

Development of an encapsulated phase change material via emulsion and coaxial electrospinning

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ABSTRACT: This article reports on the encapsulation of a phase change material (PCM) into a hydrophilic polymer, poly(vinyl alcohol) (PVOH), by means of electrospinning. Different strategies were carried out to improve the thermal buffering capacity and the stability of the developed structures when they were exposed to different relative humidity (RH) conditions. On the one hand, the thermal energy storage capacity of PVOH/PCM structures obtained through emulsion electrospinning was optimized by using different amounts of polyoxyethylene sorbitan monolaureate (Tween 20). Surfactant addition successfully increased the heat storage capacity of the developed structures, reaching an optimum performance at a concentration of 0.32% in weight with respect to the total emulsion weight. However, the hydrophilic nature of the developed structures made them extremely difficult to handle due to swelling with increasing RH. To avoid this issue an additional shell layer of poly(caprolactone) (PCL), was applied by coaxial electrospinning. In this case, the PVOH/PCM ratio (core) was optimized to reach the highest heat storage capacity per gram of sample and, then, a PCL solution was used as a shell material to hydrophobize the structures. The optimized coaxial electrospun structures were able to encapsulate about 82% of PCM. The use of both emulsion and coaxial electrospinning strategies are introduced here for the first time as advanced strategies to overcome application issues such as unintended migration and performance drop in the previously developed monophasic materials. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43903.

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INTRODUCTION

In the last decades, phase change materials (PCMs) have received great attention in many application areas because of their high energy storage density in a reduced temperature range.^{1–8} However, the use of these materials in thermal energy storage applications presents some drawbacks, such as weak thermal stability and low thermal conductivity.⁹ To overcome these problems, research efforts are currently focused on the development of new encapsulation strategies to improve the heat management capacity of these materials. Among the encapsulation techniques available, the electro-hydrodynamic processing, commonly termed as electrospinning when it generates fibers, has lately arisen as an innovative route to encapsulate PCMs. Electrospinning makes use of high voltage electric fields to produce electrically charged jets from viscoelastic polymer solutions, which upon drying produce ultrathin polymeric structures.^{7–10}

In the encapsulation area, Perez-Masia *et al.*,¹¹ reported that paraffins (such as dodecane) can be properly encapsulated by means of electrospinning, inside hydrophobic matrices such as poly(lactic acid) (PLA) and poly(caprolactone) (PCL) with a submicron drop

size, albeit PCL provides better encapsulation performance. However, a temperature mismatch between melting and crystallization phenomena (the so-called supercooling effect) was observed in the encapsulated paraffin, mainly ascribed to the reduced PCM drop size inside the fibers. They also reported that the addition of a nucleating agent in the hybrid structures, allowed a significant amount of heat storage capacity for these systems without supercooling. However, Chalco-Sandoval *et al.*,^{12,13} stated in previous works that the use of hydrophobic polymers such as poly(caprolactone) (PCL) and polystyrene (PS) as encapsulating matrices of hydrophobic PCMs (mainly paraffins), apart from resulting in significant variations in the thermal properties of the materials related to multiple crystallization events and increased supercooling degree, led to PCM migration and hence to a drop in performance during storage. This was attributed to the fact that the shell encapsulating matrices could interact with the paraffin favoring migration out of the capsule. This resulted in a decrease in the heat storage capacity of these materials over time and can potentially lead to safety issues in food packaging due to unintended migration of the PCM. Several authors stated that hydrophilic shell materials are the best candidates to encapsulate hydrophobic substances¹⁴ since they are

immiscible with the core material, favoring a phase separation between the core and the shell and thus reducing transport phenomena such as migration by permeation through the pore wall material. Nevertheless, the main disadvantage of using hydrophilic matrices is that the hybrid structures thus prepared are highly swellable and can solubilize in water at high relative humidity (RH) conditions. Therefore, the application of these types of structures seems compromised and there is a need to ensure proper protection from swelling/dissolution, preserving the integrity of the developed structures to avoid both undesirable migration from packaging to goods and diminished temperature-buffering performance.

Thus, the purpose of this work was to develop stable electrospun heat management polymeric materials with high temperature buffering capacity. To this end, the first part of the work was aimed at the development of an approach for the preparation of electrospun structures through emulsion electrospinning by using a hydrophilic material [poly(vinyl alcohol), PVOH] to encapsulate a PCM, which melted around 5 °C (RT5). PVOH, aside from being an excellent barrier material to non-polar substances such as paraffins, is characterized by having good mechanical properties, high gas barrier, chemical stability and being easily electrospinnable from water solutions.¹⁵ To optimize the incorporation of the water insoluble PCM within the hydrophilic PVOH structures a surfactant was incorporated to the polymer-PCM emulsion to produce stable solutions.

Secondly, the coaxial electrospinning processing was used to protect the PVOH/PCM hydrophilic structures from humidity by applying a hydrophobic polymeric solution of poly(caprolactone) (PCL) as a shell material. This biopolymer was selected as the shell material of the emulsion electrospun structures, because aside from being a biodegradable hydrophobic polymer, it showed stable electrospinning and from previous work, it demonstrated to provide good encapsulation yields.¹⁶

The developed core-shell structures were characterized in terms of heat storage capacity, morphology and their stability under different RH conditions was also evaluated.

EXPERIMENTAL

Materials

Rubitherm RT5, which has a melting point at 5 °C, was chosen as a PCM. RT5 is a technical grade paraffin wax based on normal paraffin waxes (C14–C18). RT5 was purchased from Rubitherm Technologies GmbH (Berlin, Germany). The poly(caprolactone) (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium). Poly(vinyl alcohol) (PVOH) was kindly donated by Plásticos Hidrosolubles (Spain). The polyoxyethylene sorbitan monolaurate (Tween 20) was supplied by Sigma-Aldrich and used as emulsifier. *N,N*-dimethylformamide (DMF) with 99% purity and trichloromethane (TCM) (99% purity) were purchased from Panreac Quimica S.A. (Castellar del Vallés, Spain) and used as solvents for the PCL. All products were used as received without further purification.

Preparation of Electrospun Hybrid Structures

Preparation of PVOH/PCM Emulsions and PCL Solutions. The PVOH/PCM emulsions were prepared by dissolving a 13% w/w of PVOH in distilled water under magnetic stirring at 25 °C for

1 h until it was completely dissolved. Afterwards, 7% in weight (wt %) of RT5 was added to the PVOH solution and different amounts of surfactant (Tween 20) were also incorporated to the PVOH/PCM dispersions (see Table I). The resulting dispersions were homogenized at 12,000 rpm for 5 min using a rotor–stator homogenizer (Ultraturrax T25, Janke and Kunkel, Germany).

In the case of coaxial electrospinning, the amount of PCM in the emulsion was increased up to 24% in weight respect to the amount of sample (wt %). Specifically, three more PCM concentrations were tested (11, 16, and 24% in weight).

The PCL solution used as shell material for coaxial electrospinning was prepared by dissolving 5% in weight (wt %) of PCL, under magnetic stirring for 1 h, in a solvent prepared with a mixture of trichloromethane:*N,N*-dimethylformamide (85:15 w/w).

Electro-Hydrodynamic Processing. The process for PCM encapsulation through high voltage spinning has been previously developed and described.¹⁷ The RT5 was encapsulated within the biopolymer matrices (PVOH and PCL) by means of a FluidnatekTM coaxial electrospinning LE-500 pilot plant system (Bioinicia S.L., Valencia, Spain) equipped with a double polarizer setup able to provide up to 60 kV and a high throughput multinozzle injector. This equipment also allows the system to operate in a laboratory mode with one nozzle for experimental design.

Initially, uniaxial electrospinning was carried out to prepare the electrospun hybrid structures from an emulsion composed of a 14% in weight (wt %) of PVOH, 7% in weight (wt %) of PCM, and different concentrations of Tween 20 (0, 0.16, 0.32, and 0.48) (cf. Table I). The distance between the emitter and the collector was set at 18 cm. The electrospun hybrid structures were obtained using a voltage of around 10 kV and a flow rate of 2 mL/h.

For the coaxial electrospinning, two different dispersions were prepared to form the core-shell electrospun hybrid structures. The core material was based on the PVOH-PCM emulsion already described in Table I and the shell material was prepared by dissolving 5% in weight of PCL in a mixture of solvents as described in the previous section. The electrospinning conditions for obtaining the coaxial electrospun nanostructures were optimized and fixed at 1 mL/h and 1.5 mL/h of flow-rate, respectively, for the inner and outer solutions; the emitter-to-collector distance was 28 cm, and a voltage of 10.8 and –1.35 kV for the emitter and collector, respectively, were used.

Characterization of the PVOH/PCM Emulsion and PCL Solution Properties

The viscosity, surface tension, and conductivity of the neat PVOH and PCL solutions and the PVOH/PCM dispersions were measured before the electro-hydrodynamic processing. The viscosity was measured using a rotational viscosity meter Visco Basic Plus L from Fungilab S.A. (San Feliu de Llobregat, Spain) using a Low Viscosity Adapter (spindles LCP and L1). The surface tension was measured using the Wilhemy plate method in an EasyDyne K20 tensiometer (Krüss GmbH, Hamburg, Germany). The conductivity was measured using a conductivity

Table I. Composition of Electrospinning-Solutions

Type of polymer	Solvents						
	Wt % (g polymer/100 g of sample)	Wt % (g surfactant/100 g of sample)	Wt % (g PCM/100 g of sample)	Wt % (g water/100 g solvents)	Wt % (g trichloromethane (TCM)/100 g solvents)	Wt % (g dimethylformamide (DMF)/100 g solvents)	
Interior	—	—	—	—	—	—	—
Exterior	13	0.00	7	100	—	—	—
PVOH	13	0.16	—	—	—	—	—
	5	0.32	—	—	—	—	15
PVOH	13	0.32	24	100	—	—	—
PCL	5	—	—	—	85	—	15

meter XS Con6+ (Labbox, Barcelona, Spain). Measurements were done at 25 °C and all tests were carried out, at least, in triplicate.

Characterization of the Electrospun Hybrid Structures

Differential Scanning Calorimetry (DSC). Thermal analysis was carried out on the just prepared structures by means of a DSC analyzer (Perkin Elmer, Inc., DSC 7, USA) from −20 °C to 20 °C in a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2, Perkin Elmer, USA). The scanning rate was 2 °C/min to minimize the influence of this parameter in the thermal properties. Small amounts (1–2 mg approximately) of dry samples were placed into aluminum pans (Perkin Elmer, DSC, BO14). An empty aluminum pan was used as a reference. The enthalpy results obtained were corrected taking into account the PCM content. All tests were carried out in triplicate.

Scanning Electron Microscopy (SEM). The morphology of the electrospun hybrid structures was analyzed using a Hitachi S-4100 microscope (Hitachi LTD, Tokyo, Japan) at an accelerating voltage of 10 kV. The electrospun hybrid structures were fixed on copper stubs using double side adhesive tape and sputter, coated with a mixture of gold-palladium. The diameters were measured by means of the Adobe Photoshop CS6 extended software from the SEM micrographs in their original magnification.

Environmental Scanning Electron Microscopy (ESEM). The effect that the relative humidity had on the morphology of electrospun hybrid structures was carried out by means of a Philips XL-30 microscope, model PV 9760 (Eindhoven, Holland) at an electron accelerating voltage of 20 kV, magnifications of 500–1,500 times, a working distance ranged from 10.2 to 10.9 mm and the diameter of the electron beam (spot) ranged from 5 to 6 mm, depending on the magnitude used to observe the image. The electrospun hybrid structures were placed directly onto the sample-holder microscopy equipment and the structures were hydrated or dehydrated by controlling the temperature and chamber pressure to favor water condensation or evaporation at different relative humidity (RH) levels.

Statistical Analysis

Results were analyzed by multifactor analysis of variance (ANOVA) using Statgraphics Centurion 15.1 software (Statpoint Technologies, INC, Warrenton, VA, USA). Fisher's least significant difference (LSD) was used at the 95% confidence level.

RESULTS

PCM Encapsulation in PVOH by Electrospinning

In the first part of this work, electrospun PVOH/PCM hybrid structures were optimized to obtain the highest thermal buffering capacity. Taking into account previous studies in which it has been demonstrated that the morphology of the structures played an important role on the energy storage capacity and PCM was better encapsulated in fibrillar structures (providing higher energy storage capacity),^{18,19} the concentration of the PVOH was optimized to obtain fibers. Therefore, based on the screening studies during electrospinning of PVOH fibers, the optimum concentration of the polymer matrix was found to be 13% in weight (wt %) in water and the amount of PCM was fixed in 7% in weight (wt %) since at this concentration, the emulsion provided better

Table II. Viscosity, Conductivity, and Surface Tension Values of the Electrospinning-Solutions Used

Dissolution	Viscosity (cP)	Surface tension (mN/m)	Conductivity ($\mu\text{S/cm}$)
Rubitherm RT5	2 (1) ^a	73 (2) ^a	0.010 (0.005) ^a
13 wt % PVOH in water	219 (1) ^b	39.9 (0.9) ^{de}	359 (1) ^b
5 wt % PCL in DFM:TCM	29 (6) ^c	34 (3) ^b	-
PVOH/PCM emulsion containing 7 wt % of PCM (without surfactant)	393 (12) ^d	45.0 (1.8) ^c	291 (3) ^c
PVOH/PCM emulsion containing 7 wt % of PCM and 0.16 wt % of surfactant	408 (18) ^e	41.2 (1.0) ^d	290 (4) ^c
PVOH/PCM emulsion containing 7 wt % of PCM and 0.32 wt % of surfactant	481 (15) ^f	37.7 (1.5) ^e	286 (5) ^c
PVOH/PCM emulsion containing 7 wt % of PCM and 0.48 wt % of surfactant	551 (21) ^g	36.5 (1.1) ^e	291 (4) ^c
PVOH/PCM emulsion containing 15.9 wt % of PCM and 0.32 wt % of surfactant	661 (10) ^h	42.8 (2.0) ^{cd}	185 (9) ^d

Mean value (standard deviation).

^{a-h}Different superscripts within the same column indicate significant differences ($P < 0.05$).

encapsulation structures and the PCM was not exuded as occurred when higher amounts of PCM were used. Taking into account these aspects, the encapsulation efficiency of these emulsion electrospun structures was optimized by adding a surfactant (Tween 20) to the PVOH/PCM emulsion systems. Tween 20 is a non-ionic amphiphilic compound, which has previously demonstrated to stabilize the electrospinning process from aqueous solutions.²⁰ The different solutions prepared were characterized in terms of viscosity, surface tension, and conductivity and the results are gathered in Table II.

The results show that the viscosity and surface tension behave differently as a function of surfactant addition. As expected, surface tension was significantly reduced with surfactant addition, fact that can be explained by the amphiphilic character of this compound,²¹ reaching a plateau value, which corresponds to the Critical Micellar Concentration (CMC) of this type of solution, since no significant differences were observed between those prepared with 0.32 and 0.48 wt %. Regarding the viscosity, it is well known that the viscosity of the solutions depends on the polymer concentration, on the viscosity of the solvents and also on the polymer-solvent interactions.^{22,23} In the present work, an increase in the viscosity values was observed upon PCM addition (without surfactant) which can be explained by the increase in the mass fraction of total solids in the emulsion. It is well known that the polymer chain can be fully extended when a good solvent is used to dissolve the polymer, which is the case of the neat PVOH in water. However, PVOH/PCM emulsions were more viscous than the PVOH solution due to the higher amount of solids in the oil in water (O/W) emulsion. It is worth noting that the viscosity values significantly increase by the addition of Tween 20, which could be mainly attributed to polymer-surfactant and PCM-surfactant interactions, resulting in a change in solution rheology. Finally, conductivity values were not significantly altered by the addition of the surfactant probably due to the absence of electrical charges in the Tween 20.

Figure 1 illustrates the morphology attained for the PVOH and PVOH/PCM emulsion-electrospun hybrid structures, showing that it was greatly influenced by both PCM addition and surfactant addition and concentration. As observed in Figure 1(A), PVOH forms uniform fibers in which more than 90% of them exhibit a diameter size below 0.5 μm , thus highlighting the more stable electrospinning of the polymer in water. However, microscopy images of PVOH/PCM fibers revealed some beaded areas which diameter varied depending on the surfactant concentration [Figure 1(B–E)]. It is worth noting that the morphology of the PVOH/PCM emulsion electrospun structures without surfactant was rather heterogeneous and the addition of PCM greatly increased the number of beaded fibers, also increasing their average size and heterogeneity [cf. Figure 1(B)]. Upon surfactant addition, a more homogeneous morphology was attained and the amount of fibers with diameters lower than 0.5 μm increased again near to 60% as the surfactant concentration increased in the emulsion electrospun hybrid structures. Many researchers had found a similar result.^{24–26} For instance, Jia and Qin²⁷ observed that in the case of non-ionic surfactants, with the increasing of the surfactant content in poly(vinyl alcohol) solutions, the diameters of the nanofibers decreased significantly. This indicates that surfactant addition effectively stabilized the emulsion and more uniform fibers and beaded areas were obtained [Figure 1(C–E)]. Therefore, during the emulsification process, surfactant plays an important role in the steric stabilization, inhibiting the droplets coalescence. In addition, an increase in the viscosity values as the surfactant concentration increased (cf. Table II), could lead to an increase in the average distance between the stabilized PVOH/PCM droplets in the emulsion, reducing droplet movement and slowing down the coalescence or aggregation of the stabilized PVOH/PCM droplets and thus, the diameter of beads obtained after the electrospinning process decreased.

For the potential application in thermal energy storage, the most desirable characteristics of the PCM hybrid structures are high latent heat and targeted phase transition temperatures.

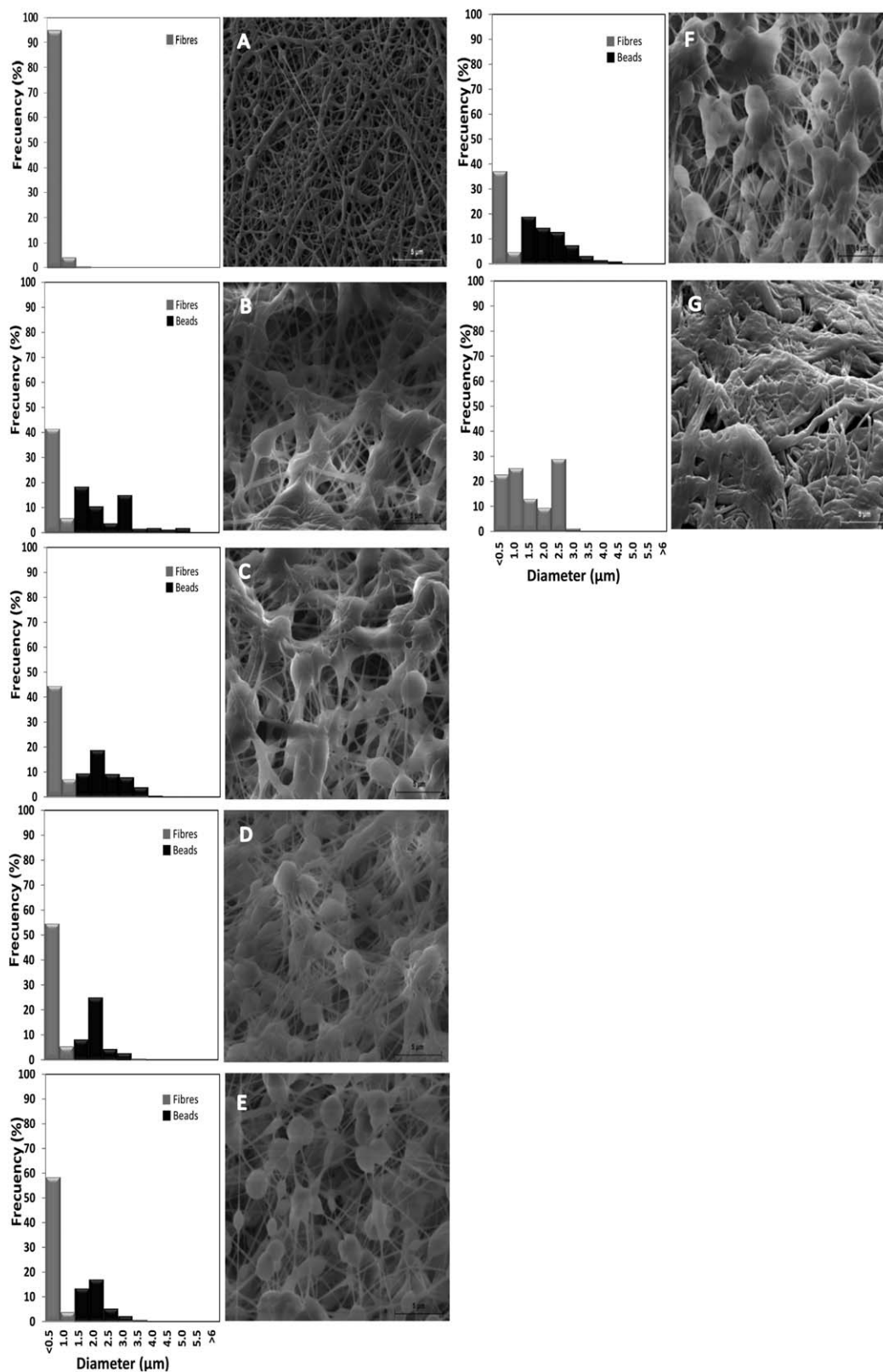


Figure 1. SEM images of the electrospun hybrid structures: electrospun uniaxial PVOH/PCM hybrid structures prepared without PCM and surfactant (A), with 7% of PCM and without surfactant (B), with 7% of PCM and 0.16% of surfactant (C), with 7% of PCM and 0.32% of surfactant (D), with 7% of PCM and 0.48% of surfactant (E), with 24% of PCM and 0.32% of surfactant (F), and electrospun coaxial PVOH/PCM/PCL hybrid structures prepared with 24% of PCM and 0.32% of surfactant (core material) and PCL at 5 wt % (shell material) (G).

Table III. Melting Enthalpy Values of PVOH/PCM Emulsion Electrospun Structures Prepared with 0.32 wt % of Tween 20 and Different PVOH/PCM Ratios

Wt % polymer/100 g of sample	Wt % PCM/100 g of sample	ΔH_m	
		[J/g PCM]	(J/g sample)
13.0	7.0	133 (4) ^a	59 (4) ^a
13.0	10.6	128 (2) ^{ab}	65 (2) ^{ab}
13.0	15.9	122 (3) ^{bc}	71 (3) ^{bc}
13.0	24.1	117 (3) ^c	76 (3) ^c

Mean value (standard deviation).

^{a-c}Different superscripts within the same column indicate significant differences ($P < 0.05$).

Therefore, the heat storage capacity of the emulsion electrospun structures based on PVOH/PCM was evaluated in terms of their thermal properties by means of DSC. Table III gathers the melting and crystallization temperatures (T_m and T_c), supercooling degree and the corresponding melting and crystallization enthalpy values (ΔH_m and ΔH_c) normalized to the PCM content of the electrospun hybrid structures. In contrast to that previously observed for PLA/PCM and PCL/PCM fibres,¹⁸ it can be observed that the melting temperature of the PVOH/PCM electrospun hybrid structures prepared without Tween 20 did not differ from that of the neat PCM (see Table III), indicating that similar PCM crystals were formed in the encapsulation structures probably due to the low compatibility between the paraffin and the hydrophilic polymer, precluding any interaction between both components. However, Pérez-Masiá *et al.*,^{11,18} observed that the melting process of PLA/PCM and PCL/PCM occurred over a broader temperature range in the hybrid structures than in the pure PCM, and the presence of two different melting peaks of the PCM, which was attributed to the formation of two different crystal populations.

Similarly, to that previously reported for PLA and PCL matrices,^{12,18,28} the crystallization phenomenon of PVOH/PCM hybrid structures occurred in multiple steps. In fact, while pure PCM crystallized at 5.4 °C, two crystallization temperatures were detected for the PVOH/PCM hybrid structures which can be ascribed to the

multiple crystallization processes of the N-alkanes ascribed to the rotator phase transitions which are observed in these paraffins when their particle size is reduced.^{12,29,30} However, the supercooling degree of PVOH/PCM hybrid structures did not differ from that obtained for the neat PCM whereas greater supercooling degree was observed for more hydrophobic matrices.^{11,13,18,31}

Concerning the electrospun hybrid structures prepared with surfactants, the onset temperature was the same but the melting temperature range was larger for the encapsulated PCM containing surfactants compared to the neat PCM and emulsion-electrospun structures without surfactants. In these cases, the PCM also showed a multiple crystallization profile and these structures showed a greater supercooling degree (calculated as the difference between the last melting and the first crystallization peaks detected) which can be explained by a reduction of the RT5 particle size, since the number of nuclei needed to initiate the crystallization process is thought to decrease with reducing the diameter of the PCM drops inside the electrospun structures. This effect agreed with the morphology attained in these cases. As previously explained, addition of surfactant resulted in beads with smaller diameters, being this decrease related to surfactant concentration.

PVOH/PCM emulsion-electrospun structures showed lower melting and crystallization enthalpy values than that of the non-encapsulated PCM, which could be ascribed to the fact that part of the PCM was not functional from an energy storage view point. Addition of surfactants greatly increased the melting enthalpy and thus, the encapsulation efficiency up to ~92% in those prepared with 0.32 wt % of Tween 20. This behavior can be explained by the fact that the surfactant decreased the surface tension between the immiscible PVOH/PCM phases by acting at the interface and, thus, the PCM was better entrapped into the PVOH matrix. It should be noted that the encapsulation efficiency was significantly reduced when 0.48% in weight (wt %) was added to the PVOH/PCM emulsion and these differences could be explained by the CMC of the solutions. As previously observed from Table II, this surfactant concentration is above the CMC and, thus, it could be expected that some of the PCM droplets were entrapped into the surfactant micelles due to amphiphilic character of this compound, thus reducing the encapsulation efficiency within the PVOH matrices.

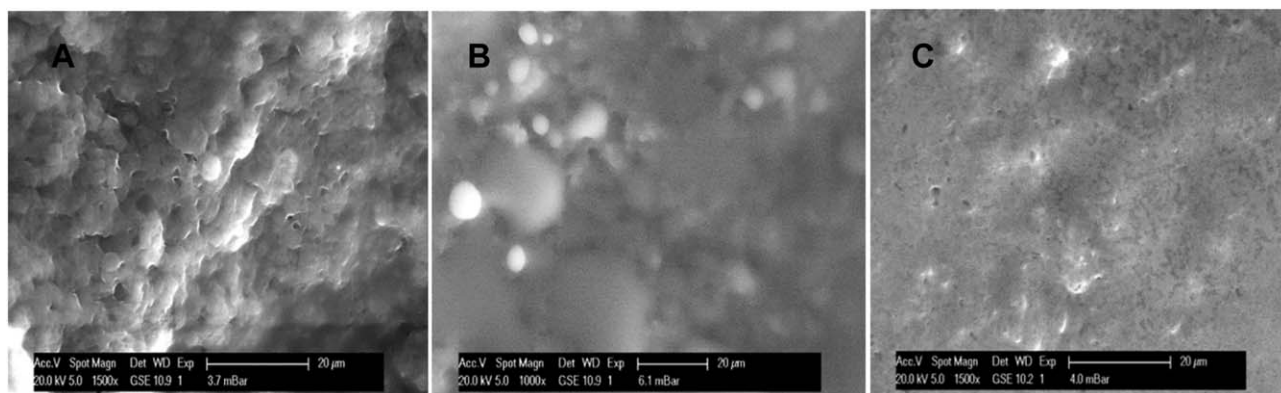


Figure 2. ESEM images of the PVOH/PCM emulsion-electrospun structures prepared with 7% (wt %) of PCM and 0.32% of surfactant conditioned at different relative humidities as follows: (A) 28% RH, (B) 46% RH, and (C) 31% RH.

Table IV. Thermal Properties of the Electrospun Hybrid Structures

Electrospun hybrid structures	T_m (°C)			ΔH_m			ΔH_c			Supercooling (°C)	Efficiency (%)
	Onset (°C)	Peak (°C)	End (°C)	J/g PCM	J/g sample	T_{c1} (°C)	T_{c2} (°C)	J/g PCM	J/g sample		
PCM-1.5°C	3.0 (0.2) ^a	7.2 (0.1) ^a	8.5 (0.2) ^a	144.7 (0.1) ^a	144.7 (0.1) ^a	5.4 (0.1) ^a	-	-144.0 (0.1) ^a	-144.0 (0.1) ^a	1.8 (0.2) ^a	100.0 (0.1) ^a
PVOH/PCM emulsion containing 7 wt % of PCM (without surfactant)	4.0 (0.2) ^b	7.2 (0.1) ^a	8.5 (0.2) ^a	99.2 (2.3) ^b	44.6 (1.0) ^b	5.4 (0.1) ^{ab}	-2.5 (0.2) ^a	-102.8 (2.2) ^b	-46.3 (1.0) ^b	1.8 (0.2) ^a	68.9 (1.6) ^d
PVOH/PCM emulsion containing 7 wt % of PCM and 0.16 wt % of surfactant	4.1 (0.2) ^b	8.2 (0.2) ^c	9.0 (0.2) ^b	129.1 (2.5) ^c	58.1 (1.1) ^c	5.9 (0.2) ^c	-3.9 (0.1) ^b	-132.9 (1.1) ^c	-59.8 (0.5) ^c	2.2 (0.1) ^{bc}	89.6 (1.5) ^b
PVOH/PCM emulsion containing 7 wt % of PCM and 0.32 wt % of surfactant	3.9 (0.1) ^b	7.9 (0.1) ^b	8.9 (0.1) ^b	133.0 (4.2) ^c	59.9 (1.9) ^c	5.9 (0.1) ^c	-3.8 (0.1) ^b	-136.4 (4.8) ^c	-61.4 (2.1) ^c	2.0 (0.1) ^{ab}	92.4 (2.9) ^b
PVOH/PCM emulsion containing 7 wt % of PCM and 0.48 wt % of surfactant	4.1 (0.1) ^b	8.2 (0.1) ^c	8.9 (0.2) ^{ab}	102.3 (1.5) ^b	46.0 (0.7) ^{be}	5.8 (0.1) ^c	-3.3 (0.2) ^c	-108.9 (2.9) ^d	-49.0 (1.3) ^{be}	2.4 (0.2) ^c	71.0 (1.1) ^d
PVOH/PCM emulsion containing 15.9 wt % of PCM and 0.32 wt % of surfactant	4.1 (0.2) ^b	8.2 (0.1) ^c	8.9 (0.2) ^{ab}	117.1 (1.3) ^d	76.1 (0.9) ^d	5.9 (0.1) ^c	-2.7 (0.2) ^d	-121.8 (0.9) ^e	-79.19 (0.6) ^d	2.2 (0.1) ^{bc}	81.4 (0.9) ^c
Coaxial electrospun structures; Core material: PVOH/PCM prepared with 0.32% surfactant and 15.9% of PCM Shell Material: PCL	4.0 (0.2) ^b	7.8 (0.1) ^b	8.7 (0.1) ^a	116.8 (2.2) ^d	48.6 (1.1) ^e	5.7 (0.2) ^{bc}	-2.6 (0.1) ^d	-94.8 (2.2) ^f	-49.8 (1.2) ^e	2.1 (0.1) ^{ab}	81.3 (1.5) ^c

Mean value (standard deviation)

^{a-d}Different superscripts within the same column indicate significant differences ($P < 0.05$).

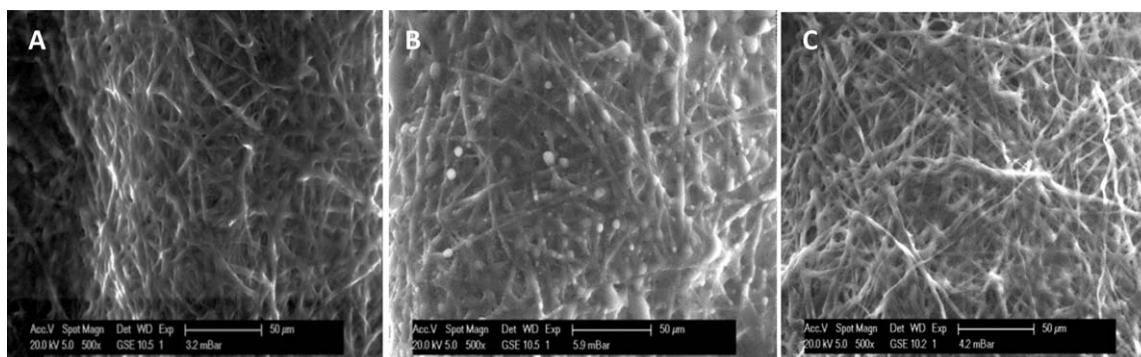


Figure 3. ESEM images of the coaxial hybrid structures prepared with PVOH/PCM emulsion (core material) and PCL (shell material) conditioned at different relative humidity conditions as follows: (A) 28% RH, (B) 46% RH, and (C) 31% RH.

The effect that relative humidity had on the morphology and the swelling phenomenon of the emulsion electrospun PVOH/PCM structures was analyzed by means of Environmental Scanning Electron Microscopy (ESEM). Figure 2 shows the surface of the PVOH/PCM emulsion electrospun structures prepared with 0.32 wt % surfactant at increasing relative humidity. ESEM images reveal a significant swelling as the relative humidity increased from 28 to 46%. The hydrophilic character of these electrospun structures was confirmed after decreasing the RH again down to 31% since the original morphology of the hybrid structures was completely lost upon water sorption if compared to the original samples observed by SEM (dry state) [cf. Figure 1(D)] and even to those previously observed at the same relative humidity [cf. Figure 2(A)]. This aspect limits the practical application of the developed hybrid structures since even at low relative humidity ($\sim 28\%$ RH), the morphology changed, making them difficult to handle. Furthermore, some of the encapsulated PCM could be released during the swelling, thus decreasing the heat storage capacity of these samples. Therefore, from the results obtained in the first part of this work, it was clearly observed that hydrophilic matrices greatly improved the encapsulation efficiency of the PCM (RT5) in comparison with previous works carried out with more hydrophobic materials,^{12,13} although this solution provided a handling problem under environmental conditions.

Encapsulation of the PCM by Coaxial Electrospinning

To overcome the above-mentioned problem, in the second part of this study, a coaxial electrospinning configuration was proposed as a feasible route to increase the hydrophobic character of the developed hybrid structures. In this case, PCL was used as a shell material of the PVOH/PCM emulsion electrospun structures (core material). Firstly, the amount of PCM was optimized to obtain the highest heat storage capacity. To this end, the amount of surfactant was fixed at 0.32 wt % according to the results previously obtained. Table IV gathers the melting enthalpy values of the developed structures, expressed as J/g sample and J/g of PCM. It was observed that the heat storage capacity per gram of sample increased as the PCM amount increased, showing not significant differences between those prepared with 15.9 wt % PCM and 24.1 wt % PCM. Taking into account that higher PCM concentration implied higher exuda-

tion phenomena, 15.9 wt % of PCM was selected to develop the coaxial electrospun structures.

The morphology of the PVOH/PCM emulsion-electrospun structures with the selected PCM concentration (15.9 wt %) was similar to those reported for lower PCM loadings, showing fibers and beaded areas with wider diameter ranges. However, when these structures were externally coated with PCL as a shell material, the morphology of the coaxial hybrid structures was completely different to their counterparts prepared with the uniaxial configuration, showing a fibrous mat with a wide range of diameter sizes and no beaded areas were detected [cf. Figure 1(G)].

Table III displays the thermal properties of the PVOH/PCM electrospun fibers prepared with 15.9 wt % of PCM containing or not PCL as a shell material. The thermal behavior of the PVOH/PCM emulsion electrospun structures was similar to that previously observed for those prepared with lower PCM ratio, although the encapsulation efficiency decreased, probably due to some leaking of the PCM from the PVOH electrospun structures. However, when the PCL was used as a shell material of the PVOH/PCM emulsion electrospun structures, the melting and crystallization temperatures were similar to their counterparts prepared without PCL. The encapsulation efficiency was even maintained by the addition of the PCL outer layer.

The effect of humidity on the morphology and stability of the electrospun coaxial hybrid structures was analyzed by ESEM and the images are shown in Figure 3. In contrast to that previously observed for the uniaxial PVOH fibers, PCL seemed to protect the electrospun structures from swelling and no changes in morphology were observed when they were exposed to increased relative humidity [cf. Figure 3(B)]. This was confirmed by decreasing the relative humidity to the initial conditions [cf. Figure 3(C)], indicating that the PCL was able to protect the electrospun structures from swelling.

CONCLUSIONS

In this work, temperature buffering hybrid structures based on PVOH/PCM were prepared by using the emulsion electrospinning technique. These structures were optimized in terms of thermal properties and morphology by using different amounts of a surfactant (Tween 20) to stabilize the emulsions and favor

incorporation of the PCM within the structures. Surfactant addition successfully increased the heat storage capacity of the developed structures, reaching optimum concentration at 0.32 wt % of Tween 20. However, the hydrophilic nature of the developed structures made them extremely difficult to handle at intermediate and high relative humidity conditions. To overcome this issue, coaxial electrospinning was proposed for the first time as a strategy to improve the stability of these structures by using PCL as a shell material in the developed PVOH/PCM emulsion electrospun structures. Although the encapsulation efficiency slightly decreased in the coaxial electrospun structures, the heat storage capacity per gram of sample increased since the PCM content could be increased within the PVOH core phase due to coaxial processing with PCL. Furthermore, the morphology of the electrospun structures prepared by the coaxial configuration remained largely unchanged when they were exposed to high RH. These materials have strong application interest in the field of temperature buffering in the food chain, with particular value as coatings or pads to be applied to superchilling packaging structures of products such as meat and fish filets to extend their shelf-life.

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