Thermal and Morphological Stability of Polystyrene Microcapsules Containing Phase-Change Materials

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Received 4 August 2009; accepted 25 July 2010
DOI 10.1002/app.33112
Published online 13 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polystyrene microcapsules with paraffin wax as the active agent [phase-change material (PCM)] were produced by a Shirasu porous glass emulsification technique and a subsequent suspension-like polymerization process. The suitability of the obtained microcapsules for textile applications was studied. The thermal properties, surface morphology, and structural stability of the PCM microcapsules were investigated with differential scanning calorimetry, thermogravimetric analysis, and environmental scanning electron microscopy. The microcapsules could be used without any appreciable damage or irreversible changes in their integrity until 135°C. Furthermore, these microcapsules were heat-resistant and could endure the curing conditions of textile coating up to 140°C for 30 min. In addition, the stability of the microcapsules under common laundering conditions was tested. It was confirmed that the microcapsules were durable enough and maintained their stability during stirring in hot water and alkaline solutions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 291–297, 2011

Key words: microencapsulation; morphology; radical polymerization; thermal properties

INTRODUCTION

Phase-change materials (PCMs) can store and release latent heat during their phase transition within a defined temperature range and can be used in thermoregulating fabrics, coatings, and foams.[1–4] Paraffin waxes, in comparison with other PCMs, have high heat-storage capacities, are easily available, and are not expensive.[5] Much research has been conducted and is indeed ongoing with the aim of exploiting this ability for energy reservoirs. The final application depends directly on the kind of material used as a PCM (melting point) and on the amount of the PCM that is encapsulated.

The confinement of PCM materials by microencapsulation facilitates their incorporation into a wide variety of applications, such as fibers, fabrics, coatings, physiotherapy devices, insulation panels, and walls.[6,7] For these applications, PCM microcapsules are required to have good thermal characteristics and mechanical strength to ensure an intact structure for their final uses and during the manufacturing processes.[8] In contrast to other applications of microcapsules, for which the core is expected to be released in a solvent, under heat, or under pressure, microcapsules containing PCMs must be stable against washing, heat, and pressure.

Zhang et al.[9] demonstrated that the thermal stability of microencapsulated *n*-octadecane can be improved with urea–melamine–formaldehyde copolymers of different molar ratios as shells and with the addition of cyclohexane in the oil phase. Jiang et al.[10] carried out a thermal stability study of phenolic resin microcapsules containing hexadecane with thermogravimetric analysis (TGA), scanning electron microscopy, and differential scanning calorimetry (DSC). These microcapsules were thermally stable up to the pyrolysis temperature of hexadecane. Shiddhan et al.[7] reported that microcapsules containing octadecane encapsulated with an urea shell, obtained by the reaction of toluene-2,4-diisocyanate and diethylene triamine, were stable against heat at 150°C for 8 h and against repeated hot-water washing. Song et al.[11] reported that the addition of silver nanoparticles significantly reinforced the strength of the polymer shell material.

For applications in thermoregulating textiles, it is crucial to know the thermal and mechanical properties of the PCM microcapsules to satisfy the requirements of the manufacturing process. Coating, lamination, finishing, melt spinning, bicomponent synthetic fiber extrusion, injection molding, and foam manufacturing are some of the convenient processes for the incorporation of PCM microcapsules into the textile structure.[4,12] In these microcapsule incorporation

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Contract grant sponsor: Asintec S.A.
Contract grant sponsor: Consejería de Ciencia y Tecnología (Junta de Comunidades de Castilla–La Mancha); contract grant number: PBC08-0243-1458.

techniques, PCMs must be permanently locked within the microcapsules and exhibit their original thermal and physical properties.[11]

However, which properties of microcapsules are required for every practical use has not been reported in great detail in the literature. Obviously, different textile applications will depend on their practical use and therefore the fusion temperature of the PCM required. Recently, we published a article concerning the production of a thermoregulating textile with PCM microcapsules and a coating technique.[13] In that article, the influence of different coating formulations and the mass ratio of the microcapsules to the coating formulation were evaluated. A cotton textile coated with WST Supermor as a polymer binder containing microcapsules (35 wt %) showed an energy storage capacity of 7.6 J/s. The shell, which consisted of polystyrene, ensured the integrity of the PCM during all the solidification and fusion cycles.

One of the most common and easiest ways of incorporating PCM microcapsules into textiles is the coating technique. For this purpose, a binder is required, and the curing of the crosslinker takes place with precise temperatures and times in a stenter facility. Most of the commercial binders need temperatures between 130 and 150°C for 5 min for the curing process.[12]

In previous works, PCMs were successfully encapsulated by a polymer cover (polystyrene) with a suspension-like polymerization technique.[14–16] The developed method has been shown to be easy, cheap, and robust for the encapsulation of paraffin for textile and similar applications. Furthermore, microcapsules with a latent heat of 104.7 J/g and an average particle size in number of 4.8 μm were obtained when an experimental design was tested to improve the characteristics of polystyrene microcapsules containing paraffin wax; a Shirasu porous glass (SPG) membrane was used to produce uniform polymeric particles.[16] These microcapsules have excellent characteristics for textile applications because of their high heat storage and low particle size. However, this affirmation requires knowledge of both the thermal and morphological stability of PCM microcapsules, that is, their durability during the incorporation process and textile end use (washing, ironing, etc). These parameters have not been studied in detail up to now.

In this study, our aim was to establish the range of temperatures in which PCM microcapsules, which were obtained in a previous study,[16] could be used without appreciable damage or irreversible changes in their integrity. Furthermore, simulations of the curing stage used to fix the PCM microcapsules onto the fabric were carried out at different temperatures in isothermal TGA experiments. Finally, the stability of polystyrene microcapsules containing paraffin wax against repeated hot-water washing was tested with DSC analyses.

EXPERIMENTAL

Microcapsule synthesis

The styrene (99 wt %) was reagent-grade (Merk Chemical, Darmstadt, Germany). It was washed with sodium hydroxide for the removal of the inhibitor, and calcium chloride was used as the desiccant. Benzoyl peroxide (97 wt %) was used as the initiator (Fluka Chemical, Buchs, Switzerland). The paraffin wax (weight-average molecular weight = 478 g/mol) was commercial-grade (Repsol YPF, Puertollano, Spain) and was used as the core material. Reagent-grade polyvinylpyrrolidone (K30; weight-average molecular weight = 40,000 g/mol; Fluka Chemical) was used as a stabilizer, and methanol was used for pouring the samples. All these reagents were used as received. Water was purified by distillation followed by deionization with ion-exchange resins. Nitrogen of a high-purity grade (99.999%) was used. A tubular SPG membrane with a pore size of 5.5 μm was used to produce microcapsules with a narrow size distribution. At the end of every experiment, the membrane was retrieved by a treatment with sodium dioctyl sulfosuccinate (Fluka Chemical, Buchs, Swtizerland; 96 wt.%), ethanol (Panreac Chemical, Barcelona, Spain), and hydrochloric acid (Prolabo Chemical, Briare, France).

Suspension-like polymerization reactions were performed in a 1-L, double-jacketed glass reactor with an SPG membrane module. A schematic diagram of this experimental setup and the detailed microencapsulation process was reported previously.[16] A Rushton turbine stirrer with six vertical blades was used in the reactor. The dimensional parameters of the equipment were reported previously.[14]

Table I shows the conditions selected for the experimental design approach carried out by Sánchez et al.[16] for the synthesis of PCM microcapsules. This recipe allows microcapsules to be obtained with high thermal storage and a low particle size, which are required for most final applications.

Environmental scanning electron microscopy (ESEM)

The surface features and diameters of the microcapsules were evaluated with an XL30 (LFD) ESEM apparatus (Philips XL30, Amsterdam). Samples were heat-treated *in situ* from room temperature to 175°C at 2.5°C/min and at 0.5 Torr for the study of the changes in the surface morphology of the PCM microcapsules.

TGA and DSC

The thermal stability of different products was determined with a TA Instruments SDT 2960 simultaneous

TABLE I
Recipe for the Production of Polystyrene Microcapsules Containing PRS Paraffin Wax by Suspension-Like Polymerization and the Experimental Conditions

Polyvinylpyrrolidone (wt %)	0.81
Milli-Q water (wt %)	81.22
Benzoyl peroxide (wt %)	0.14
Styrene (wt %)	8.56
PRS paraffin wax (wt %)	9.26
Reaction temperature (°C)	108
Reaction time	6 h
Circulation pump flow rate	150 rpm
Storage tank temperature	60°C

(New Castle, USA) DSC–TGA apparatus at a heating rate of 10°C/min under a nitrogen atmosphere.

Isothermal TGA experiments were also used to study the thermal stability of the PCM microcapsules. The weight loss of the PCM microcapsules was examined as a function of time (10, 20, 30, 40, and 60 min) under isothermal conditions at temperatures between 120 and 150°C by means of TGA. These experiments allowed us to predict the durability of the microcapsules after a curing process in textile manufacturing or in end-use treatments.

The melting points and melting heats of different materials (both those employed and obtained) were measured on a TA Instruments DSC Q100 differential scanning calorimeter equipped with a refrigerated cooling system with nitrogen as the purge gas. These measurements (error $< 4\%$) were carried out with variations in the temperature from -30 to 500°C at a heating rate of 10°C/min. Each sample was analyzed at least twice, and the average value was recorded. The amount of paraffin wax in the microcapsules could be estimated according to the measured melting enthalpy of different standard mixtures of polystyrene and paraffin wax (100 wt % paraffin, 100 wt % polystyrene, 50 wt % paraffin/50 wt % polystyrene, 75 wt % paraffin/25 wt % polystyrene, and 27 wt % paraffin/73 wt % polystyrene).

The dependence of the melting enthalpy (calculated on the basis of the endothermic peak registered between 0 and 55°C) on the paraffin wax content (according to the standard mixtures prepared) was established under the assumption of a linear fit:

$$\text{Paraffin wax content(wt\%)} = (\Delta H_m - 7.2004)/1.921 \quad (1)$$

where ΔH_m is the enthalpy of the analyzed microcapsules (J/g) and the coefficient of determination is 0.996.

Washing test

To study the stability of the PCM microcapsules under common laundering conditions for garments, washing tests were carried out. Microcapsules were washed with water (0.2 g/250 mL of water) and a commercial solid laundry detergent (0.42 g/250 mL of water) at 20, 30, 40, and 60°C for 60 min at 300 rpm with a digitally controlled magnetic stirrer. Core contents were determined by the measurement of the heats of fusion of the washed and unwashed microcapsules by DSC with the procedure presented earlier.

RESULTS AND DISCUSSION

Thermal stability of the microcapsules containing paraffin wax

The average diameters and thermal properties of the PCM microcapsules used in this work are shown in Table II. The thermal stability of the PCM microcapsules containing paraffin wax was evaluated with TGA in an N_2 atmosphere. TGA and differential thermogravimetric analysis (DTGA) thermograms of the PRS paraffin wax, polystyrene particles, and microcapsules containing paraffin wax are presented in Figure 1. A TGA plot of the PCM microcapsules shows a weight loss of 57 wt % at temperatures between 135 and 300°C, and this is attributable to the decomposition of hydrocarbon compounds of the PRS paraffin wax, as can be seen from the DTGA plot for the paraffin wax. The decomposition started at a slightly lower temperature when the paraffin was not encapsulated. This result indicates that the shell material provided good protection for the core PCM, and leakage of the core materials from the capsules was prevented, as reported in the literature.[9] Previous ESEM studies of microtomized microcapsules have demonstrated the core–shell morphology of microcapsules synthesized by this method.[16] The second weight loss (43 wt %) took place at temperatures higher than 350°C because of the decomposition of polystyrene;[17] complete decomposition of the microcapsules occurred at 460°C.

Figure 2 shows DSC thermograms of the PCM microcapsules, pure PRS paraffin wax, and polystyrene particles. The first endothermic peak occurs on DSC curves at temperatures between 0 and 55°C because of the phase-change transition of the pure paraffin wax. The assayed paraffin wax was a medium-range vacuum distillate basically consistent with a mixture of hydrocarbons (C_{19}–C_{27}) and was

TABLE II
Characteristics of Polystyrene Microcapsules Containing Paraffin Wax

Average melting heat (J/g)	Encapsulated PCM (wt %)	$dpv_{0.5}$ (μm)	$dpn_{0.5}$ (μm)
104.7	51	84.7	4.8

$dpv_{0.5}$ represents 50% of the microcapsule particles whose mean volumetric diameter was less than this value, and $dpn_{0.5}$ represents 50% of the microcapsule particles whose mean numerical diameter was less than this value.

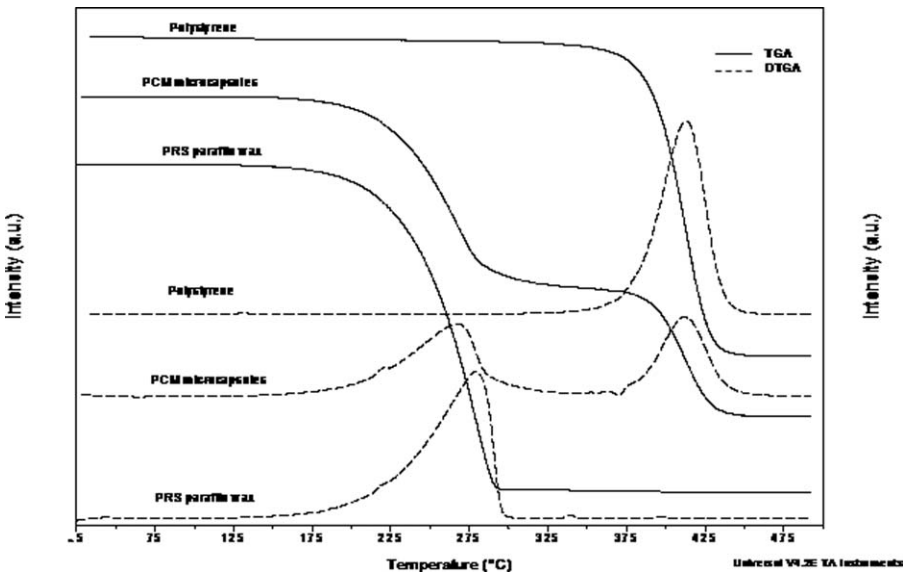

Figure 1 TGA and DTGA thermograms of polystyrene particles, PCM microcapsules, and pure PRS paraffin wax.

produced and commercialized by the petrochemical company Repsol YPF. For this reason, the temperature range in which the fusion of the solid paraffin took place was wide, and a latent heat of fusion of 106.2 J/g was obtained (52 wt % of the encapsulated paraffin wax). The shift of the melting peak of the paraffin wax from 45.6 to 43.8°C was due to a supercooling phenomenon.[10] At 73°C, the glass-transition temperature (T_g) of polystyrene was observed,[17] this T_g value being lower than the values usually found in the literature for polystyrene. This fact is attributed to the low molecular weight of the synthesized polystyrene shell.[17] Between 135 and 270°C, the decomposition of the core material appeared, whereas the last endothermic peak corresponds to the decomposition of the polystyrene shell (between 340 and 470°C). According to these results, the thermal stability of the PRS paraffin wax inside the microcapsule shells up to 135°C was demonstrated.

The change in the surface morphology of the microcapsules with temperature was studied with ESEM analyses. To clearly determine the thermal behavior of the microcapsules, we analyzed one of the biggest. ESEM micrographs showed the microcapsule damage processes *in situ* when the sample was heated (Fig. 3). As shown in Figure 3, the large analyzed microcapsule kept its integrity until 91°C. This fact implies that the phase change of the paraffin wax inside the microcapsule had no effect on the morphology and particle size. However, above T_g of

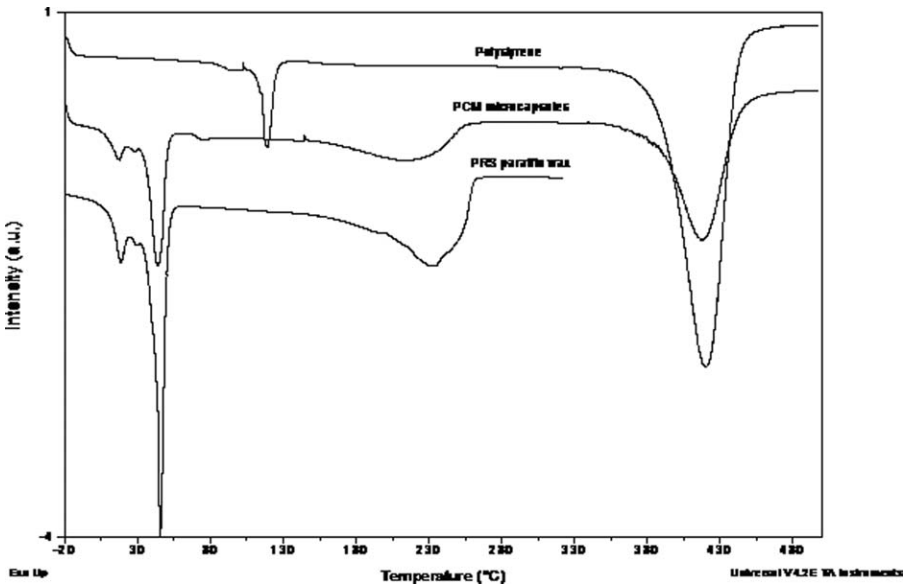

Figure 2 DSC thermograms of polystyrene particles, PCM microcapsules, and pure PRS paraffin wax.

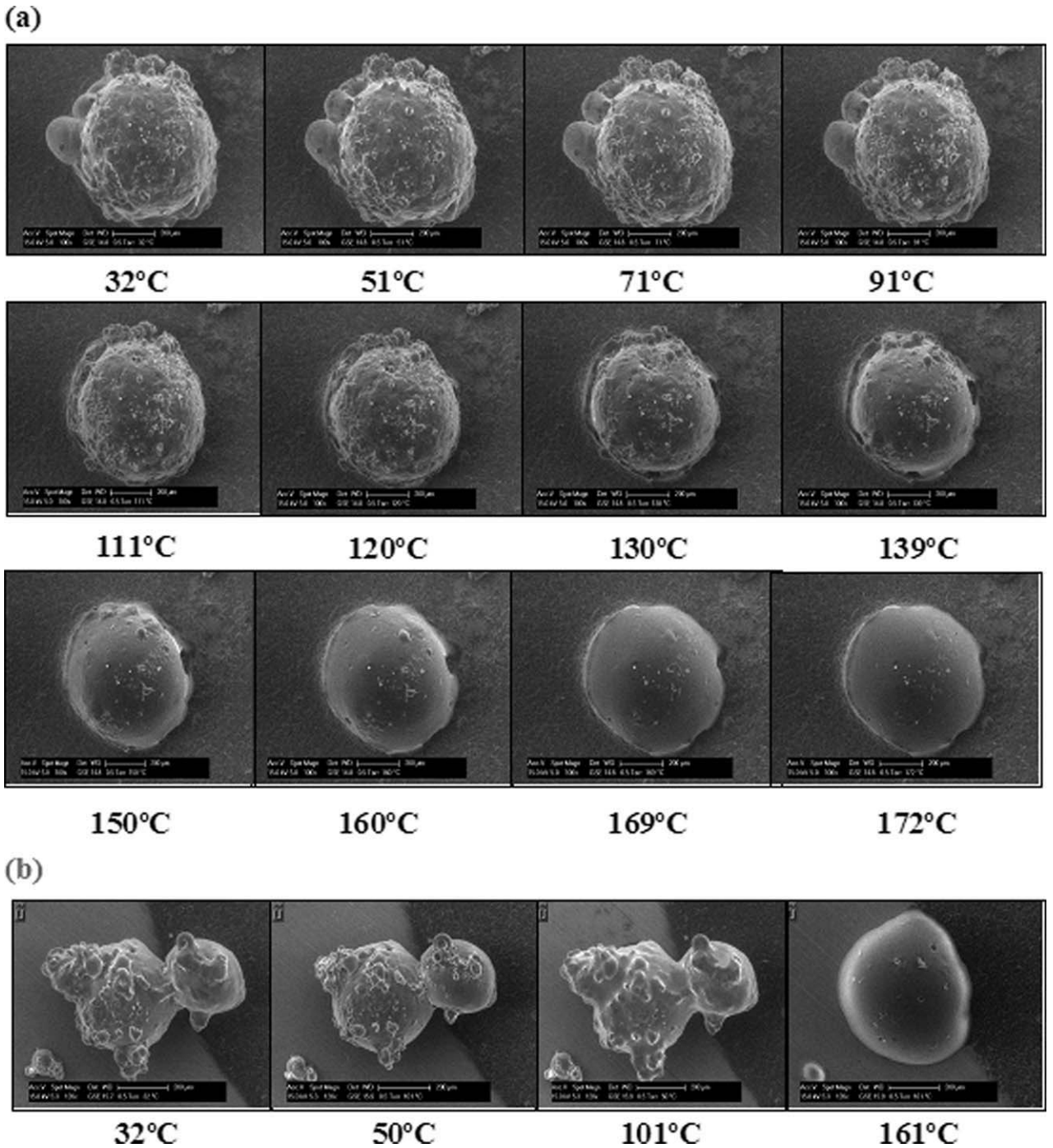

Figure 3 ESEM micrographs of (a) a PCM microcapsule heat-treated from 32 to 172°C and (b) other PCM microcapsules heat-treated from 32 to 161°C under 0.5 Torr.

the polymeric shell (73°C), the microcapsule became progressively more sticky and rubbery until it was converted into an oil drop at 172°C. Furthermore, at 135°C, the vaporization of the paraffin wax started and produced an increase in the microcapsule volume at 139°C due to the increase in its internal pressure. That agrees with the results obtained by DSC and TGA analyses. Small particles adhered to the big microcapsule (Fig. 3) and were not completely removed during the washing process. These were polymeric particles because paraffin wax would have melted at a low temperature (melting point $\approx$ 44°C). The secondary polymerization that frequently occurs in this kind of system could explain these results. To confirm the observed thermal behavior, the same ESEM thermal study using other PCM microcapsules was carried out [Fig. 3(b)]. A similar trend was found.

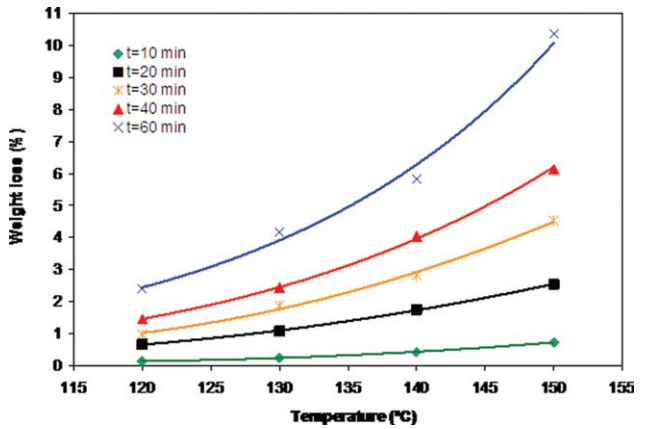

Figure 4 Effects of temperature and time (*t*) on the weight loss of PCM microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The efficacy of the prepared microcapsules at fixing onto textile materials by the coating technique was evaluated. The weight loss of the PCM microcapsules was examined as a function of time under isothermal conditions at temperatures between 120 and 150°C for 10, 20, 30, 40, and 60 min with TGA. Temperature and time treatments were selected, and we took into account the curing conditions used for the most common commercial binders. As shown in Figure 4, the weight loss of the microcapsules increased when the temperature and the time increased. A negligible weight loss of 2.5% was observed for times less than 20 min, regardless of the temperature. However, when the time was longer than 30 min, the weight loss of the PCM microcapsules with temperature increased appreciably. Therefore, these microcapsules were heat-resistant and could ensure curing conditions of 140°C and 30 min (3% weight loss). The microcapsules containing paraffin wax and synthesized in this work had thermal stability similar to that of the PCM microcapsules obtained by Song et al.[11] (130°C for 50 min).

Stability of the PCM microcapsules against water washing at different temperatures

It is interesting to know the stability of PCM microcapsules under common laundering conditions for garments. Microcapsules were stirred at 300 rpm in water with a conventional laundry detergent at 20, 30, 40, or 60°C for 1 h. These conditions were selected on the basis of those used in common garment washing. Figure 5 shows DSC curves obtained for washed and unwashed microcapsules at different washing temperatures, and we can observe the effect of the laundering on the heat-storage capacity of the PCM microcapsules. The results indicate that the PCM microcapsules were very stable against hot-water washing because the melting enthalpy remained almost constant after the washing treatments at different temperatures.

Therefore, the thermal stability of the paraffin wax inside the microcapsule shell confirmed the applicability of these materials to daily garments.

CONCLUSIONS

The thermal stability of polystyrene microcapsules containing paraffin wax, which were obtained by suspension-like polymerization, was tested. The intactness of the PCM microcapsules could be maintained up to approximately 135°C according to TGA and DSC analysis. Furthermore, an ESEM thermal study showed

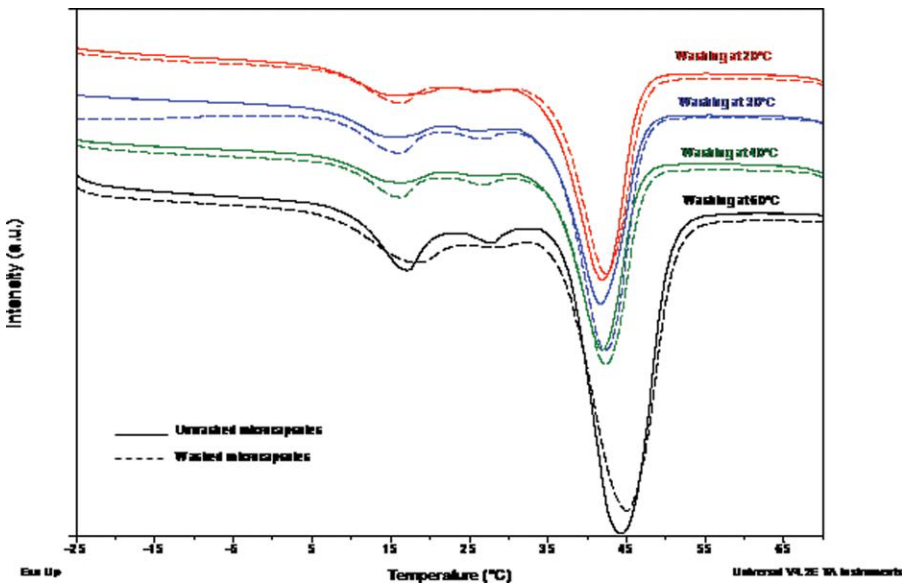

Figure 5 DSC curves of washed and unwashed microcapsules at different temperatures for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the microcapsules did not suffer any appreciable damage or irreversible changes in their integrity at temperatures below T_g of the polymeric shell (73°C).

Isothermal TGA experiments demonstrated that the PCM microcapsules were heat-resistant enough to endure the high temperatures of curing during the textile coating and manufacturing processes (140°C for 30 min).

The microcapsules retained approximately 90% of their heat-storage capacity after laundering treatments at different temperatures. Therefore, these microcapsules kept their integrity during hot washing and the chemical action of alkali laundry detergents.

In summary, the results suggest that microcapsules can be applied to any fabric or finished product with conventional finishing techniques without alterations of their thermal properties until 135°C.

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