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ORIGINAL CONTRIBUTION

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Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system

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Abstract Microcapsules containing phase-change material for thermal adaptable fiber application were synthesized and characterized. The microcapsules of about 1 μm in diameter were prepared using an interfacial polycondensation method with toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) as monomers in an emulsion system. Octadecane was used as a phase-change material and NP-10 which is nonionic surfactant, was used as an emulsifier. To investigate the reaction ratio of monomers, microcapsules were synthesized with 3 g TDI and 0–4 g DETA. Polyurea microcapsules were formed not only by reaction with TDI and DETA, but also by reaction of TDI with hydrolyzed TDI at the interface. TDI was reacted with DETA in the weight ratio of 3:1. NP-10 was reacted with TDI to form urethane. The microcapsules containing octadecane showed a phase change of octadecane at 29–30 °C. The core content measured using the heat of fusion of octadecane was less than that calculated. The efficiency of octadecane encapsulation increased as the core content decreased.

Keywords Microcapsules · Interfacial polycondensation method · Octadecane · Encapsulation · Polyurea

Introduction

Microcapsules are particles composed of a protective matrix (shell) and one or more active materials (core substance). The protective matrix or shell of the microcapsule is a natural or a synthetic polymer. The active ingredient of a microcapsule is usually a solid or liquid; however, it may also be a gas [1]. Microcapsules are prepared by polymerizing a shell of polymer around a core particle. A wide range of core materials have been encapsulated, including adhesives, drugs [2], agricultural aids, paper coatings, fragrant oils, dyes, enzymes, etc.

A given core material can be encapsulated in the form of a solution, emulsion, or dispersion process. The particle size of a microcapsule is usually determined at this step of core droplet formation [3]. In emulsion polymerization in the presence of emulsifier, the core material is emulsified in the medium. The system typically produces monodisperse particles of about 50–500 nm and has high reproducibility of encapsulation: however, in the cases of suspension polymerization involving a stabilizer, polydisperse core material droplets in the size range of about 0.1–10 μm are formed, and particle size control is governed by various additional factors, such as stirring speed, vessel configuration, shape of stirrer, etc. [4].

Microcapsules are used in a wide range of commercial products. Many application fields require the microcapsule to have desirable particle size range. For example, it is desirable to have a microcapsule size of 1–10 μm in carbonless copying paper [5]. Also, microcapsules containing pesticides have size ranges of 30–50 μm [6] and those containing perfumes have sizes of 10–50 μm [7].

Recently, microencapsulation of phase-change materials has been studied for application to thermal energy fields such as heating and air conditioning of buildings, thermal insulation materials, thermal adaptable fibers, etc. [8, 9]. Phase-change materials can absorb, store, and release large amounts of latent heat over a defined temperature range while the material changes phase or state. If the fiber is made by spinning along with microcapsules containing phase-change materials, the fiber is able to absorb or release heat when the temperature increases and decreases. This application requires only the small size microcapsule. One method to prepare microcapsules of these sizes is interfacial polymerization in an emulsion system. In the system droplets are first formed by emulsifying an organic phase consisting of the core materials and an oil-soluble reactive monomer, A, in an aqueous phase. By adding water-soluble reactive monomer, B, monomers A and B react with each other at the interface of a micelle to become a shell.

The objective of this study was to synthesize microcapsules containing phase-change material of size under 1 μm for application in thermal adaptable fibers. The microcapsules were prepared using an interfacial polycondensation method with toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) as monomers in an emulsion system.

Experimental

Materials

TDI and DETA used as shell-forming monomers were obtained from Aldrich. Octadecane (Aldrich, 99%) was employed as core material. Nonionic surfactant, NP-10 [poly(ethylene glycol) nonylphenyl ether, Sigma Chemical] was used as an emulsifier. The cyclohexane used was reagent grade.

Preparation of microcapsules

The microencapsulation was carried out in a 250-ml three-neck round-bottomed flask equipped with a mechanical stirrer. Prior to encapsulation, NP-10 (2.5 g) was dissolved in 80 ml distilled water. An organic solution of octadecane (10 ml), cyclohexane (10 ml), and TDI (3 g, 17.2 mmol) was prepared. The organic solution was added to the aqueous surfactant solution and the mixture was emulsified mechanically at a stirring rate of 300 rpm to form an oil-in-water emulsion. After stirring for 3 min, DETA diluted in 20 ml distilled water was slowly added into the emulsion system to start the interfacial polycondensation reaction between TDI and DETA at the oil–water interface. After the addition, the reaction mixture was heated to 60 °C. The resultant microcapsules were filtered and washed with distilled water to remove remaining DETA and dried in a vacuum oven.

Analysis of the microcapsules

The Fourier transform (FT) IR spectra were obtained on the microcapsules to define the structure of the shell polymer. The dry weight of the microcapsules was measured to evaluate the reaction ratio of the monomers. The thermal properties of the microcapsules containing phase-change material were evaluated using differential scanning calorimetry (DSC) (PerkinElmer, DSC 7) and the core material content was measured from the heat of fusion (ΔH_f) of octadecane. The shape of the microcapsules after polymerization was observed by optical microscopy. Scanning electron microscopy (SEM) was performed using a JSM-6330F (JEOL, Japan). One drop of the microcapsule dispersion to be investigated was placed on a nickel SEM stub and allowed to air-dry overnight. The dried sample was gold-coated.

Results and discussion

Mechanism of shell formation

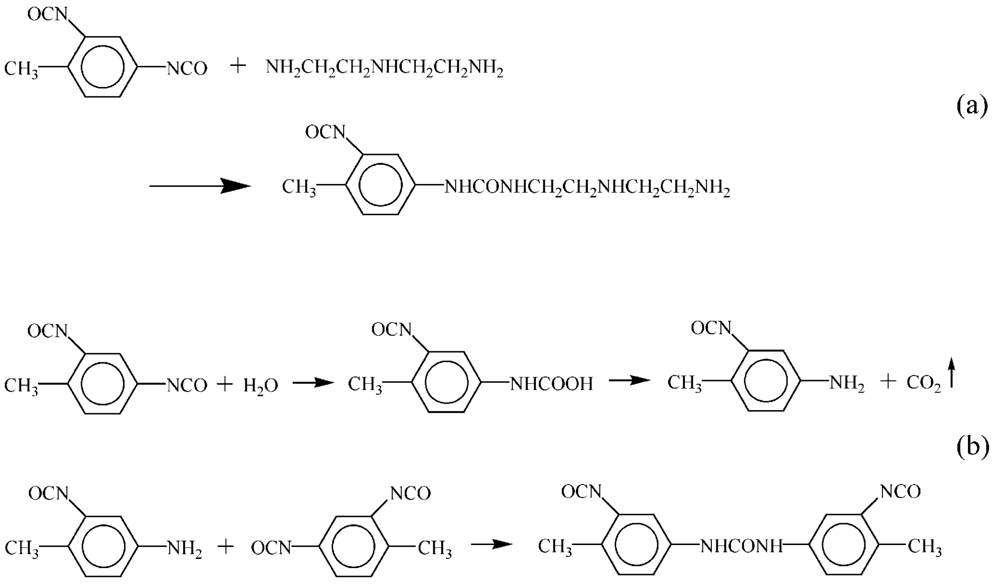
Microcapsules were prepared by the interfacial polymerization of the capsule shell formed at the surface of a droplet by polymerization of reactive monomers. When the initially formed oligomers are insoluble in the droplets, they grow and collapse at the interface, and then the polymer chains precipitated form a thin monolayer membrane around the droplets [10]. Polycondensation leads to the formation of a microscopic shell around the droplets.

The reaction scheme of shell formation is shown in Scheme 1. The polyurea shell is formed by reaction of the amine groups of DETA with isocyanate groups of TDI at the interface (Scheme 1a). Interfacial polymerization of TDI and DETA occurs rapidly at ambient temperature. On the other hand, TDI monomers can be hydrolyzed slowly at the interface to form amines which react with TDI to form the shell of the polyurea microcapsules (Scheme 1b). The latter interfacial reaction occurs on the oil side of the interface.

In order to investigate the influence of the feed ratio of TDI and DETA on the polymerization, microcapsules were synthesized by using a fixed amount (3 g) of TDI and various (0–4 g) amounts of DETA. In this case octadecane was not used and only cyclohexane was used as the core material. Because both octadecane and cyclohexane are nonpolar hydrocarbons, a similar wall-formation reaction is expected in the presence of either an octadecane–cyclohexane mixture or cyclohexane only. By omitting octadecane, the analysis of the wall-formation reaction of the microcapsule becomes easier because one does not have to consider the influence of octadecane which is not usually encapsulated quantitatively. The dry weights of the microcapsules synthesized are shown in Fig. 1. During the drying process cyclohexane was evaporated completely by diffusion through the shell. As shown in Fig. 1, the dry weight of the microcapsules increased as the DETA feed increased from 0 to 1 g, but no further increase was observed with increasing DETA weight up to 4 g. The dry weight of the microcapsules ranged from 5.69 to 5.78 g when 1 g or more DETA was used. This means that excess DETA can not react once TDI is depleted in the interface. When no DETA is used, TDI itself can make microcapsules through the reaction involving hydrolyzed TDI as in Scheme 1b.

The measured and calculated dry weights of the microcapsules are shown in Table 1. The calculated

Scheme 1 Wall-forming reaction of polyurea microcapsule



weight was obtained by assuming that TDI reacts with only 1 g DETA and 1.25 g NP-10. Regardless of the DETA feed used the measured dry weight of the microcapsules was more than that calculated. When no DETA was used, the dry weight of the microcapsules changed as the NP-10 feed changed. A surfactant weight of 2.5 g gave 4.23 g microcapsules, and 1.25 g gave 3.38 g. Because it was reported that isocyanate in a droplet successfully reacts with poly(vinyl alcohol) stabilizer in a microencapsulation system [11, 12], reaction of TDI with the hydroxyl groups of NP-10 probably takes place under similar experimental condition as in Scheme 2. The excess weight of the microcapsules is conjectured to be caused from reaction of NP-10 and TDI.

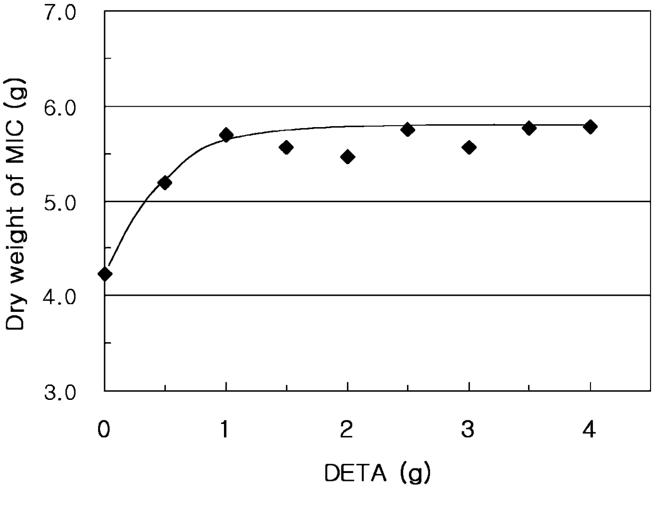


Fig. 1 Dry weight of microcapsules (*MICs*) synthesized using toluene-2,4-diisocyanate (*TDI*)/diethylenetriamine (*DETA*)/cyclohexane = 3.0 g:0–4 g:15.5 g

In order to clarify the reaction of NP-10 and TDI, synthesis of microcapsules was tried with NP-10 having no hydroxyl groups. The hydroxyl groups of NP-10 were changed to acetyl ester groups by treatment with acetic anhydride as in the reaction scheme in Scheme 3 [13].

FT-IR spectra of NP-10 and modified NP-10 are shown in Fig. 2. Spectrum a contains a characteristic absorption band at 3,453 $\mathrm{cm^{-1}}$, which is assigned to the hydroxyl group; however, the spectrum b shows no absorption band at 3,453 $\mathrm{cm^{-1}}$ and shows a new absorption band at 1,740 $\mathrm{cm^{-1}}$, which is assigned to the carbonyl group. The dry weight of the microcapsules synthesized with modified NP-10 and NP-10 is shown in Table 2. In the case of microcapsules synthesized with modified NP-10, the dry weight decreased compared to that of microcapsules synthesized with NP-10. It should be noted that the lack of hydroxyl groups in the surfactant resulted in almost no involvement of surfactant molecules in the TDI reaction.

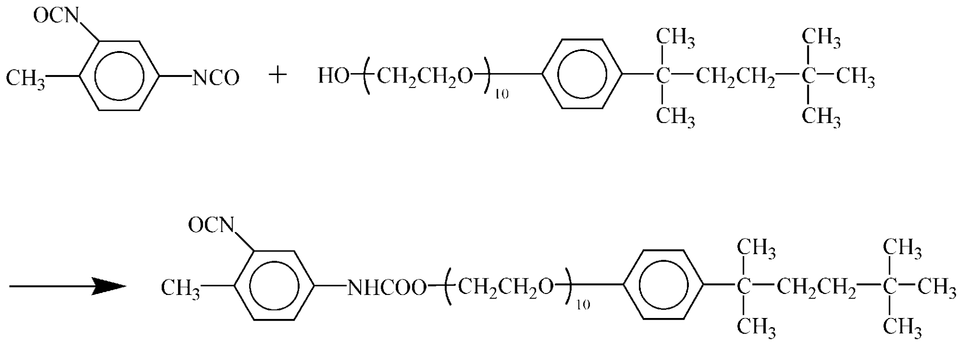
Analysis of FT-IR spectra

FT-IR analysis of microcapsules enables the definition of whether the chemical structure of the shell polymer contains chemical bonds other than the urea group, such as a urethane group, etc., along the polymer chain. The FT-IR spectra of the microcapsules are shown in Fig. 3. Spectrum a contains an absorption band at 2,276 $\mathrm{cm^{-1}}$, which is assigned to an isocyanate group. It is the spectrum of a microcapsule synthesized only with TDI. The wall-formation reaction of TDI is limited at the interface of the oil droplet because water cannot diffuse

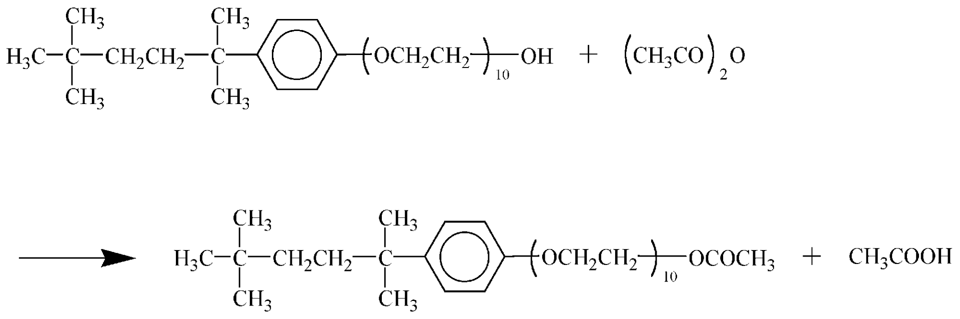
Table 1 Dry weight of microcapsules versus diethylenetriamine (*DETA*) feed weight. Toluene-2,4-diisocyanate (*TDI*), poly(ethylene glycol) nonylphenyl ether (*NP-10*)

Feed TDI (g)	DETA (g)	DETA/TDI (molar ratio)	NP-10 (g)	Dry weight of microcapsules (g)	Calculated dry weight of microcapsules (g)[a]
3.0	0	0	2.5	4.23	4.25
3.0	0	0	1.25	3.38	4.25
3.0	0.5	0.28	2.5	5.19	4.75
3.0	1.0	0.56	2.5	5.69	5.25
3.0	1.5	0.84	2.5	5.57	5.25
3.0	2.0	1.13	2.5	5.46	5.25
3.0	2.5	1.41	2.5	5.75	5.25
3.0	3.0	1.69	2.5	5.56	5.25
3.0	3.5	1.97	2.5	5.77	5.25
3.0	4.0	2.25	2.5	5.78	5.25

[a] TDI (3.0 g), DETA (1 g), NP-10 (1.25 g). Recipe: TDI, DETA, cyclohexane (20 ml)



Scheme 2 Reaction of toluene-2,4-diisocyanate and surfactant, poly(ethylene glycol) nonylphenyl ether (*NP-10*)



Scheme 3 Reaction of NP-10 and acetic anhydride

into the core of the oil droplet owing to the hydrophobic nature of the oil droplet; thus, some unreacted isocyanate groups remained in the core of the microcapsule. However, the spectra b and c do not show the absorption band at 2,276 cm^{-1}. By addition of DETA, the isocyanate group reacts fast with the amine group in DETA and there is no unreacted isocyanate group in the microcapsule core. Because DETA is compatible with the hydrophobic oil phase, it is believed to improve diffusion into the interface. Regardless of the DETA feed weight spectra b and c are almost identical. They show absorption bands at 3,364 and 1,539 cm^{-1}, which are assigned to NH, and a band at 1,664 cm^{-1}, which is assigned to the $C=O$ of the urea linkage. In spectrum a, it is possible to see that the absorption frequency of NH is slightly different from those of the others. In addition, the three spectra showed relatively weak but sharp characteristic bands of the carbonyl group of the urethane linkage at 1,709 and 1,733 cm^{-1}. As the DETA feed weight increased, the intensity of the urethane absorption peak decreased slightly. From this observation, it is possible to know that the extent of the surfactant reaction is reduced as the DETA increased owing to the competitive nature of the reaction.

Thermal characteristics of the microcapsules

The thermal properties of the microcapsules containing phase-change materials were evaluated using DSC. In

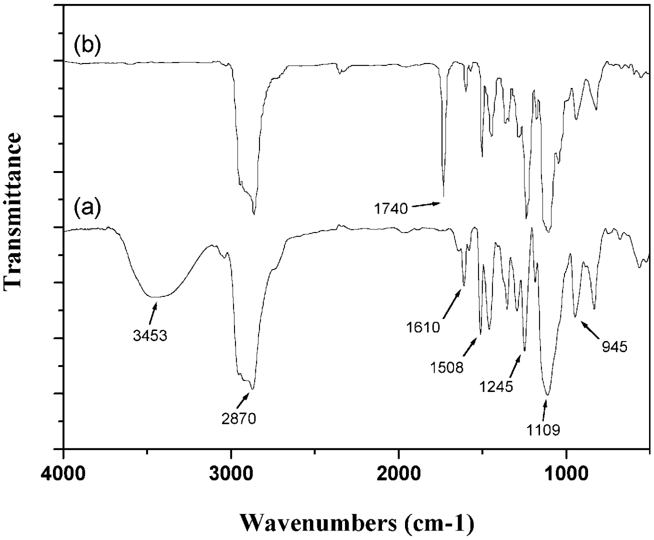


Fig. 2 Fourier transform (*FT*) IR spectra of poly(ethylene glycol) nonylphenyl ether (*NP-10*) (*a*) and modified NP-10 (*b*)

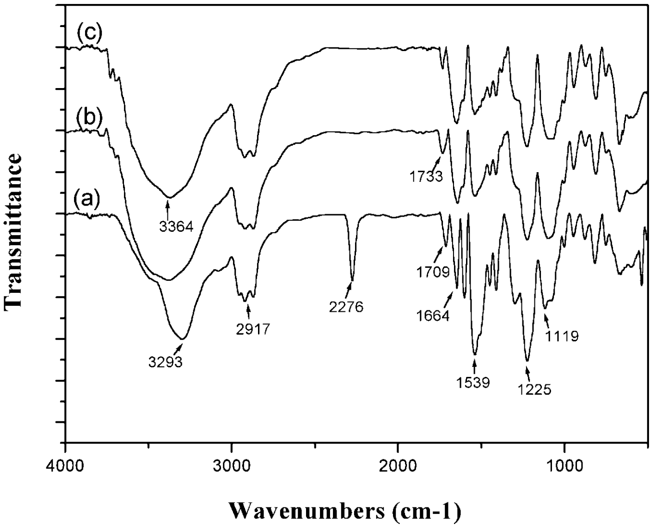


Fig. 3 FT-IR spectra of the polyurea MIC shell synthesized using 3 g TDI and 0 g DETA (*a*), 1 g DETA (*b*), and 2.5 g DETA (*c*)

order to measure the latent heat of the microcapsules as a function of the content of the phase-change materials, the microcapsules were prepared with various core–shell volume ratios. Octadecane is a phase change material desirable for application in thermal adaptable fibers owing to its availability in a reasonable phase-change temperature range and its high latent heat. The latent heat of octadecane is 241.2 Jg^{-1} and its melting point (T_m) is 28–30 °C [14]. T_m, the crystallization temperature (T_c), the latent heat of fusion (ΔH_f), and the heat of crystallization (ΔH_c) of octadecane encapsulated in microcapsules measured by DSC are shown in Table 3.

Encapsulated octadecane showed a phase change over the same temperature range as that of the bulk, and the latent heat of fusion varied according to the feed amount of octadecane. The effective specific heat of encapsulated materials undergoing a phase change depends on the physical properties of the microcapsule enclosing them. If the microcapsule is rigid, it is reported that heat transfer occurs at constant volume and no change in phase-change temperature occurs [15]. As in the data, there is no effect of the polyurea microcapsule enclosing octadecane on the melting behavior of octadecane. As the amount of encapsulated octadecane decreased, slight changes in T_m and T_c were observed probably owing to an increased ratio of surface to bulk octadecane inside the microcapsule.

The measured and calculated octadecane contents of a microcapsule are shown in Table 4. The octadecane content was obtained by measurement of ΔH_f using DSC based on the assumption that the latent heat does not change by microencapsulation. If all the octadecane used is encapsulated, the theoretical core contents are 61.5, 42.5, and 29.8 wt%, when the octadecane used is

Table 2 Dry weight of microcapsules synthesized with NP-10 and modified NP-10

TDI (g)	DETA (g)	Cyclohexane (ml)	Surfactant type	Dry weight of microcapsules (g)
3.0	0	20	NP-10	4.23
3.0	0	20	Modified NP-10	3.07
3.0	2.5	20	NP-10	5.75
3.0	2.5	20	Modified NP-10	4.15

Table 3 Thermal characteristics of microcapsules containing octadecane. Heating and cooling rate: 20 °C min^{-1}

TDI (g)	DETA (g)	Cyclohexane (ml)	Octadecane (ml)	T_m (°C)	T_c (°C)	ΔH_f (Jg^{-1})	ΔH_c (Jg^{-1})
3.0	3.5	10	10	30.8	20.9	112	110
3.0	3.5	5	5	29.6	22.5	77	66
3.0	3.5	3	3	29.5	22.7	62.6	53.6

Table 4 Core contents of microcapsulesversus feed volume of core material

Feed TDI (g)	DETA (g)	Cyclohexane (ml)	Octadecane [ml(g)]	Microcapsule Core weight by ΔH_f (wt%)	Feed octadecane, dry weight of microcapsules (wt%)[a]	Efficiency of encapsulation (%)
3.0	3.5	10	10(7.7)	46.4	61.5	75.4
3.0	3.5	5	5(3.85)	31.9	42.5	75.1
3.0	3.5	3	3(2.31)	26.0	29.8	87.2

[a] Measured dry weight of microcapsule

10, 5, and 3 ml, respectively; however, the core contents measured were 46.4, 31.9, and 26.0 wt%. Regardless of the amount of octadecane used, the core contents measured were less than the calculated values. From the measured and the calculated values, the efficiency of octadecane encapsulation was calculated. When the core material volume was larger than that of the shell material in the encapsulation reaction, the efficiency of octadecane encapsulation showed similar values of 75.4 and 75.1%. When the volume of the core materials was slightly smaller than that of the shell materials in the reaction, the efficiency of octadecane encapsulation was 87.2%.

Shape of the microcapsules

An optical microphotograph and a SEM photograph of microcapsules containing octadecane are shown in Fig. 4. The optical microphotograph was taken after polymerization, and it shows many small particles of about 0.1-μm diameter and large particles of about 1-μm diameter. The large particles have somewhat similar diameters of about 1 μm and their volume fraction is large.

When they were dried, the surface of most of the microcapsules was very smooth and the shape was very regular with diameter of about 1 μm as in the SEM photograph. By judging from the optical microphotograph, a similar inhomogeneous particle size distribution is expected in the SEM photograph; however, as in the SEM photograph, it is not easy to observe small particles. On some microcapsules, powdery clusters of small particles can be seen. The reason is probably due to the small volume fraction of small particles – their volume fraction is so small that they exist as powdery clusters or are probably embedded inside the stacked large particles.

Conclusions

For application to thermal adaptable fibers, polyurea microcapsules containing phase-change materials were successfully synthesized by interfacial polycondensation using TDI and DETA as shell monomers in an emulsion system with a low stirring speed. TDI was used as an oil-soluble monomer and DETA was used as a water-soluble monomer. Octadecane was used as a phase-change material and NP-10, a nonionic surfactant, was used as an emulsifier. A polyurea shell was formed not

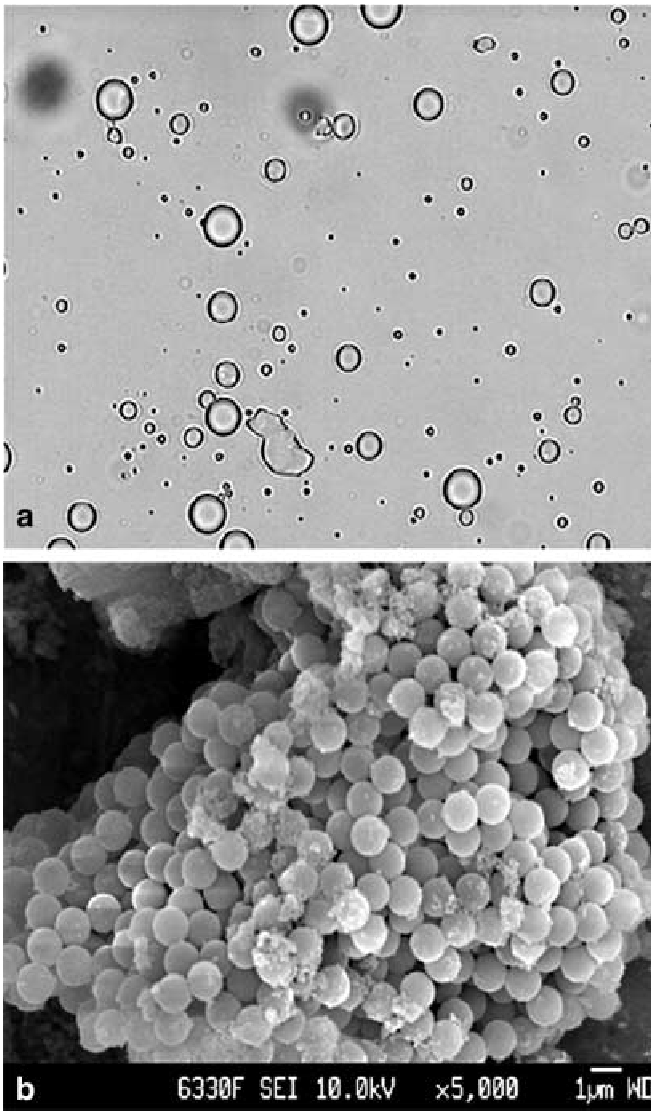


Fig. 4 **a** Optical micrograph and **b** scanning electron microscopy photograph of the MICs

only by reaction of TDI and DETA, but also by reaction of TDI and amines which are formed by hydrolysis of TDI at the interface. In this study, DETA seems to reacted with TDI in the weight ratio of 1:3 (molar ratio 1:1.77). Some portion of the nonionic surfactant, NP-10 having hydroxyl groups, reacted with TDI to form urethane. Microcapsules containing octadecane showed a phase change over the same temperature range as bulk octadecane. The core content measured using ΔH_f was less than that calculated based on the feed amount of octadecane. The efficiency of octadecane encapsulation increased as the core content decreased. SEM observation showed that the shape of most of the microcapsules was regular and the surface was smooth.

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