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## Development of natural dyed textiles with thermo-regulating properties

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## ABSTRACT

The objective of this study was to develop natural dyed fabrics with thermo-regulating properties. Microcapsules (MCs) containing *n*-octadecane and *n*-eicosane were applied to the natural indigo-dyed cotton fabrics using the dot-screen printing method. A 50/50 mixture of the two MCs was also applied. At similar loading amounts for the microcapsules, the fabrics were capable of absorbing 18.66, 14.80, and 14.68 J g<sup>-1</sup> of latent heat for the *n*-eicosane MCs, the *n*-octadecane MCs, and the mixture of the two MCs, respectively. After 20 laundering cycles, about 94% of the latent heat was retained. The color of the fabrics changed negligibly with color difference ( $\Delta E^*$ ) ranged 0.45–1.00 after MCs treatment and ranged 1.69–2.00 after 20 launderings. The latent heat was retained 70–89% after rubbing tests and 92–96% after ironing tests using a cover fabric in damp condition.

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## 1. Introduction

Nowadays, natural dyeing has been an area of interest as a green technology because of environmental problems, global warming, and the depletion of natural resources. Natural dyed textile products are gaining popularity under the global circumstances that require a high environmental consciousness to consumers. Natural dyed textile products with high value-added properties must be developed using energy-saving technology in order to improve their competitiveness in the commercial market. Therefore, the development of natural dyed fabrics with thermo-regulating properties is very important.

Microencapsulated phase change materials (PCMs) have been used to manufacture thermo-regulated fibers, foams, or fabrics [1,2]. PCM microcapsules (MCs)-treated textiles can produce a temporary cooling or warming effect in the clothing suitable for the use in hot or cold environments, and can improve the thermal comfort of the garment system. Currently, a variety of outdoor apparel items with PCM MCs are available, and the market continues to grow [3].

Hydrophobic *n*-paraffin waxes are non-toxic, inexpensive, and have a wide range of melting and crystallization temperatures depending on their carbon atoms. These waxes are able to absorb, store and release large amounts of latent heat as their physical state changes. The phase change temperature can be tailored for specific end-uses. *n*-Octadecane is suitable for all seasons clothing because its melting temperature is about 28.2 °C and, therefore,

\* Corresponding author. E-mail address: yshin@chonnam.ac.kr (Y. Shin). below the mean skin temperature of  $33.3 \degree C$  [4–9]. *n*-Eicosane has melting temperature about  $37 \degree C$  and is suitable for hot summer clothing [9,10]. Shim et al. [11] used 40% *n*-octadecane MCs and 60% hexadecane MCs for experimental ski-suits.

Although PCM MCs impart thermo-regulating properties, other comfort-related properties are affected by applying them to fabrics. The hand and durability of the PCM MCs-treated fabrics are also affected by adhesive coating processes, such as pad-dry-cure, dip. float, knife coating, etc. [12,13]. Koo et al. [14] reported about the development of thermo-regulating nylon fabrics using a dual coating method. Sánchez et al. [15] also used a coating technique by a motorized film applicator for developing thermo-regulating cotton fabrics. They coated the entire surface of fabrics with PCM MCs formulations. We adopted the dot-screen printing method, by which the dot areas were printed with PCM MCs formulations on the back side of fabrics, considering the hand changes and the color changes of the dyed fabrics. There have been no articles about the development of thermo-regulating fabrics using this printing method and taking into account the effect of PCM MCs treatment on the dyed color of fabrics.

The objective of this study was to develop natural dyed fabrics with thermo-regulating properties. The cotton fabrics that were dyed with natural indigo were treated with the PCM MCs using the dot-screen printing method. The formulations of the fixation were *n*-octadecane MCs, *n*-eicosane MCs, and a 50/50 mixture of the two MCs. The thermal properties were examined using differential scanning calorimetry (DSC). Furthermore, scanning electron microscopy (SEM) was used to observe the presence, distribution, and structure of the microcapsules. In order to investigate the efficacy of the fixation of the PCM MCs on the natural dyed fabrics, the

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Table 1
Characteristics of fabric.

Sample	Weave	Warp (cm <sup>-1</sup> )	Weft (cm <sup>-1</sup> )	Weight (g/m <sup>2</sup> )	Thickness (mm)
Cotton	1/2 Twill	57	30	126.65	0.24

color, colorfastness and physical properties including the stiffness and the air permeability were evaluated along with the durability to laundering, rubbing and ironing with respect to the thermoregulating effects.

## 2. Experimental

#### 2.1. Materials

The fabric that was used in this study was scoured and bleached 100% cotton characterized in Table 1. The natural indigo dye was prepared from *Polygonum tinctorium* using the Korean traditional niram method [16]. The melamine formaldehyde microcapsules containing *n*-octadecane ( $C_{18}H_{38}$ ,  $T_m$  28 °C, latent heat storage capacity 243 J g<sup>-1</sup>) or *n*-eicosane ( $C_{20}H_{42}$ ,  $T_m$  36.7 °C, latent heat storage capacity 247 J g<sup>-1</sup>) [17] were procured [13] from a local supplier (Human Tech., Korea). The mean particle sizes of the microcapsules were 28.06 and 23.47 µm, respectively. All of the other chemicals were reagent grade.

#### 2.2. Dyeing

The dyeing was carried out in a reduced dye bath with 16 g/L of the indigo dye and 5 g/L of sodium hydrosulfite in a liquor ratio of 1:50 at 40 °C for 30 min. The dyed samples were oxidized in air for 30 min and then subsequently rinsed in tap water and dried.

## 2.3. Fixation of the microcapsules on the dyed fabrics

The coating formulation included 40% PCM MCs, 20% rubber binder (NX-N, Hanyang Petrochemical co., Ltd., Korea), 15% acrylic binder (N-140, Hanyang Petrochemical Co., Ltd., Korea), 3% silicon emulsion (Silicone-SF, Sam Doo Co., Ltd., Korea) and 1% alkali thickener (HTH-15, Hanyang Petrochemical Co., Ltd., Korea). The three different samples were prepared using the *n*-octadecane MCs, the *n*-eicosane MCs, and a 50/50 mixture of the two MCs. The coating formulation including the PCM MCs was applied on the back side of the dyed fabrics using the dot-screen printing method. The screen, a fine nylon mesh fabric was left uncovered in the dot areas which were going to be printed, whereas the rest of dot areas which were not to be printed were sealed. Printing was done with a squeegee, which was used to squeeze the coating formulation through the fine meshes of the screen onto fabrics. The dot-printed fabrics were dried at 120 °C for 5 min and cured at 150 °C for 3 min. The addons for PCM MCs-treated fabric were calculated according to the formula:

$$\text{Add-on}(\%) = \frac{b-a}{a} \times 100$$

where a is the fabric weight of sample before treating and b, the weight of sample after treating.

#### 2.4. Characterization

The FT-IR spectra of the *n*-octadecane and *n*-octadecane microcapsules were measured using a Fourier transformed infrared spectrophotometer (FTIR, Prestige-21, Shimadzu, Japan) using the KBr pellet method at room temperature. The latent heat storage capacity and the phase change temperatures were measured with a differential scanning calorimeter (DSC2920, TA Instrument, New Castle, DE). The heating and cooling rates were  $2 \,^{\circ}$ C/min from  $10 \,^{\circ}$ C by  $50 \,^{\circ}$ C under an N<sub>2</sub> atmosphere. Average value of the latent heat storage capacity was obtained from at least three measurements. The standard deviation of DSC measurements was  $\pm 1.2 \, J g^{-1}$ .

The surface of the microcapsule-treated fabrics was observed using a field emission scanning electron microscope (FE-SEM: JSM-7500F, JEOL Inc., Japan).

The effects of laundering, rubbing and ironing of the PCM MCs-treated fabrics were evaluated by DSC and SEM analyses. Laundering durability was tested up to washing (5, 10 and 20 cycles) using the standard procedure (AATCC test method 61-1989). Washing was carried out at 40 °C for 45 min in water with a volume of 200 mL with 0.5% light detergent using a Launder-Ometer (Atlas Electric Device Co., Houston, TX). The rubbing test was carried out using a standardized Crockmeter (DL-2007, DaeLim, Co., Ltd., Korea) according to AATCC test method 8-2005. The face side and back side of PCM MCs-treated samples were rubbed for 10 cycles at a pressure of 900 g under dry condition. The ironing test was done by hot pressing of the PCM MCs-treated fabrics under dry and damp conditions (AATCC test method 133-2004). The face side of the sample was pressed at 204 °C for 15 s giving a pressure on the specimen of 40 g cm<sup>-2</sup>. All of tests were carried out three times.

# 2.5. Color and physical properties of the PCM microcapsule-treated fabrics

The color properties of the dyed fabrics were evaluated in terms of the dye uptake (expressed as the *K*/*S* value at the maximum absorption wavelength), the *H V*/*C* Munsell color values, CIE  $L^*a^*b^*$  coordinates, and the color difference ( $\Delta E^*$ ) using a Macbeth Coloreye 3100 spectrophotometer. The color fastness to washing (AATCC test method 61-1989), rubbing (AATCC test method 8-2005) and ironing (AATCC test method 133-2004) were estimated following standard procedures, as described above (Section 2.4). Light fastness was evaluated according to AATCC test method 16-2004 (option 3) using Xenon Test Chamber (Q-SUN, Xe-1-B, Q-Panel Lab Products, USA) after irradiation for 20 h. Color fastness rating was assessed by color change against the standard gray scale (values 1–5, where 1 = poor and 5 = excellent).

The stiffness (ASTM test method D 1388-64) and the air permeability (Frazier method; ASTM test method D 737-96) were evaluated using the standard procedures. Stiffness was assessed by the resistance to bending. Bending length by cantilever test was measured for the stiffness of the PCM MCs-treated fabrics. Air permeability was the rate of air flow through a fabric under differential pressure between the two fabric surfaces. The rate of air flow was measured at a prescribed pressure differential of 12.7 mm of water.

#### 3. Results and discussions

#### 3.1. Characteristics of the PCM microcapsules

Fig. 1 shows the FT-IR spectra of the *n*-octadecane and *n*-octadecane microcapsules. The absorption peaks at  $2853-2922 \text{ cm}^{-1}$  for the C–H stretching,  $1460 \text{ cm}^{-1}$  for the C–H bending, and  $721 \text{ cm}^{-1}$  for the vibration of the CH<sub>2</sub> group



Fig. 1. FT-IR spectra of (a) *n*-octadecane and (b) *n*-octadecane microcapsules.

were characteristic of *n*-octadecane. The N–H stretching vibrations at 3400 and  $1570 \,\mathrm{cm}^{-1}$  was caused by the microcapsule shell that was composed of melamine formaldehyde. Therefore, the *n*-octadecane microcapsules were successfully formed. Similar results were obtained for *n*-eicosane and the *n*-eicosane MCs.

The thermal properties of the PCM MCs were evaluated using a differential scanning calorimeter (DSC). Fig. 2 presents the DSC curves of the microcapsules containing *n*-octadecane or *n*-eicosane. The peak melting temperatures  $T_m$  of the *n*-octadecane and *n*eicosane MCs were 27.43 and 35.29 °C, respectively, during heating. These temperatures coincided with the  $T_m$  of pure PCMs. However, during cooling, the phase change occurred at lower temperatures than during heating. Furthermore, two crystallization temperature peaks, including a strong peak at 22.25 °C and a weak peak at 15.95 °C, appeared in the DSC cooling curve of the *n*-octadecane MCs, whereas three crystallization temperature peaks, including a strong peak at 32.05 °C and two smaller peaks at 27.56 and 22.09 °C, appeared in the DSC cooling curve of the *n*-eicosane MCs. A pre-



Fig. 2. DSC thermograms of the PCM microcapsules.

Table 2
Characteristics of PCM microcapsules

		•				
Core PCM	Size (µm)	$T_m$ (°C)	$T_c (^{\circ}C)$	$\Delta H_{\!f}(\mathrm{J}\mathrm{g}^{-1})$	$\Delta H_c(\mathrm{J}\mathrm{g}^{-1})$	Core/shell ratio (%)
n-Octadecane	28.06	27.43	22.25 15.95	153.9	158.1	65.1
n-Eicosane	23.47	35.29	32.05 27.56 22.09	184.9	165.2	66.9

vious report showed that the multiple peaks on the DSC cooling curves can be attributed to the liquid-rotator, rotator-crystal, and liquid-crystal transitions [18]. During heating, the PCMs changed phase from the ordered solid phase to the disordered liquid phase. Conversely, during cooling the disordered liquid phase changed to the ordered solid phase. The heat that was released from some of the capsules during cooling was possibly regained by the other capsules [19]. The crystallization behavior was affected by the average diameter of the microcapsules. The supercooling crystallization was caused by the reduced numbers of nuclei in each microcapsule because of the reduced diameter [20]. Supercooling lowered the crystallization temperature and led to release of latent heat at a lower temperature or in a wider temperature range. This supercooling crystallization phenomena of the microencapsulated *n*-octadecane and *n*-eicosane occurred when the microcapsule diameters were smaller than  $100 \,\mu m$  [18].

The phase change temperatures, including the peak melting temperature ( $T_m$ ) and the peak crystallization temperature ( $T_c$ ), and the latent heat storage capacities of the *n*-octadecane and *n*-eicosane MCs are summarized in Table 2. The phase change temperatures of the microencapsulated PCMs were similar to those of the core materials, i.e., *n*-octadecane or *n*-eicosane [17]. The latent heat of fusion ( $\Delta H_f$ ) and the latent heat of crystallization ( $\Delta H_c$ ) of the *n*-octadecane MCs were 153.9 and 158.1 Jg<sup>-1</sup>, respectively, and the  $\Delta H_f$  and the  $\Delta H_c$  of the *n*-eicosane MCs were 184.9 and 165.15 Jg<sup>-1</sup>, respectively. The *n*-eicosane MCs exhibited a higher latent heat storage capacity than the *n*-octadecane MCs. The PCM content of the MCs ranged from 65% to 67%.

## 3.2. Thermo-regulating properties of the PCM MCs-treated fabrics

Fig. 3 shows the natural indigo-dyed fabric that was treated with the PCM MCs using the dot-screen printing method, and these PCM MCs appeared as the white dot pattern on the back side of the fabric. The dots were 2 mm in diameter, and the average number of dots was 6.5/cm<sup>2</sup>. The dot pattern on the back side of the fabrics was not seen through the fabrics because the cotton fabric was thick and tight enough.



Fig. 3. Photograph of PCM microcapsule-treated fabric with dots on back side.



**Fig. 4.** DSC thermograms of the PCM microcapsules-treated fabrics: (a) *n*-octadecane MCs; (b) *n*-eicosane MCs; (c) *n*-octadecane/*n*-eicosane MCs(50/50).

The DSC curves of the PCM MCs-treated fabrics are shown in Fig. 4. The dot printed parts of the fabric were used for the DSC analysis. Endothermic peaks were observed at 26.57 and 34.36 °C in the DSC curves of the *n*-octadecane MCs-treated and the *n*-eicosane MCs-treated fabrics. The multiple endothermic peaks that appeared in the DSC curves of the PCM MCs-treated fabrics were the same as the DSC curves of the PCM MCs. The peak melting temperatures  $T_m$  of the PCM MCs-treated fabrics were slightly different than the formulated PCM MCs, but they appeared at similar temperature ranges. The fabrics that were treated with the *n*-octadecane/*n*-

eicosane MCs(50/50) exhibited the peak melting temperatures  $T_m$ of both the *n*-octadecane MCs and the *n*-eicosane MCs. The latent heat storage capacities of the treated fabrics were calculated on the basis of the DSC results of dot printed parts of the fabric. The fabrics were capable of absorbing 18.66, 14.80, and 14.68  $Jg^{-1}$  for the *n*-eicosane MCs, the *n*-octadecane MCs, and the mixture of the two MCs, respectively. Table 3 shows the peak melting/crystallization temperatures and the latent heat absorption/release capacities of the PCM MCs-treated fabrics. The latent heat absorption/release effects of the PCM MCs-treated fabrics were high and followed the order of *n*-eicosane MCs > *n*-octadecane MCs  $\ge$  *n*-octadecane/*n*eicosane MCs(50/50). A lower latent heat storage capacity was obtained with the 50/50 mixture than with each PCM MCs. It was speculated that *n*-eicosane MCs absorbed the heat gained by *n*octadecane MCs, and this led to a decrease in the overall latent heat storage capacity [19,21]. Nevertheless, the 50/50 mixture of two PCM MCs allowed widening the thermal span of the treated fabrics. It is necessary to study the effect of mixture composition ratio on thermal capacity for a better design of thermo-regulating textiles. The latent heat storage capacities of the thermo-regulating fabrics that were prepared in this study were comparatively higher than the fabrics prepared in another study. The treated fabric with a 22.9% add-on of the *n*-eicosane MCs using pad-dry-cure (PDC) method was capable of absorbing  $4.44 \text{ Jg}^{-1}$  of heat [13]. The PCM MCs-treated fabrics absorbed latent heat when PCM in the microcapsules applied to the fabric melted and emitted heat when the microcapsules on the fabric froze. The absorption (or emission) of latent heat by the microcapsules delayed the microclimate temperature increase (or decrease), enhancing the thermal comfort of the clothing system. Therefore, the fabrics that were treated with the *n*-eicosane MCs can be used for the hot summer season, and the fabrics that were treated with the *n*-octadecane MCs can be used for all seasons clothing [9]. On the other hand, the fabric that was treated with the mixture of the two MCs was expected to be suitable for a wider temperature range from hot to mild.

The laundering durability was estimated for practical use with respect to the thermo-regulating effect of the PCM MCs-treated fabrics. Laundering was repeated for up to 20 cycles. Table 4 shows the laundering durability for the latent heat storage effect of the PCM MCs-treated fabrics. Regardless of the PCM MC species, the latent heat storage capacity slightly decreased as the laundering was repeated. The PCM MCs-treated fabrics retained about 94.0% of their latent heat storage capacity after 20 launderings, indicating that the PCM MCs were firmly fixed on the fabric and relatively durable to the mechanical washing motion. Shin et al. [13] and Kwon et al. [22] used a conventional PDC method to fix the PCM MCs onto fabrics and obtained latent heat storage capacity retentions of 66% and 46-64%, respectively, after one laundering cycle. Kim and Cho [5] used a knife-over-roll coating method for the *n*octadecane MCs treatment, and obtained 52-70% of retention after 10 laundering cycles. Most of this decrease occurred after the first laundering. Therefore, the dot-printing method was a very useful method for fixing the PCM MCs onto the fabrics. The effects of rubbing and ironing on the latent heat storage capacity were also evaluated (Table 5). The latent heat storage capacity was retained about 70-89% after rubbing tests. After ironing test, the latent heat storage capacity retentions of 75-88% and 92-96% were obtained under dry and damp rubbing conditions, respectively. For better maintenance of the PCM MCs-treated fabrics, it would be helpful to use a cover fabric when ironing. The latent heat storage capacity after rubbing and ironing tests were increased in the order of *n*-eicosane MCs treated > *n*-octadecane MCs treated > *n*octadecane/n-eicosane MCs(50/50) treated fabrics.

Fig. 5 shows the SEM photographs of the *n*-octadecane MCstreated fabrics that were washed for 0–20 laundering cycles. The

#### Table 3

Thermal characteristics of the dyed/PCM microcapsule-treated fabrics.

Samples	<i>T<sub>m</sub></i> (°C)	$T_c$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> )	$\Delta H_c(\mathrm{Jg^{-1}})$
<i>n</i> -Octadecane MCs treated	26.57	23.37 16.25	14.80	14.52
<i>n</i> -Eicosane MCs treated	34.36	32.32 22.56	18.66	18.51
<i>n</i> -Octadecane/ <i>n</i> -eicosane MCs(50/50) treated	34.16 26.41	33.01 23.59 16.16	14.68	12.69

## Table 4

Effect of laundering of the latent heat storage capacity of the PCM microcapsule-treated fabrics.

Laundering (cycles)	n-Octadecane MCs		n-Eicosane MCs	<i>n</i> -Eicosane MCs		<i>n</i> -Octadecane/ <i>n</i> -eicosane MCs(50/50)	
	$\Delta H_f$ (J g <sup>-1</sup> )	Retention (%)	$\Delta H_f$ (J g <sup>-1</sup> )	Retention (%)	$\Delta H_f$ (J g <sup>-1</sup> )	Retention (%)	
0	14.80	100	18.66	100	14.68	100	
5	14.60	98.7	18.25	97.8	14.66	99.9	
10	14.24	96.2	17.88	95.8	14.17	96.5	
20	14.00	94.6	17.55	94.0	13.86	94.4	

## Table 5

Effect of rubbing and ironing on the latent heat storage capacity of the PCM microcapsule-treated fabrics.

Samples	Initial	Rubbing	Rubbing				
		Face	Back	Dry	Damp		
n-Octadecane MC	s treated						
$\Delta H_f (Jg^{-1})$	14.80	12.67	13.29	13.07	14.25		
Retention (%)		(85.4)	(89.8)	(88.3)	(96.3)		
n-Eicosane MCs tr	eated						
$\Delta H_f (Jg^{-1})$	18.66	13.14	14.59	14.13	17.28		
Retention (%)		(70.4)	(78.2)	(75.7)	(92.6)		
<i>n</i> -Octadecane/ <i>n</i> -eicosane MCs(50/50) treated							
$\Delta H_f (Jg^{-1})$	14.68	12.46	12.65	11.78	13.98		
Retention (%)		(84.9)	(86.2)	(80.2)	(95.2)		

spherical shaped microcapsules and the binder were observed on the dot area of the fabric surface before and after laundering. Some of the microcapsules were broken and some caved with increasing laundering. Similar results were observed for the *n*-eicosane MCs and the *n*-octadecane/*n*-eicosane MCs(50/50). The decrease in the latent heat storage capacity resulted from this deformation of the microcapsules on the fiber surface after laundering. The melting temperature was not affected by repeated launderings.

## 3.3. Physical properties of the PCM MCs-treated fabrics

Table 6 shows the add-on, stiffness, and air permeability of the dyed and PCM MCs-treated fabrics. After dyeing with natural indigo, the stiffness of the fabric increased by 5.4%, and the air permeability decreased by 4.8% compared to the undyed control sample. The indigo dye molecules were present inside the fiber in the form of crystalline aggregates [23], leading to the change in the microstructure of the fibers such as pores and the decreased permeability. The add-ons of the n-octadecane MCs, n-eicosane MCs, and n-octadecane/n-eicosane(50/50) MCs-treated fabrics were 17.92, 18.16, and 18.31%, respectively. After the fixation of the PCM MCs on the fabrics, the stiffness increased by 12.4-15.5%, and the air permeability decreased by about 25.9-26.6%, compared to the dyed sample. The changes in the physical properties of the treated fabrics varied depending upon the loading amount of the PCM MCs [11]. The fabric structure, thickness, and surface characteristics, such as the pore size and porosity, affected the physical properties of the fabrics. In the SEM pictures (Fig. 5), the microcapsules and binder filled some of the pores in the fabric, and the dot area (0.29 mm) was thicker than the rest of the dot area (0.24 mm). These changes made the treated fabrics stiffer and less air permeable.



Fig. 5. SEM photographs (300×, 1000×) of n-octadecane microcapsule-treated fabrics after laundering: (a) 0 cycle, (b) 5 cycles, (c) 10 cycles, and (d) 20 cycles.

## Table 6

Add-on and physical properties of dyed/PCM microcapsule-treated fabrics.

Samples	Add-on (%)	Stiffness (cm)	Air permeability (cm <sup>3</sup> /min/cm <sup>2</sup> )
Control	-	1.84	23.62
Dyed	-	1.85	22.48
Dyed/n-octadecane MCs treated	17.92	2.08	16.64
Dyed/n-eicosane MCs treated	18.16	2.18	16.78
Dyed/n-octadecane + n-eicosane MCs (50/50)treated	18.31	2.19	16.49

#### Table 7

K/S value and color fastness of the dyed fabrics.

K/S value (660 nm)	Washing		Rubbing		Ironing		Light (20 h)
	Color change	Stain	Dry	Wet	Dry	Damp	
14.15	4/5	5	4/5	4/5	5	5	4/5

#### Table 8

Effects of laundering on the color properties of the dyed/PCM MCs-treated fabrics.

Samples	Laundering (cycles)	H V/C	$L^*$	<i>a</i> *	<i>b</i> *	$\Delta E^{*}$
Dyed	-	3.7PB 3.2/4.9	33.49	-3.23	-20.68	-
Dyed/n-octadecane MCs treated	_	3.7PB 3.3/5.0	33.68	-2.96	-21.62	1.00
	5	3.7PB 3.3/5.1	34.70	-3.53	-20.78	1.25
	10	3.8PB 3.3/5.1	34.99	-3.19	-21.05	1.55
	20	3.9PB 3.4/5.1	35.38	-3.12	-21.33	2.00
Dyed/n-eicosane MCs treated	-	3.8PB 3.2/5.1	33.60	-3.04	-21.52	0.87
	5	3.9PB 3.2/5.2	33.69	-2.89	-21.98	1.37
	10	4.0PB 3.2/5.2	34.06	-2.83	-22.09	1.58
	20	4.0PB 3.3/5.3	34.95	-3.17	-21.84	1.87
Dyed/n-octadecane + n-eicosane MCs (50/50)treated	-	3.7PB 3.2/5.0	33.53	-3.39	-21.10	0.45
	5	3.8PB 3.3/5.1	34.62	-3.10	-21.16	1.24
	10	3.8PB 3.3/5.1	34.75	-3.25	-21.14	1.34
	20	3.9PB 3.3/5.1	35.12	-3.10	-21.11	1.69

 $L^*$ , lightness;  $a^*$ , red(+)/green(-) color axis;  $b^*$ , yellow(+)/blue(-) color axis;  $\Delta E^*$ , color difference.

#### 3.4. Color properties of the PCM MCs-treated fabrics

Table 7 shows dye uptake and the color fastness of the fabrics that were dyed with natural indigo before the PCM MCs treatment. The dye uptake, which was expressed as the *K*/*S* value at 660 nm, was 14.15 showing a medium color strength and the color was purple blue (3.7 PB). The color on the face of the fabric was hardly affected by the fixation of the PCM MCs on the back side of the fabric. The washing fastness was fairly good with a 4/5 rating for the color change and a 5 rating for stains. Additionally, color fastnesses to rubbing, ironing and light were relatively good with above 4/5 rating. The marks of the dot pattern were not seen through the PCM MCs-treated fabrics because the cotton fabrics were thick enough.

Table 8 shows the effects of PCM MCs treatment and laundering on the color of fabrics. The color of the fabrics dyed with natural indigo changed negligibly with color difference ( $\Delta E^*$ ) ranged 0.45–1.00 after PCM MCs treatment. Repeated laundering led to the increase in *H* (hue), *V* (value), *C* (chroma) and *L*<sup>\*</sup> (lightness) values, indicating that the color changed toward slightly more purplish, a little lighter and more saturated. Color difference ranged from 1.24 to 2.00 with increasing laundering. These differences were acceptable, and it was considered that the PCM MCs treatment process was very reliable in terms of color stability.

#### 4. Conclusion

The PCM MCs were fixed using the dot-screen printing method to impart thermo-regulating properties to the natural dyed cotton fabrics. At similar loading amounts for the microcapsules, the fabrics absorbed 18.66, 14.80, and  $14.68 \text{ Jg}^{-1}$  of latent heat for the *n*-eicosane MCs, the *n*-octadecane MCs, and the mixture of the two PCM MCs, respectively. After 20 laundering cycle, about

94% of the latent heat storage capacity was retained. On the other hand, the latent heat storage capacity was retained about 70-89% after 10 rubbing cycles. After hot pressing at 204 °C for 15 s with a pressure on the specimen of  $40 \,\mathrm{g}\,\mathrm{cm}^{-2}$ , the latent heat storage capacity retentions of 75-88% and 92-96% were obtained under dry and damp conditions, respectively. After the fixations of the PCM MCs on the fabric, the stiffness increased and the air permeability decreased. The washing fastness was fairly good at a 4/5 rating for the color change and a 5 rating for stains. Additionally, color fastnesses to rubbing, ironing and light were relatively good at a 4/5 rating. Color difference ranged from 1.24 to 2.00 with increasing laundering. It was considered that the PCM MCs treatment process was very reliable in terms of color stability. In conclusion, thermo-regulating natural dyed fabrics were developed through the fixation of the PCM MCs on the back side of the fabrics using the dot-screen printing method, while taking into account the latent heat storage capacity, durability to laundering, rubbing and ironing and color fastness.

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