



Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerisation

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ABSTRACT

The microencapsulation of phase change materials (PCMs) by a suspension copolymerisation of styrene (St) and methyl methacrylate (MMA) has been studied. The influence of the monomers/paraffin and the MMA/St mass ratio on the encapsulation process and the physical properties of the resulting microcapsules has been studied. The thermal properties, morphology, chemical composition and particle size distribution of the microcapsules were characterised by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), environmental scanning electron microscopy (ESEM), optical microscopy (OM), Fourier transform infrared spectroscopy (FT-IR) and low angle laser light scattering (LALLS). It was found that the MMA/St mass ratio has a marked influence on the polymerisation rate, affecting the conversion and the time at which the identity point is reached. As the amount of MMA is increased, the reaction time and the mean particle size decrease. On the other hand, paraffin was not encapsulated when the monomers/paraffin mass ratio was lower than 3.0 due to the shortage of copolymer. On the basis of the experimental results, an MMA/St mass ratio of 4.0 and monomers/paraffin ratio of 3.0 were established as the best conditions to produce this kind of microcapsule.

The higher reactivity and solubility of the methyl methacrylate in water, when compared to styrene, favours paraffin microencapsulation – as shown by the average storage energy capacity of the microcapsules obtained using this copolymer. Furthermore, TGA analysis shows that the thermal stabilities of both the virgin copolymer and the microcapsules containing PCMs are similar when P(St-co-MMA) is used as the shell material.

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1. Introduction

Phase change materials (PCMs) are a type of functional material that can store and release energy upon phase transition. Many companies and researchers have studied PCMs for applications in solar energy storage [1], smart housing [2], thermo-regulated fibres, fabrics, coatings and foams [3]. In all of these PCM applications, phase change materials (PCM microcapsules) are alternative systems for energy conservation.

Paraffin waxes are used as PCMs because of their low cost, high energy storage density and large scale availability [4]. Microencapsulation is often employed to encapsulate PCMs. In these processes a PCM core is encapsulated by a plastic or cross-linked polymer shell to prevent liquid from overflowing during use of the PCM. Encapsulation of the PCM core within a mechanically and chemically stable shell is currently fraught with many technical and scientific issues.

The most common methods for the microencapsulation of paraffin are interfacial polymerisation [5], emulsion polymerisation [6], in situ polymerisation [7], layer by layer deposition of polyelectrolyte [8], spray drying and coacervation [9]. However, these encapsulation techniques have some practical drawbacks. Very little PCM can be encapsulated by some of these techniques, and for some applications a large particle size is also obtained. Besides, in contrast to the other applications of microcapsules (carbonless copying paper, fire extinguishing compounds, adhesives, perfumes and fragrances, insecticides, cosmetics, fertilizers, and so forth) where the core is expected to be released in solvent under the application of heat or pressure, the microcapsules containing PCMs must be resistant towards washing, heat and pressure without disturbing the core content. Therefore, the development of a simple, cheap, robust and environmentally friendly method for encapsulating suitably sized PCMs is crucial for textile and other applications.

The suspension-like polymerisation process, by which PCM microcapsules were prepared in this work, seems to satisfy the above conditions. It has also been demonstrated that this process is governed by multiple simultaneous mechanisms such as particle

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coalescence and break-up, secondary nucleation and the diffusion of monomer to the interface. The collective effect of these mechanisms confers the size, the structure and the surface properties to the microcapsules.

The selection of an appropriate shell material, i.e. one that withstands hot and dry washing, is important for the application of microcapsules in smart textiles. Several polymers have been used as PCM shell materials and these include urea–melamine–formaldehyde [10], urea–formaldehyde [11], melamine–formaldehyde [12,13], gelatine–formaldehyde [14], toluene-2,4-diisocyanate and diethylene triamine [15] and polyurethane [16,17]. For each particular application, the microcapsules obtained showed specific limitations. In some cases, depending on the type of encapsulation method used, the synthesis can be complicated.

In previous studies, PCMs were successfully encapsulated by a single polystyrene (PSt) polymer cover [18,19]. The microcapsules obtained were spherical and had relatively high paraffin content. The use of polymethyl methacrylate (PMMA) as a shell could improve the characteristics of microcapsules and therefore broaden their fields of application. Some properties such as glass transition temperature (105 °C for PMMA vs 80 °C for PSt), modulus of elasticity (3300 MPa for PMMA vs 3200 MPa for PSt) and thermal conductivity (0.19 W/mK for PMMA vs 0.105 W/mK for PSt) [20] would affect the behaviour of textiles in which microcapsules were incorporated. Moreover, the higher reactivity and solubility in water of MMA as compared with St would improve the efficiency of paraffin encapsulation [21]. Berg et al. [22] achieved the encapsulation of hydrocarbon oils by polymerisation of MMA. Loxley and Vincent [23] reported a phase separation method to encapsulate n-hexadecane with PMMA. Yang et al. [24] studied the encapsulation of tetradecane with PMMA by in situ polymerisation for applications in fields such as heating, ventilation, air-conditioning, refrigeration and heat exchangers. Alkan et al. [25] prepared PMMA microcapsules containing docosane for thermal energy storage purposes such as solar space heating applications.

In addition, it is important to note that the final microcapsule morphology obtained by this process is strongly dependent on the mobilities between the components, compatibilities between the polymers and monomers, hydrophilicities and reactivity ratios between the monomers [26].

The aim of this work was to study the effect of methyl methacrylate monomer on the PCM microencapsulation by means of suspension-like polymerisation. The influence of the MMA/St and monomers/paraffin mass ratios on microcapsule properties such as thermal capacity, particle size distribution (PSD) and conversion profiles was studied.

2. Experimental

2.1. Materials

The monomers, methyl methacrylate (99 wt%, Merck Chemical Co.) and styrene (99 wt%, Panreac Chemical Co.), were reagent grade. Styrene and methyl methacrylate were washed with sodium hydroxide in order to remove the inhibitor. Calcium chloride was then employed as a desiccant. Benzoyl peroxide (97 wt%) was used as the initiator (Fluka Chemical Co., Ltd.). Commercial grade PRS[®] paraffin wax (Repsol YPF Co.) was used as the oily core. Reagent grade polyvinylpyrrolidone (K30, Mw 40,000 g/mol) (Fluka Chemical Co., Ltd.) was used as a stabiliser, and methanol was used to pour the samples. The reagents were all used as received. Water was purified by distillation and subsequent deionisation using ion-exchange resins. Nitrogen was high-purity grade.

2.2. Microcapsule synthesis

Suspension-like polymerisation reactions were performed in a 2-L double-jacketed glass reactor, equipped with digital control of the stirring rate and temperature, a reflux condenser and a nitrogen gas inlet tube. A schematic diagram of this experimental set-up is published elsewhere [18].

The synthesis process involved two phases: (i) a continuous phase containing water and polyvinylpyrrolidone and (ii) a discontinuous phase containing styrene, methyl methacrylate, PRS[®] paraffin wax and benzoyl peroxide.

The continuous phase was transferred to the glass reactor with mild agitation (150 rpm). The initiator was premixed with monomers and phase change material. This allowed for efficient operation and minimised the idle time. The discontinuous phase was then added to the continuous phase and was maintained under vigorous agitation (500 rpm) at a constant temperature of 98 °C. The polymerisation process was carried out for 5 h under a nitrogen atmosphere.

Once obtained, the PCM microcapsules were washed five times with methanol and filtered under vacuum to remove impurities. The purified microcapsules were dried at 25 °C for 24 h.

This process was carried out with different MMA/St mass ratios (from 2.0 to 5.0) at a fixed monomer to paraffin ratio of 3.0. The monomers/paraffin wax mass ratio was changed (from 2.0 to 4.0) at the best MMA/St mass ratio found in this work. The number of experiments carried out during this study and the respective amount of each component used for the preparation of different microcapsules containing PCMs are shown in Table 1.

2.3. Environmental scan electron microscopy (ESEM)

The surface features of the microcapsules after polymerisation were observed using an XL30 (LFD) ESEM.

2.4. Calculation of number-average diameter and volume-average diameter

Particle size and particle size distribution (PSD) were determined on a Malvern Mastersizer Hydro 2000 SM light scattering apparatus with dilute dispersions of the particles in methanol.

2.5. Differential scanning calorimetry (DSC)

The melting points and melting heats of the various materials employed and obtained were determined using a TA Instruments model DSC Q100 Differential Scanning Calorimeter equipped with a refrigerated cooling system and nitrogen as the purge gas. These measurements were performed by varying the temperature from –30 to 80 °C, with a heating rate of 10 °C/min. Each sample was analysed at least twice and the average value was recorded. Furthermore, the encapsulation ratio of paraffin wax in the microcapsule was calculated using the following equation, which is based on enthalpy values:

$$\% \text{Microcapsules paraffin content by weight} = \frac{\Delta H_m}{\Delta H_{\text{paraffin}}} \times 100\%$$

where ΔH_m is the enthalpy for the analysed microcapsules (J/g) and $\Delta H_{\text{paraffin}}$ is the enthalpy of pure paraffin wax (202.7 J/g).

2.6. Thermogravimetric analysis (TGA)

The thermal stability was characterised using a TA Instruments – SDT 2960 Simultaneous DSC-TGA at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table 1
Recipes for the production of P(St-MMA) microcapsules containing PRS® paraffin wax, by suspension-like polymerisation.

Set of experiments	MMA (g)	St (g)	PRS® paraffin wax (g)	H ₂ O (g)	BPO (g)	PVP (g)	(St + MMA)/PRS® paraffin wax (g/g)	MMA/St (g/g)
1	157	78	78.4	754.7	2.51	7.54	3.0	2.0
	176	59						3.0
	183	52						3.5
	190	46						4.0
	196	39						5.0
2	190	46	117.6	754.7	2.51	7.54	2.0	4.0
			94.8					2.5
			78.4					3.0
			67.2					3.5
			58.8					4.0

Table 2
Morphology, average diameter in volume, thermal properties of microcapsules and relative FT-IR peak intensity ratios obtained from different mass ratio of MMA/St.

MMA/St (g/g)	dpv _{0.5} (μm) ^a	Morphology (ESEM)	Average melting heat (J/g)	PCM encapsulated (wt%)	$I_{735\text{cm}^{-1}}/I_{1735\text{cm}^{-1}}$ ^a
2.0	–	Not microcapsules	–	–	–
3.0	400	Irregular	58.40	28.81	0.75
3.5	380	Spherical	87.50	43.17	0.64
4.0	182	Spherical	84.04	41.46	0.41
5.0	–	Irregular	24.90	12.28	–

^adpv_{0.5} represents 50% microcapsule particles whose mean volumetric diameter is less than this value. $I_{735\text{cm}^{-1}}$ peak intensity at 735 cm⁻¹ assigned to benzene ring deformation vibration of PSt. $I_{1735\text{cm}^{-1}}$ peak intensity at 1735 cm⁻¹ assigned to carbonyl groups of PMMA.

2.7. Fourier transform infrared spectroscopy (FT-IR)

Copolymer composition was measured by FT-IR (FTIR 16 PC, PerkinElmer) at room temperature. Microcapsules were applied on dry KBr pellets prepared using a manual hydraulic press (PerkinElmer, Spain) and these were scanned from 370 to 4400 cm⁻¹.

3. Results and discussion

3.1. Influence of mass ratio of methyl methacrylate to styrene

Experiments were carried out according to the method reported by Sánchez et al. [18] for the production of microcapsules containing PCMs with a polystyrene shell. In that case, a monomer/paraffin mass ratio of 3.0 was used and the microencapsulation of different PCMs was described. Experiments using MMA/St mass ratios in the range 2.0–5.0 at a fixed monomers/paraffin mass ratio of 3.0 were carried out in order to study the influence of the use of methyl methacrylate monomer on the microcapsule characteristics.

The data given in Table 2 are the morphology observed by ESEM, the average diameter in volume, the melting heats (average values from 3 measurements), the average proportion of paraffin and the relative proportions of St to MMA in the microcapsules prepared with MMA/St mass ratio from 2.0 to 5.0. The results show that the microencapsulation did not take place when an MMA/St mass ratio of 2.0 was used and when an MMA/St proportion of 5.0 was employed the polymer tended to polymerise outside the bead in a segregated way due to the hydrophilicity of MMA monomer. Spherical particles with a similar percentage of paraffin wax were microencapsulated using MMA/St mass ratios of 3.5 and 4.0. Thus, the amount of PCM encapsulated and the microcapsule characteristics depend on the proportions of the monomers used in the process.

According to the results, the lowest average particle size was obtained for an MMA/St mass ratio of 4.0. It is well known that small microcapsules are required for most applications [3,18,19,27]. Although the particles obtained using MMA/St mass ratios of 3.5 and 4.0 have similar average melting heats, the lower particle size observed for an MMA/St ratio of 4.0 makes this the best monomer proportion to produce microcapsules.

Chemical characterization of P(St-co-MMA) microcapsules was carried out using FT-IR spectroscopy. The relative proportions of St/MMA in the microcapsules were determined by taking into account the peak intensity ratio of the characteristic peaks of PMMA (1735 cm⁻¹) and PSt (735 cm⁻¹). The absorption peaks at 1735 and 735 cm⁻¹ can be assigned to carbonyl groups of PMMA and the benzene ring deformation vibration of PSt, respectively. As expected, a decrease in the ratio of the peak intensities was observed as the St content in the process was decreased (Table 2).

Comparison of these results with those obtained using styrene as the monomer shows that the microencapsulation improves on using methyl methacrylate, as evidenced by the energy storage capacity of the microcapsules being only 41.65 J/g (20.56% paraffin content) when the same mass ratio of styrene/paraffin (3.0) was used [18,19]. The microcapsules obtained using the copolymerisation between MMA and St have at least twice the paraffin content reported for styrene alone. Based on the inequality in interfacial tension discussed by Torza and Mason [28], this higher encapsulation efficiency can be attributed to the interfacial tension of water/PMMA (16 mN/m) being lower than the interfacial tension of water/PSt (32 mN/m), meaning that the core/shell morphology will be favoured thermodynamically during the polymerisation process [29]. Moreover, the higher polymerisation rate of MMA compared to St favours the encapsulation of the PCM material.

The latent heat per mass of microcapsules (84.04 J/g) obtained using an MMA/St proportion of ~4.0 is similar to that reported for the microencapsulation of paraffin wax with polystyrene on using a monomers/paraffin mass ratio of 1.0 and sieving the product to remove the particles with a diameter greater than 250 μm (76.22 J/g) [19]. Similarly, this value is lower than the optimal value (102.42 J/g) obtained by Sánchez et al. [27], who carried out an experimental design to improve the characteristics of microcapsules containing phase change materials with a styrene/paraffin mass ratio of 1.02 and employed an SPG (Shirasu Porous Glass) membrane to produce uniform polymeric particles (4.8 μm). Thus, one would expect an even higher paraffin content inside the microcapsule if the monomers/paraffin mass ratio was changed or an SPG membrane used in this copolymerisation process.

The morphologies of the microcapsules obtained with MMA/St proportions of 3.0, 3.5 and 4.0 by scanning electron microscopy (ESEM) are shown in Fig. 1. As can be seen, when an MMA/St mass

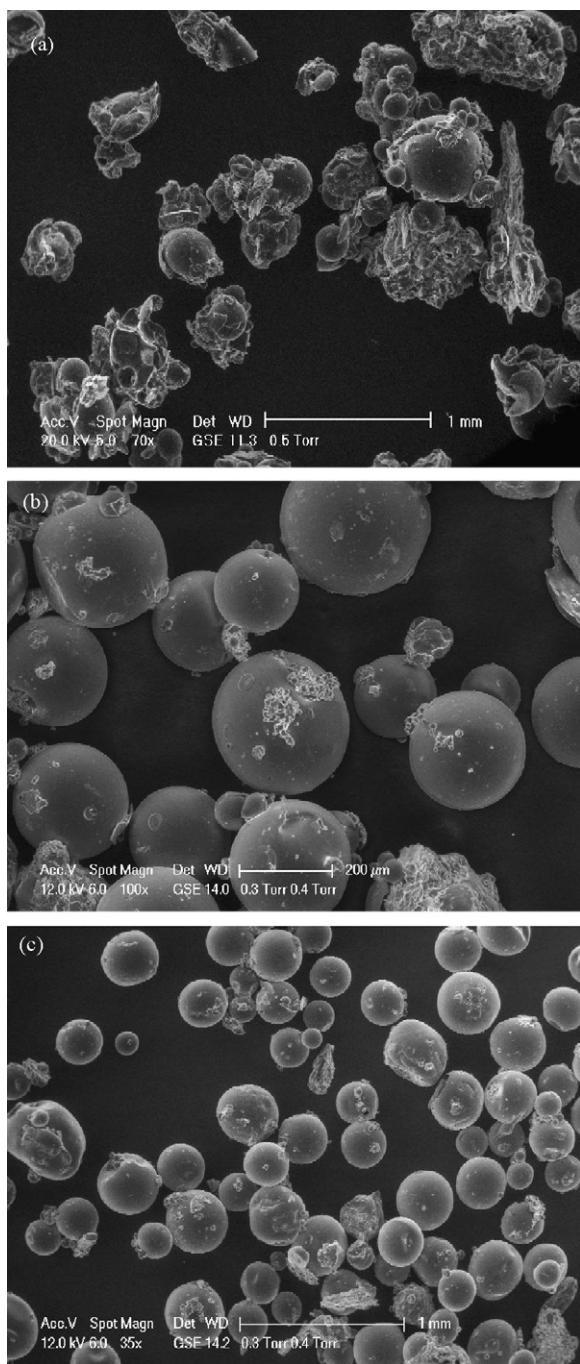


Fig. 1. ESEM micrographs of microcapsules synthesised with MMA/St mass ratios of (a) 3.0, (b) 3.5 and (c) 4.0.

ratio of 3.0 is employed (Fig. 1a), the microcapsules have an irregular form and a rough surface. However, the morphology tended to be spherical when microcapsules were prepared using MMA/St mass ratios of 3.5 and 4.0 (Fig. 1b and c), without broken particles or incomplete spheres, but the particle size distribution (PSD) seems to be non-uniform. These results indicate that the morphology improves on increasing the MMA/St mass ratio in the process from 3.0 to 4.0.

The monomer conversion and the average particle size in volume with reaction time are represented in Fig. 2. It can be seen that the higher the MMA/St mass ratio, the lower average particle size and the higher the monomer conversion.

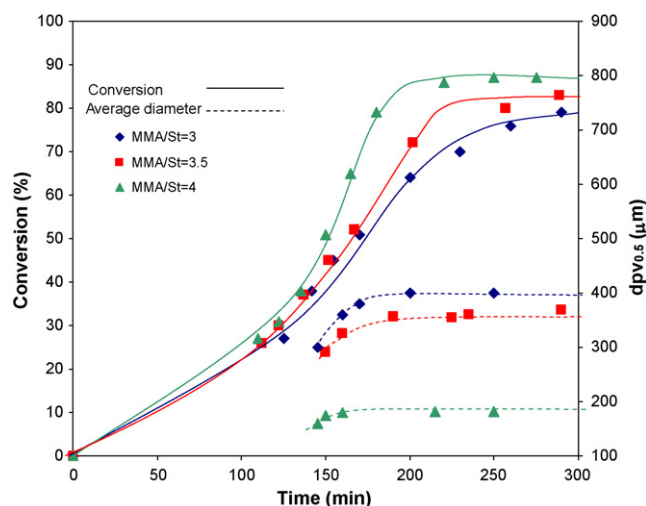


Fig. 2. Evolution of the conversion and the volume-average diameter of the microcapsules obtained using 3.0, 3.5 and 4.0 of MMA/St mass ratio during the polymerisation.

The higher conversion observed on increasing the methyl methacrylate content can be explained by the higher reactivity of this monomer with respect to styrene; the reactivity rates of styrene (M_1) and methyl methacrylate (M_2) at 90 °C are $r_1 = 0.55 \pm 0.02$ and $r_2 = 0.58 \pm 0.06$, respectively [30]. These results are in agreement with those reported by Khan and Wadehra [31] and O'Driscoll and Huang [32].

The total time for the polymerisation was 5 h. The conversion reached a plateau near to 80% in all of the experiments. In suspension polymerisation, the identity point occurs when the PSD becomes constant. Systems with a short time identity point are denoted type A; for longer times, the systems are identified as type B [33]. As seen in Fig. 2, the behaviour of this system is consistent with a type B group: the time needed to reach the identity point (around 180 min) is longer than necessary to achieve a polymer yield of 50% (around 150 min). The same results were obtained for the suspension polymerisation of St/MMA [34,35]. This means that the particles remain sticky on trying to break them up and they coalesce after a long time (about 180 min). Although the time needed to reach the identity point increases as the amount of MMA decreases, the conversion at which the identity point is reached in each experiment is always 60%. This is in agreement with the results reported by Jahanzad et al. [36]. The size of the particles increases as the length of time required to reach the identity point increases. Thus, the average diameter of the microcapsules decreases as the amount of MMA increases. This result is due to the domination of coalescence in the final sticky period, just before the identity point is reached, after which “salami”-like particles are obtained.

In a previous study it was demonstrated that the microcapsule particle diameter is inversely related to the thermal energy storage capacity [19]. In order to verify this variation and to confirm that the minimum particle size fraction of the material is mainly polymer without PCMs, the microcapsules obtained with an MMA/St mass ratio of 4.0 were sieved to the mesh sizes 0.01, 0.1, 0.25, 0.5 and 1.0 mm in order to separate them into fractions. The resulting materials were analysed by DSC. The values for melting heat per mass unit of the microcapsules under investigation were 0, 104.8, 86.8, 47.3, 26.9 J/g, respectively. Therefore, the smallest PSD fraction was found for particles of pure copolymer (i.e. without paraffin encapsulated) resulting from secondary nucleation, a process that will be described in more detail below. According to previous results [19] the proportion of paraffin wax contained in the particle decreases with increasing particle size.

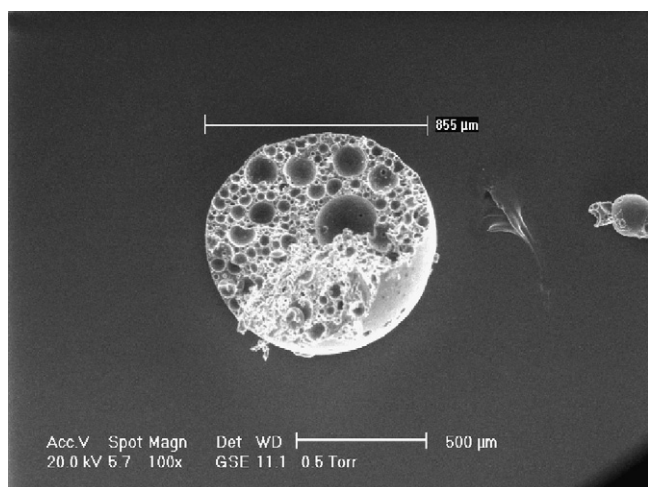


Fig. 3. ESEM cross-section of a large microcapsule prepared at mass ratios monomers/paraffin of 3.0 and MMA/St of 4.0.

The process of break up and coalescence of the particles remains active from the beginning of the suspension-like polymerisation process until the identity point is reached. At this point, the shells of the larger capsules become more consistent and contain within them microcapsules and microparticles from secondary nucleation. In this way the larger microcapsules form “salami” like structures, as can be seen in the cross-section ESEM micrograph (Fig. 3). Thus, large particles are the result of the entrapment of smaller microcapsules and microparticles without PCM encapsulation under the same shell, thus resulting in a greater relative amount of polymer. This view is consistent with the DSC results obtained.

On the basis of the results described above, the best characteristics for the microcapsules that contain PCMs were found when an MMA/St mass ratio of 4 was used.

3.2. Influence of mass ratio of monomers (methyl methacrylate and styrene) to paraffin wax

Once the best mass ratio of MMA/St had been identified, different experiments were carried out with the monomers/paraffin mass ratio changed in order to study the influence of this synthesis variable on the microencapsulation of PCM (set 2, Table 1).

In the experiments where the mass ratio of monomers to paraffin was less than 3.0, a thin layer of solid paraffin wax remained at the end of the experiment. DSC analysis of the solids on using monomers/paraffin mass ratios of 2.0 and 2.5 gave a melting heat of 0 J/g. This indicates that the encapsulation process had not worked properly under these conditions. The results obtained are consistent with those published by Hawlader and Siddhan [9,15], where the microencapsulation efficiency decreased as the ratio of core-to-coating increased.

DSC thermograms for the PCM microcapsules prepared using monomers/paraffin mass ratios of 3.0, 3.5 and 4.0 are shown in Fig. 4. The range of the phase change transition is the same as for pure PRS[®] paraffin wax, with overheating effects not observed. Furthermore, the melting heat per mass unit values for these microparticles were 84.04, 96.91 and 92.63 J/g, respectively. Consequently, the relative amount of paraffin wax encapsulated in these experiments was quite similar, with the highest value corresponding to a monomers/paraffin mass ratio of 3.5 (around 48 wt%).

It can be seen from Fig. 5 that the PSD of the microcapsules obtained exhibits a bimodal distribution in volume (Fig. 5a) and in number (Fig. 5b). This indicates that secondary nucleation could be taking place, as very small particles from 5 to 100 μm were

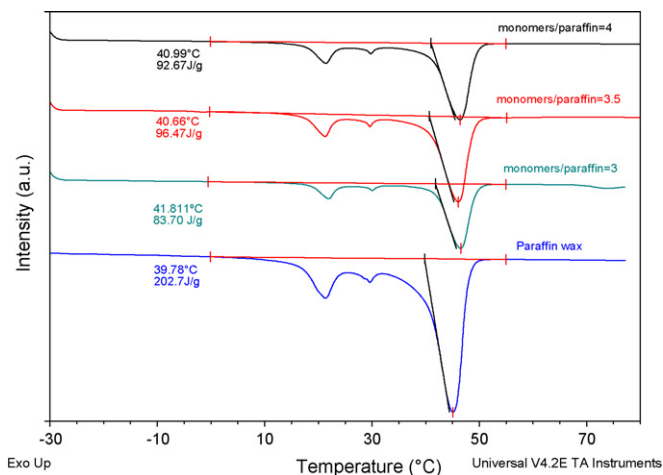


Fig. 4. DSC thermograms of microcapsules obtained using monomers/paraffin mass ratio of 3.0, 3.5 and 4.0 together with that of pure PRS[®] paraffin wax.

obtained. The hydrophilicity of the MMA monomer and the absence of inhibitors in the aqueous media favour the secondary nucleation process. Therefore, a certain amount of MMA monomer could diffuse into the aqueous phase, which implies that the microencapsulation of paraffin wax was not effective and secondary polymeric particles were formed.

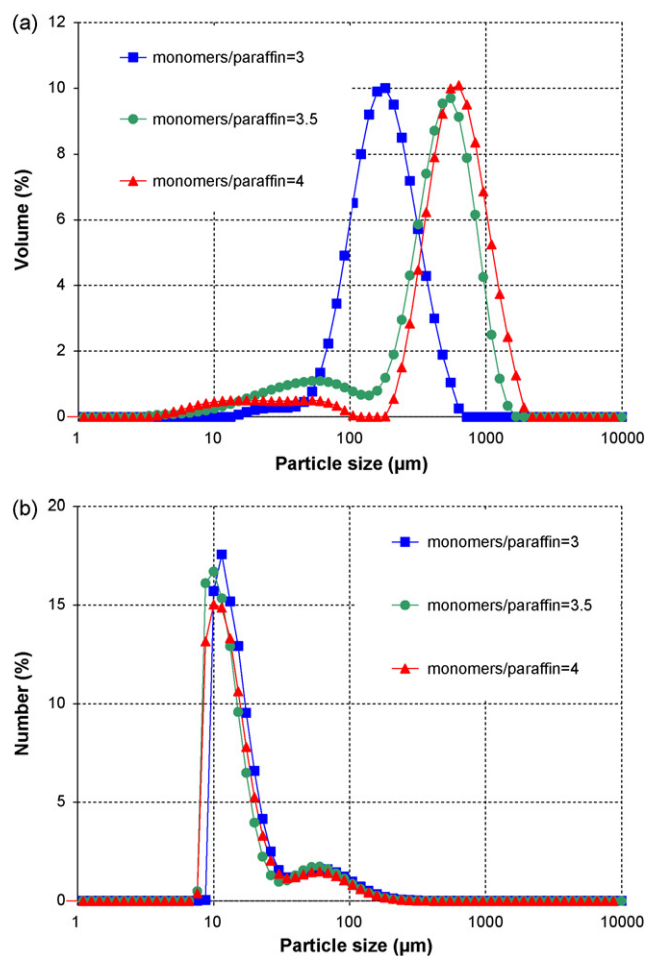


Fig. 5. Particle size distribution for microcapsules prepared using different mass ratios of monomers/paraffin: (a) in volume and (b) in number.

Table 3

Characteristics of PSt and P(St-co-MMA) microcapsules obtained using monomers/paraffin wax mass ratio of 3.0 by suspension-like polymerisation.

	dpv _{0.5} (μm) ^a	Average melting heat (J/g)	PCM encapsulated (wt.%)	Glass transition temperature (°C)	Shell decomposition temperature (°C)
Sánchez et al. [18]	238	41.65	20.56	80	340
Present work	380	87.50	43.17	99	325

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

As shown in Fig. 2, in a suspension polymerisation process each drop can be regarded as a small isolated reactor; the observed copolymerisation kinetics may correspond directly with the values for bulk polymerisation [33–35]. Nevertheless, although one would expect that the polymerisation kinetics are affected by the amount of paraffin employed, they are in fact unaffected. Conceptually, if the amount of paraffin employed is half or a third of the initial concentration of the monomers, the polymerisation rate would correspondingly decrease because of the dilution. However, such behaviour is not observed. The only possible explanation is that in the interfacial polymerisation loci, the monomer concentration is disproportionately higher than that of the paraffin. Thus, the observed polymerisation rate is almost the same as for pure monomers in the absence of paraffin. The monomers clearly dominate the paraffin in the polymerisation loci.

TGA and DTGA curves for the microcapsules with and without PCMs synthesised with an MMA/St mass ratio of 4 are shown in Fig. 6 along with that for the pure PRS[®] paraffin wax. The TGA plot of the pure paraffin wax shows a marked weight loss between 150 and 300 °C. This is due to the evaporation of paraffin wax used as the PCM. For the P(St-co-MMA) with a mass ratio of 4.0, without paraffin, a degradation step at 320 °C was observed. This is generally attributed to scission at the chain-end, initiation from the vinylidene ends [37] and random internal scission of the polymer chain. The final weight loss of the sample was observed at 450 °C. Similarly, the PCM microcapsules synthesised with a MMA/St mass ratio of 4.0 showed a weight loss between 150 and 280 °C and this is related to the evaporation of paraffin wax. Another weight loss can be seen from 325 to 450 °C and this is due to copolymer decomposition. According to these results, the copolymer and the microcapsules containing PCMs obtained using a mass ratio of MMA/St = 4 exhibit the same thermal stability.

Finally, the main characteristics of PCM microcapsules prepared in this work are shown in Table 3 along with results obtained in a previous study using a polystyrene shell [18]. Comparison of these results shows that the efficiency of paraffin encapsulation – and therefore the energy storage capacity – improves for PCM

microcapsules of P(St-co-MMA). Significant differences were not observed in the rest of the properties associated with the end-use of microcapsules, such as in thermoregulatory textiles. In addition, the thermal conductivity and mechanical strength (not shown) are enhanced when P(St-co-MMA) is used. AFM measurements were carried out on microcapsules in order to quantify the mechanical properties. The results obtained could not be quantitatively interpreted in terms of elastic properties, although it was observed that PCM microcapsules of P(St-co-MMA) have a lower deformability in comparison to PCM microcapsules made with PSt.

4. Conclusions

Paraffin wax was microencapsulated through a suspension-like polymerisation using a shell based on a copolymer of methyl methacrylate and styrene. According to the results, an MMA/St proportion of 4 and a monomer to paraffin mass ratio of 3.0 give rise to microcapsules with characteristics that are appropriate for industrial applications. In the same way, it was impossible to microencapsulate the paraffin wax when the MMA/St was equal to 2.0 and the monomer/paraffin mass ratio was lower than 3.0. The average energy storage capacity of the microcapsules obtained using this copolymer was higher than the values obtained in previous works using polystyrene as a shell material. Thus, the higher reactivity of methyl methacrylate and its higher polarity compared to styrene favour paraffin microencapsulation.

In the copolymerisation process, the monomer ratio has a marked influence on the morphology, the identity point and the average diameter of the microcapsules containing paraffin wax. The kinetics of the copolymerisation process are controlled by the monomer with the higher reactivity. In this way, as the amount of MMA increases, the time required to reach the identity point and the mean particle size decrease regardless of the amount of the core material. Furthermore, the TGA results reveal that the paraffin content does not affect the copolymer thermal stability.

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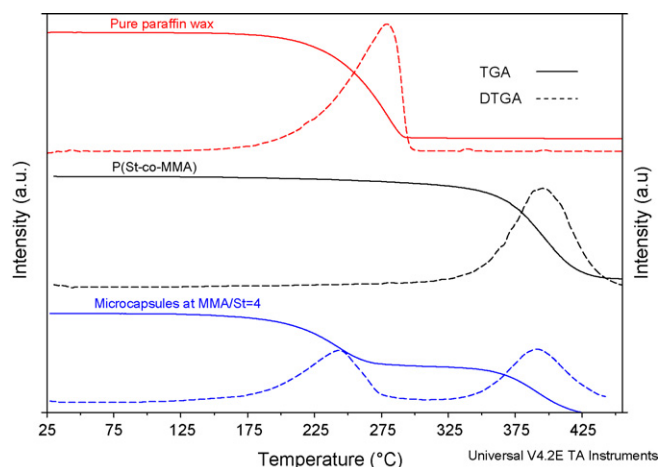


Fig. 6. TGA and DTGA curves of poly(St-co-MMA), PCM microcapsules prepared with 4.0 of MMA/St mass ratio and pure PRS[®] paraffin wax.

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