

The manufacture of microencapsulated phase change materials suitable for the design of thermally enhanced fabrics

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Abstract

Thermal comfort of a fabric is one of the important tasks of the designers that require an engineering approach. In this study, we first aimed to establish a manufacturing technique based on in situ polymerization in order to accomplish the microencapsulation of phase change materials (PCMs) that can ultimately be used in different textile applications, i.e. incorporating such products into the multi-component non-conventional fabrics. This method is suitable for the laboratory-scale work as well as the industrial-scale one, considering some important issues like energy and time savings. Four types of polyurea-formaldehyde microcapsules containing different waxes and a control group of 100% shell material were produced and then examined by DSC, particle size and SEM analyses. Furthermore, we also focused on the contributions of microencapsulated PCMs to the thermal performances of fabrics of certain passive insulation characteristics for the given cold weather and physical activity conditions, based on the model developed for a multi-layer fabric system.

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1. Introduction

The design and development of a functional textile providing an ability of dynamic heat regulation next to the skin have attracted more and more attention in recent years. Number of attempts in this field is extensive parallel to the researches in electronics, several solar energy-based systems, buildings, etc. However, successful applications are limited and still under investigation. A remarkable group of them concerns with the manufacture of microcapsules so that spherical bi-component particles consist of shells and surrounded core material [1–8].

Phase change materials (PCMs) have been applied to the textiles in a variety of processes to improve thermal comfort of end-use products, due to their high heat storage capacities. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam manufactur-

ing are some of the convenient processes for PCMs' incorporation into the structure. Well-known PCMs are linear chain hydrocarbons known as paraffin waxes (or *n*-alkanes), hydrated salts, polyethylene glycols (PEGs), fatty acids and mixture or eutectics of organic and non-organic compounds. PCMs have also been used as a core material in the microcapsule production, the prior stage of aforementioned processes for the fabrication of thermo-regulated fibers, fabrics, coatings and foams [9–11].

Microcapsule utilization in textile goods is advantageous since the encapsulation prevents PCM dispersion in the structure, reduces evaporation and reaction of PCMs with the outside environment, provides an increased heat-transfer area and a constant volume, and allows an easy application without affecting other textile properties and a normal fabric-care. In-fiber incorporation of microcapsules, for instance, could be achieved by loading the fiber with 5–10% of microcapsules, and thus, PCM could be permanently locked within the fiber exhibiting normal properties of drape, softness and strength without a need of subsequent fiber processing; or washing durability of a functional cotton fabric on which the microcapsules were applied by a printing paste also including small content of acrylic binder, which was ensured up to 15 times.

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Microcapsules are defined with the parameters such as particle diameter, thickness of shell, thermal capacity and conductivity, durability, etc. Thickness of particle walls may be less than 1 μm , and particle sizes vary within the range of less than 1 μm to more than 300 μm depending on the method of encapsulation, typically 20–40 μm in diameter. PCM content of a capsule may be up to 80–85% [12–16].

Microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are a concern for health and the environment. Physical methods are mainly spray drying or centrifugal and fluidized bed processes, which are inherently not capable of producing microcapsules smaller than 100 μm . The most suitable chemical processes are associated with the simple or complex coacervation and interfacial (or in situ) polymerization techniques.

The simple or complex coacervation is a colloidal process in which the core material in dispersed form is added to the polymer solution, and the mixture is then suspended in an aqueous phase containing a surface-active agent. Microencapsulation of both oily and water-soluble actives is possible using oil-in-water and water-in-oil techniques. As oil-in-water coacervation is more straightforward, it is widely used in the industry. Encapsulation of paraffin waxes by complex coacervation was succeeded to attain a high energy storage/release capacity of about 145–240 J g^{-1} identifying a good potential as a solar energy storage material [17]. The main limitation of this approach is the difficulty in scale up of the process.

In situ polymerization generally involves bringing together two immiscible liquids, e.g. water and organic solvent, respectively, containing complimentary, direct-acting, organic intermediates that will react with each other to establish a solid precondensate [3,9,10,15,18–26]. Condensation polymers are usually formed by the stepwise intermolecular condensation of reactive groups. The structural units of condensation polymers are usually joined by inter-unit functional groups. The in situ processes have the ability to yield microcapsules with the best quality in terms of diffusion-tightness of their walls and of a size ranging between 5 and 100 μm . Suitable polymers such as a polyamide, polyester, polyurethane, polyurea, or like substances, can be formed from resin intermediates or monomers. Additionally, in a group of study in which the microencapsulation was accomplished through an in situ polymerization technique, the effects of some process parameters such as stirring rate, pH of the reaction mixture, contents of emulsifying agent, capsule diameters and so on were studied [20–26].

In this study, we first aimed to establish a manufacturing technique based on in situ polymerization in order to accomplish the microencapsulation of PCMs that can ultimately be used in different textile applications, i.e. coating or laminating of textile surfaces or incorporating such products into the multi-component non-conventional fabrics, etc. Second, we considered this method to be suitable for the laboratory-scale work as well as the industrial-scale one while considering some important issues like energy and time savings. Furthermore, we also focused on the contributions of microencapsulated PCMs to the

thermal performances of fabrics of certain passive insulation characteristics for the given cold weather and physical activity conditions, based on the model developed for a multi-layer fabric system.

2. Experimental

2.1. Material

To produce the required microcapsules, shell materials and some auxiliaries were chosen in relation to the applied in situ polymerization technique. Monomers and auxiliaries, all by Merck, are given in Table 1. The chosen types of reaction initiator and anionic polyelectrolyte are able to serve for improving the polymerization of urea and formaldehyde whereby microcapsules having high strength and low permeability are obtainable [1]. 1,3-Benzenediol (Resorcinol) reacts with formaldehyde as a cross-linking agent, and produces resorcinol/formaldehyde resin, which enhances the shell formation and prevents bond breaking in polymerization chains [16].

Selected PCMs as being core material were those with phase transition temperatures suitable for the textile and clothing applications. Three types of paraffin waxes ($\text{C}_n\text{H}_{2n+2}$), namely, *n*-hexadecane, *n*-octadecane and *n*-eicosane, were preferred for the encapsulation since they are nontoxic, non-corrosive, chemically inert, easily available and have no unpleasant odor.

These waxes which may be encountered in textile applications are immiscible in water and thus, they offer an advantage to serve as an organic phase in interfacial polycondensation techniques. On the other hand, some other important PCMs of polyethylene glycols (PEGs), say PEG600 and PEG1000, and of a hydrated salt, say $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, were included and their contributions in encapsulation process of *n*-alkanes were also investigated.

Considering the core content, four different combinations were planned based on the chosen PCMs. Characteristics of manufactured microcapsules were checked against a control sample, which is 100% shell material. Table 2 gives the recipes applied in the experimental study, some of which indicate the mixtures of PCMs as the core. These mixtures were prepared with the aim that of widening the intervals of phase transition beside enhancing the heat absorbing and releasing capacities of capsules in order to obtain an improved performance for the stabilization of the temperature changes.

Table 1
Materials used in in situ polymerization

Material	Function in polymerization
Urea, $(\text{NH}_2)_2\text{CO}$ (60.06 g mol^{-1})	Monomer for the shell
Formaldehyde, H_2CO (30.0 mol^{-1})	Monomer for the shell
Sodium salt of dodecyl benzene sulfonic acid (SDS)	Emulsifier
Polyethenol (PVA)	Anionic polyelectrolyte
Triton X 100	Nonionic polyelectrolyte
Ammonium chloride, NH_4Cl	Reaction initiator
1,3-Benzenediol (Resorcinol), $\text{C}_6\text{H}_4(\text{OH})_2$	Binder

Table 2
Core materials and mixtures thereof

Type	Content of core			Prepolymer emulsion (g)	Percentage of core in the emulsion (%)
	Mixture	Total mass (g)	Mass to mass ratios		
Control	–	–	–	47.8	–
A	<i>n</i> -Octadecane	10.3	1.00	95.6	11
B	<i>n</i> -Octadecane/PEG600	38.4	0.13:0.87	48.9	79
C	<i>n</i> -Eicosane/ <i>n</i> -hexadecane	20.8	0.34:0.66	48.9	43
D	PEG1000/Na ₂ CO ₃ ·10H ₂ O/ <i>n</i> -hexadecane	51.2	0.50:0.39:0.11	47.8	107

2.2. Microcapsule manufacture

This experimental work concerns with the in situ polymerization of urea-formaldehyde resins encapsulating the core materials mentioned above. A double-wall reactor was designed and used to achieve laboratory-scale encapsulation process as given in Fig. 1.

As a first step, an aqueous prepolymer mixture containing, polyelectrolyte solutions of 5% of SDS, 4% of PVA, 5% of Triton X 100 and 5% Resorcinol, by mass, are mixed with 100 mL distilled water in the reactor at 20 °C. Resorcinol is added to achieve more cross-linking in urea-formaldehyde as mentioned above. The sample is stirred at 600 rpm for 10 min. Then, 30 g of urea, the nucleus material and 1–5% by mass NH₄Cl are added successively. Thus, “oil-in-water system” is prepared, and colloidal dispersions containing PCMs or mixtures thereof are formed. While this emulsion is stirring at the speed of 300 rpm, pH is adjusted to 3.50–4.00 using buffer solutions [27]. Next, the stoichiometric molar amount of 37% formaldehyde is put into the dispersion. Finally, the reaction proceeds by continuous stirring and prepolymer is synthesized during the gradual heating up to 50 °C for 40–60 min, at a constant pH Fig. 2. Suspension of polyurea-formaldehyde capsules is cooled to 25 °C,

washed with water repeatedly, then filtered and vacuum dried in a closed cabinet until almost all free formaldehyde is removed, consequently the microcapsules are recovered.

To characterize the thermal behavior of PCMs and their microcapsules, which consist of polymer shells, DSC analyses were conducted on a Perkin-Elmer/Pyris 1 type DSC under nitrogen atmosphere. During DSC analyses, test specimens were heated and cooled within a certain temperature interval ranging from 0 °C to 55 °C at 10 °C min⁻¹, which is commonly used in the experiments of polymer microcapsules [28,29]. Additionally, Phywe Cobra3 computer aided data acquisition system was connected to a double-wall calorimeter with thermocouple, and the thermal behavior of the sample was checked against that of the same amount of distilled water in a similar temperature range. In calorimeter tests, relatively lower heating and the cooling rates were preferred.

Particle size distributions of the manufactured microcapsules were determined using Master Sizer 2000 Instrument, based on the averages of five tests. SEM photos were taken to explain the structural details of the microcapsules by the SEM Instrument, type JSM 6335F NT.

The mechanical stability and leakage behavior of microcapsules were examined by the centrifugal shear force test [30].

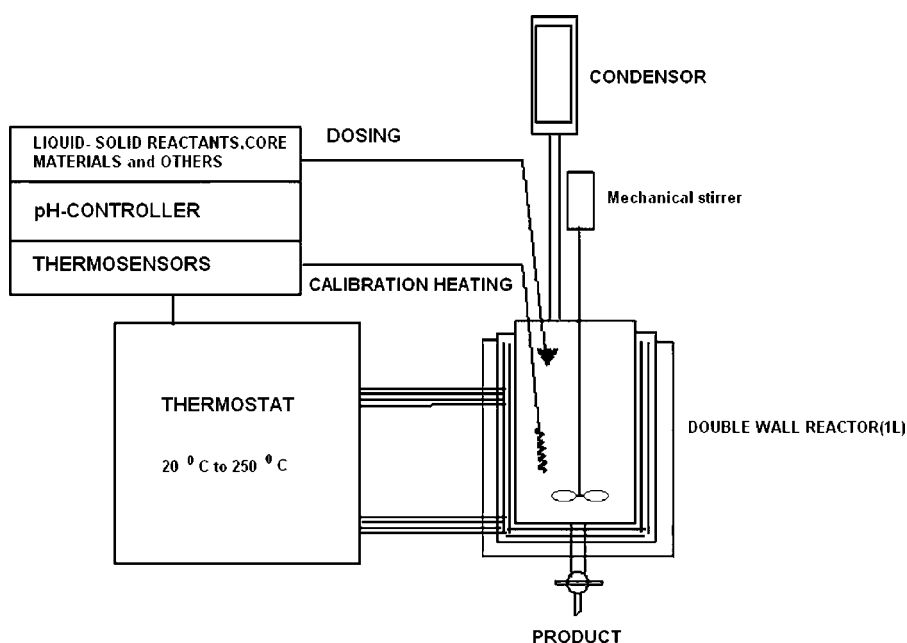


Fig. 1. The reactor designed for the manufacture of microcapsules.

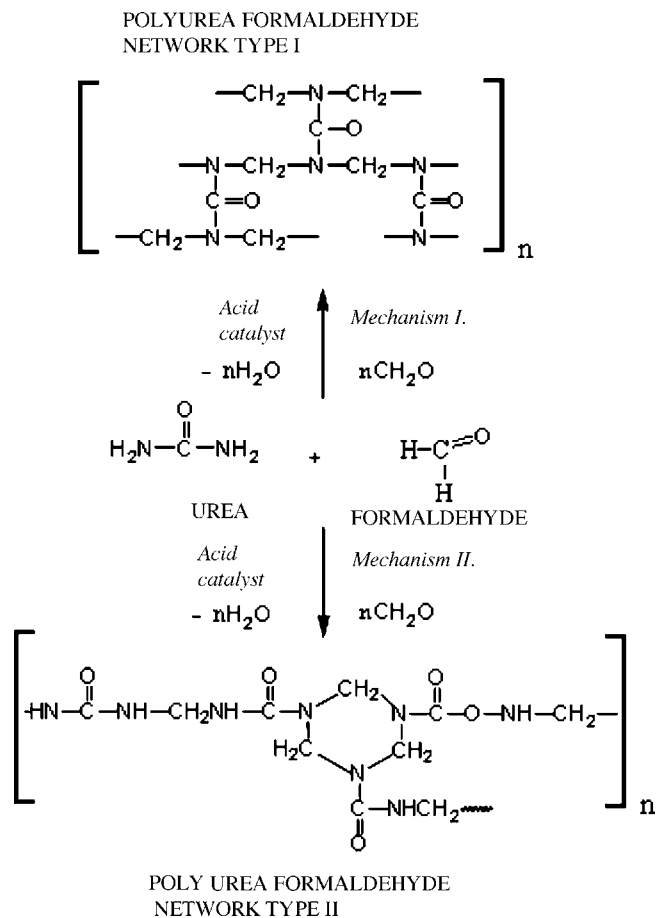


Fig. 2. In situ polymerization of urea-formaldehyde resin.

Microcapsules (0.1 g) of each sample were put into a test tube in 2 mL of water. Tubes were centrifuged at the frequency of 200 rpm and the room temperature for 2 and 4 h, respectively. Images of microcapsules were analyzed by an optical microscope for visual comparison.

3. Results and discussion

3.1. DSC results of core materials

Results obtained from DSC analyses for the PCMs used in the experimental study are given in Table 3. Fig. 3 shows DSC and calorimeter graphs of *n*-hexadecane, respectively. The phase change behavior of *n*-hexadecane is clearly seen from both DSC and calorimeter graphs given in Fig. 3 for the same temperature

interval. As illustrated from Table 3, all types of PCMs are quite satisfactory to suit thermal comfort requirements of many textile products as well as clothing. Their latent heat of fusions in terms of ΔH values (J g^{-1}) are all quite large, and thus, compatible.

3.2. Characterization of manufactured microcapsules containing PCMs

3.2.1. Particle size distribution

Test results show that capsule sizes generally vary within the range from less than 1 μm up to 500 μm (see Table 4). However, for the types B and C, 50% of microcapsules were obtained <200 μm in diameter. Furthermore, percentages of quite small particles, say <50 μm in diameter, are considerable. This is the evidence that the method of encapsulation applied in this study is appropriate to produce microcapsules containing a special core within typical ranges required for the textile applications.

On the other hand, particle size distributions are differing from each other apparently depending on the type of core material used. Microcapsules of the type A, which encircle *n*-octadecane molecules, are relatively larger than those of C. In fact, results of C imply that when smaller molecules, here mainly the molecules of *n*-hexadecane, are covered by the polymer shells, the capsule sizes obtained tend to be smaller.

In addition to this, one of the important factors of the interfacial polycondensation technique affecting the size of particle observed was the rate of stirring. The lower rates of stirring, especially after adding the second monomer into the polymerization process, may result in capsule sizes in relatively smaller diameters. But the action of this process parameter on the capsule size is not discussed here just because it is out of the scope of this paper.

3.2.2. Structures of microcapsules

When SEM photos are taken into consideration, both the general characteristics of the capsules and the differences between the samples of various types have become prominent. Fig. 6(b) shows the urea-formaldehyde polymers of control sample, without any core material. Thus, the particles are of a shape far from being spherical, and the capsule formation is basically unavailable.

However, the SEM images given in Figs. 4–6(a) illustrate the formation of the distinct microcapsules. In each image, encapsulation of the cores of a paraffin wax or a mixture thereof by the polymer shell is represented and well understood by the smooth surface morphology and the spherical shapes of the capsules. It is also seen that there are some other polymers produced which

Table 3
DSC results of PCMs

PCM	Onset T ($^{\circ}\text{C}$)	Transition interval ($^{\circ}\text{C}$)	Peak T ($^{\circ}\text{C}$)	Enthalpy, ΔH (J g^{-1})
<i>n</i> -Hexadecane (number of C atoms: 16)	17.1	10–26	22.0	185.3
<i>n</i> -Octadecane (number of C atoms: 18)	29.8	26–44	35.6	233.8
<i>n</i> -Eicosane (number of C atoms: 20) [27]	36.6	30–45	–	155.0
PEG600 (600 g mol^{-1})	10.4	06–32	21.6/27.7	106.5
PEG1000 (1000 g mol^{-1})	35.6	28–48	27.3/42.7	151.1
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (286 g mol^{-1})	34.4	33–48	38.6/43.7	235.2

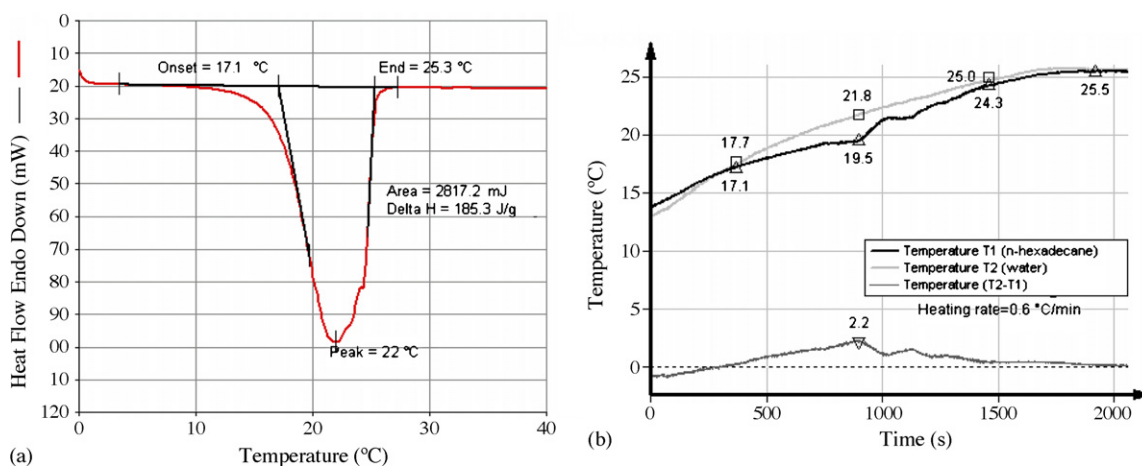


Fig. 3. (a) The DSC curve of *n*-hexadecane (heating to 55 °C at 10 °C min⁻¹; sample weight is 15.2 mg). (b) The calorimeter graph of *n*-hexadecane (heating to 26 °C at 0.6 °C min⁻¹; sample weight is 5.1 g).

Table 4

Particle sizes in micrometer correspond to the particular percentages of the size distributions

Capsule type	Capsule sizes in μm correspond to			Mean (μm)	Min. (μm)	Max. (μm)	Percentage of p. sizes $\leq 50 \mu\text{m}$	Percentage of p. sizes 51–100 μm
	10%	50%	90%					
Control	44.5	196.2	560.8	269.3	2.0	2000.0	11.6	14.6
A	47.4	411.4	1202.5	527.3	1.6	2000.0	10.5	8.0
B	33.4	201.9	704.3	296.7	3.6	1415.9	15.8	14.1
C	6.7	41.3	185.8	69.1	0.4	399.1	55.6	21.2

did not participate in the encapsulation process. This makes the microcapsule existence much more clear. In Fig. 4, capsule sizes are marked occasionally to show their dimensions in micrometer.

In addition, as mentioned above, SEM figures can give an idea about the different distribution characteristics of the samples. For instance, the capsules of C in Fig. 5 are quite small in accordance with the related results given in Table 4. Fig. 6(a) represents a greater variety of capsules of D. Besides, the image of B in Fig. 4(b) indicates that some of the capsules were formed distinctly; however, the structure is somewhat different and composed of some semi-capsules bonded together probably due

to the presence of PEG600 in the prepolymer emulsion. Free hydroxyl groups of PEG molecules tend to make physical bonds between capsules.

3.2.3. Thermal properties

Endothermic and exothermic enthalpy changes of some microcapsules during their heating and subsequent cooling in between 0 °C and 55 °C at the rate of 10 °C min⁻¹ are given as examples in Table 5 and in Figs. 7–9. In each case, the phase transition interval of the manufactured capsules greatly overlaps with that of the paraffin wax encapsulated. This implies that the

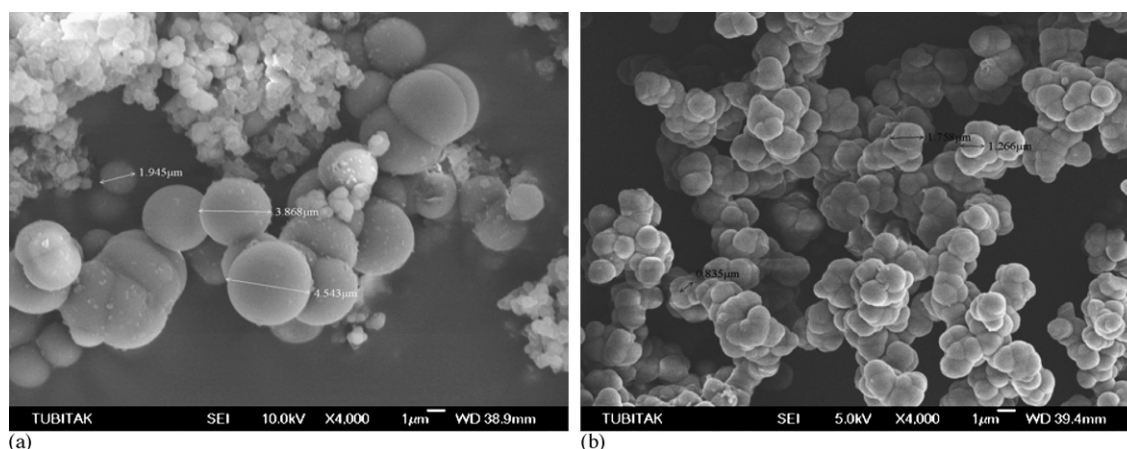


Fig. 4. (a) Microcapsules of the type A containing *n*-octadecane core; magnification 4000 \times ; 10.0 kV. (b) Microcapsules of the type B containing the mixture of *n*-octadecane and PEG600 core; magnification 4000 \times ; 5.0 kV.

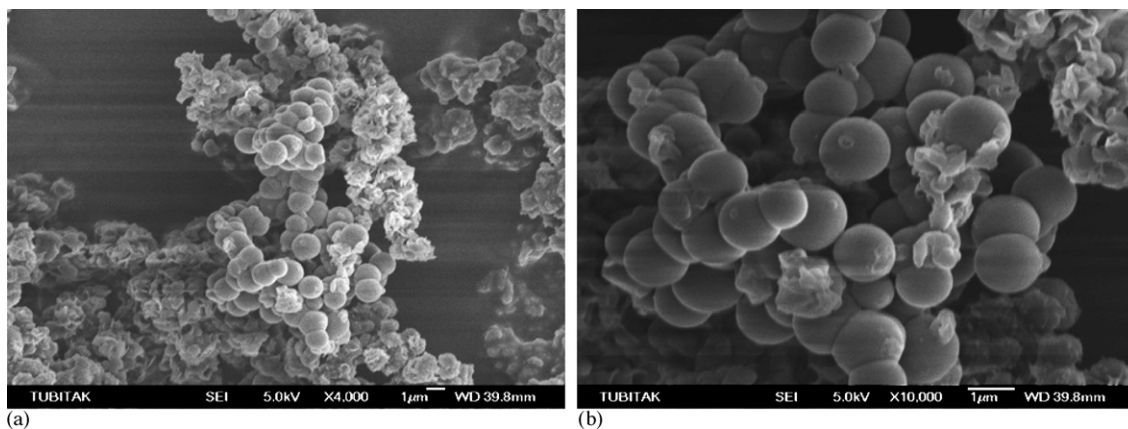


Fig. 5. Microcapsules of type C containing the mixture of *n*-eicosane and *n*-hexadecane core: (a) magnification 4000 \times ; 5.0 kV and (b) magnification 10,000 \times ; 5.0 kV.

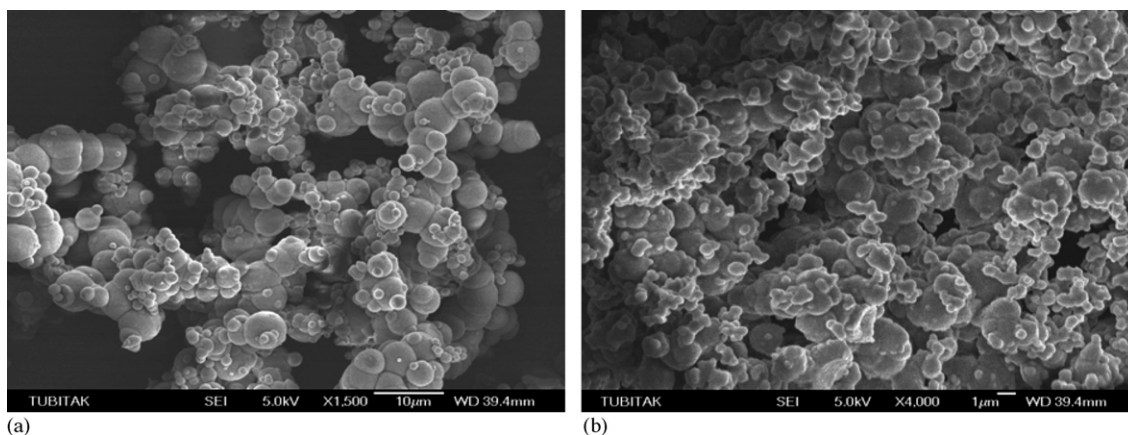


Fig. 6. (a) Microcapsules of the type D containing the mixture of PEG1000, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and *n*-hexadecane core; magnification 1500 \times , 5.0 kV. (b) Urea-formaldehyde polymers of control sample; magnification 4000 \times ; 5.0 kV.

chemical structures of paraffin waxes are not subjected to any adverse effect in microencapsulation.

These results can be regarded as a perfect evidence of a successful encapsulation process. There is a good relationship between the enthalpies obtained for the capsules and those of PCMs used, considering the amount of ingredient core materials in emulsions. The thermal property of capsule A is parallel to that of pure *n*-octadecane (see also Table 3). The phase transition behavior of capsule B is similar to that of capsule A. All ΔH values especially those obtained for the capsule types C and D are remarkable in terms of their contribution to the dynamic thermal

management of textile products. PCM contents of the microcapsules can be further increased technically; however, it should be taken into account that the micelle formation and eventually the micro-size capsule production may become more difficult.

It is also noteworthy that relatively smaller molecules of *n*-hexadecane rather than those of *n*-eicosane were encapsulated much more easily under the constant conditions in the same colloidal medium during interfacial polycondensation. Therefore, the DSC curve of the type C comprises only one fusion peak at 19.6 $^\circ\text{C}$ and the transition interval is similar to that of *n*-hexadecane (see Figs. 8 and 3).

Table 5
Phase transition characteristics of microcapsules containing paraffin waxes

Capsule type/core mixture	Heating from 0 $^\circ\text{C}$ to 50 $^\circ\text{C}$ at the speed of 10 $^\circ\text{C min}^{-1}$			Cooling from 50 $^\circ\text{C}$ to 0 $^\circ\text{C}$ at the speed of 10 $^\circ\text{C min}^{-1}$		
	Onset T ($^\circ\text{C}$)	Transition interval ($^\circ\text{C}$)	ΔH (J g^{-1})	Onset T ($^\circ\text{C}$)	Transition interval ($^\circ\text{C}$)	ΔH (J g^{-1})
A <i>n</i> -Octadecane	28.5	26.0–33.0	18.8	26.3	26.5–17.7	–17.4
B <i>n</i> -Octadecane and PEG600	28.6	26.0–32.5	3.9	26.8	27.0–25.2	–1.6
C <i>n</i> -Eicosane and <i>n</i> -hexadecane	15.5	9.0–23.5	51.7	20.4	24.5–12.0	–54.8
D PEG1000 and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and <i>n</i> -hexadecane	17.7	13.0–23.5	44.6	15.8	15.8–13.4	–42.5

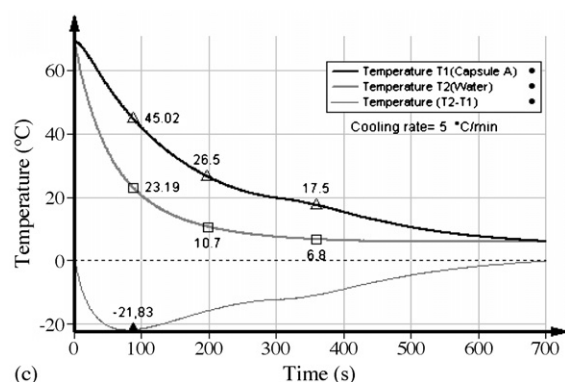
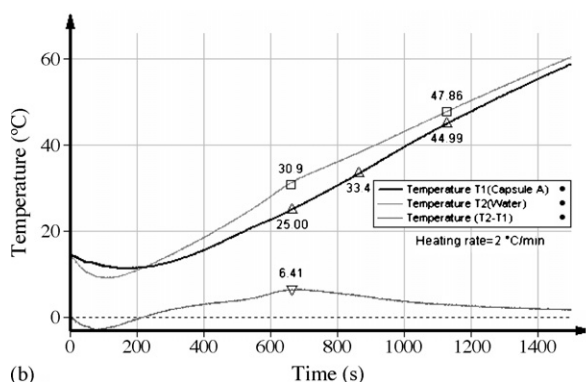
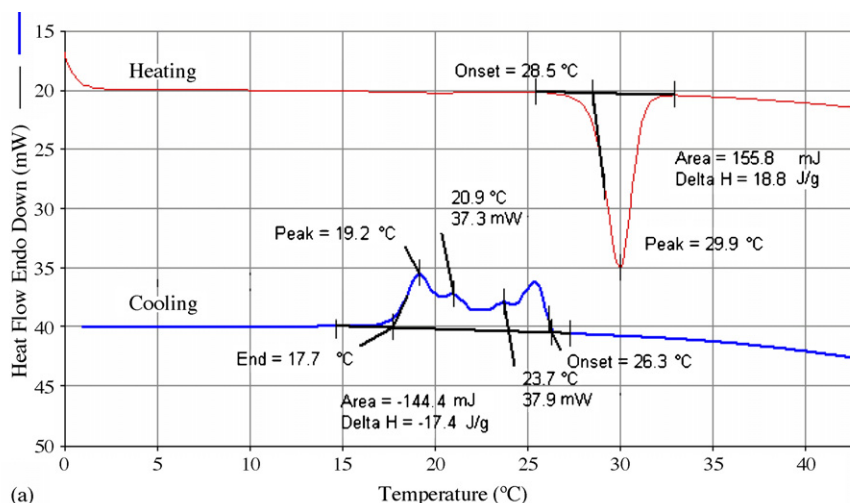


Fig. 7. (a) DSC curves obtained during heating and subsequent cooling of capsules A, containing *n*-octadecane, in between 0 °C and 55 °C at the rate of 10 °C min⁻¹; sample weight is 8.3 mg. (b) Calorimeter graph of capsule A during heating at the rate of 2 °C min⁻¹; sample weight is 1.0 g. (c) Calorimeter graph of capsule A during cooling at the rate of 5 °C min⁻¹.

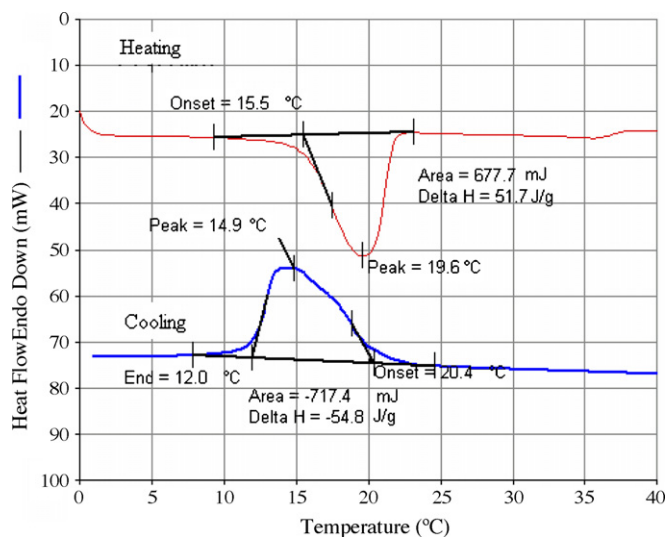


Fig. 8. DSC curves obtained during heating and subsequent cooling of capsules C, containing *n*-eicosane and *n*-hexadecane, in between 0 °C and 55 °C at the rate of 10 °C min⁻¹; sample weight is 13.1 mg.

When Figs. 9 and 3 are taken into consideration comparatively, the phase transition characteristics of capsule D are in compliance with *n*-hexadecane rather than the core mixture of it. The endothermic reaction curve of the capsules type D has a single peak at 20.0 °C, resembling the fusion peak of the pure *n*-hexadecane. Since the micelles formed within the oil-in-water system mainly contain the molecules of paraffin waxes, the water-soluble PEG in the dispersion is probably involved in intra-molecular polymerization as well as inter-capsular hydrogen bonding. On the other hand, it looks as if the hydrated salt could not participate to the encapsulation process at all.

What is more, ΔH values observed for cooling processes show that full thermal performance of the PCM contained by the polymer shell is attainable as expected, whether the environmental change is the temperature rise or drop. Another important finding related to the DSC curves given in Figs. 7–9, which is common to all, is the typical decrease of the freezing (crystallization) point. All three cooling curves represent exothermic phase transitions in relatively lower ranges of temperature when compared with their endothermic fusion ranges. If the hysteresis of the microcapsules of C and D are both considered, it is seen that phase transition peaks during heating and subsequent

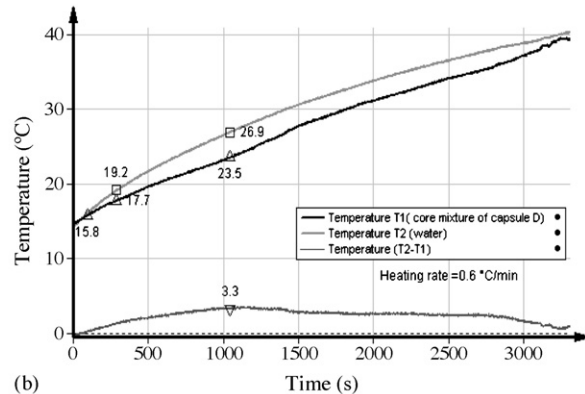
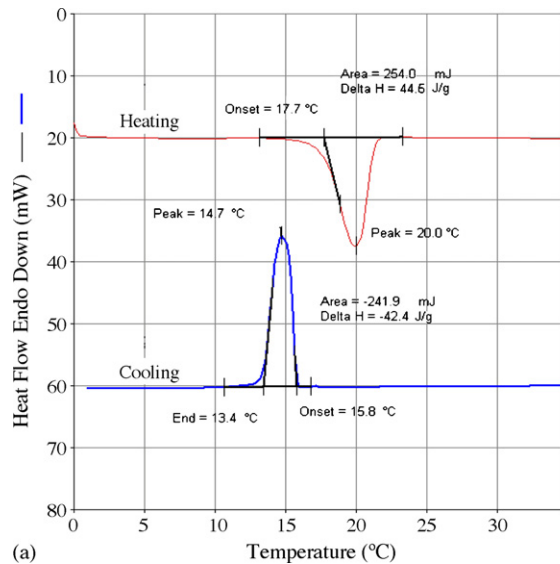


Fig. 9. (a) DSC curves obtained during heating and subsequent cooling of capsules D, containing PEG1000, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and *n*-hexadecane, in between 0°C and 55°C at the rate of $10^\circ\text{C min}^{-1}$; sample weight is 5.7 mg. (b) Calorimeter graph of core mixture of capsule D during heating at the rate of $0.6^\circ\text{C min}^{-1}$; sample weight is 7.7 g.

cooling, are 19.6°C and 14.9°C for C, and 20.0°C and 14.7°C for D.

During heating from 0°C to 55°C , the ordered structures of PCMs in solid phase gradually change towards the disordered structures in liquid phase in the cores of microcapsules. Therefore, it may reasonably be observed that the thermal behavior of the microcapsules approaches the thermal behavior of the pure substance while heat is absorbed. This also explains why transition intervals are coinciding greatly. Conversely, heterogeneous structure behavior involves in phase transitions during cooling. Cooling leads to a transition of a disordered liquid phase to an ordered solid structure. Additionally, the captured impurities other than core material during encapsulation may also cause decrease of the freezing (crystallization) point. Further possible implication is that heat released from some of the capsules during cooling may result in heat regains of some others depending on varying particle diameters yielding multiple crystallization peaks as given in Fig. 9, parallel to the literature [16]. Since the microcapsuled PCMs will be incorporated into the clothing systems for the cold weather conditions, the resultant widened hysteresis appeared in the DSC curves, due to the microencapsulation, are not at a level to impose any adverse effect on the dynamic heat exchange between a human body and the clothing system.

Fig. 10 is given to compare the enthalpy changes of microcapsules for heating and cooling, respectively. These graphs show the differences, in terms of Joules per g per $^\circ\text{C}$, between the products.

3.2.4. Mechanical properties

Mechanical stability of microcapsules is an important property to facilitate production, handling and application. As the mechanical strength of the capsules increases, their durability will also increase and the leakage possibility of the core material will decrease.

After centrifugal shear force tests for 2 and 4 h, 3 mL of water was added to each test tube to simplify the observation of the leakage of oil phase; however, any exuded oil droplet could not be detected visually for all samples. Moreover, the microscopic capsule images implied that no significant structural change after all shear force tests took place.

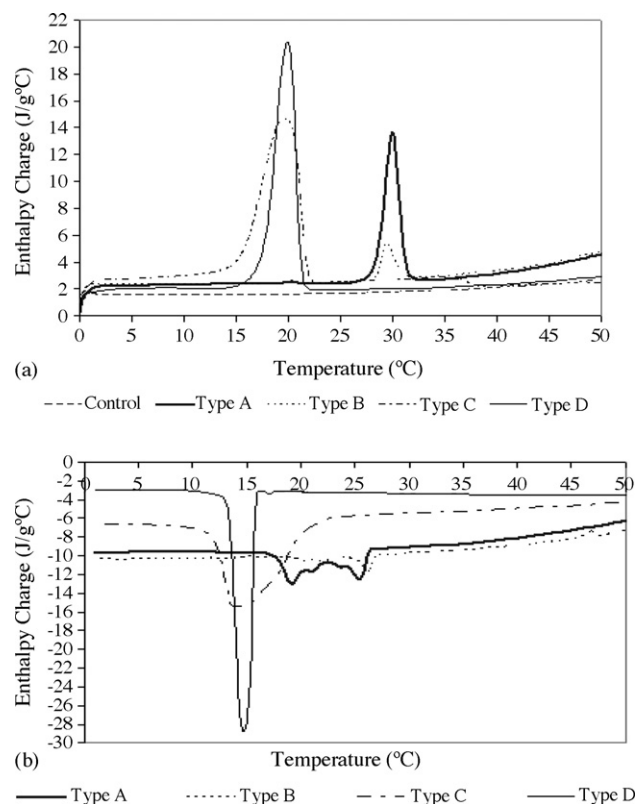


Fig. 10. Comparison of the enthalpy changes of microcapsules in terms of Joules per g per $^\circ\text{C}$: (a) heating and (b) cooling.

Table 6
Heat regulation performance of the microcapsules (type C) incorporated into three different clothing and the two-layer fabric system modeled

Type of clothing	I_{cl}		I_T			t_a (°C)	Q_M (W m ⁻²)	Q_{Loss} (W m ⁻²)	ΔQ ($Q_{Loss} - Q_M$; W m ⁻²)	Duration of the heat release [$Q'/(\Delta Q \times 60)$; min]
	clo*	m ² K W ⁻¹	clo*	m ² K W ⁻¹	K (1/ I_T ; W m ⁻² K ⁻¹)					
Trousers, long sleeve shirt	0.61	0.095	1.21	0.188	5.3	11	115	117.3	2.3	59.7
						10	115	122.6	7.6	18.0
						9	115	128.0	13.0	10.6
						8	115	133.3	18.3	7.5
						7	115	138.6	23.6	5.8
						6	115	144.0	29.0	4.7
						5	115	149.3	34.3	4.0
The two-layer fabric system modeled	0.89	0.138	1.48**	0.229	4.4	6	115	117.7	2.7	51.0
						5	115	122.1	7.1	19.5
						4	115	126.4	11.4	12.0
						3	115	130.8	15.8	8.7
						2	115	135.1	20.1	6.8
						1	115	139.5	24.5	5.6
						0	115	143.9	28.9	4.8
Trousers, long sleeve shirt, jacket	0.96	0.149	1.54	0.239	4.2	-1	115	148.2	33.2	4.1
						5	115	117.3	2.3	59.7
						4	115	121.5	6.5	21.2
						3	115	125.7	10.7	12.9
						2	115	129.9	14.9	9.2
						1	115	134.1	19.1	7.2
						0	115	138.2	23.2	5.9
Insulated coveralls, long sleeve thermal underwear, long underwear bottoms	1.37	0.212	1.94	0.301	3.3	-1	115	142.4	27.4	5.0
						-2	115	146.6	31.6	4.3
						-2	115	116.4	1.4	98.6
						-3	115	119.7	4.7	29.1
						-4	115	123.0	8.0	17.1
						-5	115	126.4	11.4	12.1
						-6	115	129.7	14.7	9.4
-7	115	133.0	18.0	7.6						
-8	115	136.3	21.3	6.4						
-9	115	139.7	24.7	5.6						
-10	115	143.0	28.0	4.9						

* 1 clo = 0.155 m² K W⁻¹ (the unit of clo is based on the insulating value of the typical American's business suit in 1941) [41].

** Interpolated.

3.3. The performance of microcapsules incorporated into a multi-layer fabric system

Heat loss to the environment normally takes place by convection, radiation and evaporation from the skin and by sensible and latent heat of perspiration; however, clothing adds thermal resistance to heat flowing. For the thermal protection, the important task of clothing is to create a stable microclimate next to the skin in order to support the body's thermoregulatory system, even if the external environment and physical activities change in a much broader range [31–39]. When a textile product is incorporated with thermally active materials, it can provide an enhanced thermal capacity in addition to the existing passive insulation characteristic of the structure to keep the body in the comfort state.

We attempt, here, to find out the functionality of our thermo-microcapsules incorporated into a two-layer fabric system. Related results given in Table 6 were based on the following model. In order to design a multi-layer clothing system with dynamic heat regulation function, it is necessary to know the total insulation value of the whole assembly depending on the structural properties and boundary layers of air in the system.

The equivalent thermal resistance of the clothing system ($1/K$) can be defined as given in Eq. (1),

$$\frac{1}{K} = \sum_{i=1}^n \left(\frac{l_i}{k_i} + \frac{1}{h_i} \right) + \frac{1}{h_a} \quad (1)$$

where k_i is the coefficient of thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$) and l_i is the thickness (m) of i th fabric layer, h_i is the convective heat-transfer coefficient of air between i th and $(i+1)$ th fabric layers ($\text{W m}^{-2} \text{K}^{-1}$), h_a is the convective heat-transfer coefficient of surrounding air at the outer fabric surface [31–37].

For the human body comfort, the difference (ΔQ) between the metabolic heat (Q_M) and the heat loss through the clothing system (Q_{Loss}) must be zero, or must be balanced by the enhanced thermal capacity (Q') of the fabric.

$$\left. \begin{aligned} \Delta Q &= |Q_M - Q_{\text{Loss}}| \\ Q_{\text{Loss}} &= K(t_s - t_a) \\ Q' &= m \times \Delta H_{\text{fus}} \end{aligned} \right\} \quad (2)$$

where t_s is the skin temperature, t_a is the temperature of ambient air, ΔH_{fus} and m are the phase transition enthalpy and mass of the microcapsuled PCM added to the product, respectively. Here, the heat loss of perspiration is not included, and the frictional resistances, the resistance of the entrapped air between layers are omitted since they are quite small. The heat loss/gain due to radiation is also neglected for the low temperature climatic conditions.

The conditions we applied to the Eqs. (1) and (2) for the two-layer fabric system are as given below.

The resultant thermal conductivity values of the first and second cloth layer of 1 mm thickness are chosen as 0.057 and 0.047 $\text{W m}^{-1} \text{K}^{-1}$ for PET and cotton fabrics, both entrapping some still air. Skin temperature (t_s) is 33 °C. ΔH_{fus} is 55 J g^{-1} corresponding to that of the type C. Air velocity (v) is 1.4 ms^{-1} .

h_a is 10.28 $\text{W m}^{-2} \text{K}^{-1}$. The weight of the fabric system is 400 gm^{-2} including 150 g microcapsules of C. The thermal resistance of the fabric system is obtained as 0.138 $\text{m}^2 \text{K W}^{-1}$ or 0.89 clo.

Table 6 illustrates the expected heat regulation function of the two-layer fabric system modeled as well as those of three different clothing systems defined in the ASHRAE Standard 55-2004 [40,41], assuming that all containing 150 g microcapsules of type C per m^2 of the surface area. In Table 6, I_{cl} is the thermal resistance of clothing alone and I_T is the total thermal resistance between the skin and the environment including clothing [35]. The conditions considered are relevant to keep a walking person on the level surface in comfort state while moving from hot to cold ambience. Based on the enhanced thermal capacity of the clothing systems, both the temperature values and the corresponding durations are given comparatively, provided that the passive insulation of the clothing is insufficient to keep the body temperature constant. As shown from Table 6, the clothing system with $I_T = 1.21$ clo (0.188 $\text{m}^2 \text{K W}^{-1}$) works well for 59.7 min at 11 °C, and the one with $I_T = 1.48$ clo (0.229 $\text{m}^2 \text{K W}^{-1}$) releases heat effectively for 51 min at 6 °C. The other two systems with better insulation values perform their function even at 5 °C and –2 °C for about 1–1.5 h. These results are satisfactory to provide a buffering effect against environmental temperature changes in addition to the passive insulation capacity of the clothing system for the human body thermal comfort.

The fabric system is expected to be bi-functional for both exothermic and endothermic activities. As the environment changes from cold to warm, the thermo-capsules will achieve thermal comfort by heat absorbing.

4. Conclusion

We have shown that the microencapsulation method presented in this study, based on in situ polymerization technique, was quite successful to produce microcapsules with an enhanced thermal capacity in relation to the PCM content. Microcapsules performed their function effectively under both heating and cooling conditions, and endothermic and exothermic phase transitions took place within the intervals coinciding with those of PCMs. In one sample (C), 77% of microcapsules obtained were $\leq 100 \mu\text{m}$ in diameter and 90% of them were smaller than 185 μm . SEM photos illustrate many distinct spheres of perfectly smooth surface morphology, some of which are even at nano-scale. No leakage of the oil phase and no significant structural destruction of the microcapsules was revealed after the centrifugal shear force tests conducted to predict their mechanical durability and long term behavior. Therefore, the manufactured thermo-capsules are evaluated fairly suitable for many textile applications.

Considering the process conditions employed in the manufacture of polyurea-formaldehyde shells encapsulating paraffin waxes, i.e. low stirring rates, low heating requirement, short polymerization duration, ordinary atmosphere and atmospheric pressure, etc., we have concluded that this procedure, completely

differing from some of the microencapsulation techniques, is adequate and easy to apply for the industrial-scale production, and does not bring difficulties, i.e. high energy consumption and long duration. Moreover, using appropriate acid catalyst (NH_4Cl), anionic polyelectrolytes such as PVA and a cross-linking agent of 1,3-benzenediol in the in situ polymerization process makes bonding of urea-formaldehyde resins strong enough and supports ecologic production.

In conclusion, capsules C and D are the convenient types to be applied to the fabric systems in order to provide an extra dynamic heat regulation function in addition to the passive insulation characteristics of the structures. The performance of capsules C, for instance, incorporated into the clothing system having a good insulation, by a reasonable amount, were found quite satisfactory as being functional at -2°C for about 1.5 h for certain simulated cold weather and physical activity conditions. The microcapsules having further increased heat capacities are also practicable through changing the ratios between PCMs and the prepolymer emulsions as a further study.

The thermal properties of fabrics including microencapsulated PCM can be designed to be dynamic and actively responsive for some special end-use fields. Against the general criticism that their action is limited by phase changing, a continuous phase transition ambience in the clothing with a relevant thermal insulation capability can be held by some arrangements, such that the outer fabric layer can act as a collector of the environmental heat and the inner layer can be functional in an interval near skin temperature for the cold weather conditions. Consequently, to enhance the thermal capacities of fabrics or to enlarge their phase transition intervals, a much better way is to use a combination of microcapsules containing different types of PCMs or paraffin waxes rather than those including a mixture of them.

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