

Preparation and Properties of Microencapsulated Octadecane with Waterborne Polyurethane

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ABSTRACT: A series of microencapsulated blends of waterborne polyurethane (WBPU) as a matrix polymer and phase change material octadecane as a domain material were prepared in the presence of emulsifier. Nylon fabrics were coated with the coating materials formulated from microencapsulated blends, thickener, and hardener. The morphology and thermal behaviors of microencapsulated octadecane and WBPU/octadecane-coated nylon fabrics were investigated using SEM, DSC, and KES-F7. The size of octadecane microspheres increased with increasing octadecane contents. However, the size of microsphere (1–6 μm) decreased with increasing emulsifier contents. ΔH_{fusion} , $\Delta H_{\text{crystallization}}$, and their filling efficiencies of octadecane in

film samples were found to increase with increasing microencapsulated blends, thickener, and hardener contents. Especially, thickener and hardener could function in trapping microencapsulated octadecane. Thermal characteristic Q_{max} ($\text{J}/\text{cm}^2 \text{ s}$) values of WBPU/octadecane-coated nylon fabrics are much higher than those of the control nylon fabric and WBPU-coated nylon fabrics, indicating that the nylon fabrics coated with WBPU/octadecane blends have cooler touch sensation compared with nylon fabrics and WBPU-coated nylon fabrics. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1596–1604, 2005

Key words: microencapsulation; polyurethane; morphology

INTRODUCTION

Microcapsules are small particles that contain an active agent or core material surrounded by a coating or shell. 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. Many workers classify capsules smaller than 1 μm as nanocapsules and those larger than 1000 μm as macrocapsules. Microcapsules are used in a wide range of commercial products and they can be developed by employing various microencapsulation methods. These microencapsulation techniques frequently result in products containing numerous variably coated particles.^{1–4} The microencapsulation is enclosed in a thin and high-molecular-weight polymeric film. The coated particles can then be incorporated in any matrix that is compatible with the encapsulating film.

Different types of coated particles can be obtained depending on the coating process used. The particles can be embedded within a polymeric or proteinic matrix network in either a solid aggregated state or a molecular dispersion, resulting in the formation of microspheres. Alternatively, the particles can be

coated by a solidified polymeric or proteinic envelope, leading to the formation of microcapsules.⁵

Recently, microencapsulation of phase change materials (PCMs) has been studied for application to thermal energy fields such as heating and air conditioning of buildings, thermal insulation materials, and thermal adaptable fibers.^{6,7} The PCMs absorb heat at their melting point upon an increase in surrounding temperatures and release the heat upon cooling. The PCMs are available with a range of transition temperature for varying applications. The heat capacity of a body can be raised or cooled in a certain temperature range by incorporating PCMs in the garments.^{8–10} A considerable amount of research into garments for protecting humans against hot and cold conditions has been reported. Some of the earliest work was reported in the late 1950s and early 1960s on garments used for maintaining thermoneutrality in pilots who endured high temperatures due to a sunlit aircraft cockpit.¹¹

Some of these PCMs change phases within a temperature range just above and below human skin temperature. This property of certain substances is triumphantly harnessed for making protective all-season outfits and for abruptly changing climatic conditions.¹² Fiber, fabric, and foam with built-in PCMs store the warmth the body creates and then release it back to the body. Since the process of phase change is dynamic, the materials are constantly changing from a solid to a liquid and back, depending upon the level of

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physical activity of the body and outside temperature. The scientific principle of temperature regulation through PCMs has been deployed in different ways for the manufacturing of textiles. These microcapsules are either embedded in the strands of synthetic fibers or embodied to the layer of a fabric. Some suspend these capsules in a variety of foams. The materials housed in capsules can withstand repeated melts and freezes at the same temperature as that of a normal human body, almost forever.

Waterborne polyurethane (WBPU) has been used for a wide range of commercial applications due to the increasing environmental regulation to reduce low-volatile organic compounds in coatings and adhesive materials.^{13–17} They are not aggressive toward plastic surfaces and they exhibit excellent adhesion to many surfaces, including glass and polymeric fibers.^{18–20} In this study, WBPU was prepared from isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl) propionic acid (DMPA), polytetramethylene ether glycol (PTMG), ethylenediamine (EDA), and triethylamine (TEA).

We have dispersed octadecane as a phase change material within the matrix network of WBPU, resulting in the formation of microspheres. WBPU/octadecane/emulsifier blends were mixed using a homogenizer. Coating materials were formulated from WBPU/octadecane/emulsifier blends, thickeners, and hardeners. Then the coating materials were embodied to a layer of fabrics. This paper focuses on the thermal behaviors of various coating materials formulated from WBPU/octadecane/emulsifier blends, thickeners, and hardeners. Their morphology and particle size were also investigated.

EXPERIMENTAL

Materials

PTMG (Mn = 2000, Hosung Petrochemical Co., Ltd.) was degassed at 70°C under vacuum overnight before use. IPDI (Merck Co.) and DMPA were used as received. EDA, *N*-methyl-2-pyrrolidone (NMP, Junsei Chemical), and methyl ethyl ketone (MEK) were dried over 4-Å molecular sieves before use. TEA (Aldrich) used as a neutralization agent, dibutyltin diacetate as a catalyst, octadecane (Aldrich) as a phase change material, emulsifier hydrogenated castor oil-12 (HCO-12, 7.2 HLB, ICI), thickener (L75N, Bayer), and hardener (Desmodur, Bayer) were used without further purification.

Synthesis of WBPU

The WBPU was synthesized using the prepolymer mixing process method.²¹ The PTMG was placed in a four-neck round-bottom flask equipped with a ther-

mometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket and degassed under vacuum at 90°C for 30 min. Then DMPA/NMP (1/1 wt ratio) was added to the flask, and the mixture was allowed to cool until 40°C under moderate stirring. IPDI was added to the flask and heated to 85°C under moderate stirring. The reaction mixture was allowed to react at 85°C until the theoretical NCO content was reached. The change of NCO content during reaction was determined using a standard dibutylamine back-titration method (ASTMD1638). MEK (10 wt %) was added to the NCO-terminated prepolymer mixture to adjust the suitable viscosity of solution. Then TEA was added to the reaction mixture for neutralizing the carboxyl group of the NCO-terminated polyurethane prepolymer. After 30 min of neutralization reaction, distilled water (65 wt %) was added to the reaction mixture under vigorous stirring. The neutralized prepolymer was chain-extended by dropping EDA at 40°C for 1 h and the reaction continued until the NCO peak (2270 cm⁻¹) in the IR spectrum had completely disappeared. All the aqueous dispersions (42 wt % solid) were obtained by evaporating MEK and then by adding the adequate amount of water.

Microencapsulation

The microspheres of octadecane were formed by blending WBPU and octadecane as PCM. The organic phase (octadecane) was dispersed into the WBPU aqueous phase in the presence of emulsifier using homogenizer (11,000 rpm for 5 min), resulting in the formation of oil-in-water emulsion. In the emulsion, the octadecane particles were embedded within the WBPU matrix in an aggregated state, resulting in the formation of octadecane microsphere. The coatings materials were formulated from WBPU/octadecane/emulsifier blends, thickener, and hardener.

Preparation of films

Films were prepared by pouring the formulated coating materials into a Teflon disk at ambient conditions. The films (typically about 0.12 mm thickness) were dried in a vacuum at 50°C for 2 days and stored in a desiccator at room temperature.

Coating on the nylon fabrics

The coating materials were coated to nylon fabrics using a steel bar and filler and then cured at 120°C for 2 min. The thickness of the coated layer was about 0.04 mm.

Characterization

Thermal property

DSC (SSC-5200, Seiko) was used to determine the melting and crystallization temperature. Heating and

TABLE I
Sample Designations and Compositions Formulated from WBPU/Octadecane/Emulsifier
Blends, Thickener, and Hardener

Sample designations	WBPU ^a (g)	Octadecane (g)	Emulsifier ^b (g)	Thickener (g)	Hardener (g)
P-1		10			
P-2	100	15	0.5	1.0	5
P-3		20			
E-1			0.1		
E-2	100	10	0.5	1.0	5
E-3			1.0		
T-1				0.8	
T-2	100	10	0.5	1.0	5
T-3				1.2	
H-1					3
H-2	100	10	0.5	1.0	5
H-3					7

^a The solid content of WBPU: 40 wt %.

^b Hydrogenated castor oil-12 (HCO-12).

cooling rates of 10 and 5°C/min were used, respectively. These heat absorptive or release characteristics can be in either the heat of fusion or the heat of crystallization; they can be associated with the phase change range (melting/crystallization range) of materials.

Particle size of WBPU

The particle size of WBPU dispersion was determined using an Autosizer (Malvern IIC). Approximately 0.15 mL of emulsion was diluted with distilled water to an appropriate concentration in the cell, followed by setting the pinhole at 200 μm. The test with a few drops of suspension was carried out after dispersion by sonicator for 1 min. The average particle diameters were measured at 25°C.

Morphology

Morphology of thin films of coating material was studied by scanning electron microscopy (SEM, Hitachi S-4200). One drop of the microcapsule dispersion was placed on a nickel SEM stub and dried overnight. The samples were coated in conventional manner with a thin layer of gold palladium to prevent changing.

Water vapor permeability

The water vapor permeability was determined using an evaporation method described in ASTM E9663-T. The mouth of the test dish is covered with test specimen, and the edges are sealed with sealing material. The whole assembly is weighed and placed in an air-circulated, temperature- and humidity-controlled chamber. The chamber has a temperature of 40 ± 2°C, 50 ± 5% relative humidity, and 0.8 m/s air movement.

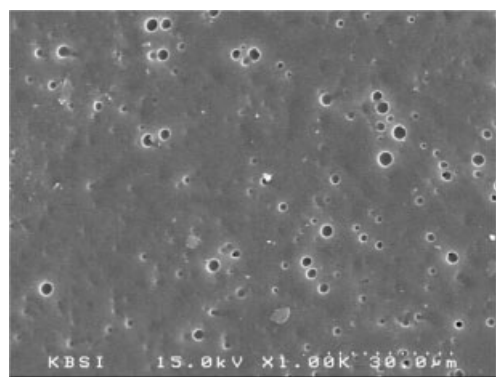
Thermal transport property

Thermal characteristics Q_{\max} of coated nylon fabrics were measured by KES-F7 (Thermolabo II, Kato Tech. Co., Ltd.). The measuring condition was 20 ± 2°C, 65 ± 5% RH, and 10 cm/s air movement. The temperature of the plate that was measured, Q_{\max} of nylon fabrics, was 30 ± 2°C. Q_{\max} (J/cm² s) was used for judging the warm/cool touch sensation felt with the initial contact of a fabric. The heat absorption starts just after touching a thin copper plate containing an amount of heat on the surface of fabrics. It is defined as the peak value of the heat flow rate from the heat capacitor to the surface of a fabric specimen measured from the moment the capacitor and surface come into contact. This transient response is similar to that occurring as heat is transferred from the surface of human skin to the heat-sensitive nerves of the skin.

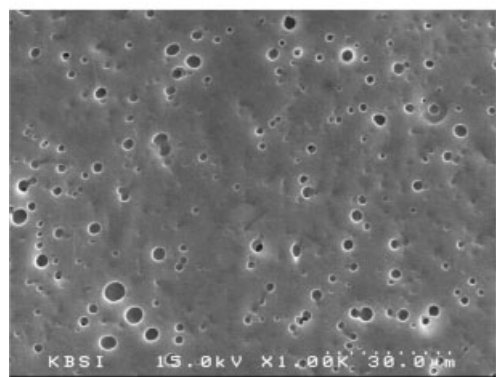
RESULTS AND DISCUSSION

Sample designations and compositions for formulated from WBPU, octadecane, emulsifier, thickener, and hardener are given in Table I.

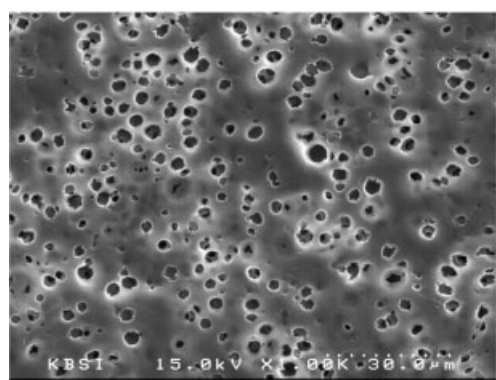
SEM photomicrographs of formulated coating films are shown in Figures 1 and 2. Figure 1 shows the morphological textures of P samples having different octadecane content, while Figure 2 shows the texture of E samples having different emulsifier content. It is seen that the mean diameter and number of microspheres increase with increasing octadecane content (see Figs. 1 and 3). As the emulsifier content increases, the mean diameter of microspheres decreases, but the number of microspheres increase (see Figs. 2 and 3). The phenomenon was explained by the fact that the emulsifier does significantly affect the dispersion of octadecane in the WBPU matrix.



(a) P-1



(b) P-2



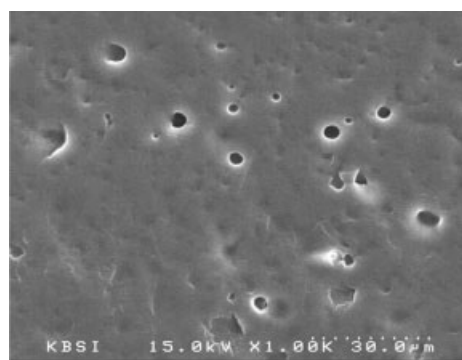
(c) P-3

Figure 1 Effect of octadecane contents on the SEM micrographs of P-series samples.

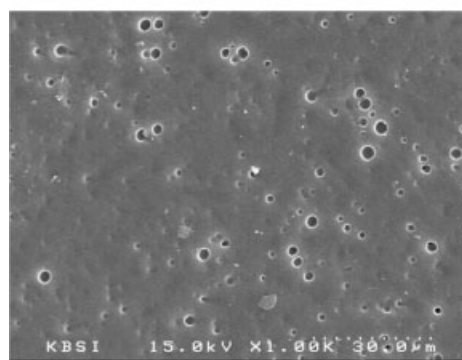
Figure 4 presents the textures of T sample (a), having different thickener content, and H sample (b), having different hardener content, respectively. The number of microspheres was found to increase more or less with increasing thickener and hardener content. This might be due to the fact that thickener and hardener could trap the microencapsulated octadecane in the matrix WBPU. The microencapsulated octadecane formed to be microspheres in this study was 1–6 μm . Generally, it is desirable to have a microcapsule size at least smaller than 10 μm for textile coatings. Based on the observation of morphology, we can conclude that the phase change material octadecane was successfully microencapsulated and the mean size of microspheres (1–6 μm) is smaller than 10 μm .

Phase change material microcapsule applied to textiles emits heat energy on the outside or absorbs heat energy from the outside, as caused by a change of phase from solid to liquid and/or from liquid to solid according to a change in skin temperature or environment temperature.²² In other words, the thermal emission (or heat absorption) is dependent on external temperature and its content. A DSC curve of bulk octadecane is shown in Figure 5. The latent heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) of octadecane are 236.6 mJ/mg and 227.6 mJ/mg, respectively.

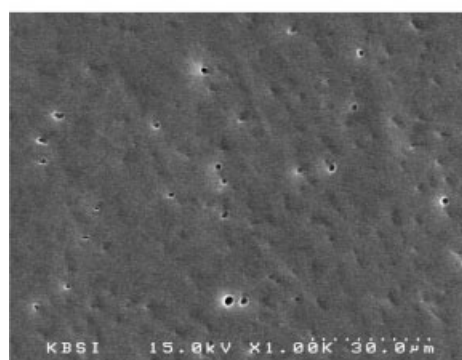
Figures 6 to 9 show DSC curves of WBPU/PCM blends films prepared from different contents of emulsifiers, octadecanes, thickeners, and hardeners. Figure 6 shows the effect of octadecane content on the DSC



(a) E-1



(b) E-2



(c) E-3

Figure 2 Effect of emulsifier contents on the SEM micrographs of E-series samples.

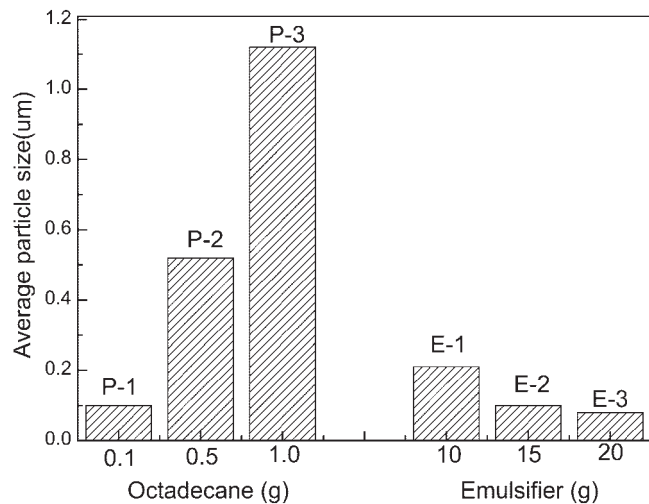


Figure 3 Effects of emulsifier and octadecane contents on the mean particle size for P- and E-series samples.

curves for P-series samples. Encapsulated octadecane showed a phase change over the same temperature range as bulk octadecane around 32.5°C (melting temperature, T_m) and 24°C (crystallization temperature, T_c). Melting temperature and ΔH_f value were increased as octadecane content increased. Figure 7 illustrates DSC curves for E-series samples. The heat of fusion (ΔH_f) was increased with increasing contents of emulsifier. This might be explained by the fact that the

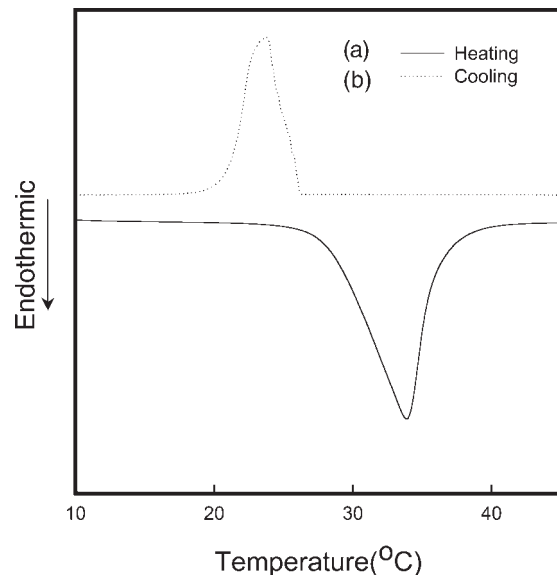


Figure 5 DSC thermograms of octadecane on (a) heating and (b) cooling scans.

emulsifier effectively dispersed octadecane in WBPU. Figure 8 shows DSC curves for the thickener effect and Figure 9 shows DSC curves for the hardener effect, respectively. This might be explained by the fact that thickener and hardener play an important role in trapping microencapsulated octadecane.

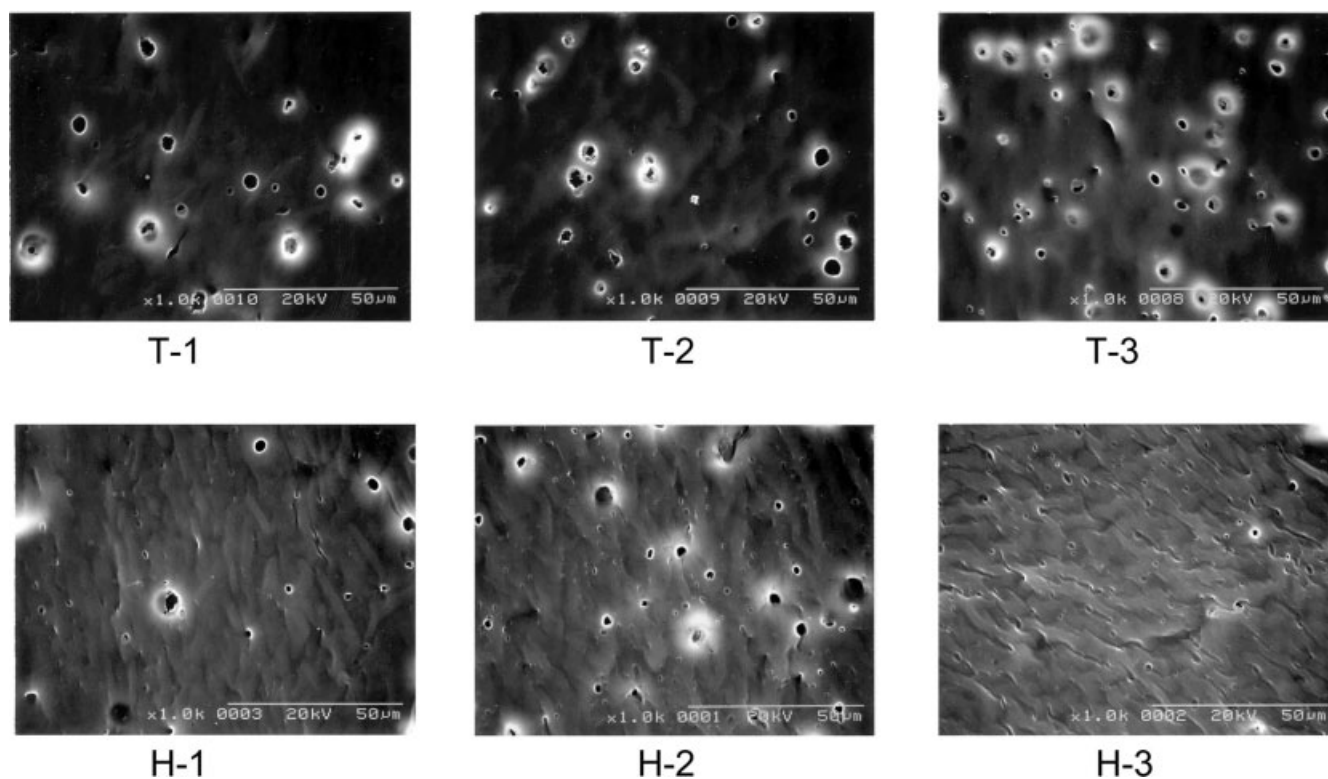


Figure 4 Effect of thickener and hardener contents on the SEM micrographs.

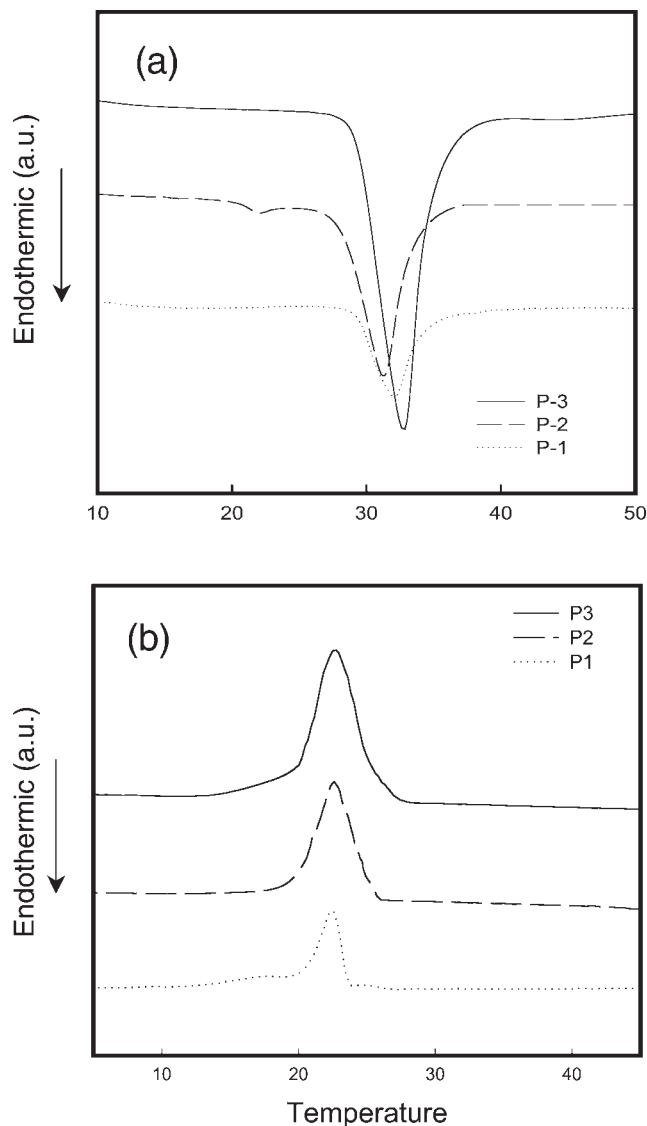


Figure 6 Effect of octadecane contents on the DSC thermograms of P-series samples on (a) heating and (b) cooling scans.

Figure 10 presents an SEM micrograph after coating onto nylon fabric. The phase change material octadecane is embedded nicely in the matrix WBPU.

Measured heat of fusion ($\Delta H_{f, \text{ meas}}$) and heat of crystallization ($\Delta H_{c, \text{ meas}}$), calculated heat of fusion ($\Delta H_{f, \text{ theo}}$) and heat of crystallization ($\Delta H_{c, \text{ theo}}$), and their filling efficiencies are listed in Table II. The filling efficiency of microencapsulated octadecane was calculated from the measured and theoretical values. If all octadecanes have microencapsulated, measured, and theoretical latent heat (ΔH_f and ΔH_c) they should have almost the same values. However, the core content measured using ΔH_f and ΔH_c was less than the theoretical content based on the feed amount of octadecane. Also, $\Delta H_{f, \text{ meas}}$ was shown to have a lesser value than $\Delta H_{c, \text{ meas}}$ regardless of octadecane content. The

size of the microcapsule cannot increase greatly the core content because it is influenced by wall materials.²³ However, the filling efficiency of microencapsulated octadecane increases significantly as core content increases in this study. This indicates that octadecane is easily embedded in the matrix WBPU with octadecane content.

The Q_{max} (J/cm² s) value and water vapor permeability with respect to different composition are shown in Table III. Q_{max} is the measure of the heat transfer properties of fabric. The signal of the heat flow associated with this absorption indicates the peak value of the heat flow, which is defined as Q_{max} . The Q_{max} value appeared after touching and was recorded

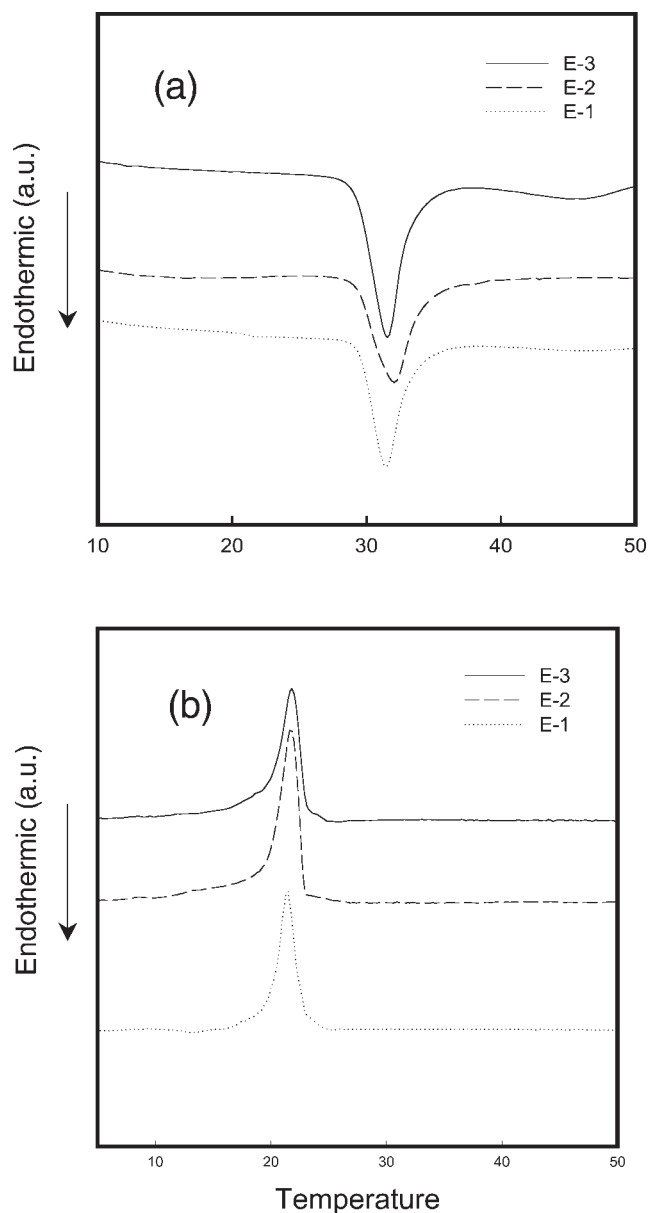


Figure 7 Effect of emulsifier contents on the DSC thermograms of E-series samples on (a) heating and (b) cooling scans.

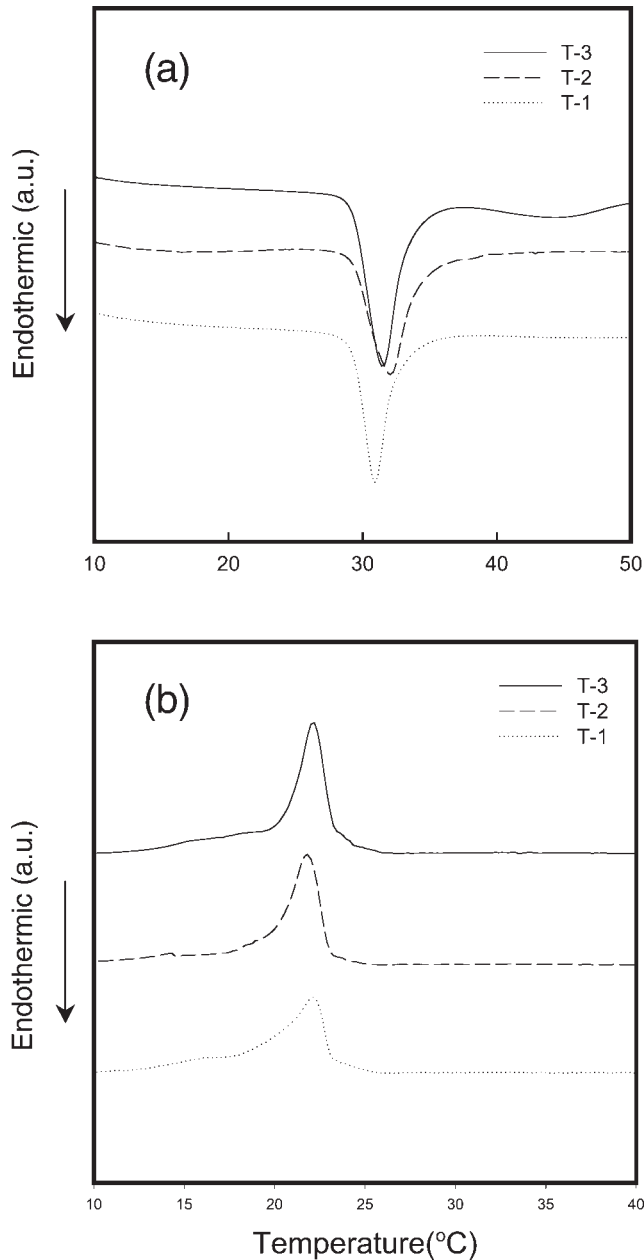


Figure 8 Effect of thickener contents on the DSC thermograms of T-series samples on (a) heating and (b) cooling scans.

to evaluate the fabric properties relating with the warm/cool feeling of fabric touch.²⁴ The heat flow rate is higher at large Q_{\max} value than at small ones. The former has a cooler touch sensation, while the latter has a warmer touch sensation. The Q_{\max} value of samples containing octadecane is than that of the control sample and WBPU-coated fabric. Q_{\max} values of WBPU/octadecane-coated fabric increased as octadecane content increased; however, Q_{\max} values were scarcely changed as emulsifier, thickener, and hardener content increased. Water vapor permeability hardly changed as emulsifier content increased. Water

vapor permeability decreased with increasing octadecane content. Octadecane may have disturbed water molecules in passing through because of its hydrophobicity.

CONCLUSIONS

We studied microencapsulation with octadecane as a phase change material in the matrix WBPU. As the concentration of octadecane increased, the size of the microspheres increased; on the other hand, an increase in emulsifier concentration resulted in a decrease in microcapsule size. By thermal analysis, crystallization

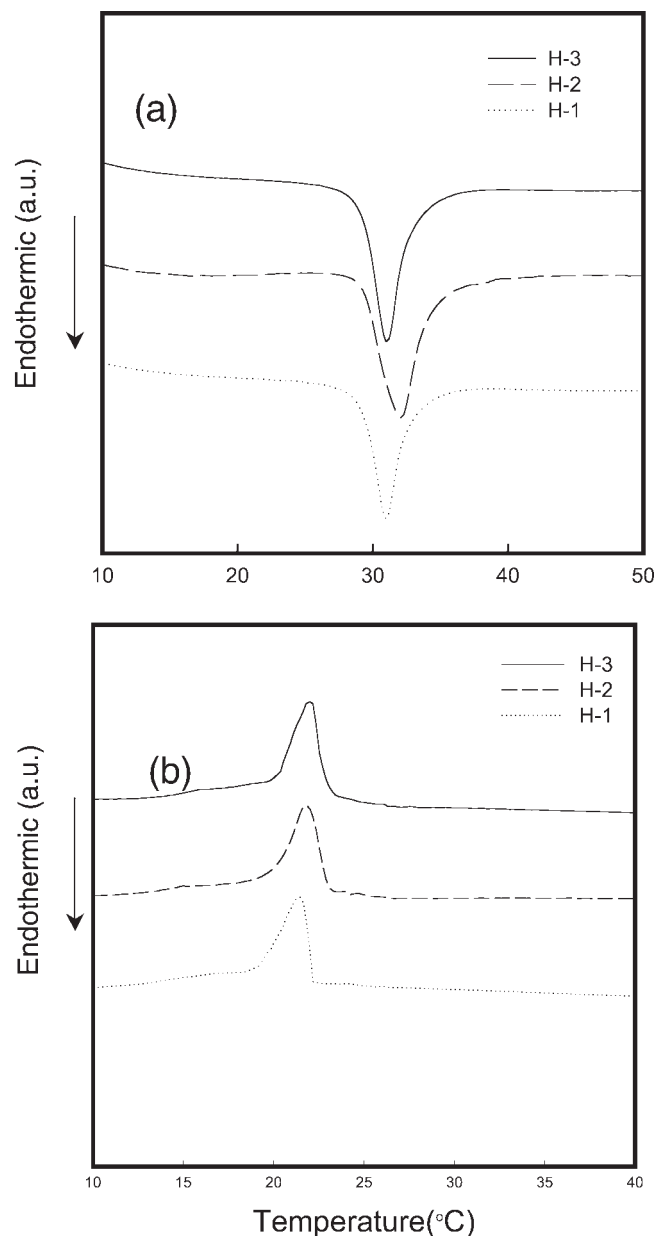


Figure 9 Effect of hardener contents on the DSC thermograms of H-series samples on (a) heating and (b) cooling scans.

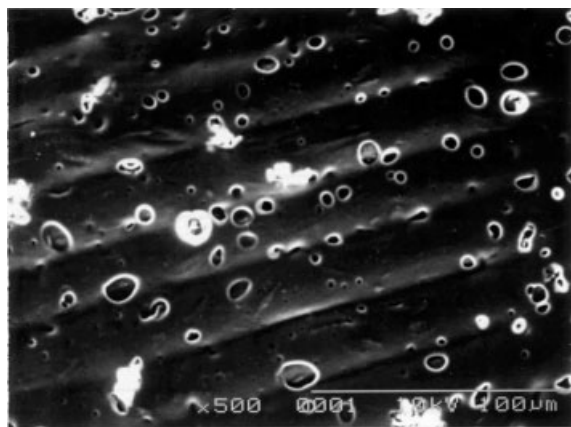


Figure 10 SEM micrograph of P-2 sample after coating onto nylon fabric.

and melting temperatures of octadecane were 23.5 and 30.5°C, and heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) were 236.6 and 227.6 mJ/mg, respectively. The filling efficiency of microencapsulated octadecane increased with increasing octadecane, emulsifier, thickener, and hardener content. In addition, thickener and hardener were found to play an important part in trapping microencapsulated octadecane. The phase change material octadecane can be embedded in matrix WBPU effectively.

Q_{\max} (J/cm² s) and water vapor permeability were measured after coating WBPU/octadecane to nylon fabric. Q_{\max} values of WBPU/octadecane-coated nylon fabric were higher than those of the control and WBPU-coated nylon fabric. This phenomenon was due to the fact that WBPU/octadecane-coated fabric

TABLE III
 Q_{\max} and Water Vapor Permeability for Controlled, WBPU, and Microencapsulated Octadecane-Coated Fabrics

Sample designation	Q_{\max}	WVP (g/m ² · day)
Control fabric	0.185	4457
WBPU	0.188	2010
P-1	0.200	1564
P-2	0.212	1537
P-3	0.242	1522
E-1	0.204	1426
E-2	0.200	1565
E-3	0.203	1555
T-1	0.203	1556
T-2	0.203	1549
T-3	0.202	1533
H-1	0.202	1548
H-2	0.205	1544
H-3	0.203	1520

indicates high heat flow rates at moment of octadecane's melting. It might be concluded to display cool contact sensitivity. Accordingly, as emulsifier, thickener, and hardener content increase, water vapor permeability almost did not change, but decreased with increasing octadecane content. This is because the hydrophobicity of octadecane prevents water molecules from passing through.

In this study, phase change material existed as microspheres embedded in the matrix (WBPU). Then coating materials could be coated onto applied fabrics directly, indicating the binding role of WBPU for fabrics. This is the first experiment to embed microencapsulated octadecane onto nylon fabrics using the coating process. This research is a profitable method for

TABLE II
The Change of Enthalpy (ΔH) and Filling Efficiencies for Microencapsulated Octadecane

Sample designation	Endothermic changes (heat of fusion)			Exothermic changes (heat of crystallization)		
	$\Delta H_{f, \text{meas}}^a$ (mJ/mg)	$\Delta H_{f, \text{theo}}^b$ (mJ/mg)	Filling efficiencies ^c of ΔH_f	$\Delta H_{c, \text{meas}}^a$ (mJ/mg)	$\Delta H_{c, \text{theo}}^b$ (mJ/mg)	Filling efficiencies ^c of ΔH_c
P-1	15.70	17.04	92.13	14.80	18.08	81.87
P-2	49.39	51.49	95.75	52.91	54.62	96.85
P-3	65.43	68.89	97.69	71.49	73.08	97.82
E-1	15.23	17.05	89.33	14.40	18.09	79.62
E-2	15.70	17.04	92.13	14.80	18.08	81.87
E-3	16.71	17.05	98.01	16.80	18.09	92.87
T-1	15.31	17.25	88.75	13.12	18.30	71.69
T-2	15.70	17.04	92.13	14.80	18.08	81.87
T-3	15.70	16.72	96.91	16.72	17.74	94.25
H-1	14.23	17.15	82.97	12.94	18.19	71.14
H-2	15.70	17.04	92.13	14.80	18.08	81.87
H-3	16.11	16.64	96.81	15.53	17.65	87.99

^a $\Delta H_{f, \text{meas}}$ (or $\Delta H_{c, \text{meas}}$, mJ/mg of octadecane); measured heat capacity of microencapsulated octadecane.

^b $\Delta H_{f, \text{theo}}$ (or $\Delta H_{c, \text{theo}}$, mJ/mg of octadecane); calculated heat capacity of microencapsulated octadecane = [weight of octadecane(mg)/total sample weight(mg)] × ΔH (mJ/mg) of pure octadecane.

^c Filling efficiencies of $\Delta H = \Delta H_{\text{meas}}/\Delta H_{\text{theo}} \times 100$.

simplification of the textile finishing process using the embedding method of PCM core material.

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