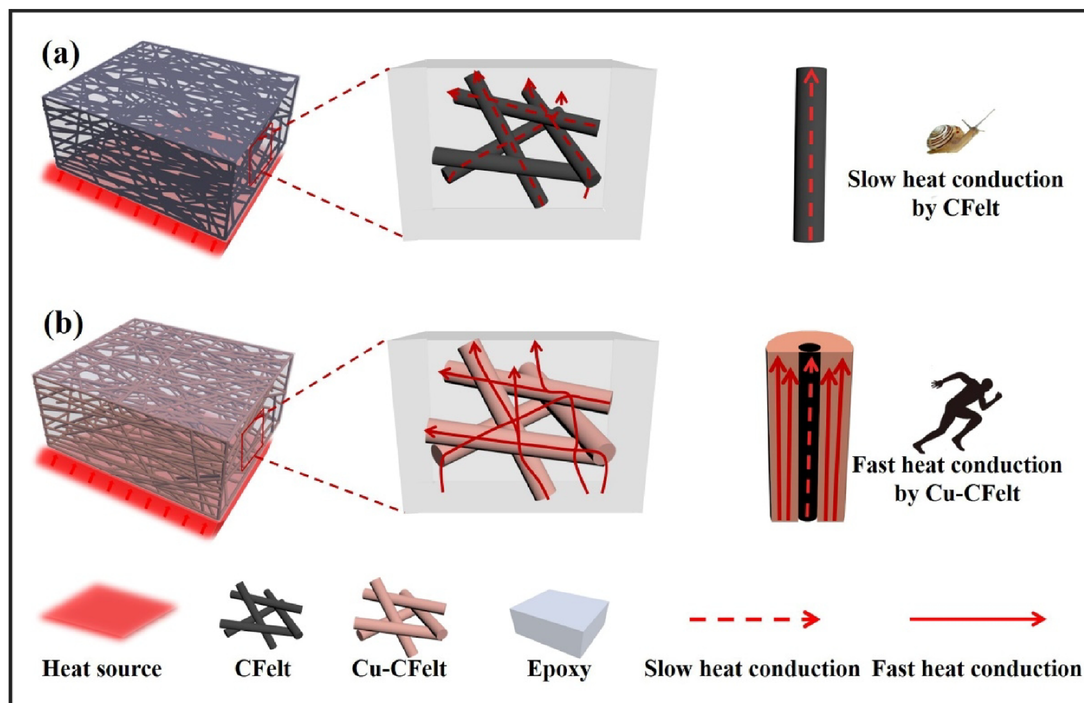


Fig. 7. Schematic illustration of the heat conduction in the (a) CFelt/epoxy and (b) Cu-CFelt/epoxy composites.

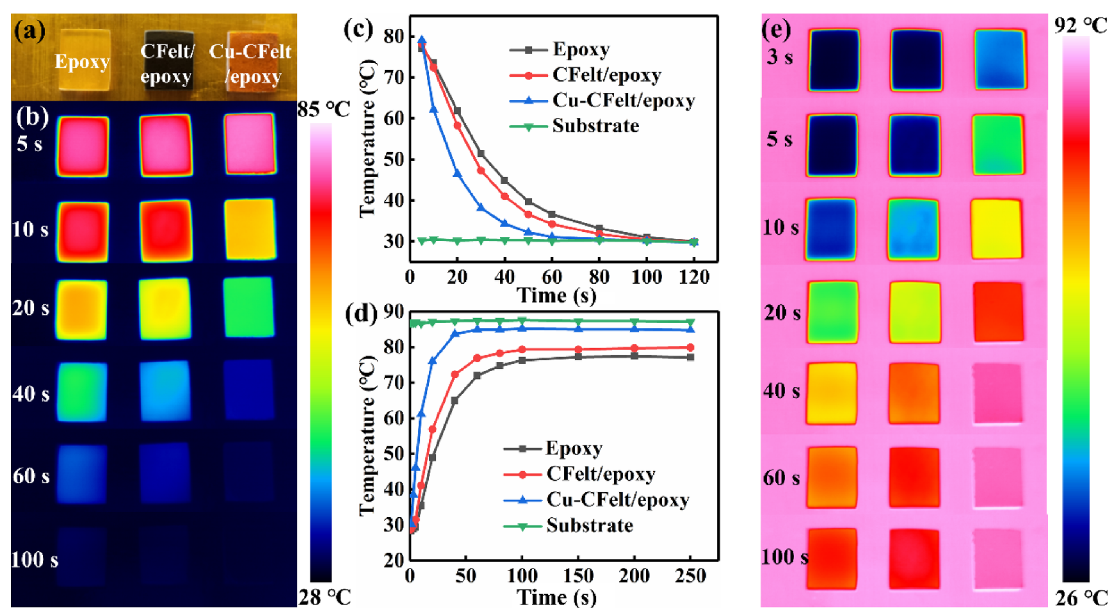


Fig. 8. Thermal management capabilities of the composites. (a) Optical photographs. (b) Infrared thermal images and (c) surface temperature variations with cooling time of epoxy, CFelt/epoxy and Cu-$CFelt_9$/epoxy composites. (d) Infrared thermal images and (e) surface temperature variations with heating time of the composites.

application of the Cu-CFelt/epoxy composites, the surface temperature variations of the composites with different working time during heating and cooling processes were detected by a portable infrared thermal imager. To estimate the heat dissipation performance, the epoxy, CFelt/epoxy and Cu-$CFelt_9$/epoxy composites with the same thickness were preheated to 80 °C and then cooled at room temperature. The order of these three samples is shown in Fig. 8a. We find that the surface temperature of Cu-$CFelt_9$/epoxy composite decreases at the highest rate (Fig. 8b and c) and it drops to 31.1 °C at 60 s, which is close to the temperature of substrate, revealing that benefitting from the high thermal conductivity, our Cu-CFelt/epoxy composites have excellent heat dissipation properties. To investigate the heat absorption capability during the heating process, the above three samples were simultaneously placed on a plate which was preheated to 80 °C for heating. As shown in Fig. 8d and e, compared with epoxy and CFelt/epoxy composite, the surface temperature of the Cu-$CFelt_9$/epoxy composite shows a much faster increasing with time, indicating that the Cu-CFelt/epoxy composites can transfer heat faster from the heater. After 60 s heating, the Cu-$CFelt_9$/epoxy composite exhibits a temperature of 84.9 °C, which is 12.9 °C and 8 °C higher than that of epoxy and CFelt/epoxy composite, respectively. We can conclude that Cu-CFelt/epoxy composites have the best heat absorption and dissipation properties compared with epoxy and CFelt/epoxy composite, which is consistent with the results of the thermal conductivity shown in Fig. 6. This reveals that the Cu-CFelt/epoxy composites have strong application potential in thermal management.

3.4. Mechanical properties of the Cu-CFelt/epoxy composites

Mechanical properties, which are very important for the application performance, lifetime and reliability of thermal management composites, were studied by three-point bending experiments. The flexural strength of epoxy, CFelt/epoxy and Cu-CFelt/epoxy can be found in Fig. 9. The flexural strength of the composites increases from 96.06 MPa (cure epoxy) to 124.55 MPa (CFelt/epoxy) after the addition of CFelt. This high flexural strength of CFelt/epoxy composites can be ascribed to the following two points: (1) CFelt has outstanding mechanical properties. (2) The surface treatment of CFelt increases the oxygen-containing functional groups and roughness of the CFelt surface and thereby causing the robust interfacial adhesion between CFelt and epoxy resin. After electroplating Cu on the CFelt skeleton, the flexural strength is 104.79 MPa for Cu-CFelt/epoxy composites, revealing a slight decrease than that of CFelt/epoxy composite. The main reason is that the interfacial compatibility between Cu-CFelt and epoxy matrix is inferior to that between CFelt and epoxy. Although the flexural strength of Cu-CFelt/epoxy composites is a little lower than that of CFelt/epoxy composites, it is still higher than that of epoxy resin. The results indicate that Cu-CFelt/epoxy composites achieve excellent thermal properties while maintain good mechanical properties. Therefore, our composites have strong potentials for engineering application.

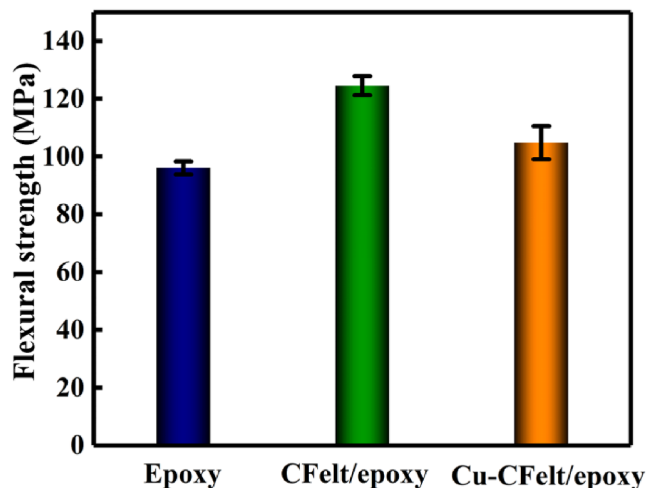


Fig. 9. Flexural strength of epoxy, CFelt/epoxy and Cu-CFelt/epoxy composites.

3.5. Electrical properties of the Cu-CFelt/epoxy composites

In many aspects of the application of thermally conductive composites, such as electronics, automotive, and aerospace industries, the conductivity is also an important parameter that needs to be considered since good conductivity can prevent the accumulation of static charge [41]. Hence, the electrical conductivity of Cu-CFelt/epoxy composites were measured. As shown in Fig. 10a, the electrical conductivity of Cu-

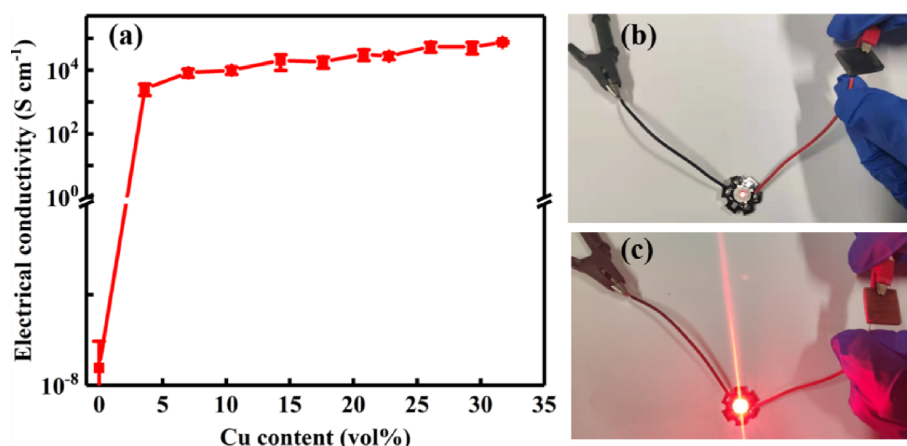


Fig. 10. (a) Electrical conductivity of Cu-CFelt/epoxy composites at various Cu contents. Digital photographs showing the LED lamp at a voltage of 2.5 V, when (b) CFelt/epoxy composite and (c) Cu-$CFelt_1$/epoxy composite were used as electrically conductive elements.

CFelt/epoxy composites increases with the increasing Cu content. The introduction of only a small amount of Cu causes a sharp increasing in the electrical conductivity. The Cu-$CFelt_1$/epoxy composite with 3.59 vol% Cu reveals the electrical conductivity of 2.6×10^3 S cm^{-1}, which is nearly 11 orders of magnitude higher than that of CFelt/epoxy composite, indicating that after 1 h electroplating, the electrical conductivity of our composites has reached the percolation threshold due to the formation of continuous Cu conduction pathway. After that, the conductivity continues to increase and eventually reaches 7.49×10^4 S cm^{-1} at the Cu loading of 31.72 vol%. To vividly demonstrate the effect of Cu on the electrical conductivity of composites, the LED lamp was separately connected with the CFelt/epoxy and Cu-$CFelt_1$/epoxy in series at a voltage of 2.5 V. As shown in Fig. 10b and c, the LED in series with CFelt/epoxy composite can only emit weak light, but the LED in series with Cu-$CFelt_1$/epoxy composite is illumined with the intense red light. Therefore, it is clear that our Cu-CFelt/epoxy composites have outstanding electrical conductivity.

4. Conclusion

Epoxy composites with ultrahigh thermal conductivity have been successfully prepared by incorporating the novel 3D interconnected Cu network supported by CFelt into the epoxy matrix. The prepared composites share advantages of both Cu and CFelt. Benefiting from the unique 3D Cu thermal conductive network, a high thermal conductivity of 30.69 W m^{-1} K^{-1} was achieved, which is nearly equivalent to 140 and 110 times the thermal conductivity of pure epoxy (0.22 W m^{-1} K^{-1}) and CFelt/epoxy composite (0.28 W m^{-1} K^{-1}), respectively. Besides, the thermal conductivity of our composites is much higher than that of most previous reported Cu-filled composites at the same filler loadings or even higher filler loadings. In addition, the investigation of the composites in thermal management shows that the Cu-CFelt/epoxy composites have good heat absorption and heat dissipation capabilities in practical applications. Moreover, the composite maintained a good flexural strength due to the strengthening of the CFelt and exhibited an ultrahigh electrical conductivity of 7.49×10^4 S cm^{-1}. In conclusion, the study offers a novel and simple route to prepare high-performance thermally conductive epoxy composites possessing large potentials for scale-up production and practical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

[1] S. Yang, W. Li, S. Bai, Q. Wang, Fabrication of morphologically controlled composites with high thermal conductivity and dielectric performance from aluminum nanoflake and recycled plastic package, ACS Appl. Mater. Interfaces 11 (2019) 3388–3399, https://doi.org/10.1021/acsami.8b16209.
[2] X. Hou, Y. Chen, W. Dai, Z. Wang, H. Li, C.-T. Lin, K. Nishimura, N. Jiang, J. Yu, Highly thermal conductive polymer composites via constructing micro-phragmites communis structured carbon fibers, Chem. Eng. J. 375 (2019), https://doi.org/10.1016/j.cej.2019.121921.
[3] J. Li, X. Zhang, C. Zhou, J. Zheng, D. Ge, W. Zhu, New applications of an automated system for high-power LEDs, IEEE-ASME Trans. Mech. 21 (2016) 1035–1042, https://doi.org/10.1109/tmech.2015.2487507.
[4] Z. Liu, J. Li, C. Zhou, W. Zhu, A molecular dynamics study on thermal and rheological properties of BNNS-epoxy nanocomposites, Int. J. Heat Mass Transfer 126 (2018) 353–362, https://doi.org/10.1016/j.ijheatmasstransfer.2018.05.149.
[5] X. Zhang, K. Wu, Y. Liu, B. Yu, Q. Zhang, F. Chen, Q. Fu, Preparation of highly thermally conductive but electrically insulating composites by constructing a segregated double network in polymer composites, Compos. Sci. Technol. 175 (2019) 135–142, https://doi.org/10.1016/j.compscitech.2019.03.017.
[6] N. Mehra, L. Mu, T. Ji, X. Yang, J. Kong, J. Gu, J. Zhu, Thermal transport in polymeric materials and across composite interfaces, Appl. Mater. Today 12 (2018) 92–130, https://doi.org/10.1016/j.apmt.2018.04.004.
[7] J.R. Choi, S. Yu, H. Jung, S.K. Hwang, R.H. Kim, G. Song, S.H. Cho, I. Bae, S.M. Hong, C.M. Koo, C. Park, Self-assembled block copolymer micelles with silver-carbon nanotube hybrid fillers for high performance thermal conduction, Nanoscale 7 (2015) 1888–1895, https://doi.org/10.1039/c4nr06390b.
[8] F. Yan, L. Liu, M. Li, M. Zhang, L. Xiao, Y. Ao, Preparation of carbon nanotube/copper/carbon fiber hierarchical composites by electrophoretic deposition for enhanced thermal conductivity and interfacial properties, J. Mater. Sci. 53 (2018) 8108–8119, https://doi.org/10.1007/s10853-018-2115-9.
[9] X. Xiao, P. Zhang, M. Li, Effective thermal conductivity of open-cell metal foams impregnated with pure paraffin for latent heat storage, Int. J. Therm. Sci. 81 (2014) 94–105, https://doi.org/10.1016/j.ijthermalsci.2014.03.006.
[10] D.-W. Jung, J.M. Kim, H.-W. Yoon, K.M. Nam, Y.-E. Kwon, S. Jeong, Y.H. Baek, Y.S. Choi, S.-J. Chang, G.-R. Yi, J.Y. Cho, G. Lee, Solution-processable thermally conductive polymer composite adhesives of benzyl-alcohol-modified boron nitride two-dimensional nanoplates, Chem. Eng. J. 361 (2019) 783–791, https://doi.org/10.1016/j.cej.2018.12.128.
[11] C. Xiao, L. Chen, Y. Tang, X. Zhang, K. Zheng, X. Tian, Enhanced thermal conductivity of silicon carbide nanowires (SiCw)/epoxy resin composite with segregated structure, Compos. Part A-Appl. Sci. 116 (2019) 98–105, https://doi.org/10.1016/j.compositesa.2018.10.023.

[12] H. Im, J. Kim, The effect of Al_2O_3 doped multi-walled carbon nanotubes on the thermal conductivity of Al_2O_3/epoxy terminated poly(dimethylsiloxane) composites, Carbon 49 (2011) 3503–3511, https://doi.org/10.1016/j.carbon.2011.04.049.

[13] W. Zhou, Thermal and dielectric properties of the AlN particles reinforced linear low-density polyethylene composites, Thermochim. Acta 512 (2011) 183–188, https://doi.org/10.1016/j.tca.2010.10.003.

[14] H. An, Z. Liu, Q. Tian, J. Li, C. Zhou, X. Liu, W. Zhu, Thermal behaviors of nanoparticle reinforced epoxy resins for microelectronics packaging, Microelectron. Reliab. 93 (2019) 39–44, https://doi.org/10.1016/j.microrel.2019.01.002.

[15] L. Zhang, X. Li, H. Deng, Y. Jing, Q. Fu, Enhanced thermal conductivity and electrical insulation properties of polymer composites via constructing Pglass/CNTs confined hybrid fillers, Compos. Part A-Appl. Sci. 115 (2018) 1–7, https://doi.org/10.1016/j.compositesa.2018.09.009.

[16] X. Wang, P. Wu, Highly Thermally conductive fluorinated graphene films with superior electrical insulation and mechanical flexibility, ACS Appl. Mater. Interfaces 11 (2019) 21946–21954, https://doi.org/10.1021/acsami.9b07377.

[17] J. Ma, T. Shang, L. Ren, Y. Yao, T. Zhang, J. Xie, B. Zhang, X. Zeng, R. Sun, J.-B. Xu, C.-P. Wong, Through-plane assembly of carbon fibers into 3D skeleton achieving enhanced thermal conductivity of a thermal interface material, Chem. Eng. J. 380 (2020), https://doi.org/10.1016/j.cej.2019.122550.

[18] H. Oh, K. Kim, S. Ryu, J. Kim, Enhancement of thermal conductivity of polymethyl methacrylate-coated graphene/epoxy composites using admicellar polymerization with different ionic surfactants, Compos. Part A-Appl. Sci. 116 (2019) 206–215, https://doi.org/10.1016/j.compositesa.2018.10.035.

[19] Y. Jiang, X. Shi, Y. Feng, S. Li, X. Zhou, X. Xie, Enhanced thermal conductivity and ideal dielectric properties of epoxy composites containing polymer modified hexagonal boron nitride, Compos. Part A-Appl. Sci. 107 (2018) 657–664, https://doi.org/10.1016/j.compositesa.2018.02.016.

[20] C.-W. Chang-Jian, E.-C. Cho, K.-C. Lee, J.-H. Huang, P.-Y. Chen, B.-C. Ho, Y.-S. Hsiao, Thermally conductive polymeric composites incorporating 3D MWCNT/PEDOT:PSS scaffolds, Compos. Part B-Eng. 136 (2018) 46–54, https://doi.org/10.1016/j.compositesb.2017.10.004.

[21] Y. Chen, X. Hou, M. Liao, W. Dai, Z. Wang, C. Yan, H. Li, C.-T. Lin, N. Jiang, J. Yu, Constructing a "pea-pod-like" alumina-graphene binary architecture for enhancing thermal conductivity of epoxy composite, Chem. Eng. J. 381 (2020), https://doi.org/10.1016/j.cej.2019.122690.

[22] Y. Li, X. Tian, W. Yang, Q. Li, L. Hou, Z. Zhu, Y. Tang, M. Wang, B. Zhang, T. Pan, Y. Li, Dielectric composite reinforced by in-situ growth of carbon nanotubes on boron nitride nanosheets with high thermal conductivity and mechanical strength, Chem. Eng. J. 358 (2019) 718–724, https://doi.org/10.1016/j.cej.2018.10.004.

[23] X. Zeng, Y. Yao, Z. Gong, F. Wang, R. Sun, J. Xu, C.P. Wong, Ice-templated assembly strategy to construct 3D boron nitride nanosheet networks in polymer composites for thermal conductivity improvement, Small 11 (2015) 6205–6213, https://doi.org/10.1002/smll.201502173.

[24] J. Chen, X. Huang, Y. Zhu, P. Jiang, Cellulose nanofiber supported 3D interconnected BN nanosheets for epoxy nanocomposites with ultrahigh thermal management capability, Adv. Funct. Mater. 27 (2017), https://doi.org/10.1002/adfm.201604754.

[25] C. Chen, Y. Xue, Z. Li, Y. Wen, X. Li, F. Wu, X. Li, D. Shi, Z. Xue, X. Xie, Construction of 3D boron nitride nanosheets/silver networks in epoxy-based composites with high thermal conductivity via in-situ sintering of silver nanoparticles, Chem. Eng. J. 369 (2019) 1150–1160, https://doi.org/10.1016/j.cej.2019.03.150.

[26] Y. Hu, Z. Chen, H. Zhuo, L. Zhong, X. Peng, R.C. Sun, Advanced compressible and elastic 3D monoliths beyond hydrogels, Adv. Funct. Mater. (2019), https://doi.org/10.1002/adfm.201904472.

[27] T.X. Huong Le, M. Bechelany, M. Cretin, Carbon felt based-electrodes for energy and environmental applications: a review, Carbon 122 (2017) 564–591, https://doi.org/10.1016/j.carbon.2017.06.078.

[28] H. Cheng, H. Xue, C. Hong, X. Zhang, Preparation, mechanical, thermal and ablative properties of lightweight needled carbon fibre felt/phenolic resin aerogel composite with a bird's nest structure, Compos. Sci. Technol. 140 (2017) 63–72, https://doi.org/10.1016/j.compscitech.2016.12.031.

[29] Y.-H. Bae, M.-J. Yu, M.C. Vu, W.K. Choi, S.-R. Kim, Synergistic effects of segregated network by polymethylmethacrylate beads and sintering of copper nanoparticles on thermal and electrical properties of epoxy composites, Compos. Sci. Technol. 155 (2018) 144–150, https://doi.org/10.1016/j.compscitech.2017.11.021.

[30] S. Yu, B.I. Park, C. Park, S.M. Hong, T.H. Han, C.M. Koo, RTA-treated carbon fiber/copper core/shell hybrid for thermally conductive composites, ACS Appl. Mater. Interfaces 6 (2014) 7498–7503, https://doi.org/10.1021/am500871b.

[31] X.-W. Zhao, C.-G. Zang, Q.-K. Ma, Y.-Q. Wen, Q.-J. Jiao, Thermal and electrical properties of composites based on (3-mercaptopropyl) trimethoxysilane- and Cu-coated carbon fiber and silicone rubber, J. Mater. Sci. 51 (2016) 4088–4095, https://doi.org/10.1007/s10853-016-9730-0.

[32] K. Ruan, Y. Guo, Y. Tang, Y. Zhang, J. Zhang, M. He, J. Kong, J. Gu, Improved thermal conductivities in polystyrene nanocomposites by incorporating thermal reduced graphene oxide via electrospinning-hot press technique, Compos. Commun. 10 (2018) 68–72, https://doi.org/10.1016/j.coco.2018.07.003.

[33] S. Liu, B. Zhao, L. Jiang, Y.-W. Zhu, X.-Z. Fu, R. Sun, J.-B. Xu, C.-P. Wong, Core–shell Cu@rGO hybrids filled in epoxy composites with high thermal conduction, J. Mater. Chem. C 6 (2018) 257–265, https://doi.org/10.1039/c7tc04427e.

[34] X. Yao, X. Gao, J. Jiang, C. Xu, C. Deng, J. Wang, Comparison of carbon nanotubes and graphene oxide coated carbon fiber for improving the interfacial properties of carbon fiber/epoxy composites, Compos. Part B-Eng. 132 (2018) 170–177, https://doi.org/10.1016/j.compositesb.2017.09.012.

[35] M. Li, C. Tang, L. Zhang, B. Shang, S. Zheng, S. Qi, A thermally conductive and insulating epoxy polymer composite with hybrid filler of modified copper nanowires and graphene oxide, J. Mater. Sci-Mater. El 29 (2017) 4948–4954, https://doi.org/10.1007/s10854-017-8454-5.

[36] H. Yuan, Y. Wang, T. Li, Y. Wang, P. Ma, H. Zhang, W. Yang, M. Chen, W. Dong, Fabrication of thermally conductive and electrically insulating polymer composites with isotropic thermal conductivity by constructing a three-dimensional interconnected network, Nanoscale 11 (2019) 11360–11368, https://doi.org/10.1039/c9nr02491c.

[37] M.C. Vu, Q.-V. Bach, D.D. Nguyen, T.S. Tran, M. Goodarzi, 3D interconnected structure of poly(methyl methacrylate) microbeads coated with copper nanoparticles for highly thermal conductive epoxy composites, Compos. Part B-Eng. 175 (2019), https://doi.org/10.1016/j.compositesb.2019.107105.

[38] L. Xu, H.-R. Wen, F. Zhang, M.M.F. Yuen, X.-Z. Fu, R. Sun, C.-P. Wong, Enhancement of thermal conductivity of epoxy adhesives by ball milling copper flakes, 18th International Conference on Electronic Packaging Technology, 2017, https://doi.org/10.1109/ICEPT.2017.8046583.

[39] A. Rai, A.L. Moore, Enhanced thermal conduction and influence of interfacial resistance within flexible high aspect ratio copper nanowire/polymer composites, Compos. Sci. Technol. 144 (2017) 70–78, https://doi.org/10.1016/j.compscitech.2017.03.020.

[40] J. Li, X. Li, Y. Zheng, Z. Liu, Q. Tian, X. Liu, New underfill material based on copper nanoparticles coated with silica for high thermally conductive and electrically insulating epoxy composites, J. Mater. Sci. 54 (2019) 6258–6271, https://doi.org/10.1007/s10853-019-03335-9.

[41] A. Moisala, Q. Li, I.A. Kinloch, A.H. Windle, Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites, Compos. Sci. Technol. 66 (2006) 1285–1288, https://doi.org/10.1016/j.compscitech.2005.10.016.