

Short communication

Preparation of CMC-modified melamine resin spherical nano-phase change energy storage materials



Xiaofeng Hu, Zhanhua Huang*, Yanhua Zhang

Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, China

ARTICLE INFO

Article history:

Received 3 February 2013

Accepted 29 August 2013

Available online 14 September 2013

Keywords:

Carboxymethyl cellulose

Melamine resin

Sphere

Phase change material

Nanocapsules

ABSTRACT

A novel carboxymethyl cellulose (CMC)-modified melamine-formaldehyde (MF) phase change capsule with excellent encapsulation was prepared by in situ polymerization. Effects of CMC on the properties of the capsules were studied by Fourier transformation infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), scanning electronic microscopy (SEM), X-ray diffractometry (XRD), and thermogravimetric analysis (TGA). The results showed that the CMC-modified capsules had an average diameter of about 50 nm and good uniformity. The phase change enthalpy of the capsules was increased and the cracking ratio decreased by incorporating a suitable amount of CMC. The optimum phase change enthalpy of the nanocapsules was 83.46 J/g, and their paraffin content was 63.1%. The heat resistance of the capsule shells decreased after CMC modification. In addition, the nanocapsule cracking ratio of the nanocapsules was 11.0%, which is highly attractive for their application as nano phase change materials.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Micro- or nano-encapsulated phase change materials are tiny particles that consist of a phase change material (PCM) core surrounded by a polymer or inorganic shell. Encapsulation of the PCM not only increases the heat transfer area, but also protects the PCM from the influences of the outside environment and enables the core material to withstand frequent changes in the volume of the storage material during phase change (Karaipekli, Sari, & Kaygusuz, 2007; Su, Huang, & Ren, 2007).

Melamine-formaldehyde (MF) resin has often been selected for the protection of PCMs, because of its low price, easily controlled preparation, high compatibility, and good thermal stability (Hwang et al., 2006; Wang, Yuan, Rong, & Zhang, 2009). However, MF resin has high hardness and brittleness, and microPCMs require considerable toughness for practical use. In contrast, carboxymethyl cellulose (CMC) is easily chemically modified and has many uses because of its abundant hydroxyl and carboxyl groups and environmental friendliness (Gilbert, 1994). The aim of this work was to fabricate novel nanoPCMs containing paraffin wax by in situ polymerization using CMC modified melamine-formaldehyde as shell material. A series of capsules with different amounts of CMC additive was prepared to investigate the influence of CMC on their performance.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (CMC, Mw = 25,000–35,000), acetic acid (36%), OP-10, melamine (>99.5%), triethanolamine, and formaldehyde (37%) were purchased from Kermel Chemical Reagents Co., Ltd. (Tianjin, China). Styrene-maleic anhydride (SMA) was purchased from Sigma Co. (St. Louis, MO, USA). Paraffin wax was obtained from Ruhr Energy Technology Co., Ltd. (Hangzhou, China).

2.2. Preparation of nanoPCMs

The preparation of nanoPCMs followed the previously described procedure (Hu & Huang, 2012) and the conditions are shown in Table 1.

2.3. Characterization

The chemical structures of the nanocapsules were analyzed using a Nicolet Magna 560 (USA) Fourier transform infrared (FT-IR) spectrometer with the KBr sampling method. The morphologies of the nanocapsules were obtained using a FEI QUANTA 200 (USA) scanning electronic microscope (SEM). The thermal storage properties of the nanocapsules were measured using a Netzsch 204E (Germany) differential scanning calorimeter (DSC) at a heating rate of 5 K/min and range of 0–40 °C under nitrogen atmosphere.

* Corresponding author. Tel.: +86 451 82192905; fax: +86 451 82192905.
E-mail address: huangzh1975@163.com (Z. Huang).

Table 1
Experiment results of the nanocapsules.

Sample number	Melamine (g)	Formaldehyde (37 wt%) (mL)	CMC (g)	Paraffin (g)	Cracking ratio (%)	The content of PCM in nanocapsules (%)
A0	2.5	4.0	0	2.5	24.6	37.2
A1	2.5	4.0	0.25	2.5	10.6	49.1
A2	2.5	4.0	0.50	2.5	11.0	63.1
A3	2.5	4.0	1.00	2.5	17.5	31.6

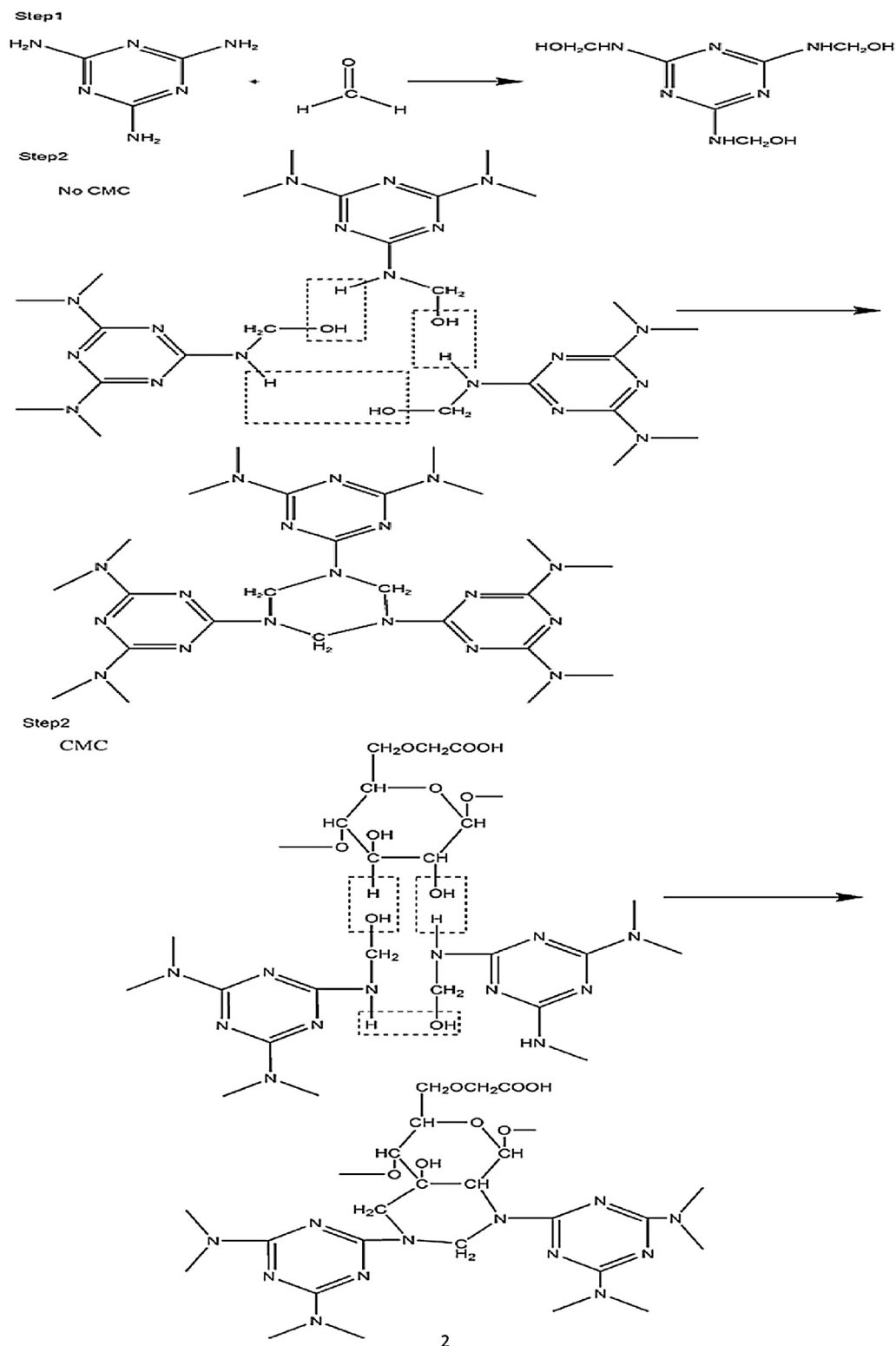


Fig. 1. Chemical reaction scheme.

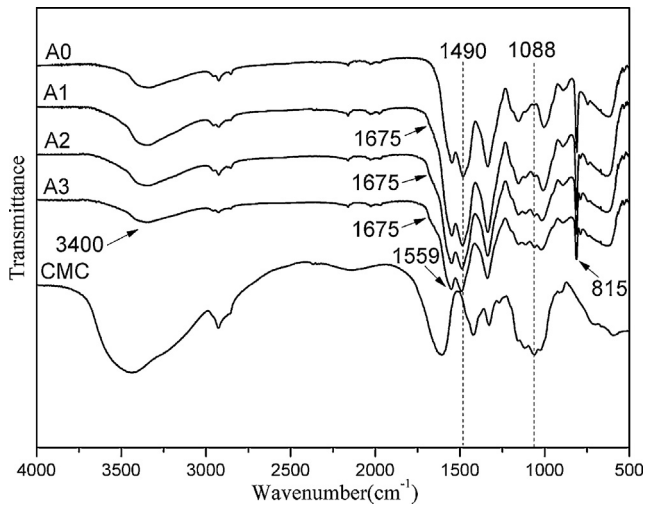


Fig. 2. FTIR spectra of CMC and nanocapsule shell material.

The phase change latent heat and phase change temperature of the nanoPCMs were obtained from the analyzed results of DSC curves using a Netzsch TA4. X-ray diffraction (XRD) patterns of the nanocapsules were obtained using a Rigaku D/MAX 2200 (Japan) diffractometer (40 kV, 30 mA, CuK α) with a scanning speed of 4°/min and scanning range of 5–50° (2 θ). The step was 0.02°. Thermogravimetric analysis (TGA) was carried out using a Netzsch TA4 (Germany) thermal analyzer. The TG instrument was calibrated with calcium oxalate from 30 to 800°C at a heating rate of 10°C/min in a static air atmosphere. DTG was also carried out to determine the maximum rate of weight loss.

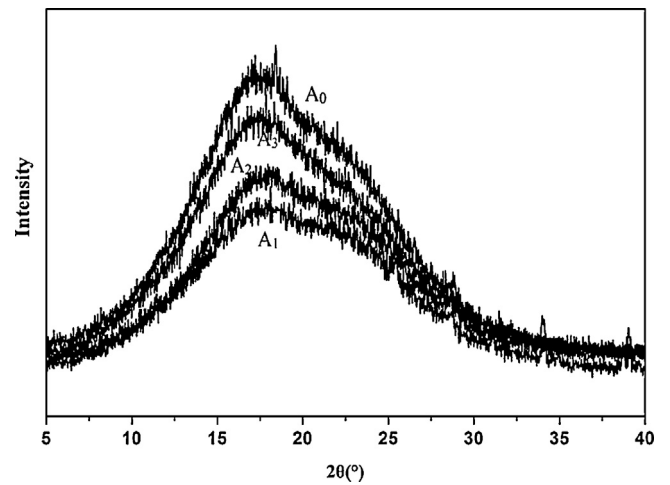


Fig. 4. X-ray diffraction patterns of nanocapsules.

2.4. Nanocapsule PCM content

The content of PCM in the nanocapsules (C_a , %) was estimated from the measured melting heat according to Eq. (1):

$$C_a (\%) = \frac{H_w}{H_p} \times 100, \quad (1)$$

where H_w is the phase change latent heat of the nanocapsules (J/g) and H_p is the phase change latent heat of the PCM.

2.5. Calculation of cracking ratio

The mechanical strength of the nanocapsules was expressed by the cracking ratio, with high mechanical strength obtained at small cracking ratios. A certain amount of nanocapsules was dispersed

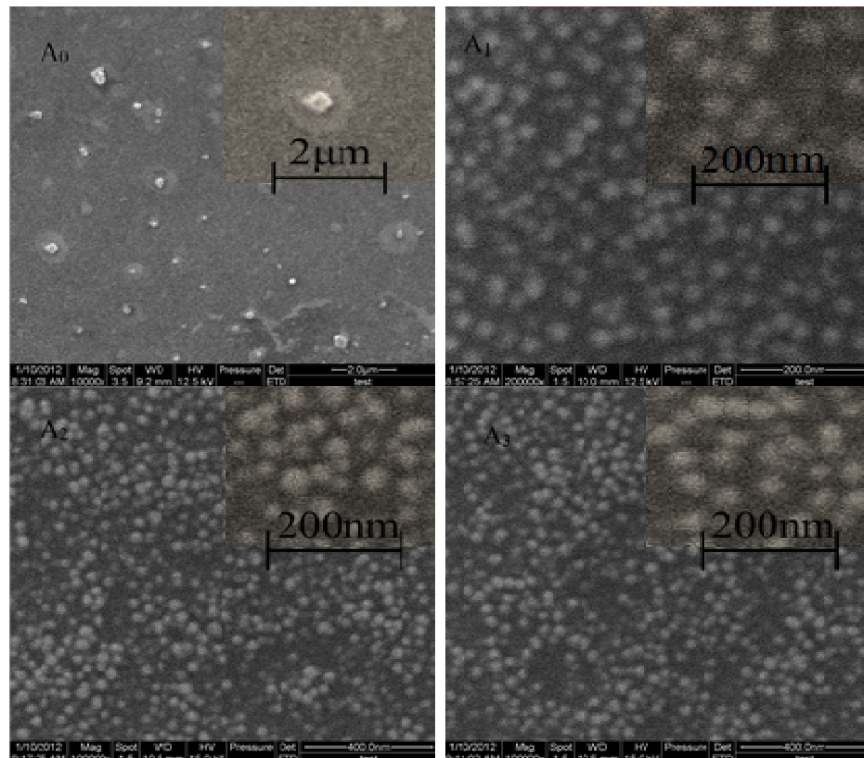


Fig. 3. SEM images of CMC-modified nanocapsules.

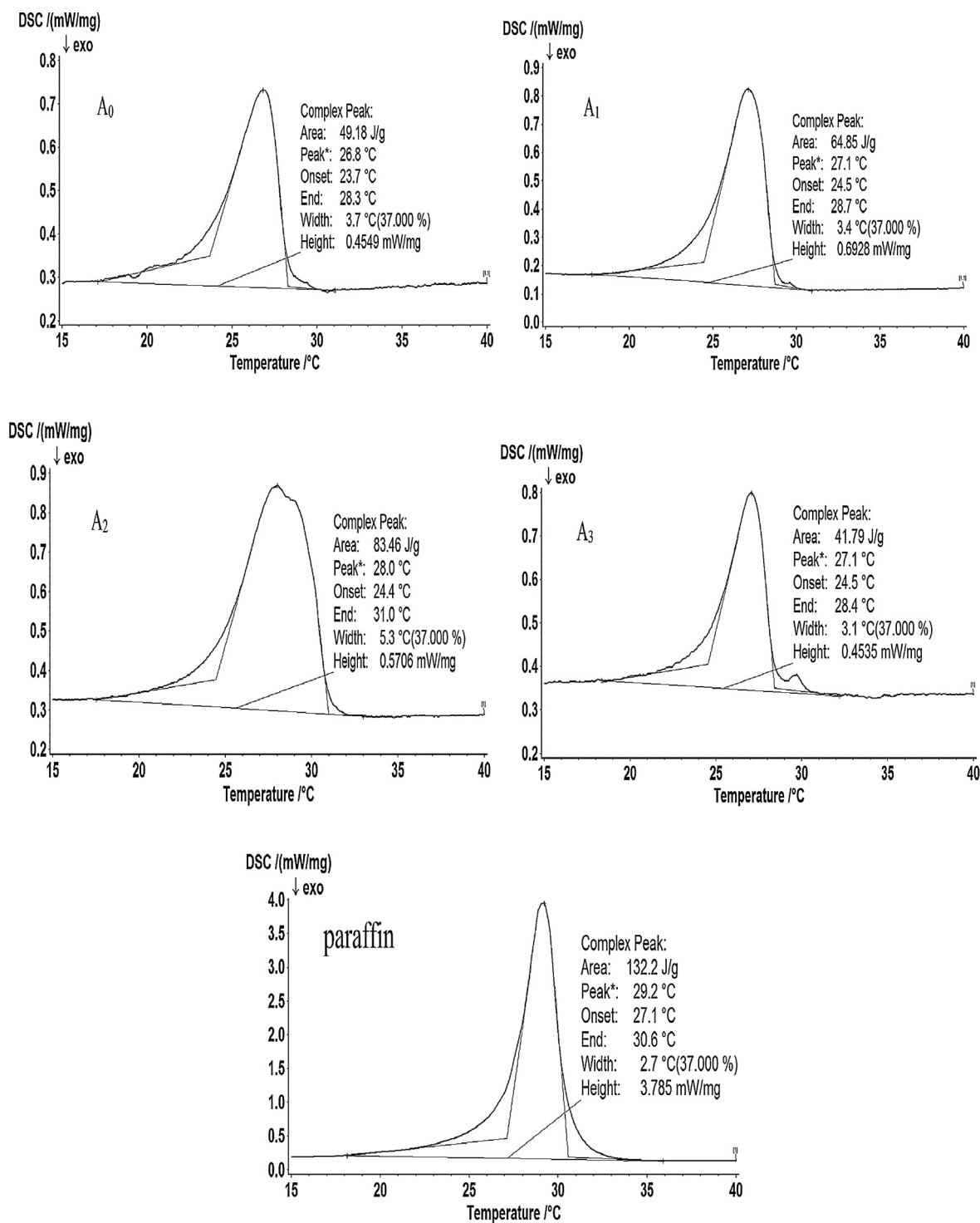


Fig. 5. DSC curves of nanocapsules and paraffin.

in distilled water, and the suspension was mechanically sheared at 5000 rpm for 10 min. The suspension was then filtered and washed once with ethanol and twice with distilled water, and dried at room temperature. The cracking ratio (N , %) can be estimated according to Eq. (2):

$$N (\%) = \frac{(W_o - W_t)}{W_o} \times 100, \quad (2)$$

where W_o is the amount of nanocapsules (g) before shearing, and W_t is the amount of nanocapsules (g) after shearing.

3. Results and discussion

3.1. Chemical structure analysis of nanoPCMs

As shown in Fig. 1, the chemical reaction scheme of CMC-modified MF consists of two steps. Step 1 is the reaction between the formaldehyde and melamine. In step 2, the MF prepolymer is modified by CMC through acid catalysis, forming a cross-linked structure. Further cross-linking reactions occur between the CMC-modified MF prepolymer molecular chains.

The FTIR spectra of CMC and nanocapsule shell materials modified with different amounts of CMC additive are presented in Fig. 2. According to the work of Benson, the peaks at 1559 and 815 cm^{-1} were assignable, respectively, to in-plane and out-of-plane triazine ring vibrations (Benson, 2003). Additionally, absorption peaks appeared at 1556 and 1490 cm^{-1} because of multiple C–N stretching in the triazine ring. The height of the peak at 1490 cm^{-1} decreased gradually with increasing CMC addition. This was because the participation of CMC in the polycondensation reaction led to the number of C–N bonds decreasing. A series of weak peaks at about 1088 cm^{-1} corresponded to C–O–C stretching vibrations. The intensity of these peaks increased with CMC addition; this indicated that the adsorption peaks were related to CMC. A weak arch shaped protuberance existing at 1675 cm^{-1} attributed to C=O stretching vibrations was the result of the limited number of C=O bonds and the width and strength of the peak near 1500 cm^{-1} . These characteristic peaks in the spectra of the nanocapsules confirmed the formation of CMC modified nanocapsules.

3.2. Morphology of nanoPCMs

Fig. 3 shows the morphological characteristics of nanoPCMs fabricated with different amounts of CMC, imaged by SEM. All nanocapsules were distributed uniformly and had regular spherical shape. The nanocapsules without CMC (A0) exhibited leakage of paraffin, but the nanocapsules modified with CMC did not. Thus, the nanocapsules containing CMC exhibited better encapsulation than the nanocapsules without CMC. It was concluded that CMC makes the nanocapsule surface more compact, mainly because CMC has abundant hydroxyl groups that enable condensation reaction with the MF prepolymer. The CMC thereby changes the shell structure of the nanocapsules, and the encapsulation effect is improved. The average diameter of A0 was about 500 nm, while that of the other three (A1, A2, A3) was about 50 nm. This change in diameter was due to the CMC slowing the polycondensation reaction rate and thus reducing the shell thickness.

3.3. Crystallography of nanocapsules

The X-ray diffraction patterns of the nanocapsules are displayed in Fig. 4. Significant differences in the X-ray diffraction patterns of the shell materials were observed for different amounts of CMC addition. Comparing A1, A2, and A3, we can see that the peak height, peak width, and peak area decreased with increasing CMC addition. It also can be seen that the diffraction peak intensity of A0 was stronger than that of A1, A2, and A3. This suggests that the crystal structure of the MF changed after the polycondensation between the CMC and parts of the MF prepolymer, which made the crystallinity and number of grains decrease. Change in the MF crystallinity directly affects the mechanical strength and encapsulation properties of the resulting PMCs (Szabo, Ravenelle, Hassan, Preda, & Mateescu, 2000). The results in Table 1 suggested that the cracking ratio of modified nanocapsules (A1–3) was lower than that of unmodified nanocapsules (A0). Because a network of CMC itself exists, excessive CMC can increase the cracking ratio.

3.4. Thermal properties of the nanocapsules

From Fig. 5, the phase change enthalpy of the nanocapsules first increased and then decreased with increasing CMC addition. However, the value was much lower than that of pure paraffin. The reduction of phase change enthalpy was likely due to the decrease of paraffin weight ratio after addition of CMC. There are complex reasons for this phenomenon. CMC has better stability at the phase inversion temperature (T_m) of paraffin, and not only makes no contribution to the phase change enthalpy, but also becomes an

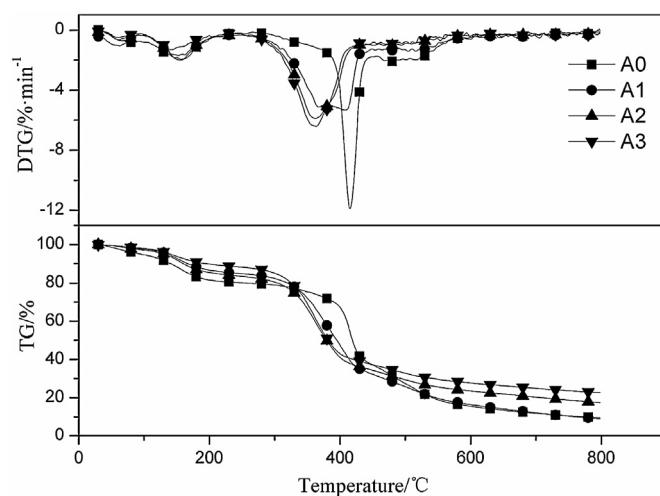


Fig. 6. TG and DTG curves of CMC-modified MF shells.

impurity phase of the paraffin. This destroys the crystalline region at lower temperature by affecting the integrity of paraffin crystallization. This is one of the reasons for the decrease of phase inversion temperature. At the same time, paraffin and the hydroxyl groups of the CMC interact through hydrogen bonds and adsorption each other. When the amount of CMC approaches a certain value, the paraffin molecules penetrate into the CMC molecules, restricting the freedom of the paraffin molecule chains at the phase inversion temperature. As a result, the phase change enthalpy is lower after the amount of CMC approaches a certain value.

3.5. Thermal stability of the CMC-modified MF shell

The thermal stability of the capsules was evaluated by TGA and DTG, as shown in Fig. 6. A two-step thermal degradation process was observed. Compared with that of A0, the TG curves of A1, A2, and A3 shifted to lower temperature and the heat decomposition rate during the second step decreased. This was because the structure of the capsule shell material changed due to the participation of CMC in the polycondensation reaction (Fig. 1) reducing the heat resistance of the shell.

4. Conclusions

In this study, nanoPCMs based on a paraffin core and CMC-modified MF shell were synthesized by an in situ polymerization method. A CMC-modified MF shell was successfully fabricated on the surface of the core material. The obtained CMC-modified microcapsules were spherical with an average diameter of 50 nm and exhibited better encapsulation and better flexibility than unmodified capsules. CMC modification also decreased the heat resistance of the capsule shells. However, the present CMC-modified microcapsules had a lower phase change enthalpy, which needs further research in the future work.

Acknowledgments

This work was supported financially by the Central University Basic Scientific Research Project of China (No. DL11EB01) and the National Natural Science Foundation of China (No. 31000277). We also thank the Postgraduate Programs Foundation of Northeast Forestry University (No. ST1P10).

References

- Benson, M. T. (2003). Density functional investigation of melamine-formaldehyde cross-linking agents. 1. Partially substituted melamine. *Industrial and Engineering Chemistry Research*, 42(18), 4147–4155.
- Gilbert, R. D. (1994). *Cellulosic polymers, blends and composites*. New York: Hanser.
- Hu, X. F., & Huang, Z. H. (2012). Preparation and characterization of CMC/melamine resin nano-encapsulated phase change energy storage materials. *Forest Engineering*, 28(4), 61–64.
- Hwang, J. S., Kim, J. N., Wee, Y. J., Yun, J. S., Jang, H. G., Kim, S. H., et al. (2006). Preparation and characterization of melamine-formaldehyde resin microcapsules containing fragrant oil. *Biotechnology and Bioprocess Engineering*, 11, 332–336.
- Karaipekli, A., Sari, A., & Kaygusuz, K. (2007). Thermal conductivity improvement of stearic acid using expanded graphite and carbon fiber for energy storage applications. *Renewable Energy*, 32, 2201–2210.
- Szabo, P. I., Ravenelle, F., Hassan, I., Preda, M., & Mateescu, M. A. (2000). Structure-properties relationship in cross-linked high-amylose starch for use in controlled drug release. *Carbohydrate Research*, 323, 163–175.
- Su, J. F., Huang, Z., & Ren, L. (2007). High compact melamine-formaldehyde microPCMs containing *n*-octadecane fabricated by a two-step coacervation method. *Colloid and Polymer Science*, 285(14), 1581–1591.
- Wang, H. P., Yuan, Y. C., Rong, M. Z., & Zhang, M. Q. (2009). Microencapsulation of styrene with melamine-formaldehyde resin. *Colloid and Polymer Science*, 287, 1089–1097.