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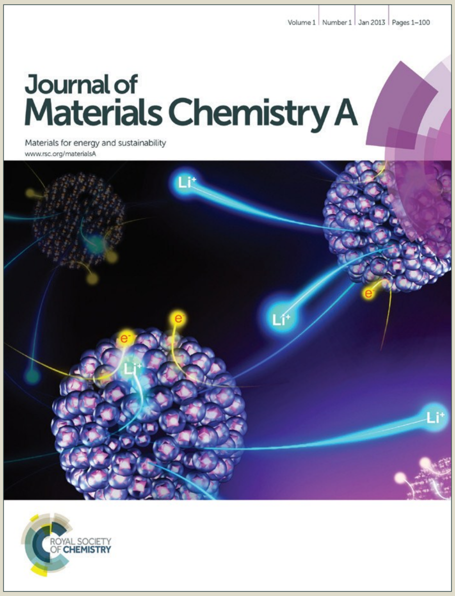

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Preparation and properties of graphene oxide-modified Poly(melamine-formaldehyde) microcapsules containing phase change materials n-dodecanol for thermal energy storage

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Abstract: A novel kind of graphene oxide-modified poly(melamine-formaldehyde) (PMF) microcapsules containing phase change materials (microPCMs) n-dodecanol was prepared by in-situ polymerization. Fourier-transform infrared spectroscopy (FTIR) and X-ray diffractometer (XRD) were used to study the chemical structure of graphene oxide (GO) and microPCMs, respectively. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to investigate the morphology of GO and microPCMs, respectively. The thermal properties of microPCMs were studied by differential scanning calorimetry (DSC), thermal constant analyzer (TCA) and thermal cycling tests. The FTIR and XRD results indicate that the phase change material n-dodecanol is encapsulated in the GO/PMF composite shell, and there is no chemical reaction between them. The SEM results show that the prepared GO-modified PMF microPCMs are spherical particles with smooth surface. The DSC results indicate that the phase change temperature and latent heat of microPCMs with 1wt% of GO are 26.40 °C and 125.2J/g, respectively. The thermal conductivity of GO/microPCMs with 4wt% GO increases by 66.29%, compared with that of microPCMs without GO according to the TCA results. Moreover, the thermal cycling tests show that the prepared microPCMs possess a good thermal stability. The GO-modified PMF microPCMs are sure to have great potential application for thermal energy storage.

Keyword: Graphene oxide; microcapsules; phase change materials; n-dodecanol; thermal energy storage

Introduction

Microcapsules containing phase change materials (microPCMs) are applied to adjust temperature or store thermal energy. When phase changing occurs in the core of microPCMs, heat is absorbed or released.[1] Microencapsulation can prevent PCMs from being exposed to the external environment as well as solve the volume changing problem in solid-liquid phase transition, therefore microPCMs have drawn greater attention than traditional PCMs.[2]

The shell material of microcapsule can be organic or inorganic. Melamine-formaldehyde (MF) resin,[3,4] urea-formaldehyde (UF) resin,[5,6] polystyrene (PS),[7] Phenolic Resin,[8] polyurethane (PU),[9] SiO_2[10] were usually used as the shell materials for the microencapsulation of PCMs. Because of low price, easily controlled preparation, high compatibility and good thermal stability,[11] MF resin has particularly been selected for the protection of PCMs. However, MF resin as well as other polymer shell material has a low thermal conductivity and the application of microPCMs is limited.

Graphene is considered to have many important potential applications since it was found in 2004[12] for its outstanding thermal, electrical and mechanical properties.[13] For its excellent performance, graphene has been used as filler to fabricate graphene/polymer nanocomposites such as graphene/poly(vinyl alcohol),[14]graphene/nylon-6.[15] Chemical oxidation-reduction method is considered to be one of the most common methods in preparing exfoliated graphene sheet.[16] In this method, graphene oxide (GO) can be obtained by intense oxidation of graphite[17] and subsequently reduced to prepare graphene. It is well known that GO has several oxygen-containing functional groups such as epoxy, carbonyl, hydroxyl groups on its surface after oxidation.[18] These functional groups provide a compatibility between GO and polymer. GO/polymer composites have been fabricated such as GO/polystyrene,[19] GO/polypropylene,[20] GO/poly (vinyl alcohol)[21,22] and GO/nylon 11.[23]

Graphene has a high thermal conductivity up to 3080-5150 w m^{-1} K^{-1}.[24] The oxygen-containing functional groups make GO can be compatible well with MF prepolymer, which is aqueous system. In this work, GO/melamine resin composite has been prepared as the wall material of microcapsule mainly to improve the thermal conductivity of microPCMs. n-dodecanol is selected as the core material of microcapsule because of its suitable phase change temperature (about 25 °C) and relatively high phase change latent heat (about 200J/g).[25] In this study, the effect of GO contents on the thermal properties, morphology and chemical structure were investigated.

Experimental Section

Materials

Graphite powder was purchased from Nanjing XFNANO Materials Tech Co. Ltd.; $KMnO_4$ (99%), H_2SO_4 (98.3%), $NaNO_3$ (AR), formaldehyde aqueous solution (37 wt%), Melamine (AR) were all purchased from Shanghai Chemical Reagent Co. (China), n-dodecanol was supplied by Aladdin Industrial Inc.; Sodium styrene-maleic anhydride copolymer (SMA1000HNa, 40 wt% aqueous solution) was purchased from Sartomer Company (USA).

Preparation of graphene oxide (GO)

GO was synthesized according to a modified Hummers method [17] from graphite, and exfoliated to give a brown dispersion in distilled water after ultrasonication. Briefly, 46 ml of concentrated sulfuric acid (98 wt%) was added firstly into a 250 ml three-neck flask in an ice bath, followed by the addition of graphite (2g) and sodium nitrate (1g). After 30 min of stirring, potassium permanganate (6g) was slowly added to the solution and kept stirring for 2 hours. The suspended solution was then stirred at 35 °C for 30 min. Next, the flask was mixed with distilled water (92 ml) slowly and the temperature of reaction was elevated to 98 °C for 15min. After that, H_2O_2 (30%, 15 ml) was added to reduce residual Oxidant. Finally, the resulting suspension was centrifuged and washed with distilled water for several times until the solution became neutral and then dried in vacuum at room temperature.

Fabrication of GO-modified PMF microPCMs containing n-dodecanol

In a 250 ml three-neck flask, melamine (20g), formaldehyde aqueous solution (43g) and different amounts of GO water dispersion were mixed together and adjusted pH to 9. Then the mixture was stirred at 70 °C for 3 h to prepare 42 wt% of GO/MF prepolymer aqueous solution.

PCM n-dodecanol (25g) and 30 ml of distilled water were emulsified mechanically with different amounts of SMA1000HNa at a stirring rate of 4,500 rpm for 60 min. The n-dodecanol emulsion was adjusted pH to 4.

The GO/MF prepolymer solution was slowly added into the n-dodecanol emulsion to start an in situ polymerization at 70 °C with a stirring rate of 400 rpm. After all of the GO/MF prepolymer aqueous solution was added, it was continuously stirred for 180 min at 70 °C with a rate of 600 rpm. Then, the resultant microcapsules in the slurry were filtered, washed with 50 wt% ethanol–water solution of 50 °C for once and distilled water for twice, and then dried at 50 °C to obtain microcapsule power.

Characterization

The size and thickness of GO sheet were measured by Atomic force microscope (AFM, Park systems XE-100) in non-contact mode. The GO dispersions (0.01mg/ml) were spin-coated onto a freshly cleaved mica surface.

The chemical structures of the microPCMs, phase change material and GO were analyzed using Fourier transform infrared (FTIR) spectrometer (Bruker Vector 33, Germany) with the KBr sampling method.

The X-ray diffraction (XRD) patterns of the samples were carried out on X-ray diffractometer (Bruker D8 ADVANCE Germany, Cu Kα radiation).

The morphologies of the microPCMs were obtained by using a scanning electronic microscope (SEM, Zeiss EVO 18 Germany). The digital photos of microPCMs were taken by Canon EOS 70D.

The thermal storage properties of the microPCMs were measured by using differential scanning calorimeter (DSC, Netzsch 204F Germany) at a heating rate (2, 5 or 10 K/min) in the rang of 0-60 °C under nitrogen atmosphere. The phase change latent heat and phase change temperature of microPCMs were obtained from the analyzing results of DSC curves using Netzsch TA4.

The thermal conductivity of the microPCMs was measured using Thermal Constant Analyzer (Hot Disk AB Company TPS2500, Sweden). To prepare samples, 18g of microPCMs for each experiment were dispersed in two containers with a depth and a diameter of 10 and 40 mm, respectively. At least five measurements were performed for each sample to ensure the repeatability of the measurement results.

The method for estimating the content of PCM in the polymeric microcapsule was in dispute, recently. In the reports of most research groups, the content of PCM in the polymeric microcapsule was estimated according to the measured phase change latent heat from DSC thermogram, assuming that the phase change latent heat of PCM didn't change before and after encapsulation. However, Chaiyasat and Okubo et. al [26] reported that the content of PCM in the polymeric microcapsule should be estimated according to the TGA measurement results. In their report, the latent heat (J/g-PCM) was decreased by encapsulation and the decrease depended on the kind of polymer shells, based on the TGA analyzing results, assuming that the thermal stability of PCM didn't change before and after encapsulation in the polymeric capsules. In fact, the thermal stability of PCM might be increased after encapsulation into polymeric microcapsules. The onset mass loss temperature of microPCMs in the first stage attributing to the decomposition of PCM, increased after encapsulation according to our previous work [3], especially for microcapsules with crosslinked polymeric shell. So, we stuck to the first popular method to estimate the content of PCM in the polymeric microcapsule, by using the equation: PCM content(%) = $H_w/H_p \times 100\%$, where H_w is the phase change latent heat of microcapsules (J/g) and H_p is the phase change latent heat of PCM (n-dodecanol of 193.9 J/g).

The encapsulation efficiency of microcapsules can be calculated as the ratio of the measured PCM content in microPCMs to the theoretical value depending on the amount of PCM and MF prepolymer added in the system of fabrication.

Results and discussion

Structure and morphology of GO sheet

The prepared GO is highly hydrophilic and easy to be exfoliated into monolayer nanosheets in water via sonication because of the oxygen-containing functional groups on its surface. The GO dispersion has good stability with brown color as show in Fig.1A. The morphology of GO nanosheets is observed by AFM (Fig.1B and Fig.1C). The size of GO is in the range of 200 nm to 500nm according to the AFM image. And the GO nanosheets have the height of about 1nm, indicating that a fully exfoliation is achieved.

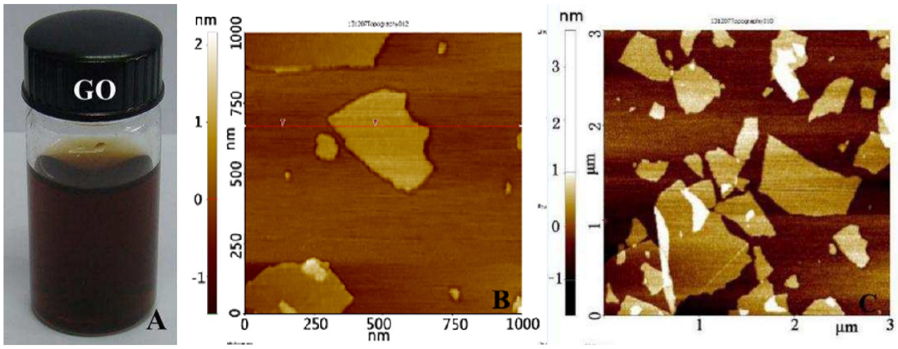


Fig.1 (A) Photograph of GO, (B and C) AFM image of GO

Generally, hydroxyl, epoxy and carboxyl groups are introduced onto the surface of GO via oxidation process.[2] FTIR spectrum of GO (Fig.2E) confirms the existence of these oxygen-containing functional groups. The broad band in the range of 3000–3600 cm^{-1} is caused by the stretching of hydroxyl groups. The peak at 1715 cm^{-1} are corresponding to the C=O bonds. The absorptions at 1405, 1221 and 1030 cm^{-1} are due to the absorption of C-O bonds of carboxyl, epoxy and hydroxyl groups, respectively. In addition, the strong peak at 1612 cm^{-1} is due to the remaining C=C bonds in GO.

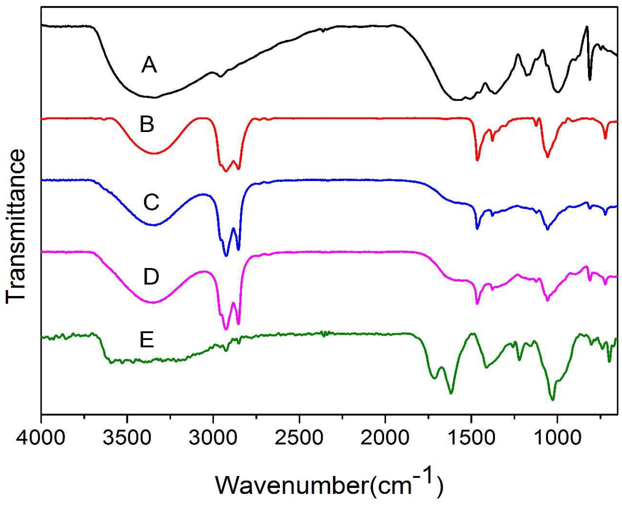


Fig.2 FTIR spectra of (A) poly(melamine formaldehyde) resin, (B) n-dodecanol, (C) microPCMs without GO, (D) GO/microPCMs and (E) GO.

Structure of microPCMs

The FTIR spectrum of MF resin is showed in Fig.2A. The strong and wide absorption peaks at approximately 3400 cm^{-1} of Fig.2A are attributed to the superposition of O–H and N–H stretching vibrations in MF resin. The weak peak at 1163 cm^{-1} of Fig.2A is corresponding to the C-O-C stretching vibrations and the peak at 995 cm^{-1} is attributed to C-O stretching vibrations of alcohol compounds owing to the existence of hydroxyl groups in MF resin. The sharp absorption peak at 810 cm^{-1} of Fig.2A is owing to the bending vibration of triazine ring, which is the characteristic peak of MF resin.

Fig.2B shows the FTIR curve of core material n-dodecanol. The strong and wide absorption peaks at approximately 3345 cm^{-1} in Fig.2B is assigned to O–H stretching vibrations of n-dodecanol. The strong peaks at 2926 cm^{-1} and 2844 cm^{-1} are associated with aliphatic C-H stretching vibrations of methyl and methylene groups respectively. In addition, the moderate strong peak at 1048 cm^{-1} is related to C–OH stretching vibration of primary alcohol.

The FTIR curves of microPCMs containing n-dodecanol without GO and with GO are showed in Fig.2C and Fig.2D. The characteristic peaks of aliphatic primary alcohol n-dodecanol at approximately 2926, 2844 and 1048 cm^{-1} can be observed in both of Fig.2C and Fig.2D, indicating that n-dodecanol has just been microcapsulated with no reaction between n-dodecanol and MF resin. The curve of Fig. 2C and D are nearly the same, confirming that the addition of GO have no influence to the chemical structure of microPCMs.

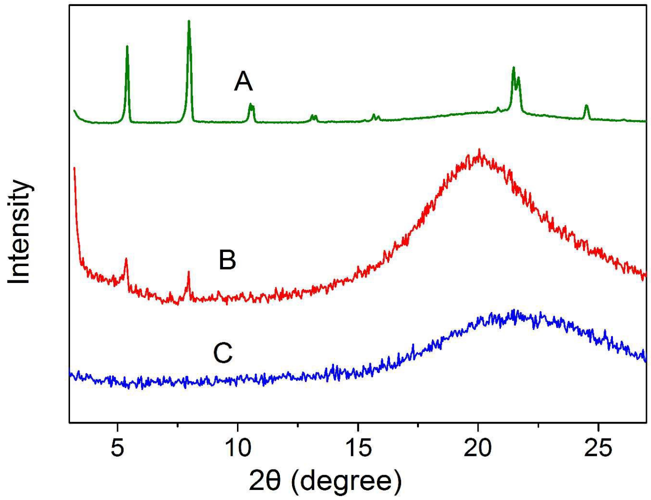


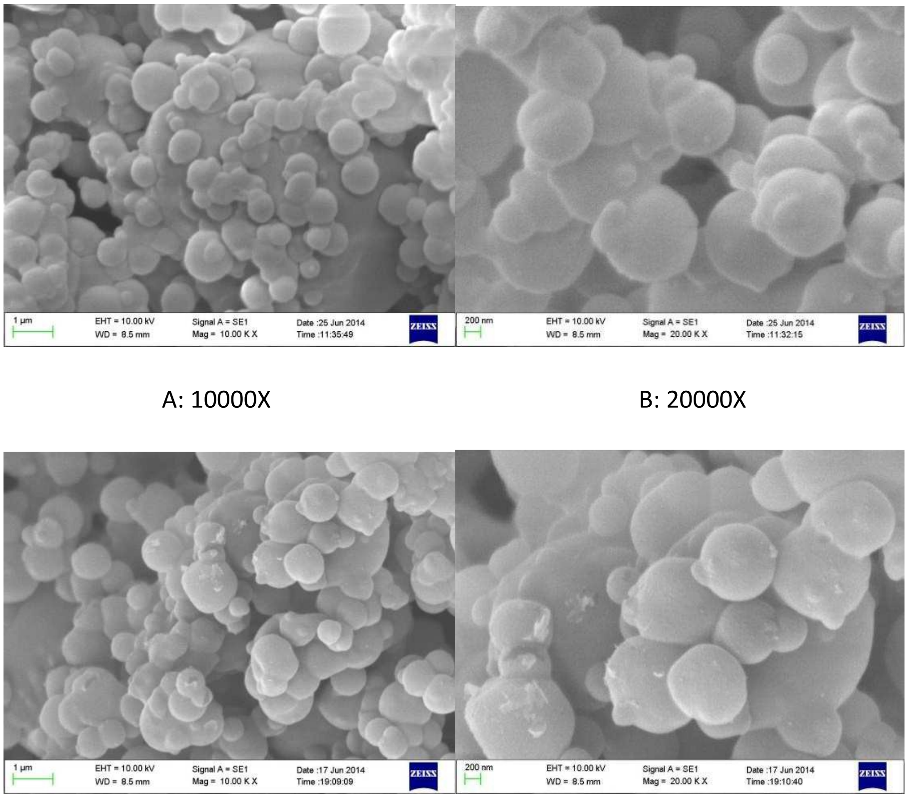
Fig. 3 XRD patterns of (A) n-dodecanol, (B) microPCMs and (C) PMF resin.

Fig.3 shows the XRD patterns of n-dodecanol, GO/microPCMs and MF resin. The sharp diffraction peaks in Fig.3A at 2θ=5.17° and 2θ=7.74° are attributed to the two diffractions of crystal planes of n-dodecanol. As shown in Fig. 3C, only a broad band at 2θ=19°~27° can be observed in the XRD pattern of MF resin, indicating that the PMF resin is amorphous. The XRD pattern of microPCMs in Fig. 3B contains both of the broad band of amorphous MF resin and the sharp diffraction peaks of n-dodecanol, whereas the intensities of peak at 2θ=5.17° and 2θ=7.74° are apparently lower than that of n-dodecanol in Fig.3A. The results suggest that there are just physical combination between n-dodecanol and MF resin, and no chemical reaction has occurred.

Morphology of microPCMs

SEM images in Fig.4 show the morphology of microPCMs with and without GO. All microPCMs have spherical shape. It can be observed that there is no destruction in the walls of microPCMs after mechanical agitation. MicroPCMs without GO have a smooth surface, while a few bugles can be observed from the surface of microPCMs with GO, which may be attributing to that some of GO wasn't embedded in the wall of microcapsules and reacted with MF prepolymer in the surface of microcapsules.

To demonstrate the form- stable performance of the prepared microPCMs, the heating test under different temperatures has been carried out. As can be seen from Fig.5, n-dodecanol melted into liquid completely after being heated at 50 °C, while the microPCMs and GO/microPCMs kept their form of dry powder during the test process. There is no liquid leaking out from microPCMs or GO/microPCMs. The result confirms that the MF resin is fully capable to prevent the leakage of the melt PCM n-dodecanol.



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B: 20000X

C: 10000X

D: 20000X

Fig. 4 SEM image of microPCMs without GO (A and B), and GO/microPCMs (C and D)

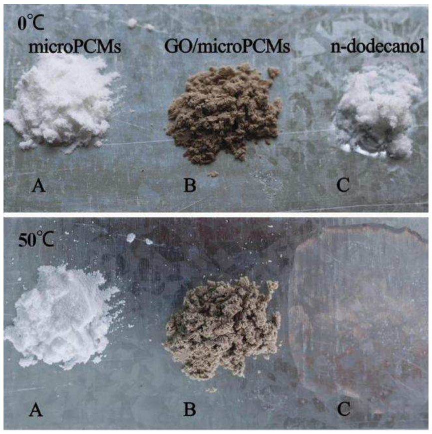

Fig. 5 Digital photos of (A) microPCMs without GO, (B) GO/microPCMs, (C) n-dodecanol at different temperatures: 0 ℃ (upper) and 50 ℃ (lower).

Thermal conductivity of GO/microPCMs

The thermal conductivity of GO/microPCMs with different contents of GO are shown in Fig. 6. The specific value of thermal conductivity and increasing percentage of GO/microPCMs are listed in Table 1.

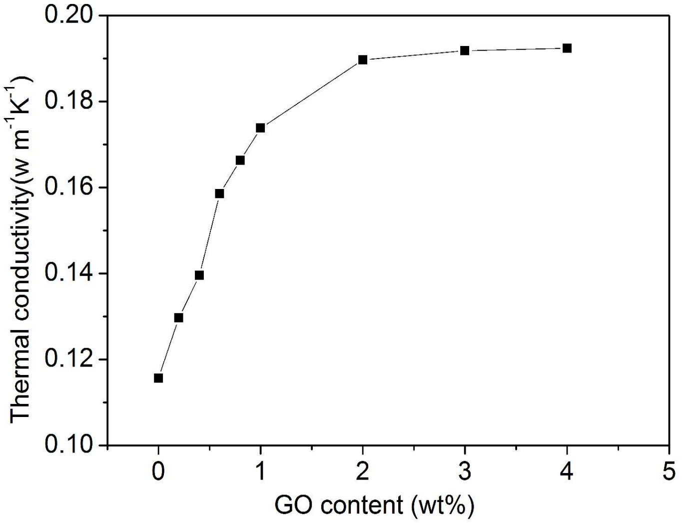

Fig. 6 Thermal conductivity of GO/microPCMs with different contents of GO

The thermal conductivity of GO/microPCMs increases with the increasing GO content in microPCMs. A significantly increase can be observed from 0.1157 to 0.1738 w m^{-1} K^{-1} when the GO content below 1wt%. The thermal conductivity of GO/microPCMs with 1wt% of GO increased by 50.21% while the thermal conductivity of GO/microPCMs with 4wt% of GO increased just by 66.29%. This can be attributing to that the oxygen-containing functional groups on the surface of GO make it excellently dispersible in MF prepolymer and the networks of GO sheets have positive influence on the thermal conductivity of GO/microPCMs. Therefore, a little amount of GO can improve the thermal conductivity of GO/microPCMs significantly. However, when the content of GO increased to 4wt%, the networks became saturated, and so little increase can be observed at the end of the curve of Fig.6.

Table1 Thermal conductivity and increasing percentage of microPCMs with different contents of GO

GO Content wt%	Thermal Conductivity $\mathrm{w\ m^{-1}\ K^{-1}}$	Increasing Percentage %
0	0.1157	0
0.2	0.1297	12.10
0.4	0.1396	20.65
0.6	0.1586	37.07
0.8	0.1663	43.73
1	0.1738	50.21
2	0.1897	63.95
3	0.1918	65.77
4	0.1924	66.29

Thermal storage properties of GO/microPCMs

Fig. 7 shows the DSC curves of pure n-dodecanol, microPCMs containing n-dodecanol and GO/microPCMs containing n-dodecanol in the first cycle of phase changing. The phase changing characteristics of the microPCMs are quite similar to that of pure n-dodecanol, which is because that there is no chemical reaction between n-dodecanol and melamine resin in preparation of the microPCMs. The temperature of phase changing peak are measured to be 26.01 °C, 26.15 °C and 26.33 °C for the microPCMs without GO, GO/microPCMs, and n-dodecanol, respectively.

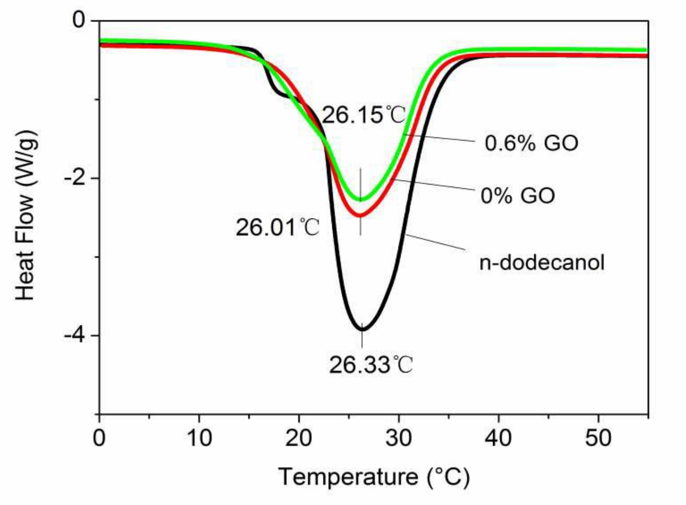

Fig.7 DSC curve for n-dodecanol, microPCMs without GO and GO/microPCMs

The phase change latent heat and the temperature of phase changing peak of microPCMs under different heating rates were showed in Fig.8 A and B, respectively. The results show that the phase change latent heat of microPCMs is almost unchanged under different heating rates of 2K/min, 5K/min and 10K/min. However, the temperature of phase changing peak of microPCMs increases with the increasing of heating rates. When the heating rate becomes high, the thermal response rate of PCMs in the inner core of microPCMs is not high enough and the peak of phase changing migrates to the right of high temperature.

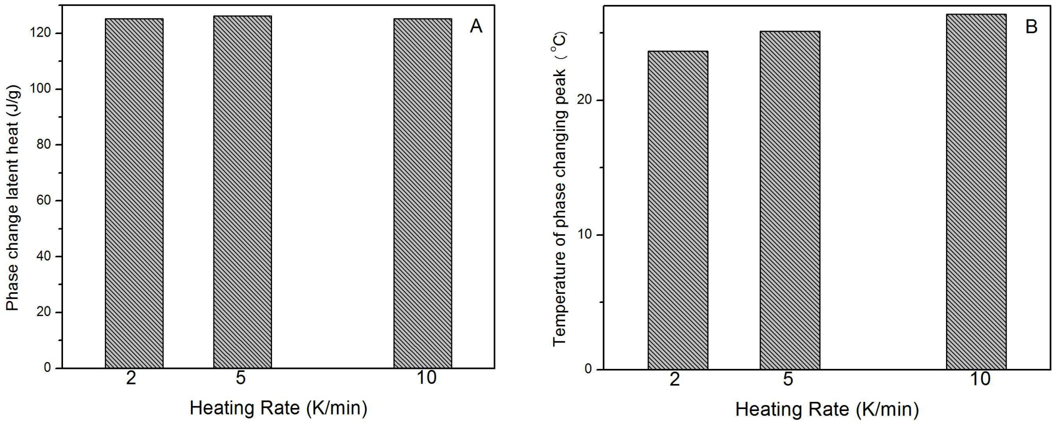

Fig.8 (A) The phase change latent heat and (B) the temperature of phase changing peak of GO/microPCMs under different heating rates

The phase change latent heat and encapsulation efficiency of the microPCMs with different contents of GO are showed in Fig.9. The phase change latent heat and encapsulation efficiency of GO/microPCMs is firstly stable and then decreasing with the increase of GO content. When the GO content is less than 1wt%, the phase change latent heat of GO/microPCMs is about 120J/g, and the encapsulation efficiency of GO/microPCMs is about 90%. When the content of GO is more than

1wt%, the dramatic decline in the curves can bee observed obviously. This can be ascribed to that the polymerization of MF prepolymer was accelerated apparently by addition of GO when the content of GO is more than 1wt%. Therefore, the encapsulation efficiency is reduced due to the rapid speed of formation of wall material.

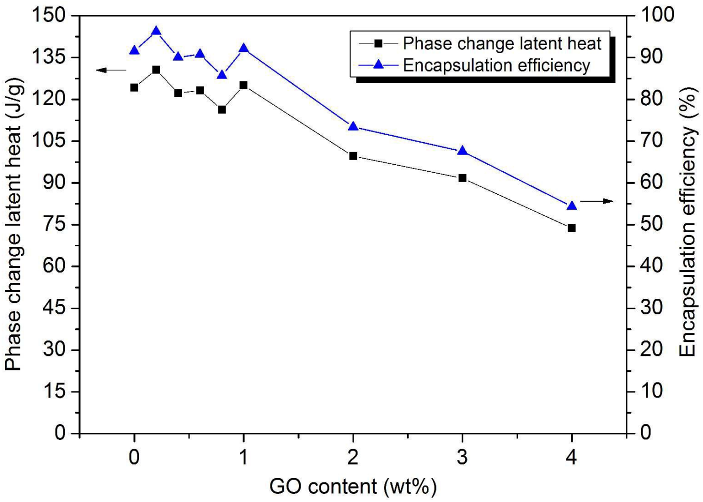

Fig.9 Phase change latent heat and encapsulation efficiency of GO/microPCMs with different contents of GO

Thermal cycle test of GO/microPCMs

Fig. 10A and B show the DSC curves during 100 thermal cycles test of the microPCMs without GO and GO/microPCMs, respectively. The DSC curves of different times of thermal cycles for phase changing including one time, 30 times, 60 times and 100 times can be fully coincide. There are no change in the phase change temperature and latent heat of microPCMs without GO and GO/microPCMs before and after tests, indicating that the microPCMs has a good thermal stability during the phase changing process.

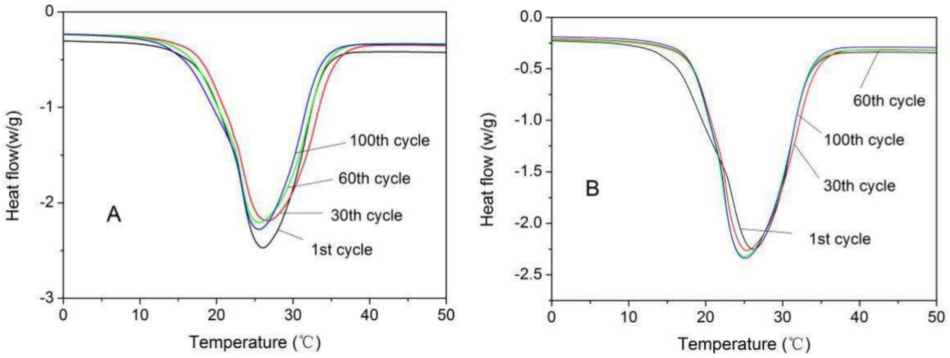

Fig.10 DSC curves of (A) microPCMs without GO and (B) GO/microPCMs for thermal cycle test

Conclusions

A novel gray microPCMs containing n-dodecanol with GO/melamine resin as the shell material was successfully prepared by in situ polymerization. The temperature of phase changing peak and latent heat of microPCMs with 1 % of GO are 26.40 °C and 125.2 J/g, respectively. The thermal conductivity of GO/microPCMs can be increased greatly by incorporating with GO. when 4wt% of GO was added in the microPCMs containing n-dodecanol, the thermal conductivity increases by 66.29% compared with that of microPCMs without GO. The prepared microPCMs all have spherical shape and relatively smooth surface. After 100 phase change cycle, the GO/microPCMs still have good thermal stability during the phase changing process. The promising results in our work demonstrated that the fabricated GO/microPCMs with high phase change latent heat and greatly improved thermal conductivity have great potential application for thermal energy storage.

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Graphical Abstract:

Graphene oxide-modified poly(melamine-formaldehyde) microcapsules containing phase change materials n-dodecanol were synthesized with improved thermal conductivity by 66.29% and high phase change latent heat of 125.2 J/g.