Development of Thermoregulating Textile Materials with Microencapsulated Phase Change Materials (PCM). II. Preparation and Application of PCM Microcapsules

Younsook Shin,[1] Dong-Il Yoo,[2] Kyunghee Son[1]

[1]*Department of Clothing and Textiles, Chonnam National University, Gwangju 500-757, South Korea*
[2]*Department of Textile Engineering, Chonnam National University, Gwangju 500-757, South Korea*

Received 30 April 2004; accepted 10 October 2004
DOI 10.1002/app.21438
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Melamine–formaldehyde microcapsules containing eicosane were prepared by *in situ* polymerization. The characterization of the microcapsules, including the particle size and size distribution, morphology, thermal properties, and stability, was carried out. The prepared microcapsules were added to polyester knit fabrics by a conventional pad–dry–cure process to develop thermoregulating textile materials. The morphology, thermal properties, and laundering properties of the treated fabrics were also investigated. The microcapsules were spherical and had melamine–formaldehyde shells containing eicosane. The microcapsules were strong enough to secure capsule stability under stirring in hot water and alkaline solutions. The heat storage capacity increased as the concentration of the microcapsules increased. The thermoregulating fabrics had heat storage capacities of 0.91–4.44 J/g, which depended on the concentration of the microcapsules. The treated fabrics retained 40% of their heat storage capacity after five launderings. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2005–2010, 2005

Key words: morphology; thermal properties; heat capacity

INTRODUCTION

Phase-change materials (PCMs) store and release thermal energy as their physical state changes.[1,2] Originally, PCM technology was developed through the National Aeronautics and Space Administration space research program of the late 1970s to the early 1980s and was used to protect delicate instruments in space from large temperature extremes.[3] More than 500 different PCMs, including water (ice), are known. The most common PCMs applied to textiles are *n*-paraffin waxes with melting temperatures (T_m's) of 36–18°C, such as heptadecane, hexadecane, octadecane, nonadecane, and eicosane. They have different phase-change temperatures, T_m and crystallization temperature (T_c), that depend on the number of carbons in their structures. These paraffin waxes cannot be incorporated directly into textiles because of their low melting point and, therefore, need to be microencapsulated.[3]

The microencapsulation of PCMs involves enclosing them in thin and resilient polymer shells so that the PCMs can be changed from solid to liquid and back again within the shells. Microencapsulated PCMs have been applied in many fields, including textiles,[4–6] heat storage systems for buildings,[7,8] and microclimate environmental control for vegetation and seeds in agriculture.[9]

In applications of PCM technology to garments and home furnishing products, PCM microcapsules are incorporated into acrylic fibers or polyurethane foams or are embedded into coating compounds and topically applied to fabrics or foams.[10,11] A variety of outdoor apparel products with PCM microcapsules, such as ski wear, hunting clothing, boots, gloves, and ear warmers, are on the market under the trade names Outlast and ComforTemp. Nonetheless, there are few reports on the formulation of PCM microcapsules and finishing onto textile fabrics or on the evaluation of their characteristics, including their thermal properties and durability.

The purpose of this study was to develop thermoregulating materials. Melamine–formaldehyde microcapsules containing eicosane were prepared by *in situ* polymerization and were characterized with respect to their structure, morphology, size distribution, thermal properties, and stability. Polyester knit fabrics were treated with the prepared microcapsules with a polyurethane binder by a conventional pad–dry–cure (PDC) process. The treated fabrics were characterized with respect to their morphology and thermal properties, and the laundering durability was evaluated for practical use.

Correspondence to: Y. Shin.
Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: R04-2000-000-00090-0.

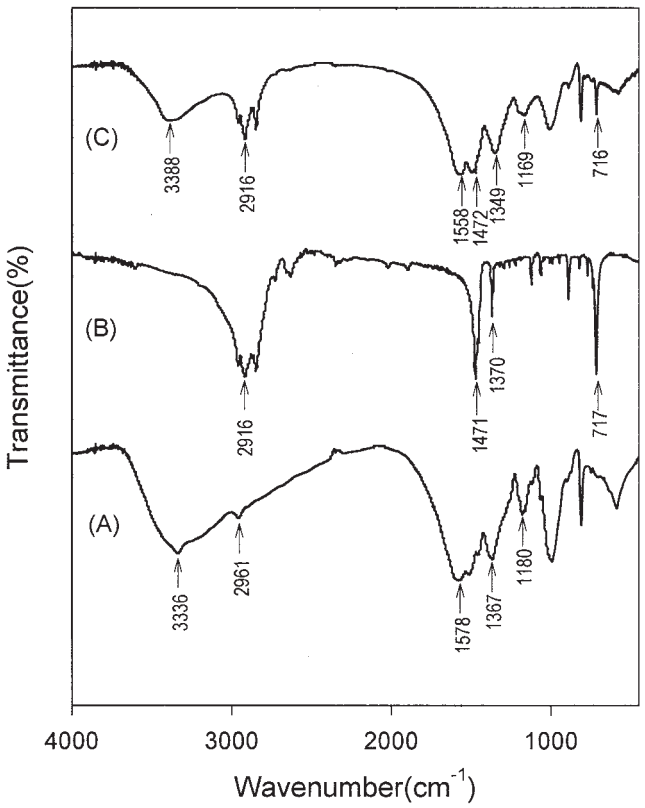

Figure 1 FTIR spectra of (A) the melamine–formaldehyde prepolymer, (B) eicosane, and (C) the microcapsules.

EXPERIMENTAL

Materials

Melamine and 37% formaldehyde as shell materials, eicosane as a core material, sodium lauryl sulfate (SLS) as an emulsifier, poly(vinyl alcohol) (PVA; weight-average molecular weight = 1500) as a protective colloid, and acetic acid and anhydrous sodium carbonate as pH controllers were used. All the chemicals were reagent-grade. The fabric was a scoured and bleached 100% polyester knit ($68 \times 58/in.^2$) with a weight of 195 g/m^2 and a thickness of 1.47 mm.

Preparation of the microcapsules

Melamine (0.1*M*) and 0.3*M* 37% formaldehyde in 100 mL of distilled water were adjusted to pH 8.5–9.0 with a 10% sodium carbonate solution and stirred at 60°C for 1 h to prepare a melamine–formaldehyde prepolymer. An oil-in-water emulsion of eicosane (10 g) in 100 mL of a 1% SLS aqueous solution was prepared via stirring at a speed of 6000 rpm. The prepared emulsion was added to the prepolymer to start *in situ* polymerization, and the pH was lowered to 4.0–5.0 with acetic acid. Subsequently, a 0.001*M* PVA solution was poured into the emulsion/prepolymer system, and the mixture was stirred at 50°C for 1 h to prevent the agglomeration of emulsion globules. The resultant microcapsules in the slurry state were filtered, washed in distilled water, and dried at room temperature to obtain a microcapsule powder. The yield of the microcapsule powder was 32%.

Characterization of the microcapsules

Infrared spectra of eicosane, the melamine–formaldehyde prepolymer, and the microcapsules were obtained with a Nicolet Impact 400D Fourier transform infrared spectrophotometer. Scanning electron microscopy (SEM) was performed with a platinum coating with a JSM-5400 (JEOL, Inc., Tokyo, Japan). Also, optical microscopy was performed for the observation of the microcapsules in the slurry state. The mean particle size and size distribution of the microcapsules were determined with an image analyzer (MS100, Malvern Instrument, Malvern, United Kingdom). A differential scanning calorimetry (DSC) instrument (DSC2920, TA Instrument, New Castle, DE) was used to measure some thermal properties. The microcapsules were heated and cooled at a rate of 2°C/min in the range of 10–50°C under an N_2 atmosphere.

Addition of the microcapsules to the fabrics

The fabric samples were impregnated with an aqueous solution composed of a plurality of microcapsules and a polyurethane binder (Snotex P110, Dae Young Chemical Co, Ltd., Seoul, South Korea), were padded up to 300% pickup by the two-dips/two-nips method,[10] were dried at 80°C for 8 min, and were cured at 130°C for 10 min. The concentrations of the microcapsules were 12.5, 25, 50, and 100% with respect to the weight of the undiluted microcapsule slurry. The concentration of the binder was 3% (on the weight of both), and liquor ratio was 32:1. The treated samples were washed and dried for further evaluation.

Evaluation of the microcapsule-treated fabrics

SEM and DSC analysis were performed both before and after laundering as described previously. The

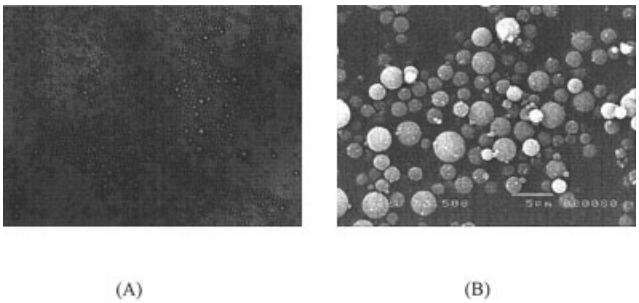

Figure 2 Morphology of the microcapsules: (A) optical micrograph (original magnification = 400×) and (B) SEM photograph (original magnification = 3500×).

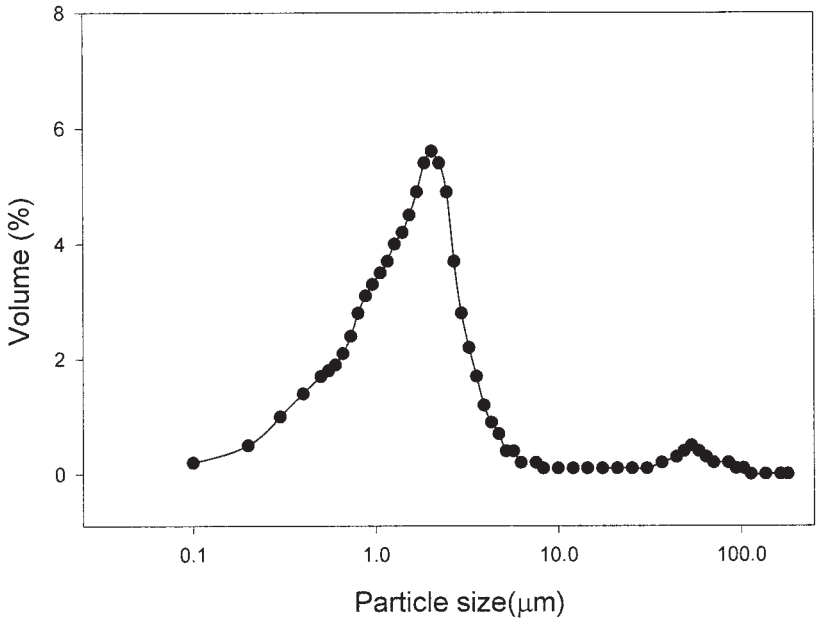

Figure 3 Particle size distribution curve of the microcapsules.

laundering durability of the treated fabrics was evaluated with an LHD-EF launderometer (Atlas Electric Devices Co., Houston, TX) according to AATCC test method 61-1989.

RESULTS AND DISCUSSION

Characterization of the microcapsules

Figure 1 shows FTIR spectra of the melamine–formaldehyde prepolymer, eicosane, and microcapsules. The N—H stretching vibration at 3300 and 1500 cm^{-1}, the C—H stretching vibration at 2900 and 1400 cm^{-1}, and the C—O stretching vibration at 1100 cm^{-1} can be observed. Specific absorption bands of the eicosane and melamine–formaldehyde prepolymer confirm that the prepared microcapsules were composed of the melamine–formaldehyde prepolymer and eicosane as the shell and core materials, respectively.

Figure 2 shows an optical micrograph of the microcapsules in the slurry state and an SEM photograph of

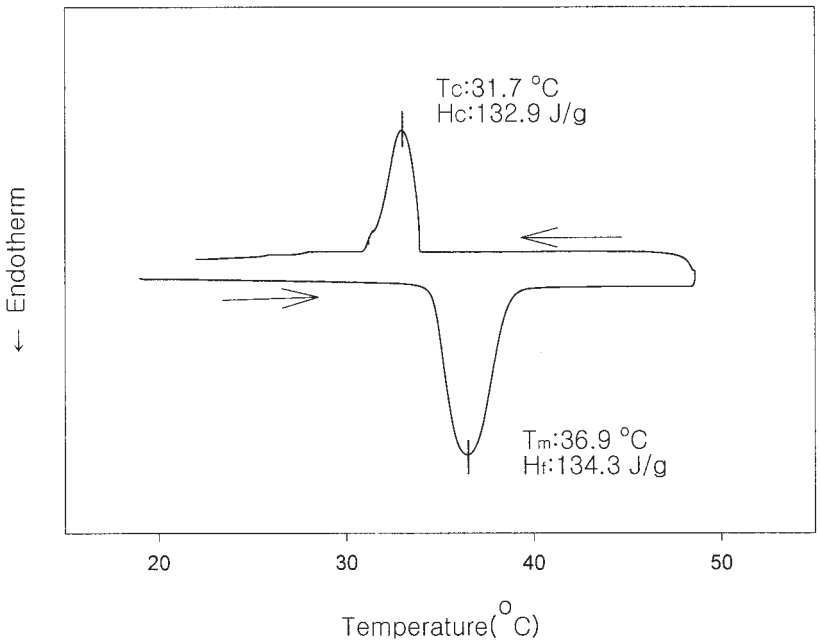

Figure 4 DSC thermogram of the microcapsules.

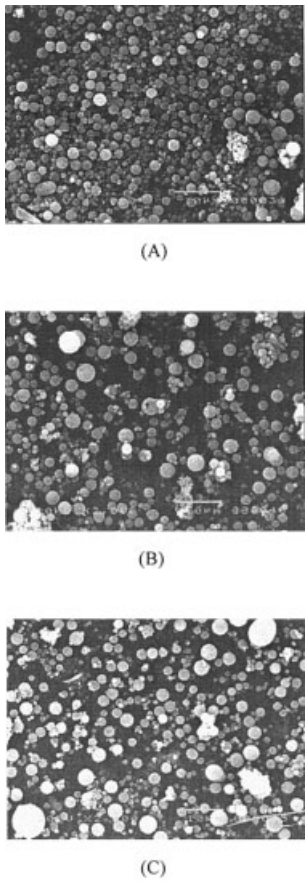

Figure 5 SEM photographs (original magnification = 2000×) of microcapsules treated with stirring under different conditions: (A) 20°C and 3 h; (B) 68°C and 3 h; and (C) pH 10, 20°C, and 3 h.

the microcapsules in the powder state. Most of the microcapsules were spheres with a smooth surface morphology. The agglomeration of the microcapsules was not observed in the slurry and powder states.

Figure 3 shows the particle size distribution of the microcapsules. The mean particle diameter of the microcapsules was 1.89 μm, and most of the microcapsules had particle sizes of 0.1–10 μm. For the addition of microcapsules to textile materials, the particle size and size uniformity are important factors.[3] Pause[11] used PCM microcapsules of 1–60 μm to improve the thermal insulation of textile materials. Colvin and Bryant[12] used microencapsulated PCMs of 30–100 μm for textile fibers, composites, foams, and so forth. They also claimed that much larger particles of 1–3 mm could be placed within clothing layers to improve breathable thermal cooling under high humidity. In comparison with previous work, the prepared microcapsules were relatively small and uniform.

Figure 4 presents a DSC thermogram of the microcapsules. The phase-change temperatures, T_m and T_c, of the microcapsules were 36.9 and 31.7°C, respectively, and they were similar to those of the core material, eicosane. The heat storage capacity of the microcapsules was 134.3 J/g. The core/shell ratio of the microcapsules was about 53%, which was higher than that of the microcapsules with a similar mean particle size manufactured by the coacervation method.[13] The core/shell ratio, representing the PCM concentration of the microcapsules, had to be as high as possible, and the shell had to be strong enough to secure capsule stability.[3]

Stability of the microcapsules

Microcapsules for textile materials should be stable against mechanical action (e.g., abrasion, shear, and pressure) and chemicals.[3] For the efficacy of the prepared microcapsules for textile materials, stability testing was performed under common laundering conditions for garments. The microcapsules were stirred in neutral (distilled water) and alkaline (pH 10) solutions at 20 and 68°C and at 380 rpm for 1 and 3 h, respectively. As shown in the SEM pictures of Figure 5, the microcapsules did not show any significant changes in their morphology and size. The heat storage capacities of the microcapsules before and after stability testing are presented in Table I. On the basis of the heat storage capacity (134.3 J/g) before the testing, more than 90% of the heat storage capacity of the microcapsules was retained after the testing, regardless of the test conditions. The results confirmed that the microcapsules were durable enough to secure capsule stability during stirring in hot water and alkaline solutions.

Morphology of the microcapsule-treated fabrics

Figure 6 shows SEM photographs of control, binder-treated, and microcapsule-treated samples. The control and binder-treated samples had very smooth appearances. The microcapsules in the microcapsule-treated samples were located at interstices between the fibers and on the fiber surface. Those microcapsules were heat-resistant and could endure the curing conditions (at 130°C for 10 min). Therefore, we spec-

TABLE I
Effect of the Water Temperature and pH on the Heat Storage Capacity of the Microcapsules

Solution		Retention of heat storage capacity (%)	
Temperature (°C)	pH	1 h	3 h
20	Neutral[a]	98	90
68	Neutral[a]	100	99
20	Alkaline[b]	99	97

[a] Distilled water.
[b] pH 10.

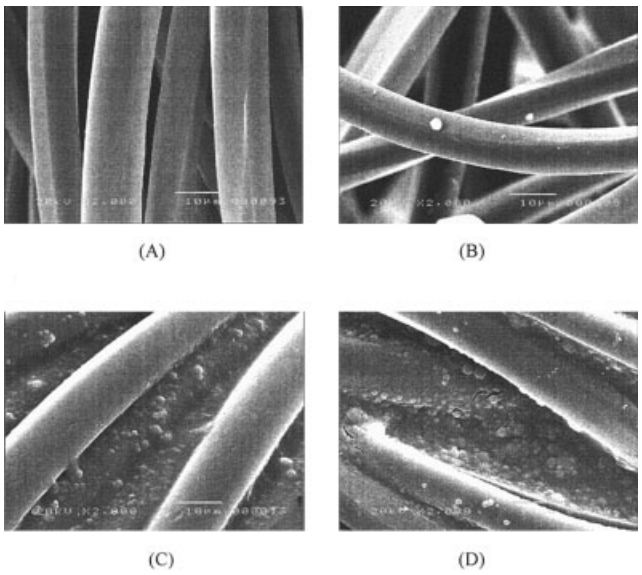

Figure 6 SEM photographs (original magnification = 2000×): (A) control, (B) binder-treated sample, (C) microcapsule-treated sample (5% addition), and (D) microcapsule-treated sample (23% addition).

ulate that the microcapsules manufactured in this study are suitable for the finishing process at high curing temperatures. Polyurea microcapsules manufactured by interfacial polymerization were melted at curing temperatures higher than 80°C.[5] On the other hand, more binder was observed in the microcapsule-treated samples than in the sample treated with the binder only. Some cracks were observed on the surface of the microcapsule-treated sample with 23% addition, which had the highest addition of the samples.

Thermal properties of the microcapsule-treated fabrics

Table II shows the heat storage capacity and T_m values according to the added amount. The heat storage capacity of the treated fabric samples increased as the addition increased. However, the heat storage capacity did not increase as much as expected even though the addition increased from 18 to 23%. This result indicated that more binder, rather than microcapsules, was attached to the fabrics at high addition percentages. The conventional PDC method used in this study seems to have limitations in loading microcapsules for high levels of thermal storage capacity. Other application methods being used currently also have some limitations in loading microcapsules. For example, microcapsules incorporated into the spinning dope of acrylic fibers have an upper loading limit of 5–10% microcapsules because the physical properties of the fibers begin to suffer above that limit, and the finest fiber available is about 2.2 dtex.[3] Although the loading can be as high as 60 wt % for coated fabrics, properties such as drape, breathability, softness, and tensile strength can be affected adversely as the loading increases.[14] Therefore, the proper treatment process for incorporating PCM microcapsules into textiles should be selected according to the performance properties and end use of the finished products.

TABLE II
Effect of The Addition Percentage on the Thermal Properties of the Polyester Knit Fabrics

Addition (%)	T_m (°C)	ΔH_f (J/g)
5	35.3	0.91
11	34.9	2.15
18	35.3	4.10
23	34.9	4.44

T_m, melting temperature; ΔH_f, heat storage capacity.

As shown in Table II, T_m of the treated fabrics was slightly lower than that of the core material, eicosane (36.1°C). Moreover, thermoregulating fabrics were obtained with heat storage capacities of 0.91–4.44 J/g, which depended on the addition of the microcapsules. They were appropriate for use in hot environments because the microcapsules on the fabrics changed phase at about 35°C.

Laundering durability of the microcapsule-treated fabrics

Figure 7 shows SEM photographs of the samples after 1, 5, 10, and 20 launderings. The sample with 23% addition was used for the laundering durability test. The microcapsules were observed on the fiber surface

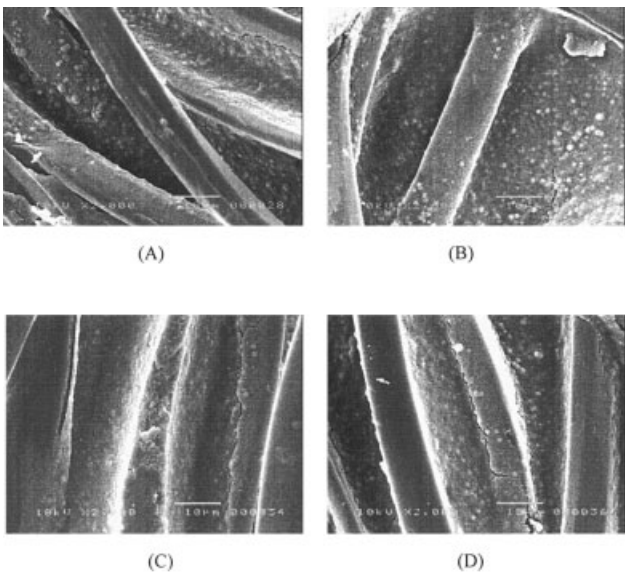

Figure 7 SEM photographs (original magnification = 1000×) of microcapsule-treated samples after laundering: (A) 1 cycle, (B) 5 cycles, (C) 10 cycles, and (D) 20 cycles.

TABLE III
Effect of Laundering on the Heat Storage Capacity of the Treated Fabrics

Laundering (cycle)	ΔH_f (J/g)	Retention (%)
0	4.44	100
1	2.94	66
5	1.82	41
10	1.13	25
20	1.14	26

and at the interstices between the fibers in the samples after one and five launderings. On the other hand, most of the microcapsules were located at interstices in the samples after 10 and 20 launderings. This result indicated that the microcapsules on the fiber surface tended to come off more easily than those at interstices during laundering.

Table III shows the effect of the laundering on the heat storage capacity (ΔH_f) of the treated fabrics. The heat storage capacity decreased as the laundering cycles increased. With respect to the heat storage capacity of the sample before laundering, 66 or 41% of the heat storage capacity was retained after one or five launderings, respectively. The largest decrease occurred after the first laundering. Microcapsules loosely attached to the fabric fell off during repeated laundering, and so the heat storage capacity of the treated samples decreased continuously up to 10 launderings; however, no more reduction in the heat storage capacity occurred thereafter. Kim and Cho[5] used an acrylic binder for coating PCM microcapsules onto fabrics and obtained 52–70% retention of the heat of fusion after 10 launderings. The selections of the appropriate binder and application method may result in a higher retention of the heat storage capacity of treated fabrics. Also, mild washing conditions would be helpful for better maintenance of microcapsule-treated materials.

CONCLUSIONS

The prepared microcapsules were spherical and had a melamine–formaldehyde resin shell containing eicosane. They were strong enough to secure microcapsule stability during stirring in hot water and under alkaline conditions and were heat-resistant enough to endure the high temperatures of curing conditions. The thermoregulating fabrics developed in this study showed heat storage capacities of 0.91–4.44 J/g. The treated fabrics retained about 40% of their heat storage capacity after five launderings.

The results suggest that microcapsules with higher core/shell ratios need to be made to improve the thermoregulating efficiency of fabrics. Also, a finishing process including binder types and loading methods needs to be studied further to improve laundering durability.

References

1. Mulligan, J. C.; Colvin, D. P.; Bryant, Y. G. J Spacecraft Rockets 1996, 33, 278.
2. Colvin, D. P.; Mulligan, J. C. U.S. Pat. 4,911,232 (1990).
3. Cox, R. Chem Fibers Int 1998, 48, 475.
4. Pause, B. J Coated Fabrics 1995, 25, 59.
5. Kim, J.; Cho, G. Text Res J 2002, 72, 1093.
6. Nuckols, M. L. Ocean Eng 1999, 26, 547.
7. Yang, R.; Xu, H.; Zhang, Y. Sol Energy Mater Sol Cells 2003, 80, 405.
8. Brown, R. C.; Rasberry, J. D.; Overmann, S. P. Powder Technol 1998, 98, 217.
9. Colvin, D. P.; Cartwright, D. K. U.S. Pat. 6,057,266 (2000).
10. Shin, Y.; Yoo, D. I.; Jang, J. J Appl Polym Sci 2001, 80, 2495.
11. Pause, B. H. J Ind Text 2003, 33, 93.
12. Colvin, D. P.; Bryant, Y. G. Adv Heat Mass Transfer Biotechnol 1998, 362, 123.
13. Shin, Y.; Son, K.; Cho, E. J Fiber Soc (Korea) 2002, 39, 224.
14. Hittle, D. C.; Andre, T. L. ASHRAE Trans 2001, 107, 175.