

# Amino multi-walled carbon nanotubes further improve the thermal conductivity of boron nitride/liquid crystal epoxy resin composites

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**Abstract.** In this work, we introduced highly thermally conductive and fibrous amino multi-walled carbon nanotubes (MCNT-NH<sub>2</sub>) into hexagonal boron nitride/liquid crystal epoxy resin (h-BN/LCER) composites to improve the thermal conductivity of the composites. First, we prepared hexagonal boron nitride@amino multi-walled carbon nanotubes (h-BN@MCNT-NH<sub>2</sub>) hybrid fillers. Then, the amino group in the hybrid filler participated in the curing process of the epoxy resin to prepare hexagonal boron nitride@amino multi-walled carbon nanotubes/liquid crystal epoxy resin (h-BN@MCNT-NH<sub>2</sub>/LCER) composites. Subsequently, its thermal conductivity was tested and analyzed using the Agari's model and microstructure of the composites, and we can come to conclude that the thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCER composites is higher than that of h-BN/LCER at the same filler content. The main reason is that the addition of MCNT-NH<sub>2</sub> plays a role in increasing the thermal conduction path of h-BN/LCER composites and decreasing the large interface thermal resistance of fillers and resin matrix. Finally, the usability and thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCER composites were verified by light-emitting diode (LED) lamps. The temperature of LED lamp using 50% h-BN@MCNT-NH<sub>2</sub>/LCER composites was eventually stabilized at 27.7 °C, it is expected that 50% h-BN@MCNT-NH<sub>2</sub>/LCER composites will be used in LED electronic products.

**Keywords:** polymer composites, thermal conductivity, amino multi-walled carbon nanotubes, hybrid filler, application in LED lamps

## 1. Introduction

In recent years, with the increasing miniaturization and multi-functionalization of electronic devices, the heat generated by integrated circuits during operation has also increased [1]. If the accumulated heat energy cannot be transferred in time, it will reduce the durability of the device [2, 3]. The material with a good thermal conductivity can release easily the heat generated in the devices in order to maintain the temperature of the device at the desired level [4]. At present, many researchers are working to improve the

thermal conductivity of polymer-based composites. Epoxy resin is often selected as a thermally conductive polymer matrix due to its good processing performance, high insulation performance, excellent mechanical properties, low water absorption, and outstanding adhesion force [5, 6]. However, the thermal conductivity of epoxy resin is about 0.2 W/(m·K), which is far from the requirement of heat conduction in its electronic package [7, 8]. Generally, highly thermally conductive inorganic fillers such as hexagonal boron nitride (h-BN) [9], aluminum nitride (AlN) [10],

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silicon carbide (SiC) nanowires [11], graphene nanoplatelets (GNPs) [12] and carbon nanotubes (CNTs) [13] are added to the epoxy resin to increase the thermal conductivity. However, due to their high interface thermal resistance, the thermal conductivity of the final composite cannot be further improved [14]. Hexagonal boron nitride (h-BN) is a two-dimensional layered material with excellent thermal conductivity [15]. Current theoretical researches show that its thermal conductivity can reach 600 W/(m·K) [16]. h-BN is a chemically inert material, which makes the interface bond with the polymer matrix weak, so its thermal conductivity cannot be well exhibited. Traditionally, h-BN is surface-modified by  $\pi$ - $\pi$  interaction and Lewis acid-base complexation between h-BN and organic molecules modifier to reduce the interface thermal resistance between the filler and the polymer [18]. Wu and Kessler [14] non-covalently modified h-BN by the  $\pi$ - $\pi$  interaction between BN and dopamine molecules and then added the modified h-BN into bisphenol E cyanate ester to prepared high-thermal conductivity h-BN/bisphenol E cyanate ester (h-BN/BECy) composites. Pan *et al.* [8] used KH550 modified h-BN to enhance the interfacial adhesion between h-BN and the matrix, and the thermal conductivity is improved compared with the unmodified h-BN composite. However, these modified methods cannot significantly improve the thermal conductivity of the composite [17, 19]. At present, the thermal conductivity of polymer-based composites has not reached the ideal thermal conductivity, which is mainly due to the large interface thermal resistance of fillers and resin matrix [20].

Recently, carbon nanotubes (CNTs) garnered much attention due to intriguing electrical, thermal, and optical properties, as well as the large aspect ratio [21]. CNTs have a thermal conductivity of up to 3000 W/(m·K), which was several tens of times the thermal conductivity of conventional thermally conductive fillers [22]. Therefore, by placing it in a polymer, the thermal conductivity of the polymer-based composite can be significantly improved, which had been confirmed by other researchers. Shi and Zhu [23] fabricated silicone-modified acrylic resin-based (Si-MA) nanocomposites. The surfaces of GNPs and CNTs were modified with *N,N'*-(cyclohexa-2,5-diene-1,4-diylidene)bis(2-hydroxy-*N*-(2-hydroxy-3-(4-(trihydroxysilyl)butoxy)propyl)-3-(4-(trihydroxysilyl)butoxy)propan-1-aminium) (TSiPD) as tGNPs and tCNTs. The tGNPs and tCNTs were added to Si-MA,

becoming Si-MA nanocomposites. The thermal conductivity with 10 wt% tGNPs obtains 2.31 W/(m·K). It is worth noting that a high thermal conductivity was obtained (2.97 W/(m·K)) with 9.9 wt% tGNPs and 0.1 wt% tCNTs, which corresponds to a 28.5% increase compared to the value of 10 wt% tGNPs. Kim *et al.* [24] investigated the thermal conductivity of multi-walled carbon nanotube-embedded cyclic butylene terephthalate thermoplastic nanocomposites. Thermal conductivity test results show that the thermal conductivity of nanocomposites gradually increases with the increase of carbon nanotubes. Guo *et al.* [25] prepared triethoxyvinylsilane (YDH-151) functionalized multi-wall carbon nanotubes (s-MWCNTs) and blended into PVDF to achieve high thermal conductive s-MWCNTs/PVDF nanocomposites. Thermal conductivity of 1.552 W/(m·K) was achieved in s-MWCNTs/PVDF composite with 10 wt% s-MWCNTs loading, about 9 times in comparison to that of pure PVDF matrix. In order to largely improve thermal conductivity, CNT-NH<sub>2</sub> were usually used. Yan *et al.* [26] research indicates that CNT-NH<sub>2</sub> can participate in the curing of epoxy resin. Therefore, if the sheet-shaped h-BN and the fibrous CNT-NH<sub>2</sub> form a hybrid filler, it can improve the thermal conduction path and reduce the thermal resistance of the interface between the filler and the matrix, thereby improving the thermal conductivity of the composite material.

In this work, we introduced highly thermally conductive and fibrous multi-walled amino carbon nanotubes (MCNT-NH<sub>2</sub>) into hexagonal boron nitride/liquid crystal epoxy resin (h-BN/LCER) composites to improve the thermal conductivity of the composites. First, we prepared h-BN@MCNT-NH<sub>2</sub> hybrid fillers. Then, the amino group in the hybrid filler participated in the curing process of the epoxy resin to prepare h-BN@MCNT-NH<sub>2</sub>/LCER composites [26]. MCNT-NH<sub>2</sub> plays a role in decreasing the large interface thermal resistance of fillers and resin matrix, thereby improving the thermal conductivity of h-BN/LCER composites.

## 2. Experiment

### 2.1. Materials

A representative liquid crystal epoxy resins (LCERs) was selected, which is composed of epoxy monomer (3,3',5,5'-tetramethyl-4,4'-biphenyl diglycidyl ether (TMBPGE)) and curing agent (4,4'-diaminodiphenylmethane (DDM)). 3,3',5,5'-tetramethyl-4,4'-

biphenyl diglycidyl ether (TMBDGE, YX-4000) were purchased from Shanghai Zhongsi Industrial Co., Ltd., China. The values of epoxy equivalent weight (EEW) of TBDGE were 185 g/eq. 4,4'-diaminodiphenylmethane (DDM, purity >97%) were provided by Aladdin Industrial Co., Ltd., China. Hexagonal boron nitride platelets (h-BN, diameter = 15  $\mu\text{m}$ , purity >99.5%) were obtained from Dandong Rijin Science and Technology Co., Ltd., China. amino multi-walled carbon nanotube (MCNT-NH<sub>2</sub>, length = 50  $\mu\text{m}$ , diameter = 8–15 nm, purity >95%, -NH<sub>2</sub> >0.45%) were obtained from Aladdin Industrial Co., Ltd., China. Ethanol (humidity <0.2%, purity >99.5%) was purchased from Aladdin Industrial Co., China.

## 2.2. Preparation of hybrid filler

### h-BN@MCNT-NH<sub>2</sub>

Figure 1a shows the process of surface treatment of h-BN. The h-BN (5 g) was dispersed in 50 ml ethanol, and then 0.2 g of MCNT-NH<sub>2</sub> was added. The mixture was loaded inside a 500 ml agate milling container containing 150 g of agate balls (8 mm:5 mm:3 mm = 3:2:1), The mixtures were milled at a rotation speed of 300 rpm for 3 h, and then the obtained product was dried in an oven at

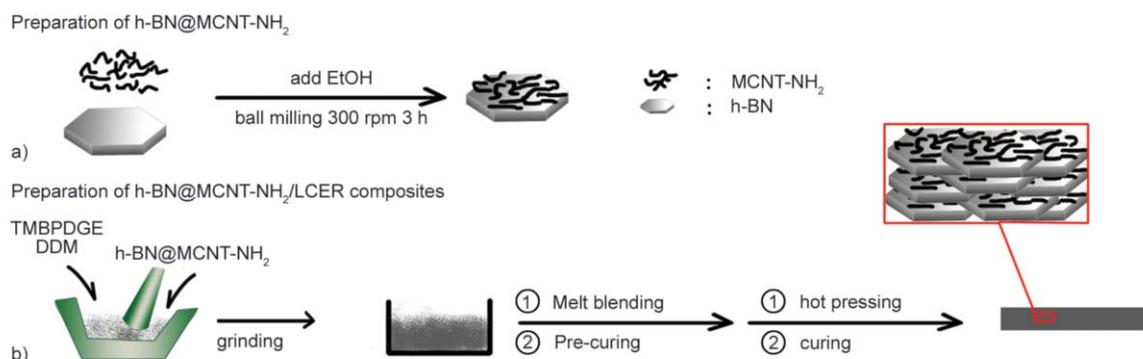
60 °C for 24 h. The final material is named as h-BN@MCNT-NH<sub>2</sub>, and the ratio of MCNT-NH<sub>2</sub> is 25 to 1.

## 2.3. Preparation of h-BN@MCNT-NH<sub>2</sub>/LCERs

In this work, h-BN@MCNT-NH<sub>2</sub>/LCER composites were fabricated, as shown in Figure 1b. First, a certain amount of hybrid filler h-BN@MCNT-NH<sub>2</sub> (h-BN:MCNT-NH<sub>2</sub> = 25:1) is ground together with DDM for 10 min to eliminate hydrogen bonds between DDM molecules. Second, TBDGE was placed in the mixture while grinding for 10 min. The mixture of uncured TBDGE-DDM with the fillers was poured into the silicone oil paper, melt-blended, and pre-cured at 160 °C for 10 min. The pre-cured sample was hot-pressed for 4 min, then cured in an oven at 160 °C for 7 h. Finally, h-BN@MCNT-NH<sub>2</sub>/LCERs was prepared. In the same way, h-BN/LCER composites with different filler contents were prepared, in which the mass fraction of boron nitride was 10, 20, 30, 40, and 50%, and the corresponding volume fraction was 5.67, 11.67, 18.2, 25.84, and 35.32 vol%. The composition of h-BN@MCNT-NH<sub>2</sub>/LCERs composites with different contents showed in Table 1. All prepared composites will be tested in the future.

**Table 1.** The composition of h-BN@MCNT-NH<sub>2</sub>/LCERs composites with different contents.

Sample code	LCER [g]	h-BN@MCNT-NH <sub>2</sub> [g]	h-BN@MCNT-NH <sub>2</sub> [wt%]	h-BN@MCNT-NH <sub>2</sub> [vol%]
LCER (TMBPDGE-DDM)	6.492	0.000	0	0.00
10% h-BN@MCNT-NH <sub>2</sub> /LCERs	6.492	0.721	10	5.61
20% h-BN@MCNT-NH <sub>2</sub> /LCERs	6.492	1.623	20	12.15
30% h-BN@MCNT-NH <sub>2</sub> /LCERs	6.492	2.782	30	19.07
40% h-BN@MCNT-NH <sub>2</sub> /LCERs	6.492	4.328	40	27.17
50% h-BN@MCNT-NH <sub>2</sub> /LCERs	6.492	6.492	50	36.57



**Figure 1.** Schematic illustration of the procedure to prepare the composites. (a) Preparation of h-BN@MCNT-NH<sub>2</sub>; (b) Preparation of h-BN@MCNT-NH<sub>2</sub>/LCER composites.

## 2.4. Characterization

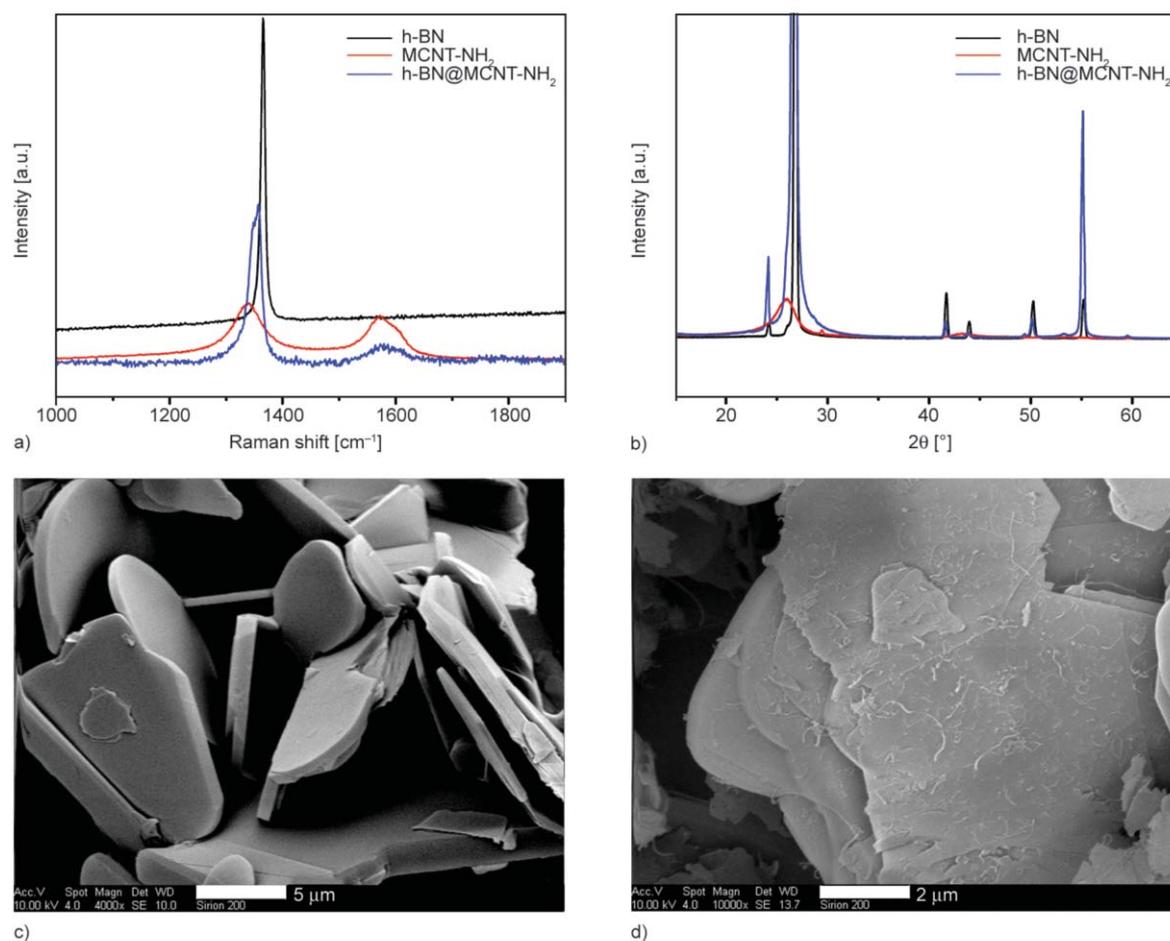
Raman spectra were measured by a Confocal Raman Microscopy (Renishaw in Via Reflex, Renishaw company, UK) with an excitation wavelength of 514.5 nm. The X-ray film and powder diffractometer (XRD, Rigaku SmartLab SE, Rigaku Corporation, Japan) was used to record the orientation behavior of the composite with a high-speed detector D/teX-Ultra. The morphologies of the fillers and composites were characterized via scanning electron microscopy (SEM, Sirion-200, FEI, USA) in an accelerating voltage of 10 kV. The thermal conductivities of composites (25 mm×25 mm×2 mm) were tested on a Hot Disk instrument (TPS 2200, AB Corporation, Sweden). Thermal properties of composites were characterized using a TGA (TG 209F3, NETZSCH, Germany) from 50 to 700 °C at a heating rate of 10 °C/min under nitrogen condition. Self-installed components verify the possibility of composite materials applied in the field of electronic packaging. The devices are 3 W LED lamps; Infrared camera

(CEM DT-980, Shenzhen Huashengchang Technology Industrial Co., Ltd., China) was used to record the temperature change of the composite material.

## 3. Results and discussion

### 3.1. Characterization of h-BN@MCNT-NH<sub>2</sub>

The preparation process of hybrid filler h-BN@MCNT-NH<sub>2</sub> was shown in Figure 1. Ethanol was used as solvent to improve the dispersibility of h-BN platelets and prevent aggregation of MCNT-NH<sub>2</sub> with each other. After h-BN and MCNT-NH<sub>2</sub> were milled at a rotation speed of 300 rpm for 3 h, hybrid filler h-BN@MCNT-NH<sub>2</sub> was prepared. In Su *et al.* [27], the hybrid filler h-BN@CNT-NH<sub>2</sub> was prepared by ultrasonic treatment, using the  $\pi$ - $\pi$  interaction force between h-BN and CNT-NH<sub>2</sub>. It can be found from the morphology SEM images of h-BN@CNT-NH<sub>2</sub> in that paper that CNT-NH<sub>2</sub> on the surface of h-BN is easier to agglomerate. We used the method of ball milling to prepare h-BN@MCNT-NH<sub>2</sub>, which can make the carbon tube adhere to the



**Figure 2.** (a) Raman spectra and (b) XRD patterns of pristine h-BN, MCNT-NH<sub>2</sub>, and h-BN@MCNT-NH<sub>2</sub>; (c) and (d) are the micromorphology of pure h-BN and hybrid filler h-BN@MCNT-NH<sub>2</sub> respectively.

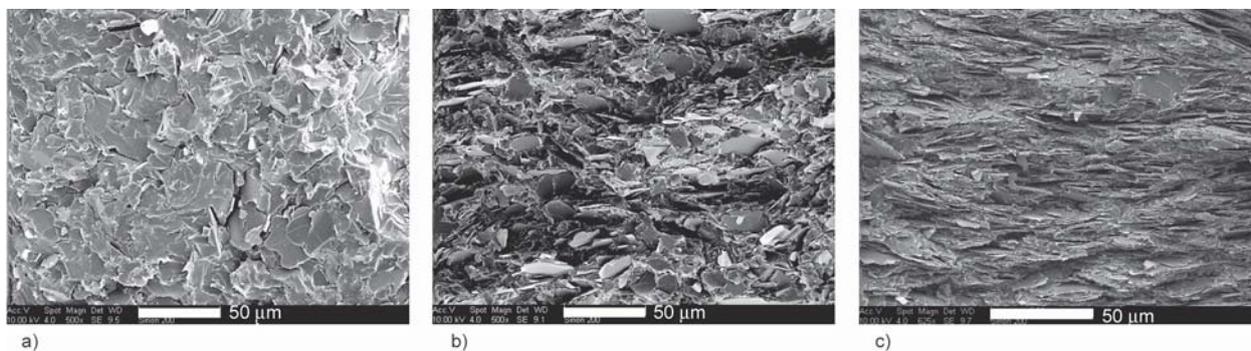
surface of boron nitride more easily and disperse more uniformly (Figure 2d). There are two possible reasons. On the one hand, the  $\pi$ - $\pi$  interaction between BN and MCNT-NH<sub>2</sub> is formed. On the other hand, due to the ball milling process, the surface of boron nitride has a certain roughness, which is easier to adhere to the carbon tube. Raman spectra of h-BN, MCNT-NH<sub>2</sub>, and h-BN@MCNT-NH<sub>2</sub> were presented in Figure 2a. The characteristic peak of h-BN appeared at 1365 cm<sup>-1</sup>, which belonged to a Raman G band due to the high frequency E<sub>2g</sub> vibration mode [28]. The G band was downshifted in the h-BN@MCNT-NH<sub>2</sub> composite from 1365 to 1357 cm<sup>-1</sup> compared to that of pristine h-BN, this effect was caused by the strong specific interactions between h-BN and MCNT-NH<sub>2</sub> [29]. This interaction may be due to the  $\pi$ - $\pi$  effect between h-BN and MCNT-NH<sub>2</sub> and the rough surface the h-BN formed during ball milling, easy to combine h-BN and MCNT-NH<sub>2</sub>.

To confirm adsorption of the MCNT-NH<sub>2</sub> on the surface of h-BN, X-ray diffraction (XRD) measurements were taken at 25 °C to h-BN, MCNT-NH<sub>2</sub>, and h-BN@MCNT-NH<sub>2</sub>. As showed in Figure 2b, a characteristic diffraction peak of h-BN was observed at 26.86° corresponding to 100 crystal planes [30]. In addition, the (002) peak slightly shifted from 26.86° (pristine h-BN) to 26.80° after hybrid filler h-BN@MCNT-NH<sub>2</sub> was made. The possible reason for the peak downshift is that the ball milling mixing promotes the  $\pi$ - $\pi$  combination of h-BN and MCNT-NH<sub>2</sub>. The microstructures of h-BN and h-BN@MCNT-NH<sub>2</sub> were observed through SEM (Figure 2c, 2d). By comparing pure h-BN with h-BN@MCNT-NH<sub>2</sub>, it can be seen that MCNT-NH<sub>2</sub> are uniformly attached to the BN surface.

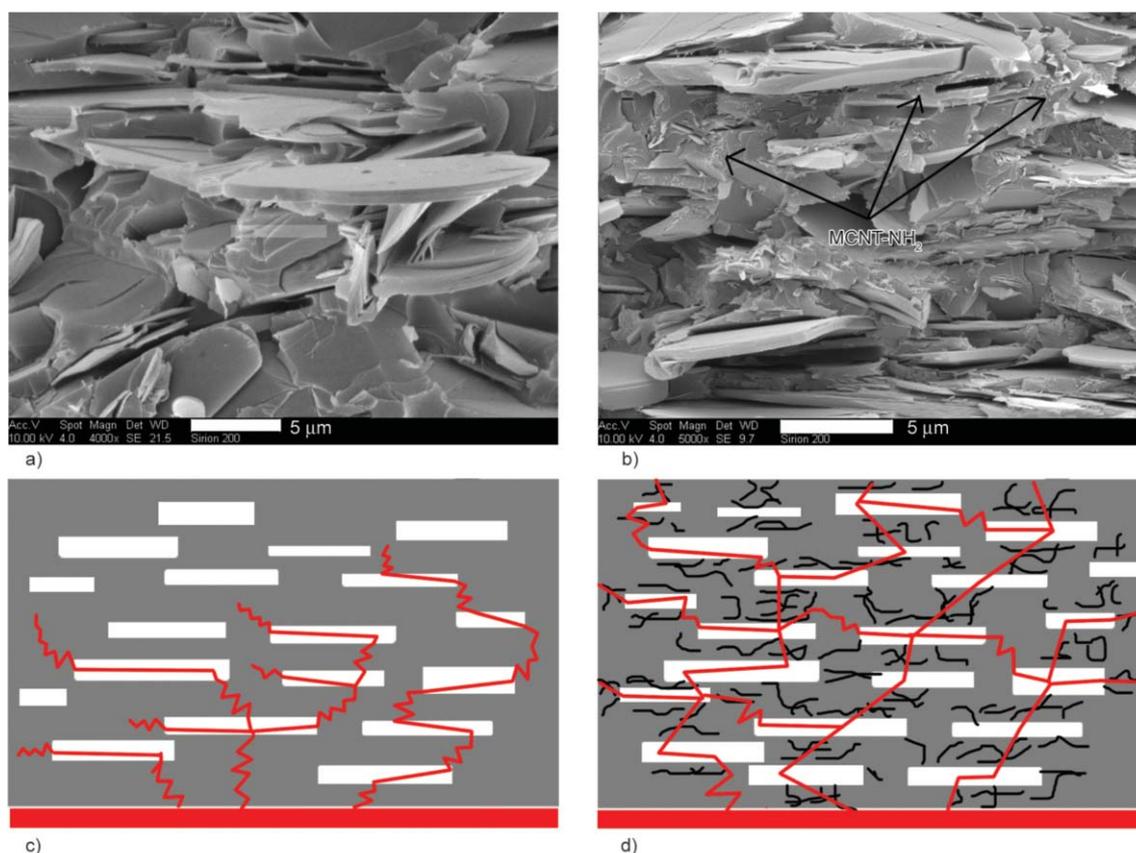
### 3.2. Morphology of h-BN@MCNT-NH<sub>2</sub>/LECRs

After pre-curing the composite, it was placed in a 3×3×0.2 cm mold, hot-pressed, and then cured in an oven to form h-BN@MCNT-NH<sub>2</sub>/LECR composites. Cross-sectional images of h-BN@MCNT-NH<sub>2</sub>/LECR were characterized via SEM. As shown in Figure 3, the dispersion and orientation of different content of fillers in the polymer can be visually observed. h-BN is relatively uniformly dispersed in the composite. With increasing the loading of filler, the horizontal structure of the thermally conductive filler is regularly arranged. The reason for the increase of h-BN arrangement is that the pressure of the hot-pressed machine does not change when the content of the filler is high, the pressure is applied to make the h-BN plates squeeze each other laterally, thereby allowing the plates to be regularly aligned horizontally.

In order to further analyze the microstructure of 50 wt% h-BN@MCNT-NH<sub>2</sub>/LECRs, the distribution of filler the composite was observed at SEM (Figure 4b) using high magnification. MCNT-NH<sub>2</sub> is slightly agglomerated because the carbon tube is introduced into the composite material through the hybrid filler. We chose 50% h-BN/LCERs for comparison, as shown in Figure 4a, the h-BN filler is dispersed in h-BN/LCER horizontally, and the surface of epoxy matrix is smooth. The low thermal conductivity of 50 wt% h-BN/LCERs compared to 50 wt% h-BN@MCNT-NH<sub>2</sub>/LECRs is attributed to thermal energy to be consumed in the composite, which is harmful to conduct thermal energy (Figure 4c). It is noted that the epoxy resin matrix at our prepared h-BN@MCNT-NH<sub>2</sub>/LCERs contains carbon nanotubes in Figure 4b. The main reason might be that the MCNT-NH<sub>2</sub> on the surface of h-BN



**Figure 3.** Cross-sectional SEM images of h-BN@MCNT-NH<sub>2</sub>/LECRs with the different content of fillers (a) 10% h-BN@MCNT-NH<sub>2</sub>/LECRs; (b) 30% h-BN@MCNT-NH<sub>2</sub>/LECRs; (c) 50% h-BN@MCNT-NH<sub>2</sub>/LECRs.



**Figure 4.** (a) The microstructure of the 50% h-BN/LCERs. (b) the microstructure of 50% h-BN@MCNT-NH<sub>2</sub>/LCERs. (c) and (d) are heat dissipation simulations of 50% h-BN/LCERs and 50% h-BN@MCNT-NH<sub>2</sub>/LCERs composites, respectively.

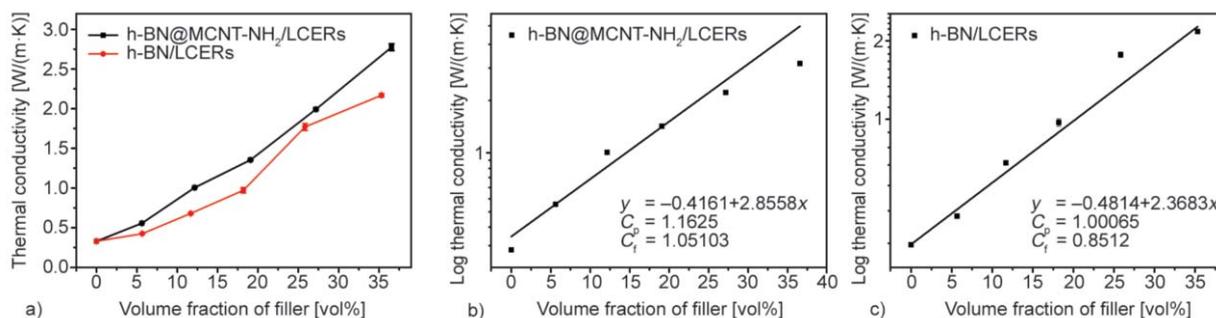
platelets participated in the epoxy resin curing process, which the amino group in MCNT-NH<sub>2</sub> can react with the epoxy monomer. The slightly agglomerated MCNT-NH<sub>2</sub> can realize the thermal conduction lap between the boron nitride sheets, which can be said to provide a thermal conduction path for the composite. MCNT-NH<sub>2</sub> plays a role in increasing the thermal conduction path of h-BN/LCERs composite and decreasing the large interface thermal resistance of fillers and resin matrix. Figure 4c and Figure 4d visually depicted the heat dissipation simulations of 50% h-BN/LCERs and 50% h-BN@MCNT-NH<sub>2</sub>/LCERs composites, respectively. where the red rectangle represents the heating element, and the red line represents a thermal conductive path, MCNT-NH<sub>2</sub> plays a crucial role in the thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCERs.

### 3.3. Thermal conductivity of the composite

The thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCERs were investigated with different loading of the filler at room temperature. As shown in Figure 5, When the content of the

filler is the same, h-BN@MCNT-NH<sub>2</sub>/LCER has a higher thermal conductivity than h-BN/LCER. In particular, h-BN@MCNT-NH<sub>2</sub>/LCERs having an h-BN@MCNT-NH<sub>2</sub> content of 50 wt% has a high thermal conductivity of 2.775 W/(m·K) at room temperature, which is about 8.43 times that of a pure LCERs. While the thermal conductivity of h-BN/LCERs with 50 wt% h-BN only reached 2.169 W/(m·K). This is due to the fact that the heat is transmitted by the vibrational modes of atoms, called phonons, with a dual character particle-wave, and the resin and h-BN are two different substances, one is crystalline, and the other is amorphous, phonon scattering easily occurs at the boundary between resin and h-BN. However, MCNT-NH<sub>2</sub> in the h-BN@MCNT-NH<sub>2</sub>/LCERs plays a role in increasing the thermal conduction path of h-BN/LCERs and decreasing the large interface thermal resistance of fillers and resin matrix. This makes h-BN@MCNT-NH<sub>2</sub>/LCERs composites have higher thermal conductivity than h-BN/LCERs.

Different theoretical models have been developed to study the thermal conductivity of composite



**Figure 5.** (a) Thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCERs vs. the volume fraction of filler, (b) and (c) represent the logarithmic values of the thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCERs as a function of volume fraction the filler, respectively.

materials, including Hatta-Taya's model [31, 32], Maxwell-Eucken's model [33], Agari's model [2, 34] and Bruggeman's model [35]. The factors that should be considered when choosing a theoretical model, such as particle size or shape, solids loading, and homogeneity of the dispersed phase in the resin matrix [33]. Assuming the heat conduction of the h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCERs composites are in an ideal condition, which is independent of isotropic and anisotropic properties. We chose the Agari's model to estimate the thermal conductivity of the composites. Agari's model was confirmed to be adaptable to thermal conductivities of varieties of polymer composite systems filled with spherical or irregular fillers [34]. Its mathematical expression is given by Equation (1):

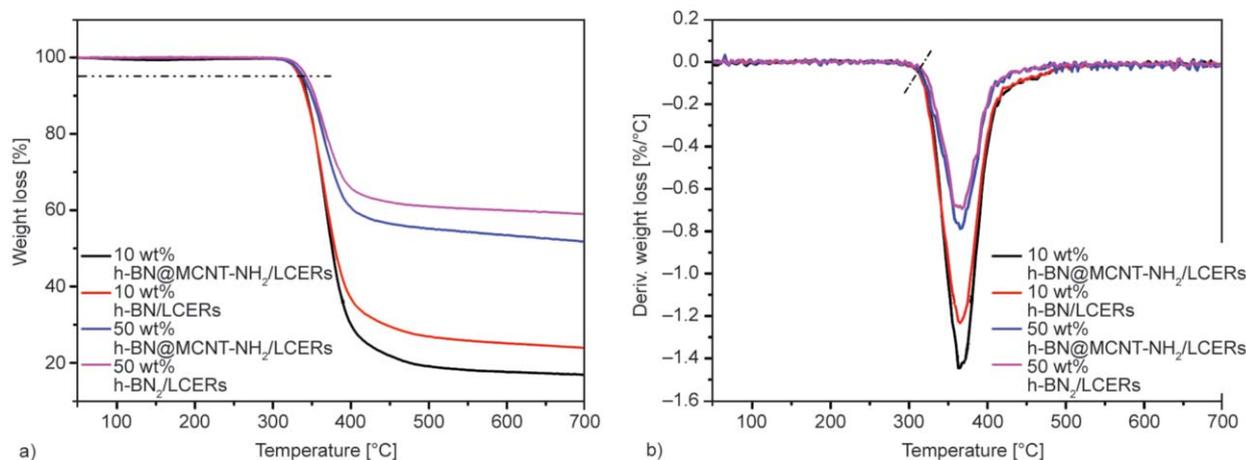
$$\log \lambda_c = C_f \cdot \log \left( \frac{\lambda_f}{C_p \cdot \lambda_p} \right) \cdot V_f + \log(C_p \cdot \lambda_p) \quad (1)$$

where  $\lambda_c$  is the thermal conductivity of a composite;  $\lambda_f$  is the thermal conductivity of fillers (200 W/(m·K)) [36];  $\lambda_p$  is the thermal conductivity of polymer resin (0.33 W/(m·K));  $V_f$  is the volume fraction of fillers;  $C_p$  measures the impact of filler on the structure of the liquid crystal epoxy resin; and  $C_f$  evaluates whether the filler can form the thermal conductive chains easily. The higher the value of  $C_f$  suggests the easier formation of the conductive chains in epoxy resin matrix [37]. Thermal conductivity of composites with different contents was presented in Figure 5a. After linearly fitting the thermal conductivity data to the volume fraction, as shown in Figure 5b and 5c, there is a certain error between the prediction of the Agari's model and the actual thermal conductivity of h-BN/LCER and h-BN@MCNT-NH<sub>2</sub>/LCERs, but it is generally acceptable. In Xiao's article, when using Agari's model to simulate the thermal conductivity

of silicon carbide nanowires (SiCw)/epoxy resin composite, there are multiple deviant points [38]. By Agari's model fitting of h-BN/LCER and h-BN@MCNT-NH<sub>2</sub>/LCERs, the corresponding value of  $C_p$  and  $C_f$  can be obtained as shown in Figure 5b and 5c. The value of  $C_p$  of h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCERs is 1.1625 and 1.0006, respectively; The value of  $C_f$  of h-BN@MCNT-NH<sub>2</sub>/LCERs and h-BN/LCER is 1.0510 and 0.8512, respectively. The value of  $C_p$  of h-BN@MCNT-NH<sub>2</sub>/LCERs is higher than of h-BN/LCERs, indicating that the hybrid filler has a greater impact on the polymer, which is attributed to the amino group in the filler participating in the curing process of epoxy resin. The value of  $C_f$  for the h-BN@MCNT-NH<sub>2</sub>/LCERs is larger than that of h-BN/LCER. It reveals that h-BN@MCNT-NH<sub>2</sub>/LCERs more easily formed thermal conductive paths in the resin matrix than h-BN/LCERs. We can seem to conclude that MCNT-NH<sub>2</sub> plays a role in increasing the thermal conduction path of h-BN/LCERs composite and decreasing the large interface thermal resistance of fillers and resin matrix.

#### 3.4. Thermal stability of the composites

Thermal stability is one of the important properties for the composites in practical application. The thermal degradation behaviors of 50% h-BN@MCNT-NH<sub>2</sub>/LCERs, 50% h-BN/LCERs, 10% h-BN@MCNT-NH<sub>2</sub>/LCERs, and 10% h-BN/LCER composites were investigated by TGA. The thermal stability of the composites was manifested in the temperature of thermal decomposition. The temperature value of 5% weight loss corresponds to at the temperature of the on-set decomposition reaction [39, 40]. It can be seen from Figure 6a that the temperature of the on-set decomposition reaction of the composite is about



**Figure 6.** (a) TGA and (b) DTG curves of 50% h-BN@MCNT-NH<sub>2</sub>/LCERs, 50% h-BN/LCERs, 10% h-BN@MCNT-NH<sub>2</sub>/LCERs, and 10% h-BN/LCER composites under nitrogen condition.

330 °C. The residual weight of composites doesn't correspond to their content of 10 and 50 wt% at 700 °C, because the nitrogen atmosphere is used in the TGA test, the polymer forms carbon residues, and it is not completely decomposed [15]. Derivative thermogravimetric analysis (DTG) curve show weight loss rate of the composites. The absolute value of the curve represents the decomposition rate of the composite. It can be seen from Figure 6b that the fastest thermal decomposition of 50 wt% h-BN@MCNT-NH<sub>2</sub>/LCERs and 50 wt% h-BN/LCERs is slower than that of 10 wt% h-BN@MCNT-NH<sub>2</sub>/LCERs and 10wt% h-BN/LCERs. The possible reason is that the addition of h-BN microplates temporarily blocked the heat that degrades the polymer matrix. Comparing the maximum decomposition rate of different types of fillers with the same content, h-BN@MCNT-NH<sub>2</sub>/LCERs is faster than h-BN/LCERs. This is because MCNT-NH<sub>2</sub> having a nanometer size cannot prevent heat insulation and can transfer heat to the resin matrix more quickly.

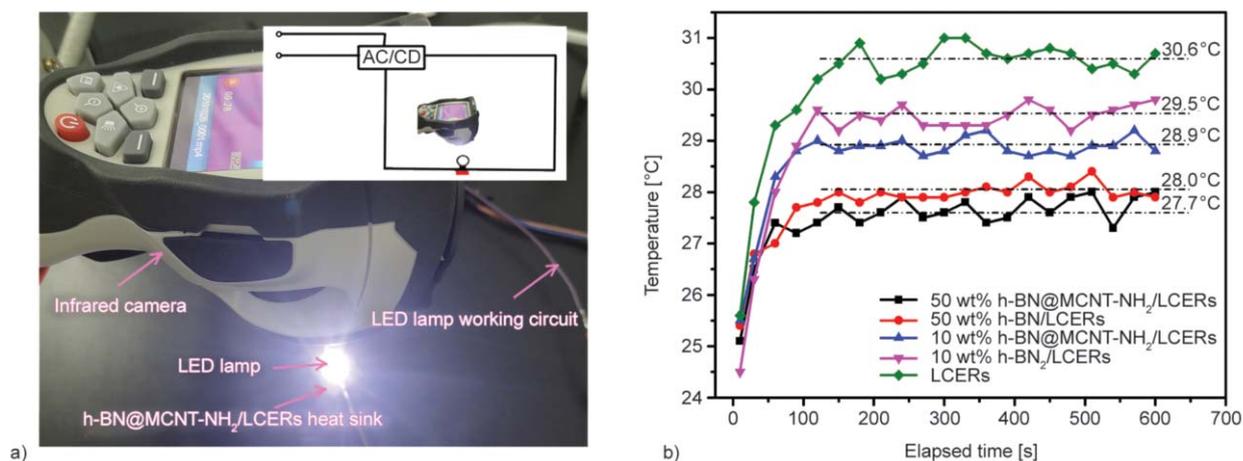
### 3.5. Application on electronic components

At present, the heat-conducting substrate of commercial LED lamps is mostly metal aluminum, but aluminum has the characteristics of difficult to process and expensive. In order to practically evaluate the usability and thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCER composites in LED lamps, we chose 3 W LED lamps and constant current converters(AC/DC) to build a conductive path with switches, as shown in Figure 7a. Composite materials with the same size (about 15 mm×15 mm×2 mm) were used as heat-transferring substrate

material under the LED lamp. The surface temperature variations of the lighted LED lamp with time were recorded by an infrared thermal imager. The temperature of the LED lamp using 50% h-BN@MCNT-NH<sub>2</sub>/LCERs, 50% h-BN/LCERs, 10% h-BN@MCNT-NH<sub>2</sub>/LCERs, and 10% h-BN/LCERs for heat dissipation was studied. It can be seen in Figure 7b that, during the running process, the temperature of the LED lamp rises rapidly within 150 seconds after startup, and then the temperature is relatively constant from 200 to 600 seconds. The temperature using 50% h-BN@MCNT-NH<sub>2</sub>/LCERs was eventually stabilized at 27.7 °C, below 50% h-BN/LCERs (28.0 °C), 10% h-BN@MCNT-NH<sub>2</sub>/LCERs (28.9 °C), 10% h-BN/LCERs (29.5 °C) and LCER (30.6 °C). This result illustrates that the 50% h-BN@MCNT-NH<sub>2</sub>/LCERs composites have better heat-transferring capability, which is in good agreement with the order of thermal conductivity of the four samples. It is verified that the thermal conductivity of 50% h-BN@MCNT-NH<sub>2</sub>/LCERs is higher in comparison with others. The above experimental results show that the 50% h-BN@MCNT-NH<sub>2</sub>/LCERs materials can guarantee timely dissipating of internally generated heat, resulting in increased lifetime and efficiency of the LED lamp eventually. Therefore, it is expected that 50% h-BN@MCNT-NH<sub>2</sub>/LCER composites will be used in LED electronic products.

### 4. Conclusions

In this work, we introduced highly thermally conductive and fibrous MCNT-NH<sub>2</sub> into h-BN/LCER composites to improve the thermal conductivity of



**Figure 7.** (a) Schematic diagram of h-BN@MCNT-NH<sub>2</sub>/LCERs composites been applied to LED and infrared camera been used to detect the heat of the surface temperature of LED lamps. (b) The surface temperature variations of the LED lamps against time.

the composites. First, we prepared h-BN@MCNT-NH<sub>2</sub> hybrid fillers. Then, the amino group in the hybrid filler participated in the curing process of the epoxy resin to prepare h-BN@MCNT-NH<sub>2</sub>/LCER composites. Subsequently, the effects of the same amount of h-BN@MCNT-NH<sub>2</sub> and h-BN were compared on the thermal conductivity of epoxy resins. The results showed that h-BN@MCNT-NH<sub>2</sub>/LCER had higher thermal conductivity. In order to explain the thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCER, we theoretically analyzed using the Agari's model and SEM to conclude that h-BN@MCNT-NH<sub>2</sub>/LCER compared to h-BN/LCER had more thermal conduction paths. The main reason is that the addition of MCNT-NH<sub>2</sub> decreased the interface thermal resistance of h-BN and LCER, and made h-BN/LCER form a thermally conductive chain. Finally, the usability and thermal conductivity of h-BN@MCNT-NH<sub>2</sub>/LCER composites was verified by LED lamps. The temperature of LED lamp using 50% h-BN@MCNT-NH<sub>2</sub>/LCERs was eventually stabilized at 27.7°C, it is expected that 50% h-BN@MCNT-NH<sub>2</sub>/LCER composites will be used in LED electronic products.

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