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A facile method to prepare oriented boron nitride-based polymer composite with enhanced thermal conductivity and mechanical properties

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ABSTRACT

Hexagonal boron nitride (BN) is often used as filler to improve the thermal conductivity of polymer matrix due to its high thermal conductivity. However, previously reported BN-based composites always have a high in-plane thermal conductivity, which is not beneficial for vertical heat dissipation. In addition, high BN content results in the deterioration of the mechanical properties. Here, we report a feasible method to prepare a BN/silicone rubber (SiR) composite with oriented BN in organosilicon matrix via a vacuum-assisted self-assembly technique. The BN/SiR composite displays a 1270% higher (2.74 W/(m·K)) thermal conductivity than that of neat organosilicon matrix (0.20 W/(m·K)). The oriented BN nanosheets increase the polymer's adhesive force and exhibit excellent compression cycle performance. In turn, these features support its superiority as thermal interface material in the light-emitting diode chips heat dissipation application.

1. Introduction

The development of the microelectronics industry is heading in the direction of higher integration, lighter in weight, and multi-function, which results in a high-density heat source that damages the chip's service life [1]. Polymers have been widely used in electronics packaging for their excellent mechanical properties, corrosion resistance, lightweight, and low cost. However, the thermal conductivity of polymers is low with a range of 0.10–0.25 W/(m·K), which can hardly meet the increasing heat dissipation requirements [2]. Therefore, how to improve the thermal conductivity of polymer has become a valuable topic for researchers today.

Hexagonal boron nitride (BN) is called “white graphene” for its two-dimensional structure [3]. It is often used as a filler to improve the thermal conductivity of polymer matrix due to its high thermal conductivity [4]. Some researchers directly mix BN with polymers. However, it requires a high filling amount of filler (>50% (volume)) to improve the composite's thermal conductivity, which in turn may

deteriorate its mechanical properties [5]. To solve this problem, researchers found that by guiding the orientation of filler particles along the same axis in the polymer matrix, the mechanical properties of the composite material can be maintained [6]. For example, Han et al. conducted a carboxylated polystyrene-coated hydroxylated BN material by a suspension polymerization process and realized a thermal conductivity of 1.13 W/(m·K) with 12 wt% BN-OH addition [7]. An constructed a well-organized 3D interconnection structure through a vacuum filtration process. The in-plane thermal conductivity of the BN/lignosulfonate/natural rubber composite material is 1.17 W/(m·K) with 25 wt% BN content [8]. In a word, high BN content in polymer matrix damages composite's mechanical properties and limits its application as thermal interface material. Furthermore, the thermal conductivity of BN-based composites is always high in the horizontal direction, which is not beneficial for vertical heat dissipation.

Here, we developed a simple and environmentally friendly method to improve the BN/silicone rubber (SiR) composite's thermal conductivity without damaging its mechanical properties. The results showed

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that BN/SiR composite has a high thermal conductivity of 2.74 W/(m·K) with excellent compression resilience performance. Moreover, various directions and thicknesses of the composite piece can be obtained according to actual applications, which is a promising property for industrial applications.

2. Experimental section

2.1. Materials

BN platelets (17-30um) were purchased from Merch Company (Germany). Silicone substrate was provided by Sigma Chemical Reagent Company. Curing agents and catalyst inhibitors were supplied by the Aladdin Company (Shanghai).

2.2. Preparation of BN/SiR composites

The bulk composites were prepared by three different methods. The following are the description :

Suction Filtration-Vacuum (SFV) method: The fabrication process is graphically shown in Fig. 1. In the first step, 5 g BN nanosheets particles were added into 50 ml ethanol at room temperature. Then the mixture solution was placed under ultrasonication to obtain a homogeneous dispersion. The well-suspension mixture was poured into a glass filter bottle, then placed on a filter paper. The mixture solution was then filtered via vacuum filtration. After filtration, the obtained BN bulk cake was dried at 80 °C. Once dried, the cake was peeled off from the filter paper carefully. After that, the organic silicon base was dropped onto the BN cake. The added organic silicon base can easily penetrate the fabricated BN cake because of its low surface tension and sufficient wettability with the BN nanosheet. Afterward, the wetting BN cake was placed

in a vacuum oven to drive away from the gas inside, and then the BN-containing organic silicon was cured at 80 °C for 5 h. Finally, the in-plane direction of BN/SiR (in-BN/SiR-SFV) composite and through-plane direction of BN/SiR (th-BN/SiR-SFV) composite were obtained.

Mix-Suction Filtration-Vacuum (MSFV) method: As depicted in Fig. 1, the SFV composite was prepared by filtration in ethanol followed with vacuum-assisted to drive away the gas from inside. Different from the SFV method, the MSFV method mixes the organic silicon base with BN nanosheet particles firstly and then filters via vacuum filtration. The following procedure is the same as the MSFV method. Furthermore, the in-plane direction of BN/SiR (in-BN/SiR-MSFV) composite and through-plane direction of BN/SiR (th-BN/SiR-MSFV) composite were obtained finally.

Random method: Random composite was prepared by a simple mix method. Typically, the homogeneously dispersed BN/SiR composite was obtained through 10 min intense stirring. Then, the homogeneous solution was cured at 80 °C for 5 h. Similarly, the in-BN/SiR-Random composite and th-BN/SiR-Random composite were prepared.

As mentioned above, the density of BN after suction filtration is constant in the SFV method process under the vacuum pump's pressure. Thus, the content of organic silicon infiltrated is fixed, and the BN mass fraction is 42%. To compare the different properties caused by the preparation method, the same amount of BN was achieved in the MSFV and the Random methods.

2.3. Characterizations

The microstructure surface of the BN/SiR composites was tested by a scanning electron microscope (SEM, FEI NOVA 4500) equipment. The BN nanosheet was determined using an X-ray diffractometer (XRD) (Pert PRO MPD, Panako Company) with Cu K α radiation ($\lambda = 0.15046$ nm), a

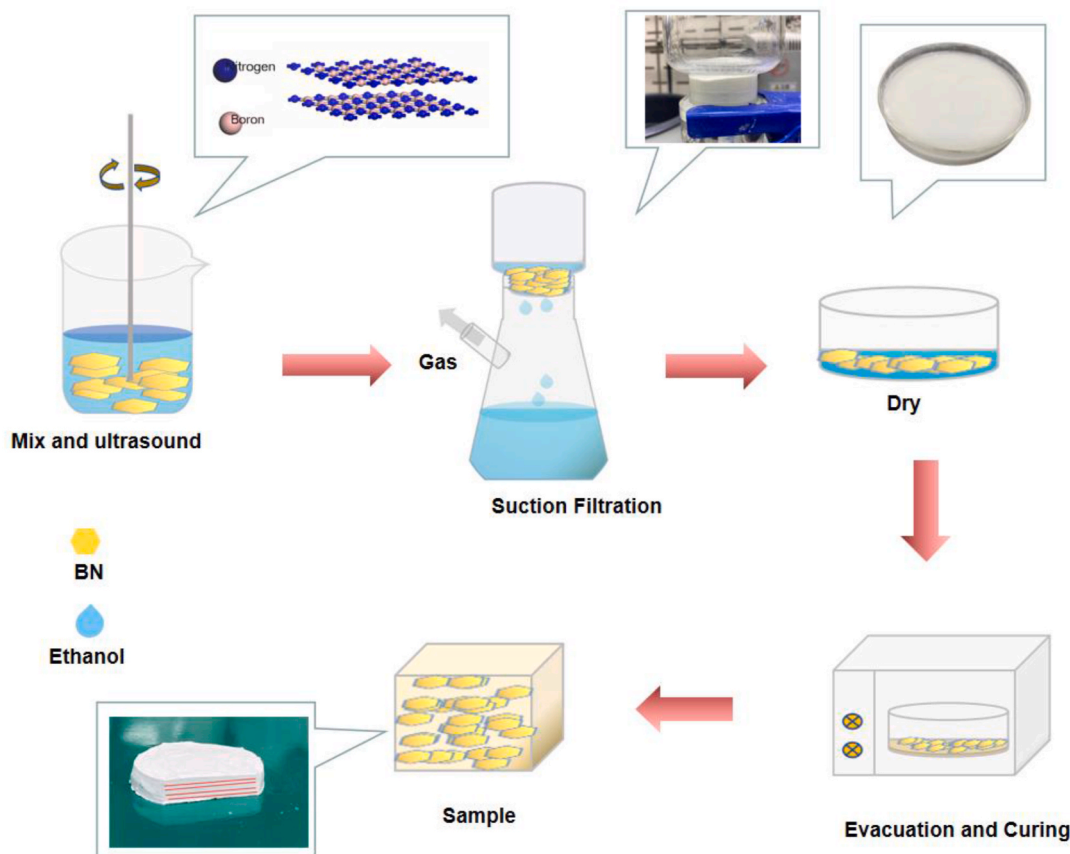


Fig. 1. Schematic diagram of the SFV method.

target current of 40 mA, and target voltage of 40 kV. The diffraction angle (2 thetas) was scanned from 5 to 80° with a step of 0.0167°/s. A dynamic mechanical performance testing machine (DMA Q800, TA Instruments) was used to study composite materials' mechanical properties and perform compression cycle tests and viscoelastic tests at room temperature. The rheological experiment was conducted with a temperature ramp 5.00 °C/min to 180.00 °C at the Multi-Frequency-Strain Module (MCR302, Anton Paar). Thermogravimetric analysis (TGA) was recorded from 30 to 800 °C with a TG-209 F1 instrument (NETZSCH, Germany) at a heating rate of 20 °C/min in airflow of 20 ml/min. A thermal imaging camera (FLIR E30, FLIR Systems, Inc., USA) was used to record the temperature changes. Laser flash diffuser LFA 467 (Germany NETZSCH) was used to detect BN/SiR composites' thermal diffusivity σ . A densitometer determined the density (ρ) of the composites. The specific heat capacity C_p was measured using Differential Scanning Calorimetry (DSC, 200 F3, NETZSCH, Germany). The material's thermal conductivity can be calculated according to the $K = \rho C_p \sigma$ formula.

3. Results and discussion

3.1. The morphology of BN/SiR composites

SEM examined the microstructural information of BN/SiR composites at different directions (Fig. 2). For BN/SiR-SFV composite, the BN nanosheets basically stack along the in-plane direction (Fig. 2a), and the parallel rows can be clearly observed (as in Fig. 2a1, 2a2). The sharp vertical grain edges of the BN nanosheet can also be seen along the through-plane direction (Fig. 2a3, 2a4), which indicates the excellent orientation of the BN/SiR-SFV composite. In Fig. 2b, there are fewer parallel BN nanosheets in the in-plane direction than that in BN/SiR-SFV composite. Some BN nanosheets locate in the composite with a certain angle to the horizontal plane. Fig. 2c shows that both vertical and parallel BN nanosheets are distributed homogeneously in the in-plane and

through-plane directions, thus indicating a random BN nanosheets dispersion state [9].

The ratio of peaks' intensity at approximately 26.9° and 41.6°, which are assigned to the (002) and (100) crystallographic planes of BN, respectively [10], represents the orientation degree of BN platelets [11]. The results are shown in Fig. 2d. The BN/SiR-SFV composite's intensity of (002) is higher than that of the BN/SiR-MSFV composite and BN/SiR-Random composite, which indicates that the BN/SiR-SFV composite has the highest orientation degree of BN nanosheets compared with the other two BN/SiR composites.

3.2. Mechanical properties

The cyclic compressive stress-strain curves of the BN/SiR composite are illustrated in Fig. 3a–e. At the beginning of the loading process, the stress-strain curve is nonlinear, which is a typical feature of soft polymer materials [12]. The stress-strain curve is then almost horizontal in the range of 0 MPa–0.01 MPa. During this period, the sample has experienced significant strain, but the stress increased slightly, which shows flexibility characteristics. After 0.01 MPa, the stress-strain curves show a much severer increasing slope. The additional stress applied to the as-deformed polymer is insufficient to create more deformation. When the stress is gradually released at a rate of -0.5 N/min, a return path is formed. From the figures, it can be found that the strain return path is different from the strain loading path, which is a typical viscoelastic behavior involving elastic and viscous components [13]. The viscoelastic behavior always represents energy loss caused by deformation hysteresis for the material. From the literature, the deformation hysteresis in the polymer material during the cyclic compression process may be due to the change of the direction or waviness of the single molecular chain during the loading-unloading cycle [14]. As shown in Fig. 3f, the in-BN/SiR-SFV composite exhibits the smallest energy loss, while the in-BN/SiR-MSFV composite and th-BN/SiR-MSFV composite shows weaker resilience properties. The deformation percentage of the

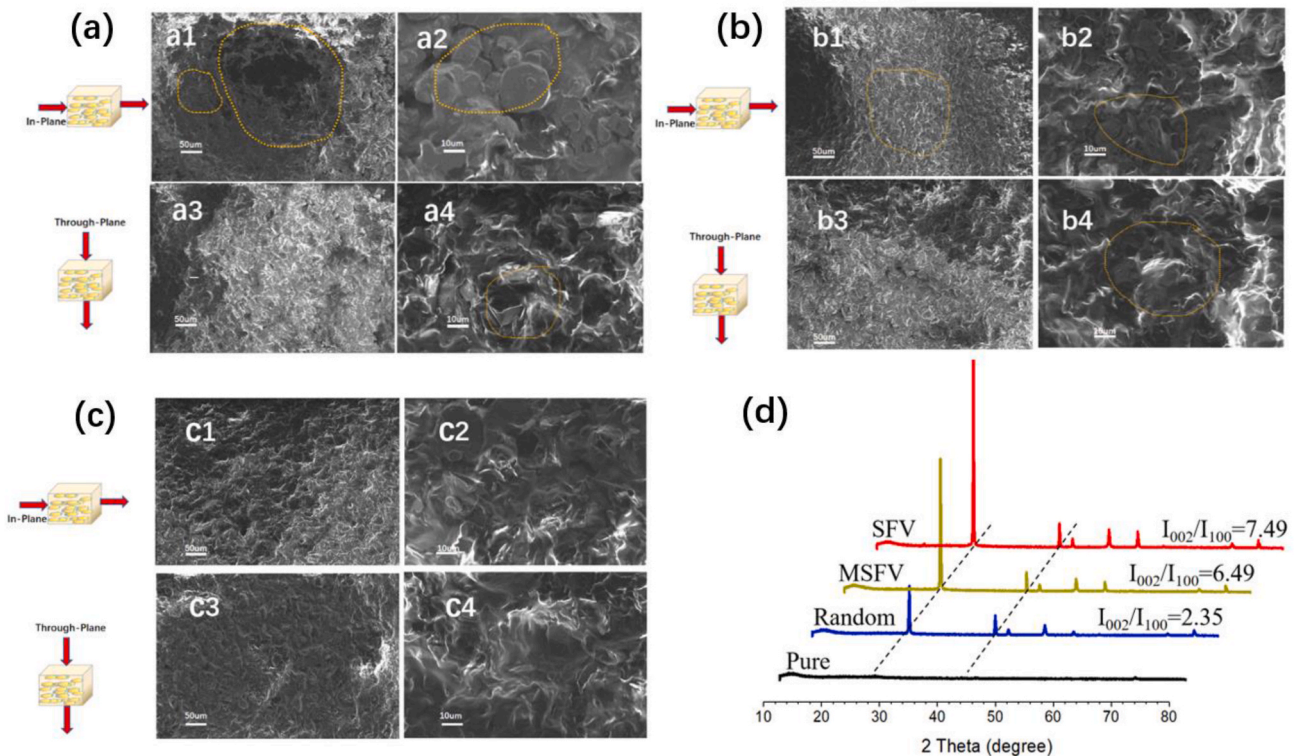


Fig. 2. SEM images of a: (a1) (a2) in-BN/SiR-SFV; (a3) (a4) th-BN/SiR-SFV; b: (b1) (b2) in-BN/SiR-MSFV; (b3) (b4) th-BN/SiR-MSFV; c: (c1) (c2) in-BN/SiR-random; (c3) (c4) th-BN/SiR-random; d: XRD patterns of BN/SiR composites.

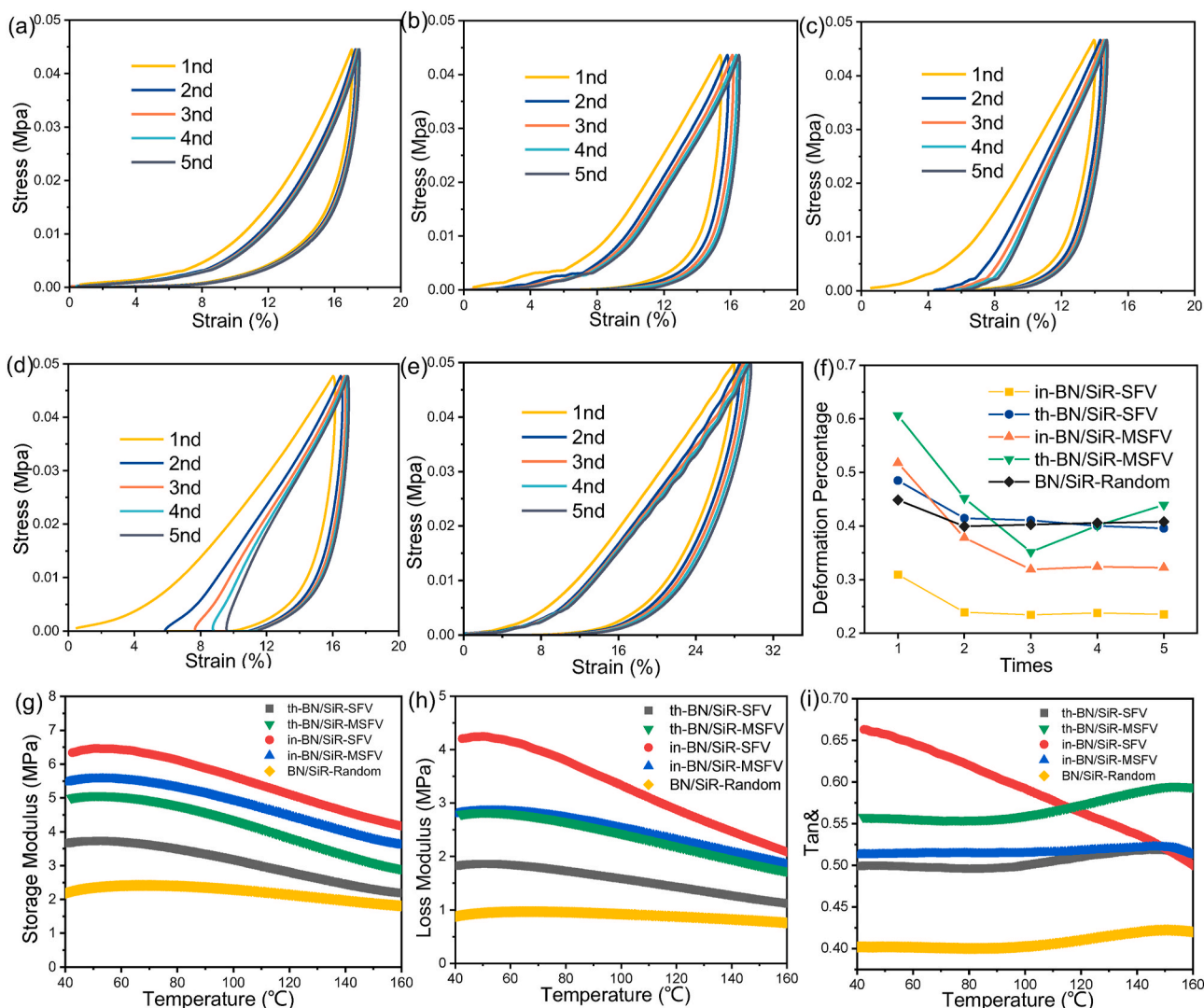


Fig. 3. Compression cycle performance of (a) in-BN/SiR-SFV; (b) th-BN/SiR-SFV; (c) in-BN/SiR-MSFV; (d) th-BN/SiR-MSFV; (e) BN/SiR-random. (f) deformation percentage of BN/SiR composites. (g) Storage modulus of BN/SiR composites; (h) Loss modulus of BN/SiR composites; (i) $\tan \delta$ of BN/SiR composites.

three composites after five cycles are as following: th-BN/SiR-MSFV > BN/SiR-Random > th-BN/SiR-SFV > in-BN/SiR-MSFV > in-BN/SiR-SFV. All experiments mentioned above show that the in-BN/SiR-SFV composite exhibits the best resilience performance and deformability, which is a required property for a good packaging thermal interface material.

The temperature dependence of the storage modulus, loss modulus, and damping coefficient ($\tan \delta$) for each composite are displayed in Fig. 3g and h, and 3i, respectively. As the temperature increases, the storage and loss modulus decrease drastically because of the transition from a glassy to a rubbery state [15]. The in-BN/SiR-SFV composite exhibits the highest storage modulus, and BN/SiR-Random composites have the lowest storage modulus value. Similarly, the composites loss storage performs the same trend compared with the storage modulus. The $\tan \delta$ results indicate that the force between the filler and matrix strengthened with temperature increasing. Since the mass fraction of BN filler of BN/SiR-SFV and BN/SiR-MSFV composite is the same, the difference between the storage modulus and loss modulus among them is mainly due to the different orientation methods in the material preparation process. The BN/SiR-SFV composite has the highest resilience performance due to the best BN nanosheets orientation [16]. The highest storage modulus indicates that the in-BN/SiR-SFV composite possesses better stress transport from rubber to fillers [17], thus exhibits a higher

ability of resistance to dynamic deformation, which was verified by the compression cycle experiment result.

3.3. Thermal conductivity

The horizontally oriented stacking of the BN nanosheet in the polymer matrix determines that most of the heat will be conducted along the horizontal direction of the composite material [18]. In addition, since the surface of the BN nanosheets is not modified, the intrinsic high thermal conductivity of the thermally conductive BN nanosheets is not changed.

In our experiment, the adhesion force of BN nanosheet in ethanol is tiny compared with that in organic silicon solution. Thus, under certain vacuum pressure, the orientation degree in the mixture (BN nanosheet/ethanol) is higher than that of the BN nanosheet/organic silicone solution. Fig. 4a presents that the in-BN/SiR-SFV composite and th-BN/SiR-SFV composite can reach 2.75 W/(m·K) and 1.04 W/(m·K), respectively. In comparison, the thermal conductivity of BN/SiR-MSFV composite reaches 1.56W/(m·K) and 1.43 W/(m·K) along the in-plane direction and through-plane direction. Since the Random method is a homogeneously mixing method, the thermal conductivity of the BN/SiR-Random composite is only 0.70 W/(m·K). The TG curve shows that the initial decomposition temperature of the three BN/SiR composites

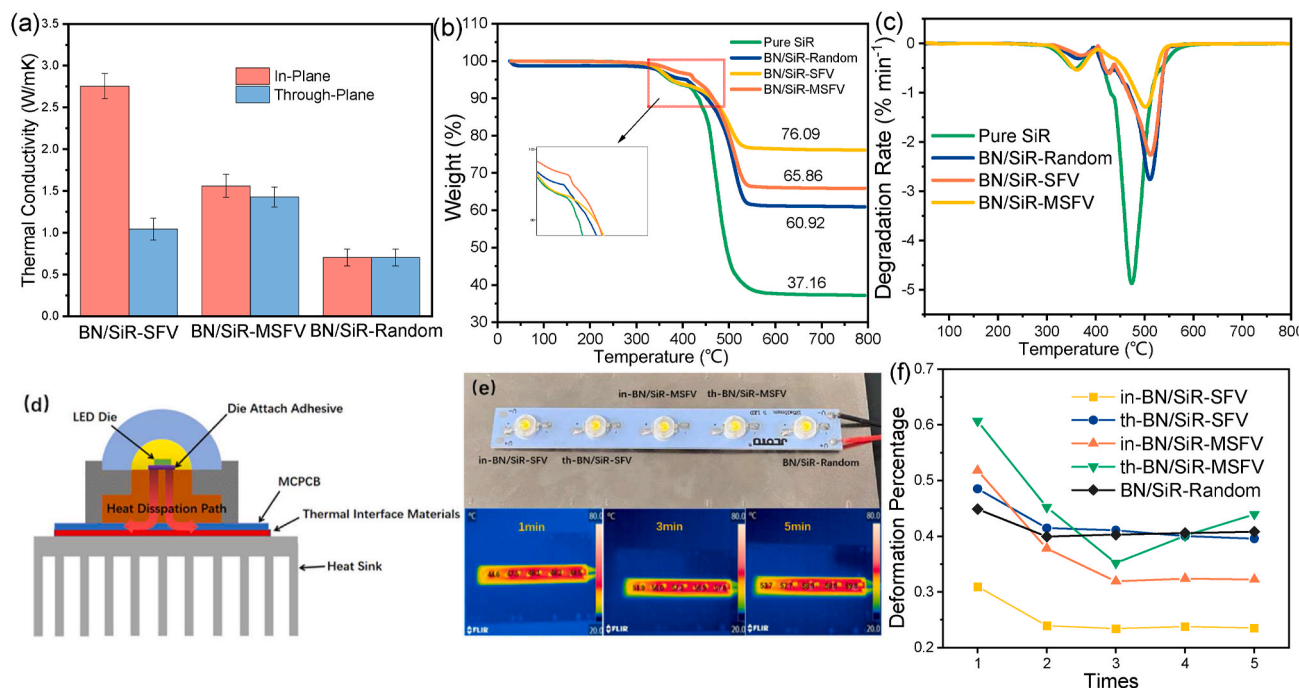


Fig. 4. (a) Thermal conductivity of BN/SiR composites; (b) TGA curves of BN/SiR composites; (c) DTG curves of BN/SiR composites; (d) LED strip structure; (e) temperature change of LEDs with different BN/SiR composites (f) IR camera image and temperature of BN/SiR composites.

presented little difference, but the final decomposition quality was quite different (Fig. 4b). Since the mass fraction of BN nanosheets in BN/SiR composites is same (42%), the main reasons for the difference may be ascribed to: (1) the horizontally oriented stacking of two-dimensional BN nanosheets provide high thermal conductivity for the composite, and thus inhibits the thermal decomposition of the quickly diffused volatile components [19]; (2) the thermally conductive filler accelerates the diffusion of heat in the composite matrix [20]. Moreover, the 10 wt% decrease of temperature for BN/SiR-SFV composite is the highest, indicating its good thermal performance.

As discussed above, the decomposition temperature of the final composite material may result from the mutual restriction of two parts. In addition, As seen in Fig. 4c, the BN/SiR-SFV composite exhibits the slowest decomposition rate in the temperature range of 0–400 °C. This further shows that the better the orientation of the BN nanosheets inside the composite, the better the thermal stability under medium-temperature conditions (300°C–400 °C).

The BN/SiR composites were attached to the light-emitting diode (LED) lights. Fig. 4d shows that the bottom of the composite is attached to a heat sink. The actual structure is shown in Fig. 4e. The LED strip lights up for 1 minute, 3 minutes, and 5 minutes, respectively. A thermal imager was used to measure the light temperature and verify the five composites' heat dissipation. As seen in Fig. 4f, with the time increase, the trend of the temperature change is almost the same. The LED attached to in-BN/SiR-SFV composite shows the lowest working temperature, while the LED attached to BN/SiR-Random composite shows the highest. The results show that the BN/SiR-SFV composite has obvious anisotropic thermal conductivity and heat dissipation performance. Moreover, the BN/SiR-SFV composite performs the best in actual heat dissipation for its highest thermal conductivity.

4. Conclusion

In this work, a BN/silicone rubber (SiR) composite with oriented BN in organosilicon matrix was prepared via a vacuum-assisted self-assembly technique. The prepared BN/SiR composite shows thermal conductivity of 1.04 W/(m·K) and 2.75W/(m·K) along the through-

plane and in-plane directions, respectively. In addition, the results of mechanical and TGA results show that the BN/SiR composite contains flexible and thermal stability. Moreover, since it is a bulk composite, the high thermal conductivity direction material can be easily obtained. Therefore, it is a valuable preparation method in packaging heat dissipation materials.

CRediT authorship contribution statement

Jing Chen: Investigation, Data curation, Writing – original draft. **Xu Liu:** Writing – review & editing. **Xiao Liang Zeng:** Methodology. **Huai Yu Ye:** Supervision. **Guo Qi Zhang:** Conceptualization.

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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