Effects of Stirring Rates and Dodecyl Mercaptan on Nanocapsules Containing N-Octadecane Prepared by Miniemulsion Polymerization

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Abstract: Nano-encapsulated *n*-octadecane (NanoPCMs) was synthesized by miniemulsion polymerization using styrene-divinybenzene co-polymer as shell and *n*-octadecane as core. The experimental results show that, the stirring rate of 6000 rpm is suitable for the nano-encapsulation. Dodecyl mercaptan (DDM) has great influence on the morphology of NanoPCMs. When DDM was employed in miniemulsion polymerization, the fabricated nanocapsules are almost spherical and their surfaces are smooth. The enthalpy of the nanocapsules is 84 $J.g^{-1}$, which corresponds to 37 wt% *n*-octadecane. The super-cooling was not observed in the DSC cooling curve.

Keywords: nanocapsule, n-octadecane, miniemulsion polymerization, styrene

1. Introduction

Phase-change materials (PCMs) can absorb, store, and release large amounts of latent heat over a defined temperature range during the melting/solidifying process [1]. However, PCMs are difficult to be used directly in practical applications because of solid-liquid state change, weak thermal stability, low thermal conductivity, volume expansion, et al. Microencapsulated phase change materials (MicroPCMs) are composed of a PCM core and a polymer or inorganic shell to maintain the shape and prevent PCM leakage during the phase change process. Nanocapsules of functional substances with a diameter lower than 1μm has been widely studied for the application of drug, dye, perfume [2] and functional textiles, et al. Zhang et al fabricated a kind of nanocapsules by *in situ* polymerization, in which melamine-formaldehyde resin was used as the shell and *n*-octadecane as the core [3]. Miniemulsion polymerization is a promising method of the direct encapsulation technique for preparing nanocapsules. The encapsulation is very sensitive to the recipe and other system parameters because of the strict thermodynamic and kinetic requirements [4-6]. Therefore, a well-defined core-shell structure is not easy to obtain. Luo et al synthesized nanocapsule of liquid substance by the interfacial confined RAFT miniemulsion polymerization [7]. In this paper, nanocapsules with polystyrene as the shell and *n*-octadecane as the core were synthesized by miniemulsion polymerization, and the effects of stirring rates and DDM on morphologies**,** thermal stable and phase change properties were also discussed.

2. Experimental

2.1 Materials

Styrene (St, purity 98 wt%, Tianjin Chemical Reagent Factory) and divinybenzene (DVB, purity 45 wt%, Tianjin Yuanli Chemical Co., Ltd.) were used as shell-forming monomers. St was washed with sodium hydroxide to remove the inhibitor and calcium chloride as the desiccant to keep for 24 h. *n*-octadecane (95 wt%, Union Lab. Supplies Limited, Hong Kong) was used as the core material. Benzoyl peroxide (BPO, purity 99 wt%, Tianjin Chemical Reagent Co., Ltd.) was used as an initiator. Sodium dodecyl sulfate (SDS, A. R., Tianjin Guangfu Chemical Co., Ltd.) and Polyoxyethylene(10) nonyl phenyl ether (NP-10, Tianjin VAS Lab Supplies Co., Ltd.) were employed as emulsifiers. Dodecyl mercaptan (DDM, A.R, Tianjin Yuanli Chemical Co., Ltd.) was used as the chain transfer agent.

2.2. Fabrication of nanocapsules

First, NP-10 and SDS were dissolved in distilled water. The oil phase of *n*-octadecane, St, DVB and BPO were prepared. The oil phase was added into the aqueous surfactant solution by continuously stirring. A miniemulsion was then obtained by emulsifying the mixture with a homomixer at stirring rate of 6000 rpm for about 10 min. The resultant miniemulsion was transferred to a 250 mL three-neck-flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen gas inlet tube. The flask was placed in a thermostatic water bath. After 15 min nitrogen purge, the temperature was raised to 90 ^{o}C and kept for 5 h with a stirring rate of 300 rpm. The resultant mixture was washed with hot water and cyclohexane, filtered to remove impurities, and then dried in an oven at 50 ^{o}C until the mass was a constant.

The fabrication process of St-DVB co-polymer as follows: the water phase was made up of 0.2 g NP-10,

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0.3 g sodium dodecyl sulfate and 100 g distilled water. The oil phase was composed of styrene, divinybenzene and benzoyl peroxide. The reaction condition was the same as the fabrication of nanocapsules. The resultant mixture was filtered and washed with hot water. The pure St-DVB co-polymer was produced.

2.3. Characterization of Nanocapsules

Spectra of *n*-octadecane, St-DVB co-polymer and nanocapsules were obtained using a Fourier Transformed Infrared Spectroscopy (FTIR, BRUKER, TENSOR37, wave number 4000-400 cm^{-1}) at room temperature.

The morphologies of the nanocapsules were examined by using a Scanning Electronic Microscope (SEM, HITACHI, S-4800). A drop of the nanocapsules dispersion was dripped on a stainless steel SEM stub and allowed air-dry overnight.

The core/shell structure of the nanocapsule was characterized by a Transmission Electron Microscope (TEM, HITACHI, H-7650). The diluted emulsion (1 wt% solid content) was mounted on carbon-coated popper grids and was left to dry at room temperature before analysis.

The samples were gold-coated. The nanocapsules size and its distribution were measured by a diameter distribution analyzer (HORIBA, LA-300).

The thermal resistance of dried nanocapsules was investigated by using a Thermogravimetric Analyzer (TG, NETZSCH, STA 409 PC/PG TG-DT) at a scanning rate of 10 ^{o}C/min in the range of 25-600 ^{o}C under a nitrogen atmosphere. Here, the thermal resistant temperature ($T_{0.05}$) is defined as the temperature at which 5% weight loss occurred.

The thermal properties of the nanocapsules were measured using a Differential Scanning Calorimeter (DSC, PERKIN ELMER, DSC7) at a heating or cooling rate of ±5 ^{o}C /min in the range of -20-80 ^{o}C in a nitrogen atmosphere. The content of *n*-octadecane in the nanocapsules can be estimated according to the measured enthalpy:

$$x = \frac{|\Delta H|}{|\Delta H_0|} \times 100\% \qquad (1)$$

where, x is the weight percentage content of *n*-octadecane; $|\Delta H|$ is the enthalpy of nanocapsules; $|\Delta H_0|$ is the melting enthalpy of *n*-octadecane.

3. Results and discussion

3.1. Effects of the stirring rate on diameter

Figure 1 shows diameter distribution curves of nanocapsules fabricated with various stirring rates during emulsifying process. The stirring rates were set as 4000, 6000, 8000 and 9000 rpm for about 10 min in the miniemulsion step, respectively. Diameter distribution curves of nanocapsules with the stirring rate of 4000 rpm appear two peaks, the average diameter is about 11 μm. By contrast, when the stirring rate is of 6000, 8000 and 9000 rpm, the average diameters are 0.4, 0.3 and 0.25 μm, respectively. The diameter of the nanocapsule decreases with the increase of stirring rate, meanwhile the diameter distribution becomes narrower.

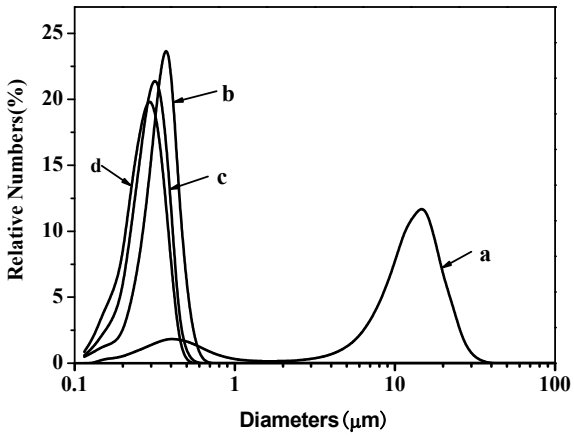


Figure 1. Diameter distribution curves of nanocapsules fabricated with various stirring rates: (a) 4000 rpm; (b) 6000 rpm; (c) 8000 rpm; (d) 9000 rpm.

3.2 Effect of DDM on morphology

Figure 2 shows SEM micrographs of nanocapsules with different contents of DDM. The nanocapsule fabricated without DDM is a hemisphere particle (Fig. 2a). When the content of DDM is 0.016 g, nanocapsules are almost spherical and their surfaces are smooth (Fig. 2b). This is probably due to the change of the surface tension between the oil phase and water phase in the presence of DDM, which acts also as an emulsifier [8].

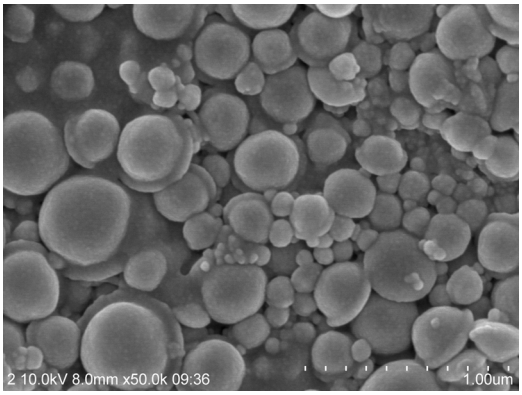
3.3 TEM of nanocapsules

The TEM image of the resultant nanocapsules is presented in Figure 3. It is visible that most of the particles have well-defined core-shell morphology. However, the solid particles composed of St-DVB co-polymer also exists. The thickness of the shell is about 40 nm.

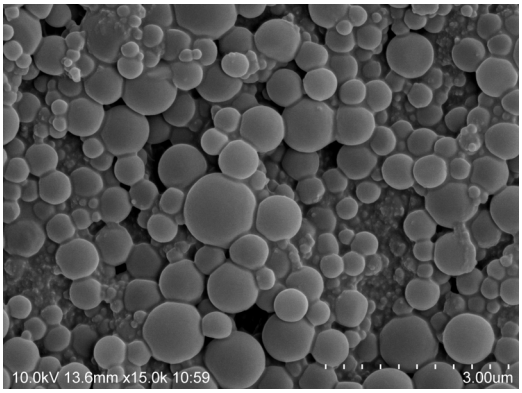
3.4 Thermal properties of nanocapsules

Figure 4 shows DSC curves of *n*-octadecane, Sample B containing 0.016 g DDM and St-DVB co-polymer. An endothermic peak and an exothermic peak are not observed in the DSC curve of St-DVB co-polymer. During the endothermic process, the enthalpies of *n*-octadecane and Sample B are 229 $J.g^{-1}$ and 84 $J.g^{-1}$, respectively. The shell composition of the nanocapsules has no effect on the melting temperature. The experimental results show that the super-cooling is not observed in the DSC

cooling curve of Smaple B, it is different from those of the previous study [3]. To some extent, the result may be affected by un-reacted monomer and other impurities. The discrepancy in effects of diameters on the crystallization temperature needs to be studied further.



(a)



(b)

Figure 2 SEM micrographs of nanocapsules with different contents of DDM: (a) sample A without DDM; (b) sample B containing 0.016 g DDM.

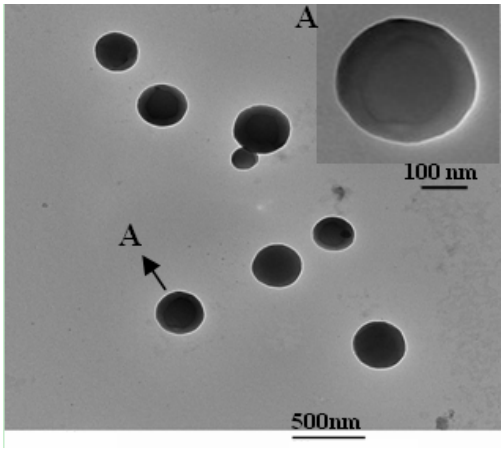


Figure 3. TEM image of Sample B containing 0.016 g DDM

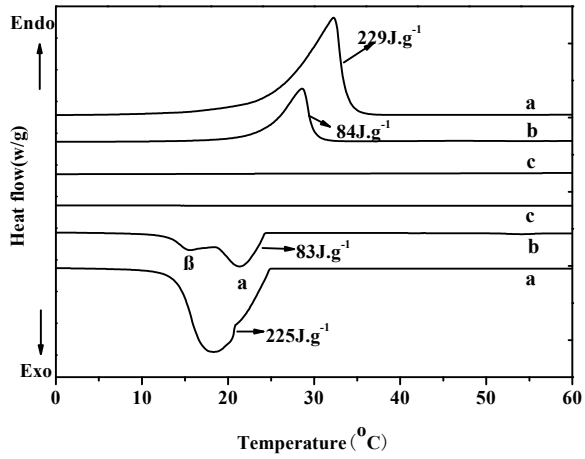


Figure 4 DSC curves of samples: (a) *n*-octadecane; (b) Sample B containing 0.016 g DDM; (c) St-DVB co -polymer.

4. Conclusions

Nanocapsules were synthesized by miniemulsion polymerization using styrene-divinybenzene co-polymer as shell and *n*-octadecane as core. When the stirring rate is above 6000 rpm, nanocapsules containing *n*-octadecane with an averaged diameter lower than 0.4μm are fabricated. Chain transfer agent- Dodecyl mercaptan also acting as an emulsifier, has great influence on morphology. When 0.016 g DDM was employed in miniemulsion polymerization, the fabricated nanocapsules are almost spherical and their surfaces are smooth. The enthalpy of the nanocapsules containing 37 wt% *n*-octadecane is 84 $J.g^{-1}$, and the super-cooling was not observed in the DSC cooling curve.

Acknowledgments

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