PREPARATION AND CHARACTERIZATION OF N-HEXADECANE/POLYCAPROLACTONE PHASE-CHANGE MICROCAPSULES VIA SINGLE-NOZZLE ELECTROSPRAYING

Shengchang ZHANG[1], **Christine CAMPAGNE**[1], **Fabien SALAÜN**[1]

[1] *ENSAIT, GEMTEX – Laboratoire de Génie et Matériaux Textiles, F-59000 Lille, France*
Correspondence: shengchang.zhang@ensait.fr Tel.:+33 (0) 3 20 25 86 91

ABSTRACT
In this study, single-nozzle electrospraying was used to prepare microencapsulated phase change materials. The effects of core/shell (n-hexadecane/polycaprolactone) mass ratios on the structure, morphology and thermal properties, were analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). A ratio about 50/50 was found as the most suitable to fabricate microcapsule with a narrow microcapsule sizes distribution, a complete core-shell structure and a smooth surface. Furthermore, the encapsulation efficiency in n-hexadecane reaches maximum at this ratio value. Finally, not only interesting latent heat can be obtained from these microcapsules, but also improved thermal stability of n-hexadecane.

Key words: phase-change microcapsule, n-hexadecane, polycaprolactone, electrospraying, structure and morphology

1. Introduction

Thermal comfort refers to the condition of mind, which expresses satisfaction with the thermal environment. The thermal sensation and thermal comfort of the human body is influenced by various factors, such as the environmental climate (rainy, cloudy, sunny), the clothing and human perceptions. Furthermore, thermal comfort is mainly governed by the existence of a microclimate between the skin and the clothing layer. The characteristics of this microclimate depend not only on the human and environmental parameters but also on the clothing factors such as the thickness of materials and the clothing insulation (i.e. porous structure or breathability). The human being a homeotherm may maintain constant its body temperature through exchanges with the environments by different phenomena as conduction, convection, radiation, and evaporation. Thermal insulation in garment provides from the use of a full structure, which entraps air [1]. Since the three last decades, a new type of materials, phase change materials (PCM), has been introduced in the textile field to improve thermal regulation. These materials can store or release a significant amount of latent heat, during their phase change transition when the increase or decrease of the surrounding temperature. Therefore, they become attractive to the energy storage system and thermal-regulated applications [2]. The possibility of keeping the wearer as long as possible in his thermal comfort zone, and at the same time to reduce the thickness of the clothing layer is a conceivable objective, with the functionalization of textile fabric with PCM materials.

The main drawbacks to use PCM in textile finishing are related to their low thermal conductivity, and since they are sometimes in a liquid state, they cannot be directly applied without being contained in a capsule to prevent any leakage during the phase change transition of PCM [3]. The microencapsulation allows increasing the specific surface contact area with air or textile to improve the heat transfers or thermal exchanges. Until now, many processes have been proposed to synthesize the microencapsulated PCMs, such as the in-situ polymerization, the interfacial polymerization, the gel-sol method, the simple or complex coacervation, the phase separation method or emulsification method, and the spray drying. The various drawbacks of the methods mentioned above in the preparation of phase-change microcapsules, are the use of toxic substances, chemical additives and surfactants, and the

difficulty in the control of structure as well as morphology (i.e. size, shape and porosity). Those problems may be overcome with the use of electrospraying process [4]. Indeed this method, as an electrohydrodynamic atomization technology, has great potential and advantages to realize polymeric microcapsules or nanocapsules in a green and simple way. In addition, it prevents particles aggregation and allows obtaining a narrow and mono-dispersed particles size distribution. The control in the size, shape and surface porosity of microcapsules is carried out via the adjustments of the solution properties and operating parameters. Besides, the functional coating of phase-change microcapsules on the surface of textiles may be achieved directly during electrospraying using the fabric as the collector. This process has the advantage to provide a functional coating with improved properties in terms of durability and thermal comfort, while maintaining the breathability and flexibility of the fabric [5].

Therefore, fabrication and development of electro-encapsulation PCMs via electrospraying is is strategically interesting, and any study that would provide new insights into the process could be of value. Moghaddam et al. [6] have prepared n-nonadecane/sodium alginate phase-change microcapsules using coaxial nozzle electrospraying. Their study aims to verify the feasibility of coaxial nozzle electrospraying to fabricate phase change microcapsules with complete core-shell structure and analyze the influences of sodium alginate concentration and process parameters on the structure, morphology and thermal properties of the obtained microcapsules. Apart from coaxial nozzle electrospraying, single-nozzle electrospraying also has potential and advantages to prepare phase change microcapsules. On the one hand, stable cone-jet mode, which is the precondition to prepare microcapsules with narrow size distribution and high encapsulation efficiency, is more accessible in single-nozzle electrospraying. On the other hand, the microcapsules with the random distribution of PCMs can be also prepared from single-nozzle electrosraying. However, until now, no publication uses electrospraying with single-nozzle to fabricate phase change microcapsules. The effects of core/shell mass ratio on the structure, morphology and thermal properties of electrosprayed phase change microcapsules have not been studied either. Furthermore, in order to reduce the release of toxic substances during the production and use of electrosprayed microcapsules, green, biocompatible and biodegradable shell materials should be also tried in electro-encapsulation process.

In this work, we have checked the ability to synthesize microcapsules containing a phase change material entrapped by a polycaprolactone (PCL) shell. The microcapsules were prepared using a single-nozzle electrospraying process with ethyl acetate as a green solvent. This study aims to investigate the influence of PCM/PCL mass ratio on the structure and thermal properties of electrosprayed particles. Microcapsules were characterized in terms of thermal properties by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA), and morphological structure by scanning electron microscopy (SEM).

2. Materials and Methods

2.1 Materials

n-Hexadecane (PARAFOL® 16-97) with a purity grade of 97 % was used as lipophilic phase to be a core material obtained from Sasol Performance Chemicals (Germany). The latent heat of raw n-hexadecane in melting and crystallization analyzed from DSC are -137.31 and 131.17 $J.g^{-1}$, respectively. The thermal degradation temperature of raw n-hexadecane ranges from 150 °C to 250 °C. A polycaprolactone (PCL) (Capa®TM 6400, mean molecular weight: 37,000 g/mol) was purchased from Perstorp (Skåne County, Sweden) and was used as wall materials. Ethyl acetate (analytical reagent) was employed as green solvent and purchased from Sigma Aldrich (France).

2.2 Preparation of n-hexadecane/PCL electrospraying solutions

PCL electrospraying solutions were prepared by dissolving 5wt% of PCL pellets in ethyl acetate at 40 °C under stirring for 1 h to allow complete dissolution, and cooled at room temperature. n-Hexadecane, in appropriated quantities to reach the mass ratio of 30/70, 50/50 and 70/30, was further added in 10 g of this solution, and stirring was maintained 2 hours for homogenization.

2.2 Fabrication of n-hexadecane/PCL phase-change microcapsules via electrospraying

A CAT000002 Electrospraying Starter Kits purchased from Spraybase® AVECATS (Kildare, Ireland) was applied to carry out the electrospraying of n-hexadecane/PCL solutions. Firstly, 10 mL mixture was added into a plastic syringe, and then the mixture was pumped into a plastic tube and further flowed out from a single nozzle (outer diameter: 460 μm, inner diameter: 260 μm). The flow rate of electrospraying solution was software controlled by syringe pump (Spraybase® AVECATS, Kildare, Ireland), and fixed at 1 mL/h in this study. The working distance from nozzle to collector was set at 17 cm. High voltage (4.0 kV) generated from a high-voltage generator (Spraybase® AVECATS, Kildare, Ireland) was applied between the nozzle and collector. During electrospraying, temperature and relative humidity were maintained at 25 °C and 45%, respectively. Finally, electrosprayed microcapsules were collected onto grounded metal dish during a collecting time of 5 h.

2.3 Measurements and characterizations

Scanning electron microscopy (SEM) (JEOL Model JSM-5900, Tokyo, Japan) was used to determine the mean diameter and the particle size distribution, as well as the surface morphology of the eletrosprayed phase-change microcapsules. The accelerated voltage was 20 kV. 100-500 random microcapsules were selected from SEM images to be analyzed via Image J software.

The thermal behavior of the electrosprayed microcapsules was recorded using differential scanning calorimetry, DSC (DSC 3+, Mettler Toledo, USA), at a heating and cooling rate of 5 °C/min heating rate under a constant stream of nitrogen (50mL/min), from -20 to 80°C. When temperature reaches to 80 °C, samples were maintained for 5 minutes to eliminate any previous thermal history and cooled at a rate of 5 °C/min. So, the melting endotherm and the crystallization exotherm of the samples were recorded in a second cycle in the same conditions.

The thermal stability of the microcapsules was analyzed by using a thermal gravimetric analyzer (TGA 3+, Mettler Toledo, USA) under inert atmosphere at a purge rate of 50 mL/min. Heating rate of 10 °C/min was use from 20 to 700 °C. For each experiment, 3 to 8 mg was used in the TGA test.

The practical loading content ($LC_p\%$), theoretical loading content ($LC_t\%$) and Encapsulation efficiency ($EE\%$) of n-hexadecane in the microcapsules were calculated via equations (1), (2) and (3) [7].

$$LC_p\% = \Delta H_{microcapsule} / \Delta H_{n\text{-}hexadecane} \times 100 \quad (1)$$

Where $\Delta H_{microcapsule}$ (J/g) and $\Delta H_{n\text{-}hexadecane}$ (J/g) are the melting enthalpy of encapsulated n-hexadecane and raw n-hexadecane, respectively. All values were determined from the second cycle in DSC analysis.

$$LC_t\% = M_{n\text{-}hexadecane} / M_t \times 100 \quad (2)$$

Where $M_{n\text{-}hexadecane}$ is the mass of n-hexadecane used in process and M_t is the total mass of PCL and n-hexadecane added in process.

$$EE\% = LC_p / LC_t \times 100 \quad (3)$$

3. Results and discussions

3.1 The morphology of electrosprayed n-hexadecane/PCL microcapsules

Spherical n-hexadecane/PCL microcapsules have been prepared with various core/shell ratios via single-nozzle electrospraying (Figure 1). The mean diameters of various samples are also reported in Table 1. From the solution without PCM, the obtained particles have a mean diameter of about 11.00 μm, a narrow size distribution, and most of them present a smooth surface and single-pore morphology. The addition of a low content of n-hexadecane in the formulation allows reducing the size of the pore, and nonporous and smooth microcapsules is obtained at higher addition of n-hexadecane. Furthermore, when the mass ratio n-hexadecane/PCL increased to 30/70, the mean diameter of microcapsules increases to 16.7 μm, and the size distribution becomes wide. Thus, on the one hand, the encapsulation of n-hexadecane in PCL matrix results in an increasing of mean diameter. On the other hand, the phase separation between n-hexadecane and PCL results in a difficulty for PCL matrix to entrap n-hexadecane molecular homogeneously based on the poor compatibility between n-hexadecane and PCL. That is why the size distribution of particles become widening under this mass ratio. With further increasing this mass ratio to 50/50, under higher concentration of n-hexadecane in PCL solution, it is accessible for major n-hexadecane molecular to mix with PCL molecular, then, the phase separation between PCL and n-hexadecane is depressed. Therefore, n-hexadecane can be entrapped homogeneously by PCL molecular in ethyl acetate, and n-hexadecane/PCL microcapsules with narrow size distribution can be fabricated (Figure 1c). Meanwhile, the mean diameter of microcapsules decreases to 15.3 μm. With further increasing this mass ratio to 70/30, it difficult for limited PCL matrix amount to encapsulate completely excessive n-hexadecane. Therefore, core n-hexadecane component is surrounded by a blend of n-hexadecane and PCL. It not only results in an increasing of mean diameter of microcapsules to 21 μm, but also a widening of size distribution.

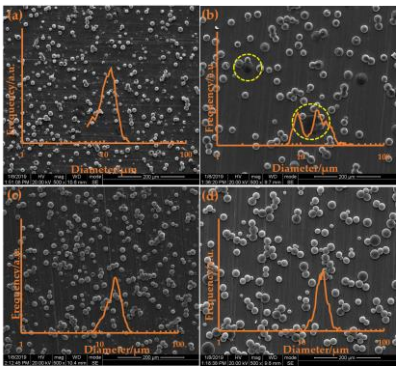

Figure 1. the SEM images of (a) neat PCL microspheres (b) n-hexadecane/PCL (30/70) microcapsules (c) n-hexadecane/PCL (50/50) and (d) n-hexadecane/PCL (70/30)

Table 1. The mean diameter of electrosprayed particles, encapsulation efficiency, loading content and latent heat of n-hexadecan in microcapsules

Mass ratio between n-hexadecane and PCL	Mean diameter/μm	Encapsulation efficiency/%	Loading content/%	Melting latent heat/(J/g)	Crystallization latent heat/(J/g)
0/100	11.0±2.5	-	-	-	-
30/70	16.7±6.4	78.3	23.5	-32.3	31.7
50/50	15.3±3.2	92.0	46.0	-63.2	61.7
70/30	21.0±5.6	84.3	59.0	-81.0	78.6

3.2 The thermal behaviours of electrosprayed n-hexadecane/PCL microcapsules

In Figure 2 and Table 1, with the increasing of the n-hexadecane amount, the latent heat of the microcapsules increase gradually, and those of PCL shell decrease. The encapsulation

efficiency and loading content of n-hexadecane in microcapsules are also listed in Table 1. When the mass ratio between n-hexadecane and PCL is 30/70, the LC_p% of n-hexadecane reaches 23.5 %, and the *EE%* is 78.3%. It might be related with the poor compatibility between n-hexadecane and PCL molecular and the phase separation process in this case. When this ratio increases to 50/50, this phase separation phenomenon is depressed, and mojor n-hexadecane molecular is entrapped by PCL matrix.Therefore, the LC_p% and *EE%* of n-hexadecane reaches 46% and 92%, respectively. The melting and crystallization latent heat of microcapsules reach 63.2 and 61.7 $J.g^{-1}$, respectively. Under these lower mass ratios, the distribution of encapsulated n-hexadecane might mainly locate in the centre of PCL matrix and be surrounded by complete PCL shell. After the first heat treatment of DSC, n-hexadecane still keep dispersed phase inside PCL matrix, which can lead to the obtention of two crystallization phases in the second cooling process from DSC according to the size of these domains and the confinement [8]. Further increasing this mass ratio to 70/30, although the LC_p% and *EE%* of n-hexadecane reaches 59% and 84.3%, respecticely, it is difficult for limited PCL to encapsulte completely excessive n-hexadecane. Major microcapsules consist of the core of n-hexadecane and the shell of a blend of n-hexadecane and PCL. Therefore, the crystal peak of n-hexadecane in this microcapsule changes to one peak due to the continuous phase of n-hexadecane in second heat treatment of DSC.

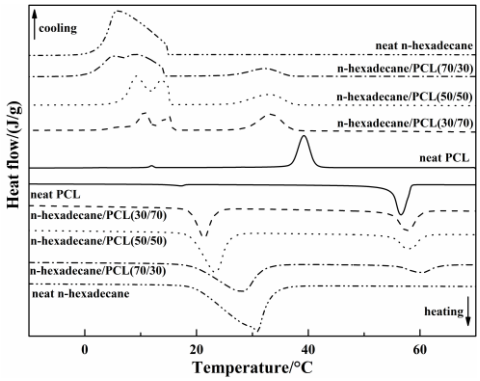

Figure 2. the DSC curves of n-hexadecane, PCL and n-hexadecane/PCL microcapsules

3.3 The thermogravimeter analysis of electrosprayed n-hexadecane/PCL microcapsules

The thermal stability of n-hexadecane/PCL microcapsules was characterized by TGA. Meanwhile, the location of n-hexadecane in PCL microcapsules can be also analyzed by TGA curves. In Figure 3, the thermal degradation of n-hexadecane carried out from 150 to 250 °C. When n-hexadecane locates inside PCL shell and is surrounded completely by PCL shell, its thermal degradation rate will be depressed. When this mass ratio increases to 30/70 or 50/50, two thermal degradation steps can be observed in TGA curves. The first step is related with the thermal degradation of n-hexadecane, and the second step is related with the thermal degradation of PCL matrix. Compared with raw n-hexadecane, the higher thermal degradation temperature of n-hexadecane in first stage indicates that n-hexadecane tends to locate inside PCL matrix under these relatively lower mass ratio. Meanwhile, compared with the microcapsules obtained from the mass ratio 30/70, the microcapsules obtained from 50/50 have higher thermal degradation temperature in the first degradation process. It indicates that the location of n-hexadecan molecular is farther from the shell and is closer to the cemtre of particles in this mass ratio 50/50. Furthermore, more complete core-shell structure and higher thermal stability of microcapsules can be obtained from this mass ratio. With further increasing this mass ratio to 70/30, three thermal degradatioin steps can be observed from TGA curves. Under this mass ratio, microcapsule consists of a core of n-hexadecane and a

shell of a blend of n-hexadecane and PCL. Therefore, the first step is related with the degradation of the n-hexadecan located on the surface of microcapsules. And the second step is related to the degradation of n-hecadecane distributed in the centre of microcapsules. The third step is related with the degadation of PCL matrix. It indicated that the complete core-shell structure of microcapsule will be destroyed under higer mass ratio between n-hexadecane and PCL.

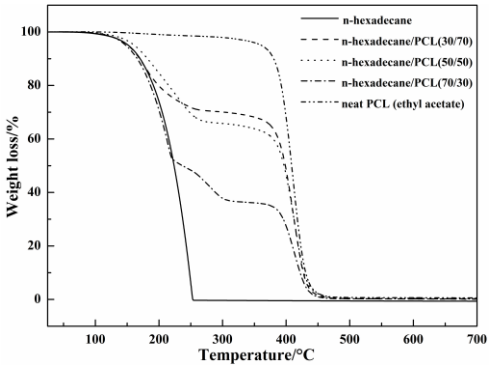

Figure 3. the TGA curves of pure n-hexadecane, PCL and n-hexadecane/PCL microcapsules

4. CONCLUSIONS

Single-nozzle electrospraying is an effective method to prepare n-hexadecane/PCL phase change microcapsules. The morphologies, structure and properties of final production are influenced by the mass ratio between n-hexadecane and PCL. When this ratio reaches 50/50, n-hexadecane/PCL microcapsule with a mean diameter of 15±3.2 μm, a complete core-shell structure, a narrow size distribution and a spherical as well as smooth morphology can be fabricated. Meanwhile, the thermal stability, loading content and encapsulation efficiency of n-hexadecane in microcapsules can be improved.

5. REFERENCES

1. F. Salaün, *The manufacture of microencapsulated thermal energy storage compounds suitable for smart textile, In Developments in heat transfer,* IntechOpen, 2011, 171-198.
2. S. Mondal, Phase change materials for smart textiles-an overview, *Applied Thermal Engineering*, 2008, 28(11-12), 1536-1550.
3. A. Sarı, C. Alkan, A. Karaipekli and O. Uzun, Microencapsulated n-octacosane as phase change material for thermal energy storage, *Solar Energy*, 2009, 83(10), 1757-1763.
4. S. Zhang, C. Campagne and F. Salaün, Influence of solvent selection in the electrospraying process of polycaprolactone, *Applied Sciences*, 2019, 9(3), 402-438.
5. C. Güneşoglu, D. Kut and M. Orhan, Performing the electrospraying process for the application of textile nano finishing particles, *Textile Research Journal*, 2010, 80(2), 106-115.
6. MK. Moghaddam, SM. Mortazavi and T. Khayamian, Preparation of calcium alginate microcapsules containing n-nonadecane by a melt coaxial electrospray method, *Journal of Electrostatics*, 2015, 73, 56-64.
7. JC. Roy, S. Giraud, A. Ferri, R. Mossotti, J. Guan and F. Salaün, Influence of process parameters on microcapsule formation from chitosan-Type B gelatin complex coacervates, *Carbohydrate polymers*, 2018, 198, 281-293.
8. H. Zhang and X. Wang, Fabrication and performances of microencapsulated phase change materials based on n-octadecane core and resorcinol-modified melamine-formaldehyde shell, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2009, 332(2-3), 129-138.