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Microencapsulation of n-hexadecane as phase change material by suspension polymerization

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Abstract: In this study, suspension polymerization is described to fabricate microcapsules containing n-hexadecane as phase change material. In the suspension polymerization, casein is employed as emulsifier and stabilizer instead of synthetic surfactant. Microcapsules with polystyrene as shell and n-hexadecane as core have an average diameter of 3~15μm and the size distribution are narrow. Thermal properties are investigated by differential scanning calorimetry (DSC) showing that the microcapsules can store and release an amount of latent heat over a temperature range nearing the melting point of pure n-hexadecane. The latent heat of fusion of microencapsulated n-hexadecane decreases after microencapsulation. The melting point of microencapsulated n-hexadecane is near but higher than that of pure n-hexadecane, and the polymerization time has little effect on the melting point.

Keywords: microencapsulation; suspension polymerization; casein; polystyrene; thermal properties

Introduction

Microcapsules are minute containers enclosing core materials within shell materials. The shell is often made of thin synthetic or natural polymers. Recently, a variety of microencapsulation techniques have been developed for applications in many areas such as drug delivery, [1] dye dispersion, [2] catalysis, [3] display media, [4] cosmetics [5] and food production [6].

Phase change materials (PCMs) can absorb, store and release large amounts of latent heat over a defined temperature range while they change their phases or states. More than 6000 kinds of materials have been found and investigated to be suitable for PCMs use [7]. PCMs is always microencapsulated, and that has been studied by many researchers [7-11] and developed by some companies like BASF. Microencapsulation of PCMs was studied for applications in thermal fields such as heating and conditioning of buildings, thermal insulation, thermal adaptable fibers and so forth.

The most common methods to prepare microcapsules of PCMs are interfacial polycondensation and in-situ polymerization. The n-octadecane (core)/polyurea (shell) microcapsules were prepared by Jeong-Sook Cho et al., [12] using an interfacial polycondensation method with toluene-2,4-diisocyanate (TDI) as oil-soluble monomer and diethylenetriamine (DETA) as water-soluble monomer in an emulsion system, they used n- octadecane as a phase change material and NP-10 [poly(ethylene glycol) nonylphenyl ether] as an emulsifier. Jun-Kyu Choi et al. [13] have prepared microcapsules containing tetradecane by in-situ polymerization, they used melamine-formaldehyde to form the polymeric shell, and styrene-maleic anhydride-monomethyl maleate copolymer (SMA) was selected as an emulsifier. In interfacial polycondensation one monomer is often dispersed through emulsifying, then, another monomer is added to react with the former at the liquid-liquid interface. In in-situ polymerization to prepare microcapsules, it is utmost important to control the reaction conditions to ensure the polymer produced should aggregate onto the liquid-liquid interface, and there is a need to make precursor polymer with low molecular weight. In the above methods, it is necessary to chose one or several surfactants to act as emulsifier. It is also important to use emulsifier in suspension polymerization to make perfect products.

Casein is an amphiphilic protein, it has excellent emulsifying properties when it is in solution and dispersed form [14, 15]. Owing to its good solubility, surface activity, heat resistance and water-holding property, casein is widely used as an emulsion stabilizing agent in foods such as ice-cream, coffee whitener, cream liqueurs and whipped toppings. [16]

In this study, our goal is to develop a new method to make microencapsules, which is easier than other methods. We only use casein to emulsify the mixture of core materials, monomers and initiators. Casein is a protein with good amphiphathy like HAS (human serum albumin), casein molecules can strongly adhere to the oil-water interface [17] and form protein multilayer [18-20] to protect and stabilize the fine oil droplets against recoalescence before microcapsules are formed. The polymerization takes place in the mini-container surrounded by casein multilayer.

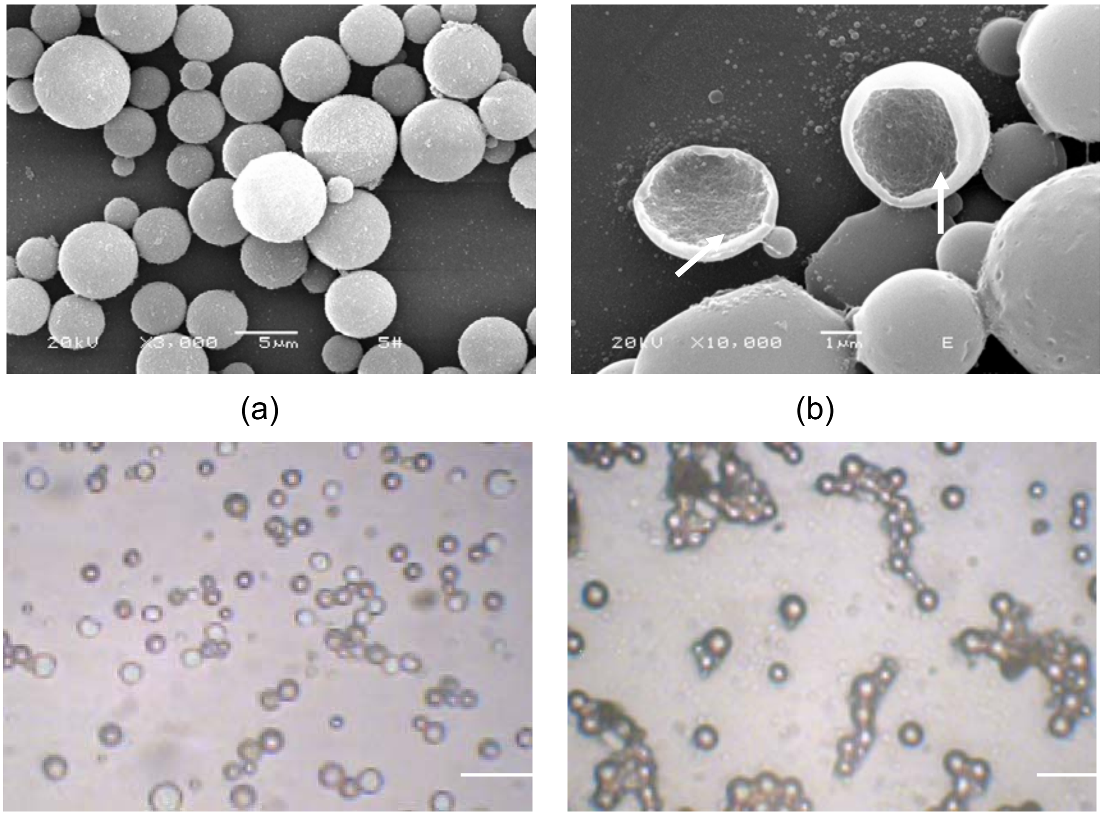
Results and discussion

Particle morphology and size distribution

SEM micrograph of microcapsules prepared with n-hexadecane is shown in Fig.1a and damaged particles made with no DVB in the recipe are shown in Fig.1b respectively. From Fig.1a, we can see that the microcapsules are spherical and the surface is smooth, and we can not tell whether the particles are hollow or multi-porous. We present another picture in Fig.1b in which the damaged particles (labelled with white arrows) clearly show the hollow structure. To obtain the damaged hollow particles, we did not use any DVB in the recipe as cross-linking agent while the other polymerization parameters remained the same. It makes the polymer shell more fragile not using DVB than using DVB in the recipe, thus the particles with no DVB are more susceptible to damage.

The concentration of casein solution affects the result of experiments. We used casein of different concentration, ranging from 0.5%(Wt) to 2.0%(Wt) in the polymerization recipe. The result is that if casein concentration is low the recoalescence of particles are likely to happen in the early course of polymerization, resulting in a few huge particles or particles coacervation. Fig.1c shows OM photograph of one sample made with the casein concentration being 1.5%(Wt), Fig.1d shows OM photograph of another sample made with casein concentration being 0.75%(Wt). In Fig.1d, most of the particles are bonded together.

Fig. 2 shows the particle size distribution of prepared microcapsules. The size of most of the resulted capsules was below 15 μm, and the size distribution was narrow. The sample had an average diameter of 5.387 μm and the microcapsules with a diameter between 3 μm and 15 μm dominated their volume fraction. With sufficient amount of casein in solution, the size of microcapsules was determined by the agitation speed of the homomixer in the stage of emulsifying.



(a) (b)

(c) (scale bar = 20μ m) (d) (scale bar = 20μ m)

Fig. 1. SEM graphs (a, b) and OM photographs(c, d) of microcapsules containing n-hexadecane as phase change material.

Fig. 3. describes the effect of agitation speed on the average particle size. The average diameter decreased when the agitation speed increased, but the effect became small and the average diameter maintained constant when the agitation speed was over 7000 rpm.

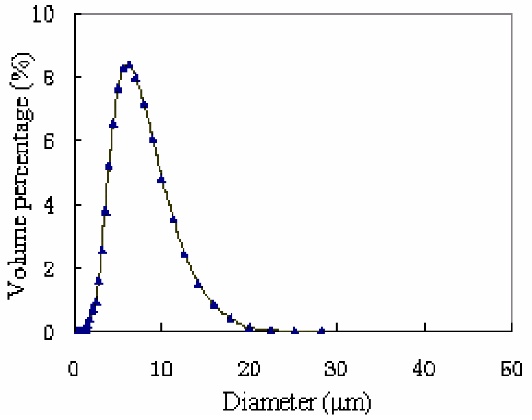


Fig. 2. Size distribution of microcapsules containing n-hexadecane.

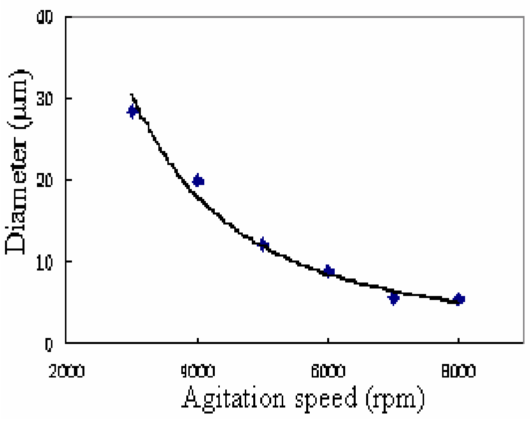


Fig. 3. Effect of agitation speed on particle size.

FT-IR spectra

FT-IR spectra of the microcapsules containing n-hexadecane is presented in Fig. 4. It is found that the C-H aromatic stretching vibration is at 3081.7cm^{-1}, 3060.1 cm^{-1} and 3025.8 cm^{-1}, the C-H stretching vibration is at 2954.4 cm^{-1}, 2923.4 cm^{-1}, 2870.5 and 2852.1 cm^{-1}. The absorption band at 1600.9 cm^{-1}, 1492.4 cm^{-1} and 1452.0 cm^{-1} belong to the phenyl ring stretching vibration. The ring in phase C-H stretching vibration is at 1027.9 cm^{-1}, and the ring out-of-plane bend at 697.5 cm^{-1}.

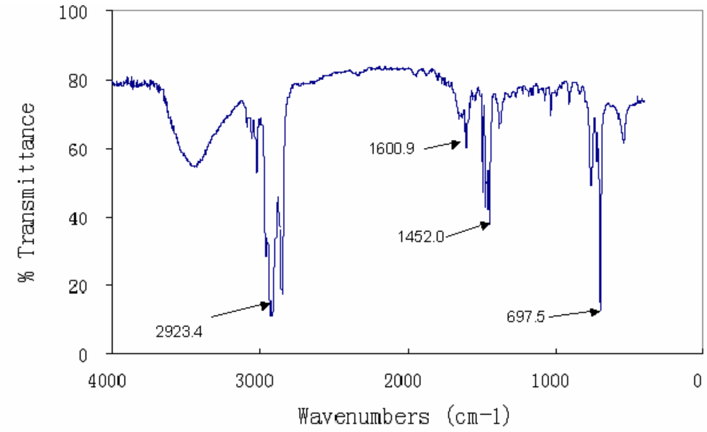


Fig. 4. FT-IR spectra of microcapsules with n-hexadecane as core and PSt as shell.

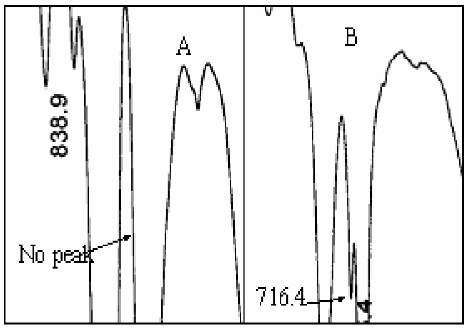


Fig. 5. FT-IR spectra of microspheres (**A**) and microencapsules(**B**).

The absorption peaks at wave numbers of 1470.1 cm^{-1}, 1377.3 cm^{-1} correspond to -CH_2- and -CH_3- respectively. Moreover, at band 716.4 cm^{-1}, there is a relatively strong absorption peak, it is attributed to $-(CH_2)_n-$, where n≥4, means the existence of aliphatic alkane (n-hexadecane). Fig. 5 shows the comparison of the FT-IR spectra of microcapsules (curve **B**) with that of microspheres (curve **A**) which had been made without HD encapsulation. In Fig. 5, curve **A** has no absorption peak near 716 cm^{-1}. From FT-IR spectra, it is clear that the microcapsules contain n-hexadecane.

Thermal properties

The thermal properties of the microcapsules were evaluated using DSC analysis, the DSC diagram of heat storage and release capacities of one sample is shown in Fig. 6. The core materials encapsulated in the PSt shell showed a phase change over a temperature range of 15.52-29.57 ^{0}C with a peak at 22.74 ^{0}C, and the latent heat of fusion was 80.25J/g. As to pure n-hexadecane, the melting point and latent heat of fusion are 16.7 ^{0}C and 236 J/g [21]. In DSC, there is no evidence of glass transition, indicating a high degree of cross-linking of polystyrene by DVB.

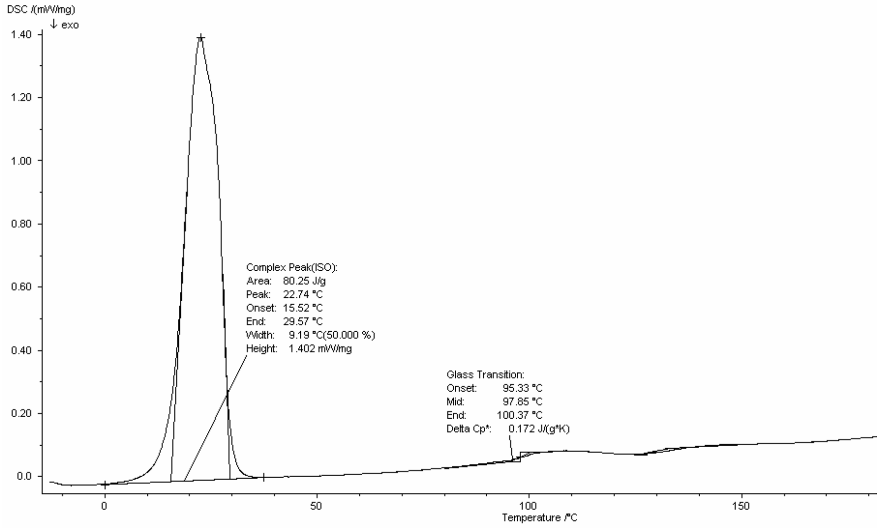


Fig. 6. DSC diagram of microcapsules.

The melting point and latent heat of fusion of encapsulated n-hexadecane exhibited some differences with those of pure one. The melting point and the latent heat of fusion of samples prepared with different polymerization time are shown in Fig. 7 and Fig. 8 respectively. From Fig.7, we see that polymerization time had little effect on the melting point of enclosing material and the melting point of microencapsulated material in the 5 samples were between 22~25 ^{0}C. We believe that the impurity of n-hexadecane raise its melting point. In the microcapsules, n-hexadecane is not the only one encapsulated, there are St and DVB that were not exhausted in the polymerization, there are also polymer molecules dispersed or dissolved in the mixture. For the five samples showed in Fig. 8, their latent heat of fusion were 124.7, 106, 86.11, 76.01 and 80.25 J/g, which were much smaller than that of pure n-hexadecane (236J/g). Jeong-Sook Cho et al. reported latent heat of fusion to be 62.6~112 J/g [12] and Xing-Xiang Zhang et al. reported 91.10~190.62 J/g [22] for encapsulated octadecane; Zou Guang-Long and coworkers reported about 50 J/g [21] of latent heat for encapsulated n-hexadecane, all were smaller than those of pure one. The decrease in heat of fusion is quite typical in microencapsulation of PCMs and it is a weak point of this technology, in this case, we think the impurity of n-hexadecane may also affect the latent heat of fusion, because the unexhausted monomers may absorb much smaller heat compared with the melting of n-hexadecane. To know exactly the reason of decrease in heat of fusion, further research should be carried out.

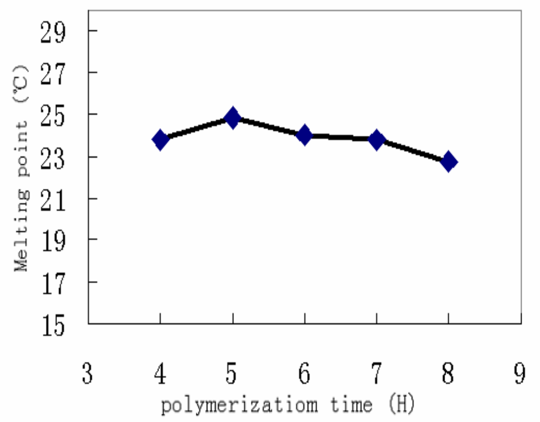


Fig. 7. Effect of polymerization time on the melting point of microencapsulated n-hexadecane.

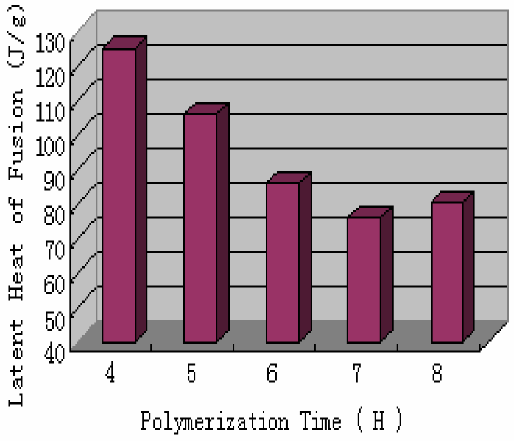


Fig. 8. Latent heat of fusion of samples with different polimerization time.

Mechanism of microcapsule formation

The schematic in Fig. 9 can describe the process for making hollow particles with phase change materials encapsulated in polymer shell. The first stage is emulsifying the oil phase into aqueous phase. Casein molecules strongly adsorb onto the oil-water interface and stabilize the fine oil droplets which then act as mini-reactors through the whole polymerization period. Precipitation polymerization takes place within the oil droplets after the temperature is elevated to 70 ^{0}C. The n-hexadecane is good solvent for monomers but non-solvent for polystyrene, and as monomer is consumed, the polymer formed becomes progressively less compatible with the monomer/alkane mixture, phase separation of polymer occurs, resulting polymer particles precipitate and move to the interface of oil droplets.

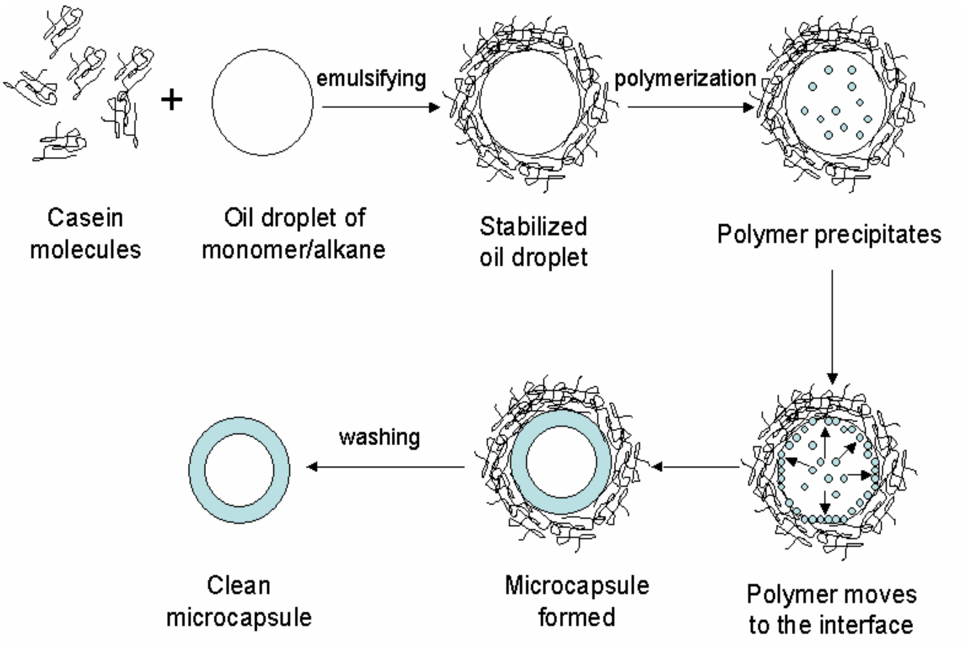


Fig. 9. Schematic of the fabrication process of microcapsule with a suspension polymerization

It is believed that this surface concentration of precipitated polymer is preferentially formed because the water-polymer interface has the lowest interfacial energy in the system [23]. The interfacial polymer can react with the monomer around them to form an enhanced polymer shell. The little amount of DVB in the monomer mixture is used as cross-linking agent to improve the shell quality.

Conclusions

In summary, polystyrene microcapsules containing n-hexadecane as phase change material was prepared by suspension polymerization using casein instead of any other kinds of synthetic surfactant as emulsifier. Unlike interfacial polycondensation and in-situ polymerization, our method is an easy method and many other monomers can be chosen to make microcapsules with different polymer shell.

The microcapsules are spherical and the surface is smooth. The diameter of most of the microcapsules was below 15 μm, and the size distribution was narrow. With sufficient amount of casein in solution, the size of microcapsules was determined by the agitation speed of the homomixer in the stage of emulsifying. The average diameter decreased when the agitation speed increased, but the effect became small and the average diameter remained constant when the agitation speed was over 7000 rpm.

The microcapsules can store and release an amount of latent heat over a temperature range nearing the melting point of pure n-hexadecane. The melting point of microencapsulated core material is near but higher than that of pure n-hexadecane, and the polymerization time has little effect on the melting point. The microcapsules are envisioned to have applications in thermal fields such as heating and conditioning of buildings, thermal insulation etc.

Experimental part

Materials

Styrene (St) that came from Damao Chemical Reagent Factory (Tianjin, PR China) was washed with 0.5 M NaOH solution and then purified by distillation under reduced pressure prior to using. Divinylbenzene (DVB) from Kelong Chemical Factory, Chengdu (PR China) was washed with 0.5 M NaOH solution to get rid of inhibitor before use. Benzoyl peroxide (BPO) purchased from Chemical Factory of Hubei University (PR China) was used as initiator and without any pre-treatment. n-Hexadecane (HD) was used as supplied from Kelong Chemical Factory, Chengdu (PR China). Casein obtained from Kelong Chemical Factory, Chengdu (PR China) was treated with EDTA (1% Wt) for 48 h to reduce metal ions before use. All chemical agents were analytically pure and all water in the experiment was de-ionized.

Preparation of microcapsules

Microcapsules of n-hexadecane were prepared by suspension polymerization. First, to obtain casein solution, 3.0 g dry pretreated casein and 0.1g Na_2CO_3 were added to 100 g de-ionized water in a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer. Then, the mixture was dissolved at 50 ^{0}C for 2 hours under mechanical stirring. 0.12 g initiator (BPO) was dissolved in 4.8 g HD. After the casein solution was cooled, the monomer mixture (6.6g St + 0.6g DVB) and 4.8 g HD with initiator dissolved were emulsified into 54 g 1.5% (Wt) casein solution by a homomixer BME-100LX (from Shanhai Weiyu machinery and electronics CO., LTD, PR China) in 8000 rpm for 20 seconds.

The above emulsion was transferred to a four-necked glass flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet nozzle. The nozzle was lifted above the surface of the emulsion after the emulsion had been purged with nitrogen for 1 hour, and the temperature was elevated to 70 ^{0}C gradually for the polymerization. The polymerization was carried out continuously at 70 ^{0}C for 8 hours. The obtained microcapsules were washed by water for at least 5 times, and then dried at 50 ^{0}C in a vacuum drying oven for 24 hours to eliminate any volatile matter (water, monomer, n-hexadecane) from the surface of the particles.

Characterization of microcapsules

The study of size and size-distribution of microcapsules were carried out on a laser analyzer for particle size (Mastersizer 2000, Malvern) which provides a Gaus curve concerning the distribution of microcapsules size (volume percentage abundance versus diameter) using the diffractive mode of light.

An optical microscope (BME M/3) and a scanning electron microscope (JEOL JSM 5900LV) were used to investigate the morphology of the surface and the inner structure of the microencapsules. As to SEM, one drop of the microcapsule dispersion was placed on a nickel SEM stub and air-dried; then the dried sample was gold-coated.

The chemical structure of the shell polymer and the core material was determined by using IR spectroscopy (Nicolet MX-1E). The sample which had been dried in a vacuum oven was ground with dried potassium bromide (KBr) powder and compressed into a disc.

The thermal properties of the capsules containing n-hexadcane were measured by differential scanning calorimetry (NETSCH DSC 204) with a N_2 flow rate of 30 ml/min. The scanning temperature range and heating rate were -30~200 ^{0}C and 10 ^{0}C /min, respectively.

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