



Non-monotonously tuning thermal conductivity of graphite-nanosheets/paraffin composite by ultrasonic exfoliation



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ABSTRACT

Organic phase change materials (PCMs) have drawn continuous attentions over time due to their large latent heat and constant-temperature solid-liquid phase transition with promising applications in thermal energy storage. Nevertheless, they suffer from the relatively low intrinsic thermal conductivity. Filling the PCMs with graphite-nanosheets (GNs) by ultrasonic exfoliating could alleviate this problem, and GNs with longer ultrasonic exfoliation time is reported to possess larger effective thermal conductivity (ETC) monotonously. In this paper, we discover a non-monotonous variation of ETC for the first time, when enhancing the ETC of paraffin with ultrasonic exfoliated GNs. The mechanism behind this phenomenon is explained by the variation of GNs morphologies over time in the paraffin. Experimental results reveal that longer exfoliation time can increase the aspect ratio and ETC, but over a critical time, the bending stiffness of GNs decrease and the particles tend to be folded with increased interfacial thermal resistance and decreased ETC. The ETC as a function of ultrasonic time shows an obvious peak value at ~ 2 min, and the ETC could be increased from 0.3 to 3.0 W/(m·K) at GNs loading of 4 wt% with negligible effect on the phase change characteristics. In addition, the GNs/paraffin composite exhibits the quick thermal response and longer working time. The present non-monotonous discovery reveals the underlying mechanism and provides suggestions on the improvement of ultrasonic exfoliation process.

1. Introduction

Organic phase change materials (PCMs), such as paraffin, fatty acids and polyethylene glycols, have drawn continuous attentions over time due to their large latent heat and wide range of melting/crystallization temperature of solid-liquid phase transitions with promising applications in thermal energy storage, electronic memory, and data storage [1–9]. Among these PCMs, paraffin is outstanding due to its appropriate melting point, large latent heat, high thermal stability, and low cost. However, the low thermal conductivity ($\kappa = \sim 0.4$ W/m·K) is the major drawback of paraffin in spite of many desirable properties, leading to low heat storage rates and limited application [10,11].

Filling the PCMs with high thermal conductivity particles is an effective scheme to enhance the effective thermal conductivity (ETC) of the composite and alleviate the problem. Traditional high thermal conductivity materials such as copper fins [12] and metal foams [13,14] offer increased ETC but are limited by manufacturing constraints and intrinsic thermal conductivity, and the foam structure has been proved to suppress the natural convection within the PCMs during the phase change process. Consequently, researchers have turned their

attentions to high thermal conductivity carbon-based nanoparticles, such as carbon nanotubes [15,16], graphite-nanosheets (GNs) [17,18], and graphene [19,20]. Due to the low cost and relatively easy preparation, the GNs have been widely investigated as thermal enhancer in PCMs. Several groups proposed the liquid-phase ultrasonic exfoliation method to exfoliate expanded graphite (EG) into nanosheets with a thickness at nanoscale (~ 5 – 10 nm) [21–24]. Successful exfoliation requires to overcome the Van der Waals force between the adjacent layers of graphite. One effective and straightforward method to reduce the strength of Van der Waals attractions is liquid immersion. EG can be successfully exfoliated in liquid environments by exploiting ultrasound to extract individual layers [25]. During ultrasonication, the micrometer-sized bubbles or voids will be generated and burst in liquids due to pressure fluctuations, which give rise to shear forces to exfoliate the EG. After exfoliation, the inter-sheet attractive forces need to be overcome by the interaction between the GNs and the solvents. Solvents with surface tension of about 40 mJ/m² are appropriate since they minimize the interfacial tension between solvent and graphite, i.e. the force that minimizes the area of the surfaces in contact [25]. If the surface tension of the solvent is high, the particles tend to adhere to

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each other and aggregate together. Unfortunately, the majority of solvents with surface tension of 40 mJ/m^2 such as N-Methyl-2-pyrrolidone (NMP $\sim 40 \text{ mJ/m}^2$), N,N-dimethylformamide (DMF $\sim 37.1 \text{ mJ/m}^2$), and ortho-dichlorobenzene (o-DCB $\sim 37 \text{ mJ/m}^2$) are harmful to the human [17,25]. Thus an appropriate solvent is also important for the exfoliation of EG. On the other hand, the effect of the ultrasonic exfoliation time on the ETC of composite is still unclear. For instance, Haddon et al. [26] demonstrated that long-time exfoliation generates thinner GNs with larger aspect ratio (the ratio of in-plane size to out-of-plane size) and a higher ETC of the composite. However, Warzoha and Fleischer [27] came to an opposite conclusion. They claimed that the thinner GNs possess a lower bending stiffness and tend to be folded in the matrix. Such folding will give rise to a larger number of interfaces with more phonon boundary scattering, leading to larger interfacial thermal resistance and lower ETC. Similarly, Fang et al. [17] also claimed that smaller nanosheets possess higher specific surface area, phonons are easily scattered at the filler/PCM interfaces, resulting in a lower ETC. We feel confused for these diametrical conclusions, thus a further study of the ETC enhancement effect on exfoliation time is significantly needed.

In this paper, we used paraffin to exfoliate the graphite into nanosheets to prepare GNs/paraffin composite, including thermal expansion step, magnetic stirring step, and ultrasonication step. Different experimental specimens were prepared by controlling the exfoliation time from 0 min to 30 min. The ETC of each specimen was measured and the trend was analyzed. The phase change characteristics and the thermal storage performance of the GNs/paraffin composite was also assessed experimentally.

2. Materials preparation and characterizations

2.1. Materials preparation

Fig. 1a shows the process of preparing GNs/paraffin composite, which consists of thermal expansion, magnetic stirring, and ultrasonic exfoliation. Firstly, the natural graphite powders (XFnano, INC) were immersed in acid solution (20 vol% HNO_3 and 80 vol% H_2SO_4) to weaken the bonds between graphite layers. Secondly, the acid treated graphite powders were put into a microwave oven with an overall power of 800 W for 40 s to produce expanded graphite (EG). Thirdly,

the EG was mixed with liquid paraffin ($\text{C}_{22}\text{H}_{46}$, RT44HC, Rubitherm) on a heating at 80°C and fully stirred for 10 h via a magnetic stirring system. After that, the mixed liquid composites were ultrasonically exfoliated in a water bath at 80°C , and the ultrasonic power was 650 W with frequency of 20–25 kHz. The paraffin not only acts as the matrix material, but also as the solvent in the ultrasonic exfoliation process to minimize the interfacial tension of the adjacent GNs layers, so as to avoid re-agglomeration. Fig. 1b shows schematic of the ultrasonic exfoliation system. We use a cell disrupter to produce ultrasonic wave to form small and energetic bubbles in the liquid medium. The bubbles burst instantaneously and release a huge amount of energy to exfoliate the EG. In order to confirm that the paraffin is able to exfoliate the EG, we measured the surface tension of the paraffin by Drop Shape Analyzer (DSA25, KRUSS). Results showed that the surface tension of paraffin is 34 mJ/m^2 , approaching 40 mJ/m^2 , indicating that paraffin can successfully exfoliate the EG into nanosheets. The ultrasonic exfoliation process ranges from 0 to 30 min to obtain GNs with different particle sizes. Finally, the prepared specimens were dried under vacuum at 80°C to remove the bubbles.

2.2. Materials characterizations

Scanning electron microscope (SEM, Quanta 200, FEI) was performed to delineate the morphology of the GNs within paraffin at different mass loadings. All the specimens were pre-treated using the approaches described by Warzoha et al. [27]. Briefly, a brittle fracture was performed on each of the specimens in order to avoid significant displacement of GNs within the paraffin. Frictional forces from conventional cutting procedures could create a high temperature which would melt the paraffin in the vicinity of the cut and alter the paraffin distribution. Note that the GNs are coated in paraffin, thus their exact geometries cannot be directly extrapolated from these images. To obtain the diameter and thickness of the GNs, a phase separation process was conducted to avoid the paraffin masking the morphology of the GNs. Toluene solvent (Sinopharm Chemical Reagents Company, China) was adopted to dissolve the paraffin that covered on the surface of GNs, followed by the centrifugal treatment (8000 r/min, 5min), ultrasonic dispersion, filtration, and drying, and then the GNs powders were obtained. Atomic force microscopic (AFM, SPM9700, Shimadzu) and SEM tests were conducted to acquire the thickness and diameter of the GNs,

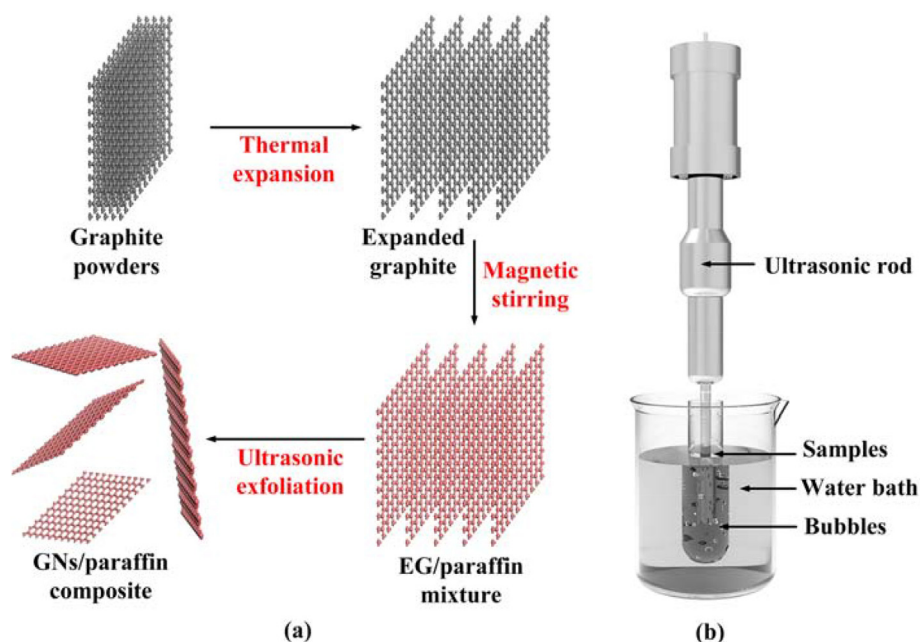


Fig. 1. (a) Process of preparing GNs/paraffin composite PCMs. (b) Schematic of ultrasonic exfoliation system.

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