

Characterization of a Novel Cost-efficient and Environmentally Friendly Graphene-enhanced Thermal Interface Material

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Abstract—With the continuous development of electronic devices, effective heat dissipation has become a major factor affecting service life. Thermal interface materials (TIM) play a key role in controlling heat dissipation of electronic devices and have thus attracted widespread attention. In this study, we used graphene flakes (GF) derived from graphene film that is wasted during the preparation of commercial large-scale graphene-enhanced TIMs as thermally conductive fillers to formulate a new TIM. The thermal conductivity of the developed TIM is 50% higher with GFs than without. Furthermore, the TIM has a tensile strength of 0.46 MPa with an elongation at break of 1225%, a maximum compression strength of 0.64 MPa at 50% compression, and high mechanical cycle stability. This report provides a cost-efficient and environmentally friendly approach to producing high-performance TIMs for electronic cooling applications.

Keywords—Thermal interface material, Graphene flakes, Cost-efficient, Environmentally friendly

I. INTRODUCTION

The continuous miniaturization and integration of electronic devices lead to a large amount of generated heat. Therefore, fast and effective heat dissipation is a key factor affecting the long-term and reliable operation of electronic equipment [1]. Increasing heat transfer at the interface is an important part of thermal management. The surfaces of rigid

objects cannot achieve close contact owing to the tiny concave-convex surface features, in which remaining gaps are filled with air. Therefore, a thermal interface material (TIM) is generally used to fill the gaps between the contact surfaces of two heterogeneous materials and improve heat dissipation [2]. Silicone rubber (SR) is often used as a matrix polymer because of its softness, high elasticity, and thermal stability. However, the thermal conductivity of SR is low, which cannot meet the heat dissipation requirements of modern electronic devices [3]. Traditionally, silicone pads are made of SR loaded with thermally conductive fillers such as metals (including Ag, Cu, Ni, Au), ceramics (including boron nitride (BN), Al_2O_3 , aluminum nitride (AlN)), carbon allotropes (including graphite, diamond, carbon nanotubes, graphene), or hybrid fillers.

Recently, fabricating a 3D continuous thermal network in polymers has become a strategy for enhancing heat dissipation in electronic devices [4]. Some researchers have introduced the 3D skeleton into polymers through freeze-drying, high-temperature heat treatment, and impregnation processes. Zhang et al. [5] used graphene aerogel to improve the thermal conductivity of SR. The thermal conductivity of the composite reached up to $1.26 \text{ Wm}^{-1}\text{K}^{-1}$ at a low filler loading of 0.5 wt%. Xue et al. [6] achieved a thermal conductivity of $0.88 \text{ Wm}^{-1}\text{K}^{-1}$ in SR modified with BN and reduced graphene sheets. In addition to constructing a skeleton by freeze-drying, Zhao et

al. [7] prepared graphene foam on a nickel foam template by chemical vapor deposition and then embedded this foam in carbon fiber/polydimethylsiloxane. The thermal conductivity of the composite reached $0.55 \text{ Wm}^{-1}\text{K}^{-1}$. Although these methods have been advantageous for producing interconnected heat transfer networks, several limitations remain. Notably, the cumbersome, expensive, and energy-consuming processes pose a significant challenge for industrial production. It is necessary to develop a cost-effective, simple, green, and scalable strategy to construct high-performance TIMs.

Owing to its beneficial thermal and mechanical properties, graphene has been widely used in the field of heat dissipation of electronics, such as the batteries in smartphones [8]. However, the large-scale use of graphene films generates a large amount of graphene-based waste. Therefore, it is desirable to reduce or reuse this waste. In this study, we formulated a new TIM using graphene flakes (GF) as thermally conductive fillers, which were derived from graphene film waste generated during the preparation of commercial large-scale graphene-enhanced TIM. The thermal conductivity of the new TIM is $1.2 \text{ Wm}^{-1}\text{K}^{-1}$, which is 445% and 50% higher than that of the silicone matrix and TIM without GFs, respectively. Additionally, the TIM has a tensile strength of 0.46 MPa with an elongation at break of 1225%, maximum compression strength of 0.64 MPa at 50% compression, and high mechanical cycle stability. This represents a novel approach for producing cost-efficient and environmentally friendly high-performance TIMs for electronic cooling applications.

II. EXPERIMENTS

2.1. Materials

In this work, graphene waste from SHT Smart High-Tech AB, Sweden was used. BN and AlN (10 μm) were obtained from Sigma-Aldrich. SR is formed by mixing a certain proportion of silicone gel A and B, which were purchased from Wacker Chemical. All of the reagents were analytical grade.

2.2. Preparation of graphene flakes

Graphene film waste was processed in a crusher for several seconds to obtain GFs with a relatively uniform texture.

2.3. Preparation of the TIM

First, silicone gel A and B were mixed in a ratio of 1.5:1 and a certain amount of AlN and BN powders were introduced. Then, GFs were added and mixed evenly using a high-speed mixer. The mixture was kept under vacuum for 30 min to remove air bubbles and subsequently poured into a mold. Finally, the sample was placed into an oven at 100 $^{\circ}\text{C}$ for 5 h to obtain the resulting TIM (GT-R/ABG). The fabrication of TIM without GFs (GT-R/AB) was the same, except GFs were not added. The mass fraction of GFs in GT-R/ABG was 1%, 2%, 3%, 4%, and 5%, abbreviated as GT-R/ABG1, GT-R/ABG2, GT-R/ABG3, GT-R/ABG4, and GT-R/ABG5, respectively.

2.4. Characterization

The size distribution of the GFs was characterized using a laser particle size analyzer (Malvern Mastersizer 3000, UK). The microstructure of the GFs was visualized by transmission

electron microscope (TEM) (FEI Tecnai F20, USA). The structure of GFs was determined by X-ray diffraction (XRD) (Rigaku Ultima IV, Japan) and Raman spectroscopy (Horiba LabRAM HR Evolution, Japan). The cross-sectional morphology of the TIM was investigated by field emission scanning electron microscopy (FE-SEM) (Helios G4 PFIB). The out-of-plane thermal conductivity of the TIM was determined using a TIM thermal resistance & conductivity measurement apparatus, which is calculated using the following equation:

$$K = \text{BLT}/R \quad (1)$$

Where R is the total thermal resistance, BLT is the bond line thickness of the sample, and K is the thermal conductivity of the sample. The mechanical properties of the TIM were evaluated using a universal testing machine (Instron, USA).

III. RESULTS AND DISCUSSIONS

GFs were obtained by crushing the graphene film waste in a crusher for several seconds. High-resolution transmission electron microscopy (HR-TEM) was used to characterize the microstructure of the resulting GFs. As shown in Fig. 1a, the GFs exhibit a wrinkled tulle shape, and their size is mainly distributed around 35 μm (Fig. 1c). A high-resolution TEM image of the edge morphology reveals that the GFs are composed of six layers of graphene (Fig. 1b). The corresponding XRD and Raman spectra of the graphene film waste and GFs were similar (Fig. 1d and e), which indicates that the pulverization process does not change the characteristic structure of the graphene [9].

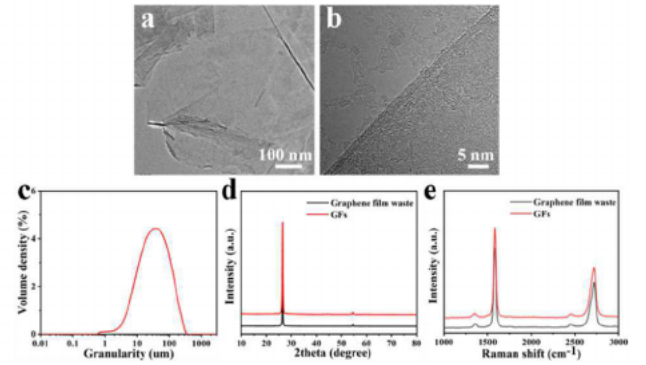


Fig. 1. (a) TEM top view of the surface of GFs. (b) High-resolution TEM image of the edge morphology of GFs. (c) Size distribution diagram of GFs. (d) XRD spectra and (e) Raman spectra of graphene film waste and GFs.

To observe the microstructure of the TIM and the filler distribution, the fractured surface of the TIM was characterized by FE-SEM. The cross-sectional morphology of the silicone matrix is relatively smooth, as a result of brittle fracture (Fig. 2a). However, the introduction of AlN and BN particles changes the morphology of the matrix (Fig. 2b). The corresponding elemental mapping of the image in Fig. 2b is shown in Fig. 2c, confirming that the B, Al, and N are uniformly dispersed in the matrix. Fig. 2(d-h) shows the cross-sectional morphology changes of GT-R/ABG with GF contents ranging from 1 to 5 wt%. The introduction of tulle-like GFs can effectively connect isolated AlN and BN particles. However, GFs begin to aggregate when their content is higher than 2 wt%. At 5 wt%, the degree of aggregation significantly increases, which is confirmed by the corresponding elemental analysis, showing that the C content in red circles is extremely high (Fig. 2i).

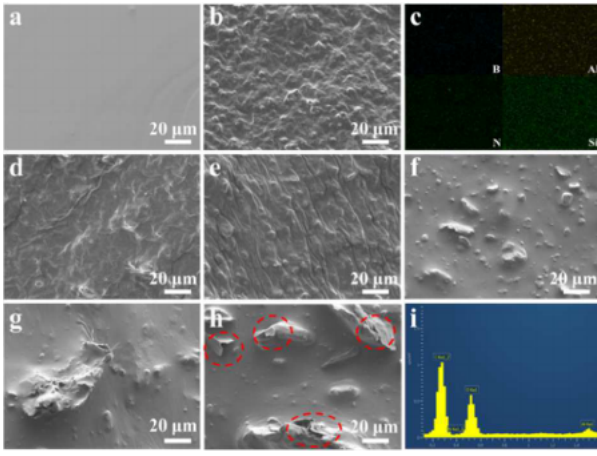


Fig. 2. (a) SEM image of the silicone matrix. (b) SEM image of the cross-section morphology of GT-R/AB. (c) Elemental mappings of (b). (d-h) SEM images of the cross-sectional morphology of GT-R/ABG with different GF contents: (d) 1 wt%, (e) 2 wt%, (f) 3 wt%, (g) 4 wt%, and (h) 5 wt%. (i) Elemental analysis of agglomerations shown in red circles in (h).

In addition to high thermal conductivity, TIMs also need high flexibility and a low elastic modulus to form complete contact between the rough interfaces. GT-R/ABG returns to its original shape after stretching and twisting (Fig. 3a). Fig. 3b shows the stress-strain curves of the TIM. The addition of AlN and BN improves the tensile strength of the silicone matrix. After introducing GFs, the stress applied on GT-R/ABG is uniformly dispersed, which is beneficial to avoid stress concentration. However, when the GF content is excessive, the aggregation of GFs results in a decrease in the tensile strength of GT-R/ABG. Furthermore, the fillers can also increase the compression strength of the silicone matrix. GT-R/AB has an ultra-high compression strength because of the high hardness of BN and AlN particles. However, after introducing GFs, the stress was uniformly dispersed by a small number of GFs, showing a relatively low compressive strength. Higher GF contents caused an increase in the compressive strength of GT-R/ABG (Fig. 3d). Therefore, the GF content has an optimal value, which is 2 wt%, where the GT-R/ABG tensile strength, elongation at break, and compression strength at 50% compression were 0.46 MPa, 1225%, and 0.64 MPa, respectively.

The mechanical stability of GT-R/ABG was evaluated by sequentially performing multiple tensile tests (10 cycles) at 50%, 100%, and 150% maximum strain (Fig. 3c). In the first cycle of every test, the SR molecule chains absorbed on the surfaces of the fillers were stretched, for which the curves showed higher energy loss coefficients. In the second cycle, the molecular chains did not have time to reabsorb on the surface of the filler, resulting in a significant shrinkage of the area enclosed by the curve. Then, subsequent cycles nearly overlap with the second cycle, demonstrating the mechanical stability of the GT-R/ABG [10].

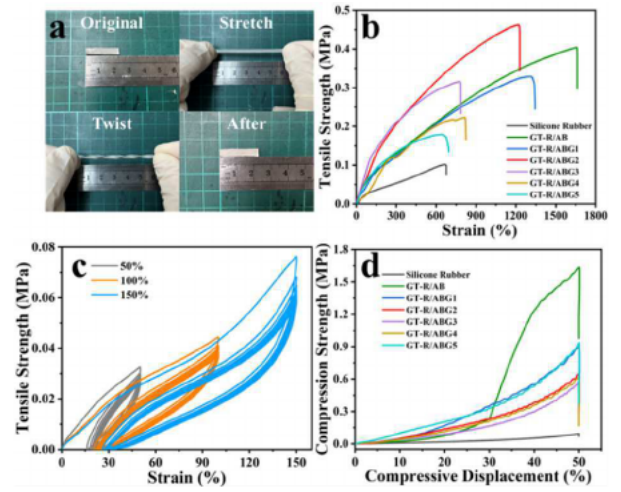


Fig. 3. (a) Optical images of the stretch and twist processes of GT-R/ABG. (b) Stress-strain curves of all samples. (c) Stress-strain curves of GT-R/ABG at the maximum strain of 50%, 100%, and 150%, repeated for 10 cycles. (d) Compression strength of all samples at the maximum compression of 50%.

Fig. 4a showed the thermal conductivity of GT-R/ABG as a function of the GF content. GT-R/ABG2 achieved an excellent thermal conductivity of $1.2 \text{ Wm}^{-1}\text{K}^{-1}$, which was 445% and 50% higher than that of the pure SR and GT-R/AB, respectively. This TIM outperforms several commercially available thermal pads, as well as some graphene-enhanced TIMs [6,7]. The isolated AlN and BN particles randomly dispersed in GT-R/AB cannot be fully interconnected, and thus, the thermal conductivity of GT-R/AB is limited by the lack of an effective heat conduction network, and severe phonon interface scattering between the fillers and matrix (Fig. 4b). In contrast, the isolated AlN and BN particles can be bridged by GFs, resulting in a more effective heat conduction network and a sharp increase in the thermal conductivity (Fig. 4c). However, excessive GF content leads to its agglomeration, which increases the interfacial thermal resistance between the matrix and fillers, resulting in a decrease in the thermal conductivity of GT-R/ABG.

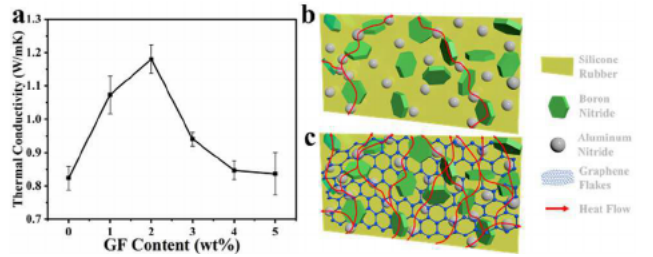


Fig. 4. (a) Variation of thermal conductivity of GT-R/ABG with different GF contents. (b, c) Proposed mechanistic model of the thermal conduction paths for (b) GT-R/AB and (c) GT-R/ABG.

IV. CONCLUSIONS

A new TIM was developed using graphene film waste in a silicone matrix in a simple, cost-effective, and environmentally friendly way, exhibiting beneficial thermal and mechanical properties. The thermal conductivity of TIM reached $1.2 \text{ Wm}^{-1}\text{K}^{-1}$, which is 445% and 50% higher than that of the silicone matrix and the TIM without GFs, respectively. Furthermore, the TIM displayed a tensile strength of 0.46 MPa, elongation at break of 1225%, a maximum compression strength of 0.64 MPa at 50% compression, and high mechanical stability. This new high-performance TIM has the potential to be applied to the thermal management of modern electronic devices.

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