Preparation and Application of Polyurethane-urea Microcapsules Containing Phase Change Materials

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Abstract: For thermal adaptable fabrics, the polyurethane-urea microcapsules containing phase-change materials (PCMs: hexadecane, octadecane and eicosane) were successfully synthesized by interfacial polycondensation using 2,4-toluene diisocyanate (TDI)/poly(ethylene glycol) (PEG400)/ethylene diamine (EDA) as shell monomers and nonionic surfactant NP-12 in an emulsion system under stirring rates of 3,000~13,000 rpm. The mean particle size of microcapsule decreased significantly with increasing the stirring rate up to 11,000 rpm, and then leveled off. The mean particle size increased with increasing the content and molecular weight (eicosane > octadecane > hexadecane) of PCMs at the same stirring rate. The mean particle sizes of microcapsules were found to decrease with increasing the NP-12 content up to 1.5 wt%, and thereafter increased a little. It was found that the melting temperature (T_m) and crystallization temperature (T_c) of three kinds of encapsulated PCMs and their enthalpy changes (ΔH_m, ΔH_c) increased with increasing PCM contents. The encapsulation efficiencies (Ee) of hexadecane microcapsule linearly increased with increasing the content of hexadecane. It was found that the stable microcapsule containing 50 wt% of hexadecane could be obtained in this study. However, Ee of octadecane and eicosane microcapsules increased with increasing PCM's contents up to 40 wt%, and then decreased a little. By considering the encapsulation efficiency, it was found that the maximum/optimum contents of octadecane and eicosane microcapsules were about 40 wt%. By the dynamic thermal performance test, it was found that the maximum buffering levels of Nylon fabrics coated with hexadecane, octadecane, and eicosane microcapsules were about −2.4/+2.9 °C, −3.6/+3.6 °C and −4.0/+4.7 °C, respectively.

Keywords: Phase change material, Microcapsule, Particle size, Encapsulation efficiency, Buffering levels

Introduction

It is well known that such phase change materials (PCMs) as paraffin waxes are cheap and have a moderate thermal energy density but a low thermal conductivity and require a large surface area. The main advantage of PCM microencapsulating is providing a large heat transfer area, the reduction of PCMs reactivity towards the outside environment and controlling the changes in the volume of storage materials as the phase change occurs. Microencapsulated PCMs were studied in the late 1970s after PCMs had long been employed as the thermal storage/control materials [1]. Microencapsulated PCMs have been used in the fabrication of thermo-regulated fibers/fabrics [2], coating [3], foams [4], coolants [5-8], solar and nuclear heat storage systems [9], and packed bed heat exchangers [10]. The fabrics coated with PCMs microcapsules have the possibility to interact with our body to balance a temperature by absorbing, storing and releasing the heat.

The wall material of the microcapsule can be formulated by using a wide variety of materials including natural and synthetic polymers as shell materials. Zang *et al.* prepared microencapsulated n-octadecane using a melamine/formaldehyde shell through *in situ* polymerization [11]. Yoshioka *et al.* obtained the PCMs microcapsule with a high thermal resistance in which the capsule shell comprised an organopolysiloxane [12]. Tadaaki synthesized PCMs microcapsules by interfacial polymerization with the aromatic polyamide shell that had a prominent thermal stability [13]. Arshady

synthesized the microencapsulated PCM with the shells of gelatin as a heat transfer media in gas-fluidized beds [14]. Microencapsulating of octadecane prepared by the interfacial polymerization of polyurea in an emulsion system was studied by Cho *et al.* [15]. Polyurethane and poly(ether urethane)-based nanocapsules were synthesized by the interfacial reaction between diisocyanate and diol (or polyol) for drug carriers [16].

Most of the PCMs undergo large changes in volume (~10 %) during melting [17]. This may cause high stresses on heat exchanger walls. The effective specific heat of encapsulated materials undergoing a phase transition depends on the physical properties of the microcapsule enclosing it. If the microcapsule is rigid, the heat transfer will occur at a constant volume and no phase change will occur. If the microcapsule is elastic, the phase change can not take place at various temperatures [8]. Polyurethanes (PUs) are an important class of polymers that have been found many applications [18-20]. Especially, polyether type polyurethanes have been studied extensively due to their excellent physical properties, resistance against infections, and superior blood compatibility [21,22].

Most studies on PCMs microcapsules have been carried out in industrial laboratories. However, there is a little information available on the optimum conditions for the PCM encapsulation with polyurethane-urea in the open literature. Moreover, the systematic data on the encapsulation efficiencies of microencapsulated PCMs and the buffering levels of coated fabrics are rarely available.

In this study, the polyurethane-urea microcapsules containing PCMs (hexadecane, octadecane, and eicosane) were prepared by interfacial polymerization using 2,4-toluene diisocyanate

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(TDI)/ethylene diamine (EDA)/poly(ethylene glycol) (PEG)/ PCMs/non-ionic surfactant NP-12 in an emulsion system. The coating materials formulated from encapsulated PCMs/ waterborne polyurethane binder were used to coat nylon fabrics. The objectives of this study are to investigate the effects of a stirring rate, the content of emulsifier, and the contents/kinds of PCMs on the mean particle sizes and the encapsulation efficiencies of microencapsulated PCMs, and on the buffering levels of nylon fabrics coated with typical microencapsulated PCMs.

Experimental

Materials

PCMs hexadecane, octadecane, and eicosane (Aldrich Chemical, Milwaukee, WI) were used as the core materials of microcapsules. Nonionic surfactant, poly (ethylene glycol) nonylphenyl ether (NP-12, Sigma Chemical, USA), was used as an emulsifier. 2,4-toluene diisocyanate (TDI, Aldrich Chemical, Milwaukee, WI) and ethylene diamine (EDA, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4Å molecular sieves for one day. Poly(ethylene glycol) (PEG, M_n = 400 g/mol, Aldrich Chemical, Milwaukee, WI) was dried over calcium hydride at a room temperature for 24 h. Dibutyl tin dilaurate (DBTDL) as a catalyst was used without any further purification.

Encapsulation of PCMs

Prior to encapsulation, NP-12 was dissolved in distilled water. The organic solutions of three kinds of PCMs and TDI were prepared, and they were added to the aqueous solution of NP-12. To obtain stable emulsions, each of these mixtures was emulsified mechanically with various stirring rates (3,000, 9,000, 11,000, 13,000 rpm) at a room temperature for 5 min to form an oil-in-water (o/w) emulsion. PEG and DBTDL were added into the o/w emulsion to start an

interfacial polycondensation reaction. The reaction mixture was reacted at 80 °C under 1,500 rpm for 1 h. and then EDA was added into the mixture to chain-extend at 60 °C under 2000 rpm for 2 h. The obtained PCMs microcapsules were filtered and washed with 30 % ethanol aqueous solution to remove the remaining TDI and PCMs on their surfaces. The sample designation, the composition of monomer/emulsifier and the feed ratio of the PCMs in the polymerization system are shown in Table 1.

Dip-coating of PCMs Microcapsules onto Nylon Fabrics

Typical microcapsules samples HD40, OD40 and ES40 were used to incorporate PCMs into fabrics. Nylon fabrics were dip-coated with microcapsule (10, 15 and 20 % owf)/ waterborne binder (5 % owf) solutions at a room temperature for 1 h. As-coated nylon fabrics were squeezed, and then dried at 90 °C for 60 min and 100 °C for 1 min.

Characterization

FT-IR spectra of pure PCMs (hexadecane, octadecane, and eicosane) and PCMs microcapsules were measured using a spectrophotometer (Nicolet impact 400D, Japan) in the wavenumber of 400~4000 cm^{-1} at a room temperature. The particle size distribution and the mean particle size of microcapsules were measured in an aqueous suspension by a particle size analyzer (Gali CIS-1, Gali Production Ltd., Israel). The particle size distribution of microcapsules was presented as a volume fraction distribution. The phase change properties of pure PCMs and PCMs microcapsules were measured using a differential scanning calorimeter (DSC, SSC-5200H MII, Seiko Ins., Japan) in the temperature range of −20 to 80 °C at a heating and cooling rate of 10.0 °C/min under a nitrogen atmosphere. The morphology of the microcapsules containing hexadecane, octadecane, and eicosane were observed through a scanning electronic microscopy (SEM, Hitachi S-4200 Field Emission SEM, Japan). According to ASTM 07024

Table 1. Effect of PCMs contents on mean particle sizes of HD, OD, and ES samples

| Specimens | Composition (mole) | | | Emulsifier | Feed PCMs | Mean particle size[a] |
	TDI	PEG	EDA	NP-12 (wt%)	(wt%)	(μm)
HD20					20 (9.2 g)	3.4
HD30	0.1	0.05	0.05	1.5	30 (16.0 g)	3.5
HD40					40 (24.6 g)	3.8
HD50					50 (36.9 g)	4.1
OD20					20 (9.2 g)	3.8
OD30	0.1	0.05	0.05	1.5	30 (16.0 g)	4.3
OD40					40 (24.6 g)	4.8
OD50					50 (36.9 g)	5.2
ES20					20 (9.2 g)	4.1
ES30	0.1	0.05	0.05	1.5	30 (16.0 g)	4.7
ES40					40 (24.6 g)	5.4
ES50					50 (36.9 g)	6.5

testing, the buffering levels of the nylon fabrics containing PCMs (the temperature differences between control fabrics and treated fabrics) were measured at a room temperature using a dynamic thermal performance tester.

Results and Discussion

Identification of Polyurethane-urea Based PCM Microcapsules

The FT-IR spectra of pure PCMs and PCMs microcapsules are shown in Figures 1(a)~(c). PCMs were identified by characteristic IR peaks, such as the aliphatic C-H bending at 2960~2840 cm^{-1}, the C-H bending near 1470 cm^{-1}, the CH_3 bending near 1370 cm^{-1}, and the inplane rocking vibration of the CH_2 group at 717 cm^{-1} [3]. The shell polymer (polyurethane -urea) of PCMs microcapsules was identified by the characteristic IR peaks, such as the C=O stretching of urethane group at 1740~1700 cm^{-1}, the urethane-urea group at 1690 ~1650 cm^{-1}, and the N-H stretching at 3450~3300 cm^{-1}. The completion of the polymerization reaction between TDI and polyol (PEG400)/EDA was confirmed by the disappearance of the NCO absorption band at 2270 cm^{-1} [16]. By comparing the IR spectra of pure PCMs with those of PCMs microcapsules, it was found that PCMs microcapsules were formed well by interfacial polycondensation using TDI and PEG400/EDA as shell monomers and nonionic surfactant NP-12 in an emulsion system.

Particle Size and Its Distribution of PCMs Microcapsules

Generally, the particle sizes of microcapsules are affected by the emulsifier content and the stirring rate in the emulsion process, etc. [3,17]. Figure 2 shows the effect of emulsifier (NP-12) content (1~3 wt%) on the mean particle size at a fixed stirring rate of 11,000 rpm for the HD20, OD20, and ES20 samples. It was found that the mean particle size of microcapsule decreased a little with increasing NP-12 content up to 1.5 wt%, and then increased significantly. From this
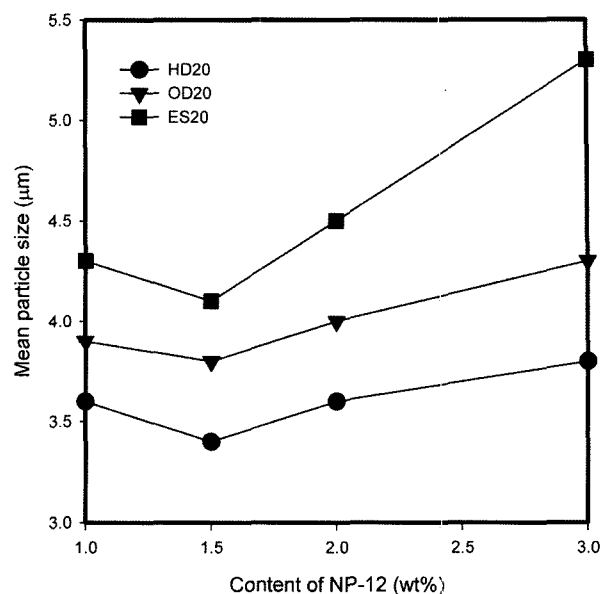

Figure 2. Effect of the NP-12 content on the mean particle size of HD20, OD20, and ES20.

result, it was concluded that the optimum content of emulsifier NP-12 to form more stable and small particles was about 1.5 wt%. Therefore, the emulsifier NP-12 was fixed at 1.5 wt% for all HD, OD, and ES microcapsules.

The effect of the stirring rate in an emulsification step on the mean particle size of typical microcapsule samples (HD20, OD20 and ES20) at a constant NP-12 content (1.5 wt%) is shown in Figure 3. The mean particle sizes of HD20, OD20, and ES20 microcapsules with different stirring rates of 3,000~13,000 rpm were in the range of 4.4~3.4 μm, 5.3~ 3.6 μm, and 6.7~4.0 μm, respectively. The mean particle size of PCM microcapsules decreased significantly with increasing the stirring rate up to 11,000 rpm, and then decreased a little. However, the mean particle size of PCM microcapsules increased with increasing the molecular weight of PCMs
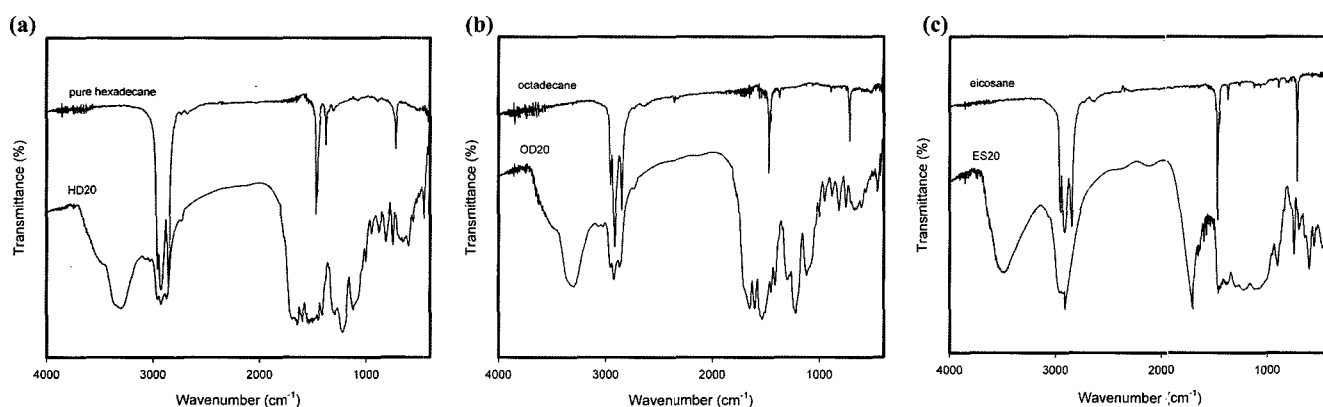

Figure 1. FT-IR spectra; (a) pure hexadecane and hexadecane microcapsule containing 20 wt% of hexadecane (HD20), (b) pure octadecane and octadecane microcapsule containing 20 wt% of octadecane (OD20), and (c) pure eicosane and eicosane microcapsule containing 20 wt% of eicosane (ES20).
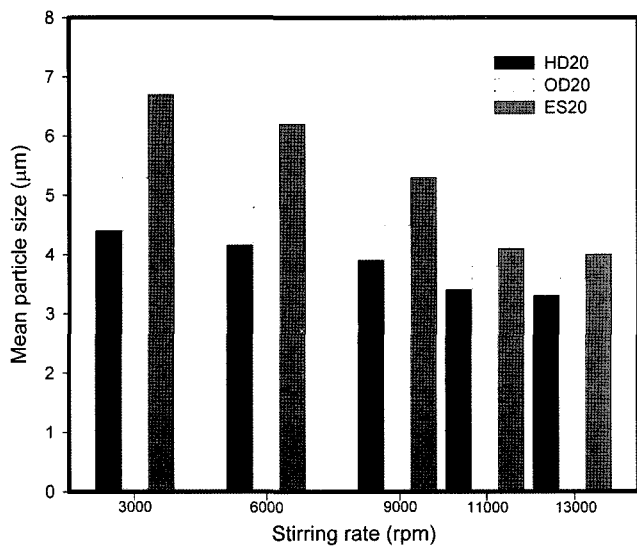
Figure 3. Effect of the stirring rate on the mean particle size of HD, OD20, and ES20.

(eicosane > octadecane > hexadecane) at the same stirring rate. This indicates that the higher the molecular weight of PCMs is the less they are likely to be dispersed in an emulsion step. Especially, when the stirring rate was above 11,000 rpm, the decrease of particle size was not significant. From these results, the optimum condition of a stirring rate was found to be 11,000 rpm. Therefore, the stirring rate was fixed at 11,000 rpm for all HD, OD, and ES samples.

The distributions of the particle size of microcapsules with different PCMs content are shown in Figure 4. The mean particle size of the HD, OD, and ES samples containing 20~50 wt% of PCMs were in the range of 3.4~4.1 μm, 3.8~5.2 μm, and 4.1~6.5 μm, respectively (see Table 1). It was found that the mean particle size increased with increasing the molecular weight of PCMs. With increasing PCMs content,

the particle size distribution of microcapsules became wider and the distribution peaks shifted to a higher size level. These behaviors are probably related to the lower dispersing ability of the higher molecular weight PCM.

Morphologies of PCMs Microcapsules

The effects of PCMs content (30, 40, and 50 wt%) on the SEM micrographs for HD, OD, and ES samples are shown in Figure 5. The microcapsules of all HD samples (HD30, HD40 and HD50) show clear spherical shapes and smooth surfaces. The spherical shape of OD30 sample remained clear. However, the microcapsules of OD40, OD50 and all ES samples showed a notably distorted and rough shape. Particularly, the shapes of the ES samples were rougher compared to those of OD samples. The mean particle sizes of microcapsules determined by SEM were found to increase with increasing PCMs content, and were almost the same with the microcapsule sizes measured using a particle size analyzer.

Thermal Behaviors of PCMs Microcapsules

The thermal properties of the microcapsules containing PCMs were evaluated using a differential scanning calorimeter (DSC). The DSC heating and cooling curves of bulk PCMs are shown in Figure 6, respectively. The heats of the fusion ($\Delta H_{f,meas}$) of pure hexadecane, octadecane, and eicosane are 192, 236, and 289 J/g, and their melting temperatures (T_m) are approximately 21.0, 34.0, and 45.0 °C, respectively. The heats of the crystallization ($\Delta H_{c,meas}$) of pure hexadecane, octadecane, and eicosane are 186, 227, and 280 J/g, and their crystallization temperatures (T_c) are near 14.4, 23.0, and 26.0 °C, respectively. The boundary temperatures between the crystallization and the melting of hexadecane, octadecane, and eicosane are about 18, 28, and 36 °C, respectively. Therefore, the textiles coated with these PCMs microcapsule emit the heat energy when the environment temperature is below the boundary temperature, but the coated textile absorbs heat
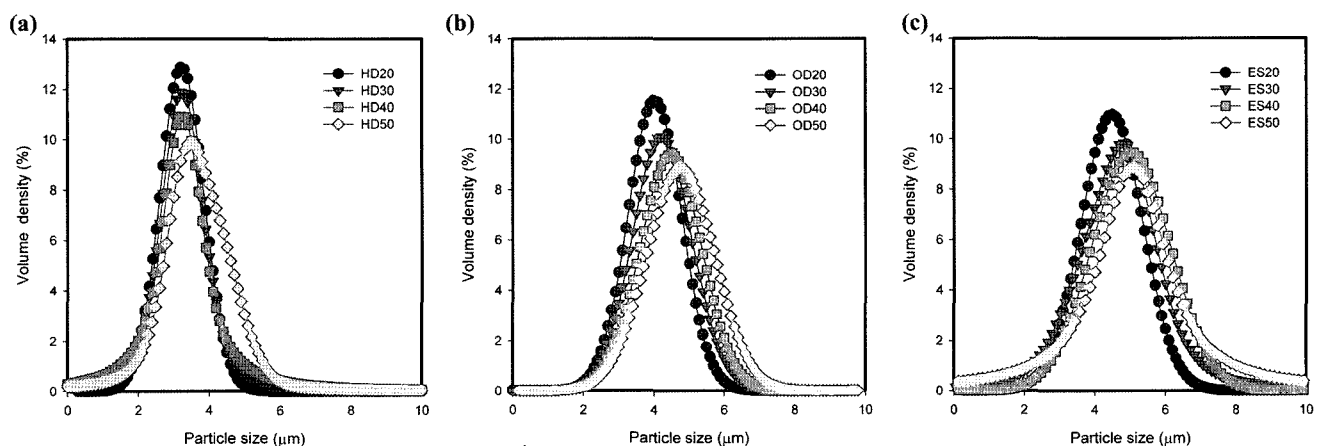

Figure 4. Particle size distribution of polyurethane-urea microcapsules containing various contents of PCMs: (a) HD, (b) OD, and (c) ES samples.
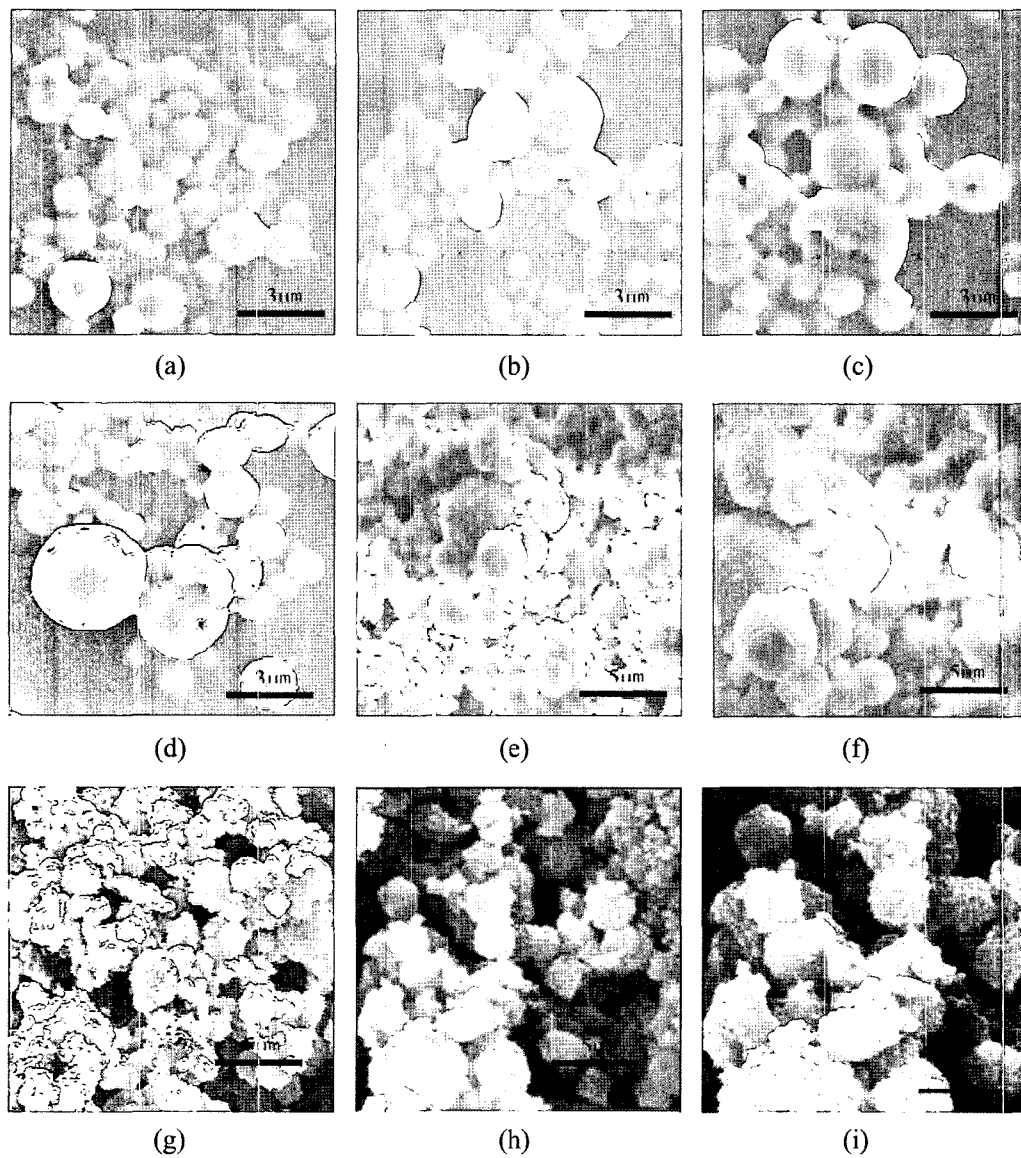
Figure 5. SEM micrographs of (a) HD30, (b) HD40, (c) HD50, (d) OD30, (e) OD40, (f) OD50, (g) ES30, (h) ES40, and (i) ES50.
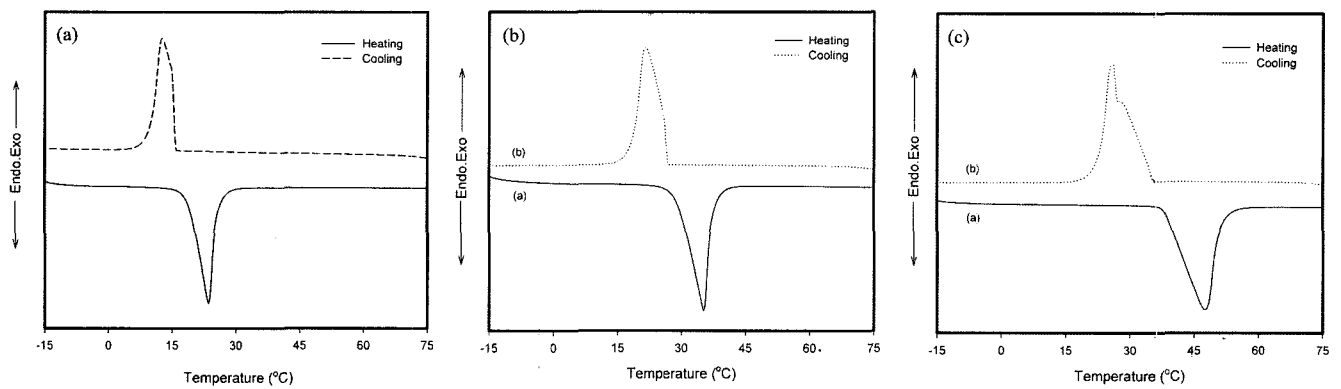

Figure 6. DSC heating and cooling curves for pure (a) hexadecane, (b) octadecane, and (c) eicosane.
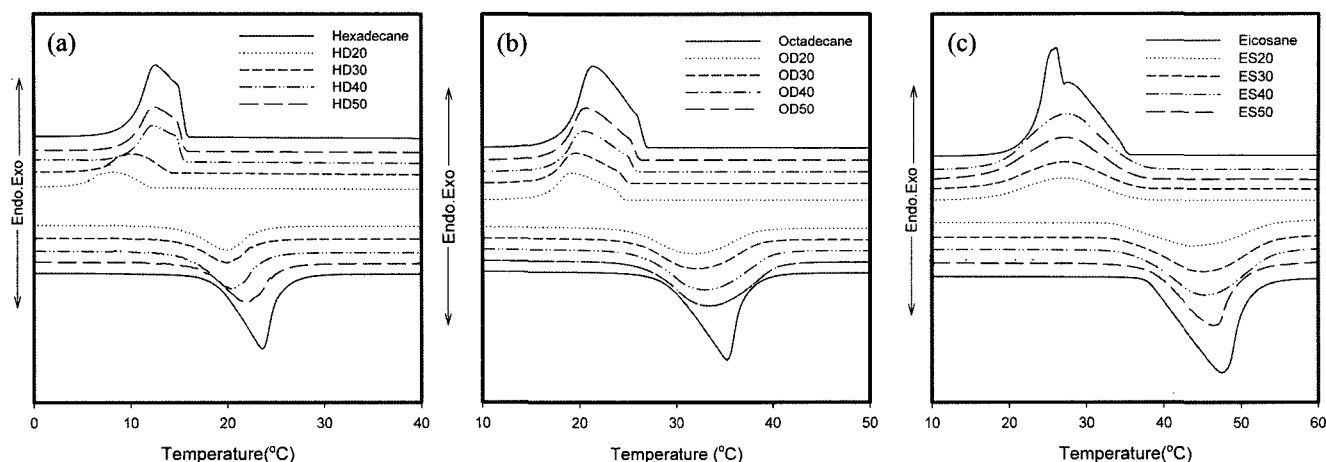
Figure 7. DSC heating and cooling curves for (a) HD, (b) OD, and (c) ES samples.

energy when placed above the boundary temperature. Upon this, the textiles containing hexadecane, octadecane, and eicosane can be used for winter, all season and summer according to these boundary temperatures.

The DSC heating and cooling curves of HD, OD, and ES samples are shown in Figures 7. It was found that the phase change transition points (T_m and T_c) of PCMs microcapsules increased a little when PCMs content increased, but they appeared at almost the same temperature ranges as those of the pure PCMs. The heat of fusion ($\Delta H_{f,meas}$) and the heat of crystallization ($\Delta H_{c,meas}$) were measured using DSC, and the theoretical heats of fusion ($\Delta H_{f,theo}$) and the heats of crystallization ($\Delta H_{c,theo}$) were calculated from fed PCM contents in polymerization systems.

The encapsulation efficiencies (Ee: $\Delta H_{f,meas}/\Delta H_{f,theo}$ and $\Delta H_{c,meas}/\Delta H_{c,theo}$) of the HD, OD, and ES samples were determined from the ratio of measured enthalpy changes ($\Delta H_{f,meas}$ $\Delta H_{c,meas}$) to theoretical enthalpy changes ($\Delta H_{f,theo}$ and $H_{c,theo}$). Ee, ΔH_{meas} and ΔH_{theo} are listed in Table 2. Ee of the HD samples linearly increased with increasing hexadecane contents up to 50 wt%. However, Ee of the OD and ES series samples increased with increasing content of the PCMs up to 40 wt%, and thereafter decreased a little. The increase of Ee might be due to the larger amount of the stable crystallized PCMs particles included in polyurethane-urea microcapsules with increasing PCMs content. By observation of encapsulation efficiency, it was found that the highest Ee of the microcapsule containing 50 wt% of HD could be obtained,

Table 2. ΔH_{meas}, ΔH_{theo}, and encapsulation efficiency (Ee) of polyurethane-urea microcapsules containing various PCMs contents

Specimens	Endothermic changes (Heat of fusion)			Exothermic changes (Heat of crystallization)		
	$\Delta H_{f,meas}$[a] (Jg^{-1})	$\Delta H_{f,theo}$[b] (Jg^{-1})	Encapsulation efficiency (Ee)[c]	$\Delta H_{c,meas}$[a] (Jg^{-1})	$\Delta H_{c,theo}$[b] (Jg^{-1})	Encapsulation efficiency (Ee)[c]
HD20	19.1	38.4	50	17.9	37.2	48
HD30	32.0	57.6	56	29.6	55.8	53
HD40	51.4	76.8	65	46.1	74.4	62
HD50	64.0	96.0	67	60.5	93.0	65
OD20	28.9	57.8	50	26.9	56.0	48
OD30	50.3	86.7	58	47.9	84.1	57
OD40	76.3	115.6	66	69.4	108.4	64
OD50	79.1	125.6	63	70.4	115.4	61
ES20	28.8	47.2	61	26.8	45.4	59
ES30	45.3	70.8	64	41.5	68.1	61
ES40	64.2	94.4	68	57.2	90.8	63
ES50	88.1	144.5	61	81.2	140.0	58

[a]$\Delta H_{f,meas}$ (or $\Delta H_{c,meas}$): measured heat capacity of polyurethane-urea microcapsules, [b]$\Delta H_{f,theo}$ (or $\Delta H_{c,theo}$): (fed PCM weight/total solid weight) × ΔH of pure PCM, [c]encapsulation efficiency of ΔH: $\Delta H_{meas}/\Delta H_{theo}$ × 100.
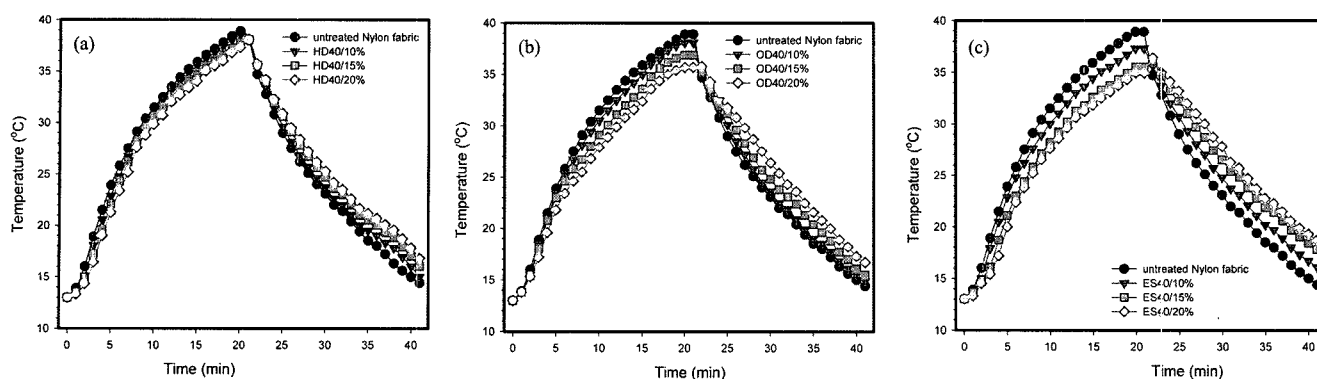
Figure 8. Thermal control efficiency of the nylon fabrics treated with 10 %, 15 %, and 20 % of PCMs microcapsules: (a) HD40, (b) OD40, and (c) ES40.

however, the optimum contents of the PCMs in OD and ES microcapsules were about 40 wt%. Therefore, we compared the temperature control performance of nylon fabrics coated with the polyurethane-urea microcapsule containing a fixed content of PCMs (40 wt%) in this study.

Buffering Levels of Coated Nylon Fabrics

One way to demonstrate the temperature control performance of the coated fabrics as compared to traditional uncoated fabrics is to measure the temperature difference (buffering level: temperature differences between control and coated fabrics) using a dynamic thermal performance test. The temperature changes as a function of elapsed times under heating and cooling steps are shown in Figure 8. Nylon fabrics were treated with the coating materials formulated from the polyurethane-urea microcapsules (10, 15, and 20 % owf) and waterborne polyurethane binder (5 % owf). The buffering temperatures of all samples increased with increasing elapsed times up to about 15 min, and then reached maximum buffering levels. The maximum buffering level of the nylon fabric treated with 10, 15, and 20 % of HD40 microcapsules were in the range of $-0.9 \sim -2.4\,°C$ (under heating condition), and $+1.1 \sim +2.9\,°C$ (under cooling condition), respectively. The maximum buffering levels of the nylon fabric contained 10 %, 15 %, and 20 % of OD40 microcapsules under heating and cooling conditions were in the ranges of $-1.0 \sim -3.6\,°C$, and $+0.7 \sim +3.6\,°C$, respectively. The maximum buffering levels of the nylon fabric treated with 10 %, 15 %, and 20 % of ES40 microcapsules under heating and cooling conditions were in the ranges of $-1.6 \sim -4.0\,°C$, and $+1.7 \sim +4.7\,°C$, respectively. From these results, it was found that the maximum buffering levels of coated nylon fabric at the phase transition point of PCMs notably increased with increasing microcapsule contents and molecular weight of PCMs. And the maximum buffering levels of HD, OD, and ES samples at their phase transition points were found to be about $-2.4/+2.9\,°C$, $-3.6/+3.6\,°C$ and, $-4.0/+4.7\,°C$. The coated nylon fabrics prepared in this study worked to keep the temperature in an optimum comfort zone,

reducing the big temperature fluctuations common in other materials and provided a superior insulation performance against the cold and the heat.

Conclusions

The polyurethane-urea microcapsules containing hexadecane, octadecane, and eicosane were successfully synthesized by interfacial polycondensation using TDI and PEG400/EDA as shell monomers and nonionic surfactant NP-12 in an emulsion system under a stirring rate of 11,000 rpm. The mean particle size of microcapsules was found to decrease as the NP-12 content increased up to 1.5 wt%, but as the content increases beyond 1.5 wt% the decrease was minor. The mean particle size of PCMs microcapsule fell significantly as the stirring rate increased up to 11,000 rpm, and thereafter the decrease became dull. At a same stirring rate, an increase in the content and the molecular weight of PCMs (eicosane > octadecane > hexadecane) also entailed an increase in the size of the mean particle. The melting temperature (T_m), the crystallization temperature (T_c), and the thermal storage/release properties of PCMs microcapsule increased as PCMs concentration increased. The encapsulation efficiency (Ee) of hexadecane microcapsules showed a linear increase with increasing hexadecane contents up to 50 wt%. However, Ee of OD and ES samples increased with increasing content of PCMs up to 40 wt%, and then decreased a little. It was found that the maximum/optimum contents of OD and ES in terms of encapsulation efficiencies of the microcapsules were about 40 wt%. By a dynamic thermal performance test, the maximum buffering level of the coated nylon fabric was found to decline as the contents of PCMs microcapsules increased. The maximum buffering levels of HD, OD, and ES samples which were measured at their phase transition points were $-2.4/+2.9\,°C$, $-3.6/+3.6\,°C$ and, $-4.0/+4.7\,°C$, respectively. These results indicate that the PCMs microcapsules prepared in this study have a high potential for coatings with high heating and cooling functions.

Acknowledgement

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