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Facile and highly efficient microencapsulation of a phase change material using tubular microfluidics

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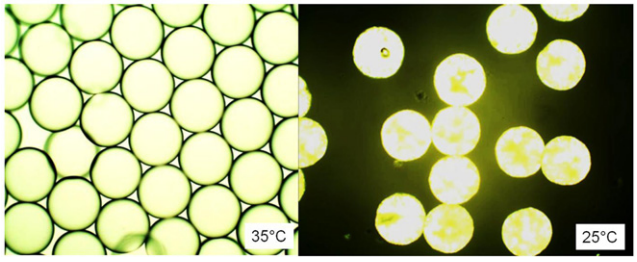
HIGHLIGHTS

- We develop a simple preparation method for highly monodisperse PCM microcapsules.
- Tubular microfluidic device facilitates controls of size and morphology of PCM microcapsules.
- Monodisperse PCM microcapsules show narrow melt-crystalline transitions.

GRAPHICAL ABSTRACT

Optical and POM images of *n*-octadecane@polyurea microcapsules prepared in a tubular microfluidic device.



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ABSTRACT

This paper presents a microfluidic approach towards the fabrication of highly monodisperse polyurea microcapsules, 35–500 μm in size, containing *n*-octadecane (phase change material, PCM). The synthesis consisted of the following two steps: (i) emulsification of *n*–octadecane, isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) in an aqueous mixture of tetraethylenepentamine (TEPA), poly (vinyl alcohol) and sodium dodecyl sulfate (SDS)and (ii) *in situ* polycondensation between TEPA and IPDI along and outside the tube length. The resulting PCM@polyurea microcapsules underwent a rapid and repeated liquid/solid phase transformation at different temperatures. The average sizes and morphology of the microcapsules were controlled by tuning the flow rate of either the continuous or discontinuous phase. The morphology, polycondensation and phase change behavior of the microcapsules were investigated by optical microscopy equipped with a thermostat plate, scanning electron microscopy, Fourier transform infrared spectroscopy and differential scanning calorimetry. The effect of the hydrophobic Fe_3O_4 nanoparticles (NPs) on the crystallization behavior was also examined in cases of microcapsules with or without NPs.

1. Introduction

The process of microencapsulation of specific materials has remarkable applications in a range of areas [1–7]. Phase change materials (PCMs) with higher thermal energy storage density, narrower operating temperature range and higher thermal conductivity have attracted overwhelming attention due to the depletion of fossil fuel resources and increasing demand for eco–friendly energy resources [8], because they can absorb or release large amounts of latent heat at their melting/crystallization temperatures. Therefore, they can be used potentially in active or pumped coolants, solar and nuclear heat storage systems and heat exchangers [9].

Recently, different polymeric materials, such as melamine-formaldehyde (MF) resins [10], urea-formaldehyde (UF) resins and

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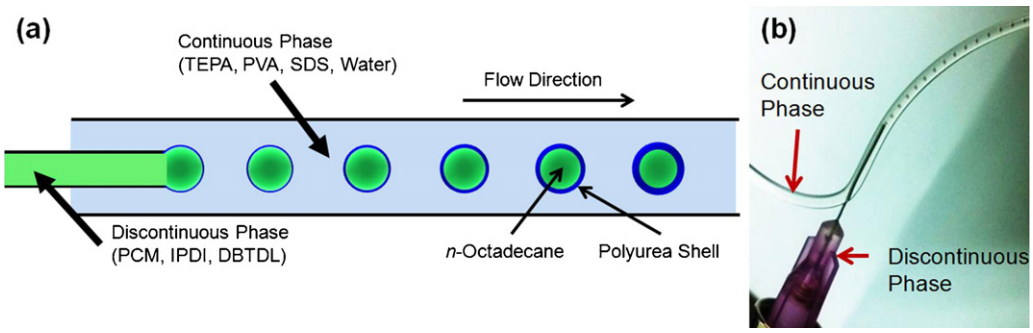

Fig. 1. (a) Schematic diagram of the fabrication of monodisperse PCM@polyurea microcapsules in a tubular microfluidic device and (b) photograph of O/W PCM droplets produced at the tubular junction. Emulsification and partial polycondensation occur in the flow stream at 35 °C.

polyurethanes (PUs) [11–14], have been selected as the core materials for protective shell preparation in microcapsules with PCMs for use in thermoregulated fibers, fabrics, foams and building materials [15–18]. Both physical (spray drying, coating processes, etc.) [19–21] and chemical (coacervation, interfacial polymerization, *in situ* polymerization, etc.) [22–26] methods have been used for the microencapsulation of PCMs. The specific size range of microcapsules can be tailored for specific applications, e.g. 1–10 μm for carbonless copying paper [27], 30–50 μm for microcapsules containing pesticides[28] and 10–50 μm for microcapsules encapsulating perfumes [29]. On the other hand, the conventional methods for the encapsulation of materials have disadvantages, such as multistep reaction procedures, large polydispersity in size, wide variability in structure and a wide range of encapsulation inefficiencies. Droplet microfluidics provides a versatile approach for the production of highly controlled and monodisperse emulsion-based templates, which can be used for various encapsulation purposes [30,31].

This paper reports a facile and an effective approach for fabricating highly monodisperse PCM@polyurea microcapsules using a tubular microfluidic technique. The *n*-octadecane, which was chosen as a PCM, is a linear hydrocarbon with $T_m \sim 27–29$ °C that has been studied extensively in nano- or microencapsulation owing to its large latent heat (214–216 J/g) [32]. Typically, PCM@polyurea microcapsules, 35–500 μm in size, were obtained by simply tuning the flow rate of either the continuous or discontinuous phase. The variation in the phase change temperature of *n*-octadecane in the presence/absence of Fe_3O_4 NPs was also studied. The current synthesis approach has an advantage over conventional and PDMS-based microfluidic methods. The tubular-based microfluidic device used does not have to undergo any tedious surface modification to create an oil-in-water (O/W) emulsion [33–37]. The fabrication of tubular-based microfluidic devices does not require any soft lithography or laser etching techniques. Therefore, the devices offer an exciting opportunity to be implanted rapidly and inexpensively in any industrial laboratory or research center for the production of polymeric particles with a range of encapsulation materials.

2. Experiment

2.1. Materials and methods

n-Octadecane (99%), sodium dodecyl sulfate (SDS, purity > 98.5%), poly(vinyl alcohol) (PVA, M_n = 85,000–146,000 g/mol, 96% hydrolyzed), tetraethylenepentamine (TEPA), isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were purchased from Sigma–Aldrich and used as received. Ultra-pure water (resistivity > 18.2 MΩ cm, Direct-Q, Millipore Co., USA) was degassed and used for all experiments. A 1 mL glass syringe (Hamilton, USA, I.D. = 4.61 mm) was used to inject the discontinuous phase and a 30 mL disposable plastic syringe (HSW, NORM-ECT, Germany, I.D. = 22.9 mm) was used in the case of a continuous phase. The tubular fluidic device was assembled by inserting a 30 G needle (NanoNC, Korea) into Tygon® microbore tubing (SAINT-GOBAIN PPL, France, I.D. = 515 μm). The flow rates of the two solutions were controlled independently in a coflow regime using two high precision infusion pumps (Legato 200, KD Scientific, USA). Fig.1 shows a schematic diagram of the microfluidic device.

2.2. Emulsification and microencapsulation

In the representative synthesis, the flow rates of the two infusion pumps were fixed to 8.0 μL/s and 0.5 μL/s for continuous (aqueous) and discontinuous (organic mixture) phases, respectively. The continuous phase is a mixture of water (94 wt%), SDS (2 wt%), PVA (2 wt%) and TEPA (2 wt%). In the case of the discontinuous phase, the PCM (*n*-ctadecane) to IPDI mass ratio was fixed to 3:1. The 0.5 wt% Fe_3O_4 NPs (refer to ESI-1) were added to the organic phase to examine the change in crystalline structure of the encapsulated PCM core. DBTDL (0.2 wt%) was added to the organic phase for complete polycondensation between IPDI and TEPA. At the tip of the needle, the organic phase breaks into spherical monodisperse droplets in an aqueous mixture to produce an O/W emulsion. The O/W droplets were then partially solidified by polycondensation along the tubing length and finally received in a collecting reservoir to perform the remainder of the polycondensation. The formation of O/W droplets and their size were closely related to capillary number (Ca, $\mu V/\gamma$, μ = viscosity, V = velocity), representing the relative effect of viscous forces vs. the interfacial tension (γ) between the two immiscible phases of co-flowing stream [38]. In this study, the Ca values were varied from 0.006 to 0.11 by adjusting the flow rate of the continuous phases.

2.3. Characterization

The complete process of emulsification and polycondensation of the PCM droplet was monitored by optical microscopy (Nikon, ECLIPSE LV 100D, Tokyo, Japan) equipped with a video camera (Moticam 2300, Motic, Beijing, China). Bright field images were also captured at different temperatures to examine the melting/crystallization behavior. The surface morphology of the dried microcapsules was observed by scanning electron microscopy (SEM, S-4300, Hitachi, Japan). Before SEM analysis, the microcapsules were vacuum dried in a freeze dryer (ILShinLab, FTD 8503, S. Korea).

Fourier transform infrared (FT-IR, FT-IR 8400S, Shimadzu, Japan) spectroscopy of the microcapsules was performed over the range, 400–4000 cm^{-1}. The samples were dried completely under vacuum before analysis. The dried sample was mixed with KBr by grinding and compressed into a pellet. The thermal properties of the