

The Application of Microencapsulated Phase-Change Materials to Nylon Fabric Using Direct Dual Coating Method

Kang Koo,¹ Youngmi Park,² Jongdeok Choe,¹ Eunae Kim²

¹School of Textiles, Yeungnam University, Gyeongbuk 712-749, Korea

²Department of Clothing and Textiles, Yonsei University, Seoul 120-749, Korea

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ABSTRACT: The fabrication of functional textiles able to provide thermal regulation and comfort for the body has attracted increasing interest in recent years. This research investigated fabric coatings containing energy absorbing, temperature stabilizing, phase-change material microcapsules (PCMMCs), and their methods of application. Specifically, a coated fabric was directly prepared by a dual-type coating method, in which the PCMMCs were dispersed in a polyurethane coating solution with no binder. The thermal performances of the dual-coated samples were evaluated by differential scanning calorimetry, and their physical characteristics were examined by scanning electron microscopy, thermal vision camera, porosity, water vapor transmission

rate (WVTR), and water entry pressure (WEP) analyses. Furthermore, the microclimate characteristics of the thermally enhanced fabrics were investigated under experimental conditions using a human-clothing-environment (HCE) simulator system. The study results confirmed the superior performance of the dual-coated fabrics in terms of thermal regulation and body comfort, compared with those coated by the dry or wet coating method, because of the improved WEP, WVTR, and thermal performance. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2337–2344, 2008

Key words: microencapsulated phase-change materials; dual coating; HCE simulator

INTRODUCTION

In the latest wearable sportswear, cold protection through thermal insulation is recognized as an important function. Such sportswear requires high-performance fabrics and the development of thermal insulation that maintains its waterproof abilities. For this purpose, a coating including a thermal insulating material in solution is typically applied to fabrics to increase their water resistance, vapor permeation, and thermal insulating ability.^{1,2}

Phase-change materials (PCMs) must have a large latent heat storage capacity and thermal conductivity, as well as a melting temperature (T_m) within the practical range of operation. Among such materials, PCM microcapsules (PCMMCs), which consist of PCMs converted into microcapsules, are more resistant to mechanical action and more chemically stable against most types of chemicals than PCMs.^{3–5}

The microencapsulation of PCMs is the process of capturing small amounts of PCMs in a shell material so that they are permanently enclosed and protected. The protective polymer shell is very durable and designed to resist the textile production methods used in fiber, weaving, knitting, and coating applications.⁶ PCMMCs have therefore been suggested as an appropriate ingredient for fabric coatings requiring remarkable heat transfer and storage capabilities.

In the embedding of a thermal insulating material into textiles, the coating formed using microencapsulated PCMs plays a very important role in providing skin comfort, thermal insulation for warmth, and improved durability. In addition, the inclusion of PCMMCs in textiles is advantageous, as such encapsulation prevents the dispersion of the PCMs in the fabric structure, reduces their evaporation, and reaction with the surrounding environment, and allows for easy utilization while preserving the original properties.⁷ However, the existing coating methods, such as the application of a wet or dry coating containing PCMMCs with commercial coating equipment, can be problematic since, according to our previous research,⁸ wet samples coated with PCMMCs exhibit good thermal insulating properties but poor durability, whereas dry-coated samples offer good durability but low resistance to mechanical action.

Correspondence to: Y. Park (ymp9397@yonsei.ac.kr).

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Therefore, to overcome these problems, we attempt here to demonstrate the improved thermal insulating properties gained through the application of PCMMCs to waterproof nylon fabrics by using the dual coating method. To accomplish this, we compare the thermal and physical properties of the prepared samples with those of nondual-coated fabrics. Furthermore, to assess the temperature regulating ability of the PCMMCs in the coating layer, we utilize a human-clothing-environment (HCE) system, which measures the microclimate temperature change between the simulated body surface and various clothing layers of functional and comfort finished textiles under transient conditions.

EXPERIMENTAL

Materials

Fabric consisting of 100% nylon was pretreated with breathable waterproof and cure. The yarn had a warp of 70 D full dull (density; 155) and a weft of 160 D full dull with air-textured yarn. The samples were conditioned by drying at room temperature for 15 min and fixating with a laboratory-scaled tenter at 150°C for 5 min. The PCMMCs were procured from a local Korean supplier (J&S Technology), and their T_m , crystallization temperature (T_c), heat of fusion (thermal storage capacity, ΔH_f), and heat of crystallization (thermal release capacity, ΔH_c) were 28.2, 16.3, 92.6, and 117.6, respectively. The average particle size of PCMMCs measured by Gracell particle analyzer (Sysmpatec, Germany) was 5–30 μm .

Hydro-microporous polyurethane (PU) resin and hydrophilic-nonporous PU resins were used as dry and wet coating solutions, respectively, while other reagents such as surfactant, color fastness crosslinking agent (Daemung Incam), *N,N*-dimethylformamide (DMF, Hanwon), color toner (Kunyang), toluene (Daechon), and dispersion agent (Bugang) as additives, were procured from local Korean manufacturers. Galwick wetting liquid with a predefined surface tension of 15.9 dyne/cm (Porous Materials, Ithaca, NY) was used as a wetting agent for the porometry measurements.

Preparations of coating solution containing PCMMCs

To prepare the coating composition, the PCMMCs were dispersed in PU resin with a polymer mixture containing a color toner, nonyellowing crosslinking agent, surfactant, and wet crosslinking and dispersion agents. This coating solution was prepared by forming dispersions with 10, 20, or 30 wt % of PCMMCs powder with respect to the weight of the PU resin, and then mixing this solution well with continuous magnetic stirring for 30 min. During mix-

ing, the bubbles from the dispersion solution were completely dissipated by using a defoamer. Aqueous dispersion solutions containing 10, 20, and 30 wt % of PCMMCs were thereby obtained for the dry, wet, and dual coatings.

Coating process

For the wet coating, the fabric samples were first coated with the coating solution, after which the DMF solvent was substituted with water by immersing the fabric in water for 5 min, to induce coagulation of the coating solution. The residual DMF was removed completely with water, and then the water was removed with a mangle and the fabric dried at 160°C for 90 s. Next, the dry coating was applied in the form of a base and top coating by means of the knife coating method. The nylon sample was coated with previously prepared PU solution by base coating process, after which the top coating containing different ratios of PCMMCs was applied, and the dry sample was cured at 160°C for 90 s.

For the dual coating system, two steps were performed to ensure that the thermally enhanced textile did not separate from the fabric. First, a wet coating was applied to fabrics and the fabrics were well dried. In the second step, a coating was applied to the wet-coated surface after the fabric drying procedure. At this time, the PCMMCs content in the wet coating solution was fixed at 10 wt %, while the following amounts of PCMMCs were used in the dry coating solution: 0, 10, 20, and 30 wt %. The overall coating process is presented in Figure 1.

Morphology test

The cross-section, morphological structure of the PCMMCs, dual-coated nylon fabrics was observed by scanning electron microscopy (SEM) with an S-4200 instrument (HITACHI, Japan) operating at an acceleration voltage of 15 kV, after the samples had been ion sputter-coated (VPS 020, ULVAC VACUUM, Japan) with a layer of white gold for 120 s. All images were taken at a magnification of 500 \times .

Thermal performance test

The thermal temperature distributions of the PCMMCs-coated samples for various times were measured using an infrared (IR) and visible vision system (NEC, TH41-464), having a thermal sensitivity of 0.06–0.03°C at 30°C, a wavelength of 8–14 μm , a measurement range of –40–2000°C, a frame rate of 1/60 s, and an imager with a resolution of 320 \times 256 pixels. The screen was observed from a distance of \sim 40 cm at 23°C, 50% relative humidity. Also, the thermal heat capacity of the sample was analyzed using a differential scanning calorimeter (DSC,

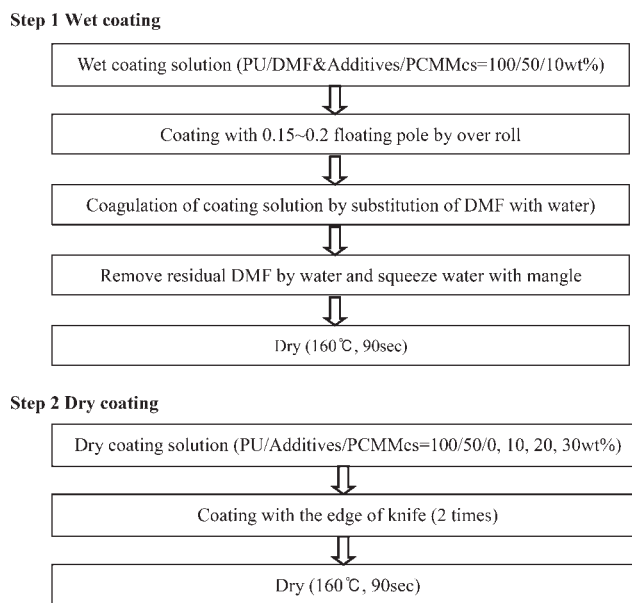


Figure 1 Dual coating process of waterproof nylon fabrics with PCMMCs.

DuPont 2010 DSC Instrument) cooled with circulating liquid nitrogen.

Measurement of WVTR and WEP

The water vapor transmission rate (WVTR) of the untreated and dual-coated samples was measured by the ASTM E 96-95 desiccant method using an LH20-11VP (Nagano, Japan). Permeation cups were filled with 40 g of CaCl_2 as a desiccant, weighed after 1 h (a_1), and then placed in a constant temperature and humidity test chamber. The absorbency of water vapor from the standardized surrounding air was measured by weighing the samples again after 1 h (a_2). This entire procedure was repeated 24 times, and WVTR was calculated as follows:

$$\text{WVTR (g/m}^2\text{24h)} = \{(a_2 - a_1)/S\} \times 24$$

where $a_2 - a_1$ is the weight change of the permeation cup with the sample (g) and S is the area of permeation (m^2). In addition, the water entry pressure (WEP) was measured according to the KS K 0591, low range, hydrostatic pressure method using a hydrostatic head tester FX 3000 (Textest, Swiss), which can operate up to pressure of 10,000 mmH_2O .

Microclimate temperature by human-clothing-environment simulator

The microclimate temperatures of the inner (the 1st layer between the skin and underwear that is PET knit) and outer (the 2nd layer between the underwear and outerwear that is treated with PCMMCs) layers with respect to the apparel wearer were deter-

mined by using an HCE simulator instrument, in which the temperature to be controlled over a wide range from the moderate to subzero state. A detailed mechanical diagram of the HCE simulator was previously published.^{9,10} The measurements from a coupled heat and moisture sensor placed between the two insulation clothing layers were recorded.

Porometry test

A capillary flow porometry (PMI, CFP-1100-A) provides a simple and nondestructive technique for the rapid and accurate measurement of the pore size and distribution.¹¹⁻¹³ The PMI porometer can measure the maximum pore size (bubble point), mean flow pore diameter, pore size distribution, cumulative flow, and gas permeability of polymeric materials, including nonwoven and woven fabrics. The test results are highly reproducible and the procedure only takes a few minutes. For the wet up/dry up processes, the sample is immersed in a wetting fluid that fills the empty pores in the sample, and gas is used to force the liquid out of the pores by gradually increasing the gas pressure. To displace the liquid inside the pores, the gas performs work on the system to compensate for the increase in the interfacial free energy. The increase in the interfacial free energy is determined by the interfacial free energy per unit area and the interfacial area, which is related to the void structure of the material.⁷ In this study, to determine the pore characteristics of the dual-coated samples, each sample was immersed in a Galwick wetting liquid, which filled its pores, and then pressure was applied with compressed air. The flow started at a low pressure with a zero flow rate to remove some of the substances that were present in the pores. With increasing pressure, more pores became vacant, and the flow rate increased. The flow rate was determined as a function of pressure for both the dry up/wet up processes and was used to calculate the pore characteristics.

Durability test

The durability of the washing treatment was tested according to the laundering methods described in ISO-6330 6A. This consisted of evaluation by WEP analysis, according to the standard course, using a home drum washer (WD-R801B, LG, Korea).

RESULTS AND DISCUSSION

SEM investigation of PCMMCs dual-coated nylon fabrics

The SEM studies indicated that the coating layer consisted of very strong, piled PCMMCs, having a

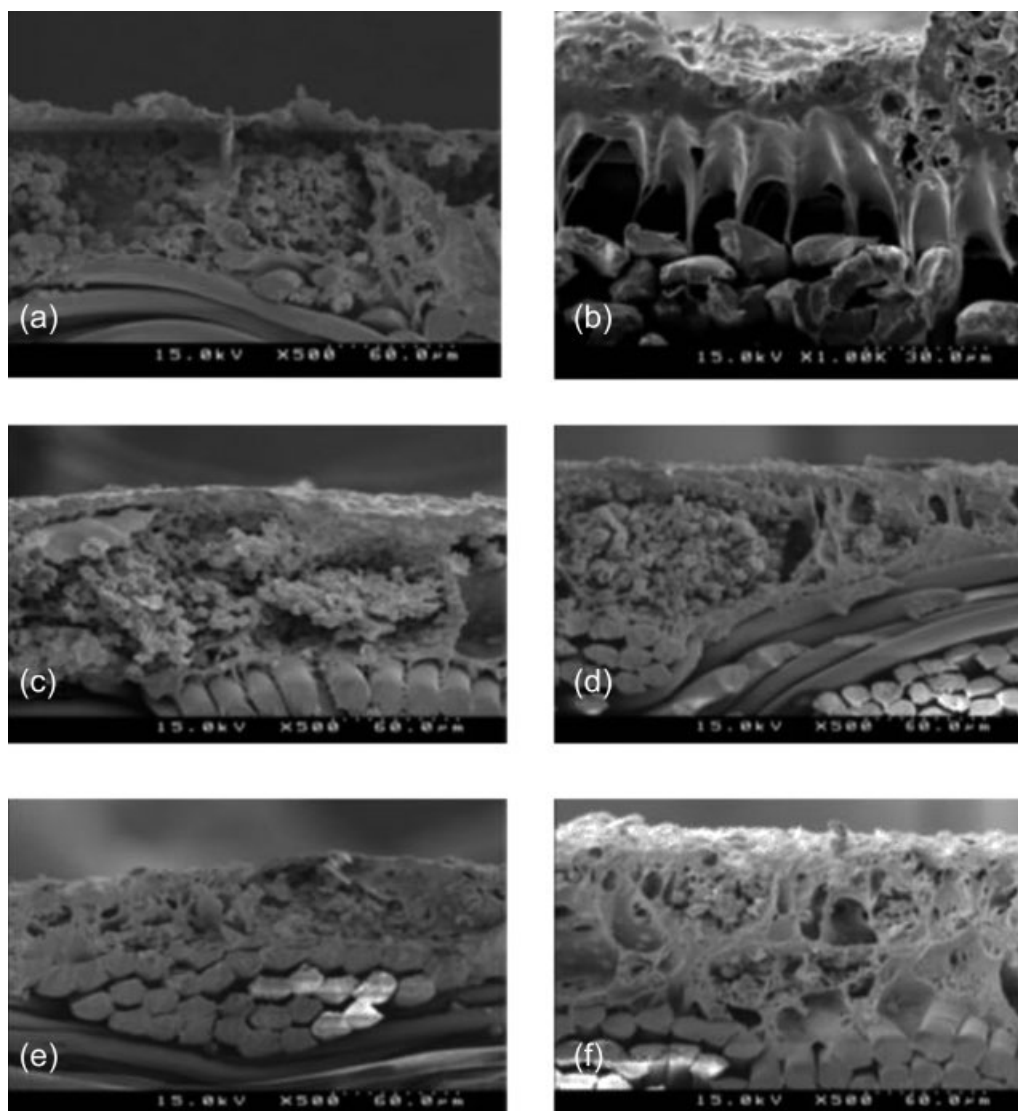


Figure 2 SEM images of the dual-coated nylon fabrics with different PCMMCs content; (a) wet 10%, (b) dry 10%, (c) wet 10%/dry, (d) wet 10%/dry 10%, (e) wet 10%/dry 20%, (f) wet 10%/dry 30% ($\times 500$).

smooth and regular global shape. Moisture/air exchange occurred between the porous PU phases. The interface of the PCMMCs layer affected the thermal insulation of the nylon fabrics. A cross-sectional image of the dual-coated nylon fabrics with different PCMMCs compositions is shown in Figure 2. Regarding the overall dual coating mechanism, the globular-shaped microcapsules were observed to be piled up with a certain thickness corresponding to that of the wet coating step. It was also noted that the microcapsules were more easily distributed into the microporous PU resin during the wet coating process than in the dry coating solution. The hydrophilic-nonporous PU solution-coated layer, which indicated the dry coating part, exhibited a very thin layer suggesting that the nonporous PU resin was not coated. This confirmed the durability and physical properties of the dual-coated fabric.

Thermal characteristics by DSC

The DSC curves of the dual-coated fabrics shown in Figure 3 were obtained to evaluate the thermal performances of the fabrics as a function of the PCMMCs content. The main phase transition peak during the heating at around 28°C represents the PCMMCs solid to liquid phase change, while the other peak during cooling at around 20°C corresponds to the PCMMCs liquid to solid phase transition. With increasing PCMMCs content, the thermal release and storage capacity slowly increased to 5.37–8.52 and 5.38–6.83 J/g, respectively. The thermal release capacity corresponding to the solid-liquid phase-change capacity of the dual-coated fabrics containing 10, 20, and 30 wt % of PCMMCs was 2.23, 3.15, and 3.21 J/g higher than that of the wet coating sample, respectively. This indicated that the increase of the thermal release capacity might have resulted

from the thermal behavior of the PCMMCs when desorbing heat was applied. If the PCMMCs hysteresis is considered, the phase transition peak during the cooling of the dual-coated fabrics containing 10, 20, and 30 wt % of PCMMCs was 3.74, 3.96, and 3.68°C higher than that of the wet 10%/dry 0 wt % sample, respectively. Accordingly, the increased thermal capacity of all the dual-coated samples may have provided a satisfactory thermal release enthalpy, therefore making this material suitable for application in cold weather clothing.

Temperature distribution behavior by infrared and visible vision camera

PCMs typically absorb energy during the heating process if a phase-change occurs. Otherwise this energy can be transferred to the environment in the phase-change range during the reverse cooling process. The insulation effect afforded by the PCMs is dependent on the environment temperature and time. Thermography utilizes the IR spectral band. To perform the temperature distribution analysis, a thermal vision camera was used to detect IR radiation and convert this information into an image, where each pixel corresponded to a temperature value. In this experiment, the image was equivalent to the temperature range from 24 to 36°C.

Figure 4 shows a comparison of the surface temperature distribution of the various PCMMCs-coated samples by different coating method. Even though the samples were coated under the same condition, such as dry and dry 30% which means with and without 30 wt % PCMMCs in coating solution during the dry coating process, respectively, the temperature change was around 2–3°C, indicating major differences. The temperature of the dual-coated sample was clearly maintained higher than that of the dry-

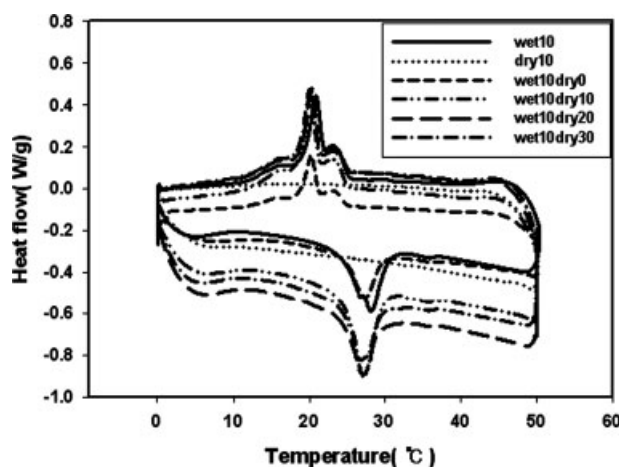


Figure 3 The DSC curves of the dual-coated nylon fabrics with different PCMMCs content.

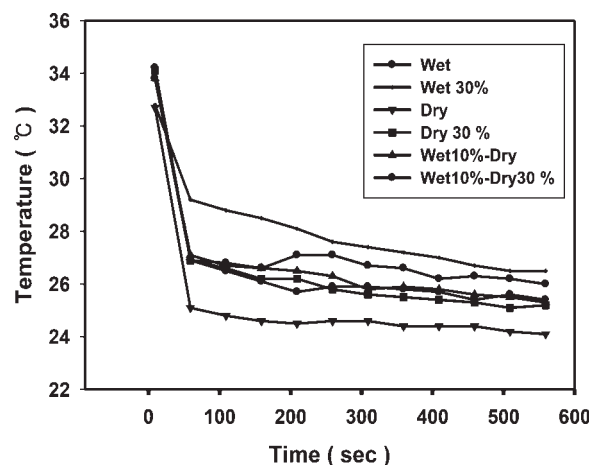


Figure 4 Temperature distribution of various differently coated fabrics as a function of time.

or wet-coated samples, except the sample of PCMMCs 30 wt %. However, the main characteristic of the dual-coated sample treated with wet 10%/dry 30 wt % PCMMCs was that it only improved the physical stability of the PCMMCs on the surface of the nylon fabrics, whereas the wet 10%/dry 0% dual-coated sample increased the surface temperature. Therefore, an appropriate combination of PCMMCs in the dual coating could achieve the best physical and thermal effects. In this case, the dual-coated samples performed better than the wet- or dry-coated samples did alone.

Water vapor transmission rate

The WVTR measurements indicated that the pores of the dual-coated fabrics were responsive to the moisture content. As shown in Figure 5, as the PCMMCs content was increased to 10 wt %, the WVTR of both the dry and dual-coated samples was clearly increased. As the PCMMCs content was increased beyond 10 wt %, and the WVTR value of the dry sample decreased because of the application of the nonporous-type PU coating solution. Consequently, as can be seen in Figure 2(b), if the PCMMCs were lost during the dry coating process, the coated layer became more porous than the untreated one, which raised the WVTR above that of the PCMMCs-untreated sample, whereas the WVTR of the wet 10%/dry 0% dual-coated samples tended to slightly decrease with increasing PCMMCs content up to 10 wt %, and then continuously increased with further increase in PCMMCs content, because of the microporous PU resin used in the coating solution. In Figure 5, the WVTR of the wet/dry sample, which included not PCMMCs during the wet coating step but 10, 20, 30 wt % PCMMCs during the dry coating step, was higher than that of the wet 10%/

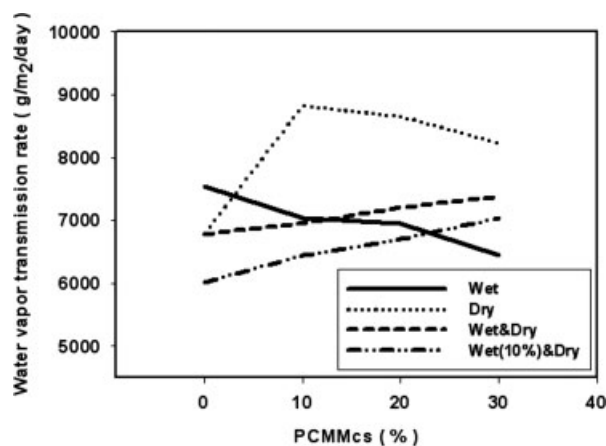


Figure 5 WVTR of various differently coated fabrics as a function of PCMMCs content.

dry 0% dual-coated sample because of the well-packed structure induced by the PCMMCs inclusion. This may have been related to the introduction by the nonporous PU resin of new empty sites in the coating layer because of the removal of PCMMCs during the dry coating process and the consequently high WVTR value. The dual-coated nylon fabrics prepared in this process demonstrated the ability to respond to external thermocontrol and to provide thermal insulation, which supports a new approach in the development of functional textiles with thermal and controllable, water vapor comfort.

Water entry pressure of PCMMCs dual-coated nylon fabrics

After dual coating, the WEP change of the wet-, dry-, wet 0%/dry 0%, and wet 10 wt %/dry 0%-PCMMCs-coated fabrics is presented in Figure 6. The water droplets rolled onto the surface of the coating layer treated fabrics. The results presented in the fig-

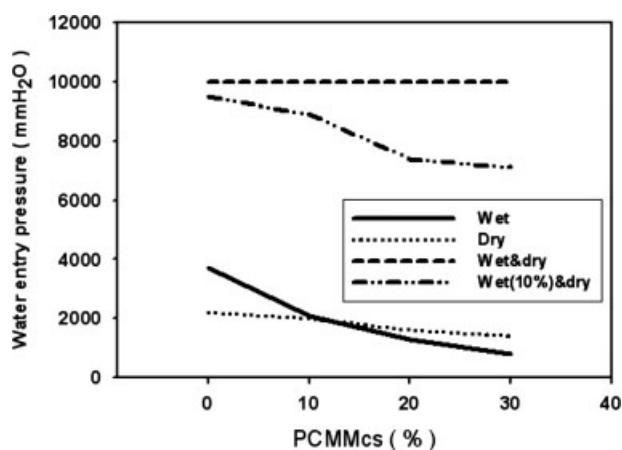


Figure 6 WEP of various differently coated fabrics as a function of PCMMCs content.

TABLE I
Pressure (*P*) and Diameter (*D*) Change at Mean Flow and Bubble Point

Samples	Mean flow		Bubble point	
	<i>P</i> (psi)	<i>D</i> (μm)	<i>P</i> (psi)	<i>D</i> (μm)
Noncoating	0.64	10.37	0.61	10.87
PU dual-coating	5.71	1.16	5.04	1.31
PCMMCs 30 wt % dual-coating	8.72	0.76	6.90	0.96

ure confirmed the high WEP of the dual-coated nylon textiles compared with dry or wet coating. In the wet/dry dual coating process, the WEP of the waterproofed fabrics remained almost constant after the coating, whereas it decreased from 10,000 to 6800 mmH₂O after the wet (10%) and dry process, despite the PCMMCs addition, because of either the slipping out or breakage of the PCMMCs during the processing, as shown in Figure 2(b). This can be explained by the WEP increase induced by the dual coating. These results supported the potential of the dual coating-induced PCMMCs layer to confer good WEP properties to waterproof nylon.

Maximum and mean flow pore size

As can be seen in Table I, which shows the pore size change of the samples at mean flow and bubble point pressure, the bubble point and mean flow varied considerably for each sample. There were significant differences in the pressure and diameter between the control samples and the PCMMCs-treated ones. Because of the PCMMCs addition, the pressures associated with the bubble point and mean flow were always higher than those of the control sample, up to 10-fold higher for the sample containing 30 wt % PCMMCs. This tendency was caused by the dependence of the pressure and diameter of the bubble point and mean flow on the coating condition, because of the attainment of a proper compressive strength. These results confirmed the significant effect of the dual coating on the air penetration of the samples.

Thermal comfort of samples under simulated multilayer systems

Microclimate temperature evaluation of clothing material is difficult and complicated to achieve. The performance of a clothing system in the transient state has not previously been investigated, with the exception of the thermal insulation properties. Especially, the importance of the thermal performance of breathable waterproof fabrics under extreme conditions has become increasingly recognized. For the thermal comfort of the human body, it is important for clothing to create a regular microclimate to pro-

vide a thermoregulatory system for the skin, and thereby protect it from the environmental changes caused by extreme conditions. To investigate the functionality of the thermoregulatory PCMMCs for clothing, we simulated two virtual layers of clothing systems with the skin temperature being constantly maintained at 34°C. Figure 7 shows the microclimate temperature change of the nylon fabrics with and without PCMMCs at the 1st (a) and 2nd layers (b) as the transient conditions were varied from 35 to -10°C. As shown in Figure 7, the PCMMCs-coated sample tended to retain a higher temperature than the untreated samples did due to the heat released from the PCMMCs during the phase transition. Consequently, the clothing will provide thermal comfort by releasing heat in conditions of extreme cold.

Durability test

Generally, the efficiency and duration of the thermal effects achieved by these thermally improved fabrics, which were prepared by the new coating technology, depended on the latent heat storage and release

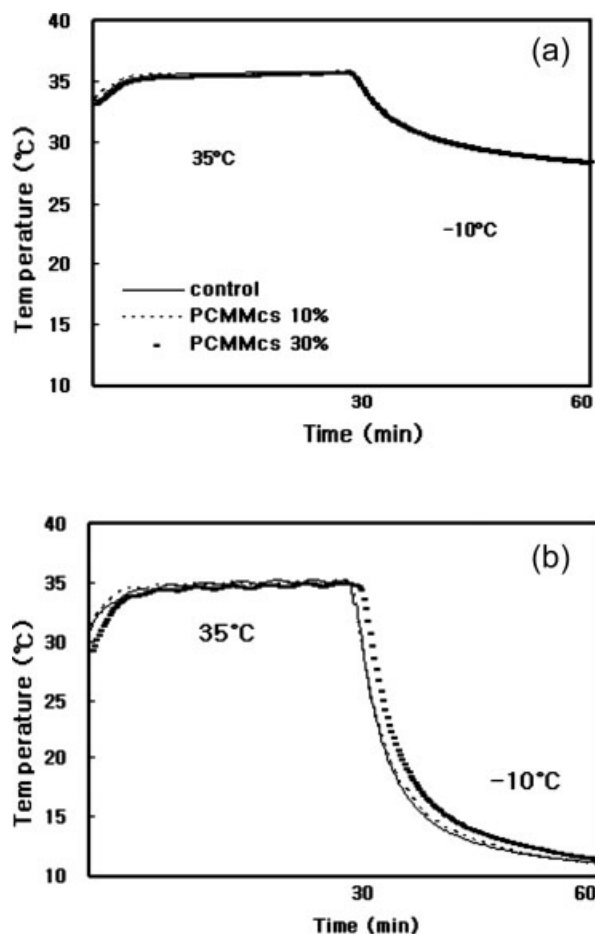


Figure 7 Microclimate temperature change of nylon fabrics with and without PCMMCs at 1st (a) and 2nd layers (b), during the transient conditions from 35 to -10°C.

TABLE II
Washing Durability of Dual-Coated
Fabrics Estimated by WEP

Component (wet/dry)	Water entry pressure (mmH ₂ O)	
	Before washing	After washing
PCMMCs 0 wt %/0 wt %	10,000	10,000
PCMMCs 10 wt %/0 wt %	9,500	9,000
PCMMCs 10 wt %/10 wt %	8,900	7,800
PCMMCs 10 wt %/20 wt %	7,400	6,500
PCMMCs 10 wt %/30 wt %	7,100	5,800

capacity, PCMMCs content, textile substrate structure, such as its density and waterproof properties, and the correspondence between the phase-change temperature range and the application temperature range.

In this study, the durability of the dual-coated fabrics was investigated by conducting WEP analyses after the samples were washed 10 times. As listed in Table II, WEP slightly decreased after each washing cycle, but tended to retain over 80% of its original value after 10 cycles over. Although this thermoregulatory material coating technique avoided significant damage to the microcapsules during the washing procedure, the resulting coating lacked durability against washing. By increasing the PCMMCs content of the washed samples, their WEP decrease rates were gradually increased from 5.3 to 18.3%. This increase may have been caused by the formation of a weak physical complex between the PU and fabrics on the sample surfaces, or by mechanical action during the washing, even though the improved decrease rate had a comparatively weak effect on the washing. This phenomenon may also have affected the water repellency properties.

CONCLUSIONS

This study has investigated the thermal and physical properties of PCMMCs-coated waterproof nylon fabrics based on the wet/dry, dual coating process without any binder treatment. As the PCMMCs content was increased, the WVTR of dual-coated fabrics was generally increased, whereas the WEP was decreased increasingly. The SEM photographs showed that PCMMCs were clearly observed when they formed part of the wet-coated layer. The DSC analysis showed that the maximum exothermic peaks of the dry and dual-coated fabrics occurred near the phase-change temperature of PCMMCs. The thermal release capacity and thermal insulation of the coated fabrics increased with increasing PCMMCs content. From these results, the dual-coated fabrics are expected to perform better than those coated by the dry or wet coating method, because of the enhancement of WEP, WVTR, and their thermal performance.

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