Preparation and Characterization of Novel Polyamide Paraffin MEPCM by Interfacial Polymerization Technique

Ju Wei, Zhenzhong Li, Ling Liu, Xiang Liu

School of Textile and Materials Engineering, Dalian Polytechnic University, Dalian, Liaoning, China
Correspondence to: Dr. J. Wei (E-mail: weiju423@yahoo.com.cn)

ABSTRACT: A novel polyamide-paraffin microencapsulated phase change material (MEPCM) was prepared by interfacial polymerization technique using 1,3,5-benzenetricarbonyl chloride (TMC) and ethylenediamine as monomers and 30# paraffin as core material. Morphology, chemical composition, thermal properties of the MEPCM were studied by scanning electron micrograph, FT-IR spectrum, differential scanning calorimeter analysis and thermogravimetric analysis. The solvent resistances of the MEPCM were also studied by observing the morphology changes of the MEPCM under optical microscope. Results indicate that the MEPCMs prepared under optimal conditions have spherical shape with average diameter of 6.4 μm, and the polyamide shell has successfully packaged the paraffin core. The MEPCM has a high efficiency in storing and releasing heat. The latent heat is 121.7 J/g and the microencapsulation ratio is 87%, 5% weight loss temperature is 260°C. The MEPCM is stable in H_2SO_4 solution ($\omega = 0.98$), NaOH solution ($\omega = 0.40$), ethanol, acetone, ether, dimethylformamide while can be destroyed by $ZnCl_2$ solution ($\omega = 0.60$). © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Energy shortage has been a more and more critical challenge for the world. Utilization of renewable energy provides an effective solution for this problem.[1] For renewable energies, phase change materials (PCMs) play an essential role, it can absorb or release large latent heat at their melting points as surrounding temperature increases or decreases. Paraffin waxes are the most widely used PCMs because of their advantages such as being chemically stable, nontoxic, noncorrosive, odorless, and easily available. Despite the advantages, paraffin waxes are in liquid state at temperature above its phase change point and will leak from the substrate. For this reason, it cannot be mixed into the substrate materials directly, which restricts its applications. Microencapsulation technique solved this problem well. With the microencapsulation technique, the PCMs are packaged in the capsules whose shell is composed of macromolecules to prevent its contact with the substrate materials, which greatly expanded the application fields of PCMs. Microencapsulated phase change material (MEPCM) can be used in active or pumped coolants,[2] solar, and nuclear heat storage systems and thermoregulating textiles.[3–5]

The properties of the MEPCMs are decided by both the core and the shell materials. The latent heat properties are mainly decided by the core materials, but the other important properties such as chemical and thermal stability, release properties, compatibility with the substrate materials are all decided by the structure of the shell, which depends on the monomers and the microencapsulation technique that used. Microencapsulation technique mainly includes interfacial polymerization (IP),[6,7] *in situ* polymerization,[8–10] complex coagulation,[11,12] emulsify polymerization,[13,14] and spray-drying,[15] etc. Among them, IP technique has the advantage of high-reaction speed, high ratio of coverage, good disperse property, etc. Cho et al.[16] synthesized a type of polyurethane MEPCM by IP techniques using toluene-2,4-diisocyanate (TDI) and diethylenetriamine as monomers. The average diameter is 1 μm, latent heat of fusion (ΔH_f) is about 112 J/g and the core content is about 46.4 ∼ 61.5%. Compared with other microencapsulation techniques, studies on preparing MEPCMs by IP technique are fewer. MEPCMs used for different products have different requirements on properties. It is very necessary to develop various types of MEPCMs to meet with various requirements of application.

The authors synthesized a polyurea (PU) MEPCM using TDI and piperazine as monomers earlier.[17] To improve MEPCM properties further, the authors synthesized a new type of polyamide (PA) paraffin MEPCM by IP technique in this article and probed its properties such as morphology, diameter distribution, chemical structure, thermal properties, solvent resistance, core content, etc. The originality lies in the nature of the oil-phase monomer, which provides superior properties for the PA MEPCMs. The PA MEPCMs can disperse in water and organic solvent easily, show good-thermal stability and chemical stability. Thus, it has the advantage of being utilized in manufacturing thermal regulating fibers by melt spinning or wet spinning method.

EXPERIMENTAL

Materials

1,3,5-Benzenetricarbonyl chloride (TMC; C.P., Qingdao Benzo Chemical) and ethylenediamine (EDA; A.R. Tianjin Fuchen Chemical Reagent) were used as shell-forming monomers. 30# paraffin wax (Henan Nanyang Paraffin Wax Fine Chemical Plant) was used as a core material. Nonionic surfactant, OP-15, OP-10 (C.P., Shanghai Wenhua Chemical Pigment), Cationic surfactant, hexadecyl trimethyl ammonium bromide (CTBA), anionic surfactant, sodium dodecyl sulfate (SDS; C.P. Tianjin Kermel Chemical Reagent) were used as an emulsifier. All the chemicals were of reagent grade and used without further purification.

Preparation of Microcapsules

The aqueous solution containing 1 wt % emulsifier was prepared by dissolving the agents in distilled water. The oil solution was prepared by dissolving TMC in 40°C paraffin wax. The aqueous solution was mechanically stirred at a rate of 9000 r/min. Oil solution and EDA was respectively dropped into the aqueous solution for a time span of 7 s. Mass ratio of EDA and aqueous solution was 1:100. The stirring rate was slowed down to 600 r/min 1 min later. During the process, interfacial polymerization reaction took place between TMC and EDA at the oil–water interface. The reaction lasted for 30 min, and then the resultant microcapsules were filtered, washed and dried.

Encapsulation Efficiency

Dried capsules about 1 g were washed with 25 mL of toluene. Unencapsulated paraffin wax or partially encapsulated paraffin wax was dissolved in toluene. The encapsulation efficiency was calculated as the ratio of the weight of washed and dried capsules to the original weight of sample.[15]

Chemical Structures

The infrared experiments were performed in a PerkinElmer spectrum one-B spectrometer. KBr was ground to a fine powder and mixed with MEPCM samples (2% w/w). KBr blended with MEPCM were dried and poured onto the transmission sample holder before IR spectra acquisition.

Morphologies

For surface observation, a scanning microscope JEOL JSM-6700F scanning electron microscopy (SEM) was used. Each sample was fixed on a standard-sample holder and sputter

Table I. Effect of TMC Concentration on Encapsulation Efficiency

TMC concentration (%)	Encapsulation efficiency (%)
2	20
4	70
6	89
10	99

Reaction temperature: 40°C and emulsifier: OP-15.

coated with gold. They were then examined with a SEM with suitable acceleration voltage (15 kV) and magnification.

Diameter Distribution

MEPCMs were dispersed by alcohol and dropped on a slide. Diameters of 300 MEPCMs were tested under the optical microscope and the volume average diameter D_V was calculated according to the following formula.

$$D_V = \sqrt[3]{\sum (N_i \times D_i^3) / \sum N_i}$$

N_i—number of microcapsules in a diameter range, D_i—class mid-value in a diameter range.

Chemical Resistance

The dried MEPCMs were immersed in acid, alkaline, or organic solvents at 25°C for 1 h, then observed their morphology changes under optical microscope to judge its chemical resistance.

Thermal Analysis

Thermal analyses of MEPCMs were carried out on a differential scanning calorimeter, DSC analyzer (Mettler Toledo, DSC822e). Mass of core material content was measured from the heat of fusion (ΔH_f). Dried MEPCM samples were tested with a heating rate of 10°C/min in air atmosphere. Each sample was analyzed at least twice and the average value was recorded. Thermal stability characterization was performed on a differential thermal analyzer (Henven HJ-2) at a scanning rate of 10°C/min in air atmosphere.

RESULTS AND DISCUSSION

Effect of TMC Concentration on Encapsulation Efficiency

During the process of preparing MEPCMs by IP technique, the oil phase was emulsified into the water phase. Monomers diffused from oil and water phase, respectively, to the interface and polymerized with each other to form a thin film around the little oil droplets. After forming the nascent cell, the following polymerization was a diffusion-controlled process. An excess of EDA was used as the acid acceptor. Shell thickness and encapsulation efficiency were mainly determined by the TMC concentration. Effect of TMC concentration on encapsulation efficiency is shown in Table I.

From Table I, the authors can see that with the increasing of the TMC concentration in oil phase, encapsulation efficiency increases, indicating that core materials cannot be encapsulated completely with low-oil monomer concentration.

Table II. Effect of Reaction Temperature on Encapsulation Efficiency

Temperature (°C)	Encapsulation efficiency (%)
35	75
40	99
45	86
50	82

TMC concentration: 10% and emulsifier: OP-15.

Effect of Reaction Temperature on Encapsulation Efficiency

Reaction temperature has an important effect on encapsulation efficiency. For TMC, hydrolysis rate increases with the rising of the temperature and diffusion coefficient decreases with the declining of the temperature, which are both unfavorable for the formation of the shell. Effect of reaction temperature on encapsulation efficiency is shown in Table II.

From Table II, the authors can see that the highest encapsulation efficiency was got at 40°C.

Effect of Emulsifier Type on Encapsulation Efficiency and Diameter

To make the emulsion stable, certain surfactants are used to form an adsorption layer at the liquid–liquid interface, which may affect the polymerization more or less. The structure of the adsorption layer depends on the chemical structure of the surfactant that was used as the emulsifier. To investigate effect of emulsifier type on microencapsulation, nonionic, anionic, cationic surfactants were chosen as emulsifier to prepare the MEPCMs. Encapsulation efficiency and average diameter of the MEPCMs are shown in Table III.

From Table III, the authors can see that the encapsulation efficiency of OP-15 is highest and the average diameter of OP-15 is lowest except OP-10. The reason can be ascribed to the differences of adsorption layer structure and emulsion stability mechanism. For cationic and anionic surfactants, the surface of the droplets consists of charged hydrophilic irons. Stability of the emulsion depends on electrostatic repulsion mechanism. For nonionic surfactants, the surface of the droplets consists of hydrophilic polyoxyethylene chain. Stability of the emulsion depends on steric repulsion mechanism. Results indicate that

the adsorption layer formed by nonionic surfactants is more advantageous for diffusion and polymerization of the monomers when compared with ionic surfactants. Encapsulation efficiency and average diameter difference between OP-10 and OP-15 can be ascribed to HLB (hydrophile–lipophile balance) value. OP-10 and OP-15 have similar chemical structures as follows:

$$C_8H_{17}-\text{C}_6H_4-(CH_2CH_2O)_n-H$$
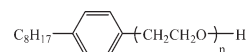
The value of "n" in above formula is 10 for OP-10 and 15 for OP-15. HLB value increases with the rising of "n" value. HLB value of OP-15 that is 15 meets with the optimum HLB value of paraffin/water system described in this article, while HLB value of OP-10 is 13.3-14. MEPCMs prepared by OP emulsifier have narrower particle size distribution than that of SDS and CTBA.

Chemical Characterization of the Polyamide MEPCM

For MEPCMs prepared by the IP technique, the structure of the shell depends largely on the type of the monomers. First, monomer type decides the polymer type of the shell, thus decides its thermal stability, chemical stability, and compatibility with the substrate materials. Second, monomer reactivity influences the thickness of the shell, the higher reactivity the monomer has, the smaller the amount it can be used, thus deduced the thickness of the shell and improved the core content. Third, monomer functionality decides the cross-link degree of the shell, thus influences the density of the shell, difunctional monomers produce linear macromolecules winding around the core randomly so that the resultant shell is inevitably semipermeable, monomers having more than two functionalities will produce cross-link structure, which is denser. TMC is a trifunctional monomer that has high reactivity and usually is used for preparing reverse osmosis and nanofiltration membranes. Formerly, authors used TMC as monomer to polymerize with three kinds of diamines, prepared composite membranes with ideal-filtration properties.[18] Considering the importance of cross-link degree of MEPCM shells, the authors chose TMC as the oil-phase monomers to interfacially polymerize with EDA, synthesized a new type of PA MEPCM. The chemical schematic is showed as follows.
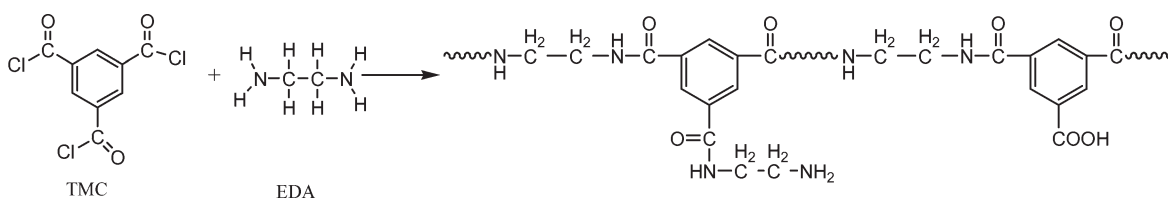
Chemical characterization of the PA MEPCM was carried out using FTIR spectroscopy method. Figure 1 shows the transmittance spectra of characteristic peaks for pure paraffin and MEPCM.

From Figure 1, the authors can see that in the pure-paraffin spectrum, the peaks at 2957, 2918, 2850 cm^{-1} are C—H stretching peaks and the peaks at 1467, 1378, 721 cm^{-1} are characteristic for paraffin compounds. The similar results were also reported for

Table III. Effect of Emulsifier Type on Encapsulation Efficiency and Diameter

Emulsifier	Encapsulation efficiency (%)	Average diameter (μm)
OP-10 (nonionic)	95	6.2
OP-15 (nonionic)	99	6.4
SDS (anionic)	85	8.9
CTBA (cationic)	76	10.2

TMC concentration: 10% and reaction temperature: 40°C.

Figure 1. FTIR spectra of paraffin and MEPCM.

MEPCMs containing paraffin.[13] In the MEPCM spectrum, besides the characteristic peaks of paraffin at 2957, 2918, 2850, 1467, 1378, 721 cm^{-1}, there are some new peaks appeared. Peaks at 3427 cm^{-1} is due to N—H stretching and peaks at 1651 cm^{-1} can be assigned to polyamide I, 1542 cm^{-1}, polyamide II, 1289 cm^{-1}, polyamide III. The above peaks indicate that the MEPCMs are composed of polyamide shell and paraffin core as expected and the chemical structure of paraffin remains unchanged. It also can be observed that the characteristic peaks of polyamide are much smaller than that of the paraffin, which indicates that the core content of MEPCM is very high.

Morphology of the MEPCM
Microencapsulation of the paraffin can be observed directly by SEM method. A SEM photograph of polyamide MEPCMs are shown in Figure 2.

From Figure 2, the authors can see that morphologies of MEPCMs prepared by IP technique are quite different from MEPCMs prepared by *in situ* polymerization, emulsion polymerization, and complex coacervation techniques. MEPCMs prepared by *in situ* polymerization[7] have flocculation characteristic. MEPCMs prepared by emulsion polymerization[13] and complex coacervation[15] have very smooth surface. The polyamide MEPCMs prepared by IP technique under optimum conditions are mainly spherical and their profiles are clear without adhesive phenomenon, which indicates that the paraffin has been packaged well, but impurities and cracked shells can be observed, if use SDS and CTBA as emulsifiers. From the 2000 magnified photograph, the authors can see that there are some crimples on the surface of the MEPCMs, the crim-
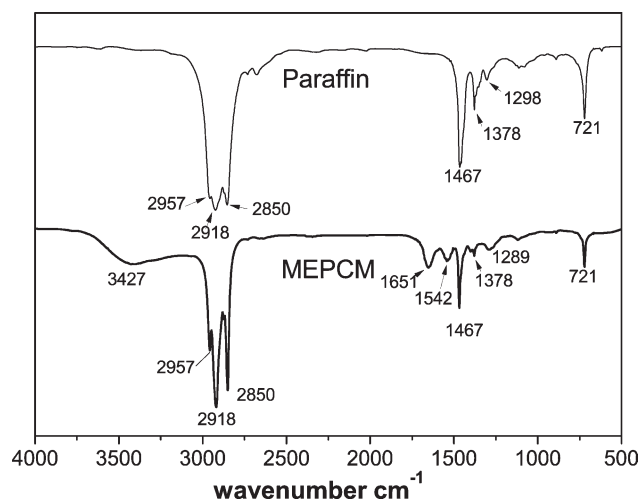
ples on big capsules are deeper than that of the small one. The crimples are probably produced during the formation process of the MEPCMs. The reasons can be of those two aspects. First paraffin is of liquid state at the preparation period but turns to solid state after preparation. Since the density of solid is bigger than liquid, so the volume of core material certainly decreases when the system is cooled down. At the meantime the polyamide shell did not shrink obviously thus lead to the crimple appearance on the surface of the capsules. Secondly, when the oil phase is added into the liquid system, at the beginning of the polymerization, monomer concentration of oil phase is high, when the reaction proceeding on, oil-phase monomer exhausted gradually, volume of oil droplets decreased continuously, at the same time, the initially formed membranes have bigger area, so will sink after the reaction. The sink of the shell also has some advantages, it can provide some pre-expand space for the core materials avoiding the leakage of the core when the MEPCMs are heated during usage.

Particle Size Distribution of the MEPCMs
Particle size distribution (PSD) of MEPCMs is very important for its usage. Different application purpose requires different diameter distribution. For example, MEPCMs used for thermo regulating fibers had to have small size and be uniform to
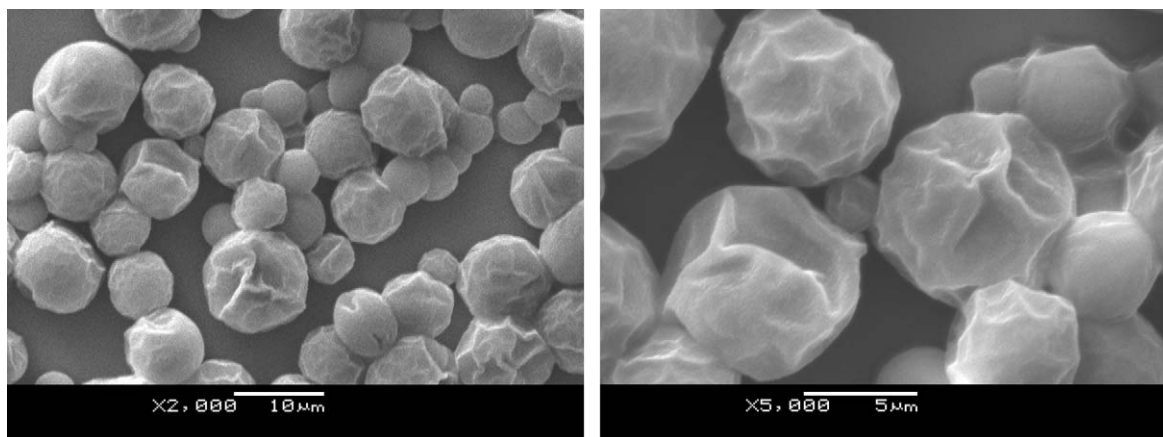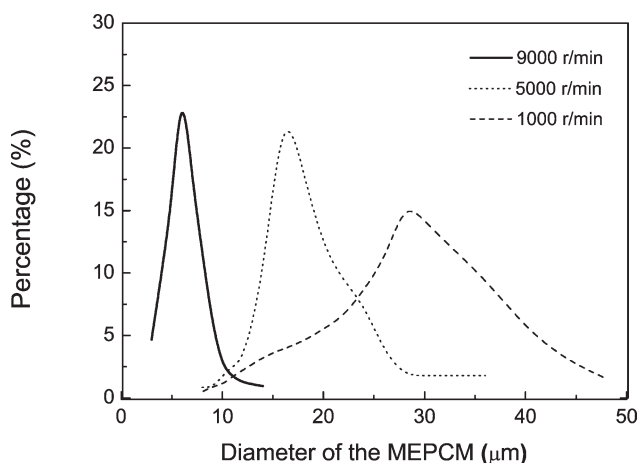

Figure 2. SEM image of MEPCM.

Figure 3. Diameter distribution of MEPCMs.

Figure 5. TG curves of paraffin and MEPCMs.

ensure the successful spinning and fiber size. As being discussed in the published reports, diameter of MEPCMs is influenced by several factors such as the type and concentration of emulsifier, the speed and time of the stirring, etc.[7]

Preparing MEPCMs by IP technique, the emulsifying process had to be finished quickly; otherwise, the already-formed shell of capsules will be destroyed by high-speed flow. Prolonging the emulsify time is not a valid method of reducing particle size, nevertheless, increasing the emulsify speed is feasible. Influence of emulsify speed on the PSD are shown in Figure 3.

From Figure 3, the authors can see that the mean diameter of the MEPCMs decreased with the increasing of emulsifying speed, at the meantime, the diameter distribution turned to narrow. Comparably, MEPCMs prepared at an emulsifying speed of 9000 r/min is relatively more proper for preparing thermal regulating fibers.

CHEMICAL STABILITY OF THE MEPCM

MEPCMs used for thermal regulating fibers require good chemical stability. The MEPCMs are usually added into the polymer solution to spin the fiber. If the shell material cannot stand the solvent, the MEPCM will be destroyed. Several solvents were chose to investigate chemical stability of the MEPCM. The MEPCM
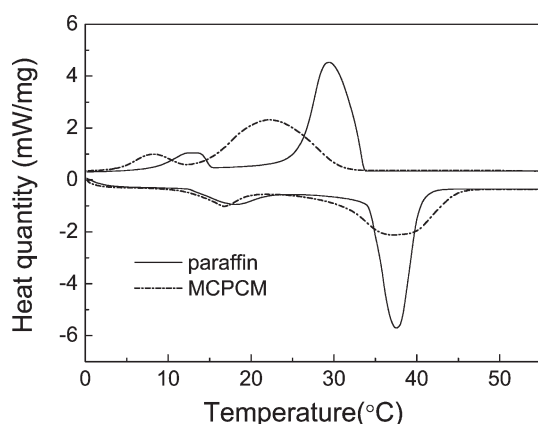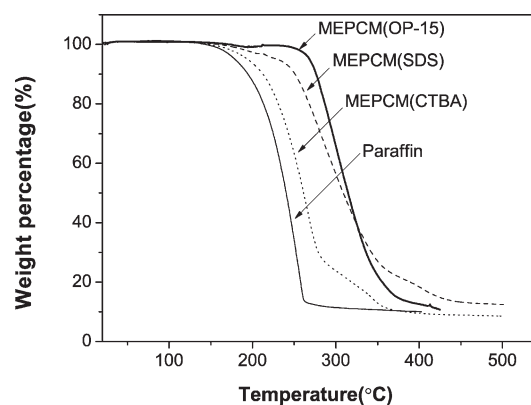

Figure 4. DSC curves of paraffin and MEPCM.

remains its shape and properties after being immersed in H_2SO_4 solution ($\omega = 0.98$), NaOH solution ($\omega = 0.40$), ethanol, acetone, ether, dimethylformamide, DMSO for an hour, however, it can be destroyed by $ZnCl_2$ solution. The superior chemical stability of the MEPCM can be ascribed to cross-link structure of the shell and also related to the aromatic-molecular structure.

Thermal Characteristics of the MEPCM
Figure 4 is DSC curves of paraffin and MEPCM prepared at the optimal process.

From Figure 4, the authors can see that the MEPCMs have high efficiency in storage and releasing heat. For the MEPCMs, melting process starts at 29°C and ended at 44°C during the heating process. Crystallization process started at 31°C and ended at 14°C during the cooling process. Latent heats of melting and freezing of paraffin were measured to 122.1 and 121.7 J/g, respectively. For the paraffin, melt process start at 34°C and ended at 41°C during the heating process. Crystallization process start at 33°C and ended at 25°C during the cooling process. Because of thermal conductivity of the shell, phase changing temperature spans of the MEPCMs are wider than that of the paraffin. Latent heats of melting and freezing of paraffin were measured to 139.8 and 139.4 J/g, respectively. The encapsulation ratio R of paraffin was calculated with the following equation based on enthalpy values at 87.7%.

$$R = \frac{H_{\mathrm{MEPCM}}}{H_{\mathrm{PCM}}} \times 100\,(\%)$$

where H_{MEPCM}, H_{PCM} are measured enthalpies of microcapsules containing paraffin and paraffin itself, respectively.

Thermal Stability of the MEPCM
Thermal stability of the MEPCM was evaluated by means of thermogravimetric analysis (TGA). Figure 5 shows the TGA curves of pure paraffin and PA MEPCMs prepared by different emulsifiers. The data are obtained by increasing the temperature at a rate of 10°C/min from room temperature to 600°C. In Figure 5, pure paraffin starts to lose weight at approximately 150°C, and it just remain 13% weight when the temperature raised to 265°C. Comparably, the 5% weight-loss temperatures of the MEPCMs prepared by OP-15, SDS, CTBA are 260, 230, 194, 179°C, respectively. T_e temperature of MEPCM prepared

by OP-15 is 265°C. The results indicated that the paraffin has been packaged by the shell materials. Otherwise, the MEPCM will have a nearly same T_e temperature as the paraffin for paraffin leaking from the shells. Thermal stability of the MEPCM prepared by OP-15 is better than that of the SDS and CTBA. Although, the PA shell of the MEPCM prepared by OP-15 is very thin, but since it has cross-linked molecular structure, it still can protect the core paraffin quite well.

CONCLUSION

A new type of PA-shell MEPCM-containing paraffin is successfully prepared by IP technique using TMC and EDA as monomers. The optimal-preparation process is 1% EDA concentration, using OP-15 as the emulsifier, mass ratio of TMC and paraffin is 1:9 and the emulsify time is 1 min, reaction temperature is 40°C. FT-IR results confirmed that the shell of the MEPCM is PA and the core is paraffin. SEM analysis indicates that the MEPCMs have spherical shape and there are some crimples on the surface of the MEPCM. The average diameter of the MEPCM is 6.4 μm. According to the calculation results of DSC test, the latent heat of the MEPCM is 121.7 J/g and the core content is 87.7%. TG analysis confirmed the high-thermal stability of the MEPCM, which 5% weight loss temperature in air atmosphere is 260°C.

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