

THERMAL CONDUCTIVITY OF 3D GRAPHENE FILLED POLYMER COMPOSITE

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Summary: *Graphene foam (GF), graphene sheet (GS) and carbon black (CB) were filled into polydimethylsiloxane (PDMS) to make novel polymer composites. The thermal properties of those composites were investigated. It is found that at 0.5 and 0.7 wt% graphene foam, the thermal conductivity of GF/PDMS composites increases from 0.40 to 0.56 Wm⁻¹K⁻¹, which are 200-300% that of pure PDMS, and about 20% higher than that of GS/PDMS composite. Furthermore, the adding of CB into the space of GF network and the interior of GF arms reinforces the thermal transportation, manifested by the increased thermal conductivity with 6 wt% CB. The coefficient of thermal expansion of 0.7 wt% GF/PDMS is (80-137)×10⁻⁶/K within 30-150 °C, much lower than those of 0.7 wt% GS/PDMS composite and pure PDMS. In addition, thermal stability of 0.7 wt% GF/PDMS composite is superior over 0.7 wt% GS/PDMS composite, and they are further improved by CB adding. All above results demonstrate that the GF filled polymer composite is a good candidate for thermal interface materials.*

1 INTRODUCTION

Heat dissipation has attracted tremendous attention for miniaturization of electronic devices generating hot-spot temperatures rising, which promoting the development of thermal interface materials (TIMs) with high thermal conductivity [1-4]. Graphene foam (GF) is composed of graphene with interconnected structure and inherits the excellent thermal, electrical and mechanical properties of graphene [5-8]. In terms of thermal conductivity of polymer matrix TIMs, the GF is expected to have high improvement due to its interconnected structure which forming naturally thermal transportation path. Pettes et al. [5] discovered that

the thermal conductivity of GF composed of few-layer graphene and ultrathin graphite was affected by the etchant for the sacrificial nickel, increased from 0.26 to 1.7 $\text{Wm}^{-1}\text{K}^{-1}$. Zhang et al. [9] found that the thermal interface resistance of GF at Si-Al interface was as low as $0.04 \text{ cm}^2\text{KW}^{-1}$. Chen et al. [10] reported that the thermal diffusivity of graphite foam/epoxy composite with 91.45 wt% epoxy was raised to $6.541 \text{ mm}^2/\text{s}$, which was 45.7 times higher than the pure epoxy. Ji et al. [7] filled ultrathin-graphite foams into phase change materials (PCMs), getting an increase of 18 times in thermal conductivity compared with paraffin wax. However, the GF applied in polymer matrix TIMs has rarely been reported.

In this work, the GF was grown by CVD on Ni substrate. The graphene sheets were obtained by breaking GF into thin pieces under ultrasonic agitation. In this way, they have the same growth condition. GF was infiltrated with liquid PDMS, graphene sheet (GS) was mixed with liquid PDMS, while carbon black (CB) was dispersed in PDMS and then the mixture was infiltrated with PDMS. The curing process was same for all composites. The microstructures and thermal conductivity of composites are investigated.

2 MATERIALS AND EXPERIMENTAL METHODS

2.1 COMPOSITES PREPARATION

The nickel foam with 1.5 mm in thickness was put in the quartz tube placed in a furnace (SGL-1200, Shanghai Daheng Co. Ltd.). It was heated to 1000 °C under Ar (500sccm) and H_2 (200 sccm) and kept for 20 min. After that, CH_4 (12 sccm) was introduced for 10 or 20 min for different thickness of graphene. Then, the samples was cooled to room temperature. 4 wt% poly(methyl methacrylate) (PMMA) was dip-coated and solidified on the surface of GF and 3M HCl was used to etch the nickel. The GF was obtained after dissolving PMMA with acetone. GS was get to sonicate GF in the ethanol.

The GF was filled with liquid PDMS (Sylgard184, Dow Corning, base agent/curing agent = 10/1 in weight). It was cured at 80 °C for 4h after removing the bubbles to get GF/PDMS composite. For GS/PDMS composites, GS was dispersed in acetone. Then, the base agent was added to blend with it. The curing agent was put into the mixture after acetone evaporation. The solicitation process is the same with GF/PDMS composite. For CB/GF/PDMS composites, the fabrication is almost the same with GS/PDMS composites except using acetone.

2.2 CHARACTERIZATION

Transmission electron microscope (TEM, Tecnai G2 F20, FEI) and scanning electron microscope (SEM, S-4800, HITACHI) was applied to observe the microstructure of studied materials. Atomic force microscope (AFM, MFP-3D-BIO, AR) was used to measure the thickness of GS. Laser flash method (LFA447, Netzsch) and heat flux method (DRL-III, Hunan Xiangyi Instruments Co. Ltd.) were utilized to measure the thermal conductivity of samples. The thermal properties of studied materials were obtained by dynamic

thermogravimetric analysis (Q600 SDT, TA), optical thermal expansion instrument (DIL-806, BHR).

3 RESULTS AND DISCUSSIONS

The morphologies of GF, GS and CB are presented in Figure 1. As shown in Figure 1(a), the arms of GF are interconnected with each other to form a three dimensional network. The diameter of circles surrounded by arms is about 300-500 μm . The width of arms is about 40 μm . The GS is semitransparent which is shown in Figure 1(b). Its thickness measured with AFM presented in Figure 2 is about 4 nm. From the Figure 1(c), it can be seen that the CB exists in a form of particle with the diameter of about 100 nm.

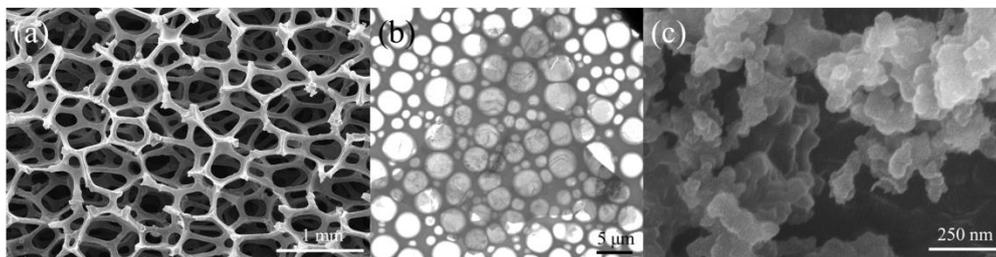


Figure 1: Morphologies of SEM images of (a) GF and (c) CB. (b) TEM image of GS.

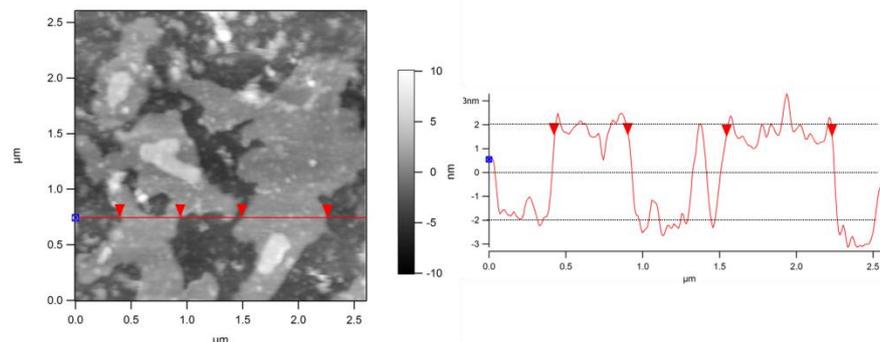


Figure 2: AFM image of GS on Si substrate.

The SEM images of a series of composites are displayed in Figure 3. The ripples or wrinkles appear in the surface of GF and GS, which also were observed by others [6, 12]. In Figure 3(a), PDMS not only occupied the space between the arms but also the interior of arms. The dimension of GS in GS/PDMS composites shown in Figure 3(b) reveals the existence of aggregation of GS in comparison with the data obtained by AFM. From the Figure 3(c), CB dispersed uniformly in the hollow arms and the space between the arms. No obvious gap between the struts indicates good filling of PDMS.

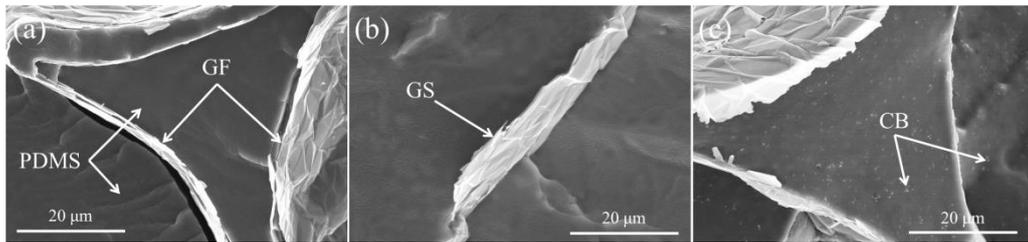


Figure 3: SEM images of freeze-fractured surfaces of (a) GF/PDMS, (b) GS/PDMS, (c) CB/GF/PDMS composites.

The thermal conductivity of materials studied are given in Figure 4. For 0.7wt% GF/PDMS composite, the thermal conductivity is $0.56 \text{ Wm}^{-1}\text{K}^{-1}$, which is about 300% that of PDMS and 20% higher than that of 0.7 wt% GS/PDMS composite. This phenomenon may be ascribed to the interconnected structure of GF, which supplies the channels for fast thermal transportation. But for GS filled composite, the channels for thermal transportation will form just when the amount of GS reaches a certain value called percolation threshold. Moreover, more interfaces and boundaries appear in GS/PDMS composite compared with GF/PDMS composite, which is adverse for fast thermal transportation [5, 9, 12, 13].

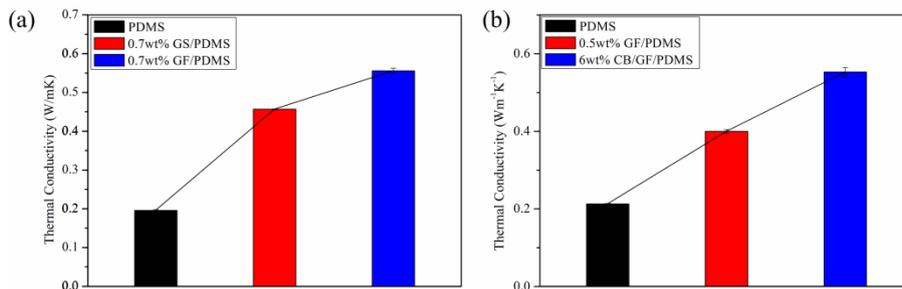


Figure 4: Thermal conductivity of the materials studied.

For different weight fraction of GF/PDMS composites, it can be found that the thermal conductivity of 0.7 wt% composite is 40% higher than that of 0.5 wt%. Because the integrity of GF depends on the graphene growth condition such as time duration, flow of CH_4 , etc. Figure 5 gives SEM images of neat Ni foam and graphene grown on Ni foam with CH_4 introduced for different time. At 3 min, a large part of Ni foam surface is still bare without graphene. At 5 and 10 min, most of Ni surface is covered by graphene, but the bare area still exists and some residual stay on the surface. At 20 min, the integrity of graphene is excellent. The longer time can guarantee the integrity of GF, which is beneficial for higher thermal conductivity.

For CB/GF/PDMS composite, the GF used is identical with that of 0.5 wt% GF/PDMS composite. When adding 6 wt% CB, the thermal conductivity is increased from $0.40 \text{ Wm}^{-1}\text{K}^{-1}$ to $0.55 \text{ Wm}^{-1}\text{K}^{-1}$. Owing to higher thermal conductivity of CB compared with PDMS, the addition of CB can improve the capability of thermal conduction of PDMS.

Furthermore, the mixture of CB and PDMS can infiltrate the hollow arms of GF to further improve the thermal conductivity.

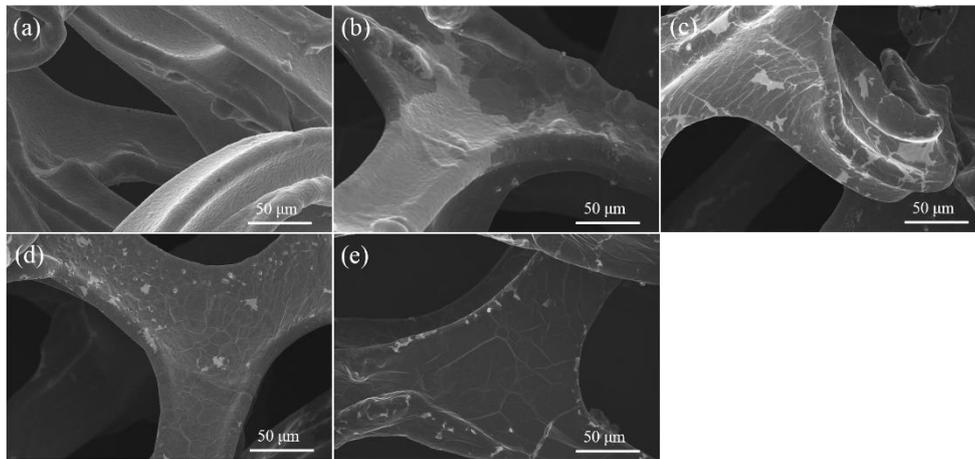


Figure 5: SEM images of (a) neat Ni foam, (b)-(e) graphene grown on Ni foam with CH_4 introduced for 3 min, 5 min, 10 min and 20 min respectively.

The curves of weight loss versus temperature of materials studied are plotted in Figure 6 at the rate of $20\text{ }^\circ\text{C}/\text{min}$ under the nitrogen atmosphere. As shown in the Figure 6(a), the addition of GF obviously improves the thermal stability in comparison with PDMS and GS/PDMS composite. Take $T_{25\%}$ (temperature at 25% weight loss) for an example, it is increased $67\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$ in contrast with PDMS and GS/PDMS composite. Adding 6 wt% CB further increases the $T_{25\%}$ about $50\text{ }^\circ\text{C}$ compared with 0.5 wt% GF/PDMS composite in Figure 6(b).

The weight loss is mainly caused by the molecular chain interruption with the ascending temperature, forming volatiles to escape the surface of sample and evaporating, leading to the polymer decomposition [14, 15]. Filling of GF, GS or CB could hinder the movement of volatiles to enhance the thermal stability of composites [16-18]. In preparation of GS/PDMS composite, GSs tend to form agglomeration which decreases the specific surface area. While the shape and dimension of GF is fixed without the problem of agglomeration to more effectively prevent the movement and escaping of volatiles, showing better thermal stability. Similarly, the filling of CB act as barriers to volatiles make a further improvement in the thermal stability.

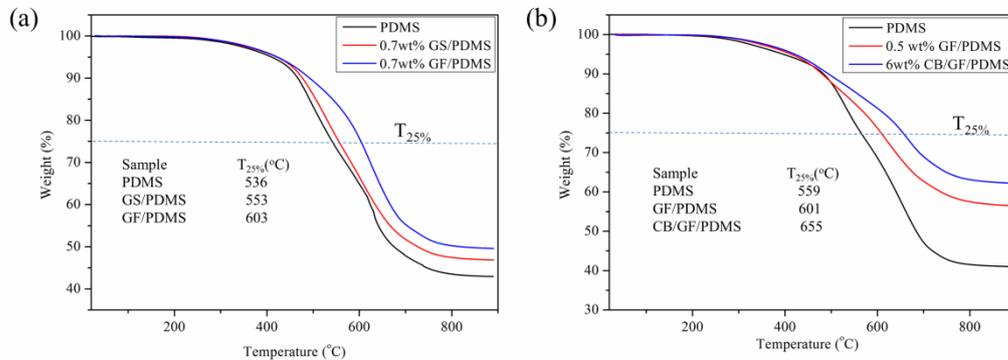


Figure 6: TGA a curves of the materials studied.

The coefficient of thermal expansion (CTE) from 30 to 150 °C are listed in Table 1. It can be found that the CTE of GF/PDMS composite is $80\text{-}137 \times 10^{-6}/\text{K}$ at 30-150 °C, which is apparently lower than that of PDMS and GS/PDMS composite at any the same temperature. Due to the negative CTE and extremely stiffness of graphene, GF and GS may confine the chain movement of PDMS, giving rise to lower CTE. On account of the interconnected and hollow structure of GF, it may more effectively hold back the thermal expansion of PDMS compared with GS.

Temperature(°C)	30	50	70	90	110	130	150
CTE($10^{-6}/\text{K}$)							
PDMS	285	289	288	280	277	275	271
0.7wt%GS/PDMS	125	160	183	194	203	210	217
0.7wt%GF/PDMS	80	84	88	105	123	131	137

Table 1: Variation of coefficient of thermal expansion with temperature

4 CONCLUSIONS

A series of graphene foam (GF) filled polymer composites are prepared such as GF/PDMS composites with different weight fraction of GF, CB/GF/PDMS composite at 6wt% of CB. The GS/PDMS composite and pure PDMS are also manufactured for comparison. In this work, their microstructures and thermal properties are investigated. It is found that the thermal conductivity of 0.7 wt% GF/PDMS composite is 0.56 Wm⁻¹K⁻¹, 200%, 40% and 20% superior to PDMS, 0.5 wt% GF/PDMS and 0.7 wt% GS/PDMS composites. This result proves the effectiveness of interconnected and integral network of GF on the thermal transportation inside the composite. Furthermore, the thermal conductivity was increased 38% with the addition of CB at 6 wt% compared with 0.5 wt% GF/PDMS composite. Besides, the GF endows the composites with better thermal stability and dimensional stability in comparison with PDMS and GS/PDMS composite, and the filling of CB can make a further improvement.

In summary, aforementioned results indicate that the GF based polymer composite is promising applied in thermal engineering management like phase change materials, electronic devices, etc. Besides, the addition of carbon blacks can further improve the thermal properties of composites.

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REFERENCES

- [1] C. Zweben, Advances in photonics thermal management and packaging materials. Integrated Optoelectronic Devices 2008. *International Society for Optics and Photonics*, 2008.
- [2] R. Prasher, Thermal interface materials: historical perspective, status, and future directions. *Proceedings of the IEEE*, **94**, 1571-1586, 2006.
- [3] S. Ghosh, I. Calizo, D. Teweldebrhan, E.P. Pokatilov, D.L. Nika, A.A. Balandin, et al., Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Applied Physics Letters*, **92**, 151911, 2008.
- [4] K.M.F. Shahil, A.A. Balandin, Thermal properties of graphene and multilayer graphene: Applications in thermal interface materials. *Solid State Communications*, **152**, 1331-40, 2012.
- [5] M.T. Pettes, H.X. Ji, R.S. Ruoff, Shi L. Thermal transport in three-dimensional foam architectures of few-layer graphene and ultrathin graphite. *Nano Letters*, **12**, 2959-64 2012.
- [6] Z.P. Chen, W.C. Ren, L. Gao, B. Liu, S. Pei, H.M. Cheng, Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nature Materials*, **10**, 424-428, 2011.
- [7] H.X. Ji, D.P. Sellan, M.T. Pettes, X. Kong, J. Ji, L. Shi, et al., Enhanced thermal conductivity of phase change materials with ultrathin-graphite foams for thermal energy storage. *Energy & Environmental Science*, **7**, 1185, 2014.
- [8] J. Jia, X. Sun, X. Lin, X. Shen, Y.W. Mai, J.K. Kim, Exceptional electrical conductivity and fracture resistance of 3D interconnected graphene foam/epoxy composites. *ACS Nano*, **8**, 5774-5783, 2014.
- [9] X.F. Zhang, K.K. Yeung, Z.L. Gao, J.K. Li, H.Y. Sun, H.S. Xu, et al., Exceptional thermal interface properties of a three-dimensional graphene foam. *Carbon*, **66**, 201-209, 2014.
- [10] X. Chen, Y. Lu, X. Zhang, F. Zhao, The thermal and mechanical properties of graphite

- foam/epoxy resin composites. *Materials & Design*, **40**, 497-501, 2012.
- [11] S.J. Chae, F. Günes, K.K. Kim, E.S. Kim, G.H. Han, S.M. Kim, et al., Synthesis of large-area graphene layers on poly-nickel substrate by chemical vapor deposition: wrinkle formation. *Advanced Materials*, **21**, 2328-2333, 2009.
- [12] J.H. Yu, X.Y. Huang, C. Wu, P.K. Jiang. Permittivity, thermal conductivity and thermal stability of poly(vinylidene fluoride)/graphene nanocomposites. *IEEE Transactions on Dielectrics and Electrical Insulation*, **18**, 478-484, 2011.
- [13] A.A. Balandin. Thermal properties of graphene and nanostructured carbon materials. *Nature Materials*, **10**, 569-581, 2011.
- [14] J.Y. Lee, Y. Liao, R. Nagahata, S. Horiuchi, Effect of metal nanoparticles on thermal stabilization of polymer/metal nanocomposites prepared by a one-step dry process. *Polymer*, **47**, 7970-7979, 2006.
- [15] S. Kim, D. Kavitha, Identification of pyrolysis reaction model of linear low density polyethylene (LLDPE). *Chemistry Letters*, **35**, 446-447, 2006.
- [16] W.G. Jeffrey, L.J. Catheryn, B.M. Alexander, H. Richard, Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites. *Chemistry of Materials*, **12**, 1866-1873, 2000.
- [17] H.L. Qin, S.M. Zhang, C.G. Zhao, M. Feng, M.S. Yang, Z.J. Shu, et al., Thermal stability and flammability of polypropylene/montmorillonite composites. *Polymer Degradation and Stability*, **85**, 807-813, 2004.
- [18] Y. Cao, J. Feng, P. Wu, Preparation of organically dispersible graphene nanosheet powders through a lyophilization method and their poly(lactic acid) composites. *Carbon*, **48**, 3834-3839, 2010.