



# Poly(urea-formaldehyde) microcapsules containing commercial paraffin: in situ polymerization study

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## Abstract

Microcapsules containing Rubitherm® RT-42 paraffin wax (core) and a poly(urea-formaldehyde) shell were prepared by an in situ polymerization. The influence of prepolymerization/polymerization time, the reaction temperature, and the monomers/phase change material (PCM) mass ratio on the encapsulation process and the physical properties of the resulting microcapsules was studied. The morphology, chemical composition, and particle size distribution of the microcapsules were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). It was found that the structure of the generated poly(urea-formaldehyde) microcapsules strongly depended on the reaction time. The content of encapsulated Rubitherm® RT-42 increased with increasing reaction temperature until a limit, ranging the optimum reaction temperature from 60 to 70 °C. Finally, it was found that the optimal monomers/PCM mass ratio was 0.8. The poly(urea-formaldehyde) microcapsules obtained containing the RT-42 paraffin can be used as thermal energy storage systems.

**Keywords** In situ polymerization · Microcapsules · Poly(urea-formaldehyde) · Phase change materials

## Introduction

Thermal energy storage is a very important issue in industry, domestic scope, and construction. The potential use of phase change materials (PCMs) as an efficient way to store energy has been investigated for years. Although PCMs take advantage of their latent heat, a leakage occurs when PCM becomes liquid or reaches the liquid state [1]. To prevent this phenomenon, both encapsulation and microencapsulation of PCM are required. Thus, a strong and impermeable shell, wrapped to the PCM core, is able to maintain the PCM encapsulated in an unlimited number of phase change cycles.

PCM microencapsulation has been widely used for building applications. Microencapsulated PCMs have been incorporated to cement, concrete [2], wallboards [3], gypsum plaster [4], sandwich panels [5], and slabs [6]. Textile applications have been another important industrial field in which PCM microcapsules have been used [7, 8].

Encapsulated PCM slurry has been investigated for its use in solar panels [9], heat exchangers [10, 11], and air conditioning systems [12].

Paraffins are one of the most suitable PCMs due to their low cost, stability, non-corrosive and non-toxic character in nature, and the wide range of melting temperatures available determined by the number of carbons contained in their structure (ranging from 30 to 90 °C for C18–C50 chain lengths) [13].

There are several techniques to encapsulate phase change materials, physical-mechanical methods as the spray drying, physico-chemical methods such as coacervation and sol-gel, and chemical methods such as interfacial, suspension, and emulsion polymerization [13]. Chemical methods are widely used to encapsulate PCMs due to the simplicity of the experimental facilities required.

Amino polymers, combination of melamine or urea with formaldehyde, are also widely used to encapsulate PCMs. The procedure of manufacture of these proceeds through in situ polymerization, which can be carried out in one or two steps. This method produces high-quality materials referred to its polymeric sealing wall [14]. Different works have reported the encapsulation of *n*-octadecane using melamine-formaldehyde as the polymeric wall [15–17]. Li et al.

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evaluated the residual amount of formaldehyde present in the final product, poly(urea-formaldehyde) microcapsules containing commercial paraffin, finding that it was about  $68.6 \text{ mg kg}^{-1}$  [17], thus demonstrating the low toxicity of the microcapsules obtained [18].

More recently, Mohaddes et al. encapsulated *n*-eicosane obtaining a melting enthalpy of  $162.4 \text{ J g}^{-1}$  [19]. For their part, Xin et al. carried out a study for the optimum curing temperature of the polymeric resin (urea-formaldehyde), resulting in a paraffin encapsulation efficiency and melting enthalpy of 52.8% and  $74.2 \text{ J g}^{-1}$ , respectively [20]. Finally, Yin et al. encapsulated *n*-hexadecanol with 79.1% of efficiency and  $171 \text{ J g}^{-1}$  of melting enthalpy [21].

The application of PCM microcapsules in thermal energy storage systems requires that these materials have good thermal properties, mechanical and thermal stability, a suitable size, an adequate shell polymer cross-linking, and no leakage issues. Therefore, it is not surprising that the optimization of the synthesis conditions has been a priority of many researchers. Thus, Salaün et al. analyzed factors like phase volume ratio, types and content of surfactants, stirring rate, pH, reaction time, core/shell ratio, and monomer mole ratio and found out the optimum synthetic conditions for melamine-formaldehyde microcapsules containing *n*-hexadecane [22].

Most of the researchers who have previously carried out the in situ polymerization technique for the manufacture of PCM microcapsules have employed the two-step method [19–21, 23–25], based on the use of at least two reaction vessels: one for the suspension preparation and other for the prepolymerization reaction. It is reckoned that the one-step method would be more suitable for the future industrial scaling up design, since a low investment in equipment is required. Nevertheless, the results reported for this method have not been completely satisfactory. With the purpose of combining the advantages of both methods, the development of a two-step synthesis route in a single reaction vessel to obtain poly(urea-formaldehyde) microcapsules is required.

The aim of this work was to study the synthesis route of poly(urea-formaldehyde) microcapsules (PUF-MC) containing a commercial paraffin (Rubitherm® RT-42). In addition, the influence of the prepolymerization/polymerization time, reaction temperature, and monomer/PCM mass ratio on the physical properties of the resulted materials were evaluated.

## Experimental

### Materials

RT-42 paraffin wax from Rubitherm® was employed as the core material of the synthesized microcapsules. Urea from

Sigma-Aldrich chemical company and formaldehyde (37–38 wt%) from Panreac Chemical Company were used as monomers. Hydrochloric acid and sodium hydroxide were purchased from Sigma-Aldrich and Panreac, respectively, and used as pH control agents. An emulsifier, poly(ethylene-alt-maleic anhydride), EMA, and an anti-agglomeration agent, polyvinyl alcohol (PVA), were purchased from Sigma-Aldrich chemical company. Resorcinol from Fluka chemical company and ammonium chloride from Panreac chemical company were employed as the cross-linking agent and the reaction initiator, respectively. All the chemical materials were used without further purification.

### Preparation of poly(urea-formaldehyde) microcapsules

PCM microencapsulation was carried out through an in situ polymerization method, using a jacketed glass reactor with a three-necked lid, mechanical stirring, a reflux condenser, an oil thermostat bath, and a nitrogen gas inlet tube.

The synthesis of PCM microcapsules was done as follows:

- Firstly, 200 mL of the PVA solution (1.25 wt% in water) and 50 mL of the EMA solution (2.5 wt% in water) were added to the reactor. This mixture was heated at  $50 \text{ }^\circ\text{C}$  with a stirring rate of 400 rpm. Subsequently, the first monomer (urea) was added whereas NaOH (1 M) was dropwised to raise a value of pH equal to 9.
- Secondly, the addition of Rubitherm® RT-42 was carried out under a vigorous stirring rate (1000 rpm) for 15 min to form the emulsion system.
- Then, formaldehyde solution was incorporated to the reactor and the temperature was increased. This prepolymerization reaction took place at basic pH.
- Once the prepolymerization reaction time was finished, pH was fixed at a value of 3 using a 1-M HCl solution. Finally, resorcinol and ammonium chloride were added allowing the polymerization reaction to proceed.

The amounts of each reagent and the reaction conditions used are summarized in Table 1.

### Characterization of the microcapsules

The melting point and the melting heat of Rubitherm® RT-42 and the resulting microcapsules were evaluated using a 2 Star<sup>c</sup> System differential scanning calorimetry (DSC) from Mettler Toledo company. A nitrogen constant flow of  $50 \text{ mL min}^{-1}$  was used as the purge during the experiments. The experiments were performed in the range of temperature from  $-20$  to  $90 \text{ }^\circ\text{C}$  at a scanning speed of  $10 \text{ K min}^{-1}$ . The degree of encapsulation of Rubitherm® RT-42 was calculated using the

**Table 1** Reaction conditions and amounts of reagents used in the preparation of poly(urea-formaldehyde) microcapsules

Set of experiments	PCM (g)	Urea (g)	Formaldehyde (37 wt%) (g)	Monomers/PCM (g/g)	Prepolymerization-polymerization time (h)*	T (°C)	Surfactant type	Amount of surfactant (g)**
1	16	5	4.7	0.6	1–3 2–2 2–3	60	EMA-PVA	1.25–2.5
2	16	5	4.7	0.6	2–3	60 70 80	EMA-PVA	1.25–2.5
3	16	4.1 5.0 6.6 8.2	3.9 4.7 6.2 7.8	0.5 0.6 0.8 1.0	2–3	70	EMA-PVA	1.25–2.5

\*Prepolymerization-polymerization conditions

\*\*EMA-PVA amount

following equation, which is based on the enthalpy values determined by the DSC:

$$\text{RT-42 content (wt\%)} = \frac{\Delta H_{\text{PUF-MC}}}{\Delta H_{\text{RT-42}}} \times 100$$

where  $\Delta H_{\text{PUF-MC}}$  is the melting enthalpy of the PCM inside the microcapsules ( $\text{J g}^{-1}$  of microcapsules) and  $\Delta H_{\text{RT-42}}$  is the melting enthalpy of Rubitherm® RT-42 ( $156 \text{ J g}^{-1}$ ).

The total amount of PUF microcapsules produced was weighted and the mass yield percentage was calculated using the following equation that takes into consideration the initial weight of Rubitherm® RT-42 and the monomers used for the synthesis.

%Mass yield of PUF–MC

$$= \frac{\text{Weight of PUF-MC}}{\text{Weight of RT-42 + urea + formaldehyde}} \times 100$$

The morphology and mean diameter of the obtained microcapsules were observed using a Phenom Pro-X scanning electron microscopy (SEM) and the ParticleMetric software. To improve the imaging of samples, a gold coating of samples was performed using a Q150R rotary-pumped sputter coater. The mean diameter was calculated with the ParticleMetric software using images of more than 10 particles.

The composition of the polymeric shell and the presence of encapsulated PCM were studied using an UATR two Fourier transform infrared spectroscopy (FT-IR) from Perkin Elmer company. The wavenumber range was  $4000\text{--}500 \text{ cm}^{-1}$ .

## Results and discussion

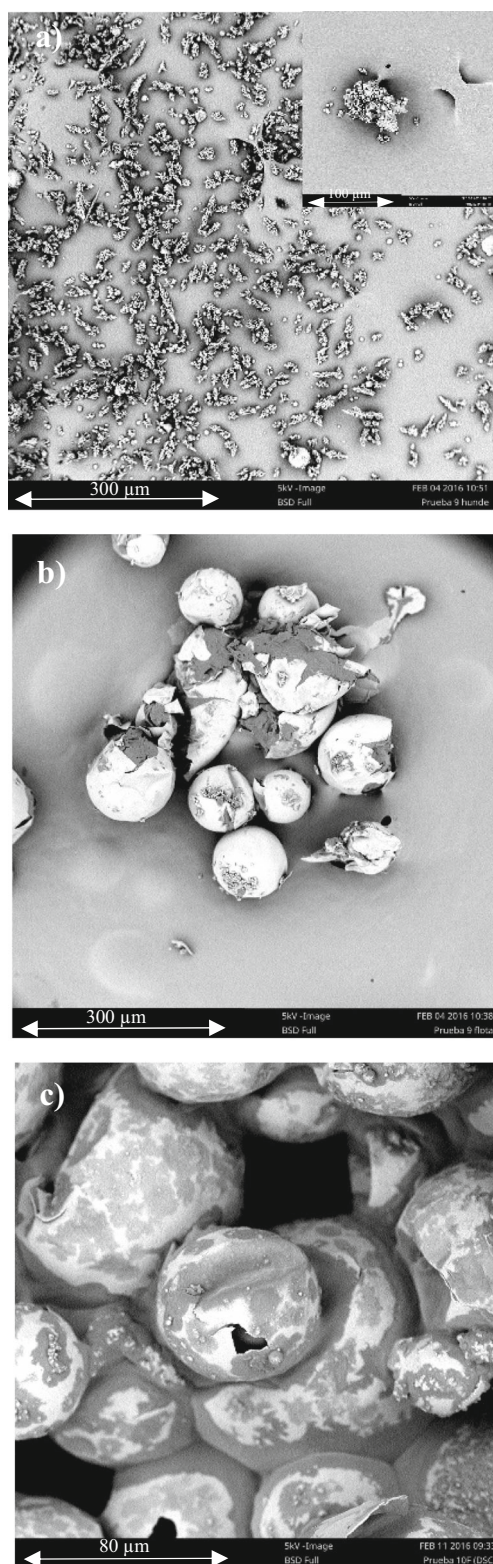
The microencapsulation reaction was carried out through an in situ polymerization, using urea and formaldehyde as

monomers. This reaction can be carried out in one or two steps. To reduce costs for its scaling-up process, the synthesis route was firstly performed in only one step. Thus, all the reactants were added to the reaction medium at the same time (the reagents' amount was the same as that in set 1, Table 1). Temperature and pH were fixed at  $60 \text{ }^\circ\text{C}$  and 3, respectively, and the reaction time was fixed at 4 h.

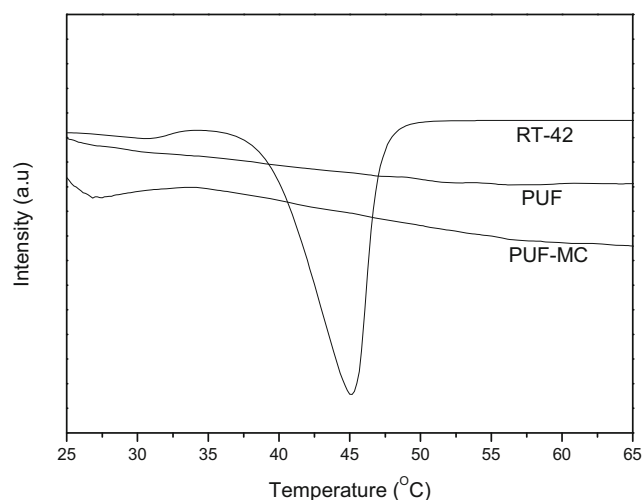
After the polymerization reaction, it was observed that a large amount of free solid Rubitherm® RT-42 formed a thin layer on the surface of the reaction medium, indicating that certain amount of the PCM added was not effectively encapsulated. In addition, after cooling and settling, two different products were obtained: one was floating over the aqueous suspension whereas the other one was settled at the bottom of the reactor vessel. These products were analyzed by DSC and SEM techniques.

Figure 1 shows SEM micrographs of both obtained products. An agglomeration of poly(urea-formaldehyde) particles and few PUF microcapsules were observed in the settled fraction (Fig. 1a). A higher magnification of the agglomeration (included in Fig. 1a) confirmed that some nanoparticles of PUF are formed as a consequence of the precipitation of high molecular weight prepolymer in the aqueous solution [26]. On the other hand, the floating products were microcapsules with an imperfect polymeric covering layer (Fig. 1b). To demonstrate that the microencapsulation did not take place properly, these microcapsules were heating above the melting point of the used PCM ( $38\text{--}48 \text{ }^\circ\text{C}$ ). In Fig. 1c, a magnified image of the leakage of the paraffin is shown, resulting in hollow microcapsules with wrinkled structures.

Figure 2 shows the DSC profiles of the obtained microcapsules (PUF-MC), the particles of poly(urea-formaldehyde) without PCM encapsulated (PUF), and the phase change material (RT-42). It was observed that the amount of PCM encapsulated was negligible. Considering these results, it seems



**Fig. 1** SEM micrographs of the products obtained using the one-step method. **a** Settled fraction composed by an agglomeration of poly(urea-formaldehyde) particles and few PUF microcapsules, **b** floating products were microcapsules with an imperfect polymeric covering layer, and **c** hollow microcapsules with wrinkled structures and the leakage of paraffin

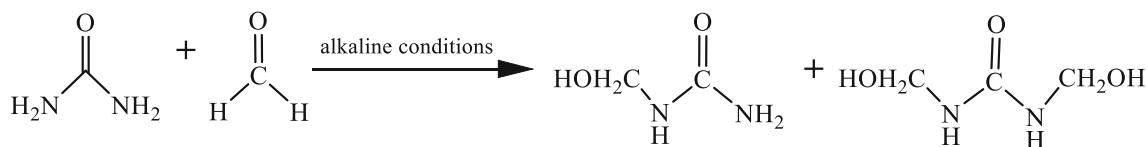


**Fig. 2** DSC profiles of the microcapsules obtained using the one-step method (PUF-MC), poly(urea-formaldehyde) (PUF), and Rubitherm® RT-42 (RT-42)

clear that the formation of microcapsules containing Rubitherm® RT-42 was not successfully carried out.

Next, the reaction mechanism of urea and formaldehyde was divided into two pathways. Firstly, for the formation of the prepolymer, a nucleophilic addition of urea and formaldehyde to form monomethylol and dimethylol urea under alkaline conditions was performed (Fig. 3). Subsequently, for the polymerization process, the hydroxymethyl groups of the mono- and dimethylol molecules reacted under acidic conditions with the imino group and the hydroxymethyl groups of other molecules, resulting in the cross-linking reactions. This second process could be improved with the addition of a cross-linking agent as  $\text{NH}_4\text{Cl}$  [20]. Monomer molecules (monomethylol and dimethylol urea) can be attached to the surface of paraffin droplets leading to their encapsulation. The pH was carefully controlled since it promotes the reaction of urea with formaldehyde in the interface of paraffin droplets, producing a film of urea-formaldehyde polymer as a microcapsule shell [31].

The morphologies of the resulting particles, which are floating and those which are at the bottom of the reaction medium, synthesized through the two-step synthesis process described in section “[Preparation of poly\(urea-formaldehyde\) microcapsules](#),” were studied by SEM. Figure 4a shows spherical microcapsules with heterogeneous particle size distribution. These microcapsules floated due to the low density of the encapsulated paraffin. However, the settled product consisted of broken microcapsules and agglomerated PUF particles (Fig. 4b). DSC analyses of both products were performed. The average latent heat per mass of floated particles was  $75.9 \text{ J g}^{-1}$  (which corresponds to a percentage of Rubitherm® RT-42 encapsulated equal to 48.6 wt%), whereas that of the settled particles was  $0 \text{ J g}^{-1}$ , which means that the encapsulation process did not proceed. This finding means

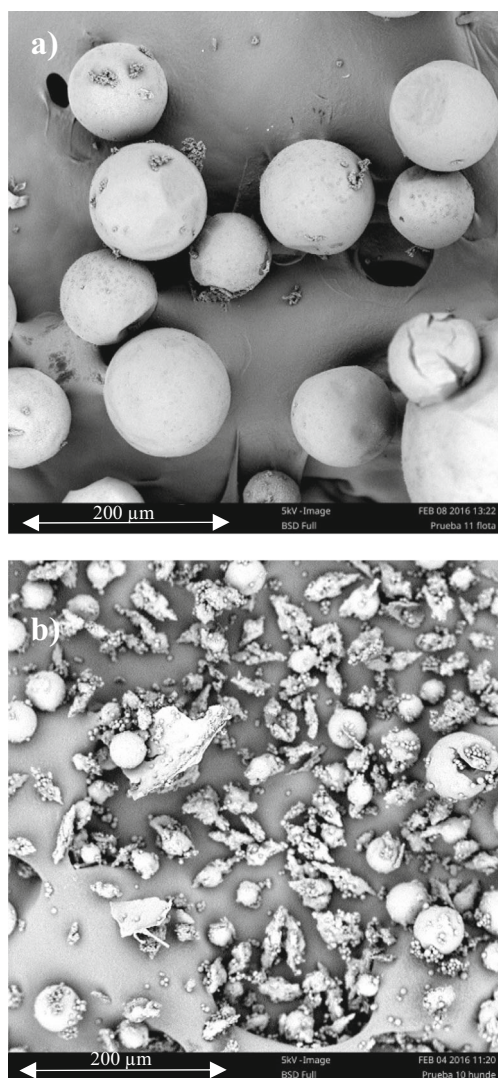


**Fig. 3** Scheme of the prepolymerization reaction for the formation of monomethylol and dimethylol urea under alkaline conditions

that the microencapsulation only took place successfully for the floating product, being its mass yield of 41.6 wt%.

Chemical characterization of the PUF microcapsules (PUF-MC) and Rubitherm® RT-42 (RT-42) was carried out using FT-IR spectroscopy (Fig. 5). The FT-IR spectrum of PUF-MC showed bands in the 3500–3000  $\text{cm}^{-1}$  region corresponding to the stretching vibration of the N–H and O–H bonds. A C–H stretching or bending vibration was observed at 1477  $\text{cm}^{-1}$ ,

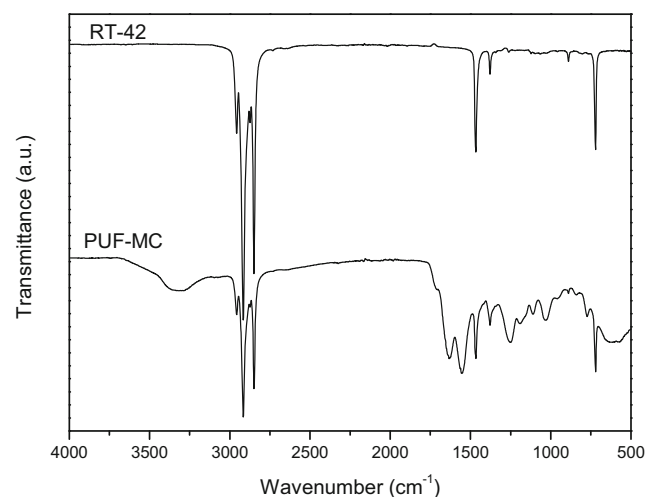
a N–H stretching vibration at 1565  $\text{cm}^{-1}$ , and a C=O stretching vibration at 1625  $\text{cm}^{-1}$ ; a C–N stretching vibration was detected at 1250  $\text{cm}^{-1}$ , whereas ether bridges were observed at 1130  $\text{cm}^{-1}$  [27, 28], thus confirming the formation of a poly(urea-formaldehyde) shell in sample PUF-MC. The absorption peaks corresponding to RT-42 at 2957, 2924, and 2854  $\text{cm}^{-1}$  were also detected in the PUF-MC spectrum [29], thus demonstrating the encapsulation of Rubitherm® RT-42.



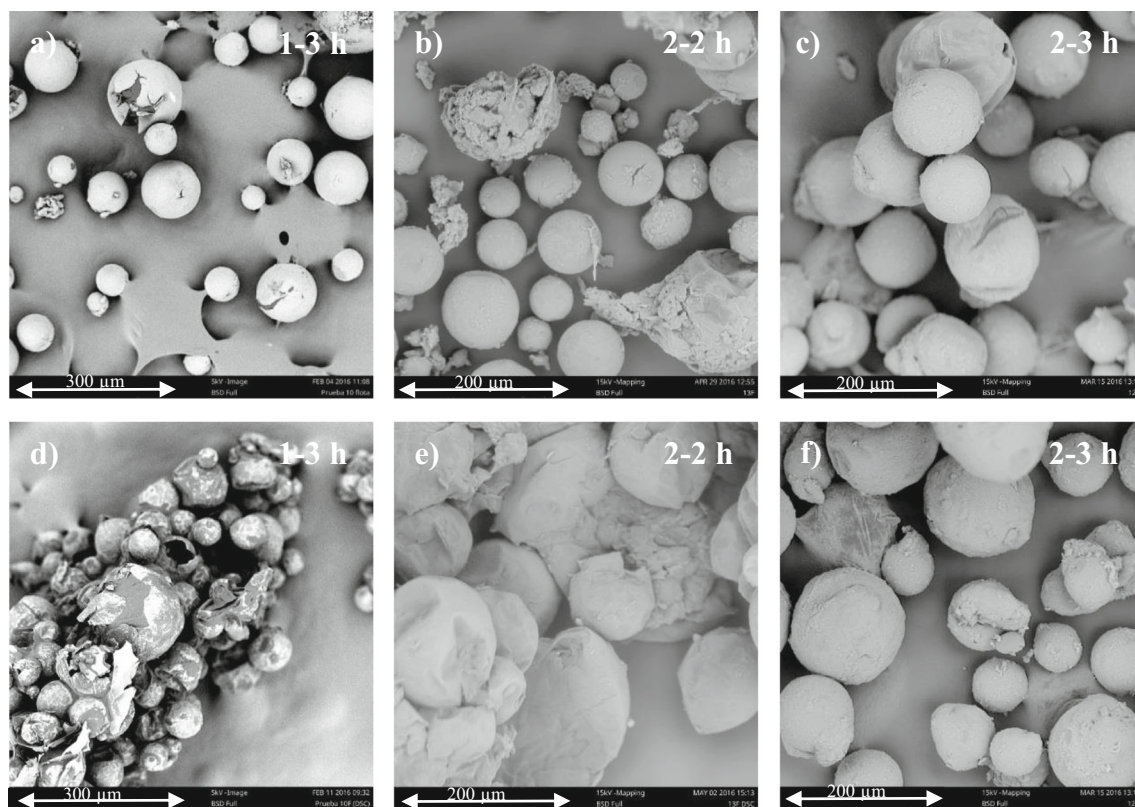
**Fig. 4** SEM micrographs of the resulted products using the two-steps method. **a** Floating spherical microcapsules with heterogeneous particle size distribution and **b** settled product consisted of broken microcapsules and agglomerated PUF particles

### Influence of prepolymerization/polymerization reaction time

The effect of the prepolymerization and polymerization times on the PUF microcapsules synthesis using 1–3, 2–2, and 2–3 h was evaluated (set 1, Table 1). The resulting PUF microcapsules were visualized by SEM analyses (Fig. 6a–c). As can be seen, the aspect of the microcapsules improved when the prepolymerization time increased from 1 to 2 h. For the latter, microcapsules obtained at polymerization times of 2 and 3 h showed a perfect polymeric covering layer (Fig. 6b, c, respectively). However, microcapsules obtained in experiments 2–3 showed an irregular morphology (Fig. 6c). These results clearly indicate that the structure of the generated PUF microcapsules strongly depends on the reaction time.



**Fig. 5** FT-IR spectra of the phase change material (RT-42) and the microcapsules obtained (PUF-MC)



**Fig. 6** SEM micrographs of the PUF microcapsules obtained using 1–3, 2–2, and 2–3 h prepolymerization/polymerization times. **a–c, d–f** After heating them above their melting point

Table 2 reports the amount of Rubitherm® RT-42 encapsulated, the PUF microcapsules mass yield, the mean diameter, and the morphology of the microcapsules obtained.

DSC profiles for the PUF microcapsules prepared using different reaction times are shown in Fig. 7. The melting heats per mass unit of the microcapsules prepared (combination of pre- and polymerization times 1–3, 2–2, and 2–3) increased with the reaction time until a maximum was reached ( $65.8$ ,  $118.5$ , and  $103.6 \text{ J g}^{-1}$ , respectively). Therefore, the highest RT-42 encapsulated content was obtained ( $94.8 \text{ wt}\%$ ) for the combination of pre- and polymerization times of 2–2 h. The physical stability of these microcapsules was evaluated by heating these samples above their melting point. The resulting materials were observed by means of SEM (Fig. 6d–f). Thus, only the PUF microcapsules obtained using the combination of pre- and polymerization times 2–3 h (Fig. 6f) maintained their structure without any appreciable leakage of Rubitherm® RT-42.

On the basis of the results obtained, PUF microcapsules synthesized using the combination of pre- and polymerization times 2–3 h were selected as the reference for further studies due to the fact that the highest PUF microcapsules yield ( $50.2 \text{ wt}\%$ ) and an acceptable encapsulation efficiency ( $74.4 \text{ wt}\%$ ) were obtained and a perfect polymeric shell was observed.

### Influence of reaction temperature

The effect of the reaction temperature on the thermal properties and morphology of the prepared microcapsules were investigated (set 2, Table 1). It was studied temperatures higher than the melting point of Rubitherm® RT-42 ( $\geq 48 \text{ }^\circ\text{C}$ ) to ensure a liquid phase. In addition, it was checked that at low reaction temperatures ( $\leq 60 \text{ }^\circ\text{C}$ ), the organic phase was not well dispersed in the aqueous medium. According to Carfagna [30], the urea-formaldehyde system predominantly reacts in the water phase.

Table 2 reports RT-42 content, mass yield, mean diameter, and morphology of the microcapsules obtained. The higher the reaction temperature, the higher the RT-42 content and the PUF microcapsule yield were. According to Rochmadi et al. (2010), microcapsule formation increased with the increase of temperature due to the participation of the hydrogen of the amino group in the reaction and the formation of a methylene bridge structure [31]. However, at  $80 \text{ }^\circ\text{C}$ , the microencapsulation was not successful. In this sense, Xin et al. 2014 [20] reported that at temperatures higher than  $70 \text{ }^\circ\text{C}$ , the polymerization speed of the urea-formaldehyde system is too fast, resulting in larger particles with a wider particle size distribution [32]. Therefore, the process of microencapsulation of RT-42 Rubitherm® should be developed between  $60$  and  $70 \text{ }^\circ\text{C}$  [33].

**Table 2** Encapsulation efficiency, mass yield, average diameter, and morphology of the poly(urea-formaldehyde) microcapsules obtained from different set of experiments

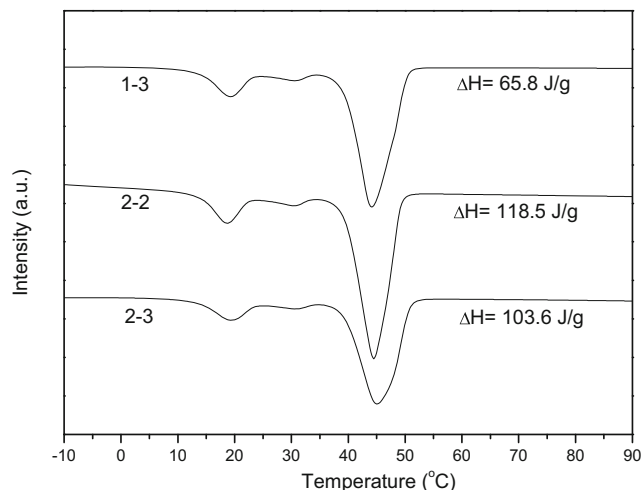
Set of experiments	RT-42 content (wt%)	PUF-MC mass yield (%)	Mean diameter from SEM ( $\mu\text{m}$ )	Morphology from SEM	
Prepolymerization-polymerization time (h)	1–3	48.6	41.6	133	Spherical with smooth surface and cracks
	2–2	94.8	39.8	132	Spherical with smooth surface and PUF aggregates
	2–3	74.4	50.2	160	Irregular with rough surface
Temperature ( $^{\circ}\text{C}$ )	60	74.4	50.2	160	Irregular with rough surface
	70	84.7	68.1	145	Spherical with smooth surface and PUF aggregates
	80	0.00	36.5	–	Not microcapsules observed
Monomers/PCM mass ratio (g/g)	0.5	–	–	–	Not microcapsules observed
	0.6	84.7	60.9	75	Spherical with smooth surface and PUF aggregates
	0.8	90.6	44.4	172	Spherical with smooth surface
	1.0	102.3	35.7	142	Spherical with smooth surface and cracks

SEM micrographs of the PUF microcapsules synthesized using different reaction temperatures are shown (Fig. 8). Microcapsules prepared at  $60^{\circ}\text{C}$  presented an irregular form and a rough surface (Fig. 8a). At  $70^{\circ}\text{C}$ , the morphology of the particles synthesized tended to be spherical with smooth surface whereas the particle size distribution seems to be less uniform (Fig. 8b). At  $80^{\circ}\text{C}$ , no PUF microcapsules were formed (Fig. 8c).

A reaction temperature of  $70^{\circ}\text{C}$  was selected in the next study due to the PUF microcapsules obtained at this temperature presented the highest RT-42 content (84.7 wt%) and a maximum PUF microcapsules yield was obtained (60.9 wt%).

### Influence of monomers/PCM mass ratio

The formation of methylol groups mostly depends on the formaldehyde/urea molar ratio. Molar ratio higher than 1.8 improved the tendency to form highly methylolated species

**Fig. 7** DSC profiles of the microcapsules obtained at different prepolymerization-polymerization times

[34, 35]. In addition, Xin et al. 2013 reported that the highest encapsulation efficiency was obtained when the molar ratio of formaldehyde/urea was equal to 1.8. In this study, a closest value to this molar ratio (1.88) was used [36].

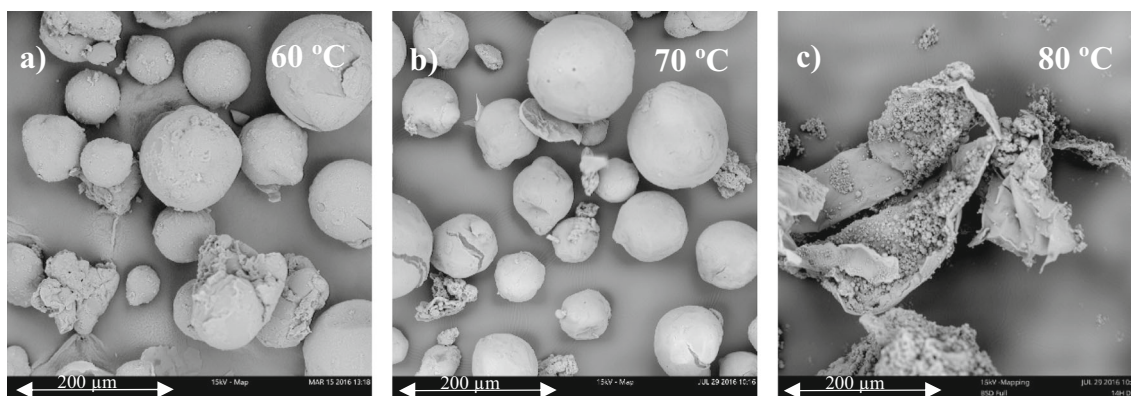
The influence of the monomers/PCM mass ratio on the PUF microcapsules formation was studied (Table 1, set 3). The experiment carried out using a mass ratio of 0.5 (Table 2) was not successful. This fact could be a consequence of the shortage of the polymer chains that could not completely cover the total amount of Rubitherm® RT-42 added.

The higher the monomers/PCM mass ratio, the higher the RT-42 contained in the PUF microcapsules was (84.7, 90.6, and 102.3 wt% corresponding to 132.4, 141.6, and 159.9  $\text{J g}^{-1}$ , respectively) (Table 2). On the contrary, the PUF microcapsule yield decreased when the monomers/PCM mass ratio was higher than 0.6, which means that the formation of PUF aggregates increased, and accordingly the PCM content in the microcapsule can be increased due to the higher availability of the shell material (Table 2).

Figure 9 shows the SEM micrographs of the PUF microcapsules after heating them above the melting point of Rubitherm® RT-42. Figure 9a confirms the presence of an excess of PCM promoted an easy breakage of the microcapsule shell. The surface of the microcapsules became rough with increasing values of the monomers/PCM mass ratio. According to the SEM micrographs, microcapsules obtained using 0.8 of monomers/PCM mass ratio maintained its physical stability after heating (Fig. 9c). Thus, an optimum value of the monomers/PCM mass ratio of 0.8 was selected.

### Conclusion

Rubitherm® RT-42 paraffin wax was successfully encapsulated by means of in situ polymerization using poly(urea-

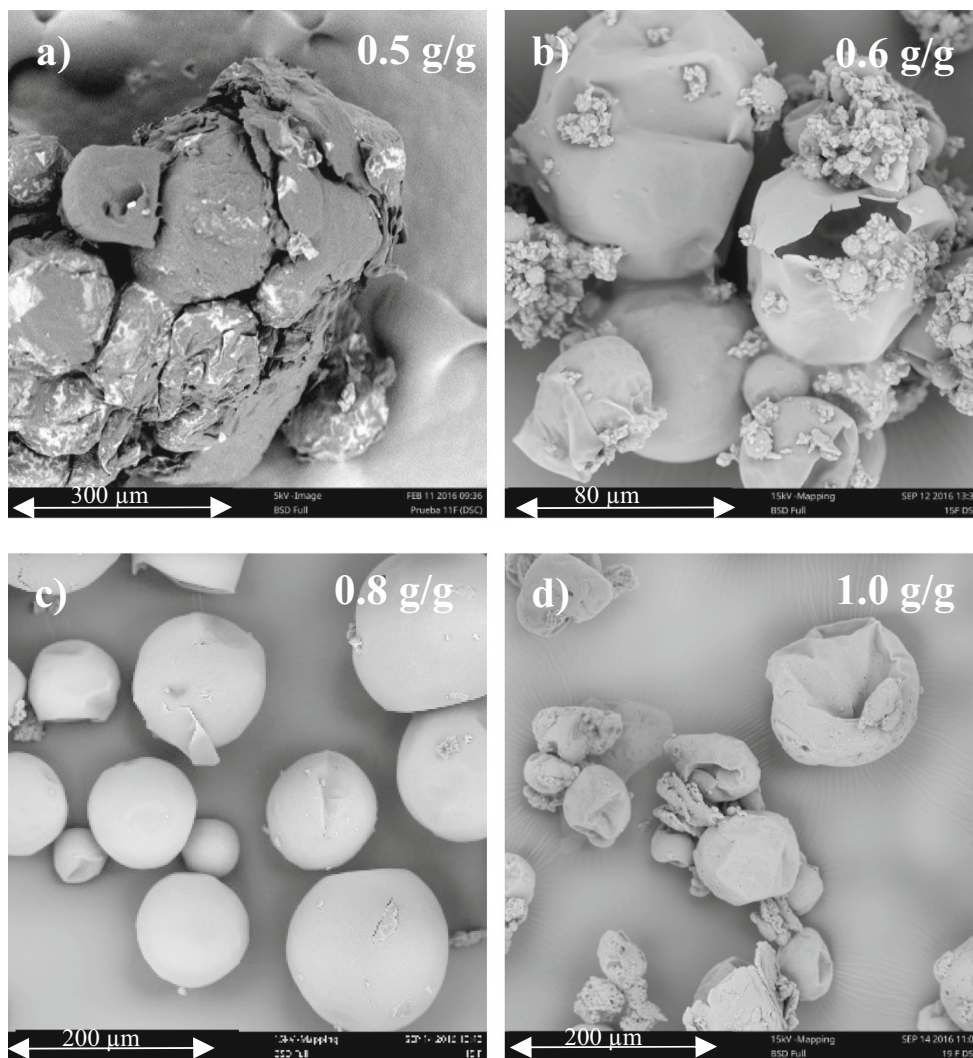


**Fig. 8** SEM micrographs of the microcapsules obtained at **a** 60 °C, **b** 70 °C, and **c** 80 °C

formaldehyde) as the shell. The reaction conditions and the amounts of reagents were sequentially studied and optimized to obtain a high encapsulation efficiency (90.6 wt%). The structure and occurrence of the PUF microcapsules strongly depended on the prepolymerization/polymerization time, being the optimum combination 2–3 h. The highest

encapsulation of Rubitherm® RT-42 and formation of spherical microcapsules with a smooth surface was obtained at 70 °C and using a monomers/PCM mass ratio of 0.8. The stability, non-corrosive, and non-toxic character in nature and low cost of the paraffin wax make possible the microcapsules here prepared suitable to be used in different

**Fig. 9** SEM micrographs of the microcapsules obtained at different monomers/PCM mass ratios after heating them above their melting point. **a** 0.5 g/g, **b** 0.6 g/g, **c** 0.8 g/g, and **d** 1.0 g/g





industrial applications (solar panels, heat exchangers, and air conditioning systems).

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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