Journal of Fiber Bioengineering & Informatics 5:1 (2012) 51–58
http://www.jfbi.org | doi:10.3993/jfbi03201204

# Preparation and Characterization of Microencapsulated $n$-octadecane as Phase Change Materials

Ruimin Cui [a], Xiaoyan Liu [a,b,*], Weidong Yu [a], Lanxi He [a]
Qingchuan Jia [a], Xiaomei Liu [a]

[a] *College of Textiles, Dong Hua University, Shanghai 201620, China*
[b] *Key Laboratory of Textile Science & Technology, Ministry of Education, Shanghai 201620, China*

**Abstract**

In this paper, a kind of microcapsule containing phase change material of $n$-octadecane was successfully synthesized based on in situ polymerization where trimethylol melamine and hexamethylol melamine were shell materials. We used different emulsification time, reaction time and different treatment to improve the quality of the microcapsules. The microcapsule and coated fabric were characterized by the optical microscope, Scanning Electronic Microscope (SEM), laser diameter distribution machine and Differential Scanning Calorimeter (DSC). The optical microscope and SEM pictures showed that this microcapsule has good surface configuration. Particle size with laser diameter distribution machine displayed that grains of the microcapsule were distributed evenly. The DSC results revealed the phase-changing temperature and enthalpy of the microcapsule.

*Keywords*: Phase Change Materials; Fabric; Microcapsule; Heat Regulation

## 1 Introduction

In recent years, functional textiles have been developed to enhance and broaden textile performance [1]. Among these, the demands of dynamic heat regulation fabric have attracted more and more attention [2]. Thermoregulated textile is a type of intelligent textile, which can change its temperature according to the environment.

Phase Change Materials (PCMs) have been used to manufacture thermoregulated textiles to improve thermal comfort of the wearer [3]. PCMs are entrapped in a microcapsule to prevent their leakage during their liquid phase [4]. These compounds possess the ability to absorb and store large amounts of latent heat during the heating process and can release this energy during the cooling process.

The selection of a PCMs formulation depends typically on the final required phase change temperature. PCMs will change phase with the temperature between the body and the outer garment

*Corresponding author.
*Email address:* xiaoyanliu@dhu.edu.cn (Xiaoyan Liu).

layer. Indeed, for textile applications [5], PCMs should have a temperature range to make the human body feel comfortable, i.e. from 18℃ to 35℃. To avoid any liquid PCMs diffusing within a fibrous substrate, these compounds need to be contained in a capsule. However, the thermal stability and mechanical property of present microcapsules are not adequate, therefore many studies have been carried out to improve the microcapsules' thermal and mechanical stabilities [6].

The shell material is very important for the thermal stability of the microcapsules. There are some materials that can be used as the shell of microcapsules, for example melamine-formaldehydes [7], Methyl Methacrylate (MMA) [8] and so on. In this paper, we used trimethylol melamine and hexamethylol melamine as the microcapsules shell due to their high reactivity, as they can shorten reaction time in situ polymerization method and improve the utilization of material. In addition, melamine-amine and hexamethylol melamine have high tensile strength, compression strength, good acid-alkali resistance and better sealing.

Microcapsules can change phases in a proper temperature range. The well known microcapsules applied to textiles are $n$-alkanes with melting temperature ($Tm$) of 18-36℃, hexadecane, heptadecane, octadecane, nonadecane, and eicosane [9, 10]. Their melting temperatures are suitable to manufacture thermoregulated fabrics. Paraffin waxes are preferred due to their high latent heat, and they are chemically inert, non-toxic and non-corrosive. Herein pure compound octadecane was used as microcapsules core material, and its melting temperature is 28℃ where people feel comfortable [11].

# 2 Experimental

## 2.1 Material

Trimethylol melamine and hexamethylol melamine used as shell materials were purchased from Shanghai Dijin Chemical Co. Ltd., China. Octadecane and paraffin were chosen as the core material. Octadecane was prepared for the encapsulation which was purchased from Sinopharm Chemical Reagent Co. Ltd., China. Paraffin was purchased from Shanghai Huayong Paraffin Co. Ltd., China.

Ammonium hydroxide and ethylic acid were used to modify pH value, which were purchased from Sinopharm Chemical Reagent Co. Ltd, China. Emulsifier XP was used as an emulsifying agent which was purchased from Shanghai Dijin Chemical Co., Ltd., China. Dispersing agent NNO was purchased from Anyang Suburb Shuanghuan Assist Agent Chemical Co., Henan, China. Absolute ethyl alcohol was purchased from Changshu Yangyuan Chemical Co. Ltd.

## 2.2 Microcapsule Preparation

Trimethylol melamine and hexamethylol melamine were used to encapsulate the core materials in this experiment.

Emulsifier XP was added into the distilled water as the emulsion, where the stirring rate was 10000 rpm at 55℃. The emulsion was adjusted to pH 4.0-5.0. Then trimethylol melamine and hexamethylol melamine were added separately into the emulsion, in which the stirring rate was

500 rpm, lasting 90-120 mins. After the reaction, the dispersing agent was added into the solution. Lastly, the pH value was adjusted to 7.0-8.0. The experimental illustration was shown in Fig. 1.

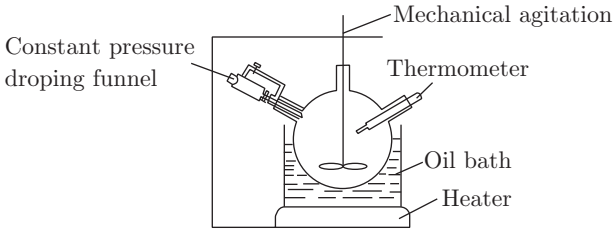



Fig. 1: The microcapsules preparation sketch

### 2.3 Microcapsules Treatment on the Fabrics

Microcapsules were coated on the fabric. The coating formulation was prepared by mixing microcapsules with the coating binder. In this study different commercial binders were used for the fixation of the microcapsules on the textile substrate. The original textile was set on a plate to assure the fabric was flat and smooth. Then a gauge thickness of 0.01 mm was selected, where the knife speed was slow to allow a homogeneous coating. Finally, the fabric substrate was coated with the microcapsule solution and binder. After coating, the fabric was firstly pre-cured at 80 ℃ for 30 mins, then dried at 120 ℃ for 5 mins.

### 2.4 Test Method

To characterize the thermal behaviour of PCMs and their microcapsules, Differential Scanning Calorimeter (DSC) analyses were conducted on a Perkin-Elmer/Pyris 1 type DSC under nitrogen atmosphere. During DSC analyses, the specimens were heated and cooled within a certain temperature ranging from 0 ℃ to 80 ℃ at 2 ℃ per mins, which is usually used in the experiments of polymer microcapsules.

Particle size distributions of the manufactured microcapsules were determined using a Ls13320 Laser Particle Size Analyzer.

SEM photos were taken to display the structural details of the microcapsules by JSM 6335 FNT. Optical microscope was also used to character the surface morphology of the microcapsules.

## 3 Results and Discussion

### 3.1 DSC Results of Microcapsules

The DSC curve of microcapsulated was shown in Fig. 2. It can be found that *n*-octadecane melted from 26.8 ℃ to 32 ℃, which is comfortable to humans. Its latent heat of fusions in terms of $\Delta$H values (140.1 J/g) was quite large.

The phase change behavior of *n*-octadecane was clearly seen from Fig. 2. In this Figure we could see that the *n*-octadecane was quite satisfactory to suit thermal comfort requirements of many textile products.

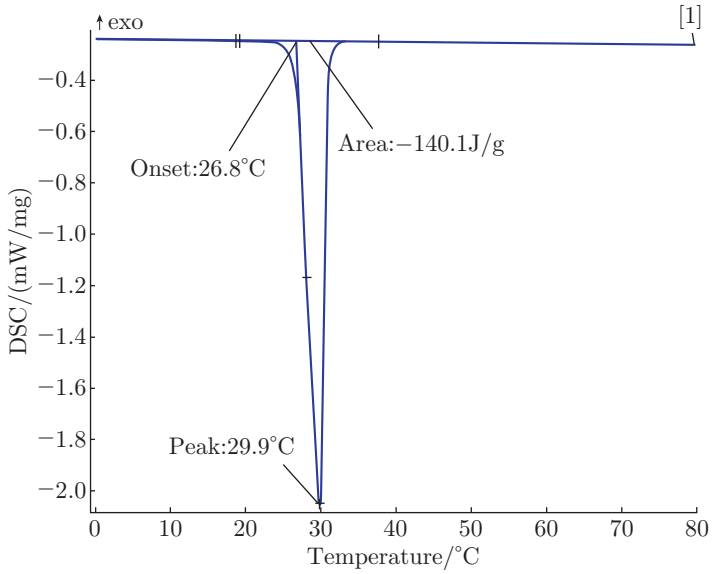
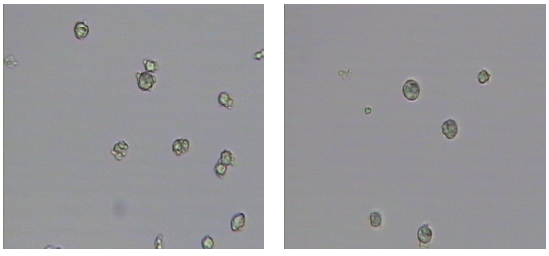



Fig. 2: DSC curve of microcapsules

## 3.2 Optical Microscope Observation of the Microcapsules

During emulsification, the stirring rate couldn't be set too low, otherwise, the *n*-octadecane micelle grain diameter will be large, and the microcapsules grain diameter will also be too large. Lastly, the stirring rate was determined as 10000 rpm. The addition of emulsifier was to make sure all the *n*-octadecane droplet could be contained by the emulsifier, and the amount of emulsifier was two times of the core materials. The phase volume ratio of the dispersed organic phase to the continuous phase was fixed to 0.5 to obtain narrow size distribution and a mean diameter of the dispersed particles within the range from 2 to 4 μm after 5 mins of stirring.

To observe the morphology of microcapsules, the optical microscope was firstly used as shown in Fig. 3. It can be observed that the microcapsules dispersed evenly and had uniform diameter. Compared to the stirring time of 5 mins with 3 mins, the diameter of microcapsules under the former time was smaller than the latter.

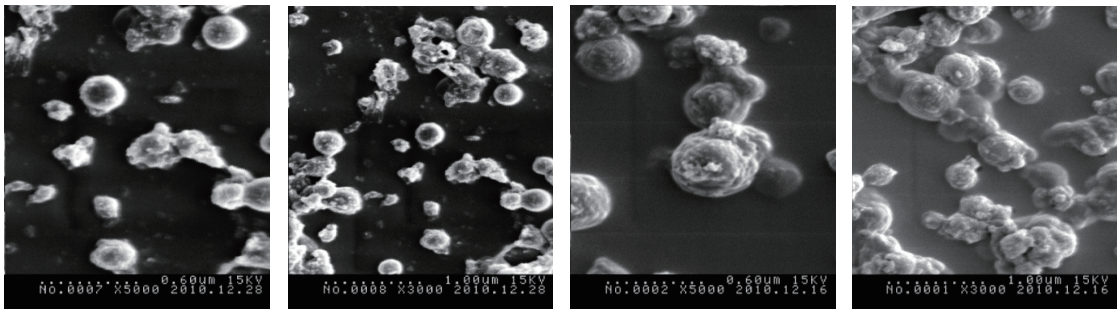


(a) (b)

Fig. 3: Optical microscope of microcapsules: (a) *n*-octadecane: XP=1:2, 10000 rpm, 3 minutes, 16×40, (b) *n*-octadecane: XP=1:2, 10000 rpm, 5 minutes, 16×40

## 3.3 SEM of the Microcapsules

At the same time, the different core materials of *n*-octadecane and paraffins were compared in this experiment. Both of the images of the microcapsules with different core materials were shown in Fig. 4. In Fig. 4 (a) and (b), the *n*-octadecane was used as core materials. In Fig. 4 (c) and (d), the core materials was paraffins. With the same fabric process, the surface morphology of *n*-octadecane was smoother and the particle size was smaller than paraffins. This may be because the *n*-alkanes chain in *n*-octadecane was smaller than paraffins. Moreover, from Fig. 4, it could be found that the size of microcapsules of *n*-octadecane was smaller than the ones of paraffins.



(a) (b) (c) (d)

Fig. 4: SEM of the microcapsules with different core materials: (a) *n*-octadecane×5000; (b) *n*-octadecane ×3000; (c) paraffins×5000; (d) paraffins×3000

## 3.4 Particle Size Distribution

In order to discover the dispersion of the microcapsules in the solution clearly, the particle size was measured by a Ls13320 Laser Particle Size Analyzer.

Fig. 5 illustrates how the microcapsules sizes varied within the range from less than 1 μm to 60 μm. Because the microcapsules particle was very small, they were easy to aggregate; therefore a different action step was used to reduce the microcapsules aggregation.

In Fig. 5 (a), the dispersing agent was added to the sample at a stirring rate of 600 rpm for 10 minutes; Fig. 5 (b) shows ultrasonication for 1 hr after the Fig. 5 (a) procedure; Fig. 5 (c) shows the sample without dispersing agent was ultrasoniced for 1 hr.

The particle size diameter is shown as the Table 1.

Table 1: Particle size of the samples with different treatment

| Samples | 0.5 g dispersing agent | 0.5 g dispersing agent ultrasonication 1 hr | Ultrasonication 1 hr |
|---|---|---|---|
| Mean diameter (μm) | 14.23 | 5.256 | 18.31 |

It could be seen the diameters of particle size were different from each other, which may result from the different type of treatment.

The Fig. 5 (b) showed the smallest particle size, i.e. the one that had dispersing agent added and then ultrasonication as the best treatment, where the particle size was evenly distributed and the average value was 5.256 μm, which was the smallest of the three treatments.

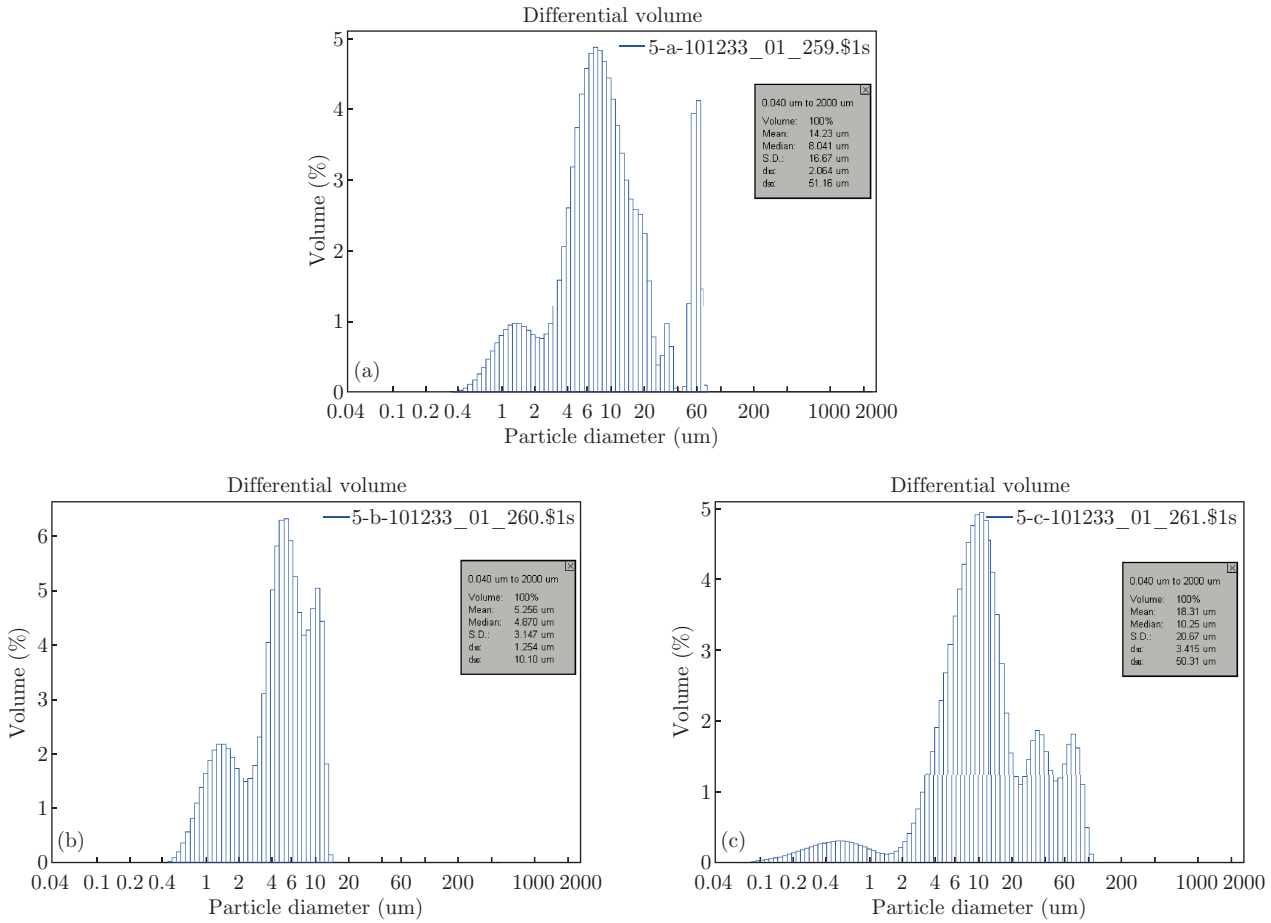



Fig. 5: Particle size distribution of the microcapsules with different after-treatment: (a) 0.5 g dispersing agent; (b) 0.5 g dispersing agent+ultrasonication 1 hr; (c) ultrasonication 1 hr

Obviously, the dispersing agent can reduce the particle aggregation, moreover, the distribution of particles will be more even and be smaller after ultrasonication treatment.

The particle size distributions also changed when the reaction time was different. In Fig. 6 (a), trimethylol melamine and hexamethylol melamine were added, and heated for 1 hr and 1.5 hr respectively at 55 ℃; Fig. 6 (b) trimethylol melamine and hexamethylol melamine were added, and heated for 1.5 hr and 2 hr respectively at 55 ℃.

The particle size diameter is shown in Table 2.

Table 2: Particle size of the samples with difference reaction time

| Samples | 1 hr+1.5 hr | 1.5 hr+2 hr |
|---|---|---|
| Mean diameter (μm) | 5.256 | 4.314 |

The mean diameter of microcapsules was 5.256 μm under the former condition, while the average diameter decreased to 4.314 μm when the reaction time increased. Actually, it could be seen that 50% of microcapsules were smaller than 3.851 μm in Fig. 6 (b), and some were lower than 1.234 μm.

Based on the particle distribution under the above condition, we can summarize that the dispersing agent and ultrasonication were important during the encapsulation, and the reaction

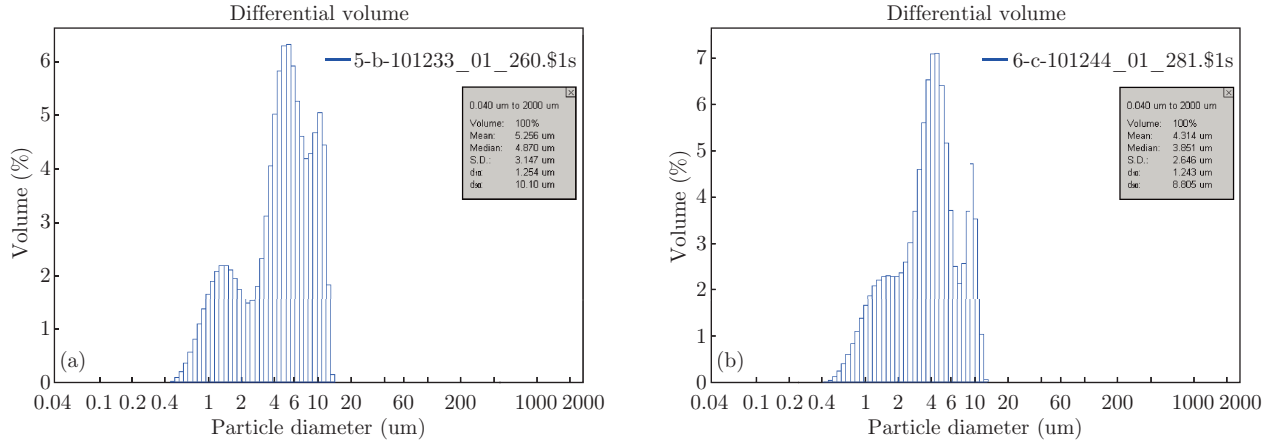



Fig. 6: particle size distribution of the microcapsules with different reaction time: (a) 1 hr+1.5 hr; (b) 1.5 hr+2 hr

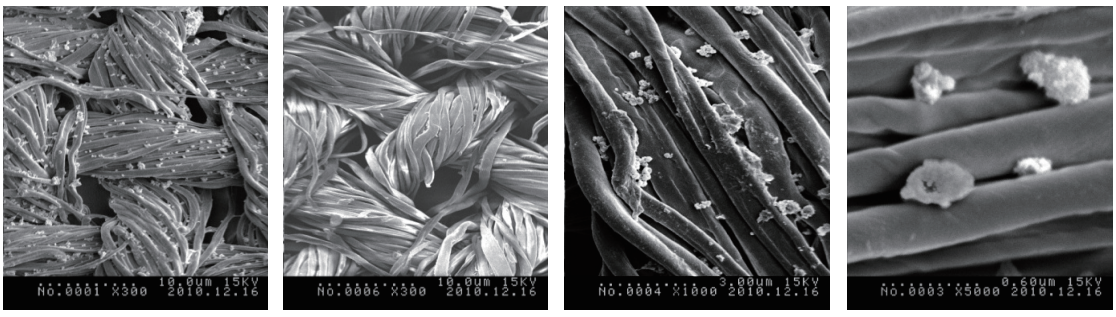
time also took effect during the interfacial polycondensation. The reaction was sufficient when the time increased, but once the reaction time rose to a certain extent, the influence was not obvious.

In addition, the stirring rate was also one of the important factors affecting the size of particle. The lower the stirring rate was, especially after the second monomer was added into the polymerization process, the larger the capsule sizes became.

## 3.5 The Morphology of the Fabrics Treated with Microcapsules

The coating fabrication was prepared by mixing microcapsules with the coating binder, and some commercial binders were applied for the fixation of the microcapsules on the textile substrate, and the chitosan was finally chosen as the binder. Chitosan formed a component adhesive film on the fabric surface with high cohesiveness, and microcapsules was also stuck to the fabric firmly. The film of the chitosan and microcapsules made the fabric having a good rubbing fastness and softness, without adhering to the knife in printing and net printing, and not blocking the fabric hole. Compared with other adhesives, chitosan has special advantages such as antibacterial, biodegradable and biocompatible, and having higher absorption to water imbibition and higher whiteness. In this paper, 10g of microcapsules solution and 15 g of chitosan were prepared, which was then coated on the fabric.

The morphology of the original and treated fabric is shown in Fig. 7. In Fig. 7 (c), microcapsules



(a) (b) (c) (d)

Fig. 7: SEM of fabric: (a) coated fabric × 300, (b) original fabric × 300, (c) coated fabric × 1000, (d) coated fabric × 5000

dispersed evenly on the fabric. The core and the shell of the microcapsule can be seen clearly in the Fig. 7 (d).

# 4 Conclusion

The microcapsules were synthesized in this paper based on the core of *n*-octadecane and shell of both of trimethylol melamine and hexamethylol melamine in situ polymerization, while only one material was used as shell in many research. The DSC curve confirmed that *n*-octadecanes serviced as the core materials were suitable for fabrics application in the microcapsule. Seen from the particle size distribution, the procedure of dispersion and ultrasonication was necessary, and the 2 hr reaction time was better. Using chitosan as the binder, the coating fabrication was obtained. Observed in the SEM, microcapsules were distributed evenly on the fabric surface.

# Acknowledgement

This work was supported by the Key Laboratory of Textile Science & Technology, Ministry of Education (SP1001), and Shanghai University Students Innovation Program (101-03-0127021).

# References

[1] Koo K, Choe J, Park Y. The application of PCMM -s and SiC by commercially direct dual-complex coating on textile polymer. Applied Surface Science 2009, 255: 8313-8318.

[2] Wang SX, Li Y, Hu JY, Tokura H, Song QW. Effect of phase-change material on energy consumption of intelligent thermal-protective clothing. Polymer Testing 2006, 25: 580-587.

[3] Nelson G. Application of microencapsulation in textiles. International J 2002; 242: 55-62.

[4] Nelson G. Microencapsulation in textile finishing. Review of Progress in Coloration 2001; 31: 57-64.

[5] Mondal S. Phase change materials for smart textile-an overview. Applied Thermal Engineering 2008; 28: 1536-1550.

[6] Jiang MJ, Song XQ, Ye GD, Xu JJ. Preparation of PVA/paraffin thermal fiber by in situ microcapsulation. Composites Sci and Tech 2008, 68: 2231-2237.

[7] Nihal S, Emel O. The manufacture of micro encapsulated phase change materials suitable for the design of thermally enhanced fabrics. Thermochimica Acta 2007; 452: 149-160.

[8] Xu J, Wan X, Zhang BQ, Wang Y, Guo BH, Zhang YP, Wang X. Preparation of phase, change material wax/p (MMA-co-AA ) core-shell microcapsules. Acta Polydmerica Sinica 2009; 11: 1154-1156.

[9] Fang GY, Hui L. Preparation and characterization of nano-encapsulated n-tetradecane as phase change material for thermal energy storage. Chemical Engineering J 2009; 153: 217-221.

[10] Sánchez P, Victoria M. Development of thermo-regulating textiles using paraffin wax microcapsules. Thermochimica Acta 2010; 498: 16-21.

[11] Salaün F, Devaux E. Thermoregulating response of cotton fabric containing microencapsulated phase change materials. Thermochimica Acta 2010; 506: 82-93.