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ORIGINAL CONTRIBUTION

Microencapsulation of PCMs with a polystyrene shell

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Abstract Microencapsulation of different phase change materials (PCMs) with a polymer shell of polystyrene by suspension polymerization has been carried out. This method based on a suspension polymerization allows the encapsulation of non-polar PCMs, while that it was not possible to encapsulate the polar PCMs (polyglycols). This study deals with preparation and characterization of encapsulated paraffin wax. Thermal properties, the morphology and the particle size distribution of the microcapsules obtained were determined by differential scanning calorimetry, scanning electron microscopy and laser diffraction, respectively. This encapsulated paraffin wax could be considered to have good potential for energy storage.

Keywords Phase change materials · Microencapsulation · Suspension polymerization · Paraffin wax · Styrene

Introduction

The microencapsulation of phase change materials (PCMs) to be employed in textile materials with medical applications for hot and cold therapies or in high-tech clothes for extreme weather conditions is a great challenge for technicians and scientists. Up to now, some attempts to develop a cheap and technically easy process for the encapsulation of paraffin waxes have been done. The most common methods used are interfacial polymerization [1], emulsion polymerization [2], in situ polymerization [3], spray drying and coacervation [4].

Although the PCM is responsible for the storage and adsorption or release of thermal energy, the encapsulation of them needs a physically and chemically stable shell. This is the main technical and scientific problem. For that reason, the development of an easy, cheap and robust method for the encapsulation of PCMs is so important for textile applications.

The PCMs have to be materials with high heats of fusion. They can absorb or release the latent heat when the temperature of the material undergo or overpass the temperature of phase change. A variety of PCMs available are well known for their thermal characteristics; these materials exist in the market (hydrated salts, paraffins or waxes, organic, inorganic and fatty acids), and they can be encapsulated by a polymer cover [5].

The election of the appropriate material depends on the final application the materials that melt below 5 °C are used to impart warmth to a user's skin under cold weather conditions, while the materials that melt around 30 °C would be suitable to provide some sensation of freshness from the clothes.

Some conventional encapsulation methods like complex coacervation or gellation create the "shell" of the microcapsule by precipitating the polymer shell from the continuous phase, in an out-inside process. Complex coacervation results from the mutual neutralization of two or more oppositely charged colloids in aqueous solution. As a result of this reduction, the coacervated particles separated out into two new phases: rich and poor phases in colloid concentration. For example, the positively charged gelatin ($pH<8$) forms a complex coacervate with negatively charged gum Arabic [4].

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Another possible method to obtain microcapsules with a polymer cover and a PCM core would be to carry out a suspension-like polymerization process. This process generally involves the dispersion of the monomer, mainly as a liquid in small droplets, into an agitated stabilizing medium usually consisting of water containing small amounts of suspension and dispersion agents. The initiator is dissolved in the monomer–PCM mixture, and it could be chosen to control the site of the free radical generation as desired, i.e. within the droplet or in the water phase external to the droplet. In the case of PCM microencapsulation, the initiator must own a certain polarity in such a way that the site of free radical generation will be the interface between water and the oil droplet, maintaining the paraffin inside the polymer-covering layer that is being formed. In this way, this method can be understood as an “inside-out” approach for PCM microencapsulation.

Taking this in mind, it seems obvious that the complex interaction between the polymer system (initiator, monomers and polymer) and the continuous phase (usually water and suspension agent) on the surface of the droplets will be mainly responsible for the success in the encapsulation and the particles properties.

Ma et al. [8] developed a suspension-like polymerization process to encapsulate a PCM. They carried out a microencapsulation method to retain hexadecane (HD) inside a shell formed by a mixture of *N*,*N*-dimethylaminoethyl methacrylate and styrene as monomers. They found several problems to get microcapsules depending on small changes in the operating conditions. They observed that if the amount of monomers was not enough, the HD was not completely encapsulated; namely, as the relative amount of PCM increases in the recipe, it was more difficultly encapsulated by the polymer.

Recently, Jonsson et al. [9] prepared by suspension polymerization acrylonitrile–methacrylonitrile copolymer particles with a core/shell structure. They observed that the monomer feed composition and the polymerization temperature were also important parameters in determining the particle morphology of suspension-polymerized *co*-acrylonitrile polymer particles.

Berg et al. [6] examined several water/polymer/oil systems and found that the encapsulation of hydrocarbon oils via the free radical polymerization of vinyl monomers was critically dependent upon the type of emulsifier used. This seems to be related to the minimization of interfacial energy for the particles dispersed in water. Later, Sundberg et al. [7] studied other water/polymer/polymer systems and observed that the thermodynamic properties of the particles were independent of particle size and the method of emulsion processing. Again, the experimental evidence showed that the morphology of particles formed via in situ polymerization (as in synthetic latex) is mainly controlled by interfacial tensions.

For a given formulation, the obtaining or not of core/shell particles, hemispheres, individual particles or other possible morphologies depends mainly on the value of the minimum total free energy change. To sum up, a core/shell morphology will be thermodynamically favoured during polymerization if $\gamma_{wo}>(\gamma_{wp}+\gamma_{op})$ in which γ_{wo} is the interfacial tension of the water and the oil interphase, γ_{wp} is the interfacial tension of the water/polymer interface and γ_{op} is the interfacial tension of the oil/polymer interface. The described water/polymer/oil system will correspond to the water/polystyrene/PCM system developed in this research [7].

The microencapsulation method developed in this work is simpler than other methods referenced in literature. In this work, we used the suspension polymerization technique to prepare microcapsules. Styrene was selected to form the shell, and several kinds of PCMs are studied as core materials. The influence of the type of PCM used on the heat capacity of microcapsules, the particle size distribution (PSD) and on the microcapsules yield of each experiment is studied.

Materials and methods

Materials

Styrene (99 wt%) was of reagent grade (Panreac Chemical). Styrene was washed with sodium hydroxide to remove the inhibitor and calcium chloride as the desiccant. Benzoyl peroxide (97 wt%) was used as an initiator (Fluka Chemical). PRS® paraffin wax was of commercial grade (Repsol YPF), tetradecane (99 wt%) was of reagent grade

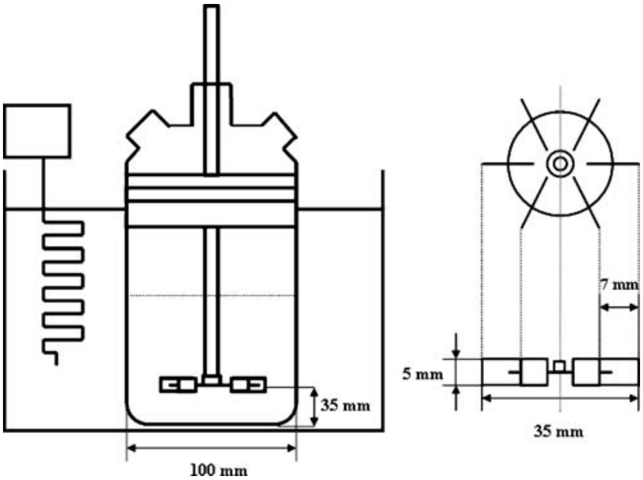


Fig. 1 Detail of the experimental set up with indication of equipment dimensions

Table 1 Recipe for the obtaining of microcapsules containing PRS® paraffin wax and experimental conditions used

	Ingredients	Measure
Discontinuous phase (g)	Polyvinylpyrrolidone (PVP)	3.77
	Water (mili-Q)	377.40
Continuous phase (g)	Benzoyl Peroxide (PBO)	1.26
	Styrene (St)	78.40
	PRS® paraffin wax	27.04
Reaction temperature (°C)		110
Stirring rate (rpm)		900
Reaction time (h)		6

(Fluka Chemical), polyethyleneglycol (PEG) 1000 was of reagent grade (Panreac Chemical), Rubitherm® RT 27 was of commercial grade (Rubitherm GmbH), Rubitherm® RT 20 was of commercial grade (Rubitherm GmbH), nonadecane (99 wt%) was of reagent grade (Sigma-Aldrich Chemical) and polyethyleneglycol 800 was of reagent grade (Clariant) and were used as an oily core. Polyvinylpyrrolidone (K30, Mw 40,000 g/mol) was of reagent grade (Fluka Chemical) and was used as a stabilizer, and methanol was used to pour the samples. All these reagents were used as received. Water was purified by distillation followed by deionization using ion-exchange resins. Nitrogen was of high-purity grade.

Microcapsules synthesis

Microencapsulations were carried out in a 1-l glass reactor equipped with digital control of stirring rate, an oil thermostat bath, a reflux condenser and a nitrogen gas inlet tube. The experimental setup is shown schematically in Fig. 1. Rushton turbine stirrer with six vertical blades was used in the reactor. Dimension parameters of the equipment are also shown in Fig. 1.

The synthesis process involves two phases: a continuous phase containing water and polyvinylpyrrolidone and a discontinuous phase containing styrene, PCM and benzoyl peroxide (Table 1). The recipe shown in Table 1 is based on one used in a previous work dealing with a suspension polymerization process [10, 11].

Table 2 Properties of commercial PCMs investigated

Compound	Molecular weight (g/mol)	Melting temperature (°C)
PRS® Paraffin wax	168–240	40–45
Tetradecane FLUKA	198.4	5–7
PEG 800 CLARIANT	760–840	25–30
PEG 1000 PANREAC	900–1,100	35–40
Rubitherm® RT27	258	28
Rubitherm® RT20	244	22
Nonadecane	268.52	32–34

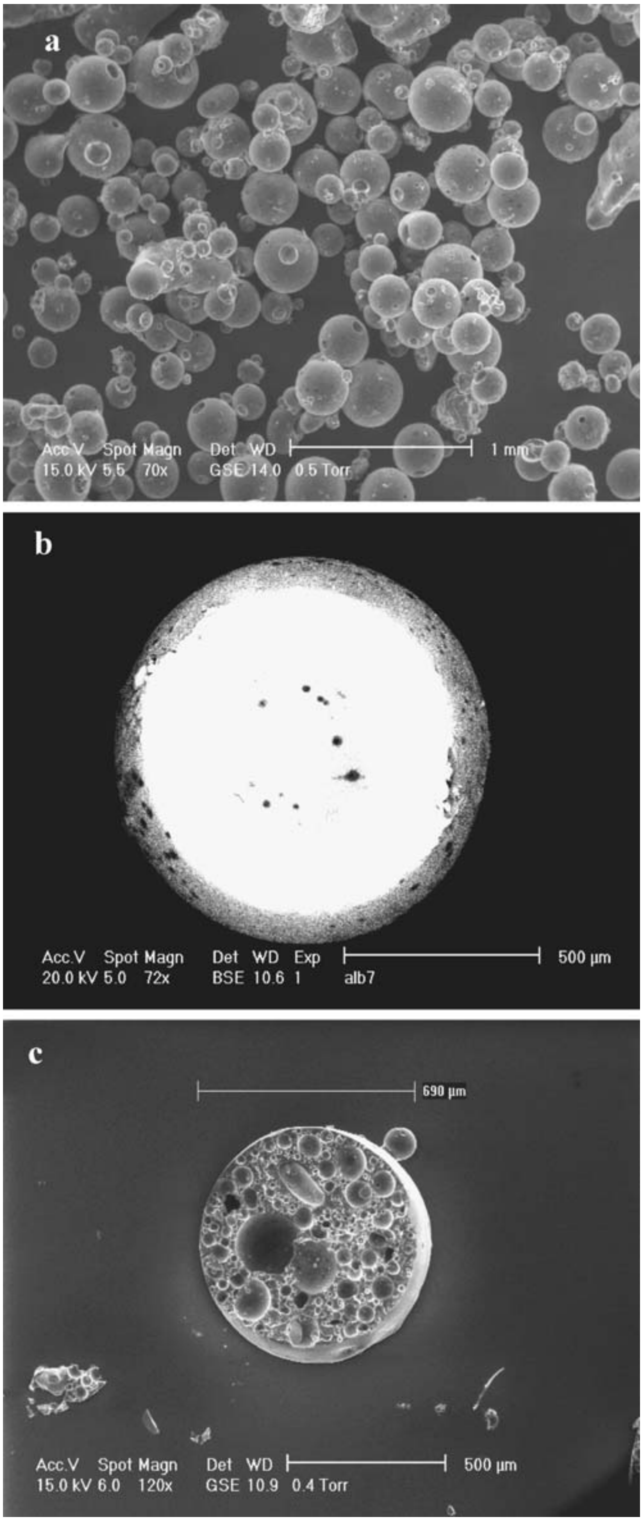


Fig. 2 SEM micrographs of microcapsules containing PRS® paraffin wax. **a** General view of a batch of microparticles and **b** and **c** cross-sections of single microparticles

The continuous phase was transferred to a glass reactor with mild agitation. As the initiator was already mixed with the monomer and PCM, efficient operation was required to minimize the idle time. Next, the discontinuous phase was added into the continuous phase maintained under vigorous agitation. The reaction media was bubbled with nitrogen, and the temperature was set at 110 °C in the thermostat bath.

Temperature was maintained in a fixed value during the experiments. The polymerization process was carried out for 6 h under a nitrogen atmosphere.

Once obtained, the polymerized microcapsules were repeatedly washed with methanol and filtrated to remove impurities. The purified microcapsules were dried at room temperature.

This process was carried out with different core materials; the detailed component of each system is listed in Table 2.

Environmental scan electron microscopy observation

The surface features of the microcapsules after polymerization were observed by using a XL30 (LFD) microscope for environmental scan electron microscopy (ESEM).

Gel permeation chromatography measurement

The molecular weight distribution (MWD) of the polymer forming the polymer shell and the relative amount of PCM encapsulated were measured by gel permeation chromatography (GPC) using a chromatograph model 150-GPCV LC of Waters (USA). Tetrahydrofuran was used as an elution solvent. Poly(styrene) standards from Waters were used for MWD calibration.

Calculation of number-average diameter and volume-average diameter

Particle size and PSD were determined on a Malvern Mastersizer Hydro 2000 SM light-scattering apparatus in a diluted dispersion of the particles in methanol.

Differential scanning calorimetry

Measurements of melting point and melting heats of different materials employed and obtained were performed in a differential scanning calorimetry (DSC) model DSC Q100 of TA Instruments. These measurements were done varying the temperature in the range from −30 to 80 °C with a heating rate of 10 °C/min.

Thermogravimetric analyzer (thermogravimetry and differential thermal analysis)

The weight loss of the microcapsules with temperature was investigated by using a thermogravimetric analyzer (TGA) model TGA7 of Perkin Elmer TGA7 at a rate of 10 °C/min in an atmosphere of helium.

Results and discussion

Microencapsulation technique

With the recipe presented in Table 1 and the operational method described in the “Materials and methods,” the

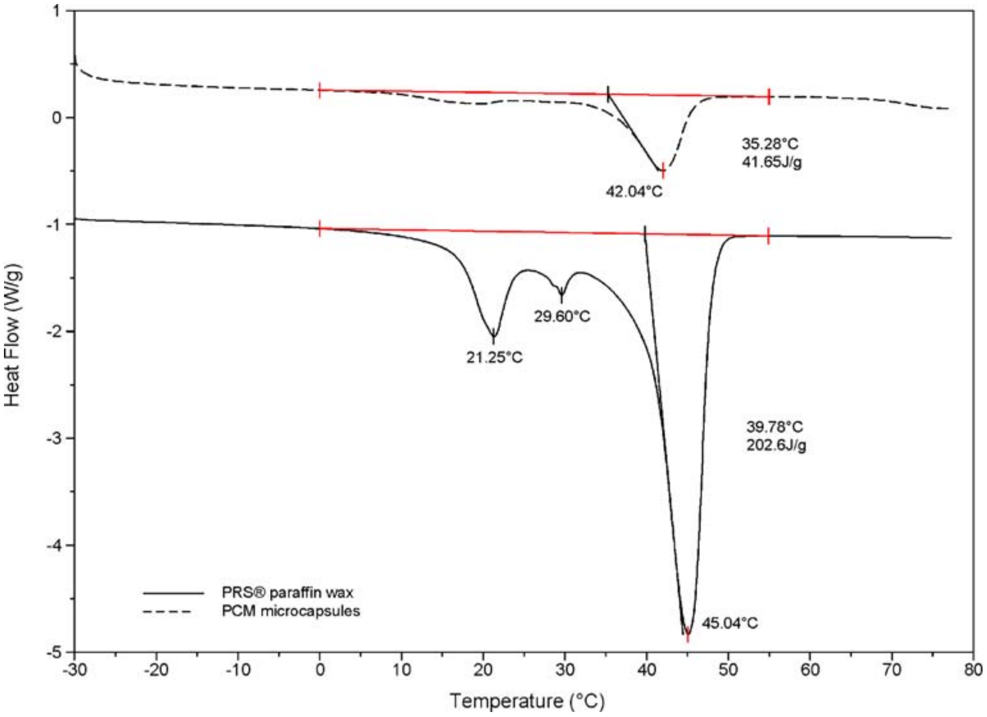


Fig. 3 DSC thermograms of microcapsules containing PRS® paraffin wax and the pure PRS® paraffin wax

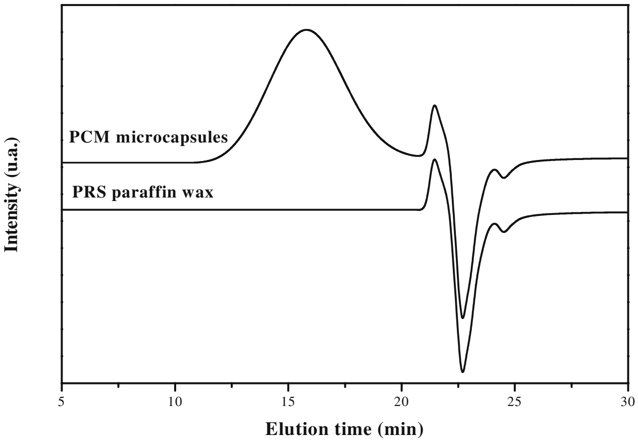


Fig. 4 GPC chromatograms of microcapsules obtained containing PRS® paraffin wax and the pure PRS® paraffin wax. *Peak I*= polystyrene (shell); *Peak II*=PRS® paraffin wax (core)

encapsulation of a PRS® paraffin wax was apparently obtained. The first visual appreciation in an optical microscope and after that in the ESEM (Fig. 2) indicated that spherical microspheres were obtained with a relatively homogeneous external appearance and a wide distribution of sizes. In these preliminary experiments, the mass ratio of paraffin to polystyrene was maintained in 27:78. In this initial stage, this proportion ensures the success of the microencapsulation. Further studies about this parameter and others are being carried out to optimize the thermal microcapsules performance.

According to Sundberg et al. [7], for a given formulation, the obtaining or not of core/shell particles, hemispheres, individual particles or other possible morphologies depends mainly on the value of the minimum total free energy change and on the main location of the initiator during the polymerization process. Styrene is slightly soluble in water (0.03 g/100 ml 20 °C), but the paraffin employed is absolutely insoluble in water. The Solubility parameter of polystyrene is 8.5–9.6 cal$^{1/2}$ cm$^{-3/2}$, paraffin (eicosane) is 8.07 cal$^{1/2}$ cm$^{-3/2}$ and water is 23.4 cal$^{1/2}$ cm$^{-3/2}$.

On the other hand, the interfaces of importance were those between the water and each oil, the interfacial tension of the water/polystyrene and the water/paraffin interface, and between two oils, the interfacial tension of the polystyrene/paraffin interface.

Torza and Mason [13] arrived at the following inequality for the conditions necessary for polystyrene to encapsulate paraffin: $\gamma_{wo} > (\gamma_{wp} + \gamma_{op})$, which is the interfacial tension of water/paraffin>(interfacial tension of water/polymer+interfacial tension of polystyrene/paraffin).

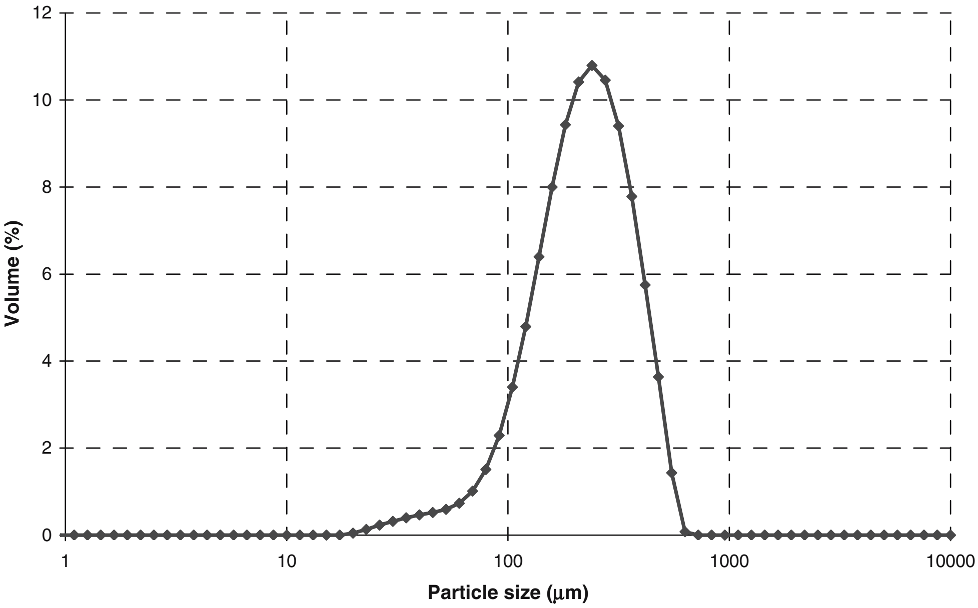
In this case, this would take the following approximate values: (≈20)>((≈13)+5). One value like this would justify the success of the encapsulation process.

Nevertheless, at the end of the experiment, after cooling and settling, a certain amount of free solid paraffin wax forming a thin layer was observed on the surface of the reaction medium. In the first moments, it seemed indicate that the encapsulation process could be not successful.

The matter of question was to confirm if the paraffin wax has been encapsulated or otherwise the microcapsules were only constituted by polystyrene. To get that purpose, the presence of paraffin in the washed microparticles was experimentally measured by means of DSC and GPC measurements.

The DSC thermograms of the microparticles together with that of pure PRS® paraffin wax are shown in Fig. 3. This first paraffin wax assayed is a medium-range vacuum

Fig. 5 Particle size distribution for different microcapsules obtained



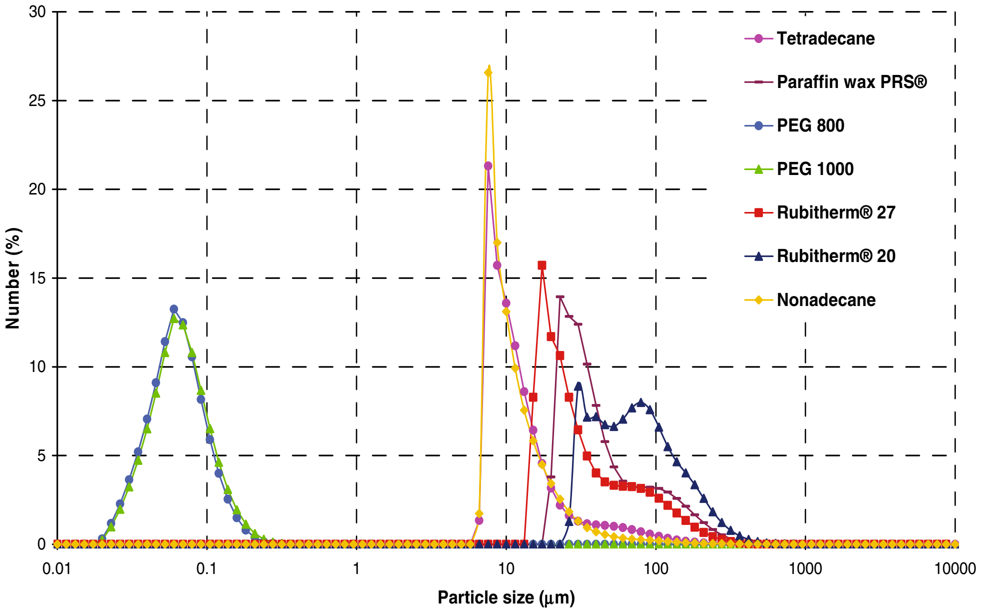


Fig. 6 Particle size distribution for different PCMs studied

distillate basically consistent in a mixture of hydrocarbons C19–C27 produced and commercialized by the petrochemical company Repsol-YPF (Spain). For that reason, the temperature range in which the fusion of the solid paraffin takes place is wide and goes from 0 to 55 °C with three peaks at 21.25, 29.60 and 45.04 °C, being the phase change enthalpy of the paraffin of 202.6 J/g. It can be observed in Fig. 3 that the DSC curve of the microcapsules exhibits the same range of transition phase than the pure paraffin wax. The shift of the peak up to 42.04 °C can be due to a supercooling phenomenon. A similar behaviour has been described for similar microencapsulated PCM systems in which the supercooling crystallization phenomena occurred when the diameter of microcapsules was smaller than 100 µm [14].

Obviously, the latent heat of the microcapsules, which was of 41.65 J/g, was smaller than pure paraffin wax. This value indicates that not all the paraffin of the initial recipe had been encapsulated as expected from the fact that a thin layer of paraffin has been obtained at the end of the experiment. The proportion of core paraffin to shell polymer was actually about 20%, while the proportion in the recipe was 33%. The experimental results show that PRS® paraffin wax had been successfully encapsulated inside the microcapsules and that although the PCM microcapsules have a considerable heat storage capacity, this can be improved modifying the recipe and the encapsulation method.

On the other hand, GPC chromatogram of microcapsules obtained was compared to GPC chromatogram of the pure PRS® paraffin wax (Fig. 4). The GPC analysis of microcapsules shows the presence of two peaks corresponding to substances existed, one with a higher molecular weight (48,025 g/mol) corresponding to the polystyrene (cover) and the other with 471 g/mol corresponding to a low-weight product (PRS® paraffin wax). The proportion between the integrated area of the peaks corresponding to PRS® paraffin, and the polymer shell was approximately 18% by weight confirming the previous DSC results and the success in the encapsulation.

Surface morphology of microcapsules obtained was studied by scanning electron microscopy (SEM). From Fig. 2a, it was evident that the microcapsules obtained were spherical, with no broken particles or incomplete spheres but with a small hole in most of them and with a broad PSD from visual observation of the micrographs. Figure 2b shows the cross-section of a typical microcapsule with a paraffin core and a polymer shell. It was also seen that

Table 3 Average diameters and thermal properties of microcapsules containing different PCMs

PCM	$dpv_{0.5}$ (µm)[a]	$dpn_{0.5}$ (µm)[b]	Melting heat (J/g)	PCM encapsulated (wt%)
PRS® paraffin wax	237.81	38.01	41.65	20.56
Tetradecane	254.59	11.24	48.92	39.10
PEG 800	0.13	0.07	0	0
PEG 1000	0.14	0.07	0	0
Rubitherm® 27	212.54	27.85	58.83	28.69
Rubitherm® 20	311.42	64.87	12.01	10.92
Nonadecane	442.03	10.48	119.80	49.36

[a] $dpv_{0.5}$ represents 50% microcapsule particles whose mean volumetric diameter is less than this value.

[b] $dpn_{0.5}$ represents 50% microcapsule particles whose mean numeric diameter is less than this value.

some of the capsules are formed by a great number of smaller microcapsules occluded inside, as shown in Fig. 2c.

The PSD of the microcapsules obtained is shown in Fig. 5. The PSD in volume shows unimodal distributions of particle sizes ranging in the interval between 20 and 700 μm. The average diameter of microcapsules was 237 μm, which would be a little high for its further application in the textile industry.

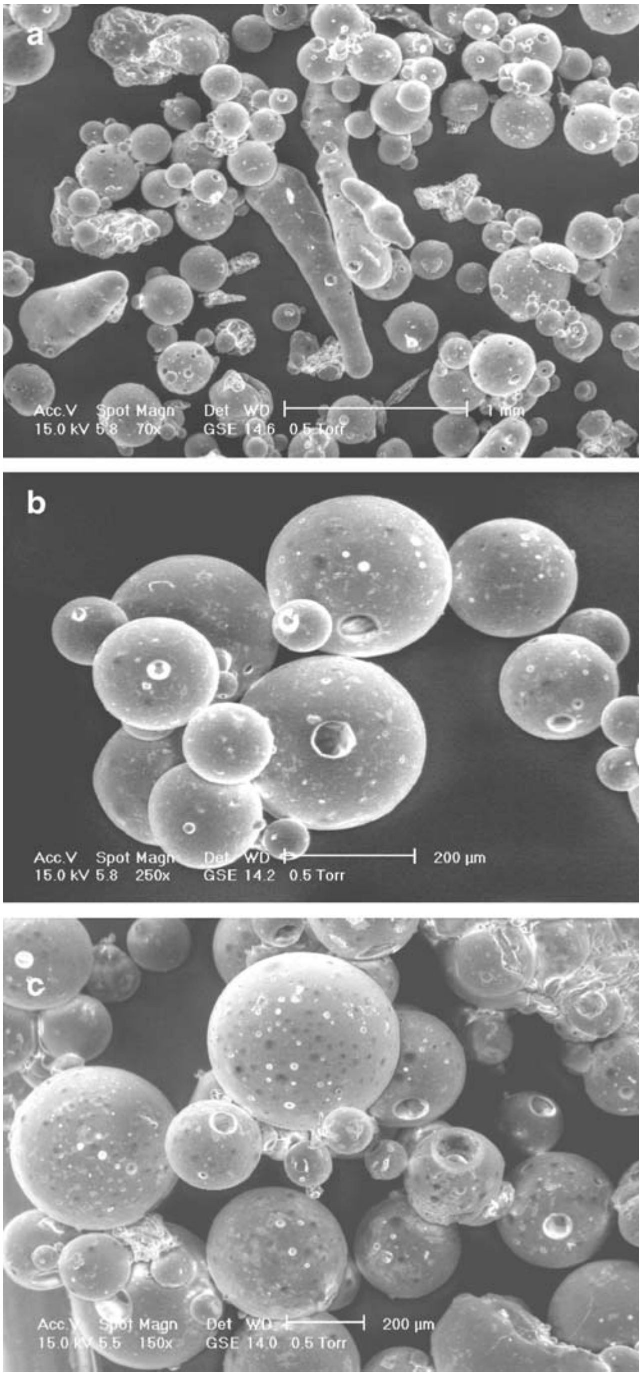


Fig. 7 SEM micrographs of microcapsules with **a** Rubitherm® 27, **b** tetradecane and **c** PRS® paraffin wax as the core

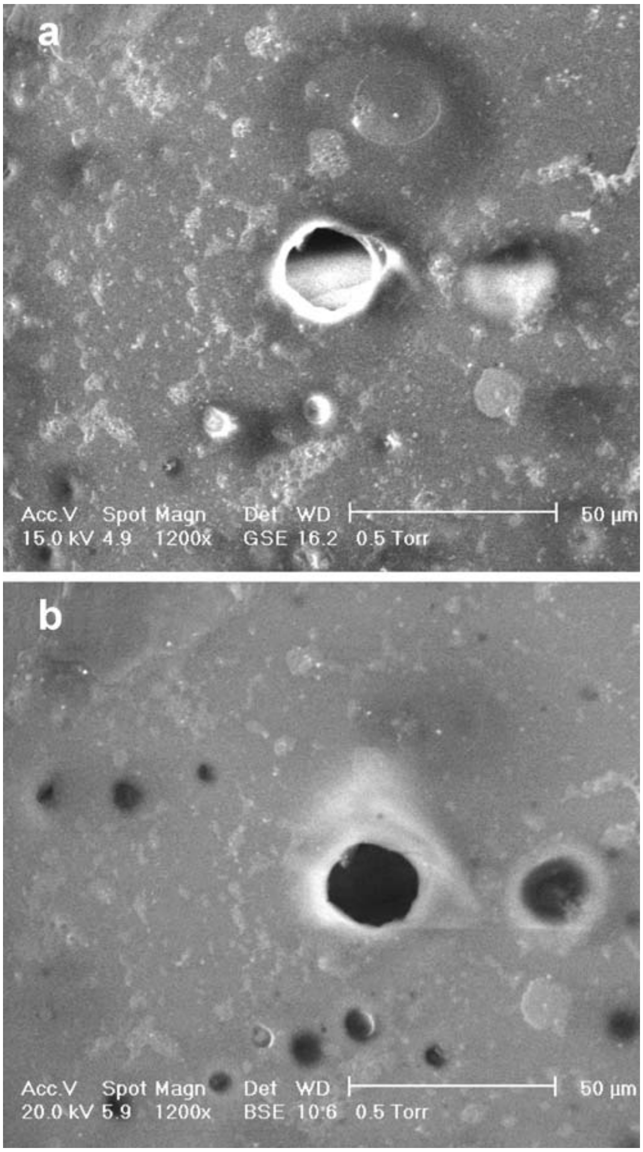


Fig. 8 SEM micrographs of microcapsules containing PRS® paraffin wax **a** with BSE detectors **b** without BSE detectors

Influence of PCM type

Depending on the application of the microcapsules, it would be important to have a wide catalogue of materials susceptible to be applied for different thermal regulation purposes. In addition, it was important to know what kinds of PCM materials were appropriate for use with this encapsulation method, so that different kinds of commercial PCMs with different chemical nature and melting temperatures were assayed with the same recipe and experimental conditions than those reported in Table 1. PEG 800 and 1000 are two types of PEG with an average molecular weight of 800 and 1,000, respectively. Rubitherm RT20 and RT27 are two commercial paraffin waxes of undefined compositions and melting points of 20 and 27 °C, respectively. The other products are paraffin of defined composition like tetradecane and nonadecane.

PSDs in number of the materials obtained after the polymerization process using these PCM materials are shown in Fig. 6. Table 3 reports the average diameter, the melting heats, the average proportion of paraffin in the capsules and the yield in microcapsules of each experiment.

In the experiments for the encapsulation of paraffin nature, PCMs different amounts of microcapsules containing PCMs were obtained. The PSD of those materials exhibit a bimodal distribution, with a high percentage of small particles with an average diameter greater than 10 µm as can be seen in Fig. 6. The melting heats of the microcapsules containing the different types of paraffin are higher than that obtained in the preliminary experiments using PRS® paraffin.

The mean diameter in number of the microcapsules increases in this way: Rubitherm® RT20>Paraffin wax PRS®>Rubitherm® RT27>Nonadecane>Tetradecane. However, the average diameter in volume increases in this way: Nonadecane>Rubitherm® RT20>Tetradecane>Paraffin wax PRS®>Rubitherm® RT27. Nonadecane and tetradecane showed that depending on the PCM encapsulated, the relative relation between big-size and small-size particles changes.

It can be seen that PEG 1000 and PEG 800 have similar PSDs, with an average diameter less than 1 µm. This fact indicates that probably the encapsulation has not worked and only PS microparticles had been obtained. Furthermore, a separate phase composed mainly by glycol was observed in the bottom of the reaction vessel at the end of the reaction because the density of this PCM is higher than water. The DSC of the microcapsules obtained showed that the peak corresponding to the phase transition of PCM does not appear to give a melting heat of 0 J/g (Table 3), confirming that the PEG had not be encapsulated.

This surface polymerization process has necessarily to be related with the formation of a monomer–polymer outer layer covering the PCM core in each drop. An adequate hydrophobic nature of the PCM must favour the encapsulation process. Probably, a PEG with a certain hydrophilic character does not favour the segregation of a polymer cover in the surface of the PEG drops, and the styrene trends to create only separate polymer particles such if a emulsion polymerization occurs [12]. Besides, the greater density of PEG than water makes the PEG settle, and this fact can also make the encapsulation more difficult.

It is also noteworthy that the smallest latent heats of the microcapsules obtained including a paraffin compound as core were obtained for Rubitherm® RT27 and Rubitherm® RT20. This fact is probably due to the inclusion in the composition of these products of a certain amount of oxygenated compounds (waxes) that modifies the surface conditions for polymer shell formation allowing the encapsulation of a minor proportion of paraffin under the same polymerization conditions.

The morphologies of the microcapsules obtained in each case can be observed on the SEM graphs shown in Fig. 7. The particles obtained with Rubitherm show irregular shapes and rough surfaces, so that it could be stated that even small amounts of a slightly polar compound in the PCMs affect strongly to the encapsulation process, making the encapsulation more difficult and obtaining an irregular shape.

However, with paraffin wax PRS®, nonadecane and tetradecane, the microcapsules produced had a spherical

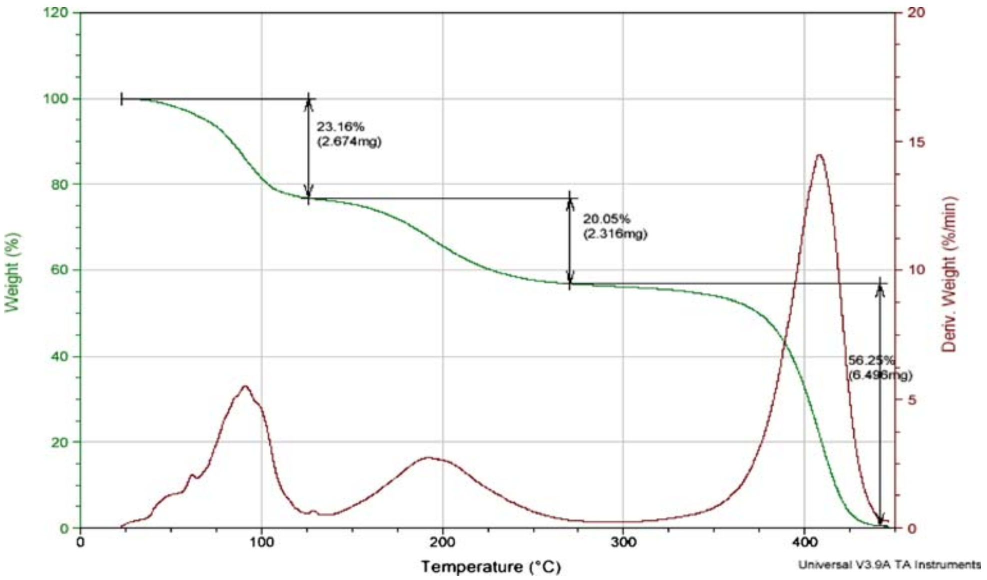


Fig. 9 TG and DTA curves of microcapsules containing paraffin wax PRS®

shape with a broad particle size. Most of the microcapsules have smooth surfaces, but dimples (like craters) were found on some of the microcapsules. Moreover, the scanning electron microscope with backscattered detectors demonstrated that the composition of the surface of the supposed holes was composed by polystyrene and not by paraffin; that is, a small layer of polymer remains covering the holes (see Fig. 8). This fact ensures that the core materials cannot get away of the capsule maintaining the PCM inside. These craters could be produced during the solidification of the paraffin in the cooling period after the polymerization because the contraction of the core material is greater than that of the shell producing a small deformation (like a hole) in the weakest part of the capsule [14]. This thin part of the shell would be the most likely place for the PCM to escape during temperature cycling. Nevertheless, it has been confirmed that after five laundering cycles at 60 °C, the latent heat of the microcapsules remain unchanged in 41.5 J/g, confirming that there is not an appreciable release of PCM during the washing tests.

Keeping in mind the possible application of these microcapsules in fabrics, the thermal stability of the material was tested by means of thermogravimetry (TG) and differential thermal analysis (DTA) analyses (Fig. 9). The analyses was done on microcapsules as obtained after the polymerization and washing process with no further drying, as if a post-washing test were done on a real textile. The TGA plot of the microcapsules showed a loss of 23 wt % below 100 °C because of the elimination of methanol and water (drying of surface wetting agents), and between 120 and 250 °C, other weight loss (21 wt%) was observed, attributed to the paraffin wax. Finally, at temperatures higher than 300 °C, an additional weight loss of 57 wt% took place; this weight loss was due to the polystyrene. Therefore, the thermal stability of the paraffin wax PRS® inside the microcapsule shell up to 120 °C was demonstrated confirming the applicability of these capsules in daily garment.

Paraffin wax PRS® was selected as a PCM for further studies. Paraffin wax is an attractive, chemically stable and non-toxic material. It has high latent heat capacity over a suitable temperature range to be used in the fabrication of thermo-regulated fibres, fabrics, coating and foams [12]. On the other hand, paraffin PRS® and other quite similar paraffin products are easily available from many manufacturers and are usually less expensive than other PCMs with a given formulation.

Summary

A cheap and technically feasible process for the encapsulation of PCMs has been developed. A method based on a suspension free radical polymerization process has been used for the encapsulation. This PCM encapsulation method had not been previously described in literature, nor patented.

Different PCMs (paraffin wax PRS®, tetradecane, Rubitherm® RT27, Rubitherm® 20, nonadecane) can be encapsulated by this method and form a core-shell structure. However, PEG cannot be encapsulated because of its hydrophilic nature. It is possible to obtain particles where almost the 50% by weight of microcapsules is PCM. SEM and laser diffraction techniques show that spherical microcapsules with a broad PSD were obtained.

It has been observed that the diameter, the melting heat and the amount of microcapsules obtained in each experiment vary with the kind of PCMs used.

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