In situ formation of a cellular graphene framework in thermoplastic composites leading to superior thermal conductivity†

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Based on the fast growth of the device performance, there has been an increasing demand for handling the issue of thermal management in electronic equipments. Therefore, it is of great significance to improve the thermal conductivity of thermoplastics, which are commonly used in electronic components. However, the difficulty of graphene dispersion and strong interfacial phonon scattering restrict the heat dissipation performance of graphene/thermoplastic composites, especially in the case of polypropylene (PP) or polyethylene (PE). Here, we propose a single-step and versatile approach to fabricate graphene/thermoplastic composites with a remarkable thermal conductivity enhancement. The composites were prepared by coating graphene on polymer powder first, followed by hot pressing. As a result, an interconnected graphene framework can be developed in the thermoplastic matrix, leading to significant heat transfer enhancement of the composites. At a 10 wt% graphene content, the thermal conductivity reaches 1.84, 1.53, 1.43, and 1.47 W m⁻¹ K⁻¹ for PE, PP, PVA (poly(vinyl alcohol)), and PVDF (poly(vinylidene fluoride)) composites, respectively. Our finding provides a path to develop a variety of highly thermally conductive thermoplastic composites for use in heat dissipation and other thermal applications.

Introduction

The evolution of semiconductor manufacturing technology in recent decades has led to higher levels of integration and miniaturization of electronic components. However, accompanying the rapid improvement of the performance of electronic devices, the removal of excess or waste heat is becoming an increasingly critical issue.¹,² Thus, there has been a growing demand for the development of heat dissipation materials for use in electrical, electronic and energy industries.³ Polymers have been widely utilized as component parts in electronic equipments and integrated circuit packaging. Unfortunately, the thermal conductivity of conventional polymers is lower than 0.5 W m⁻¹ K⁻¹, which restricts their applications in high-power and high-heat-flux electronic devices.⁴–⁶ Therefore, various nanomaterials have been used as fillers such as silver or copper nanowires, boron nitride nanosheets, carbon nanotube, and graphene, to develop polymer-based composites with improved thermal conductivity.⁷–¹³

Graphene, a monolayer of sp²-bonded carbon atoms arranged in a two-dimensional honeycomb lattice, has received significant attention in both academia and industry.²,¹⁴–¹⁶ Owing to its excellent thermal, mechanical, and electrical properties, graphene exhibited significant potential to be incorporated into polymer matrices for the development of high performance polymer composites.¹⁷–¹⁹ To obtain desired thermal properties of the composites, a key factor is to accomplish homogeneous dispersion of graphene with a fine interface in the polymer matrix.²⁰ However, the ease of graphene aggregation in polymers is a fundamental issue, which is attributed to the strong π–π interaction between graphene sheets. Moreover, the poor interface between graphene and polymers based on weak van der Waals interaction leads to additional phonon scattering, thus degrading the thermal properties of the resulting composites.²¹,²² Although the chemical functionalization of graphene has been commonly employed to overcome this
problem,\textsuperscript{14} it remains a particular challenge to achieve good dispersion of graphene in nonpolar polyolefins, like polypropylene (PP) and polyethylene (PE). This is due to the low interaction energy and large polarity difference between graphene and PP/PE.\textsuperscript{20,23–25} So far, only a few studies have been done for investigating the thermal conductivity enhancement (TCE) of graphene/polyolefin composites, but the results are still not satisfactory.\textsuperscript{14} TCE is defined as $(\kappa - \kappa_m)/\kappa$, where $\kappa$ and $\kappa_m$ are the thermal conductivity of the composite and the matrix, respectively. Song et al. prepared a PP composite with 5 wt% graphene loading showing a TCE of 97% ($\kappa: 0.40$ W m$^{-1}$ K$^{-1}$) by a two-step process: first coating graphene with PP latex and then melt blending the coated graphene with the PP matrix.\textsuperscript{26} Kalaitzidou et al. utilized a melt-mixing method to fabricate a graphene/PP composite with a TCE of 380% ($\kappa: 1.20$ W m$^{-1}$ K$^{-1}$) at a high filler content of $\approx 43$ wt%.\textsuperscript{27} In consequence, the development of other processes is necessary in order to further improve the thermal conductivity of graphene/polyolefin composites.

The creation of a three-dimensional (3D) graphene framework in nonpolar polyolefins represents a potential solution for the issue of the difficulty of graphene dispersion.\textsuperscript{28} In general, 3D graphene monoliths can be developed by using self-assembly techniques, such as hydro-thermal or sol-gel methods, followed by freeze-drying treatment.\textsuperscript{29,30} Alternatively, 3D graphene can be obtained by growth on Ni foams using chemical vapor deposition, followed by etching of Ni.\textsuperscript{31} To date, a variety of 3D graphene monoliths (sponges, foams, and aerogels) have been incorporated into polymer matrices, to obtain composites with enhanced physical properties.\textsuperscript{32–39} However, in all the above-mentioned methods, 3D graphene was first prepared and then filled with the polymer to fabricate the resulting composite, leading to the fact that the process is complicated, time consuming, and difficult to scale up. Therefore, this shows a strong demand for a simple and versatile approach to fabricate 3D graphene/polyolefin composites with high thermal conductivity.

Herein, we propose a simple and scalable approach to prepare hot-pressed PP composites embedded with a cellular graphene framework by one-step fabrication, which is time and cost-efficient as compared to conventional two-step processes. At the same graphene content, the thermal conductivity of PP composites with the formation of an interconnected graphene framework is twice higher than those of melt-blended samples with randomly distributed graphene.\textsuperscript{22} In addition, this concept was successfully applied to other thermoplastic systems like polyethylene (PE), poly(vinyl alcohol) (PVA), and poly(vinylidene fluoride) (PVDF). Under optimized hot-pressing conditions, the TCE of thermoplastic composites is in the range of 500–670% at a 10 wt% graphene content, demonstrating the feasibility and universality of our proposed method.

**Experimental**

**Materials**

Graphene nanoplatelets (GNPs) prepared by intercalation and exfoliation of graphite were supplied by Ningbo Morsh Technology Co., Ltd., China. PP and PE powders were purchased from Samsung, Korea. PVA and PVDF powders were obtained from Anhui Wanwei Co. Ltd. and 3F Co. Ltd. (China), respectively. Dehydrated ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the materials were used without further purification.

**Sample preparation**

Before mixing with polymer powders, a calculated amount of GNPs was washed with dehydrated ethanol to remove the adsorbed moisture. GNPs and PP were sonicated in ethanol for 5 min, separately, and then they were mixed together under magnetic stirring for 40 min. The ethanol was removed by filtration to obtain GNP/PP powder, followed by drying in an oven at 80 °C for 2 h. A stainless steel mold with 12.7 mm in diameter was used to contain the GNP/PP powder, and then GNP/PP composites were fabricated by uniaxial hot pressing for 10 min under 10 MPa at various temperatures. The thickness of the samples after hot pressing is around 1.30 mm, which nicely fit the holder of a laser flash apparatus (LFA). And the value of thermal conductivity $\kappa$ was calculated by the following equation: $\kappa = \alpha \times C_p \times \rho$, where $\alpha$ is the thermal diffusivity, $C_p$ is the specific heat capacity, and $\rho$ is the measured density of the samples. $C_p$ is theoretically evaluated from the ratio of GNPs (0.72 J kg$^{-1}$ K$^{-1}$) in the polymer matrix (PP: 1.93 J kg$^{-1}$ K$^{-1}$), which is in agreement with experimental values (Fig. S1†) and the density of the GNP/PP composite is in the range of 0.88–0.93 g cm$^{-3}$ (880–930 kg m$^{-3}$).\textsuperscript{40,41}

**Characterization**

The lateral size and thickness of GNPs were determined by using an optical microscope (OM) (Leica, Germany) and atomic force microscope (AFM) (Dimension 3100, Veeco, USA), respectively. The quality of GNPs was investigated by Raman Spectroscopy (Renishaw plc, Wotton-under-edge, UK) with a laser wavelength of 532 nm, as well as X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD, Kratos Analytical, Japan). The microstructure of GNPs was studied by transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan). The morphology of GNP and GNP/PP composites was observed by field emission scanning electron microscopy (FE-SEM) (Quanta FEG 250, FEI, USA). Thermogravimetric analysis (TGA) was performed using a PYRIS Diamond$^{TM}$ system (PerkinElmer, USA) to confirm the weight percent of GNPs in the polymer matrix. The measurements were carried out under nitrogen in the range from 30 °C to 800 °C at the heating rate of 20 ºC min$^{-1}$. The $C_p$ and melting point of the polymers were evaluated by using a differential scanning calorimeter (DSC) (PYRIS Diamond$^{TM}$, PerkinElmer, USA). The thermal diffusivity of the composites was determined by using a LFA 457 MicroFlash$^{®}$ system (NETZSCH, Germany). The IR-photos were captured by using an infrared camera (Fluke, Ti400, U.S.A.).

**Results and discussion**

Scheme 1 is the schematic diagram of the fabrication process of GNP/PP composites, and also illustrates the concept of this
study, in which a cellular graphene framework can be in situ developed and embedded in polymer matrices during hot pressing. Our method is simple, feasible, easy to scale up, and compatible with the polymer manufacturing process in the industry. In the first step of the experiment, GNPs were deposited on PP micropowder by simply mixing them in ethanol with magnetic stirring. GNPs preferred to be physically attached to the surface of the microparticles due to their relatively strong adhesive interaction, based on the high aspect ratio (>550) and ultrathin nature of GNPs. After drying, the obtained black powder was further hot pressed to form a GNP/PP composite with a characteristic microstructure. The detailed characterization of GNPs can be found in Fig. S2–S4,† in which the average lateral size and the thickness of GNPs are 5.4 ± 0.3 μm and 10.6 ± 0.3 nm, respectively. In addition, the higher carbon content (61.8%) and \( I_2D/I_G \) ratio (0.58) derived from XPS and Raman spectra (Fig. S4†), respectively, indicate fewer defects in GNPs than in reduced graphene oxide.42,43

Fig. 1a and b display the SEM images of the PP powder before and after coating with GNPs (10 wt% loading), respectively. The pristine PP powder presents a granular shape with an irregular contour, and the particle size is in the range of 100–150 μm. After deposition, we found that the surface of the powder particles is covered by a thin layer of GNPs (see Fig. 1c), and the particle size mostly remains the same. A black piece of the GNP/PP composite detached from the mold was obtained after hot pressing. In the cross-sectional view of the composite in Fig. 1d, it can be seen that the PP powder has been partially melted and merged together because of high pressure and high temperature. As the sample surface was carefully polished, the evidence of the formation of a cellular graphene framework within the polymer matrix is revealed as shown in Fig. 1e and f.44,45 The boundary of the PP granules is surrounded by trim strips composed of GNPs, which are connected together to form a continuous 3D framework throughout the entire composite. Note that the PP powder particles were not fully covered by GNPs, resulting in the preservation of the mechanical strength of the composite. The thermal properties of GNP/PP composites obtained under various fabrication conditions were systematically investigated.

The dependence of thermal diffusivity (a) and thermal conductivity (c) on GNP loading and hot-pressing temperature is presented in Fig. 2a–c, respectively. In Fig. 2a and b both the thermal diffusivity and conductivity of the samples show a linear increase as more GNPs were incorporated, despite different hot-pressing temperatures. Fig. 2c exhibits the thermal conductivity as a function of hot-pressing temperature (Fig. S5a† thermal diffusivity). Interestingly, we noticed that
160 °C is an optimized temperature to achieve maximum thermal conductivity of the samples, even though GNP content varies in a wide range. With the filler content of 2 and 10 wt%, the thermal diffusivity of the composites increases from 0.13 (neat PP) to 0.31 and 0.92 mm$^2$ s$^{-1}$, respectively, with about 240 and 710% improvement. And the thermal conductivity of a 12 wt% GNP-loaded sample can reach 1.63 W m$^{-1}$ K$^{-1}$. We found that this temperature (160 °C) is just the melting point of PP powder used in our study (see the DSC curve of PP in Fig. S6†). It is speculated that, when the pressing temperature is lower than 160 °C, voids and pores might remain in the composite because PP is partially melted, leading to poor thermal conductivity. In contrast, when the temperature is too high, the decrease in the thermal conductivity is due to agglomeration and precipitation of GNPs because of the low viscosity of fully melted PP. In order to discuss the effect of PP particle size on the thermal conductivity of the resulting composites, PP particles with the sizes of 40–80, 100–150, and 200–250 μm were mixed with 10 wt% GNPs, separately, as the starting materials for further hot pressing. The SEM images of the GNP-coated PP powders and GNP/PP composites fabricated with different particle sizes are presented in Fig. S7.† As shown in Fig. 2d, again, good thermal conductivity can be obtained when the samples were prepared at 160 °C (Fig. S5b† thermal diffusivity). In addition, the composites made using 100–150 μm PP particles exhibit a higher thermal conductivity (max: 1.53 W m$^{-1}$ K$^{-1}$) than others. For the case of small PP particles (40–80 μm), the large surface curvature is unfavorable for the surface attachment of GNPs, because our GNPs have a lateral size of about 5.5 μm and are not very flexible due to the multilayer nature. In contrast, the graphene framework would become discontinuous owing to the large deformation of PP particles with the size of 200–250 μm during hot pressing. Fig. 2e displays the typical TGA curves of neat PP and a 10 wt% GNP-loaded composite respectively. The addition of GNPs results in shift toward higher temperatures, suggesting an improvement of the thermal stability of GNP/PP composites as compared to that of neat PP. And the difference between two samples indicates that the loss of GNPs (~0.3 wt%) is negligible during hot pressing.

The comparison of our result with the previous literature using various nanocarbons as fillers for PP-based composites is exhibited in Fig. 3a. Based on of the same filler content of 5 wt%, it can be seen that the thermal conductivity of our sample is 0.82 W m$^{-1}$ K$^{-1}$ (TCE: 272%) is twice as good as the best results obtained using melt-blending processes. 22,27,46–49 This can be attributed to the fact that the heat flow through an interconnected, thermally percolating framework of GNPs is more efficient than that in the case of a uniform distribution of nanocarbon fillers in the PP matrix, as illustrated in Fig. 3b. Moreover, at the same loading of 5 wt%, the thermal conductivity of our GNP/PP sample is almost double than that of the PP composite embedded with a 3D graphite network, indicating the benefit of the use of graphene fillers. 22 As a result, our proposed process enables us to overcome the issue of fabricating highly thermally conductive PP composites, including the difficulty of graphene dispersion and strong phonon scattering at the graphene/PP interface.

The concept of in situ formation of a cellular graphene framework in polyolefin composites by hot pressing is not only beneficial to the thermal conductivity of PP matrices, but also available to other thermoplastic systems such as PE, PVA, and PVDF. As revealed in Fig. 4a, the thermal conductivity of GNP/thermoplastic composites at 10 wt% filler loading shows the dependence on the pressing temperature (Fig. S8† thermal
diffusivity). Again, we found that the thermal conductivity of the samples reaches a maximum as the hot-pressing temperature is close to the melting point of the thermoplastic matrix (see DSC curves in Fig. S6†). Under the optimized temperature, the thermal conductivity of PE, PVA, and PVDF-based composites reaches 1.84, 1.43, and 1.47 W m\(^{-1}\) K\(^{-1}\), respectively.

The dependence of the thermal diffusivity of the samples on the environmental temperature is presented in Fig. 4b. The decrease in the thermal diffusivity can be attributed to the enhanced phonon scattering effect with the increase of the temperature.\(^{29}\) In Fig. 4c, the TCE of the thermoplastic composites at 10 wt% GNP loading is evaluated to be 457 (PE), 595 (PP), 580 (PVA), and 673% (PVDF), and compared them to those of neat thermoplastics. The results demonstrate that our method can be applied to considerably improve the thermal conductivity of common thermoplastics. For instance, an ultrahigh molecular-weight PE composite with 10 wt% GNP loading was prepared by Gu et al. using ball milling followed by hot pressing.\(^{31}\) But, the TCE of Gu’s sample is just 51% of that of the GNP/PE composite we made with the same filler content. Consequently, compared to other thermoplastic composites filled with graphene or white graphene (hexagonal boron nitride), our samples can achieve a higher TCE at a relatively low filler content because of the formation of effective conduction paths based on the 3D graphene framework (see Table S1†). Fig. 4d presents the capability of large-scale production of GNP/thermoplastic composites with the size of 10 × 10 cm based on our proposed process.

A test was performed to verify the increase of the heat dissipation performance of 10 wt% GNP-loaded composites and neat thermoplastics, which were set on the same hot plate and their surface temperature was recorded by using a calibrated infrared (IR) camera. The size of each circular sample is 12.7 mm in diameter and 1.3 mm in thickness. All the samples were initially kept at room temperature and then heated simultaneously. The evolution of the surface temperature at the intervals of 0, 20 and 80 s was captured by using the IR camera, as shown in Fig. 5a. It can be seen that the surface temperature of the composites is obviously higher than that of neat thermoplastic when the heating time is longer than 20 s. Fig. 5b presents that the temperature rise of the composites is much faster than that of neat thermoplastics at the initial heating stage. After 80 s heating, the surface temperature difference at

Conclusions

In summary, we report a time- and cost-efficient approach to fabricate graphene/thermoplastic composites with considerably improved thermal conductivity. Our concept is to uniformly coat GNP on the surface of polymer powder by mixing in ethanol first, followed by drying and then hot pressing. Different from the samples made by melt-blending or solution-mixing processes, a feature of a cellular graphene framework embedded in thermoplastic matrices can be observed in our samples. The in situ formation of the thermally percolating framework of GNP during hot pressing enables significant enhancement of the thermal conductivity of the resulting composites. At 10 wt% loading of GNP, the thermal conductivity of PE, PP, PVA, and PVDF-based composites reaches 1.84, 1.53, 1.43, and 1.47 W m\(^{-1}\) K\(^{-1}\), respectively. And the corresponding TCE is 457 (PE), 595 (PP), 580 (PVA), and 673% (PVDF). Moreover, we found that the hot-pressing temperature shows a pronounced dependence on the melting point of the used thermoplastics for achieving a maximum thermal conductivity. Based on this observation, other thermoplastic composites with a high thermal conductivity at a relatively low graphene content can be fabricated for different thermal applications.

Acknowledgements

The authors are grateful for the financial support by the National Natural Science Foundation of China (51573201, 51501209 and 201675165), Program for International S&T Cooperation Projects of the Ministry of Science and Technology of China (2015DFA50760), Public Welfare Project of Zhejiang Province (2016C31026), Science and Technology Major Project of Ningbo (2016B10038 and 2016S1002), and International S&T Cooperation Program of Ningbo (2015D10003). The authors also thank the Chinese Academy of Science for Hundred Talents Program, Chinese Central Government for Thousand Young Talents Program, 3315 Program of Ningbo, and The Key Technology of Nuclear Energy (CAS Interdisciplinary Innovation Team, 2014).

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Published on 02 March 2017. Downloaded by Ningbo Institute of Materials Technology and Engineering, CAS on 20/04/2017 07:46:44.


