Materials Science & Engineering B 226 (2017) 86–93

Contents lists available at ScienceDirect

Materials Science & Engineering B

journal homepage: www.elsevier.com/locate/mseb

Multifunctional poly (melamine-urea-formaldehyde)/graphene microcapsules with low infrared emissivity and high thermal conductivity

Zhen Qiao, Jian Mao*

College of Materials Science and Engineering, Sichuan University, No. 24, South Section 1, Yihuan Road, Chengdu 610064, Sichuan, China

ARTICLE INFO

Keywords:
Phase change materials
Graphene
Thermal properties
IR emissivity

ABSTRACT

In this study, compact melamine urea formaldehyde (MUF) microcapsules containing paraffin phase change materials (PCMs) were prepared via in situ polymerization. The graphene sheets coated onto the shell of microcapsules, defined as "MUF@Graphene composites". The thermal conductivity of the microcapsules was enhanced without influencing their enthalpy by coating graphene sheets. The graphene sheets were visible in SEM images of MUF@Graphene composites. The thermal conductivity was 0.1944 W/mk for MUF microcapsules, and was 1.0540 W/mk for MUF@Graphene composites (10 wt%). The encapsulation ratio of all samples exceeded 80% and all samples exhibited favorable thermal stability. The IR emissivity of MUF microcapsules was 0.95, and was 0.64 for MUF@Graphene composites (10 wt%) .

1. Introduction

Phase change materials (PCMs) can store energy and adjust temperature during phase change process [1]. Organic PCMs are a particularly well-suited candidate for energy storage owing to their especially high latent heat [2–4]. The disadvantages inherent to organic PCMs, such as unreliable storage capacity, unwanted malleability and poor service life, can be ameliorated to some extent by encapsulation. The primary drawback of traditional organic PCMs is their low thermal conductivity, which becomes especially problematic after encapsulation with copolymer or inorganic materials [5,6].

Phase change microcapsules can be used in infrared (IR) shielding coatings to maintain a stable temperature at around the melting temperature when the inner temperature increases or decreases [7,8]. However, phase change microcapsules own high IR emissivity, which restricts the application of in IR shielding field [9]. By the way, low thermal conductivity of most PCMs can reduce the heat transfer rate between inner objects and outer infrared shielding coating, which can make the temperature difference between inside and outside being obvious. It is also against for the IR shielding application.

Graphene, which possesses high thermal conductivity and ultralow electrical resistivity [10–14], is currently considered an ideal candidate for improving the physical properties of microcapsules [15,16], and it also has favorable low density [17–21].

And according to the Stefan–Boltzmann law, the IR radiation energy of an object is $M = \varepsilon\sigma T^4$, where M is the radiant emittance, σ is the Boltzmann constant, ε is the IR emissivity, and T is the absolute temperature. For opaque objects, the IR emissivity ε can be expressed as [22]

$$\varepsilon = 1-R \quad (1)$$

where R is the reflectivity of an opaque object. Usually, reflectivity is consistent with surface conductivity [6,23–26], so graphene could be used to decrease the IR emissivity of phase change microcapsules

In this paper, graphene was used to modify melamine urea formaldehyde (MUF) microcapsules (paraffin as core materials and MUF copolymer as shell materials) in effort to improve their thermal conductivity, while retaining a higher phase change enthalpy value. Feasible composite structures, MUF@Graphene (core@shell), were prepared and their surface characteristics, thermal conductivities, phase change enthalpies thermal stability and IR emissivity were investigated.

2. Preparation

Analytically reagents were purchased from Chengdu Kelong Chemical Reagent Company (China) unless otherwise specified. The preparation procedure is depicted in Fig. 1.

MUF composites were prepared through in situ polymerization. Step 1 (MUF preparation), 9.00 g urea, 22.50 g formaldehyde (37 wt% aqueous solutions) and 50 mL deionized water were mixed into a 250 mL three-neck round-bottomed flask equipped with a mechanical stirrer, after urea dissolved, the pH value of the solution was adjusted to 8–9 with triethanolamine (TEA), then the solution was heated to 60 °C

* Corresponding author.
E-mail address: maojian@scu.edu.cn (J. Mao).

http://dx.doi.org/10.1016/j.mseb.2017.08.016
Received 6 June 2017; Received in revised form 31 July 2017; Accepted 16 August 2017

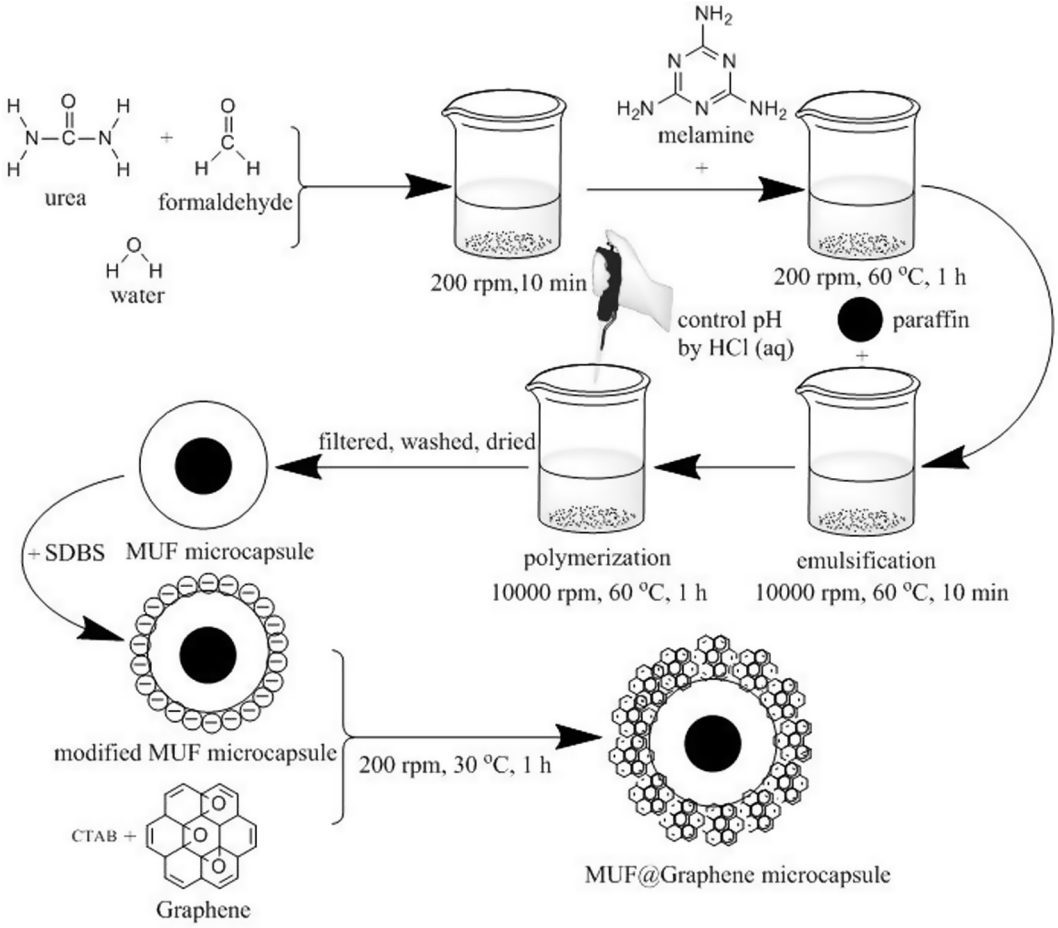

Fig. 1. Preparation of MUF microcapsules and MUF@Graphene composites.

and stirred for 60 min. After stirring, 0.93 g Melamine and 100 mL (0.5 wt%) sodium dodecyl benzene sulphonate (SDBS, as surfactant) solution was added to the solution, the reaction product was as the monomer. Step 2 (emulsification), a certain amount of paraffin was added to the mixture after melted, then, the whole suspension was stirred by Fluko FA25 high-shear dispersing emulsifier device (Fluko, German) at 10,000 rpm for 10 min. Step 3 (in situ polymerization), the pH value of the suspension was controlled to 2.00 slowly and carefully by dropping HCl (0.1 mol/L) during the agitation. After the polymerization, the suspension was kept at water bath (60 °C) for 120 min to ensure the polymerization reacted completely. The products were finally filtered and washed several times with deionized water, and dried at room temperature.

MUF@Graphene composites were prepared by dispersing 1.00 MUF microcapsules and 0.01 g SDBS (anionic surfactant) in 50 mL ethanol and ultrasonicated for 10 min. Graphene sheets (Deyang Carbonene Company, China) and 0.01 g hexadecyl trimethyl ammonium bromide (CTAB, cationic surfactant) were then dispersed into 50 mL deionized water and ultrasonicated for another 10 min. Finally, the two suspensions were mixed under vigorous stirring for 60 min (cationic surfactant could combine with anionic surfactant well), filtered and washed several times with deionized water, and dried at room temperature.

An extraction experiment was conducted to wash out the un-encapsulated paraffin in the samples before they were characterized. Prior to the characterization experiment, the microcapsules products were added to a flask with 250 mL petroleum ether, stirred for 2 h, and filtered and dried at room temperature for 48 h.

3. Characterization

The microstructure and morphology of the as-prepared samples were obtained on a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). Transmission electron microscope (TEM) images and high resolution transmission electron microscope (HRTEM) images were acquired on a Tecnai G2 F20 transmission electron microscope (Hillsboro, OR). XPS (X-ray photoelectron spectroscopy) was performed using a Thermal Scientific Escalab 250 Xi (Waltham, MA) using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV). Fourier transformed infrared (FT-IR) spectra were recorded on a Tensor 27 (Bruker, Germany) from 500 cm^{-1} to 4000 cm^{-1}. Raman spectra of the samples were recorded at room temperature on a LabRAM HR Raman spectrometer (France) with an argon ion laser. The phase change temperature and enthalpy of samples were measured with a differential scanning calorimeter (DSC) (DSC-1/700, METTLER TOLEDO, Switzerland) as the sample was heated from 20 °C to 80 °C and then cooled to 20 °C at rate of 5 °C/min under a constant stream of nitrogen. The thermal conductivity was measured with a hot wire thermal conductivity instrument (Xiatech TC3010, China). To test the thermal conductivity, we firstly pressed the sample into circular plate (weight = 3.00 g, diameter = 50.00 mm, thickness = 5.00 mm), and then put the hot wire between two samples. To make sure the sample can make good contact with the hot wire, we placed a weight on the top of the stacked samples. For each sample, we performed three measurements and obtained an average value as its thermal conductivity. And the measurements were carried out at room temperature. The thermal stability was measured by thermal gravimetric analysis (TGA) (TGA/DSC-2, METTLER TOLEDO, Switzerland). The IR emissivity at wavelengths of 1–14 μm was measured on an IR-2 IR emissivity