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Development of Temperature Buffering Material Concepts Based on Electro-Hydrodynamic Processing of Interest in the Food Cold Chain

TESIS DOCTORAL

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CERTIFICAN: que la presente memoria titulada **DEVELOPMENT OF TEMPERATURE BUFFERING MATERIAL CONCEPTS BASED ON ELECTRO-HYDRODYNAMIC PROCESSING OF INTEREST IN THE FOOD COLD CHAIN**, que para aspirar al grado de Doctor, presenta Wilson Rolando Chalco Sandoval, realizada bajo su dirección en el Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), reúne las condiciones adecuadas para su presentación como tesis doctoral, por lo que AUTORIZAN al interesado a su presentación.

Valencia, 28 de Mayo de 2015.

Fdo:

José María Lagarón Amparo López Rubio María José Fabra Rovira

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ABSTRACT

The use of latent heat storage materials containing phase change materials (PCM's) is an effective way of buffering thermal fluctuations and has the advantages of high-energy storage density and the isothermal nature of the storage process. The aim of this work was to develop novel heat management materials based on the encapsulation of PCM's for different applications of interest in refrigerated foods. To this end, the electro-hydrodynamic processing was used to encapsulate commercial PCM's with transition temperatures of interest in refrigeration and superchilling within different polymer and biopolymer matrices.

Initially, materials with heat management capacity to be used in refrigeration equipment and packaging applications were designed. To this end, thick slabs, multilayer heat storage structures and polystyrene foam trays containing ultrathin fiber-structured polystyrene/PCM coatings were fabricated through the encapsulation of commercial phase change materials (specifically paraffin's) within different polymeric matrices. The morphology, thermal properties, encapsulation efficiency and temperature profile of the just prepared structures and after three months of storage at 4 and 25ºC were evaluated.

However, the developed electrospun heat management materials showed a multiple crystallization profile, increased supercooling degree (difference between the melting and crystallization temperatures), low encapsulation efficiency and partial diffusion out of the PCM from the electrospun structures during ageing. Therefore, different strategies were been carried out to counteract these drawbacks. One the one hand, thermal energy storage systems including a PCM which crystallize at -1.5ºC were optimized by adjusting the solvent composition in order to obtain hybrid electrospun fibers with thermal properties similar to those of the neat PCM. On the other hand, a hydrophilic shell material based on polyvinylalcohol (PVOH) was used to encapsulate the PCM by using the emulsion electrospinning technique in order to improve the encapsulation efficiency. However, the hybrid structures thus prepared were highly soluble in water at high relative humidity conditions and an extra layer of a more hydrophobic material (polycaprolactone) through coaxial electrospinning was used to protect them from swelling. The use of the coaxial configuration was a good strategy to preserve the morphology of the electrospun structures when exposed to high relative humidity.

RESUMEN

El uso de materiales de almacenamiento de calor latente que contienen materiales de cambio de fase (PCM's) es una manera eficiente de amortiguar las fluctuaciones de temperatura y presenta las ventajas de proveer alta densidad de almacenamiento de energía y la naturaleza isotérmica del proceso de almacenamiento. El objetivo de este trabajo fue desarrollar nuevos materiales con capacidad de gestión de calor mediante la encapsulación de PCM's para diferentes aplicaciones de interés en alimentos refrigerados. Para ello, se utilizó el procesado electrohidrodinámico para encapsular PCM's comerciales con temperaturas de transición de fase de interés en refrigeración y superenfriamiento dentro de matrices poliméricas y biopoliméricas.

Inicialmente, se diseñaron materiales con capacidad de gestión de calor para ser utilizados en equipos de refrigeración y aplicaciones de envasado. Con este propósito, se fabricaron bloques, estructuras multicapa y bandejas de poliestireno que contenían un recubrimiento de fibras nanoestructuradas ultrafinas mediante la encapsulación de materiales de cambio de fase (especialmente parafinas) dentro de diferentes matrices poliméricas. Se evaluó la morfología, propiedades térmicas, eficiencia de encapsulación y perfil de temperatura de las estructuras recién preparadas y después de tres meses de almacenamiento a 4 y 25ºC.

No obstante, se observó que los materiales electroestirados con capacidad de gestión de calor presentaron un perfil de cristalización múltiple, un incremento en el grado de subenfriamiento (diferencia entre las temperaturas de fusión y de cristalización), baja eficiencia de encapsulación y una difusión parcial del PCM de las estructuras electroestiradas durante el periodo de almacenamiento. Para contrarrestar estos efectos, se llevaron a cabo dos estrategias diferentes. Por un lado, se optimizaron los sistemas de almacenamiento de energía térmica incluyendo un PCM que cristaliza a -1.5ºC mediante el ajuste de la composición de los disolventes con el fin de obtener fibras hibridas electroestiradas con propiedades térmicas similares al PCM puro. Por otro lado, para mejorar la eficiencia de encapsulación se utilizó un material hidrófilo basado en polivinilalcohol (PVOH) como material de recubrimiento para encapsular el PCM usando la técnica de electroestirado a partir de una emulsión. Sin embargo, se observó que las estructuras hibridas preparadas fueron altamente solubles en agua y en condiciones de alta humedad relativa. Por tanto, para protegerlos se incorporó una capa adicional de un material más hidrofóbico (policaprolactona) mediante la técnica de electroestirado coaxial. El uso de la configuración coaxial fue la mejor estrategia para preservar la morfología de las estructuras electroestiradas cuando éstas fueron expuestas a condiciones de alta humedad relativa.

RESUM

L'ús de materials d'emmagatzematge de calor latent que contenen materials de canvi de fase (PCM) és una manera eficaç d'esmorteir les fluctuacions tèrmiques. A més a més presenta els avantatges de posseir una alta densitat d'emmagatzematge energia així com la naturalesa isotèrmica del procés d'emmagatzematge. L'objectiu d'aquest treball va ser desenvolupar productes amb capacitat de gestió de calor mitjançat l´ encapsulació de PCM per a diferents aplicacions d'interès en la conservació d´aliments refrigerats. Amb aquesta finalitat, es va utilitzar el processament electro-hidrodinàmic per encapsular PCM comercials dins de diferents matrius polimériques i biopolimériques, amb temperatures de transició d'interès en el procés de conservació d´aliments refrigerats.

Inicialment, es van dissenyar materials amb capacitat de gestió de calor per ser utilitzats en equips de refrigeració i en el envasat d´aliments refrigerats. Per a tal fi, es van dissenyar blocs, materials multicapa i safates de poliestirè que contenien un recobriment nanoestructurat i ultrafí amb encapsulats de materials de canvi de fase comercials (específicament parafines) dins de diverses matrius polimèriques. Es va caracteritzar la morfologia, les propietats tèrmiques, l´eficiència de encapsulació i la capacitat d'emmagatzematge d´energia just en el moment en el que es van preparar i després de tres mesos d´emmagatzematge a 4 y 25ºC.

No obstant això, els materials desenvolupats van mostrar un perfil de cristal·lització múltiple, un augment del grau de subrefredament (diferència entre les temperatures de fusió i de cristal·lització), una baixa eficiència d'encapsulació i una difusió parcial del PCM de les estructures electroestirades durant el període d´emmagatzematge. Per tant, diferents estratègies han estat portades a terme per contrarestar aquests inconvenients. D'una banda, amb la finalitat d'obtenir fibres híbrides electroestirades amb propietats tèrmiques similars a les de la PCM pur, es van optimitzar els sistemes d'emmagatzematge d'energia tèrmica que incloïen un PCM que fon a -1,5 ºC variant la composició dels dissolvents. D'altra banda, es va utilitzar un material de la closca hidròfil basat en polivinílic alcohol (PVOH) per encapsular el PCM mitjançant l'ús de la tècnica d´electroestirat d´una emulsió per tal de millorar l'eficiència d'encapsulació. No obstant això, les estructures híbrides així preparades van ser altament soluble en aigua a altes condicions d'humitat relativa i va ser necessari utilitzar una capa addicional d'un material més hidròfob (policaprolactona) a través de la configuració coaxial de l´equip d´electroestirat. L'ús de la configuració coaxial va ser una bona estratègia per preservar la morfologia de les estructures electroestirades quan s'exposen a altes humitats relatives.

INDEX PAGE

INDEX PAGE

I. INTRODUCTION

1. PHASE CHANGE MATERIALS (PCM's)

Cold storage has-been extensively used during the last decades for food preservation. Cold acts slowing down or even hampering the microbiological or physicochemical deterioration of food products, thus guaranteeing their quality and safety. One of the most important methods of cold preservation and distribution of food products to the main world market is chilling (refrigeration). Refrigeration temperatures (from 2 to 8ºC) are used for preventing or slowing down microbial, chemical and/or enzymatic activity. However, superchilling has emerged as a potential method for extending shelf-life of food products by partial freezing. Superchilling implies temperatures in the borderline between chilling and freezing where a minor part of the product's water content is frozen by lowering the temperature 1-2ºC below its freezing point. The shelf-life of superchilled foods can be extended by 1.5–4 times relative to chilled food and is an attractive alternative to freezing and conventional chilling.[1-4]

Many industries and supermarkets require their products to be stored, transported and commercialized at low temperatures without temperature fluctuations for preserving food quality and safety. It is well known that those temperature fluctuations could cause negative effect to the quality of the food, inducing for example recrystallization in ice creams and drip loss of meat and seafood and therefore could induce great economical losses to supermarkets and devalue the quality of frozen food.

Breakdowns of the cold chain are likely to occur during food commercialization, which lead to temperature fluctuations of the product, having negative effects on both food quality and safety as a consequence of crystal ice growth, acceleration of chemical reactions and/or microorganism growth, which could result in a reduction of quality and may shorten the shelf-life of the food products.

On the other hand, cold storage systems are partially responsible for ozone depletion and global warming, because of the refrigerants used

(Chlorofluorocarbons-CFCs and Hydrochlorofluorocarbons HCFCs) and the energy consumption of equipment due to the too frequent compressor activations which increases the energy-derived costs.

The development of thermal energy storage (TES) systems has been envisaged as one of the best options to counteract the above-mentioned food-related and environmental problems dealing with cold preservation. According to various studies these systems can produce substantial energy savings (up to 50%) and CO_2 emission reductions.[5,6] TES systems store thermal energy by using sensible heat of solids or liquids, latent heat of phase change materials (PCM’s) or chemical reaction of some compounds.[7] Amongst all of them, latent heat storage using PCM’s is one of the most efficient methods to store thermal energy. These substances undergo a phase transition at a specific temperature and, as a result, they are able to absorb, store and release the latent heat when isothermal conditions are altered (cf. Figure 1).[8-11] Therefore, the use of PCM's provides higher heat storage capacity and more isothermal behavior-compared to sensible heat storage.[12,13] A large number of compounds that melt and solidify at different temperatures can be identified as PCM's. However, PCM's should also present suitable physical, chemical and kinetic properties in order to be used in energy storage systems.[14]

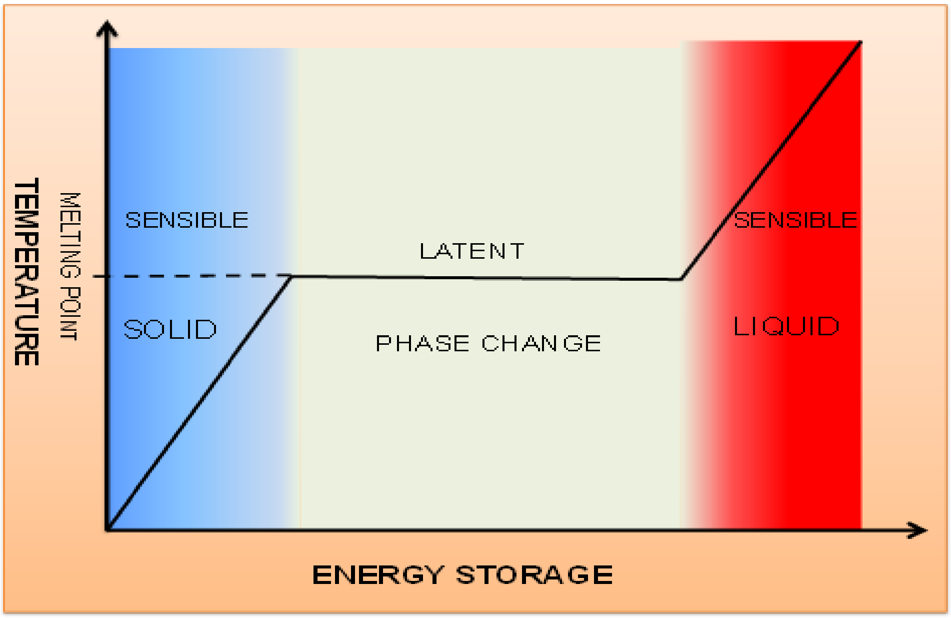

Figure 1. Thermal behavior of phase change materials (PCM's)

1.1. Classification of PCM's. Advantages and disadvantages

PCM's are generally classified into two categories: inorganic materials, such as salt hydrates, and organic materials, such as paraffin's or fatty acids. Inorganic PCM's are attractive materials for use in thermal energy storage due to their high volumetric storage density (~350 MJ/m^3), relatively high thermal conductivity (~0.5 W/m°C) and moderate costs compared to organic PCM's, with few exceptions. However, the problems of phase segregation and supercooling (lag between the melting and crystallization temperatures) have limited their applications. On the other hand, organic PCM's present moderate thermal storage densities (~200 kJ/kg or 150 MJ/m^3) and a wide range of melting temperatures. They undergo negligible supercooling and are chemically inert and stable with no phase segregation. However, they have low thermal conductivity (~0.2 W/m°C).[15] In Figure 2, several PCM's are illustrated with their corresponding temperature ranges and enthalpy energy storage characteristics. Tables 1 to 4 also detail some of the PCM's found in the literature.

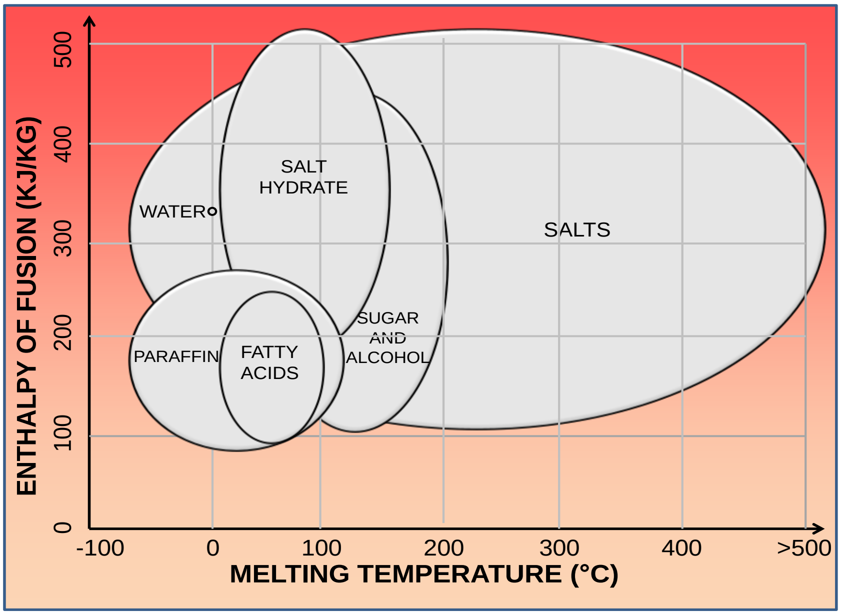

Figure 2. Types of phase change materials according to its melting temperature and melting enthalpy.

Table 1. Paraffin's with potential use as PCM

Paraffin’s	Melting Temperature (°C)	Latent heat of fusion (kJ/kg)
Paraffin C10	-30.0	-
Paraffin C11	-26.0	-
Paraffin C12	-9.6	216
Paraffin C13	-6.0	-
Paraffin C14	5.5	165
Paraffin C15	10.0	205
Paraffin C16	16,7	237,1
Paraffin C17	21,7	213
Paraffin C18	28.0	244
Paraffin C19	32.0	222
Paraffin C21-C34	40.2 - 75.9, respectivity	200-269, respectivity

Table 2. Fatty acids with potential use as PCM

Fatty acids	Melting Temperature (°C)	Latent heat of fusion (kJ/kg)
Acetic acid	16.7	184
Polyethylene glycol 600	20.0-25.0	146
Capricacid	36.0	152
Eladicacid	47.0	218
Lauricacid	49.0	178
Myristicacid	58.0	199
Palmiticacid	55.0	163
Stearicacid	69.4	199

Table 3. Inorganic substances with potential use as PCM

Composition	Melting Temperature (°C)	Latent heat of fusion (kJ/kg)
Al(NO3)3 (30.5 wt.%) + H2O	-30.6	131
NaCl (22.4 wt.%) + H2O	-21.2	222
16.5 wt.% KHCO3 + H2O	-6.0	-
Na2SO4 (31 wt.%)	4.0	234
K2HPO46H2O	14.0	109
Mn(NO3)2 6H2O	27.0	148
CaCl2 12H2O	29.8	174
LiNO3 3H2O	8.0	253
Na2SO4 10H2O	32.4	241
Na2CO3 10H2O	32.0	267
Na2S2O3 5H2O	48.5	210
Ni(NO3)2 6H2O	57.0	169
LiCH3COO 2H2O	70	150
KAl (SO4)2 12H2O	91	184
MgCl2 6H2O	117	167

Nevertheless, organic PCM's, and specifically paraffin's, are normally preferred in most applications since they are chemically more stable than other PCM's, do not degrade after repeated cycling and supercooling and corrosion does not pose as a significant problem. Moreover, paraffin's cover a large temperature range and they have been found to have self-nucleating properties,[16,17] being moreover highly compatible with a wide variety of materials.[18] Thus, several companies (Rubitherm GmbH,[19] Cristopia,[20] Climator,[21]TEAP[22], etc).[9,13,23] are already commercializing this kind of PCM's.

Table 4. Some commercial PCM's available in the market

Composition	Melting Temperature (°C)	Latent heat of fusion (kJ/kg)	Supplier
SN33 (Salt solution)	-33.0	245	TEAP
MPCM (Paraffin)	-30.0	140-150	MicrotekLaboratories
Climsel C-21 (Salt solution)	-21.0	306	Climator
SN 21 (Salt solution)	-21.0	240	Cristopia
TH 16 (Salt solution)	-16.0	289	TEAP
STLN 10 (Salt solution)	-11.0	271	Mitsubishi Chemical
RT - 9 HC (Paraffin)	-9.0	260	RubithermGmbH
RT - 4 (Paraffin)	-4.0	179	RubithermGmbH
TH 4 (Salt solution)	-4.0	386	TEAP
RT 0 (Paraffin)	0.0	225	RubithermGmbH
RT5 (Paraffin)	5.0	180	RubithermGmbH
MPCM (6) (Paraffin)	6.0	157-167	MicrotekLaboratories
ClimSel C7 (Salt solution)	7.0	130	Climator
RT 10 (Paraffin))	10	150	RubithermGmbH
RT 21 (Paraffin)	21	160	RubithermGmbH
ClimSel C24 (Salt solution)	24	170	Climator
RT 27 (Paraffin)	27	179	RubithermGmbH
ClimSel C32 (Salt solution)	32	185	Climator
RT 35 (Paraffin)	35	170	RubithermGmbH
RT 47 (Paraffin)	47	170	RubithermGmbH
ClimSel C58 (Salt solution)	58	340	Climator
RT 60 (Paraffin)	60	144	RubithermGmbH
ClimSel C70 (Salt solution)	71	320	Climator
T 80 HC (Paraffin)	79	240	RubithermGmbH
RT 90 HC (Paraffin)	90	200	RubithermGmbH

1.2. Encapsulation of PCM's

As previously commented, PCM's are able to absorb and release a large amount of latent heat during their phase transition process, thus providing high energy storage capacity. Nevertheless, the use of these materials in thermal energy storage applications present some drawbacks, such as weak thermal stability, low thermal conductivity and the fact that some of them are liquid at ambient temperature and, thus, they are not easy to handle.[14,24] The encapsulation of the PCM's is a plausible solution to avoid these problems. By introducing these materials inside a shell material the following advantages are found:

- PCM is protected against the influences of the outside environment.
- The heat transfer area is increased.
- The changes in volume of the PCM, as the phase transition occurs, are withstood.
- A solid matrix is provided, thus allowing an easier handling of the materials.

In conclusion, the encapsulation of the PCM's makes them more suitable to be applied in many fields, such as building, protection of temperature sensitive products, air conditioning applications, solar energy storage systems, greenhouses, temperature regulating textiles, electronics devices and biomedical systems.[24-26] Moreover, micro- and nanoencapsulation of PCM's increase their application in many of these fields, since the reduced size structures could be better incorporated within different materials. Furthermore, the microcapsules increase the heat transfer area of the PCM's, thus enhancing the heat exchange performance as compared to big PCM structures or to the pure PCM.

There are many methods for the encapsulation of PCM's, which are generally classified in physical and chemical procedures. Figure 3 shows different techniques that have been used for this purpose. According to the literature, the most widely explored techniques for PCM microencapsulation have been: spray drying (for the physical technologies) and in-situ polymerization (for the chemical methods).[10,16,27,28] According to different studies physical methods usually result in relatively large size microstructures which reduce the efficiency of heat transfer.[10,29] A substantial drop in heat storage capacity with the physical methods as compared to that of chemical methods has been generally observed. However, chemical methods require aggressive conditions of temperature, pressure or pH in order to form the structures. In order to overcome these issues, the **electro-hydrodynamic technology** has recently arisen as an innovative approach to encapsulate PCM's.[30] This technique makes use of high voltage electric fields to produce electrically charged jets from viscoelastic polymer solutions which on drying, by the evaporation of the solvent, produce ultrathin polymeric structures.[31] This methodology produces different kind of structures depending on multiple conditions including solution properties (polymer concentration, viscosity, electrical conductivity, surface tension and solvent volatility), environmental conditions (temperature, air velocity and humidity) and process conditions (voltage, spinning distance and flow rate). When ultrathin continuous fibers are obtained, the process is called “electrospinning”. When size-reduced capsules are attained, the process is normally referred to as “electrospraying” due to the non-continuous nature of the structures obtained. This technique allows the control of the morphology and size of the structures by adjusting the process parameters, thus avoiding the heat transfer efficiency problem. Furthermore, electro-hydrodynamic electro-hydrodynamic technology does not require extreme conditions for the structures formation, so different polymers can be used as matrix materials, including biopolymers such as proteins, polysaccharides or biodegradable polyesters.

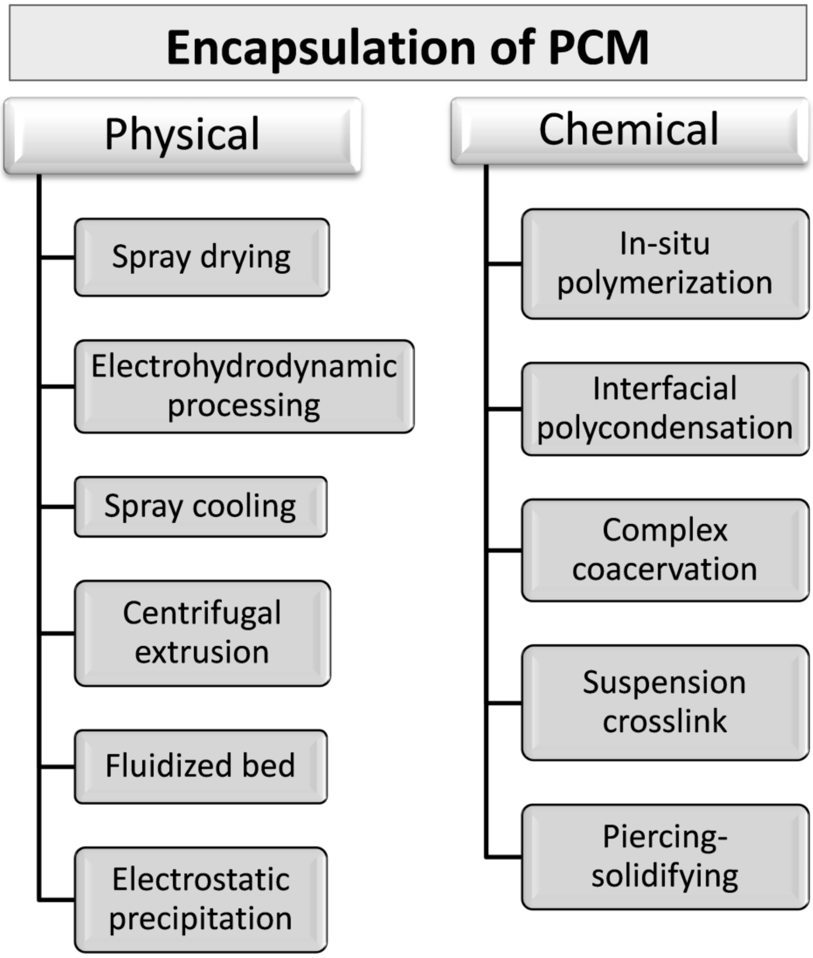

Figure 3. Methods of encapsulation of PCM's

Electro-hydrodynamic technology has been successfully used for the microencapsulation of different substances, including PCM's as it will be later explained.[26] Using this technology there is no limitation in terms of the substance to encapsulate, independently of the chemical nature of the encapsulating matrix, as uniaxial, coaxial or multiaxial electrospinning configurations might be employed. Conventional electrospinning (uniaxial) setups are based on needle systems, the polymer solution is conduced to a spinneret attached to a syringe. This configuration allows to encapsulate a material which require being spinnable. The coaxial configuration consists of two concentrically arranged needles connected to two reservoirs which contain different solutions, one with the polymer matrix and one with the core material. This configuration presents the possibility of including a core material which does not require being spinnable as it will be entrapped by the outer polymeric shell. The triaxial electrospinning configuration is another novel recent modification of traditional electrospinning. Via this technique, three different solutions could be electrospun into one nano-/micro structure with concentric three-layer morphology. Moreover, this technology can microencapsulate materials from the melt as well as from polymer solutions, enhancing even further the number of encapsulation matrices that can be used.

1.3. Use of the electro-hydrodynamic process for microencapsulation of PCM's

Although this technology has been traditionally focused on textile applications, the use of electrospun structures for different purposes has attracted a great deal of attention in the last years. Nowadays, this technology is also being explored for microencapsulation purposes with successful results.[8,24,32-35] This technology is not yet used commercially for encapsulation purposes, however it has several advantages over other well-established encapsulation technologies including:

- Ultrafine or even nanosized structures with a huge surface-to-volume ratio can be obtained

- It allows the control of the morphology and size of the structures by adjusting the process parameters

- It does not require the use of extreme conditions of temperature, pH, pressure, etc. for the formation of structures, thus, being an ideal method for protecting sensitive encapsulated compounds

- There is no limitation in terms of the substance to encapsulate as different electrospinning configurations can be used (coaxial or even triaxial).

- In general, very high encapsulation efficiency (about 98%) is obtained.

Electro-hydrodynamic technology has been mainly used for the design of heat management materials for building applications. Thus, synthetic polymers have been usually selected as matrix materials. Regarding PCM's, those which present a phase transition in the human comfort range temperatures (20-35ºC) have been commonly studied. For instance, some authors[8,35,36] encapsulated different fatty acids (lauric acid, myristic acid, palmitic acid and stearic acid) within polyethylene terephthalate (PET) fibers. These fibers presented proper encapsulation efficiency and enthalpy values and keep their heat management properties after several cycles. However, these structures presented some supercooling degree. In other work, McCann et al.[37] used the melt coaxial electrospinning to develop nanofibers based on three different paraffin's (octadecane, hexadecane, and eicosane) encapsulated in polyvinylpyrrolidone (PVP). Results showed that it was possible to encapsulate up to 45%wt. of paraffin within the PVP, and the materials showed an enthalpy of 114 J/g.

A novel application of microencapsulated PCM's is the preservation of perishable products, such as food or biomedical substances. In this area, PCM's structures could be incorporated within packaging structures in order to increase the thermal energy storage capacity of the packaging. Since packaging is normally used for relatively short shelf-life products, bio-based matrices are preferred for this application in order to avoid waste disposal problems. In this context, Perez-Masia and co-workers[32,33,38] developed novel thermal energy storage systems from polymers and biopolymers by means of the electro-hydrodynamic electro-hydrodynamic technique to protect products along the cold chain. Initially they encapsulated dodecane (a paraffin with a phase transition around -10ºC) in different bio-based matrices. They saw that biopolyesters were a plausible option to encapsulate organic PCM's (paraffin's) by means of electrospinning, due to a proper affinity between the matrices and the PCM. Specifically, it was seen that polycaprolactone (PCL) provided better encapsulation performance (encapsulation efficiency and enthalpy values) than other matrices. Moreover, in this work supercooling was effectively reduced by adding different nucleating agents. These authors also encapsulated

Rubitherm-RT5 within biopolyesters. RT5 is a commercial mixture of paraffin's which present a phase transition around 5ºC without supercooling degree. This temperature is commonly used to keep the refrigerating conditions of foodstuffs in retail and display cabinets at supermarkets or in household refrigerators, thus increasing the applicability of the capsules developed. This work compared different matrices and studied the effect of the morphology of the encapsulation structures (fibers or spheres) on thermal properties and encapsulation efficiency. They concluded that PCM was better encapsulated in fiber structures and also in PCL structures. Therefore, PCL fibers were used to evaluate the energy storage ability of the materials after the incorporation of the PCM. It was seen that PCL fibers containing the PCM almost tripled the time needed to reach room temperature when compared to the pure PCL fibers, thus demonstrating the heat management capacity of this type of structures. Otherwise, Chen et al.[39] also used bio-based matrices to encapsulate PCM's. They prepared ultrafine fibers composed of polyethylene glycol as PCM and cellulose acetate as shell material. The results showed that the ultrafine fibers had cylindrical shape with smooth surface and high latent heats of fusion and crystallization (86 J/g). The composite fibers were stable after 100 heating - cooling cycles, showing good thermal stability and reliability.[7] Additionally, they encapsulated a commercial PCM (Rubitherm-RT5) with a phase transition around 5ºC in polystyrene (PS). In this work capsules and fibers were attained, showing that fibers were more convenient for PCM encapsulation, since better efficiencies and enthalpy values were obtained.

However, several problems derived from PCM encapsulation have been noted such as:

- The supercooling effect which produces a delay in the crystallization temperature of the material, causing a difference between the melting and the crystallization temperatures. This phenomena occurred when the diameter of microstructures was smaller than 100 mm.[40]

- Multiple crystallization process of encapsulated PCM, which was attributed to what is called the rotator phase transition (liquid-rotator, rotator-crystal, and liquid-crystal transitions). For example, three crystallization peaks were observed in n-octadecane and n-eicosane when these paraffin's were microencapsulated.[41,42]

- Low encapsulation efficiency of the PCM is another problem that has been encountered in some works, possibly attributed to the lack of optimization of the encapsulation procedure or to interactions between the PCM and the polymers or additives.

- PCM diffusion out of the encapsulating matrix along storage which may be due to the fact that the shell matrices could interact with the paraffin favoring PCM's migration and, thus, the hydrophobic shell material seemed to act as permeable matrices for PCM's.

Given that this is a rather novel research area, further studies on fully functional technologies that can optimize the encapsulation of PCM's, maximizing the heat management capacity of the materials and minimizing the changes in the thermal behavior of the PCM's as a consequence of encapsulation are required. Furthermore, for the practical applications of the materials, their behavior during storage should be also characterized and a focus on material design should also be put on.

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II. OBJECTIVES

2. GENERAL AND SPECIFIC OBJECTIVES

The general objective of this work was to develop novel heat management materials based on the encapsulation through electrospinning of phase change materials (PCM's), specifically paraffins, with first order transition temperatures of interest in food preservation, within various polymer matrices.

For this purpose, several specific objectives were planned. The first one consisted on the optimization of the electrospinning conditions to develop encapsulation structures based on polyester matrices containing a commercial paraffin (RT5) with a transition temperature around 5ºC.

The second specific objective was to develop materials for different applications of interest in refrigerated food. One of them was the development of slabs based on polymers matrices containing RT5 for increasing efficiency and reducing energy consumption in refrigeration equipments. The second application focus consisted on the development of PS foam trays containing an ultrathin fiber-structured polyester/PCM coating of interest in refrigerated food products packaged in trays such as meat and fish products. The third application of this PCM encapsulated-based material was based on the development of polyester-based multilayer films with heat storage capacity for food packaging applications

The third specific objective was to evaluate the effect of storage time and temperature on the heat storage capacity of the developed materials. It is important to understand the behavior of these materials under different storage conditions as they are aimed to be introduced in packaging structures or in refrigeration equipments.

The fourth specific objective was to develop novel heat management materials of interest in superchilling applications based on polyester matrices containing a mixture of commercial paraffin's which presented a phase transition at around -1.5ºC.

Finally, the fifth objective was to find new strategies to counteract the drawbacks observed when microencapsulating PCM's related to supercooling effect, multiple crystallization and leaking of the PCM.

III. RESULTS AND DISCUSSION

1. GENERAL INTRODUCTION TO RESULTS

The current thesis work has been carried out within the context of the FP7 European Project FRISBEE and completed the initial research work carried out and reported in the thesis work of Perez-Masiá[1] related to microencapsulation of PCM's using electrospinning. Based on these previous results, novel heat management materials consisting on microencapsulated phase change materials (PCM's), specifically paraffins, obtained through electrospinning were developed. Most of the work carried out involved the use of a commercial paraffin (with commercial name RT5) which had a transition temperature around 5ºC. Different material formats were implemented to be used in various applications for refrigerated food.

The first research work (chapter 1) focused on the design of a material to be used in refrigeration equipments, with the aim of increasing energy efficiency and reducing both energy consumption and the use of refrigerants which are harmful to the environment. To this end, polycaprolactone (PCL) and polystyrene (PS) were selected as encapsulation polymeric matrices as, apart from being materials either being already used in refrigeration equipments (like PS) or with a great potential to substitute current materials used (in the case of PCL), they showed very good results in terms of energy storage capacity. After an initial optimization of the electrospinning process to develop fiber mats containing high amounts of encapsulated PCM's, thick slabs, which could be introduced in the walls of refrigeration equipments, were obtained using a hot-plate hydraulic press. The effects of storage temperature (4 and 25°C) and ageing (3 months) on the performance of these PS/RT5 and PCL/RT5 slabs were investigated so as to understand the behavior of these heat management materials during service.

In chapter 2, the development of a novel heat management material for refrigerated meat and fish trays is reported. Specifically, a PS foam tray containing an ultrathin fiber-structured polystyrene/PCM coating was fabricated. In order to improve the adhesion between the PS tray and the electrospun

PS/PCM layer, a soft heat treatment was applied. The performance of the ultrathin fiber-structured polystyrene/PCM coating was also investigated during ageing (3 months) at two storage temperatures (4 and 25°C).

The third chapter of this thesis work, reports on the development of a heat management material to be used in food packaging applications with the aim of counteracting potential temperature variations during the commercialization of refrigerated foods. To this end, multilayer heat storage structures were developed based on PS films coated with a PCL/PCM electrospun layer and, in some cases, with another external PCL electrospun layer. The PCL/PCM fibrous mats were directly electrospun onto the PS films and an additional PCL electrospun layer (without PCM) was also deposited in some experiments, as previously mentioned. As in the case of the slabs presented in chapter 1, with the purpose of evaluating the performance of the multilayer structures developed with time, a study evaluating the effect of storage temperature (4 and 25°C) and ageing (3 months) was also carried out.

It should be mentioned that the three types of materials developed in this first part of the thesis were fabricated using a Bioinicia's Fluidnatek coaxial electrospinning pilot plant equipment designed with a scanning high throughput multinozzle injector containing 20 coaxial nozzles.

From the first part of this thesis, it was observed that, in general, the thermal properties of the various developed materials somehow differed from the ideal behavior desirable for a heat management material, since microencapsulation was seen to modify the crystallization pattern and to increase the supercooling degree (i.e. the difference between the melting and crystallization temperatures of the paraffin). Furthermore, another objective of this thesis was to develop thermal energy storage systems for superchilling applications. Chapter 4, includes the results obtained for novel heat management polymeric materials with a phase transition temperature around -1.5ºC, which were optimized so as to have melting and crystallization temperatures and a supercooling degree similar to that obtained for the pure PCM. The development of these materials was focused on studying how the use of various solvents with different physicochemical properties modified solution properties and, thus, the electrospinning process. Based on preliminary results, solvent mixtures were used in the optimized electrospinning solutions which were prepared with polycaprolactone (PCL), polystyrene (PS) and high-impact polystyrene (HIPS) as polymeric matrices and the PCM was obtained from a mixture of commercial paraffins which presented a phase transition at around -1.5ºC.

Another drawback observed from the first part of this thesis was related to the leaking of encapsulated PCM during the storage period. In chapter 5, different strategies have been carried out to counteract this phenomenon. On one hand, optimization of emulsion electrospun structures based on a hydrophilic polymer (PVOH), RT5 and a non-ionic surfactant was carried out. A hydrophilic polymer was selected to minimize the interactions with the hydrophobic paraffin and prevent its leakage. However, this system was highly sensitive to humidity and, thus, it could not be used as such for refrigerated food products application. Therefore, a second strategy based on a coaxial electrospinning methodology was implemented to incorporate a hydrophobic polymer (PCL) as outer shell material to protect the PVOH-PCM structures. PCL was chosen as shell material due to it is biodegradable character, good spinnability and the excellent encapsulation yields observed in previous works.

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CHAPTER I

Electrospun Heat Management Polymeric Materials of Interest in Food Refrigeration and Packaging

CHAPTER I: Electrospun Heat Management Polymeric Materials of Interest in Food Refrigeration and Packaging

ABSTRACT

The use of latent heat storage materials using phase change materials (PCM's) is an effective way of buffering thermal fluctuations and has the advantages of high-energy storage density and the isothermal nature of the storage process. The aim of this work was to develop slabs with energy storage capacity for their application in refrigerated foods. To this end, polycaprolactone (PCL) and polystyrene (PS) were used as encapsulating matrices of a PCM, specifically RT5 (a paraffin which has a transition temperature at 5ºC), by using electro-hydrodynamic processing. The effect of storage temperature (4ºC and 25ºC) and time on the morphology and thermal characteristics of the PCL/RT5 and PS/RT5 slabs was evaluated. Results showed that RT5 can be properly encapsulated inside both polymers, although PCL provided better encapsulation efficiency. Encapsulation efficiency was affected not only by the polymer matrix but also by storage time at 25ºC. The greatest encapsulation efficiency (98.6%) and optimum heat management performance was achieved for PCL/PCM slabs stored at 4ºC, corresponding to materials composed of ~44 wt % of PCM (core material) and ~56 wt % of the PCL shell material. These temperature buffering materials can be of great interest to preserve the quality of packaged foods and to increase efficiency and reduce energy consumption in refrigeration equipment.

KEYWORDS: biopolymers and renewable polymers; polystyrene; crystallization; differential scanning calorimetry (DSC); fibers

1. INTRODUCTION

Refrigeration systems have been used during the last decades as a main method of food preservation. In fact, it is well-known that frozen and freezing temperatures are required during transport and storage in order to maintain the quality and safety of many foodstuffs. It is worth to note that food quality is often compromised by temperature fluctuations during food commercialization which, amongst others, contributes to the formation of heterogeneous crystal growth. However, refrigeration is one of the heavy energy consumers. Furthermore, the ozone layer depletion and greenhouse gases emission associated to the use of air conditioners and refrigerators that make use of chlorofluorocarbons and hydrochlorofluorocarbons (CFCs and HCFCs) as refrigerants represent great environmental concerns. The phase-out of CFCs and HCFCs according to the Montreal Protocol urges the researchers to find out environmentally friendly new substitutes for refrigerants or novel technologies to reduce the amount of refrigerant used in these systems as well as to reduce the energy consumption of these. As a result, researchers are focused on developing technical options for improving the energy performance of household refrigerators and one of the most innovative options is the use of phase change materials (PCM's). PCM's are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release the latent heat when isothermal conditions are altered.[1] PCM's could be used during transport or storage, for the protection of solid foods, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products, and many others.[2] The most commonly used PCM's are paraffin waxes, fatty acids, eutectics, and hydrated salts.[3] The paraffin compounds fulfil most of the requirements for being used as PCM's, as they are reliable, predictable, nontoxic, chemically inert, and stable below 500ºC. They also show little volume changes on melting and have low vapour pressure in the molten form.[4] On the other hand, the inorganic substances, like salt hydrates, usually suffer from supercooling and phase separation during their applications which often compromises the temperature buffering behavior of these materials and cause random variations or progressive drifting of the transition zone over repeated phase change cycles. Furthermore, corrosion is another shortcoming of these materials.[5]

Direct application of PCM's is difficult because they have weak thermal stability, low thermal conductivity, and some of them are liquid at ambient temperature and, thus, are not easy to handle or to be directly incorporated into packaging structures and refrigeration equipment.[6] Therefore, the encapsulation of the PCM in a shell material is a plausible solution to avoid all these problems. Microencapsulated PCM is a form of PCM encapsulated in natural and synthetic polymeric capsules, which range in size from less than 1 mm to more than 1000 mm. The microcapsules protect the PCM against the influences of the outside environment, increasing the heat-transfer area, and permitting the core material to withstand changes in volume of the PCM, as the phase change occurs allowing small and portable thermal energy storage systems.[5] One methodology being increasingly used for the microencapsulation of materials is electro-hydrodynamic processing. This processing technique has proven to be a suitable method for encapsulation of several components, including biomedical substances, functional food ingredients, PCM's, and others substances within polymer matrices.[7–9] The electro-hydrodynamic processing commonly termed as electrospinning is a technique whereby long nonwoven ultrafine structures, typically fibers with diameters of several tens to several hundreds of nanometers, may be formed by applying a high-voltage electric field to a solution containing polymers.[10] The basic principle of electrospinning is to apply high voltage on the polymer solution or melt that would overcome polymer surface tension and induce the jet formation. Applied tip-to-collector electric field causes surface charge repulsion of solution which deforms spherical drop of viscoelastic polymer solution on needle tip into conical shape (Taylor's cone). When electrostatic forces of surface charge repulsion overcome polymer surface tension, charged jet ejects from Taylor's cone and deforms uniaxially through electric field toward grounded collector. Simultaneously, with rapid whipping of the jet, the evaporation of the solvent leaves dried fibers behind.[11] It is believed that higher electric field causes spreading of main jet into numerous secondary fibers with smaller approximately equal diameter regarding the main jet. Due to instability of polymer jet, deformation depends on the electric field strength. Therefore, it is necessary to adjust electrospinning parameters for uniform nanofibers fabrication. To produce fibers, a large number of highly specific conditions including solution properties (polymer concentration, viscosity, electrical conductivity, surface tension, and solvent volatility), environmental conditions (temperature, air velocity, and humidity), and process conditions (voltage, spinning distance, and flow rate) must be met. The aim of this work was, on one hand, to develop heat management materials based on the encapsulation of a PCM which melts at 5ºC (RT5-core material) inside two different polymeric matrices ((polycaprolactone (PCL) and polystyrene (PS) (shell material)) by means of the electro-hydrodynamic processing and, on the other hand, to study the effects of storage temperature and ageing on the performance of these PS/RT5 and PCL/RT5 slabs. It is important to understand how these materials will behave as a function of temperature and time, because these encapsulated structures are aimed to be introduced in packaging structures or in refrigeration equipment, in order to counteract temperature fluctuations and to increase the energetic efficiency of the devices, respectively.

2. MATERIALS AND METHODS

2.1. Materials

Rubitherm RT5, a technical grade paraffin wax, was chosen as the PCM for cool storage. It is based on a cut resulting from refinery production and it consists entirely of normal paraffin waxes (C14-C18). RT5 was purchased from Rubitherm Technologies GmbH (Berlin, Germany). The PCL grade FB100 was supplied by Solvay Chemicals (Belgium). PS commercial grade foam was supplied by NBM (Valencia, Spain). N,N-dimethylformamide (DMF) with 99% purity and trichloromethane (99%) were purchased from Panreac Quimica S.A. (Castellar del Vallés, Spain). All products were used as received without further purification.

2.2. Preparation of Films

2.2.1. Preparation of PS/PCM and PCL/PCM Solutions.

The electrospinning solutions were prepared by dissolving the required amount of PS and PCL, under magnetic stirring, in a solvent prepared with a mixture of trichloromethane : DMF (70 : 30 w/w) in order to reach a 10% or 13% in weight (wt.%) of PS or PCL, respectively. Afterward, 45 wt % of PCM (Rubitherm 5) with respect to the polymer weight was added to the polymer solutions, and stirred at room temperature until it was completely dissolved.

2.2.2. Electro-hydrodynamic Processing.

The full process of the PCM encapsulation through electro-hydrodynamic processing has been previously developed (patent application number: P201131063). Based on previous knowledge, PCL/PCM and PS/PCM solutions were prepared according to Pérez-Masiá et al.,[9] in order to produce fibrillar structures. Thus, PCM's were microencapsulated within two different polymeric matrices (PS and PCL) by means of a Fluidnatek® electrospinning pilot plant tool from Bioinicia S.L. (Valencia, Spain) equipped with a variable high-voltage 0–60 kV power supply. PCL/PCM or PS/PCM solutions were electrospun under a steady flow-rate using a motorized high throughput multinozzle injector, scanning horizontally toward a metallic grid used as collector. The electrospinning conditions for obtaining both PCM-containing polymer structures were optimized and fixed at 55 mL/h of flow-rate, tip-collector distance of 26 cm, and the voltage of the collector and injector were set at 52 kV and 44 kV, respectively.

2.2.3. Preparation of PS/RT5 and PCL/RT5 Slabs.

Based on screening studies (data not shown) on the energy storage capacity of electrospun fiber mats, PS/RT5 and PCL/RT5 slabs (3 X 1 X 1 cm) were developed in order to increase the temperature buffering capacity of the materials. To this end, the electrospun fiber mats, obtained in a pilot plant electrospinning equipment, were slightly pressed using a hot-plate hydraulic press at 63ºC for 90 s.

2.2.4. Slabs Conditioning and Storage.

Samples were equilibrated in desiccators at 0% HR by using silica gel and at two different temperatures 4ºC and 25ºC for 3 months. PCL/PCM and PS/PCM slabs were taken from the desiccators stored at 4ºC and 25ºC at different time intervals (0, 7, 15, 30, 45, 60, and 90 days) and differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) analysis were carried out.

2.3. Characterization of Slabs

2.3.1. Scanning Electron Microscopy (SEM).

The morphology of the electrospun PCL/PCM and PS/PCL fibers and slabs was examined using SEM on a Hitachi microscope (Hitachi S-4100). Samples were frozen in liquid N2 and cryofractured to observe the cross section of the samples. Then, they were fixed to beveled holders using conductive double side adhesive tape, sputtered with a mixture of gold-palladium, and observed using an accelerating voltage of 10 kV. The diameters of the electrospun mats were measured by means of the Adobe Photoshop CS4 software from the SEM micrographs in their original magnification. The calculation of the number-average diameter was done by measuring 300 fibers diameters.

2.3.2. Differential Scanning Calorimetry.

Thermal analyses of electrospun fibers and slabs were carried out on a DSC analyzer (Perkin Elmer DSC 7, US) from -20 to 20ºC in a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2, Perkin Elmer, US). The scanning rate was 2ºC/min in order to minimize the influence of this parameter in the thermal properties. The amount of material used for the DSC experiments was adjusted so as to have a theoretical PCM content of 1–2 mg approximately. The enthalpy results obtained were, thus, corrected according to this PCM content. All tests were carried out, at least, in duplicate.

2.3.3. Attenuated Total Reflectance Infrared Spectroscopy.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR) spectra of polymers (PCL and PS), pure RT5 and PCL/PCM and PS/ PCM slabs were collected at 25ºC in a FTIR Tensor 37 equipment (Bruker, Germany). The spectra were collected in the different materials by averaging 20 scans at 4 cm^{-1} resolution. The experiments were repeated twice to verify that the spectra were consistent between individual.

2.3.4. Temperature Profiles.

The temperature profiles of slabs with and without PCM were compared. To this end, PCL and PS slabs were frozen at -18ºC for 1 day. Then, the surface temperature was registered at room temperature (20ºC) by using an infrared thermometer MS Plus provided by PCE Instruments (Tobarra, Spain).

2.3.5. Statistical Analysis

A statistical analysis of data was performed through analysis of variance (ANOVA) using Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD). Homogeneous sample groups were obtained by using LSD test (95% significant level).

3. RESULTS

3.1. Morphology

The morphology of the electrospun structures was analysed through scanning electron microscopy (SEM). Microstructural images provide information about the morphology of the slabs and allow us to gain a better understanding of thermal properties of slabs. Initially, the morphology of PS/PCM (a) and PCL/PCM (b) fibres were observed since the microstructure of the fibres could aid to explain the encapsulation efficiency of the different materials, as well as their thermal performance during storage time. Figure 1 shows the cross-sections of both cryofractured fibres. Control PCL and PS fibres are also included for comparison purposes.

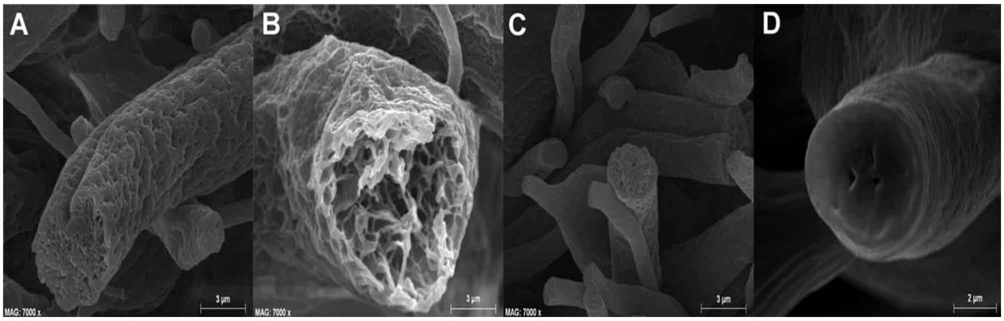

Figure 1. SEM images of electrospun fibers: (A) polystyrene/PCM, (B) polycaprolactone/PCM, (C) control polystyrene fibers, and (D) control polycaprolactone fibers.

From these images, it can be observed that the incorporation of RT5 led to the formation of several channels inside the fibrillar structures where the PCM was supposed to be allocated (compare with PS and PCL control fibres in Figures 1C and 1D, respectively, where no such channels were observed). These channels were much bigger in PCL/PCM structures than in PS/PCM electrospun fibres, which could help explain the differences in thermal properties as it will be detailed below. Noticeable differences were observed between both types of fibres. PCL/PCM fibres were thicker and both encapsulation structures presented a porous surface, although in the case of PS/PCM fibres, pore size was much smaller. There are several studies which indicate that the use of volatile solvents or high relative humidity can contribute to produce porous nanofibres.[12-16] However, in the present study the porous structure is thought to derive from the encapsulation of the PCM since the fibres with no PCM did not exhibited such a porous structure. In fact, the pores were actually the areas where the PCM was most likely to be located and, therefore, account for the capsule size obtained by the processing technique.

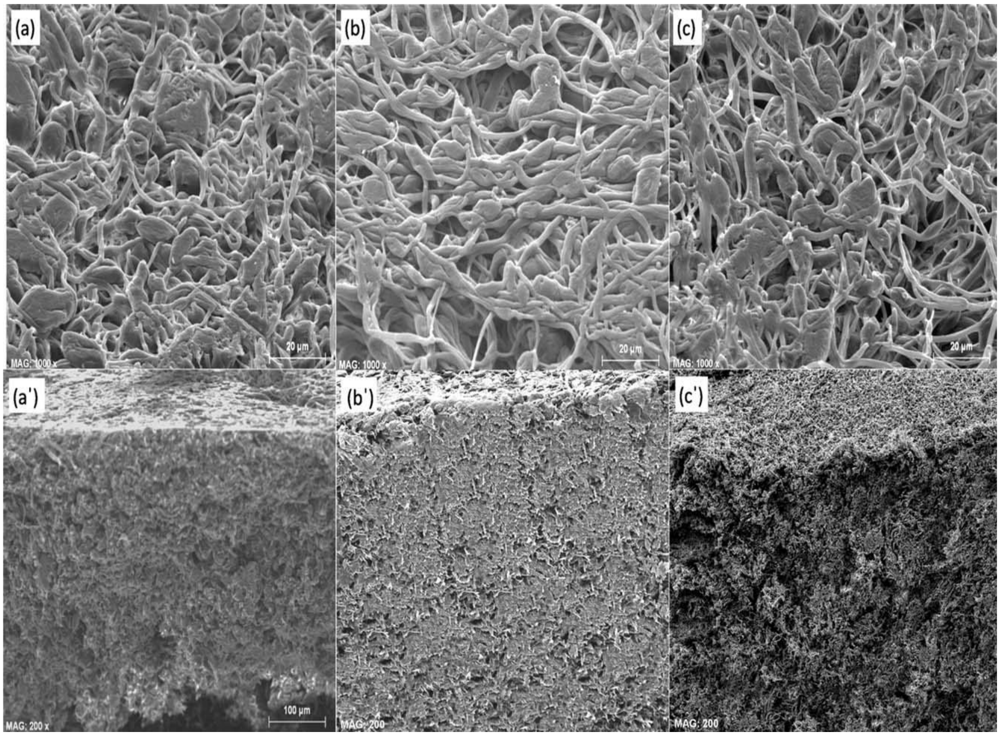

Figure 2. SEM images of surface (a–c) and cross-section (a'–c') of electrospun PS/PCM fibers: (a–a') nonstored slabs, (b–b') stored slabs for 3 months at 4ºC, (c–c') stored slabs for 3 months at 25ºC.

Figures 2 and 3 show the surface (a-c) and cross-sections (a'-c') of non-stored and stored (at 4 and 25ºC) slabs of PS/PCM and PCL/PCM, respectively. From surface images, it is clearly observed that the fibres obtained from the PCL/PCM solution were thicker (fibre diameters ranged from 0.55 to 11.91 µm) while in PS/PCM slabs, many beaded areas (1.96 - 19.77 µm) were distinguished within the fibrous mats and not significant morphological differences were observed between non-stored and stored slabs (diameter of fibres ranged from 0.35 to 3.89 µm).

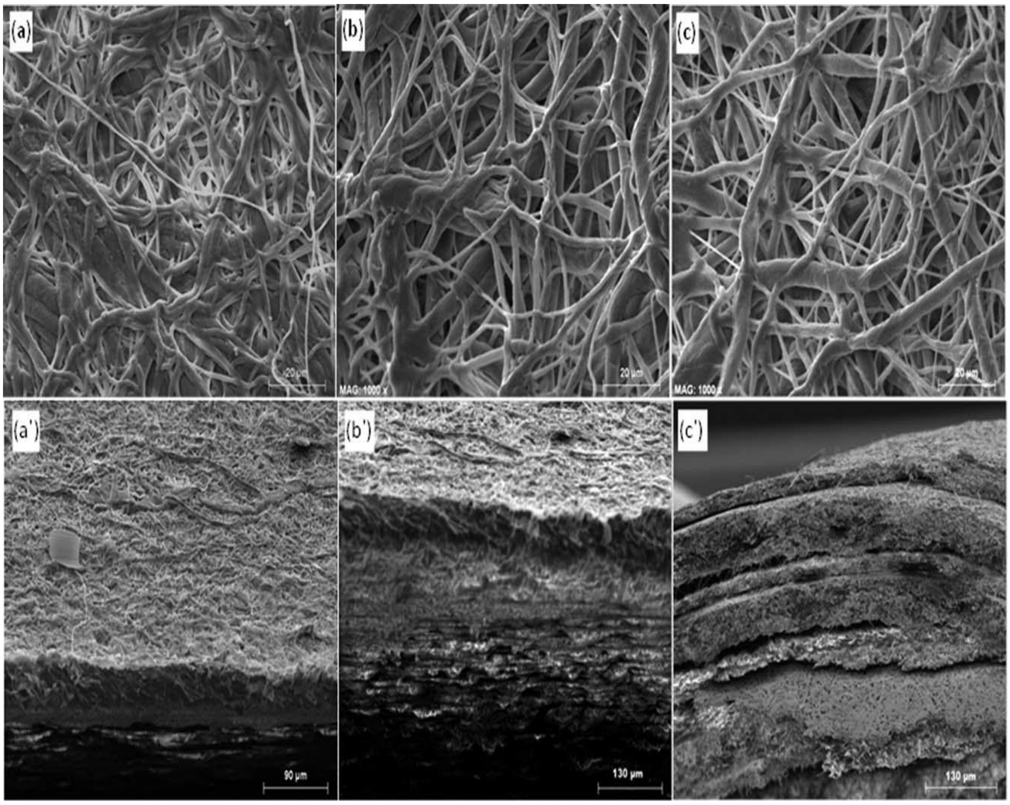

Figure 3. SEM images of surface (a–c) and cross-section (a'–c') of electrospun PCL/PCM fibers: (a–a') nonstored slabs, (b–b') stored slabs for 3 months at 4ºC, (c–c') stored slabs for 3 months.

Remarkable changes can be discerned from the cross-section images. Non-stored PS/PCM (Figure 2a') and PCL/PCM (Figure 3a') slabs were more compact than the ones stored at 25ºC (figure 2c' and 3c'). However, the appearance of slabs stored at 4ºC (figure 2b' and 3b') was similar to that observed for non-stored slabs, probably due to the physical state of the PCM. As commented on above, the phase transitions of RT5 take place around 5ºC and, thus, the PCM was in a solid state at 4ºC and remained in the porous structure during storage. On the opposite, PCM was in a liquid state at room temperature (25ºC), which clearly contributed to modify the structure of the slabs. In this sense, it is worth to note that stored PCL/PCM slabs at 25ºC were delaminated after three months, probably due to the morphology of fibres which facilitated the PCM (which was liquid at room temperature) migration out of the encapsulating pores.

3.2. Thermal Properties of Electrospun Structures

The thermal behaviour of the PCL/PCM and PS/PCM structures was analysed by DSC and it was also used to ascertain the degree of PCM incorporation. Firstly, the thermal behaviour of pure RT5 is shown in Figure 4.

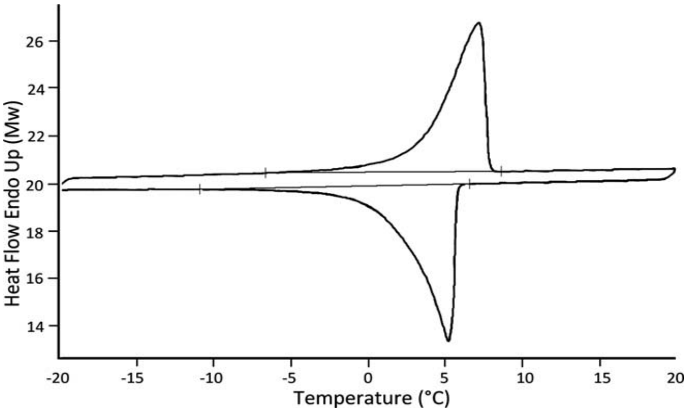

Figure 4. DSC thermograms of Rubitherm 5.

The PCM melted at ~7.20ºC and crystallized at ~5.26ºC, in a narrow temperature range, having an enthalpy of 144.7 J/g. However, the thermal properties of RT5 varied when this PCM was encapsulated within the polymer (PS or PCL) matrices and upon ageing.

Thermal properties (enthalpy values, melting and crystallization temperatures, and supercooling degree) of the internal and external parts of the PS/RT5 slabs analysed by DSC at 2ºC min^{-1} are given in Tables 1 and 2, respectively.

Similarly, the corresponding data of internal and external parts of PCL/PCM slabs are displayed in Tables 3 and 4, respectively.

From Tables 1 and 2, it can be observed that when RT5 was encapsulated in the PS matrix, the melting enthalpy was lower than that of the non-encapsulated PCM. This difference could be explained by part of the PCM not being properly encapsulated, and/or by an interaction of the PCM with the encapsulating polymer, thus partially hindering paraffin crystallization. As expected, the crystallization and melting enthalpy of slabs were significantly higher at the internal part of the slabs, probably due to the slight heat-treatment suffered from the outer zones during the slab-formation. On the other hand, the melting temperature of pure RT5 was in the same range as the melting temperature of the slabs, indicating that similar PCM crystals were formed in the encapsulation structures. Furthermore, in the internal parts of PS/PCM slabs, the melting temperature was not significantly affected by the storage temperature and time. However, in the external parts of the paraffin-containing PS structures, the melting temperature increased during storage at 25ºC. Regarding the melting and crystallization enthalpies, a slight decrease was observed with time upon storage at 25ºC (in both the internal and external parts of the slabs), which again could be explained by a partial diffusion out of the PCM.

Table 1. Thermal Properties of the Internal Part of PS/RT5 Slabs

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		T_{c3} (ºC)		ΔH_c (J/g PCM)		Supercooling (ºC)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	$7.3(0.1)^{a,1}$	$7.4(0.1)^{a,1}$	$119(2)^{a,1}$	$119(2)^{ab,1}$	$9.1(0.1)^{a,1}$	$9.1(0.1)^{a,1}$	$5.0(0.1)^{a,1}$	$5.0(0.1)^{ab,1}$	$-9.6(0.1)^{a,1}$	$-9.6(0.1)^{a,1}$	$117(1)^{ab,1}$	$117(1)^{ab,1}$	$2.4(0.1)^{a,1}$	$2.7(0.1)^{a,1}$
7	$7.1(0.3)^{a,1}$	$7.5(0.1)^{a,1}$	$122(2)^{b,1}$	$120(1)^{b,1}$	$9.0(0.2)^{a,1}$	$9.3(0.1)^{a,1}$	$4.5(0.2)^{bcd,1}$	$5.2(0.1)^{ab,2}$	$-10.4(0.2)^{bc,1}$	$-10.6(0.1)^{a,1}$	$121(5)^{bc,1}$	$121(2)^{c,1}$	$2.6(0.1)^{a,1}$	$2.4(0.1)^{a,1}$
15	$6.8(0.7)^{a,1}$	$7.3(0.7)^{a,1}$	$128(2)^{d,1}$	$121(3)^{ab,1}$	$8.9(0.4)^{a,1}$	$9.2(0.6)^{a,1}$	$4.5(0.3)^{bc,1}$	$5.1(0.4)^{ab,1}$	$-10.6(0.5)^{b,1}$	$-10.5(0.5)^{a,1}$	$129(5)^{c,1}$	$119(3)^{bc,1}$	$2.4(0.5)^{a,1}$	$2.3(0.3)^{a,1}$
30	$6.9(0.1)^{a,1}$	$7.4(0.1)^{a,1}$	$125(2)^{cd,1}$	$131(5)^{c,1}$	$8.7(0.1)^{a,1}$	$9.2(0.2)^{a,2}$	$4.3(0.1)^{b,1}$	$5.0(0.1)^{ab,2}$	$-10.4(0.1)^{bc,1}$	$-10.6(0.4)^{a,1}$	$125(1)^{bc,1}$	$130(3)^{d,1}$	$2.6(0.1)^{a,1}$	$2.4(0.1)^{a,1}$
45	$7.0(0.1)^{a,1}$	$7.2(0.5)^{a,1}$	$115(2)^{ab,1}$	$114(2)^{ab,1}$	$8.7(0.1)^{a,1}$	$9.0(0.3)^{a,1}$	$4.4(0.1)^{b,1}$	$4.7(0.4)^{a,1}$	$-10.4(0.6)^{bc,1}$	$-10.4(0.1)^{a,1}$	$117(1)^{ab,1}$	$118(1)^{ab,1}$	$2.6(0.1)^{a,1}$	$2.4(0.1)^{a,1}$
60	$7.2(0.2)^{a,1}$	$7.3(0.1)^{a,1}$	$112(3)^{a,1}$	$114(1)^{ad,1}$	$8.9(0.1)^{a,1}$	$9.0(0.1)^{a,1}$	$4.6(0.1)^{bca,1}$	$4.9(0.1)^{ab,2}$	$-9.7(0.4)^{bc,1}$	$-10.1(0.1)^{a,1}$	$113(3)^{bd,1}$	$116(4)^{ad,1}$	$2.7(0.3)^{a,1}$	$2.4(0.1)^{a,1}$
75	$7.4(0.4)^{a,1}$	$7.5(0.3)^{a,1}$	$113(2)^{ab,1}$	$114(1)^{ad,1}$	$9.0(0.3)^{a,1}$	$9.2(0.2)^{a,1}$	$4.8(0.1)^{ad,1}$	$5.1(0.1)^{ab,1}$	$-9.8(0.4)^{ab,1}$	$-9.9(0.2)^{a,1}$	$118(2)^{bd,1}$	$116(2)^{ad,1}$	$2.6(0.2)^{a,1}$	$2.4(0.2)^{a,1}$
90	$7.2(0.1)^{a,1}$	$7.4(0.2)^{a,1}$	$110(1)^{a,1}$	$111(1)^{d,1}$	-	-	$4.7(0.2)^{acd,1}$	$5.2(0.1)^{b,1}$	$-9.9(0.2)^{abc,1}$	$-9.2(0.2)^{a,1}$	$112(4)^{d,1}$	$111(1)^{d,1}$	$2.5(0.3)^{a,1}$	$2.2(0.3)^{a,1}$

a–e: Different superscripts within the same column indicate significant differences due to storage time ($P < 0.05$); 1 and 2: Different superscripts within the same line indicate significant differences due to the temperature used ($P < 0.05$). Mean value (standard deviation).

Table 2. Thermal Properties of the External Face of PS/RT5 Slabs

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		T_{c3} (ºC)		ΔH_c (J/g PCM)		Supercooling (ºC)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	6.9(0.1)^{a,1}	6.8(0.1)^{a,2}	69(1)^{a,1}	69(1)^{a,1}	9.1(0.1)^{a,1}	9.6(0.1)^{a,2}	4.1(0.1)^{a,1}	4.1(0.1)^{a,1}	-9.8(0.1)^{abc,1}	-9.1(0.1)^{a,2}	71(1) ^{ab,1}	68(1)^{ab,2}	2.8(0.1)^{a,1}	2.7(0.1)^{a,1}
7	7.0(0.2)^{a,1}	7.5(0.3)^{ab,1}	70(2)^{ab,1}	68(1)^{ab,1}	9.2(0.2)^{b,1}	9.1(0.8)^{ad,2}	4.3(0.2)^{a,1}	4.6(0.4)^{bc,1}	-9.5(0.4)^{bc,1}	-9.1(0.1)^{a,1}	70 (1)^{ab,1}	68(2)^{abc,1}	2.7(0.1)^{a,1}	2.9(0.1)^{a,1}
15	7.1(0.3)^{a,1}	7.4(0.1)^{ab,1}	69(1)^{ab,1}	62(1)^{c,2}	9.3(0.2)^{bcd,1}	9.1(0.1)^{c,1}	4.5(0.6)^{a,1}	4.5(0.1)^{ab,1}	-9.7(0.1)^{abc,1}	-9.0(0.3)^{ab,1}	69 (1)^{a,1}	64(1)^{acd,1}	2.5(0.1)^{a,1}	2.9(0.1)^{a,1}
30	7.4(0.1)^{bc,1}	7.7(0.6)^{b,1}	73(3)^{b,1}	70(4) ^{a,1}	9.6(0.2)^{cd,1}	9.5(0.3)^{ad,1}	4.8(0.5)^{a,1}	4.7(0.2)^{bcd,1}	-9.5(0.2)^{abc,1}	-9.0(0.4)^{ab,1}	76(1)^{b,1}	71(1)^{b,1}	2.7(0.5)^{a,1}	3.0(0.4)^{a,1}
45	7.2(0.1)^{abc,1}	7.5(0.1)^{ab,1}	74(2) ^{b,1}	64(2)^{bc,2}	9.2(0.1)^{bc,1}	9.3(0.1)^{cd,1}	4.5(0.3)^{a,1}	4.6(0.1)^{ab,1}	-9.9(0.1)^{ab,1}	-9.6(0.1)^{abc,2}	76(1)^{b,1}	62(1)^{cd,1}	2.7(0.3)^{a,1}	2.9(0.1)^{a,1}
60	7.6(0.2)^{c,1}	7.6(0.2)^{ab,1}	71(2)^{ab,1}	63(1)^{c,2}	9.6(0.1)^{d,1}	9.4(0.1)^{ad,1}	4.8(0.1)^{a,1}	5.0(0.1)^{cd,1}	-9.3(0.1)^{c,1}	-8.5(0.5)^{abc,1}	72(5)^{b,1}	59(4)^{acd,1}	2.7(0.1)^{a,1}	2.6(0.1)^{a,1}
75	7.2(0.2)^{ab,1}	7.7(0.6)^{b,1}	72(4) ^{ab,1}	59(2)^{c,1}	8.9(0.1)^{b,1}	9.9(0.1)^{b,2}	4.4(0.5)^{a,1}	5.0(0.1)^{cd,1}	-9.6(0.2)^{abc,1}	-8.4(0.1)^{bc,1}	69(5)^{ab,1}	62(1)^{acd,1}	2.7(0.6)^{a,1}	2.6(0.6)^{a,1}
90	7.0(0.1)^{a,1}	7.9(0.2)^{b,2}	69(1)^{ab,1}	59(4)^{c,1}	9.0 (0.2)^{a,1}	9.8(0.2)^{a,1}	4.4(0.7)^{a,1}	5.1(0.2)^{d,1}	-9.9(0.1)^{a,1}	-8.3(0.6)^{c,1}	69(1)^{a,1}	60(3)^{d,2}	2.6(0.6)^{a,1}	2.8(0.1)^{a,1}

a–d: Different superscripts within the same column indicate significant differences due to storage time ($P < 0.05$); 1 and 2: Different superscripts within the same line indicate significant differences due to the temperature used ($P < 0.05$).Mean value (standard deviation).

Table 3. Thermal Properties of the Internal Part of PCL/RT5 Slabs

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		T_{c3} (ºC)		ΔH_c (J/g PCM)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	7.7(0.1)^{a,1}	7.3(0.5)^{ab,1}	131(1)^{a,1}	131(1)^{a,1}	5.4(0.1)^{a,1}	5.3(0.2)^{a,1}	1.8(0.1)^{a,1}	1.8(0.1)^{a,1}	130 (1)^{a,1}	130(1)^{a,1}	2.3(0.1)^{a,1}	2.0(0.3)^{a,1}
7	7.6(0.1)^{a,1}	7.6(0.5)^{ab,1}	132(1)^{a,1}	126(1)^{ab,2}	5.4(0.1)^{a,1}	5.4(0.3)^{ab,1}	1.9(0.1)^{ab,1}	2.0(0.1)^{b,1}	131(1)^{ab,1}	127(2)^{b,2}	2.2(0.1)^{bc,1}	2.2(0.5)^{a,1}
15	7.6(0.3)^{a,1}	7.8(0.1)^{ab,1}	135(4)^{a,1}	126(1)^{ab,2}	5.3(0.4)^{a,1}	5.7(0.1)^{b,1}	2.0(0.2)^{bc,1}	2.6(0.1)^{c,2}	137 (4)^{de,1}	125(1)^{b,2}	2.3(0.1)^{ab,1}	2.1(0.1)^{ab,1}
30	7.6(0.3)^{a,1}	8.1(0.3)^{b,1}	138(3)^{ab,1}	121(1)^{b,2}	5.5(0.3)^{ab,1}	6.1(0.1)^{c,2}	2.1(0.2)^{bcd,1}	3.9(0.2)^{d,2}	136(1)^{cd,1}	120(1)^{c,2}	2.1(0.1)^{ab,1}	2.0(0.3)^{ab,1}
45	7.6(0.1)^{a,1}	8.1(0.1)^{b,1}	135(3)^{bc,1}	121(1)^{b,2}	5.5(0.1)^{ab,1}	6.3(0.2)^{d,2}	2.2(0.1)^{cde,1}	4.1(0.1)^{de,2}	135(1)^{bcd,1}	116(3)^{d,2}	2.1(0.1)^{bc,1}	1.8(0.1)^{ab,2}
60	7.5(0.1)^{a,1}	8.1(0.2)^{b,1}	140(1)^{c,1}	120(3)^{b,2}	5.5(0.1)^{ab,1}	6.5(0.2)^{d,2}	2.3(0.1)^{de,1}	4.2(0.1)^{e,2}	141(2)^{e,1}	118(2)^{cd,2}	2.1(0.1)^{b,1}	1.7(0.1)^{ab,2}
75	7.3(0.1)^{a,1}	8.1(0.1)^{a,1}	137(1)^{d,1}	107(1)^{c,2}	5.5(0.1)^{ab,1}	6.5(0.1)^{d,2}	2.2(0.1)^{cde,1}	4.2(0.2)^{e,2}	138(1)^{de,1}	108(1)^{e,2}	1.8(0.1)^{c,1}	1.6(0.2)^{ab,1}
90	7.6(0.1)^{a,1}	8.3(0.6)^{ab,1}	133(1)^{d,1}	106(4)^{c,2}	5.6(0.1)^{b,1}	6.5(0.1)^{d,2}	2.4(0.1)^{e,1}	4.2(0.1)^{e,2}	133(1)^{abc,1}	106(3)^{e,2}	1.7(0.1)^{c,1}	1.6(0.3)^{b,1}

a–e: Different superscripts within the same column indicate significant differences due to storage time ($P < 0.05$); 1 and 2: Different superscripts within the same line indicate significant differences due to the temperature used ($P < 0.05$). Mean value (standard deviation).

Table 4. Thermal Properties of the External Face of PCL/RT5 Slabs

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		T_{c3} (ºC)		ΔH_c (J/g PCM)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	7.5(0.1)^{a,1}	7.5(0.1)^{a,1}	110(1)^{ab,1}	110(1)^{ab,1}	5.5(0.1)^{a,1}	5.5(0.1)^{a,1}	2.0(0.1)^{a,1}	2.0(0.1)^{a,1}	109(1)^{a,1}	109(1)^{ab,1}	2.0(0.1)^{a,1}	2.1(0.1)^{a,1}
7	7.2(0.1)^{a,1}	7.6(0.1)^{a,2}	107(1)^{a,1}	107(1)^{abc,1}	5.0(0.1)^{a,1}	5.5(0.1)^{a,2}	1.9(0.1)^{a,1}	2.3(0.1)^{ab,2}	111(1)^{ab,1}	106(1)^{b,1}	2.2(0.1)^{a,1}	2.1(0.1)^{a,2}
15	7.4(0.1)^{a,1}	7.8(0.1)^{b,2}	114(3)^{bc,1}	103(1)^{ac,2}	5.3(0.1)^{a,1}	5.7(0.1)^{b,2}	1.9(0.6)^{a,1}	2.9(0.1)^{b,2}	115(4)^{bc,1}	105(1)^{a,1}	2.1(0.1)^{a,1}	2.1(0.1)^{a,1}
30	7.5(0.2)^{a,1}	8.0(0.1)^{b,1}	124(5)^{d,1}	106(2)^{ac,2}	5.5(0.1)^{a,1}	6.1(0.1)^{c,1}	2.5(0.7)^{a,1}	4.1(0.5)^{c,2}	123(4)^{de,1}	108(1)^{ab,2}	2.1(0.1)^{a,1}	1.9(0.2)^{ab,1}
45	7.5(0.2)^{a,1}	8.0(0.2)^{bc,1}	114(1)^{bc,1}	111(4)^{b,1}	5.3(0.4)^{a,1}	6.3(0.2)^{d,2}	3.6(0.1)^{b,1}	4.5(0.2)^{cd,2}	115(2)^{bc,1}	112(4)^{b,1}	2.2(0.1)^{a,1}	1.7(0.4)^{bc,2}
60	7.6(0.1)^{a,1}	8.1(0.2)^{bc,1}	118(3)^{c,1}	101(1)^{d,2}	5.4(0.1)^{a,1}	6.5(0.1)^{de,2}	4.6(0.1)^{c,1}	4.7(0.1)^{cd,2}	118(2)^{cd,1}	99(3)^{c,2}	2.2(0.2)^{a,1}	1.7(0.2)^{bc,2}
75	7.5(0.3)^{a,1}	8.0(0.2)^{bc,1}	124(1)^{d,1}	99(3)^{d,2}	5.3(0.3)^{a,1}	6.5(0.7)^{e,2}	4.3(0.2)^{bc,1}	4.7(0.6)^{cd,2}	127(2)^{e,1}	96(3)^{c,2}	2.2(0.1)^{a,1}	1.5(0.9)^{c,2}
90	7.7(0.4)^{a,1}	8.3(0.1)^{c,1}	115(2)^{bc,1}	100(2)^{d,2}	5.4(0.3)^{a,1}	6.7(0.1)^{f,2}	4.7(0.8)^{d,1}	4.7(0.1)^{d,2}	114(2)^{abc,1}	97(3)^{c,2}	2.2(0.1)^{a,1}	1.5(0.1)^{c,2}

a–d: Different superscripts within the same column indicate significant differences due to storage time ($P < 0.05$); 1 and 2: Different superscripts within the same line indicate significant differences due to the temperature used ($P < 0.05$). Mean value (standard deviation).

In contrast with the similarities in the melting temperature between pure RT5 and encapsulated PCM, the crystallization event was considerably different. While pure RT5 crystallizes at 5.26ºC, a greater supercooling degree was observed in both internal and external zones of the PS/PCM slabs. The supercooling effect was probably due to the reduction of the PCM particle size, since the number of nuclei needed to initiate the crystallization process decreased with reducing the diameter of the RT5 drops inside the fibres. Moreover, a multiple crystallization profile was seen for the encapsulated PCM and, specifically, three crystallization temperatures were detected for the slabs. This can be mainly ascribed to the different diameter of PCM droplets.[17,18] Zhang[19] assigned the multiple crystallization processes of the N-alkanes to the rotator phase transition which is observed in these paraffin's when their particle size is reduced. A rotator phase is defined as lamellar crystals, which exhibit long-range order in the molecular axis orientation and centre-of-mass position but lack rotational degrees of freedom of the molecules about their long axis. In these cases, more than one peak is observed in the DSC analysis during the crystallization process that corresponds to the different crystallization mechanisms followed. The first peak belongs to the heterogeneously nucleated liquid-rotator transition, the second one includes the rotator-crystal transition and the last one is attributed to the homogeneously nucleated liquid-crystal transition.[18]

These multiple crystallization profile can be related with the particle size of RT5 droplets. As commented on above, the encapsulation of RT5 led to the formation of pores inside PCL or PS fibres, which were larger for PCL fibres. However, it appears that microemulsions were formed during the preparation of PS-based solutions, leading to the formation of smaller pores within the electrospun fibres, which resulted in the heterogeneous crystallization phenomena observed. Similar to that observed for PS/PCM slabs, there were not significant changes between the melting temperatures of pure RT5 and PCL/RT5 slabs. It is important to note that the melting enthalpy of PCL/RT5 slabs was significantly higher than that of PS/RT5 slabs, fact which could also be attributed to a greater encapsulation efficiency probably related with the larger size of PCL/RT5 fibres. Once again and probably as a result of the heat-treatment used for the formation of slabs, melting and crystallization enthalpies were lower at the external parts of the PCL/PCM slabs. The melting temperature as well as melting and crystallization enthalpies did not vary significantly in PCL/PCM slabs stored at 4ºC. However, a significant increase in the melting temperature together with a decrease in the melting and crystallization enthalpies were observed in PCL/RT5 slabs stored at 25ºC. This could be ascribed to the PCM diffusion throughout the PCL matrix along storage.

Two crystallization temperatures were detected for the PCL/PCM slabs which can be assigned to the crystallization behaviour of lamellar crystals described above, with the second and third transitions appearing as a single peak.[19] These differences between PCL and PS crystallization behaviour could be also explained by the different particle size of the PCM droplets, which was greater in PCL fibres. Similar behaviour was observed in PCL/dodecane hybrid structures.[11]

The presence of PCM in the slabs was also qualitatively evaluated by ATR-FTIR spectroscopy. Figure 5 shows the ATR-FTIR spectra of the pure PS fibres, the pure RT5 and the PS/RT5 slabs analysed at 20ºC. At this temperature, the pure RT5 is characterized by the –CH2 and –CH3 stretching vibration bands at 2956, 2922 and 2854 cm^{-1}. These bands were also observed in the PS/RT5 slabs even though they were overlapped with the spectral bands from the PS, thus confirming the PCM encapsulation in the PS matrix. It is worth noting that the intensity of the characteristic bands from the paraffin was greater at the internal part of the slabs and decreased in those stored at 25ºC (Table 5). This is directly related with the enthalpy values commented on above.

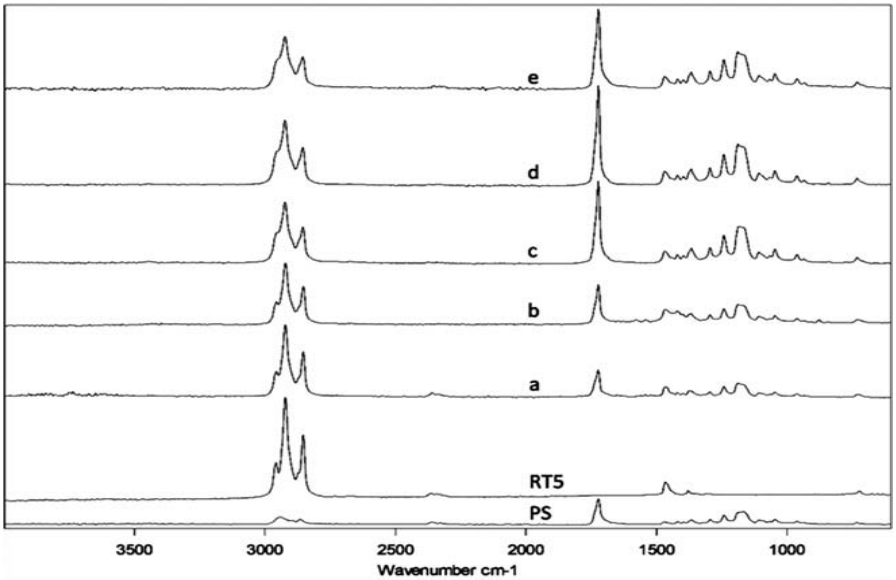

Figure 5. ATR-FTIR spectra of the pure PS polymer, pure RT5, and non- stored and stored PS/PCM hybrid electrospun materials measured at 4ºC and 25ºC, at the internal and external part of the slabs. (a) PS/RT5 non- stored slabs, (b) and (c) internal PS/RT5 slabs stored for 3 months at 4ºC and 25ºC, respectively, as well as (d) and (e) external PS/RT5 slabs stored for 3 months at 4ºC and 25ºC, respectively.

Figure 6 compares the ATR-FTIR spectra of the pure PCL fibres, the pure PCM and the internal and external parts of the non-stored and stored PCL/RT5 slabs analysed at 20ºC. Once again, the –CH2 and –CH3 stretching vibration bands at 2956, 2922 and 2854 cm^{-1} appeared in all PCL/RT5 slabs even though they were also overlapped with the spectral bands of PCL.

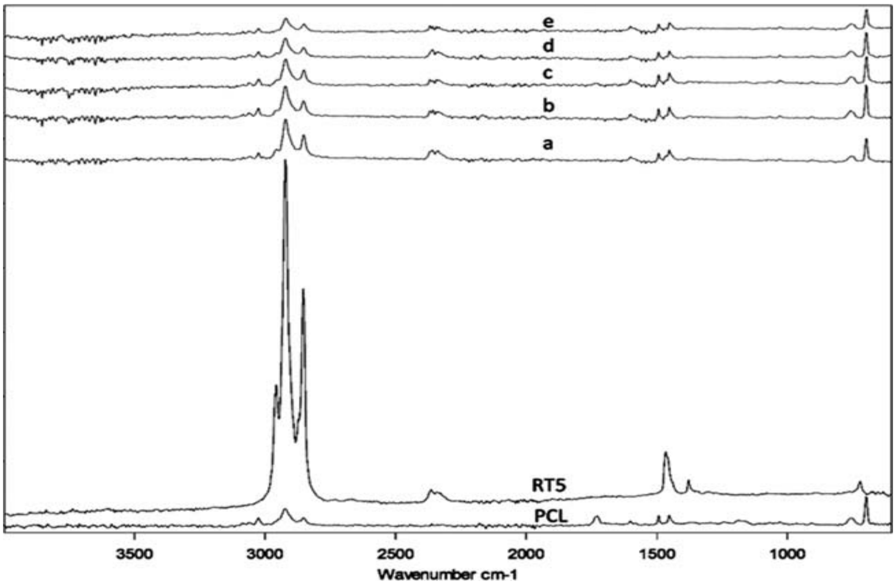

Figure 6. ATR-FTIR spectra of the pure PCL polymer, pure RT5, and nonstored and stored PCL/PCM hybrid electrospun materials measured at 4ºC and 25ºC, at the internal and external part of the slabs. (a) PCL/RT5 nonstored slabs, (b) and (c) internal PCL/RT5 slabs stored for 3 months at 4ºC and 25ºC, respectively, as well as (d) and (e) external PCL/RT5 slabs stored for 3 months at 4ºC and 25ºC, respectively.

Similarly to that observed for the PS-based slabs, the relative intensity of the PCM bands with respect to the polymer ones was greater both in the internal parts of the slab and upon storage at 4ºC (Table 5). Again, these results are in agreement with enthalpy values.

Table 5. Ratio of RT5 and PS or PCL

Material	Intensity			Ratio(RT5/PS o PCL)
	2921.87 cm^{-1}	698.16 cm^{-1}	1724.19 cm^{-1}	
Rubitherm 5 (RT5)	1.0354	-		-
Polystyrene (PS)	0.0519	0.0898		0.5778
PS/RT5 non-stored slabs	0.1369	0.0773		1.7711
Internal PS/RT5 slabs stored for 3 months at 4°C	0.0998	0.1029		0.9696
Internal PS/RT5 slabs stored for 3 months at 25°C	0.0766	0.0824		0.9289
External PS/RT5 slabs stored for 3 months at 4°C	0.0576	0.0761		0.7573
External PS/RT5 slabs stored for 3 months at 25°C	0.0364	0.0613		0.5939
Polycaprolactone (PCL)	0.0604		0.2551	0.2368
PCL/RT5 non-stored slabs	0.7090		0.2770	2.5594
Internal PCL/RT5 slabs stored for 3 months at 4°C	0.6613		0.4499	1.4699
Internal PCL/RT5 slabs stored for 3 months at 25°C	0.5796		0.8288	0.6992
External PCL/RT5 slabs stored for 3 months at 4°C	0.6327		0.8774	0.7211
External PCL/RT5 slabs stored for 3 months at 25°C	0.5521		0.8312	0.6642

3.3. Evaluation of the PCM Encapsulation Efficiency and Loading

The PCM encapsulation efficiency and loading capacity of the hybrid structures were evaluated from the enthalpy results obtained through DSC. The encapsulation yield was calculated by dividing the experimental by the expected theoretical melting enthalpies obtained for PS or PCL materials. The theoretical melting enthalpy was obtained considering the quantity of RT5 added to the electrospinning solution (45 wt.-%) and multiplying this by the experimental enthalpy of the pure RT5. Figure 7 and 8 shows the encapsulation efficiency and the calculated total amount of the PCM encapsulated in the PS and PCL slabs, respectively. Both (internal and external) parts of slabs stored at 4 and 25ºC were analysed.

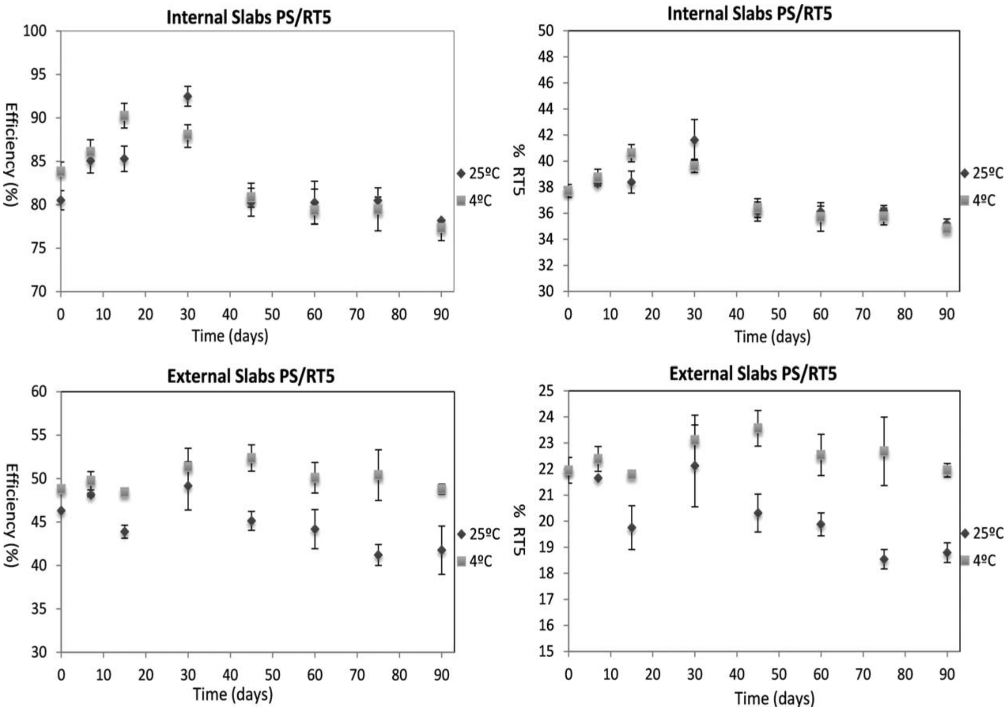

Figure 7. Encapsulation efficiency and the calculated amount of the RT5 (%) encapsulated in the PS fibers during ageing at 4ºC and 25ºC.

PCL structures presented greater encapsulation efficiency than PS and the encapsulation yield was always higher at the internal part of the slabs, as previously anticipated by the thermal and morphological characterization. The greater encapsulation efficiency of PCL structures could be related with the greater diameter and internal structure observed in these fibres which could retain a higher amount of the PCM. A similar behaviour was also observed by Pérez-Masiá[11] working with PCL/dodecane (porous fibres) and PLA/dodecane hybrid structures (thinner and non-porous fibres).

On the other hand, the lower encapsulation efficiency observed in the outer layers was probably related with the slight heat-treatment used for the formation of the PCL/PCM and PS/PCM slabs. It may be noted that the encapsulation yield at the external part of the slabs significantly decreased with the storage time at 25ºC. However, the internal part of the hybrid structures behaved differently depending on the matrix and temperature used. For instance, the encapsulation efficiency in the PS/RT5 hybrid structures decreased by up to 14.90% for the internal part of slabs stored at 90 days, having not significantly differences between those stored at 4 or 25ºC. This was more noticeable in the case of the internal part of the PCL/PCM structures stored at 25ºC, where the encapsulation efficiency decreased by up to 18.86% for slabs stored 90 days. However, no significant variations were observed in the PCL/PCM structures stored at 4ºC. As commented on above, this could be attributed to the different physical state of the PCM at 4 and 25ºC together with the porous structures of PCL fibres.

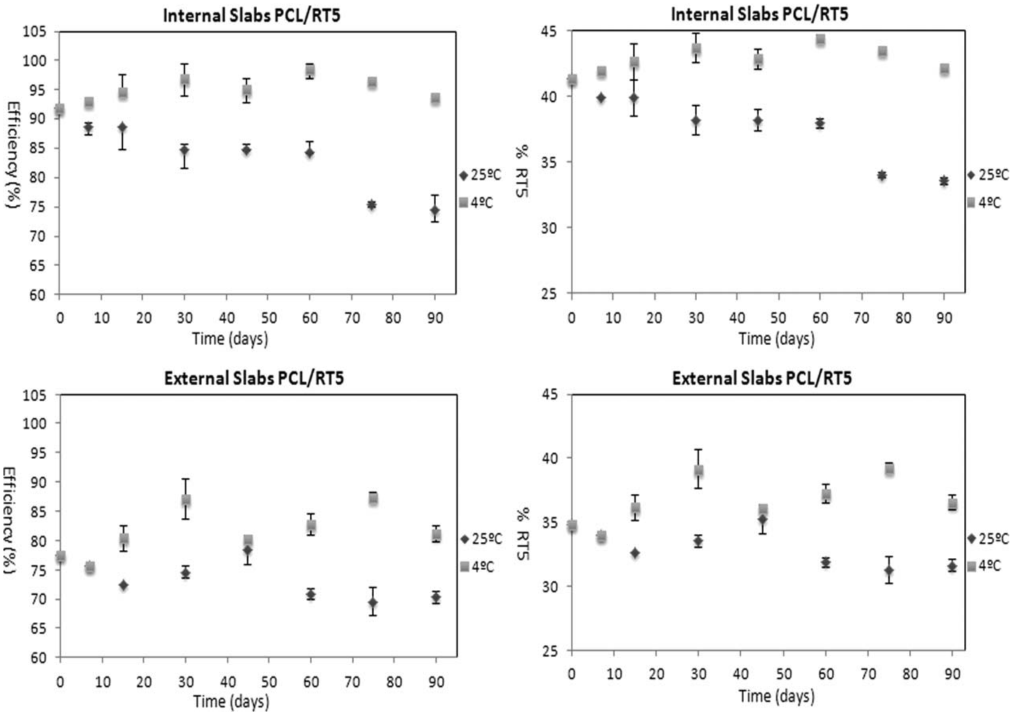

Figure 8. Encapsulation efficiency and the calculated amount of the RT5 (%) encapsulated in the PCL fibers at 4ºC and 25ºC.

From the results, it can be concluded that the greatest encapsulation efficiency (98.56%) was achieved for PCL/PCM slabs stored at 4ºC, which retained the encapsulated PCM during storage and were, thus composed of 44.35 wt.% of PCM (the core material) and 55.65 wt.% of the PCL shell material.

3.4 Temperature profile of PS/PCM and PCL/PCM slabs.

The thermal behaviour of the PCM was also evaluated by recording the temperature profiles of PCL and PS slabs stored at -18ºC and analysed at room temperature (20ºC). Figure 9 compares the temperature profiles of the PS/PCM (a) and PCL/PCM (b) slabs with their counterparts without PCM, as they pass through the melting range of RT5. The IR probe is expected to provide thermal information mostly coming from the surface of the material where lower encapsulation efficiency values were observed.

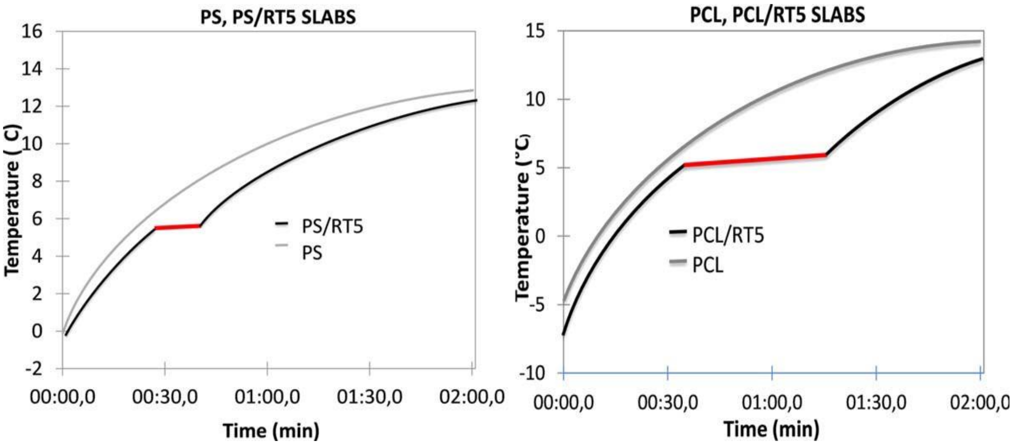

Figure 9. Surface temperature as a function of time for PS/PCM (a) and PCL/PCM (b) slabs.

As expected, the increased effective specific heat over the melting region has the effect of slowing down the rate of temperature rise locally. In both cases, the slope of the time-temperature curve of the PCL/PCM and PS/PCM slabs decreased and even plateau for some time in the melting range of the PCM for both encapsulation structures, but it was more pronounced in the PCL hybrid structures, which could thus be more effective at temperature buffering.

4. CONCLUSIONS

In this work, heat management materials based on the encapsulation of a PCM (RT5) inside PS or PCL were successfully developed. Melting behaviour of the encapsulated RT5 was similar to that of pure RT5. However, a multiple crystallization profile was observed for the encapsulated PCM. While pure RT5 crystallizes at 5.26ºC, a greater supercooling degree was observed in both internal and external zones of the PS/PCM and PCL/PCM slabs, probably due to the reduction of the PCM particle size.

Results showed that PCL/PCM slabs were able to encapsulate a greater amount of the RT5 than those obtained with PS. The encapsulation efficiency decreased in the PS/PCM and PCL/PCM slabs stored at 25ºC which was attributed to the progressive diffusion out of the PCM from the capsules during aging (which was in liquid state at this temperature). However, no significant changes during aging were observed in those stored at 4ºC, showing that PCL/PCM slabs stored at 4ºC had the greatest encapsulation efficiency (98.56%). Therefore, the developed PCL/PCM hybrid structures would be able to encapsulate a heat storage capacity equivalent to ~44 wt% of PCM, at 4ºC for at least three months.

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CHAPTER II

Use of phase change materials to develop electrospun coatings of interest in food packaging applications

CHAPTER II: Use of phase change materials to develop electrospun coatings of interest in food packaging applications

ABSTRACT

In the present study, a heat management PS foam tray containing an ultrathin fiber-structured PS/PCM coating was prepared by using high throughput electro-hydrodynamic processing. To this end, polystyrene (PS) was used as the encapsulating matrix of a commercial phase change material (PCM) called RT5 (a blend of paraffin's with a transition temperature at 5ºC), by using the electrospinning technique. With the aim of imparting heat management capacity to the trays, the PS tray was coated by the PS/PCM ultrathin fiber mats and a soft heat treatment was applied to improve the adhesion between the layers. Results showed that RT5 could be properly encapsulated inside the PS matrix, with a good encapsulation efficiency (ca. 78%) and the developed PS fibers had a heat storage capacity equivalent to ~34 wt.% of the neat PCM. The effect of storage time and temperature was evaluated on the heat storage capacity of the developed PS-trays with the ultrathin fiber-structured PS/PCM layer. The heat storage capacity was affected not only by the storage time, but also by the temperature. This work adds a new insight on the development of heat management polymeric materials of interest in food packaging applications, in order to preserve the quality of refrigerated packaged food products. Although the electro-hydrodynamic processing seems to be a promising alternative to develop heat management materials, further works will be focused on the improvement of heat storage capacity and efficiency of the developed packaging materials along storage time.

Keywords: Phase change material · Electro-hydrodynamic processing · Heat Management materials · Food packaging · Encapsulation

1. INTRODUCTION

Maintaining the cold chain during the commercialization of certain food products is one of the key aspects to ensure food safety and food quality. Refrigeration temperatures (from 2 to 8ºC) are used for preventing or slowing down microbial, physiological and chemical changes in food produced by microbial, chemical and/or enzymatic activity. Along the cold chain there can be temperature variations which will consequently have negative effects on food due to crystal ice growth, acceleration of chemical reactions and/or microorganism growth, which could result in a reduction of quality and may shorten the shelf-life of the food products. Therefore, there is a great interest on finding new strategies to reduce temperature fluctuations along the cold chain. In this sense, the packaging can be designed to play an active role to maintain the food temperature within desired limits and, thus, to ensure the quality, safety and increase the shelf-life of the products (James et al., 2006). However, traditional commercial packages such as low-density polyethylene, polystyrene, etc. do not provide any protection for maintaining the cold chain.

Phase change materials (PCM's) are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release latent heat with a very small variation in temperature (Jin et al., 2010). PCM's could be used during transport, storage and distribution stages to maintain the cold chain of solid food, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products and many others (Alkan et al., 2011; Azzouz et al., 2009; Oró et al., 2012; Salunkhe and Shembekar, 2012; Zalba et al., 2003). The most commonly used phase change materials are paraffin waxes, fatty acids, eutectics and hydrated salts (Farid et al. 2004). Paraffin compounds fulfill most of the requirements for being used as PCM's, as they are reliable, predictable, non-toxic, chemically inert and stable below 500ºC. They also show little volume changes on melting and have low vapor pressure in the melt form (Sharma et al., 2009).

For the correct use of PCM's, as they experiment a phase change from solid to liquid at the target temperature, they must be encapsulated. In this context, there are two main encapsulation types: the nano- or micro- and the macroencapsulation. Traditionally, for building and transport applications, macroencapsulation in containers have been carried out. However, nano- and microencapsulation present a number of advantages for the development of other types of heat-storage materials, like improvement of the heat transfer through its greater specific surface. Therefore, microencapsulation of PCM's is a plausible solution because it allows protecting them against the influences of the outside environment, increasing the heat-transfer area, and permitting the core material to withstand changes in volume of the PCM which take place as the phase change occurs, thus, allowing the development of small and portable thermal energy storage systems (Alkan et al., 2011).

An strategy already proposed to impart thermal buffering capacity to standard packaging materials is based on the development of thermal energy storage structures through the addition of, for example, PCM's (Chalco-Sandoval et al., 2014, Gin and Farid 2010 and Oró et al., 2012) within the polymeric structures (Oró et al., 2013). This strategy has been used by several researchers such as Yannick (2006) who patented a method to manufacture an insulated container used to transport and store ice cream, and Laguerre et al., (2008) who developed and validated a mathematical model to predict the product temperature at certain locations within an insulated container equipped with PCM. However, little information exists in the literature about the incorporation of encapsulated PCM structures into polymeric matrices for food packaging purposes, either in the form of multilayer or in nanocomposites. Chalco-Sandoval et al., 2014 developed PS multilayer-based heat storage structures based on PS films coated with polycaprolactone (PCL)/PCM electrospun layers. An additional PCL electrospun layer (without PCM) was also electrospun in some cases to retain PCM during film storage.

Electro-hydrodynamic processing is one technique increasingly being used for the microencapsulation of substances. Besides being a very simple technique, some advantages of this technique for encapsulation include that no temperature are needed, thus, being an ideal method for protecting sensitive encapsulated compounds. This technique has proven to be a suitable method for encapsulation of several components, including biomedical compounds, functional food ingredients, PCM's and others substances within polymer matrices (Goldberg et al., 2007; Lopez-Rubio et al., 2012; Pérez-Masiá et al., 2013). Furthermore, this technique has been successfully used to improve barrier properties of food packaging biopolymeric materials by using multilayer structures (Fabra et al., 2013, 2014), serving the electrospun hybrid structures as a self-adhesive. The electro-hydrodynamic processing, commonly termed as electrospinning, is a technique whereby long non-woven ultrafine structures, typically fibers with diameters of several tens to several hundreds of nanometers, may be formed by applying a high-voltage electric field to a solution containing polymers (Teo and Ramakrishna., 2006). As a result of the applied electric field, a polymer jet is ejected from the tip of a capillary through which a polymer solution is pumped, accelerated toward a grounded target and deposited thereon (Arecchi et al., 2010). Thus, the combination of the PCM with the electrospinning could provide new solutions for developing smart packaging systems with controlled barrier properties and heat management capacity.

The aim of this work was to develop heat management materials of interest in food packaging for refrigeration applications by means of developing a electrospun coating incorporating a PCM which melts at 5ºC (RT5), to be used onto polystyrene (PS) foam trays. The effects of storage temperature and ageing on the performance of the trays were also evaluated. PS was chosen due to it is a polymer widely used for food packaging applications.

2. MATERIALS AND METHODS

2.1. Materials

Rubitherm RT5, a technical grade paraffin wax, was chosen as the PCM for refrigerated storage. It is based on a cut resulting from refinery production and it consists entirely of normal paraffin waxes (C14-C18). RT5 was purchased from Rubitherm Technologies GmbH (Berlin, Germany). Polystyrene trays, which were foamed white trays, having a density of 20 $Kg \cdot m^{-3}$, were purchased from Poliestirenos Asturianos S.L (Asturias, Spain). The dimensions of the PS trays were 0.22, 0.14, 0.025 m length, width and height, respectively. Polystyrene (PS) commercial grade foam was supplied by Traxpo (Barcelona, Spain). N, N-dimethylformamide (DMF) with 99% purity and trichloromethane (99 %) were purchased from Panreac Quimica S.A. (Castellar del Vallés, Spain). All products were used as received without further purification.

2.2. Preparation of polystyrene-based tray structures

2.2.1. Preparation of heat management PS-trays.

PS trays were coated with PS/PCM mats produced by means of the high throughput electro-hydrodynamic processing. The full process of the PCM encapsulation through a high voltage spinning methodology has been previously developed (patent application number: ES 2 395 306 A1). The electrospun PS/PCM fibers were prepared according to Perez-Masia et al., (2013), by dissolving the required amount of PS, under magnetic stirring, in a solvent prepared with a mixture of trichloromethane:N,N-dimethylformamide (70:30 w/w) in order to reach a 10% in weight (wt.-%) of PS. Afterward, 45 wt % of PCM (Rubitherm 5) with respect to the polymer weight was added to the polymer solutions, and stirred at room temperature until it was completely dissolved. PS/PCM fiber mats were directly electrospun onto a metal collector over 5 hours by means of a Fluidnatek® electrospinning pilot plant equipment from Bioinicia S.L. (Valencia, Spain) equipped with a variable high-voltage 0-60 kV power supply. PS/PCM solutions were electrospun under a steady flow-rate using a motorized high throughput multinozzle injector, scanning vertically towards a metallic grid used as collector. The distance between the needle and the collector was 28 cm and experiments were carried out at ambient temperature. The voltage of the collector and injector were set at 52 kV and 44 kV, respectively.

The electrospun PS/PCM coatings presented a whitish appearance and, with the aim of obtaining a continuous pellicle, the PS/PCM coating (~ 50g) was deposited onto the PS trays and was annealed at 145ºC for 1.5 min using a hot-plate hydraulic press (Carver, Inc., Wabash, USA) which also favoured the adhesion between materials.

2.2.2. Samples conditioning and storage

Samples were equilibrated in desiccators at 0% RH by using silica gel and at two different temperatures 4 and 25ºC for three months. PS-trays containing the PS/PCM coating were taken from the desiccators at different time intervals (0, 7, 15, 30, 45, 60 and 90 days) and DSC and FTIR analysis were carried out.

2.3. Characterization of PS trays with the ultrathin fiber-structured PS/PCM coating

2.3.1. Scanning Electron Microscopy (SEM).

SEM was conducted on a Hitachi microscope (Hitachi S-4100) at an accelerating voltage of 10 kV. Samples were cryo-fractured after immersion in liquid nitrogen and subsequently sputtered with a gold–palladium mixture under vacuum before their morphology was examined using SEM. The thickness of the coating layer was measured by means of the Adobe Photoshop CS3 extended software from the SEM micrographs in their original magnification.

2.3.2. Differential Scanning Calorimetry (DSC)

Thermal analyses of the samples were carried out on a DSC-7 calorimeter (Perkin Elmer Inc., Norwalk, USA) from -20 to 20ºC under a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2) (Perkin Elmer Inc., Norwalk, USA). The scanning rate was 2ºC/min in order to minimize the influence of this parameter in the thermal properties. The amount of material used for the DSC experiments was adjusted so as to have a theoretical PCM content of 1-2 mg approximately. The enthalpy results obtained were, thus, corrected according to this PCM content. All tests were carried out in triplicate.

2.3.3. Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR).

ATR-FTIR spectra of polystyrene (PS) polymer, PS tray, pure RT5 (PCM), PS/PCM fibers and PS tray structures were collected at 25ºC in a FTIR Tensor 37 equipment (Bruker, Rheinstetten, Germany). The spectra were collected in the different materials by averaging 20 scans at 4 cm^{-1} resolution. The experiments were repeated twice to verify that the spectra were consistent between individual samples.

2.3.4. Temperature profiles.

The temperature profiles of the PS trays with and without the PS/PCM coating were compared. To this end, all samples were frozen at -18ºC for 1 day. Then, the surface temperature evolution was registered at room temperature (20ºC) by using an infrared thermometer MS Plus (PCE Instruments, Tobarra, Spain).

2.3.4. Optical properties.

Internal transmittance of the PS/PCM coating and PS-trays was determined through the surface reflectance spectra with a spectrocolorimeter CM-3600 (Minolta Co, Tokyo, Japan) with a 10 mm illuminated sample area. Measurements were taken from three replicates by using both a white and black background and Kubelka-Munk theory for multiple scattering was applied to the sample reflection spectra. Internal transmittance (Ti) was calculated from the reflectance of the sample layer backed by a known reflectance and the reflectance of the film on an ideal black background (Hutchings 1999). Moreover, CIE-L*a*b* coordinates (CIE, 1986) were obtained by the infinite reflection spectra of the samples, using D65 illuminant/10° observer in order to calculate the whiteness index (WI) of the samples (Eq. (1)).

$$\mathrm{WI} = 100-((100-\mathrm{L})^2+\mathrm{a}^2+\mathrm{b}^2)^{0.5}$$
(1)

where L* (Luminosity) and a*b* are CIE-Lab colour parameters

2.4. Statistical Analysis.

Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, USA) was used for carrying out statistical analyses of data through analysis of variance (ANOVA). Fisher's least significant difference (LSD) was used at the 95% confidence level.

3. RESULTS

3.1. Morphology and optical properties

The main objective of this work was to develop PS trays containing PS/PCM coatings to maintain the chilling temperature of fresh food products along the cold-chain. The PS/PCM coating was previously observed by SEM (cf. Figure 1a). The surface images, showed a dense but opened structure with many beaded areas (10.3 ± 4.2 μm) within the fibrous (1.6 ± 0.6 μm) mat, and the cross-section images of the PS-trays (cf. Figure 1b) gave an idea of the coating´s thickness (~78μm) and compactness.

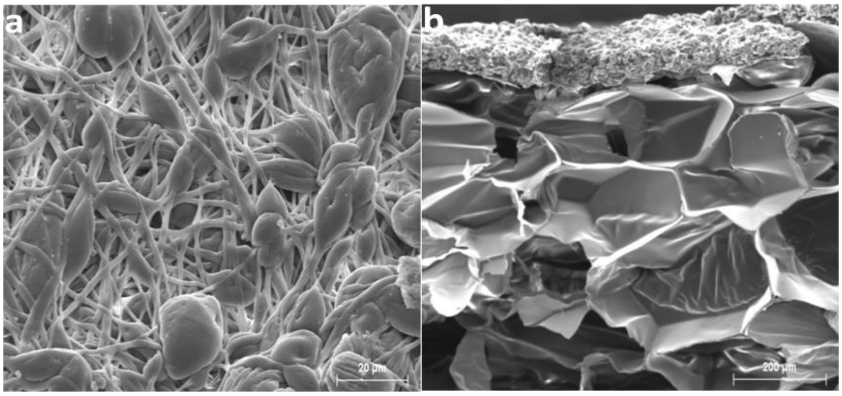

Figure 1. Cross-section SEM image of pure PS (left) and PS/PCM (right) fibers. The scale markers correspond to 2 μm. Arrows indicate the channels where PCM is supposed to be located.

Figure 2 shows the cross-sections of pure PS and PS/PCM cryofractured fibers. From these images, it can be observed that upon PCM incorporation, the surface morphology of the fibers was changed. While highly porous fibers were obtained for pure PCL, more compact structures were generated when PCM was added. Moreover, the cross-section of the loaded fibers also showed multiple channels (indicated with arrows) inside the fibrillar PS structures where the PCM was supposed to be allocated.

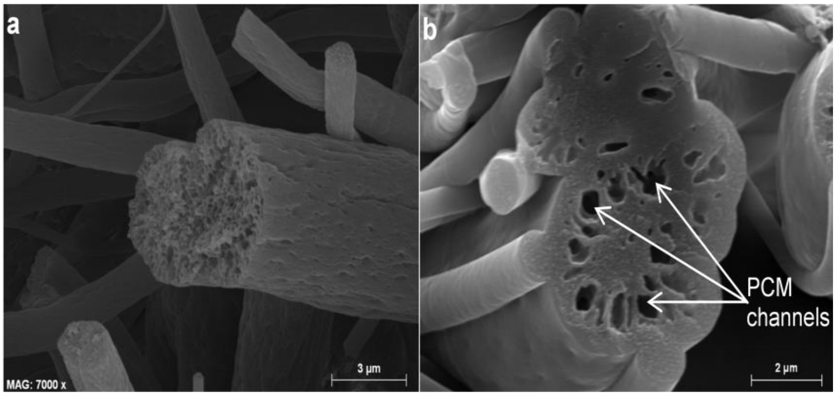

Figure. 2. Surface (a) and cross-section (b) SEM images of the PS tray with the ultrathin fiber-structured PS/PCM coating. Scale markers correspond to 20 and 200 µm for the surface and cross-section, respectively.

Optical properties of the PS trays containing, or not, the PS/PCM coating were evaluated and compared by means of the internal transmittance (Ti) where an increase in the internal distribution of transmittance is ascribed to an increase in transparency. Spectral distribution curves of internal transmittance are plotted in Figure 3. Lower Ti values (Ti ≤ 15%) were obtained in all the samples as compared to those previously obtained for multilayer structures prepared with PS (Ti ≥ 50%) which can be ascribed to the different nature of the PS used (Chalco-Sandoval et al., 2014). Considering these results, PS-trays and the corresponding PS-trays containing the ultrathin fiber-structured coating can be considered to have low transparency. The highest internal transmittance values were found for the PS tray whereas Ti values decreased with the addition of the electrospun PS/PCM coating. This can be ascribed to the fact that transmittance and haze of composite films or multilayer films are mainly affected by differences in refractive indices between polymer matrix and fillers or between the different compounds which constitute the film´s structure (Zhou and Burkhart., 2010). Jeeju et al., 2012 also observed a significant decrease in the transmittance values of the PS nanocomposites by the addition of zinc oxide nanoparticles. They reported that the transparency of the neat PS was nearly 100% whereas the transparency of the composite PS/ZnO film was around 70% in the visible region.

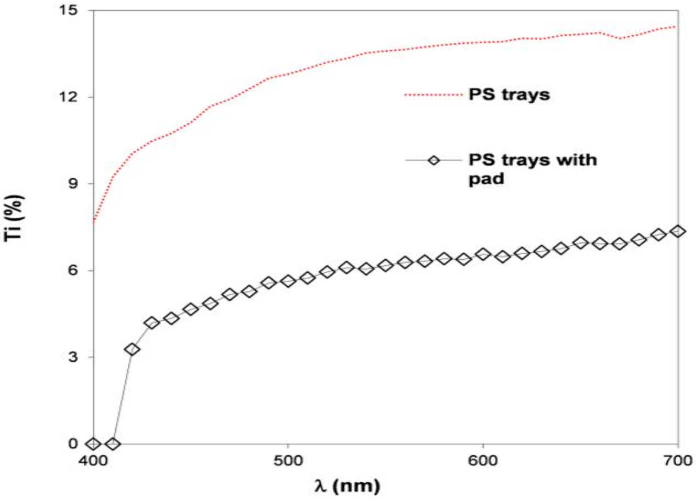

Fig. 3. Spectral distribution of internal transmittance (Ti) of PS trays with and without the ultrathin fiber-structured PS/PCM coating.

From the reflectance spectra of an infinite thickness sample, Lightness (L*), hue (h*ab), Chroma (C*ab) and Whiteness Index (WI) of each sample were obtained (Table 1). PS trays containing PS/PCM coating showed higher lightness and WI than PS-trays, coherent with their lower internal transparency. Both samples showed low Chroma values, corresponding with the white appearance of them. Whiteness is an attribute of colors of high luminous reflectance and low purity situated in a relatively small region of the color space. Thus, the white color attribute is distinguished by its high lightness (L*) and its very low (ideally zero) saturation(C*ab).

Table 1. Color coordinates (L, h and C) and whiteness index (WI) of PS-trays containing or not PS/PCM pad.

Samples	L*	h*	C*	WI
PS-tray	90.5 (0.4)^{a}	102 (0.9)^{a}	0.10 (0.06)^{a}	90.5 (1.1)^{a}
PS-tray with PS/PCM pad	93.3 (0.6)^{b}	98 (1.0)^{b}	0.22 (0.05)^{a}	93.3 (0.5)^{b}

$^{a-b}$: Different superscripts within the same column indicate significant differences between samples

3.2. ATR-FTIR analysis of PS/PCM coating

The presence of PCM onto the PS trays and within the PS/PCM fibers was qualitatively evaluated by ATR-FTIR spectroscopy. Figure 4 shows the ATR-FTIR spectra of the PS tray (with and without the PS/PCM coating) and the pure RT5 analyzed at 20ºC. At this temperature, the pure RT5 is characterized by the –CH2 and –CH3 stretching vibration bands at 2956, 2922 and 2854 cm^{-1} (Sebek et al., 2013; Perez-Masia et al., 2013) and these bands were also observed in the PS/PCM coatings even though they were overlapped with the spectral bands from the PS.

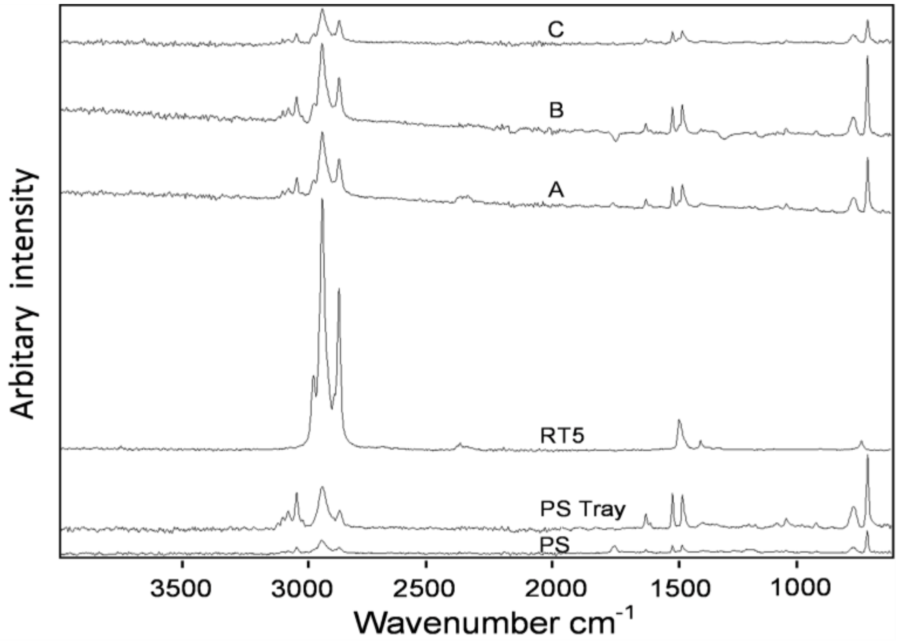

Fig. 4. ATR-FTIR spectra of the neat PS polymer, PS tray, pure RT5 and non-stored/stored PS tray with the PS/PCM coating measured at 4 and 25ºC. (A) Non-stored PS tray containing the PS/PCM coating; (B) and (C) PS tray containing the PS/PCM coating stored for 3 months at 4 and 25ºC, respectively.

From Figure 4 it can be clearly observed that the intensity of the characteristic bands of the PCM was greater in non-stored samples, indicating a greater amount of PCM within the structures, which was directly related with the enthalpy values commented on above, since higher crystallization and melting enthalpies implied greater encapsulation efficiency. In order to qualitatively evaluate PCM loading, the relative intensity of a PCM band with respect to a polymer spectral band was calculated in non-stored and stored structures and the results are compiled in Table 2. Specifically, the bands at 2956 cm^{-1} and 1493 cm^{-1} were selected for RT5 and PS, respectively. Similarly to that observed for PS-based multilayer structures (Chalco-Sandoval et al., 2014), the calculated spectral band ratio of the non-stored PS trays structures was greater (1.29 ± 0.2) than in stored ones (1.1 ± 0.3 and 0.84 ± 0.2 for samples stored at 4 and 25ºC, respectively). Furthermore, the relative intensity of the PCM bands decreased after 3 month of storage, mainly in those stored at 25ºC. The greater decrease in samples stored at 25ºC was closely related to the partial diffusion out of the paraffin and thus, with the lower enthalpy values found in the stored samples.

3.3. Thermal properties of the developed PS trays with the ultrathin fiber-structured PS/PCM coating.

The thermal properties of the PS trays containing the electrospun PS/PCM coating were analyzed by DSC during three months of storage and this technique was also used to determine the RT5 encapsulation efficiency. Table 2 gathers the enthalpy values, melting and crystallization temperatures as well as the supercooling degree of the pure RT5 and the PS-trays containing the electrospun PS/PCM coating.

Table 2. Thermal properties of the Rubitherm 5 (RT5) and the PS trays structures. Mean value (standard deviation).

Time (days)	Tm (ºC)		ΔHm (J/g PCM)		Tc$_1$(ºC)		Tc$_2$ (ºC)		ΔHc (J/g PCM)		Supercooling (ºC)	
	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
Pure RT5	7.2 (0.1)		142 (3)		5.3 (0.2)				142 (3)		1.9 (0.2)	
0	7.2(0.1)^{a1}	7.2(0.1)^{a1}	107(1)^{a1}	107(1)^{a1}	5.7(0.2)^{a1}	5.7(0.1)^{a2}	3.2(0.1)^{a1}	3.2(0.1)^{a2}	109(1)^{a1}	107(1)^{a1}	1.5(0.2)^{a1}	1.5(0.1)^{a1}
7	7.3(0.1)^{a1}	7.3(0.1)^{a1}	104(1)^{b1}	98(1)^{b2}	5.7(0.1)^{a1}	5.7(0.1)^{a2}	3.3(0.1)^{ab1}	3.3(0.1)^{ab2}	103(1)^{b1}	98(1)^{b2}	1.6(0.1)^{a1}	1.6(0.1)^{a1}
15	7.4(0.1)^{ab1}	7.4(0.1)^{ab1}	95(1)^{c1}	87(1)^{c2}	5.8(0.1)^{ab1}	5.8(0.2)^{ab1}	3.4(0.1)^{bc1}	3.4(0.1)^{b2}	93(3)^{c1}	87(1)^{c2}	1.6(0.1)^{a1}	1.6(0.3)^{a1}
30	7.5(0.2)^{b1}	7.7(0.1)^{c1}	92(3)^{c1}	70(1)^{d2}	5.9(0.1)^{b1}	6.1(0.1)^{c1}	3.5(0.2)^{bcd1}	3.6(0.1)^{c2}	92(5)^{c1}	70(1)^{d2}	1.6(0.1)^{a1}	1.6(0.3)^{a1}
45	7.7(0.2)^{bc1}	7.8(0.1)^{c1}	85(1)^{d1}	55(2)^{e2}	6.1(0.1)^{c1}	6.2(0.1)^{c2}	3.6(0.1)^{cde1}	3.9(0.1)^{d2}	82(2)^{d1}	55(2)^{e1}	1.6(0.1)^{a1}	1.6(0.1)^{a1}
60	7.7(0.2)^{bc1}	8.0(0.1)^{cd1}	80(1)^{e1}	49(3)^{e2}	6.2(0.1)^{cd1}	6.4(0.2)^{cd2}	3.7(0.2)^{de1}	3.9(0.1)^{d2}	80(1)^{d1}	49(1)^{f2}	1.6(0.1)^{a1}	1.6(0.2)^{a1}
75	8.0(0.1)^{c1}	8.3(0.1)^{d1}	79(1)^{e1}	47(4)^{f2}	6.3(0.1)^{d1}	6.6(0.1)^{d1}	3.9(0.2)^{ef1}	4.1(0.2)^{de2}	79(1)^{d1}	47(4)^{fg2}	1.7(0.1)^{a1}	1.7(0.1)^{a1}
90	8.1(0.1)^{d1}	8.5(0.1)^{e2}	75(2)^{f1}	44(2)^{f2}	6.5(0.2)^{de1}	6.8(0.1)^{e1}	4.1(0.1)^{f1}	4.4(0.1)^{e2}	73(3)^{e1}	44(2)^{g2}	1.6(0.1)^{a1}	1.7(0.1)^{a1}

$^{a–f}$ Different superscripts within the same column indicate significant differences due to storage time ($p < 0.05$).

^{1,2} Different superscripts within the same line indicate significant differences due to the temperature used ($p < 0.05$).

The melting temperature of the PS trays with the coating was in the same range as the melting temperature of the pure RT5 (~7.2ºC), indicating that similar PCM crystals were formed within the encapsulation structures. Nevertheless, while pure RT5 crystallizes at 5.3ºC, a greater supercooling degree was observed for PS-trays containing the coating. This phenomenon can be ascribed to a reduction of the RT5 particle size, since the number of nuclei needed to initiate the crystallization process decreased with reducing the diameter of the RT5 drops inside the fibers. In fact, two crystallization temperatures were detected for the paraffin blend contained within the PS trays which can be ascribed to the multiple crystallization processes of the N-alkanes ascribed to the rotator phase transitions which are observed in these paraffin's when their particle size is reduced (Zhang et al., 2012; Delgado et al., 2012; Zhang et al., 2004).

As deduced from Table 2, the thermal behavior of the PCM varied when it was encapsulated and upon ageing since PS trays containing the ultrathin fiber-structured PS/PCM coating showed lower melting and crystallization enthalpy values than those of the non-encapsulated PCM. This fact could be explained by lower encapsulation efficiencies than theoretically calculated and also by the PCM diffusion throughout the PS matrix along storage. Moreover, one should also consider the potential PCM-PS interactions which could hinder paraffin crystallization. Similar to the results previously reported for multilayer structures prepared with PS and PS/PCM fibers (Chalco-Sandoval et al., 2014), the storage temperature was the determining factor in the reduction of melting and crystallization enthalpies of the samples with time, showing a decrease of ~56-58% and ~30-40% in samples stored at 25ºC and 4ºC, respectively. This can be ascribed to the physical state of the PCM since the paraffin was in solid state (crystallized) at 4ºC and, thus, better retained within the fibrous mat. However, the liquid state of the PCM at room temperature could facilitate its diffusion throughout the PS matrix favoring PCM-PS interactions which could also hinder paraffin crystallization with storage time. The loss of heat management capacity over the storage time was significantly greater than that previously reported for the PS/PCM and PCL/PCM slabs (Chalco-Sandoval et al., 2014) probably due to the greater thickness of the slabs, which thus better protected the PCM from the heat treatment applied.

3.4. Evaluation of the RT5 Encapsulation Efficiency and Loading.

The encapsulation efficiency was calculated by dividing the experimental melting enthalpy obtained for the hybrid materials by the experimental melting enthalpy obtained for pure RT5, considering the quantity of the PCM added to the electrospinning solutions. The encapsulation efficiency is closely related with the heat storage capacity of the PS trays. Figure 5 shows the encapsulation yield and the calculated total amount of the encapsulated PCM derived from the DSC results of the hybrid structures stored at 4 and 25ºC. PS fibers were able to encapsulate a heat storage capacity equivalent to ~34 wt.-% of the PCM (core material) which corresponded to an encapsulation efficiency of ca. 78%. Similarly, Do et al., 2013 reported that eicosane/poly(vinylidene fluoride) composite nanofibers were able to encapsulate PCM with a heat storage capacity equivalent to ~32.5 wt.-% and, Pérez-Masiá et al., 2013 also reported an encapsulation efficiency of 83% of polycaprolactone/PCM hybrid structures which had a heat storage capacity equivalent to ~37 wt.-%.

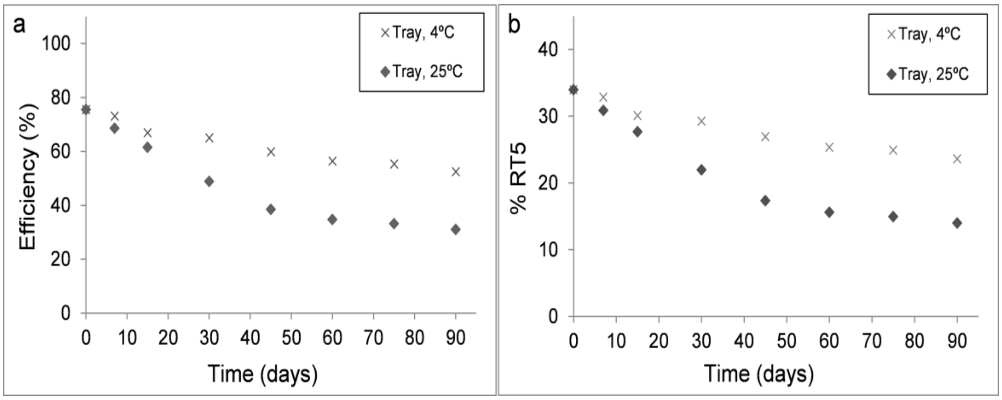

Fig. 5. Encapsulation efficiency and the calculated amount of the RT5 (%) encapsulated in the PS-tray systems. (a) Efficiency (%) at 4ºC and 25ºC; (b)% RT5 at 4ºC and 25ºC.

The storage temperature played an important role in the reduction of the heat storage capacity, showing a decrease up to 56-58% in PS trays stored at 25ºC and 30-40% in samples stored at chilling temperature (4ºC). The decrease in the encapsulation efficiency and thus, in the heat storage capacity of the PS trays stored at 25ºC could be ascribed to the heat treatment applied during the coating formation and also to the liquid state of the RT5 when stored at 25ºC, similar behavior was observed in the polystyrene and polycaprolactone slabs (Chalco-Sandoval et al., 2014). Furthermore, it is hypothesized that the porous structure of the electrospun PS fibers also facilitated PCM leakage during storage.

3.5. Heat storage capacity of PS trays with the ultrathin fiber-structured PS/PCM coating.

The thermal buffering capacity of the encapsulated RT5 was measured by recording the temperature profiles of the PS trays with and without the PS/PCM coatings (Figure 6) stored at -18ºC and analyzed at room temperature (20ºC). From Figure 6, it is clearly observed that the presence of the coating containing the PCM, effectively extended the time needed to increase the temperature above the chilling temperature of food products when compared to the neat PS tray, even though this time extension should be greater for real food packaging applications. The increase in time is related to the latent energy for melting the PCM, but also to the insulation effect of the PS/PCM coatings. The slope of the time-temperature curve of the PS trays containing PS/PCM trays decreased in the melting range of the PCM. Chalco–Sandoval et al., (2014) observed a similar behavior for polystyrene/RT5 slabs and polycaprolactone/RT5.

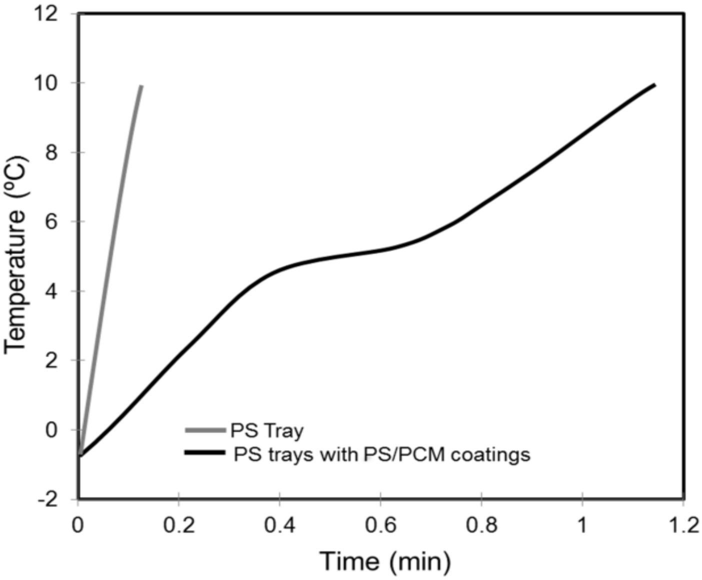

Fig. 6. Surface temperature as a function of time for PS tray with and without the ultrathin fiber-structured PS/PCM coating.

4. CONCLUSIONS

In this work, heat management materials consisting on PS trays coated with the electrospun PS/PCM layers have been developed. A temperature mismatch between melting and crystallization phenomena (the so-called supercooling effect) was observed in the PS-trays containing the electrospun PS/PCM layer, mainly ascribed to the reduced PCM drop size inside the fibers. Results showed that PS fibers were able to encapsulate a heat storage capacity equivalent to ~34 wt.-% of the PCM (core material) which corresponded to an encapsulation efficiency of ca. 78%. The storage temperature was the determining factor in the reduction of heat management capacity over the storage time, showing a decrease of ~56-58% in those stored at 25ºC and 30-40% in samples stored at chilling temperature (4ºC). Although electrospinning seems to be a promising technology to develop heat management materials, further works need to be developed to improve the encapsulation efficiency and heat storage capacity of the developed polymeric materials over storage time.

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CHAPTER III

Development of polystyrene-based films with temperature buffering capacity for smart food packaging

CHAPTER III: Development of polystyrene-based films with temperature buffering capacity for smart food packaging

ABSTRACT

One of the main factors affecting the quality of perishable products is represented by temperature variations during storage and distribution stages. This can be attained through the incorporation of phase change materials (PCM's) into the packaging structures. PCM's are able to absorb or release a great amount of energy during their melting/crystallization process and, thus, they could provide thermal protection to the packaged food. Thus, the objective of this research was to develop polystyrene (PS)-based multilayer heat storage structures with energy storage and hence temperature buffering capacity for their application in refrigerated foods. To this end, polycaprolactone (PCL) was used as the encapsulating matrix of a phase change material (PCM) called RT5 (a commercial blend of paraffin's with a transition temperature at 5ºC), by using high throughput electro-hydrodynamic processing. The PCL/PCM fibrous mats were directly electrospun onto PS films and an additional PCL electrospun layer (without PCM) was also deposited in some experiments to improve the overall functionality of the PCM. The attained morphology, thickness, deposition time, temperature and multilayer structure played an important role on the energy storage capacity of the developed PS-based multilayer structures. Results obtained from a differential scanning calorimeter (DSC) show that RT5 can be properly encapsulated inside the PCL matrix and the encapsulation efficiency and, thus, the heat storage capacity was affected not only by the multilayer structure, but also by the storage time and temperature. The thermal energy storage/release capacity was of about 88–119 J/g. As a result, this work demonstrates the potential of these materials for an efficient temperature buffering effect of relevance in food packaging applications, in order to preserve the quality of refrigerated packaged food products.

KEYWORDS: electro-hydrodynamic processing, phase change material, encapsulation, thermal energy storage and smart food packaging

1. INTRODUCTION

Refrigeration plays an important role in food preservation, as low temperatures aid in preventing or slowing microbial, physiological and chemical changes in food produced by microbial and/or enzymatic activity. Temperature fluctuations in the cold chain during the storage and distribution stages have negative effects on food due to crystal ice growth, acceleration of chemical reactions and/or microorganisms growth, which could result in a reduction of quality and may shorten the shelf-life of the food products. Therefore, strategies to buffer potential temperature fluctuations during the commercialization of foods are highly desirable.

Packaging can be designed to play an active role to maintain the food temperature within desired limits and, thus, to ensure the quality, safety and increase the shelf-life of the products (James et al., 2006). Usually, the limited thermal insulation and poor thermal buffering capacity of standard packaging do not provide any protection for maintaining the cold chain. But there are different strategies that could contribute to improving the thermal buffering capacity of a package, being one of them the development of thermal energy storage (TES) structures through the addition of phase change materials (PCM's) (Gin and Farid, 2010; Oró et al., 2012) within the polymeric structures (Oró et al., 2013). This strategy has been recognized as one of the most preferred forms of energy storage, mainly due to the high energy storage density provided by the PCM's and the nearly isothermal heat storage characteristics that can be attained (Melone et al., 2012). Phase change materials (PCM's) are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release the latent heat with a very small variation intemperature (Jin et al., 2010). PCM's could be used during transport, storage and distribution stages to maintain the cold chain of solid food, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products and many others (Oró et al., 2012). The most commonly used phase change materials are paraffin waxes, fatty acids, eutectics and hydrated salts (Farid et al., 2004). The paraffin compounds fulfill most of the requirements for being used as PCM's, as they are reliable, predictable, non-toxic, chemically inert and stable below 500ºC. They also show little volume changes on melting and have low vapour pressure in the melt form (Sharma et al., 2009). Direct applications of PCM's are difficult since they have weak thermal stability, low thermal conductivity and some of them are liquid at ambient temperature and, thus, are not easy to handle or to be directly incorporated into packaging structures (Fang et al., 2009). Therefore, the encapsulation of the PCM in a shell material is a plausible solution to avoid all these problems. Microencapsulated PCM is a form of PCM encapsulated in natural or synthetic polymeric capsules, which range in size from less than 1 lm to more than 1000 lm. The microcapsules protect the PCM against the influences of the outside environment, increasing the heat-transfer area, and permitting the core material to withstand changes in volume of the PCM, as the phase change occurs allowing small and portable thermal energy storage (TES) systems (Alkan et al., 2011).

One technique increasingly being used for the microencapsulation of materials is electrohydrodynamic processing. This technique that comprehending electrospinning and electrospraying has proven to be a suitable method for the encapsulation of several components, including biomedical substances, functional food ingredients, PCM's and others substances within polymer matrices (Goldberg et al., 2007; Perez-Masia et al., 2013). Electrospinning is a technique whereby long non-woven ultrafine fibres with diameters of several tens to several hundreds of nanometers may be formed by applying a high-voltage electric field to a polymeric solution (Teo and Ramakrishna, 2006). As a result of the applied electric field, a polymer jet is being ejected from the tip of a capillary through which a polymer solution is pumped, accelerated towards a grounded target and deposited thereon (Arecchi et al., 2010).

The aim of this work was, on the one hand, to develop heat storage materials by means of incorporation of a PCM substance with a first order thermal transition at 5ºC (RT5) in polystyrene (PS) films and, on the other hand, to study the effects of storage temperature and ageing on the performance of these films. It is important to understand how these materials will behave as a function of temperature and time, since these encapsulated structures are aimed to be introduced into packaging structures, in order to counteract temperature fluctuations and better maintain the cold chain, respectively.

2. MATERIALS AND METHODS

2.1. Materials

Rubitherm RT5, a technical grade paraffin wax consisting of a blend of normal paraffin waxes (C14-C18), was purchased from Rubitherm Technologies GmbH (Berlin, Germany). Polystyrene (PS) commercial grade foam was supplied by NBM (Valencia, Spain). The polycaprolactone (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium). N,N-dimethylformamide (DMF) with 99% purity and trichloromethane (99% purity) were purchased from Panreac Quimica S.A. (Barcelona, Spain). All products were used as received without further purification.

2.2. Preparation of polystyrene-based multilayer structures

2.2.1. Preparation of polystyrene films

For obtaining the polystyrene (PS) films, pellets of PS were first melt-mixed by means of a mixer (Plastogragh®, Brabender®, Germany) at 175°C and 100 rpm for 3 min. Once the melted product was obtained, films were prepared by compression-moulding using a hydraulic press (Carver 4122, USA), at 175°C and 60000 psi of pressure during 3 min.

2.2.2. Preparation of PCL/PCM electrospinning solution

The electrospinning solution was prepared by dissolving the required amount of PCL, under magnetic stirring, in a solvent prepared with a mixture of trichloromethane:N,N-dimethylformamide (70:30 w/w) in order to reach a 13% in weight (wt.-%) of PCL. Afterwards, 45 wt.-% of PCM (Rubitherm 5) with respect to the polymer weight was added to the polymer solution, and stirred at room temperature until it was completely dissolved.

2.2.3. Electrospinning process

The full process of PCM encapsulation via electro-hydrodynamic processing is a proprietary method previously described (patent application number: P201131063). According to this process, PCL/PCM solutions were prepared as described in (Perez-Masia et al., 2013), in order to produce fibrillar structures. Thus, the PCM was submicroencapsulated within polycaprolactone (polymer matrix) by means of a multinozzle high throughput Fluidnatek® electro-hydrodynamic pilot processing tool commercialized by Bioinicia S.L. (Valencia, Spain). This tool is equipped with a variable high-voltage 0-60 kV power supply. The PCL/PCM solution was electrospun under a steady flow-rate using a multinozzle injector. The electrospinning conditions for obtaining PCM-containing polymer structures was optimized and fixed at 55 ml/h of flow-rate, tip-collector distance of 26 cm and the voltage of the collector and injector were set at 26 kV and 22 kV, respectively. The PCL/PCM nanofibres were directly electrospun over the polystyrene film. Two different deposition times (15 and 45 min) were evaluated in the PS-multilayer structures to see how deposition time affected thermal, tensile, optical and barrier properties. A second series of PS-multilayer systems were prepared by electrospinning a PCL layer (15 min) onto the electrospun PCL/PCM layer in order to assess the protection of this additional layer on the heat storage capacity.

2.2.4. Preparation of polystyrene multilayer structures

Once the PCL/PCM and/or PCL nanofibers were collected onto the polystyrene compression molded films, a curing step at 60°C for 1 min was applied in an oven to enhance adhesion.

2.2.5. Polystyrene multilayer conditioning and storage

Samples were equilibrated in desiccators stored at 0% RH by using silica gel and at two different temperatures (4 and 25ºC) for three months. Polystyrene multilayers were taken from the desiccators at different time intervals (0, 7, 15, 30, 45, 60 and 90 days) and analysed by DSC and FTIR.

2.3. Characterization of polystyrene PS-multilayer structures

2.3.1. Scanning Electron Microscopy (SEM)

The morphology of polystyrene multilayers structures was examined using SEM on a Hitachi microscope (Hitachi S-4100). Samples were frozen in liquid N_2 and cryofractured to observe the cross-section of the samples. Then, they were fixed on copper stubs using double side adhesive tape, coated with a mixture of gold-palladium, and observed using an accelerating voltage of 10 kV.

2.3.2. Differential Scanning Calorimetry (DSC)

Thermal analyses of PS multilayer structures were carried out on a DSC-7 calorimeter (Perkin Elmer Inc., USA) from -20 to 20ºC in a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2, Perkin Elmer, USA). The scanning rate was 2ºC/min in order to minimize the influence of this parameter in the thermal properties. The amount of material used for the DSC experiments was adjusted so as to have a theoretical PCM content of 1-2 mg approximately. The enthalpy values obtained were, thus, corrected according to this PCM content. All tests were carried out in duplicate.

2.3.3. Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR).

ATR-FTIR spectra of PCL, pure RT5 and PS multilayers structures were collected at 25ºC in a FTIR Tensor 37 equipment (Bruker, Germany). The spectra were collected in the different materials by averaging 20 scans at 4 cm^{-1} resolution. The experiments were repeated twice to verify that the spectra were consistent between individual samples.

2.3.4. Temperature profiles.

The temperature profiles of PS multilayers structures with and without PCM were compared. To this end, polystyrene multilayers were frozen at -18ºC for 1 day. Then, the surface temperature evolution was registered at room temperature (20ºC) by using an infrared thermometer MS Plus provided by PCE Instruments (Tobarra, Spain).

2.3.5. Optical properties

Film transparency was evaluated through the internal transmittance of the samples where an increase in the spectral distribution of transmittance (Ti) is associated with more homogeneous and transparent samples. To this end, measurements were taken from three replicates per sample by using both a white and a black background and Kubelka-Munk theory for multiple scattering was applied to the sample reflection spectra. Internal transmission was calculated from the reflectance of the sample layer backed by a known reflectance and the reflectance of the sample on an ideal background (Collins, 1994).

2.4. Statistical Analysis.

Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used for carrying out statistical analyses of data through analysis of variance (ANOVA). Fisher’s least significant difference (LSD) was used at the 95% confidence level.

3. RESULTS

3.1. Morphology and transparency of PS multilayer structures

The microstructure of the multilayer films was qualitatively analysed aiming to describe the effect of PCL/PCM and PCL nanostructured outer layers deposition onto PS films and to compare the effect of deposition time and the film processing conditions. Figure 1 shows SEM images from the cross-section of the PS multilayer structures. In the films prepared with one layer of PCL/PCM nanofibers (Figs. 1A and 1C), a thicker PCL/PCM layer (ca.44 μm, Fig 1C) was obtained for the longest deposition time (45 min), as expected, which corresponded to a greater amount of fibrous materials (~1.7 g) deposited onto the PS film. In contrast, a thinner layer was obtained in PS-multilayer structures when PCL/PCM fibres were electrospun during just 15 min (ca. 18 μm, Fig 1A). In this case, the amount of PCL/PCM fibrous materials was estimated to be ~0.82g. This amount of the electrospun PCL/PCM deposited layer was estimated by weighting the PS film before and after collection of the electrospun material.

As commented above, some PS multilayer systems were prepared with an additional layer of PCL nanofibres (without PCM) (Figs. 1B and 1D) with the aim of preventing PCM diffusion throughout the PCL matrix, thus, improving the heat storage capacity of the films along storage. Even though this PCL layer was not easily distinguished from the inner PCL/PCM layer, it was clearly observed that PS-multilayer structures prepared with both layers were thicker (ca. 27 and 65 μm for Figure 1B and 1D respectively) than their counterparts prepared with only one layer of PCL/PCM (Figs. 1A and 1C).

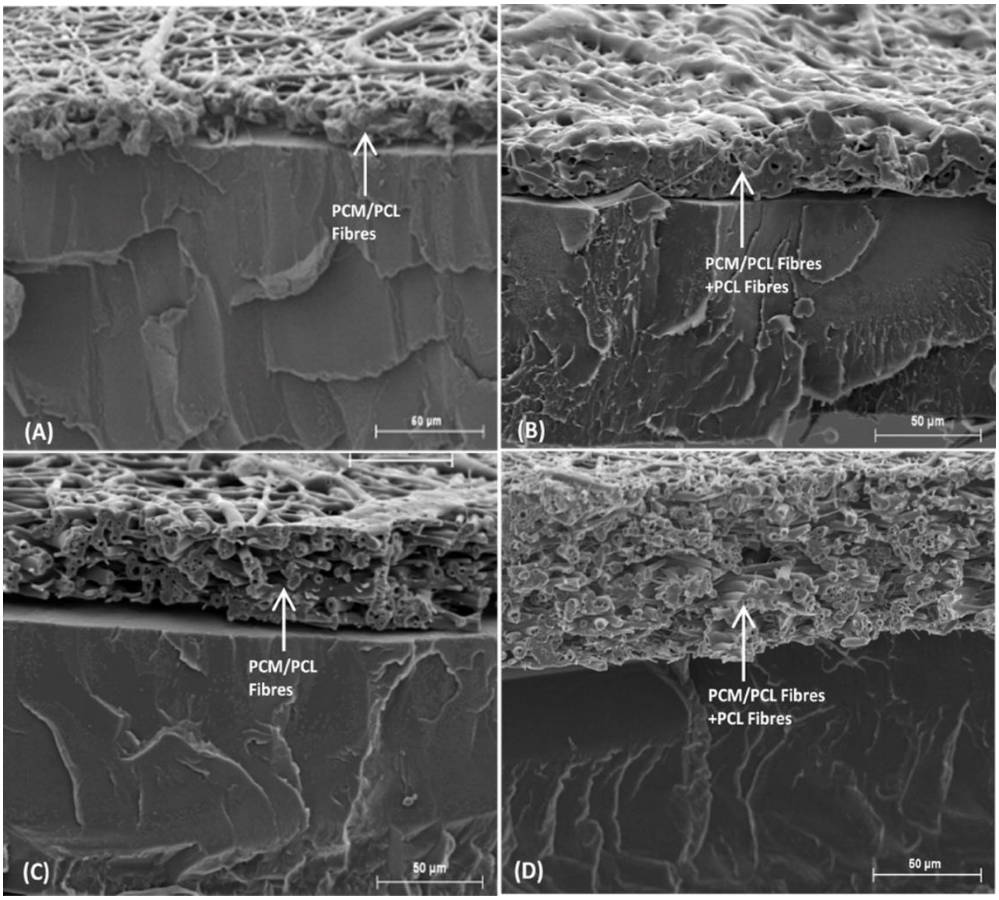

Figure 1. SEM images of the cryo-fractured sections obtained from PS multilayer structures containing different electrospun layers: (A) 15 min of electrospun PCL/PCM fibres deposition; (B) 15 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres; (C) 45 min of electrospun PCL/PCM fibres deposition; (D) 45 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres.

The transparency of the films is directly related with the surface and internal structure of the multilayer structures (Fabra et al., 2014) and is a key property in many applications, especially in food packaging where visual inspection of the contents is of key relevance. Thus, the effect of PCL/PCM and PCL layers onto PS films were evaluated by means of the internal transmittance (Ti), where an increase in the internal distribution of transmittance is ascribed to an increase in transparency. Spectral distribution curves of internal transmittance are plotted in Figure 2. The highest Ti value and, thus, the greatest transparency, was found for the PS film, whereas Ti values decreased in PS multilayer structures prepared with the electrospun PCL/PCM or PCL layers, and this decrease in transparency depended on the film-processing conditions (deposition time and number of layers). Transparency of PS multilayer structures significantly decreased for the greatest PCL/PCM deposition time (45 min) in line with the greater thickness obtained in this case. PS-multilayer systems prepared with an additional PCL layer followed the same pattern described for PS multilayer systems prepared with the electrospun PLC/PCM layer; although these PS multilayer structures showed lower Ti values than their counterparts prepared with one layer.

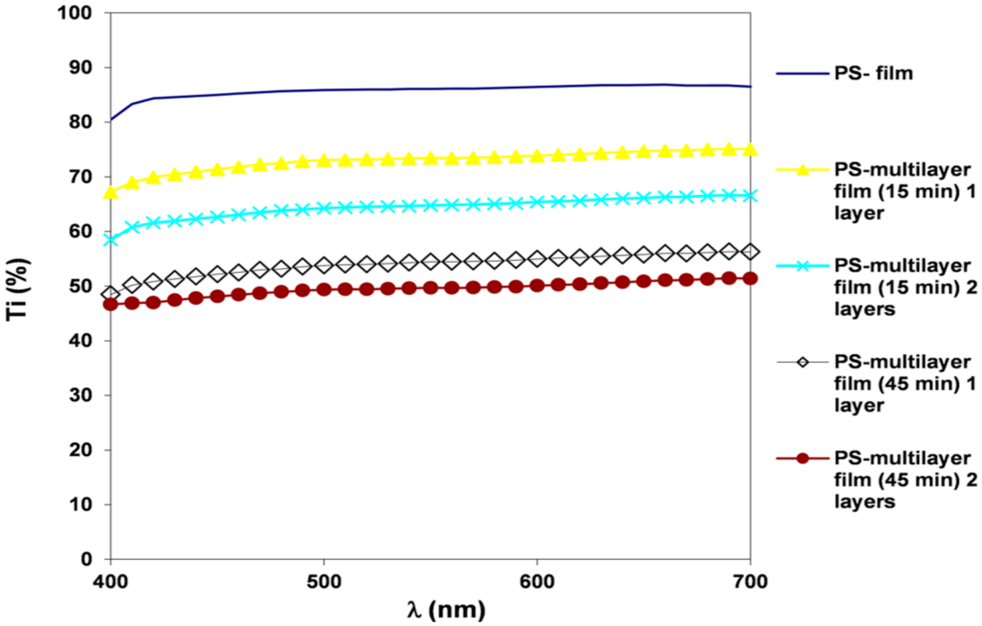

Figure 2. Spectral distribution of the internal transmittance of the PS multilayer structures

3.2. Thermal properties of the PS-multilayer structures

The thermal behaviour of the PS multilayer structures was analysed by DSC during three months storage and it was also used to determine the degree of RT5 encapsulation. The thermal properties (enthalpy values, melting and crystallization temperatures and supercooling degree) of the PS multilayer structures prepared with the different processing conditions are shown in Tables 1-4. RT5 melts at ~7.2ºC and crystallizes at ~5.3ºC, having an enthalpy of 144.7 J/g (Chalco-Sandoval et al., 2014). The melting temperature of the PS-multilayer structures was in the same range as the melting temperature of the pure RT5, indicating that similar PCM crystals were formed in the encapsulation structures. However, the crystallization phenomenon was different. While pure RT5 crystallizes at 5.3ºC, a greater supercooling degree was observed in all PS-multilayer structures. This supercooling effect can be explained by a reduction of the RT5 particle size, since the number of nuclei needed to initiate the crystallization process decreased with reducing the diameter of the RT5 drops inside the fibres. In fact, two crystallization temperatures were detected for the multilayer systems which can be ascribed to the multiple crystallization processes of the N-alkanes to the rotator phase transition which is observed in these paraffin's when their particle size is reduced (Delgado et al., 2012; Wang et al., 2004; Zhang et al., 2012). A rotator phase is defined as lamellar crystals, which exhibit long-range order in the molecular axis orientation and centre-of-mass position but lack rotational degrees of freedom of the molecules about their long axis. In these cases, more than one peak is observed in the DSC analysis during the crystallization processes that correspond to the different crystallization mechanisms followed. The first peak belongs to the heterogeneously nucleated liquid-rotator transition, the second one includes the rotator-crystal transition and the last one is attributed to the homogeneously nucleated liquid-crystal transition (Wang et al., 2004).

As shown in Tables 1 to 4, the thermal properties of the RT5 varied when it was encapsulated and upon ageing, showing lower melting enthalpy values than that of the non-encapsulated PCM. This difference could be ascribed on the one hand, to the fact that the PCM was not properly encapsulated and, on the other hand, to the presence of PCM-PCL interactions which could hinder paraffin crystallization. This could also explain the slight increase in the melting temperature observed in most of PS multilayer structures upon ageing at 4 and 25ºC. The reduction on the melting and crystallization enthalpies depended on the storage temperature, the PCL/PCM deposition time and the number of layers used for the multilayer. It is worth noting that the heat storage capacity of PS multilayer structures prepared with the lowest PCL/PCM deposition time (15 min) was lost after only 30 days at 25ºC, whatever the number of layers used. This could be ascribed to the liquid state of the PCM at room temperature which facilitates its diffusion throughout the PCL matrix. However, the PCL layer seemed to protect the PCM in these PS multilayer structures when the storage temperature was 4ºC, as in this case, the paraffin was in solid state (crystallized) and, thus, better retained within the fibres. At 4ºC, while melting and crystallization enthalpies of stored PS multilayer structures prepared with PCL/PCM and PCL layers decreased ~12%, a greater decrease was observed in those prepared with only the PCL/PCM layer (~66%).

Table 1. Thermal properties of the PS-multilayer structures prepared after 15 min of electrospun PCL/PCM fibres deposition. Mean value (standard deviation).

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		ΔH_c (J/g PCM)		Supercooling (ºC)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	7.7(0.1)^{ay}	7.7(0.1)^{ay}	85(1)^{ay}	85(1)^{ay}	6.5(0.1)^{ay}	6.5(0.1)^{ay}	4.6(0.1)^{ay}	4.6(0.1)^{ay}	85(1)^{ay}	85(2)^{ay}	1.2(0.1)^{ay}	1.2(0.1)^{ay}
7	7.7(0.1)^{ay}	8.0(0.1)^{az}	78(1)^{by}	53(1)^{bz}	6.3(0.1)^{ay}	6.8(0.1)^{az}	4.6(0.1)^{ay}	4.7(0.1)^{ay}	78(1)^{by}	53(1)^{bz}	1.3(0.1)^{ay}	1.2(0.1)^{ay}
15	7.7(0.1)^{ay}	8.5(0.1)^{bz}	72(1)^{cy}	24(1)^{cz}	6.3(0.1)^{ay}	7.0(0.1)^{bz}	4.6(0.1)^{ay}	4.8(0.1)^{abz}	65(3)^{cy}	24(1)^{cz}	1.4(0.1)^{ay}	1.5(0.1)^{bz}
30	7.6(0.1)^{a}		59(1)^{d}		6.3(0.1)^{a}		4.6(0.2)^{a}		58(1)^{d}		1.3(0.1)^{a}	
45	7.6(0.2)^{a}		51(1)^{e}		6.3(0.2)^{a}		4.8(0.1)^{bc}		52(2)^{e}		1.3(0.1)^{a}	
60	7.7(0.3)^{a}		44(1)^{f}		6.4(0.2)^{a}		4.8(0.1)^{bc}		44(1)^{f}		1.3(0.1)^{a}	
75	7.7(0.1)^{a}		37(3)^{g}		6.4(0.1)^{a}		4.8(0.1)^{bc}		38(5)^{g}		1.3(0.1)^{a}	
90	7.7(0.1)^{a}		29(1)^{h}		6.3(0.1)^{a}		4.9(0.2)^{d}		29(1)^{h}		1.4(0.1)^{a}	

$^{a\text{-}h}$ Different superscripts within the same column indicate significant differences due to storage time ($p < 0.05$).

$^{y\text{-}z}$ Different superscripts within the same line indicate significant differences due to the temperature used ($p < 0.05$).

Table 2. Thermal properties of the PS-multilayer structures prepared after 15 min of electrospun PCL/PCM fibres deposition and with the additional layer of PCL fibres. Mean value (standard deviation).

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		ΔH_c (J/g PCM)		Supercooling (ºC)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	7.3(0.1)^{ay}	7.3(0.1)^{ay}	105(1)^{ay}	105(1)^{ay}	5.9(0.1)^{ay}	5.9(0.1)^{ay}	4.4(0.1)^{ay}	4.4(0.1)^{ay}	104(1)^{ay}	104(1)^{ay}	1.4(0.1)^{ay}	1.4(0.1)^{ay}
7	7.3(0.1)^{ay}	7.5(0.1)^{aby}	104(1)^{ay}	76(1)^{bz}	6.0(0.1)^{aby}	6.1(0.1)^{aby}	4.4(0.1)^{ay}	4.6(0.1)^{bz}	103(1)^{ay}	77(3)^{bz}	1.4(0.1)^{ay}	1.4(0.1)^{ay}
15	7.5(0.1)^{by}	7.7(0.2)^{by}	105(1)^{ay}	49(1)^{cz}	6.1(0.1)^{bcy}	6.1(0.1)^{by}	4.6(0.1)^{aby}	4.9(0.1)^{cz}	106(1)^{ey}	48(1)^{cz}	1.4(0.1)^{ay}	1.4(0.1)^{ay}
30	7.5(0.1)^{by}	7.7(0.2)^{by}	101(2)^{by}	13(1)^{dz}	6.2(0.1)^{cy}	6.2(0.1)^{by}	4.6(0.3)^{abcy}	5.3(0.1)^{dz}	100(2)^{by}	13(1)^{dz}	1.3(0.2)^{ay}	1.4(0.4)^{ay}
45	7.6(0.1)^{bc}		100(1)^{b}		6.3(0.2)^{cd}		4.8(0.1)^{bcd}		98(1)^{bc}		1.3(0.2)^{a}	
60	7.7(0.1)^{cd}		99(2)^{b}		6.4(0.1)^{ef}		4.9(0.1)^{cd}		98(1)^{c}		1.3(0.1)^{a}	
75	7.8(0.1)^{d}		95(1)^{c}		6.5(0.1)^{gh}		5.0(0.1)^{de}		94(1)^{d}		1.3(0.1)^{a}	
90	7.9(0.1)^{e}		94(1)^{c}		6.6(0.1)^{h}		5.3(0.1)^{e}		93(1)^{d}		1.3(0.1)^{a}	

$^{a\text{-}h}$ Different superscripts within the same column indicate significant differences due to storage time ($p < 0.05$).

$^{y\text{-}z}$ Different superscripts within the same line indicate significant differences due to the temperature used ($p < 0.05$).

Table 3. Thermal properties of the PS-multilayer structures prepared after 45 min of electrospun PCL/PCM fibres deposition. Mean value (standard deviation).

Time	T_{m1} (ºC)		ΔH_m (J/g PCM)		T_{c1}(ºC)		T_{c2} (ºC)		ΔH_c (J/g PCM)		Supercooling (ºC)	
(days)	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	$7.2(0.1)^{ay}$	$7.2(0.1)^{ay}$	$97(1)^{ay}$	$97(1)^{ay}$	$6.0(0.1)^{ay}$	$6.0(0.1)^{ay}$	$4.5(0.1)^{ay}$	$4.5(0.1)^{ay}$	$94(1)^{ay}$	$94(1)^{ay}$	$1.2(0.1)^{aby}$	$1.2(0.1)^{ay}$
7	$7.1(0.1)^{by}$	$7.3(0.1)^{az}$	$91(1)^{by}$	$92(1)^{by}$	$6.1(0.1)^{aby}$	$6.0(0.1)^{aby}$	$4.5(0.1)^{ay}$	$4.6(0.1)^{ay}$	$90(1)^{ay}$	$91(1)^{bz}$	$1.0(0.2)^{ay}$	$1.3(0.1)^{aby}$
15	$7.1(0.1)^{by}$	$7.5(0.1)^{abz}$	$90(1)^{by}$	$88(1)^{cz}$	$6.1(0.1)^{aby}$	$6.1(0.2)^{aby}$	$4.5(0.1)^{ay}$	$4.5(0.5)^{ay}$	$87(1)^{aby}$	$86(2)^{cy}$	$1.0(0.2)^{ay}$	$1.4(0.3)^{aby}$
30	$7.3(0.1)^{ay}$	$7.6(0.1)^{bcz}$	$85(1)^{cy}$	$81(2)^{dz}$	$6.2(0.1)^{abcy}$	$6.2(0.4)^{aby}$	$4.6(0.1)^{aby}$	$5.0(0.6)^{ay}$	$80(6)^{bcy}$	$78(1)^{dy}$	$1.1(0.1)^{aby}$	$1.4(0.4)^{aby}$
45	$7.4(0.1)^{cy}$	$7.7(0.1)^{bcz}$	$81(1)^{dy}$	$72(1)^{ez}$	$6.1(0.1)^{aby}$	$6.3(0.1)^{aby}$	$4.6(0.1)^{aby}$	$5.0(0.1)^{az}$	$78(1)^{cy}$	$71(1)^{ez}$	$1.3(0.1)^{bcy}$	$1.4(0.1)^{aby}$
60	$7.7(0.1)^{dy}$	$7.7(0.1)^{bcy}$	$74(2)^{ey}$	$62(2)^{fz}$	$6.3(0.1)^{bcy}$	$6.3(0.2)^{aby}$	$4.6(0.1)^{ay}$	$5.0(0.2)^{az}$	$73(4)^{cdy}$	$60(1)^{fz}$	$1.4(0.1)^{bcy}$	$1.4(0.1)^{aby}$
75	$8.0(0.1)^{ey}$	$7.8(0.2)^{cy}$	$71(1)^{fy}$	$56(1)^{gz}$	$6.5(0.1)^{cy}$	$6.3(0.1)^{aby}$	$4.7(0.1)^{bcy}$	$5.0(0.1)^{az}$	$69(1)^{dey}$	$57(2)^{gz}$	$1.5(0.1)^{cy}$	$1.6(0.3)^{aby}$
90	$8.0(0.1)^{ey}$	$8.2(0.3)^{dy}$	$64(2)^{gy}$	$47(2)^{hz}$	$6.5(0.3)^{cy}$	$6.5(0.5)^{by}$	$4.8(0.2)^{cy}$	$5.2(0.6)^{ay}$	$63(5)^{ey}$	$48(1)^{hz}$	$1.6(0.3)^{cy}$	$1.8(0.3)^{by}$

$^{a\text{-}h}$ Different superscripts within the same column indicate significant differences due to storage time ($p < 0.05$).

$^{y\text{-}z}$ Different superscripts within the same line indicate significant differences due to the temperature used ($p < 0.05$).

Table 4. Thermal properties of the PS-multilayer structures prepared after 45 min of electrospun PCL/PCM fibres deposition and with the additional layer of PCL fibres. Mean value (standard deviation).

Time (days)	T$_{m1}$ (ºC)		ΔH$_m$ (J/g PCM)		T$_{c1}$(ºC)		T$_{c2}$ (ºC)		ΔH$_c$ (J/g PCM)		Supercooling (ºC)	
	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C	4°C	25°C
0	7.0(0.1)^{ay}	7.0(0.1)^{ay}	119(1)^{ay}	119(1)^{ay}	5.4(0.1)^{ay}	5.4(0.1)^{ay}	3.8(0.1)^{ay}	3.8(0.1)^{ay}	119(1)^{ay}	119(1)^{ay}	1.6(0.1)^{ay}	1.6(0.1)^{ay}
7	7.0(0.1)^{ay}	7.0(0.1)^{ay}	115(1)^{by}	114(1)^{by}	5.4(0.1)^{ay}	5.5(0.1)^{aby}	3.8(0.1)^{aby}	3.9(0.4)^{ay}	111(1)^{by}	113(1)^{bz}	1.6(0.1)^{ay}	1.5(0.1)^{ay}
15	7.3(0.1)^{by}	7.0(0.1)^{ay}	113(1)^{cy}	110(1)^{cz}	5.4(0.1)^{ay}	5.8(0.2)^{abcy}	3.9(0.1)^{aby}	3.9(0.1)^{ay}	111(2)^{by}	110(1)^{by}	1.6(0.1)^{ay}	1.5(0.3)^{ay}
30	7.4(0.2)^{by}	7.3(0.1)^{by}	108(1)^{dy}	99(1)^{dz}	5.7(0.1)^{by}	5.9(0.4)^{abcy}	4.2(0.1)^{abcy}	4.2(0.2)^{aby}	109(3)^{bcy}	97(1)^{cz}	1.6(0.1)^{ay}	1.5(0.3)^{ay}
45	7.5(0.1)^{by}	7.4(0.2)^{by}	104(1)^{ey}	91(1)^{ey}	5.8(0.1)^{by}	6.1(0.1)^{bcy}	4.5(0.1)^{bcy}	4.4(0.1)^{abcy}	104(1)^{cy}	91(3)^{cz}	1.6(0.1)^{ay}	1.4(0.1)^{ay}
60	7.5(0.1)^{by}	7.5(0.1)^{by}	100(1)^{fy}	80(2)^{fz}	5.9(0.1)^{by}	6.1(0.2)^{bcy}	4.6(0.2)^{cdy}	4.6(0.1)^{abcy}	97(1)^{dy}	81(4)^{dz}	1.7(0.1)^{ay}	1.4(0.2)^{ay}
75	7.6(0.1)^{cy}	7.8(0.1)^{cy}	94(1)^{gy}	72(1)^{gz}	6.3(0.1)^{cy}	6.3(0.1)^{cdy}	4.8(0.2)^{cdy}	4.8(0.1)^{abcy}	91(4)^{ey}	72(1)^{ez}	1.5(0.1)^{ay}	1.4(0.2)^{ay}
90	7.7(0.1)^{cy}	7.9(0.1)^{cy}	88(1)^{hy}	61(1)^{hz}	6.4(0.2)^{cy}	6.4(0.1)^{dy}	5.0(0.1)^{dy}	5.1(0.1)^{cy}	89(6)^{ey}	60(1)^{fz}	1.5(0.1)^{ay}	1.4(0.4)^{ay}

$^{a\text{-}h}$ Different superscripts within the same column indicate significant differences due to storage time ($p < 0.05$).

$^{y\text{-}z}$ Different superscripts within the same line indicate significant differences due to the temperature used ($p < 0.05$).

The storage temperature was the determining factor in the variations of melting and crystallization enthalpies of PS multilayer structures prepared with the greatest PCL/PCM deposition time (45 min), showing a decrease of ~50% in the films stored at 25ºC. Crystallization and melting enthalpies of PS multilayer structures stored at chilling temperatures showed a reduction of up ~25-33% after 90 days of storage.

3.3 Evaluation of PCM encapsulation in PS multilayer structures

The presence of RT5 in the PS multilayer structures was qualitatively evaluated by ATR-FTIR spectroscopy. Figures 3 shows the ATR-FTIR spectra of the pure PCL polymer, the pure RT5 and the non- stored PS-multilayer structures analysed at 20ºC.

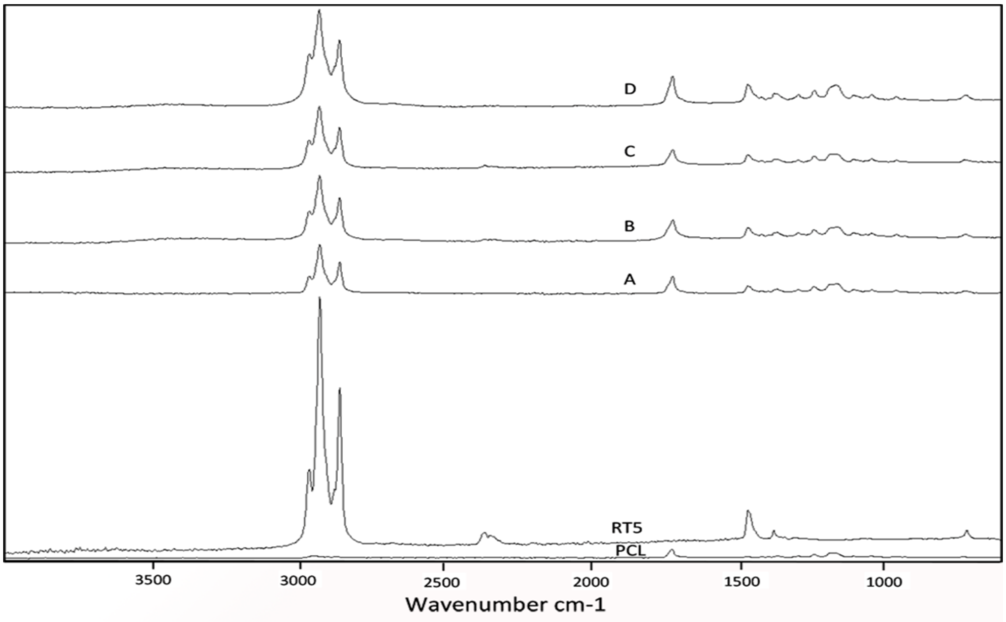

Figure 3. ATR-FTIR spectra of the pure PCL polymer, pure RT5 and non-stored PS multilayer structures: (A) 15 min of electrospun PCL/PCM fibres deposition; (B) 15 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres; (C) 45 min of electrospun PCL/PCM fibres deposition; (D) 45 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres.

At this temperature, the pure RT5 is characterized by the –CH2 and –CH3 stretching vibration bands at 2956, 2922 and 2854 cm^{-1}. These bands were also observed in the PS-multilayer structures even though they were overlapped with the spectral bands from the PCL, thus confirming the RT5 encapsulation in the PCL matrix. Figure 4 compares the ATR-FTIR spectra of the pure PCL fibres, the pure RT5 and the stored PS multilayer structures analysed at 20ºC. A similar pattern was observed in this case.

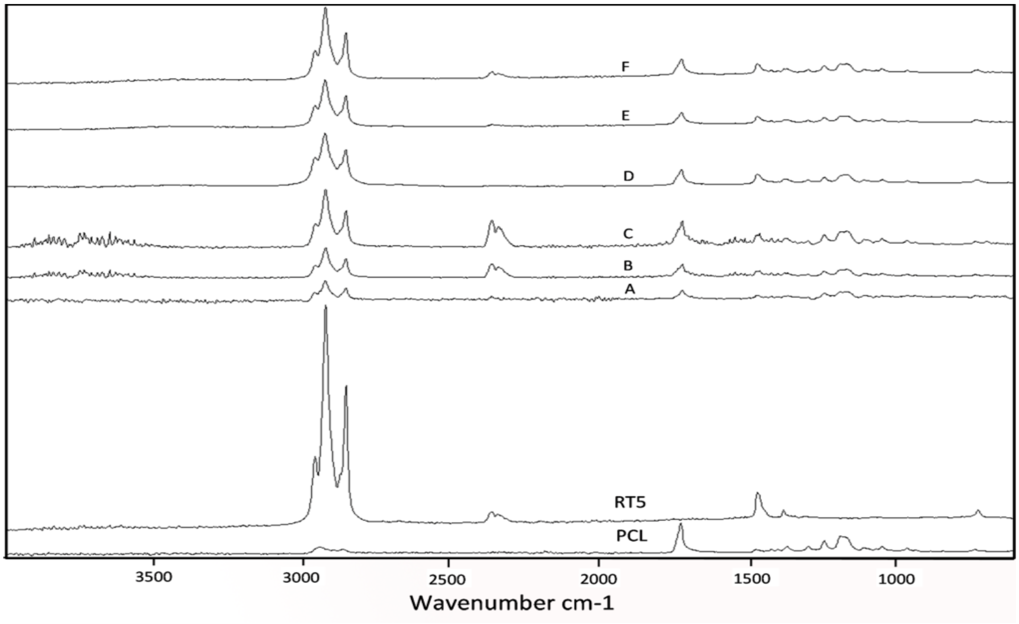

Figure 4. ATR-FTIR spectra of the pure PCL polymer, pure RT5 and stored PS multilayer structures measured at 4 and 25°C: (A) 15 min of electrospun PCL/PCM fibres deposition stored at 4°C; (B) 15 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres stored at 4°C; (C) and (D) 45 min of electrospun PCL/PCM fibres deposition stored at 25 and 4°C, respectively; (E) and (F) 45 min of electrospun PCL/PCM fibres deposition and 15 min de electrospun PCL fibres stored at 25 and 4°C, respectively.

Once again, the–CH2 and –CH3 stretching vibration bands at 2956, 2922 and 2854 cm^{-1} appeared in all PS multilayer structures even though they were also overlapped with the spectral bands of PCL. The relative intensity of the RT5 bands with respect to the polymer ones was calculated in non-stored and stored structures (Table 5) and it was calculated taking into account the bands at

2921,87 cm-1 and 1724,19 cm^{-1} for RT5 and PCL, respectively. As expected, the relative intensity of the non-stored PS multilayer systems was greater than in stored ones, accordantly with the higher heat storage capacity of these multilayer systems, as it will be detailed below. The relative intensity of the RT5 bands decreased after 3 months of storage, being more evident in those stored at 25ºC. It is worth to note that the relative intensity of the characteristics bands from the PCM was greater in PS multilayer systems stored at 4ºC. Similar results have been recently reported in PCL/RT5 slabs which can be explained by the porous structure observed for PCL fibres, which allowed the diffusion of PCM, which is liquid at 25ºC (Chalco-Sandoval et al., 2014).

Table 5. Ratio of RT5/PCL of non-stored and stored samples at 4 and 25ºC.

Material	Non-stored	Stored 3 months at 4°C	Stored 3 months at 25°C
RT5			
PCL	0.13	0.13	0.13
PS-15'-1	2.89	1.99	-
PS-15'-2	3.06	2.46	-
PS-45'-1	3.93	3.35	2.35
PS-45'-2	4.10	3.48	3.08

3.4 Evaluation of the PCM Encapsulation Efficiency and Loading

The RT5 encapsulation efficiency and loading capacity were calculated by dividing the experimental melting enthalpy obtained for the PS multilayer structures by the experimental melting enthalpy obtained for pure RT5, considering the quantity of the PCM added to the electrospinning solutions (45 wt.-%). Figure 5 shows the encapsulation efficiency and the calculated total amount of the PCM encapsulated in the PS-multilayer structures stored at 4 and 25ºC, respectively. In this case, the encapsulation efficiency is more closely related with the heat storage capacity of these multilayer structures during the storage time. As shown, the presence of PCL layer played an important role in PS-multilayer structures stored at 4ºC, showing greater heat storage capacity even though for PS-multilayer systems prepared with the lowest PCL/PCM deposition time (Figs. 5A and 5C).

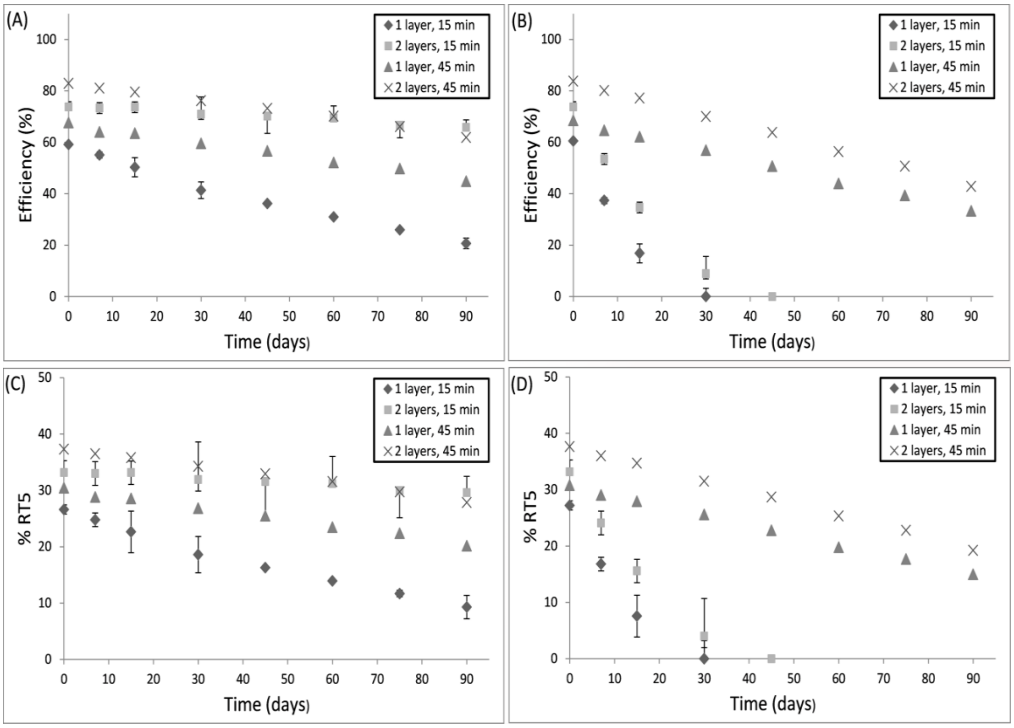

Figure 5. Encapsulation efficiency and the calculated amount of the RT5 (%) encapsulated in the PS multilayer structures during ageing at 4 (A and C) and 25ºC (B and D).

However, at 25ºC, multilayer systems prepared with the higher amount of PCL/PCM presented greater encapsulation efficiency and thus, greater heat storage capacity, than those prepared with the lowest deposition time, whatever the number of layers used during film-formation. Once again, the presence of the additional layer of PCL seems to protect the PCM, although this effect disappeared in those prepared with the lowest amount of PCL/PCM fibres. It may be noted that the heat storage capacity of the PS multilayer structures significantly decreased with the storage time at 25ºC. For instance, the encapsulation efficiency and thus, the heat storage capacity of PS multilayer structures prepared with the lower amount of electrospun PCL/PCM fibres decreased by up to 100% for PS multilayer structures stored at 30 days, and between 25 and 28% for those prepared with the highest amount of PCL/PCM fibres.

No significant variations were observed in the PS multilayer structures prepared with both layers (PCL/PCM and PCL fibres) at 4ºC. This could be attributed on the one hand, to the physical state of the PCM at 4ºC and 25ºC together with the porous structures of the PCL fibres and the PCL protection layer (without PCM). In fact, PS-multilayer structures stored at 4ºC significantly decreased the encapsulation efficiency with the storage time when the PCL/PCM layer was not protected by a PCL layer.

From the results, it can be concluded that the greatest heat storage capacity was achieved for PS multilayer structures prepared with both layers PCL/PCM and PCL, stored at 4ºC, which retained the encapsulated RT5 during the storage.

3.5 Heat storage capacity of PS multilayer structures.

The thermal buffering capacity of the encapsulated RT5 was also assessed by recording the temperature profiles of the PS multilayer structures stored at -18ºC and analysed at room temperature (20ºC). Analyses were preformed after three months of storage at 4 or 25ºC. Figure 6 compares the temperature profiles of the PS and the PS multilayer structures prepared with PCL/PCM and/or PCL layers, stored at 4 and 25ºC. No data was shown for multilayer systems prepared with the lowest deposition time and stored at 25ºC since the encapsulation efficiency of these films disappeared after 30 days of storage.

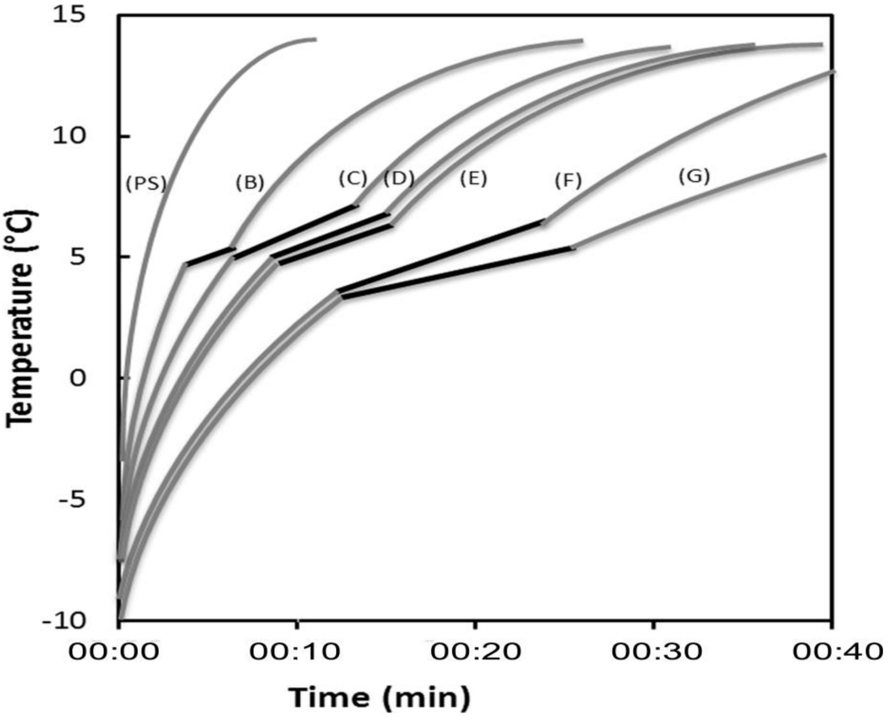

Figure 6. Surface temperature as a function of time: (A) 15 min of electrospun PCL/PCM fibres deposition stored at 4°C; (B) 15 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres stored at 4°C; (C) and (D) 45 min of electrospun PCL/PCM fibres deposition stored at 25 and 4°C, respectively; (E) and (F) 45 min of electrospun PCL/PCM fibres deposition and 15 min of electrospun PCL fibres stored at 25 and 4°C, respectively.

As expected, PS multilayer structures prepared with PCL/PCM layers behaved differently than PS films. In all cases, the slope of the time-temperature curve of the PS-multilayer structures decreased in the melting range of the PCM. PS multilayer structures showed higher thermal buffering capacity for the longest PCL/PCM deposition time. Furthermore, it is clearly observed that the presence of the additional layer of PCL nanofibres (without PCM) successfully delayed the diffusion of PCM, thus improving the temperature buffering of these multilayer structures along the storage. This fact was more marked in PS-multilayer structures stored at 4ºC.

Thus, in agreement with the DSC results, the most effective at temperature buffering was the PS multilayer film stored at 4ºC and prepared with the longest deposition time of PCL/PCM and with the additional layer of PCL fibres, where even a plateau for some time in the melting range of the RT5 can be observed.

4. CONCLUSIONS

In this work, PS multilayer-based heat storage structures were developed based on PS films coated with PCL/PCM electrospun layers. An additional PCL electrospun layer (without PCM) was also electrospun in some cases to improve PCM efficiency. The results show that the melting behaviour of the encapsulated PCM was similar to that of the pure PCM but a multiple crystallization profile was observed for the encapsulated PCM. While the pure PCM crystallizes at 5.3ºC, a greater supercooling degree was observed in all PS-multilayer structures. This supercooling effect can be explained by a reduction of the PCM particle size.

The heat storage capacity of these PS multilayer structures was affected not only by the film multilayer structure, but also by the storage time and temperature. The heat storage capacity decreased in PS-multilayer systems stored at 25ºC. PS multilayer structures showed higher thermal buffering capacity for the longest PCL/PCM deposition time and at chilling temperatures. The presence of the additional PCL layer also improved the temperature buffering capacity of these multilayer structures along storage. These active packaging materials has a the thermal energy storage/release capacity was of about 88–119 J/g.

The greatest efficiency (65%) and optimum heat storage performance was achieved for PS-multilayer structures prepared with both layers (PCL/PCM and PCM) stored at 4ºC, whatever the electrospun deposition time used, corresponding to materials composed of 27 wt.-% of PCM (core material).

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CHAPTER IV

Optimization of solution composition for the encapsulation of a phase change material in polymeric matrices by electro-hydrodynamic processing

CHAPTER IV: Optimization of solution composition for the encapsulation of a phase change material in polymeric matrices by electro-hydrodynamic processing

ABSTRACT

In this work, a PCM with a phase transition temperature set at -1.5ºC was encapsulated inside polycaprolactone (PCL), polystyrene (PS) and high-impact polystyrene (HIPS) matrices by means of electro-hydrodynamic processing in order to develop thermal energy storage systems for food superchilling applications. Different solvents were screened to prepare the electrospinning solutions which were seen to directly affect the properties of the obtained structures in terms of morphology, heat storage capacity, supercooling degree and thermal behavior. As a strategy to improve the heat management properties of the developed hybrid structures, solvents with different physicochemical properties (dielectric constant, viscosity and solubility, among others) were mixed in optimized ratios. Aside from more homogeneous electrospun fiber morphologies, the use of polymer solutions prepared with solvent mixtures resulted in improved thermal properties of the hybrid heat management materials, which showed melting and crystallization temperatures and a supercooling degree similar to that obtained for the pure PCM. The best encapsulation efficiency was achieved for PCL-based hybrid structures, which showed that ~92 wt.-% of the incorporated PCM, effectively remained within the polymeric matrice.

Keywords: electro-hydrodynamic processing, electrospinning, phase change materials, superchilling, temperature buffers, active packaging, intelligent packaging, thermal properties, heat management.

1. INTRODUCTION

A possible approach to control thermal variations during storage and distribution of refrigerated food products, maintaining the preservation temperature constant and, thus, preventing temperature fluctuations which can lead to food quality losses, is through packaging structures with thermal energy storage capacity. This can be attained through the incorporation of phase change materials (PCM's) into the packaging structures. PCM's are substances that can absorb, store and release large amount of thermal energy at a nearly constant temperature[1-3] buffering the thermal variations of the environment and, thus, they could contribute to the preservation of packaged food quality and safety. The use of PCM's in energy storage systems has been recently applied in different fields such as building materials, air conditioning applications, solar energy storage systems, greenhouses, temperature regulating textiles, electronic devices, pharmaceutical products and biomedical systems.[4,5] PCM's are available in a wide range of temperatures and can be even tailor designed to have their phase transition at any temperature. Specifically, in the food packaging area, PCM's are replacing dry ice containers used during the transport and storage of perishable foodstuffs. Some of the advantages of using PCM's include the weight reduction of the containers in comparison with dry ice and, their reusability during many thermal cycles.

A variety of PCM's are available, but the most commonly used phase change materials are paraffin waxes, fatty acids, eutectics and hydrated salts.[6] The paraffin compounds fulfill most of the requirements for being used as PCM's, as they are safe, predictable, non-toxic, chemically inert and stable below 500ºC.[1] However, one problem is their handling, since they are liquid at ambient temperature and, what is more important, they need to undergo a phase change (i.e. from liquid to solid and vice versa) at the target temperature to exert the desired functionality. Microencapsulation of the PCM's is a plausible solution because it allows protecting them against the influences of the outside environment, increasing the heat-transfer area, and permitting the core material to withstand changes in volume of the PCM which take place as the phase change occurs, thus, allowing the development of small and portable thermal energy storage systems.[7] Different encapsulation techniques have been reported in the literature such as spray drying and coacervation,[8] emulsion polymerization,[9-11] layer-by-layer deposition of polyelectrolytes[12] or electro-hydrodynamicprocessing.[13,14]

The electro-hydrodynamic processing (comprising electrospraying and electrospinning) is a technique being increasingly used for the microencapsulation of substances. This technique has recently proven to be useful for the encapsulation of different compounds, including biomedical substances, functional food ingredients and phase change materials with significant yielding and flexibility in design, giving raise to micro-, submicro- and nano-sized structures.[13-15] Electrospinning is used to generate ultrathin fibers with diameters of several tens to several hundreds of nanometers by applying a high-voltage electric field to a polymeric solution.[16] As a result of the applied electric field, a polymer jet is ejected from the tip of a capillary through which a polymer solution is pumped, accelerated toward a grounded target and deposited thereon.[17]

The electrospinning process is governed by the solution properties (mainly viscosity or rheological properties, electrical conductivity and surface tension), processing conditions (voltage, tip to collector distance, flow rate, etc.) and ambient parameters (temperature, humidity, etc.).[18-21] Particularly, the properties of the solvent used (dielectric constant, density, solubility, boiling point, surface tension, etc.) play an important role in the conformation of the polymer chains and, thus, in the final properties of the electrospun material.[19,20] Therefore, it is of outmost importance to understand how the solution properties, which depend on the solvent chosen to dissolve/disperse the polymer, affect the morphology and molecular organization of the electrospun fibres and, thus, their encapsulation capacity.

The selection of a desirable solvent or solvent system as the carrier of a particular polymer is fundamental for optimization of the electrospinning process. It is well-known that the use of a solvent for a particular polymer in which it is highly soluble, makes the polymer chains to swell and expand, favouring polymer/solvent interactions. However, when a solvent of poor solubility for a particular polymer is used, polymer-polymer self-interactions preferentially occur.[22]

Some works have demonstrated that the mean electrospun fibre size of polycaprolactone (PCL) and polyvinylchloride (PVC) can be reduced when they are dissolved in highly polar media or in solvents with high dielectric constant such as hexafluoro-2-propanol-HFP, dimethylformamide or trifluoroethanol-TFE.[20,22-24]

Thus, the main purpose of this work was to optimize the electrospinning solutions, in terms of the solvent or solvent system used, of some polymers for encapsulating a PCM which melts at superchilling temperature. The PCM was obtained from a mixture of commercial paraffin's which presented a phase transition at around -1.5ºC. This temperature is commonly used to maintain the food quality and to prolong the shelf-life of certain refrigerated foodstuffs and this process in commonly known as superchilling. Superchilling, which is also called deep chilling or partial freezing, is often used to describe a process in which food products (generally fish) are stored below its freezing point without becoming a solid. The difficulty lies in the temperature control, which needs to be between 0ºC and not fall below -1.7°C, which would cause damage to for instance meat products. The shelf life of superchilled foods can be extended by 1.5–4 times relative to chilled food and is an attractive alternative to freezing and conventional chilling.[25-28]

Three different shell materials were selected: polycaprolactone (PCL) due to its biodegradability, good physical properties and excellent commercial availability and two petroleum-based matrices, polystyrene (PS) and high impact polystyrene (HIPS) currently used in refrigerating equipment and food packaging. The electrospinning solutions were optimized so as to maximize the thermal performance of the electrospun structures. To this end, the effect of the solvent or solvent mixtures on the solution properties, encapsulation morphology and on the thermal properties of the electrospun structures were evaluated.

2. MATERIALS AND METHODS

2.1. Materials

The PCM (-1.5ºC) was obtained by mixing two commercially available paraffin waxes in a 54:46 (w/w) ratio of Rubitherm RT4® (RT4): Rubitherm RT-4® (RT-4) at 25ºC and 300 rpm for 10 min. Both technical grade paraffin waxes were purchased from Rubitherm Technologies GmbH (Berlin, Germany) and the melting points were 4 and -4ºC, respectively. The polycaprolactone (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium). Polystyrene (PS) commercial grade foam was supplied by Traxpo (Barcelona, Spain). High impact polystyrene (HIPS) was supplied by Ferro (Almazora, Spain). N, N-dimethylformamide (DMF) with 99% purity, tetrahydrofuran (THF) with 99.5% purity and trichloromethane (TCM) (99 % purity) were purchased from Panreac Quimica S.A. (Castellar del Vallés, Spain). Toluene (T) with 99.5% purity was purchased from WES (We Enable Science, Llinars del Vallés, Spain). All products were used as received without further purification.

2.2. Development of electrospun fibers

2.2.1. Preparation of polymer solutions

The electrospinning solutions were prepared by dissolving the required amount of PCL, PS and HIPS, under magnetic stirring, in a solvent or mixture of solvents (see Table 1). The PCL was used at 15% w/w, while the PS and HIPS were used at 25% w/w. Besides, 45% w/w of PCM with respect to the polymer weight was added to the polymer solutions and stirred at 40ºC until it was completely dissolved.

Table 1. Composition of electrospinning solutions

Type of polymer	wt.-%g polymer/ 100 g polymers and solvent	Solvents			
		wt.-% g Trichloromethane (TCM)/100 g solvents	wt.-% g Dimethylformamide (DMF)/100 g solvents	wt.-% g Toluene (T))/100 g solvents	wt.-% g Tetrahy drofuran (THF)/100 g solvents
PCL	15	100	-	-	-
		-	100	-	-
		-	-	100	-
		17	65	18	-
PS	25	-	100	-	-
		-	-	-	100
		-	65	-	35
HIPS	25	-	100	-	-
		-	-	-	100
		-	65	-	35

2.2.2. Electrohydrodynamic processing

The process for PCM encapsulation through high voltage spinning has been previously developed and described.[29] The paraffin was encapsulated within the polymer matrices (PCL, PS or HIPS) by means of a high throughput Fluidnatek™ electrospinning LE-500 pilot plant system (Bioinicia S.L., Valencia, Spain) equipped with a variable high-voltage 0-60 kV power supply and a multinozzle inyector which can also work in a laboratory mode using a single nozzle for experimental design. Table 2 gathers the electrospinning conditions (flow rate, emitter to collector distance and the applied voltage) used for each polymeric solution.

Table 2. Electrospinning conditions

Electrospinning solutions	Flow rate (ml/h)	Tip to collector distance (mm)	Voltage of the injector (kV)	Voltage of the collector (kV)
PCL/PCM prepared with TCM	2	280	4.2	3.8
PCL/PCM prepared with DMF	3	250	6.7	7.8
PCL/PCM prepared with T	3	270	4.4	5.4
PCL/PCM prepared with TCM/DMF/T	5	260	6.1	7.2
PS/PCM prepared with DMF	3	230	8.8	9.8
PS/PCM prepared with THF	3	220	5.7	6.7
PS/PCM prepared with DMF/THF	5	240	6.5	7.5
HIPS/PCM prepared with DMF	3	240	8.5	9.6
HIPS/PCM prepared with THF	3	220	5.7	6.1
HIPS/PCM prepared with DMF/THF	5	250	6.0	6.8

2.3. Characterization of the solutions properties

The apparent viscosity and surface tension of the solutions were measured before the electro-hydrodynamic processing. The apparent viscosity of the solutions 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 (spindle LCP). The surface tension was measured using the Wilhemy plate method in an EasyDyne K20 tensiometer (Krüss GmbH, Hamburg, Germany). Measurements were done at 25°C and all tests were carried out, at least, in triplicate.

2.4. Characterization of the electrospun hybrid fibers

2.4.1. Scanning Electron Microscopy (SEM).

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

2.4.2. Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out using a DSC analyzer (Perkin Elmer, Inc., DSC 7, USA) in order to evaluate the thermal storage capacity of the hybrid materials. The thermal properties of the dry samples (~2 mg) were analyzed from -20ºC to 20ºC in a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2, Perkin Elmer, USA). The scanning rate was 2°C/min in order to minimize the influence of this parameter in the thermal properties. The enthalpy results obtained were corrected taking into account the theoretical PCM content. All tests were carried out in triplicate.

2.4.3. Attenuated Total Reflectance Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra of electrospun structures were collected at 25ºC in a FTIR Tensor 37 equipment (Bruker, Rheinstetten, Germany). The spectra were collected in the different materials by averaging 20 scans at 4 cm^{-1} resolution. The analyses were carried out in triplicate to verify that the spectra were consistent between individual samples.

2.5. 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.

3. RESULTS

It is well-known that the electro-hydrodynamic process strongly depends on the solution properties. In this sense, stable electrospinning is only achieved when the viscosity is high enough to produce the necessary polymer entanglements to form the fibers. On the other hand, the surface tension is also a crucial parameter for the process, since high surface tension values could overcome the electrostatic forces generated by the high voltage applied and the electrical conductivity of the solution, thus, hindering the Taylor cone formation and the subsequent electrospinning process.[30,31] Therefore, in the first part of this work, the effect of different solvents on the electrospinning capacity, the morphology and the heat management properties of the electrospun structures were evaluated and, in the second part of the work, different electrospinning solutions were prepared by using mixed solvent systems with different physicochemical properties. The different solvents used together with their properties are compiled in Table 3.

Table 3. Properties of solvents.

Solvents	Surface tension (mN/m)	Viscosity (cP)	Dielectric constant	Solubility for PCL	References
Tricloromethane	28.2*	10.8*	4.8**	Partial to high***	*[48] **[49] ***[23]
Dimethylformamide	37.9*	6.8*	36.7**	Poor***	
Tetrahydrofuran	28.2*	2.0*	7.5**	Partial to high***	
Toluene	29.1*	2.3*	2.4**	High***	

3.1. Electrospun fibers obtained from neat solvents

Based on screening studies dealing with the electrospinning of polycaprolactone, polystyrene and high impact polystyrene, the concentration of each polymer was adjusted to obtain a stable electrospinning process avoiding dripping of the solutions. Several solvents were also evaluated to prepare the initial electrospinning solutions as it will be described below. The optimum concentration of the PCL matrix in solution was found to be 15% (w/w), while greater amounts (25% w/w) were needed in the case of the PS and HIPS matrices. On the other hand, the maximum amount of PCM which could be incorporated in the polymer solutions without altering the electrospinning process was estimated to be 45% in weight with respect to the polymer weight. It is worth to note that other formulations were also tested but they could not be properly electrospun or they were thermodynamically unstable and phase separation occurred during the electrospinning process. These effects explained why some of the formulations using the considered solvents were not characterized (cf. Tables 1 and 2). Besides, others solvents such as cyclohexane, pyridine, dichloromethane and acetone were also tested. However, in these cases, the polymer solutions were too viscous or the solvents were thermodynamically immiscible with the polymer and/or with the PCM and phase separation occurred during the electrospinning process.

3.1.1. Electrospun heat management polycaprolactone-based fibers

PCL pellets were dissolved in pure trichloromethane (TCM), N, N-dimethylformamide (DMF) and toluene (T). These solvents were selected because, on the one hand, they provided appropriate physico-chemical properties to the polymer solutions and, on the other hand, they did not show phase separation during the electrospinning process. The properties of the solutions obtained using the different solvents are compiled in Table 4, while Figure 1 shows the corresponding SEM images of the obtained electrospun PCL-based fibers.

Table 4. Viscosity and surface tension values of the electrospinning solutions used. Mean value (standard deviation).

Dissolution	Viscosity (cP)	Surface tension (mN/m)
PCL/PCM prepared with TCM	2390(38)^{a}	26(1)^{ab}
PCL/PCM prepared with DMF	1560(33)^{b}	30(1)^{c}
PCL/PCM prepared with T	618(1)^{c}	28(1)^{abc}
PCL/PCM prepared with TCM/DMF/T	1253(1)^{d}	27(2)^{abc}
PS/PCM prepared with DMF	1042(2)^{e}	29(1)^{bc}
PS/PCM prepared with THF	467(14)^{h}	25(1)^{a}
PS/PCM prepared with DMF/THF	604(19)^{c}	27(1)^{ab}
HIPS/PCM prepared with DMF	1224(6)^{f}	27(2)^{abc}
HIPS/PCM prepared with THF	625(8)^{d}	25(4)^{a}
HIPS/PCM prepared with DMF/THF	994(4)^{g}	26(1)^{abc}

a-h: Different superscripts within the same column indicate significant differences due to different polymers and solvents used ($p < 0.05$).

From the results obtained it was clearly observed that the surface tension of the electrospinning solutions did not explain the differences observed in the morphology of the electrospun fibers since only slight differences in surface tension were observed between samples. In contrast, the viscosity seemed to play an important role on the ability of the solution to be electrospun and on the morphology attained in each case. 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.[34,35] In this specific work, the polymer concentration was kept constant and, thus, the differences observed in the viscosity values could be ascribed to differences in solvent viscosity and to polymer-solvent interactions.[19,22,35,36] In fact, the viscosity of the solvents used (cf. Table 3), seemed to effectively affect the final viscosity of the polymer/PCM solutions (cf. Table 4).

Figure 1 shows that the average diameter of the PCL-based electrospun hybrid fibers varied from 0.1 to 25 µm depending on the solvent used. A significant decrease in the diameter of the electrospun fibers was seen when the dielectric constant of the solvent increased (see Table 3). In this sense, as observed from images 1A to 1C, the smallest average fiber diameters were obtained using the solvent with the greatest dielectric constant, i.e. DMF.

It is also worth to note that the applied voltage for the electrospinning solutions prepared with DMF was significantly higher than that used with their counterpart solutions prepared with TCM or T (see Table 2) which could also contribute to smaller fiber diameters and to a narrower size distribution.[37-39] In fact, Bhardwaj and Kundu[35] and Guarino et al.[20] pointed out that an increase in the electrical conductivity of the polymer solutions, which was the case for the solutions prepared with DMF, usually requires greater applied voltages for electrospun fiber formation. Similar effects were also observed in dextran membranes[40] and in poly-L-lactide nanofibers.[38]

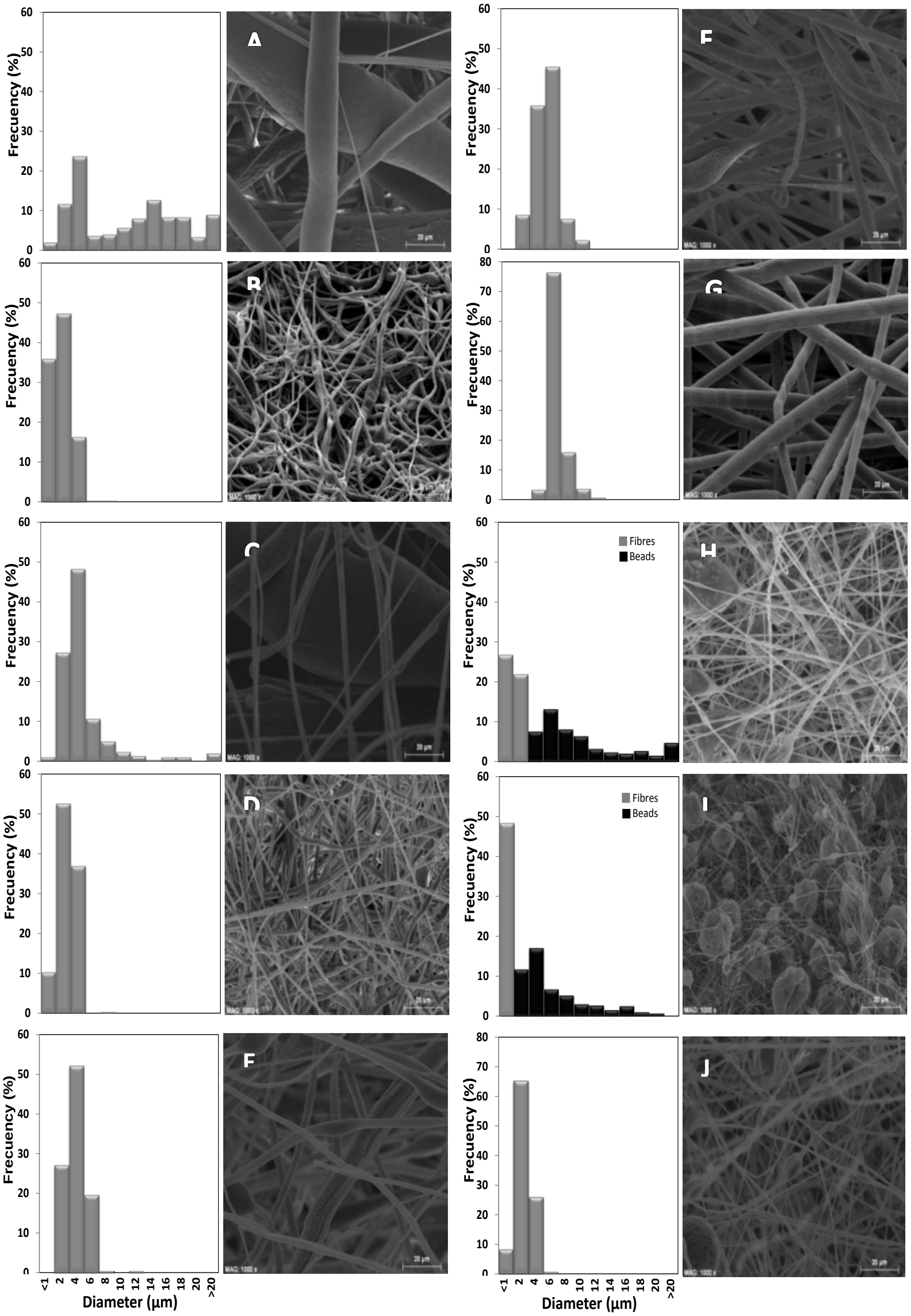

Figure 1. SEM images of electrospun hybrid systems: electrospun PCL/PCM structures prepared with TCM (A), DMF (B), T (C) and TCM/DMF/T (D); electrospun PS/PCM structures prepared with DMF (E), THF (F) and DMF/THF (G); electrospun HIPS/PCM structures prepared with DMF (H), THF (I) and DMF/THF (J). Scale markers correspond to 20 µm.

The morphology of the PCL fibers obtained with T ranged between those prepared with TCM or DMF. On the one hand, it is assumed that the dielectric constant of the PCL-T solution will be lower than that prepared with DMF, according to the lower dielectric constant value reported for the neat T (see Table 2). The relatively low dielectric constant value (2.4) of this solvent could have contributed to the larger average electrospun fiber diameter and to the less homogeneous distribution in diameter size obtained in this case. On the other hand, toluene provided lower viscosity to the polymer solution than TCM, fact that could partially explain the lower proportion of larger diameter fibers obtained in the case of T when compared to the structures obtained from the TCM solutions.

For the potential application of the encapsulated PCM's as thermal energy storage devices, good thermal performances in terms of high latent heat and adequate phase transition temperatures are required. In order to evaluate the thermal storage capacity of the electrospun fibers, thermal properties (enthalpy values, melting and crystallization temperatures and supercooling degree) of the pure paraffin and electrospun hybrid materials were analyzed by DSC at 2ºC min^{-1} and the results are given in Table 5.

The enthalpy values can serve to estimate the encapsulation efficiency and, from Table 5, it can be clearly observed that the lowest enthalpy value corresponded to the PCL hybrid structures obtained from the DMF solution. This result could be explained by both the low solubility of PCL in this solvent, which probably interfered in the polymer/PCM interactions and also to the small diameter of the fibers obtained, which has been previously related to low encapsulation yields.[14]

Table 5. Thermal properties of electrospun hybrid structures. Mean value (standard deviation).

Electrospun hybrid structures	Tm_1 (ºC)	ΔHm (J/g PCM)	Tc_1(ºC)	Tc_2 (ºC)	Tc_3 (ºC)	ΔHc (J/g PCM)	Supercooling (ºC)	Efficiency (%)
PCM-1.5ºC	$0.1(0.2)^{ab}$	$145.3(0.4)^{a}$	$-1.5(0.2)^{abc}$	-	-	$-144.8(0.3)^{a}$	$1.6(0.2)^{a}$	$100.0(0.1)^{a}$
PCL/PCM prepared with TCM	$1.1(0.2)^{c}$	$144.8(0.1)^{a}$	$-1.1(0.2)^{ad}$	$-2.6(0.3)^{a}$	-	$-143.5(2.8)^{a}$	$2.2(0.1)^{b}$	$99.6(0.1)^{a}$
PCL/PCM prepared with DMF	$0.6(0.1)^{de}$	$95.5(1.3)^{b}$	$-1.2(0.1)^{ad}$	-	-	$-94.2(1.6)^{b}$	$1.8(0.1)^{a}$	$65.7(0.9)^{b}$
PCL/PCM prepared with T	$1.0(0.3)^{ce}$	$129.4(1.4)^{cd}$	$-2.6(0.5)^{e}$	-	-	$-128.3(1.9)^{cd}$	$3.6(0.2)^{c}$	$89.1(1.0)^{cd}$
PCL/PCM prepared with TCM/DMF/T	$0.2(0.1)^{abf}$	$133.6(0.1)^{c}$	$-1.5(0.1)^{ab}$	-	-	$-133.1(1.2)^{c}$	$1.7(0.2)^{a}$	$91.9(0.1)^{c}$
PS/PCM prepared with DMF	$0.6(0.2)^{df}$	$68.4(1.0)^{e}$	$-1.9(0.2)^{c}$	$-4.4(0.1)^{b}$	-	$-68.5(0.5)^{e}$	$2.5(0.1)^{b}$	$47.1(0.7)^{e}$
PS/PCM prepared with THF	$0.4(0.2)^{abdf}$	$126.2(4.7)^{d}$	$-1.0(0.3)^{ad}$	$-4.9(0.1)^{c}$	$-16.2(0.1)^{a}$	$-123.5(1.8)^{d}$	$5.3(0.1)^{d}$	$86.8(3.2)^{d}$
PS/PCM prepared with DMF/THF	$0.1(0.2)^{ab}$	$104.1(1.0)^{f}$	$-1.6(0.1)^{bc}$	-	-	$-102.9(2.7)^{f}$	$1.7(0.1)^{a}$	$71.6(0.6)^{f}$
HIPS/PCM prepared with DMF	$1.7(0.1)^{g}$	$54.2(2.9)^{g}$	$-0.9(0.1)^{d}$	$-12.9(0.2)^{d}$	-	$-48.08(0.6)^{g}$	$2.5(0.1)^{c}$	$37.3(2.0)^{g}$
HIPS/PCM prepared with THF	$0.4(0.1)^{bdf}$	$106.0(2.9)^{f}$	$-2.7(0.1)^{e}$	$-2.9(0.2)^{a}$	$-15.3(0.4)^{b}$	$-103.8(4.0)^{f}$	$3.3(0.3)^{c}$	$73.0(2.0)^{f}$
HIPS/PCM prepared with DMF/THF	$0.0(0.1)^{a}$	$83.1(0.3)^{h}$	$-1.8(0.1)^{bc}$	-	-	$-76.1(3.0)^{h}$	$1.8(0.1)^{a}$	$57.2(0.2)^{h}$

a-h: Different superscripts within the same column indicate significant differences due to different polymers and solvents used ($p < 0.05$).

In the case of PCL fibers prepared in TCM and T the intermolecular interactions were probably higher due to the high solubility of both the polymer and the paraffin in these solvents, which may have favored the intertwining of the polymer chains being able to trap a larger amount of PCM. To corroborate the encapsulation efficiency results, an additional qualitative evaluation was carried out using ATR-FTIR spectroscopy.

Figure 2 shows the ATR-FTIR spectra from 500 to 3500 cm^{-1} at 25ºC of the pure PCM, the neat PCL and the hybrid PCL-structures. The pure RT5 is characterized by the C-H stretching bands at 2956, 2922, and 2854 cm^{-1}, while in the case of PCL, the main vibrational mode corresponds to the C=0 stretching at ~1724 cm^{-1}. For the qualitative analysis of PCM encapsulation, the band at 2956 cm^{-1} was selected for the paraffin, as it was not overlapped with bands from the PCL, and the carbonyl stretching band was selected for the PCL.

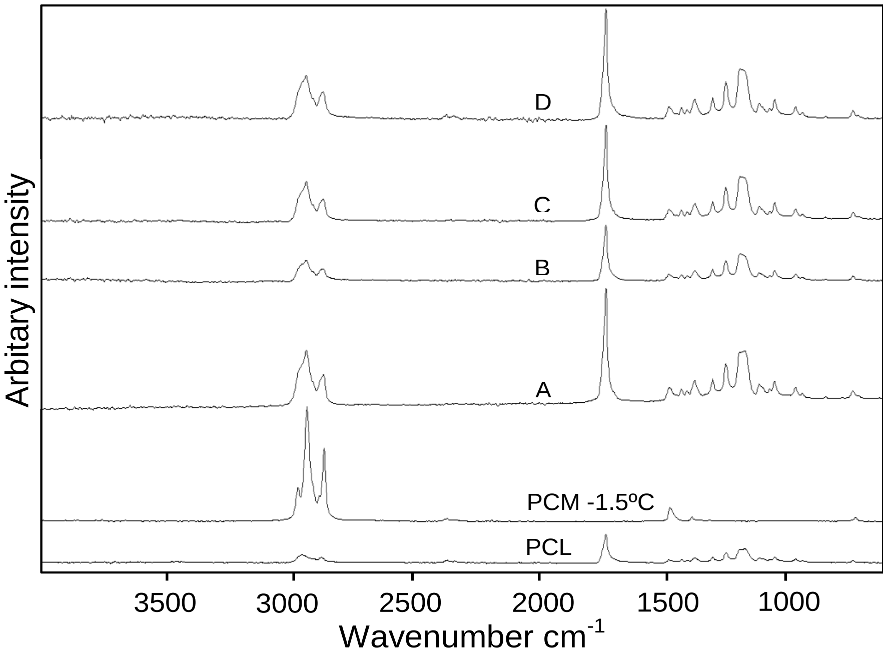

Figure 2. ATR-FTIR spectra of the electrospun PCL structures, pure PCM and electrospun PCL/PCM hybrid structures. Electrospun PCL/PCM structures prepared with TCM (A), DMF (B), T (C) and TCM/DMF/T (D).

Table 6. Ratio of PCM-1.5ºC and PCL, PS or HIPS. Mean value (standard deviation).

Electrospun PCL, PS and HIPS hybrid structures	Bands intensity (cm^{-1})			Ratio (PCM-1.5ºC/PCL, PS or HIPS)
	2956	1724	1492	
PCM -1.5ºC	0.30(0.01)	-	-	-
Polycaprolactone (PCL)	-	0.26(0.01)	-	-
PCL/PCM prepared with TCM	0.32(0.01)	1.00(0.01)	-	0.32(0.01)^{a}
PCL/PCM prepared with DMF	0.11(0.01)	0.48(0.01)	-	0.24(0.01)^{c}
PCL/PCM prepared with T	0.23(0.01)	0.81(0.01)	-	0.28(0.01)^{b}
PCL/PCM prepared with TCM/DMF/T	0.23(0.01)	0.81(0.01)	-	0.29(0.01)^{b}
Polystyrene (PS)	-	-	0.09(0.05)	-
PS/PCM prepared with DMF	0.02(0.08)	-	0.04(0.07)	0.51(0.07)^{a}
PS/PCM prepared with THF	0.06(0.03)	-	0.07(0.03)	0.87(0.03)^{c}
PS/PCM prepared with DMF/THF	0.05(0.07)	-	0.08(0.06)	0.71(0.06)^{b}
High Impact Polystyrene (HIPS)	-	-	0.25(0.10)	-
HIPS/PCM prepared with DMF	0.08(0.05)	-	0.12(0.11)	0.71(0.08)^{a}
HIPS/PCM prepared with THF	0.15(0.03)	-	0.08(0.06)	1.72(0.05)^{c}
HIPS/PCM prepared with DMF/THF	0.12(0.06)	-	0.11(0.07)	1.06(0.06)^{b}

a-c: Different superscripts within the same column indicate significant differences due to different solvents used ($p < 0.05$).

The ratio of these two bands can serve as an indication of the amount of PCM actually incorporated within the electrospun structures. Table 6 displays the relative intensity of the PCM band with respect to the PCL spectral band. In agreement with the enthalpy results obtained by DSC, the calculated spectral band ratio of the PCL hybrid structures prepared with DMF was lower than that of their counterparts prepared with TCM or T, thus confirming the results of lower melting enthalpies and lower encapsulation efficiency obtained by DSC analysis.

Aside from the enthalpy of the structures, which provides an indication of the heat storage capacity of the materials, it is important that the phase transition occurs close to the target temperature set (in this case close to superchilling temperatures) and with a low supercooling degree (i.e. the smallest possible difference between the melting and crystallization temperatures). From Table 5, it can be observed that the solution prepared with DMF provided melting and crystallization temperatures closer to that of the non-encapsulated PCM and, also, a lower supercooling degree when compared with the PCL-based fibers obtained from the TCM or T solutions. Furthermore, in the case of the structures prepared from the TCM solution, two crystallization peaks were detected ascribed to different crystallization mechanisms as described by some authors.[13,41,42] These differences in the thermal behavior could be explained by the different solubility of the fiber components in the different solvents used. It appears that the poor solubility of PCL in DMF, makes the interactions of the polymer with the paraffin difficult and, consequently, the PCM is able to melt and crystallize at a temperature similar to that of pure RT5. However, this also results in a lower encapsulation efficiency of these structures.

Summarizing, it has been observed that the physico-chemical properties of the solvents (mainly viscosity and dielectric constant) play an important role in the final properties of the solutions and, consequently, on the morphology and diameter of the electrospun fibers obtained thereof. Moreover, it has been demonstrated that the solubility of the fiber components (in this case the polymer and the paraffin) in the solvents is crucial in determining the thermal properties (enthalpy values, melting and crystallization temperatures and supercooling degree) of the final electrospun hybrid encapsulating fibers.

3.1.2. Electrospun heat management of PS and HIPS hybrid fibers

Based on previous studies,[43-47] the best candidates to dissolve the polystyrene (PS) and high-impact polystyrene (HIPS) were DMF and tetrahydrofuran (THF) since both provided appropriate electrospinning properties to the polymer solutions. Jarusuwannapoom et al.[45] concluded that DMF is the best solvent since it provided PS fibers with highest productivity and optimal morphological characteristics due to its high boiling point, solution conductivity and high dielectric constant compared to other solvents. Whereas that Casper et al.[43] and Jaziri et al.[44] used THF to dissolve PS with very good results. As commented above, other solvents were also tested but they did not provided suitable solubility, viscosity, surface tension and/or conductivity to polymeric solutions. Again, by looking at Table 4, it can be seen that the use of different solvents did not have a major effect on the surface tension of the PS and HIPS electrospinning solutions prepared from DMF, which were more viscous than their counterparts prepared from THF because both the viscosity of the solvent (6.81 cP) and solubility of the polymers in DMF were greater than those in THF, favoring polymer-solvent interactions and causing a more extended conformation of the polymer chains, thus resulting in increased viscosity.

Once again, the effect that the solvent had on the fibers morphology was clearly observed in the case of DMF (*cf.* Figure 1E and 1H). Comparing the PS and HIPS electrospinning solutions prepared with neat solvents, it was found that the highest the dielectric constant of the solvent, the smaller the average diameter of the electrospun fibers whatever the polymer used. Jun et al.[38] highlighted that a low conductivity of the electrospinning solution results in insufficient elongation of the jet by the electrical forces needed to produce uniform fibers. This was the case of HIPS prepared with THF (*cf.* Figure 1H) where non-uniform fibers containing beaded areas were obtained.

It is also worth to note that, whatever the polymer used, the applied voltage for the electrospinning solutions prepared with DMF were significantly higher than those used with their counterparts prepared with the other solvents (see Table 2) which could also contribute to smaller fiber diameters and to a narrower size distribution.[37-39]

The thermal properties of the hybrid structures prepared with PS and HIPS were closely related to the attained morphology and, thus, to the physico-chemical properties of the electrospinning solutions. Similarly to the results previously reported for PCL, solutions prepared with DMF provided lower melting and crystallization enthalpies for the encapsulated PCM than their counterparts prepared with THF. In fact, the encapsulation efficiency of PS and HIPS solutions prepared with DMF were very low, not only due to the small fiber diameters, as in the case of the PCL structures, but also due to the lower solubility of the paraffin in this specific solvent, which probably interfered with a proper PCM encapsulation in these matrices.

Figures 3 and 4 show the ATR-FTIR spectra from 500 to 3500 cm^{-1} of the pure PCM, the neat polymer and the hybrid electrospun structures for PS and HIPS, respectively. As for the PCL-based structures, the band at 2956 cm^{-1} was selected for the PCM because it did not overlap with any from the polymers. Regarding the PS and HIPS infrared spectra, the band at $\sim$1493 cm^{-1}, corresponding to carbon-carbon stretching vibrations in the aromatic rings[48] was used for the qualitative estimation of the encapsulation efficiency.

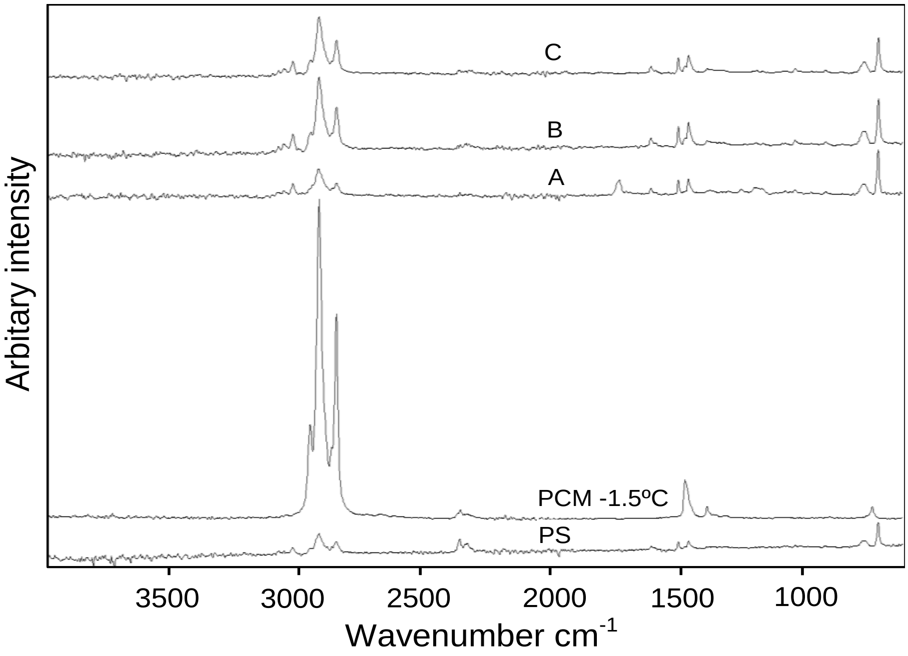

Figure 3. ATR-FTIR spectra of the electrospun PS structures, pure PCM and electrospun PS/PCM hybrid systems. Electrospun PS/PCM structures prepared with DMF (A), THF (B) and DMF/THF (C).

The relative intensity of the PCM band with respect to the PS or HIPS spectral bands, as observed from Table 6, confirmed that the amount of paraffin encapsulated was greater in the structures prepared from the THF solutions, even though more heterogeneous fiber morphologies were obtained with this solvent.

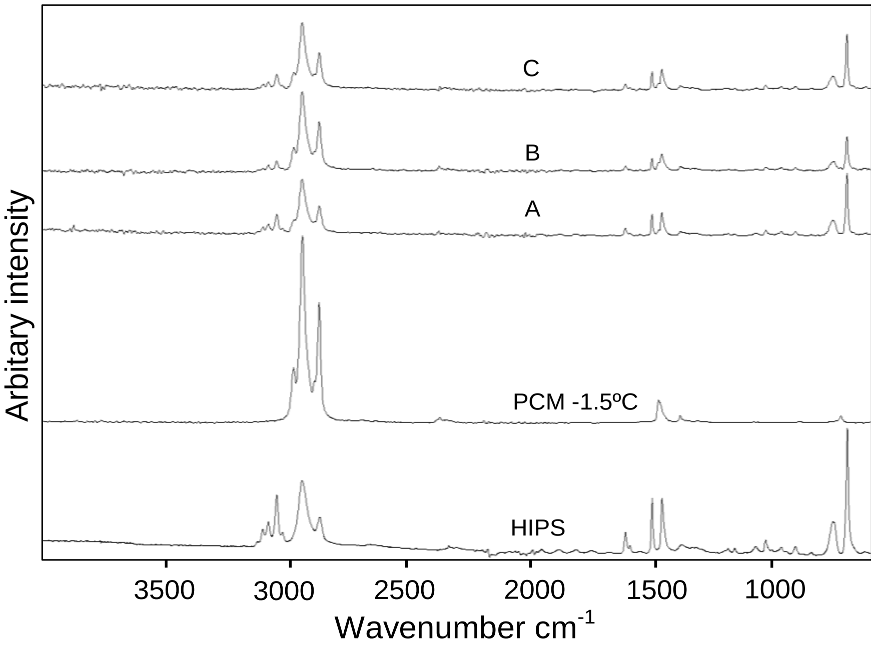

Figure 4. ATR-FTIR spectra of the electrospun HIPS structures, pure PCM and electrospun HIPS/PCM hybrid structures. Electrospun HIPS/PCM structures prepared with DMF (A), THF (B) and DMF/THF (C).

Regarding the melting and crystallization behavior of the paraffin encapsulated in PS and HIPS, in general, greater differences were observed from the values obtained for the non-encapsulated PCM, if compared with the PCL-based electrospun fibers. Moreover, for both polymers, independently of the solvent used, crystallization occurred in multiple stages which, as explained before, could be attributed to the different crystallization mechanism as well as to the different populations of crystals found along the fibers and beads.[13,41,42] Greater supercooling was also observed, being more pronounced in the case of the structures prepared from the THF solutions, fact which is not desirable for heat management materials.

The results obtained in this first part of the study showed that the thermal properties of the structures obtained from the polymer solutions prepared with pure solvents significantly differed from the ideal behavior desirable for a heat management material, since the encapsulation efficiency, the melting and crystallization temperatures and the supercooling degree of the hybrid structures were significantly affected by the polymer (shell material) and by the solvent used to prepare the electrospinning solutions.

3.2. Optimization of the heat management properties by mixing solvents.

In order to develop polymer solutions suitable for electrospinning, and giving raise to structures with high heat storage capacity, low supercooling degree, and melting and crystallization temperatures close to the neat paraffin, a strategy to modify solution properties based on using solvent mixtures was proposed. Based on the results obtained in the first part of this study and on the solvent properties (cf. Table 3), different solvent mixtures were prepared and some preliminary tests were carried out to adjust solvent composition with the aim of obtaining hybrid fibers with thermal properties similar to those of the neat PCM (results not shown).

Table 1 includes, the optimum solvent mixture compositions for each polymer studied. Based on the preliminary tests, a 65% v/v of DMF in the solvent mixtures was found to be the optimum independently of the polymer used. As expected, the viscosity values of the electrospinning solutions prepared with the solvent mixtures (cf. Table 4) ranged between those obtained with the pure solvents, thus confirming that solvent viscosity greatly determines the final viscosity of the polymer solutions.

DMF provided high dielectric constant values, more uniform and smooth fibers, a single melting and crystallization peak and a supercooling degree similar to that of the pure PCM. To counteract the low encapsulation efficiency obtained when using only this solvent, the best strategy was to add solvents which provided complementary properties in terms of viscosity and component solubility.

In the case of PCL-based structures, DMF was mixed with both TCM and T. These solvents provided partial to high solubility to both the polymer and the PCM, generating fibers with diameters ranging from 1 to 4 microns (cf. image 1D) and providing relatively high encapsulation efficiency.

The thermal behavior of these PCL hybrid structures prepared from a mixture of solvents was also better when compared to that of the structures obtained from solutions with a single solvent (see Table 5). The supercooling degree and the melting and crystallization temperatures were similar to those obtained for the non-encapsulated PCM. Regarding the encapsulation efficiency of the optimized structures, calculated from the melting enthalpy, it was slightly lower (92%) than that from the PCL fibers prepared with TCM (99%) but, greater than the encapsulation yield of the structures prepared with DMF (66%). In the case of PS and HIPS, DMF (65% v/v) was mixed with THF (35% v/v) to counteract the low solubility of PCM in the former. THF was also a good solvent for both polymers, providing good encapsulation efficiency when used alone.

The development of PS/PCM fibers using such solvent mixture, resulted in more homogeneous and uniform fibers (*cf.* Figure 1G), with a relatively narrow size distribution. Similarly, the combination of DMF and THF was also favorable in terms of fiber morphology for the structures prepared with HIPS, resulting in more uniform fibers with diameters ranging from 1 to 4 µm (*cf.* Fig 1J). The supercooling degree was successfully reduced in all cases, reaching values similar to those obtained for the bulk PCM. The melting and crystallization temperatures of the optimized hybrid structures were in the same range as those from the neat PCM and, thus, eliminating the multiple crystallization behaviour observed when using neat solvents. This is a clear advantage for the practical application of these materials, as the phase transition should occur, as it has been previously mentioned, at the targeted temperature and in a narrow temperature range, thus avoiding large supercooling degrees. The encapsulation efficiency of the PS (~72%) and HIPS (~57%) structures obtained from the solutions prepared with the solvent mixture was intermediate between that obtained using only DMF(~47% and ~37% for PS and HIPS, respectively) and THF (~87% and ~73% for PS and HIPS, respectively).

The relative encapsulation efficiency was also qualitatively estimated using FTIR, which supported the DSC results obtained (see Table 6). Interestingly, these results imply that the encapsulation efficiency is not only determined by the size of the encapsulation structures or the affinity between the polymer and the substance to encapsulate, but it also depend on the overall properties of the electrospinning solutions.

4. CONCLUSIONS

In this work, the effect of using different solvents on the electro-hydrodynamic processing, morphology, thermal properties and encapsulation efficiency of various electrospun heat management polymeric materials has been evaluated. To this end, a PCM which melts around -1.5ºC was successfully encapsulated within PCL, PS and HIPS matrices. Results showed that the optimized hybrid encapsulating structures were reached using mixtures of solvents in which each solvent provided a desired property (conductivity, viscosity, compatibility with the polymer, etc.) for the electrospinning process. The optimized electrospun hybrid structures presented a supercooling effect similar to that obtained for the neat PCM.

The PCL matrix was able to encapsulate higher amounts of PCM than PS and HIPS matrices, providing a greater heat storage capacity.

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CHAPTER V

Development of temperature buffering encapsulated phase change material in polyvinyl alcohol (PVOH) and polycaprolactone (PCL) via emulsion and coaxial electrospinning of interest in the food cold chain

CHAPTER V: Development of temperature buffering encapsulated phase change material in polyvinyl alcohol (PVOH) and polycaprolactone (PCL) via emulsion and coaxial electrospinning of interest in the food cold chain

ABSTRACT

This paper reports on the encapsulation of a paraffin based phase change material into a hydrophilic high gas and oil barrier polymer, polyvinyl alcohol (PVOH), by means of electro-hydrodynamic processing. 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 a surfactant (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 (wt.-%) with respect to the total emulsion weight, showing under these conditions an encapsulation efficiency of ~90%. However, the hydrophilic nature of the developed structures made them extremely difficult to handle due to swelling with increasing RH, since PVOH is a water soluble polymer. To avoid this issue an additional encapsulating shell layer of a more hydrophobic material, polycaprolactone (PCL), was applied by coaxial electrospinning. In this case, the PVOH/PCM ratio (core material) was optimized to reach the highest heat storage capacity per gram of sample and, then, a polycaprolactone (PCL) solution in TCM/DMF was used as a shell material in order to hydrophobize the developed structures. Thermal properties showed that the optimized coaxial electrospun structures were able to encapsulate about 82% of PCM. Although the encapsulation efficiency slightly decreased in the coaxial electrospun structures, the heat management capacity per gram of sample increased since it was possible to increase the content of the PCM in the PVOH core fraction due to coaxial processing. The use of the coaxial configuration is shown as an adequate strategy to preserve the morphology of the electrospun structures when exposed to high relative humidity as inferred from environmental scanning electron microscopy (ESEM) experiments.

Keywords: Coaxial electrospinning, Electro-hydrodynamic processing, Phase change materials, Temperature buffering, Active fibres, Cold chain, Emulsion electrospinning, Polyvinyl alcohol, Polycaprolactone

1. INTRODUCTION

In the last decades, phase change materials (PCM's) 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 generated fibers, has lately arisen as an innovative route to encapsulate PCM's. Electrospinning makes use of high voltage electric fields to produce electrically charged jets from viscoelastic polymer solutions which on drying produce ultrathin polymeric structures.[7-10]

In the encapsulation area, Chalco-Sandoval et al.,[11,12] stated in previous works that the use of hydrophobic polymers such as polycaprolactone (PCL) and polystyrene (PS) as encapsulating matrices of hydrophobic PCM's (mainly paraffin's), apart from resulting in significant variations in the thermal properties of the materials related to multiple crystallization events and increased supercooling degree (defined as the difference between the melting and crystallization temperatures), did not properly protect the core material during storage of the materials. This was attributed to the fact that the shell encapsulating matrices could interact with the paraffin favouring migration of the PCM's and, thus, the hydrophobic shell material seemed to act as permeable matrices for PCM's. In fact, they demonstrated that there was a partial diffusion out of the paraffin during ageing whatever the temperature used during the storage period of time. This resulted in a decrease in the heat storage capacity of these materials over time. Several authors stated that hydrophilic shell materials are the best candidates to encapsulate hydrophobic substances[13] since they are immiscible with the core material, favouring a phase separation between the core and the shell and reducing migration. Nevertheless, the main disadvantage of using hydrophilic matrices is that the hybrid structures thus prepared are highly swellable in water at high relative humidity conditions which means that they could potentially released the encapsulated PCM. 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.

Thus, the purpose of this work was to develop stable electrospun heat management polymeric materials with high temperature buffering capacity of interest in refrigeration applications. To this end, the first part of the work was aimed at the developing of an approach for the preparation of electrospun structures through emulsion electrospinning by using a hydrophilic material (polyvinylalcohol –PVOH-) to encapsulate a PCM which melted around 5ºC (RT5). PVOH, apart from being an excellent barrier material to non-polar substances such as paraffin's, is characterized by having good mechanical properties, high gas barrier, chemical stability and being easily spinable in water.[14] In order 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 polycaprolactone (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 good spinning properties and from previous work it demonstrated to provide good encapsulation yields.[15]

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

2. MATERIALS AND METHODS

2.1. Materials

Rubitherm RT5 which has a melting point at 5ºC 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 polycaprolactone (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium). Polyvinylacohol (PVOH) was kindly donated by Plásticos Hidrosolubles (Spain). The polyoxyethylene sorbitan monolaureate (Tween20) 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.

2.2. Preparation of electrospun hybrid structures

2.2.1. Preparation of PVOH/PCM emulsions and PCL solutions.

The PVOH/PCM emulsions were prepared by dissolving a 13% w/w of PVOH in distiller water under magnetic stirring at 25ºC for 1 hour 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 1). The resulting dispersions were homogenized at 12000 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 one hour, in a solvent prepared with a mixture of trichloromethane: N,N dimethylformamide (85:15 w/w).

2.2.2. Electro-hydrodynamic Processing

The process for PCM encapsulation through high voltage spinning has been previously developed and described.[16] The RT5 was encapsulated within the biopolymer matrices (PVOH and PCL) by means of a Fluidnatek™ 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 1). 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.

Table 1. Composition of electrospinning-solutions

Type of polymer		wt.-% (g polymer/100 g of sample)	wt.-% (g surfactant/100 g of sample	wt.-% (g PCM/100 g of sample	Solvents		
Interior	Exterior				wt.-% (g water/ 100 g solvents	wt.-% (g trichloromethane (TCM)/100 g solvents)	wt.-% (g dimethylformamide (DMF)/100 g solvents)
UNIAXIAL							
PVOH	-	13	0.00	7	100	-	-
			0.16				
			0.32				
			0.48				
COAXIAL							
PVOH		13	0.32	24	100	-	-
	PCL	5	-	-	-	85	15

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 1 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.

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

2.4. Characterization of the electrospun hybrid structures

2.4.1. Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out on the just prepared structures by means of a DSC analyser (Perkin Elmer, Inc., DSC 7, USA) from -20ºC to 20ºC in a nitrogen atmosphere using a refrigerating cooling accessory (Intracooler 2, Perkin Elmer, USA). The scanning rate was 2°C/min in order to minimize the influence of this parameter in the thermal properties. Small amounts (1-2 mg approximately) of dry samples were placed into aluminium pans (Perkin Elmer, DSC, BO14). An empty aluminium 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.

2.4.2. 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.

2.4.3. Environmental Scanning Electron Microscopy (ESEM).

The effect that the relative humidity had on the morphology of electrospun hydrid 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 500–1500 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, 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 favour water condensation or evaporation at different relative humidity (RH) levels.

2.4. 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.

3. RESULTS

3.1. PCM encapsulation in EVOH by electrospinning

In the first part of this work, electrospun PVOH/PCM hybrid structures were optimized in order to obtain the highest thermal buffering capacity. Based on the screening studies during electrospinning of PVOH, 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 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 improve the electrospinnability of aqueous solutions.[17] The different solutions prepared were characterized in terms of viscosity, surface tension and conductivity and the results are gathered in Table 2.

Table 2. Viscosity, conductivity and surface tension values of the electrospinning-solutions used. Mean value (standard deviation).

Dissolution	**Viscosity (cP)**	**Surface tension (mN/m)**	**Conductivity (μS/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}	34.0(3.0)^{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}

a-h: Different superscripts within the same column indicate significant differences ($p < 0.05$).

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,[18] reaching a plateau value which corresponds to the Critical Micellar Concentration (CMC) of this type of solution, since not significant differences were observed between those prepared with 0.32 and 0.48 wt.-%. Regarding the viscosity, an increase 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 nothing 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 1A, PVOH forms uniform fibres in which more than 90% of them exhibit a diameter size below 0.5 µm, thus highlighting the good spinnability of this polymer in water. However, microscopy images of PVOH/PCM fibres revealed some beaded areas which diameter varied depending on the surfactant concentration (Figures 1B-1E). It is worth nothing 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 fibres, also increasing their average size and heterogeneity (cf. Figure 1B). Upon surfactant addition, a more homogeneous morphology was attained and the amount of fibres with diameters lower than 0.5 µm increased again near to 60% as the surfactant concentration increased in the emulsion electrospun hybrid structures. This indicates that surfactant addition effectively stabilized the emulsion and more uniform fibres and beaded areas were obtained (Figure 1C-1E).

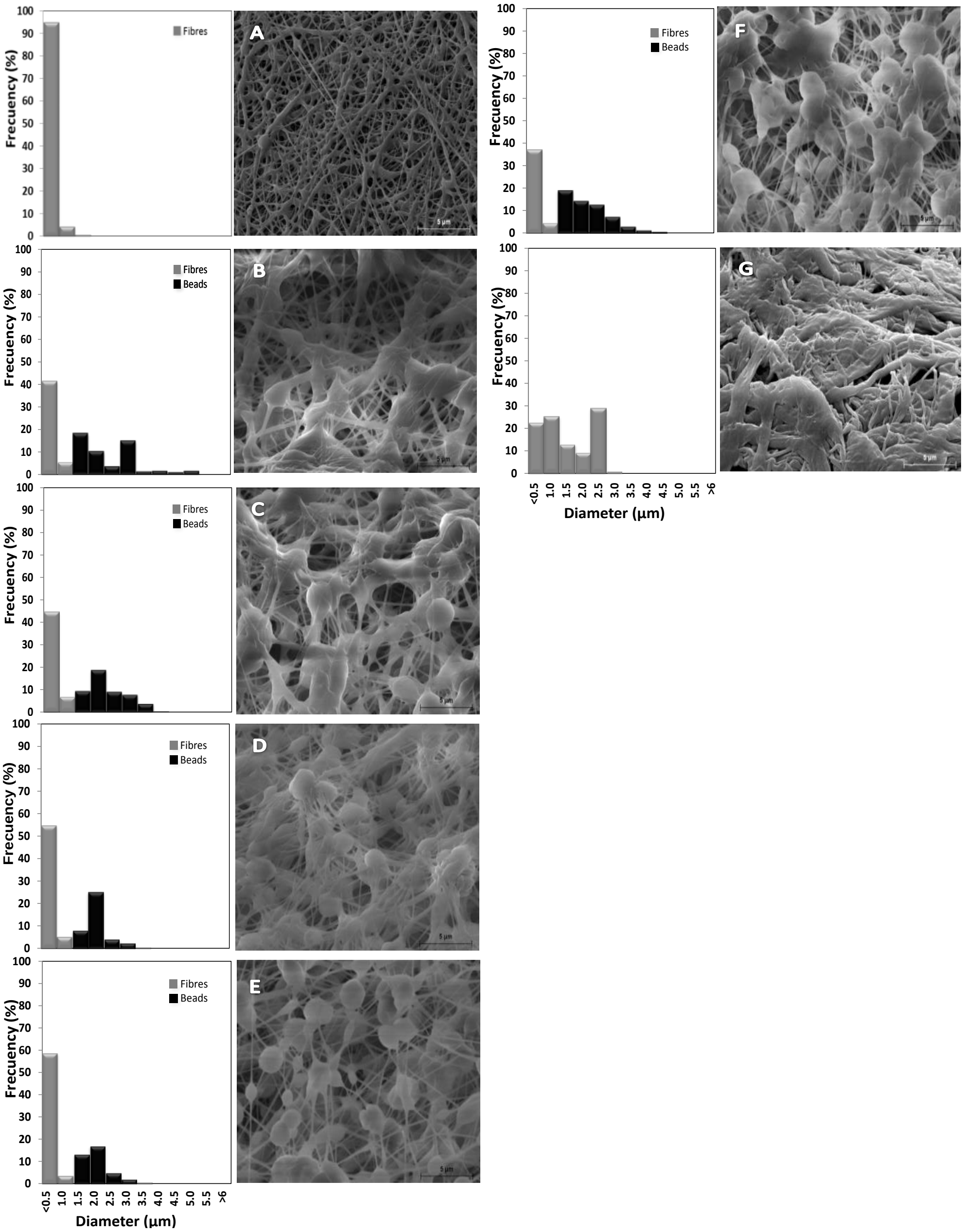

Figure 1. SEM images of the electrospun hybrid structures: electrospun uniaxial PVOH/PCM hybrid structures prepared without PCM and surfactant (A), with 7% of PCM and without surfactant (B), with 7% of PCM and 0.16% of surfactant (C), with 7% of PCM and 0.32% of surfactant (D), with 7% of PCM and 0.48% 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).

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 2), 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. 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 3 gathers the melting and crystallization temperatures (Tm and Tc), supercooling degree and the corresponding melting and crystallization enthalpy values (· Hm and · Hc) normalized to the PCM content of the electrospun hybrid structures. From this Table, 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, 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.

Table 3. Thermal properties of the electrospun hybrid structures. Mean value (standard deviation).

Electrospun hybrid structures	Tm (ºC)			ΔHm		Tc$_1$ (ºC)	Tc$_2$ (ºC)	ΔHc		Supercooling (ºC)	Efficiency (%)
	Onset (ºC)	Peak (ºC)	End (ºC)	J/g PCM	J/g sample			J/g PCM	J/g sample		
PCM-1.5ºC	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}

a-g: Different superscripts within the same column indicate significant differences ($p < 0.05$).

However, the crystallization phenomenon was different. While pure PCM crystallized at 5.4ºC, 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 paraffin's when their particle size is reduced.[19-21] 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. The phase change material will hence be effective on a larger temperature range. In these cases, 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 decreased 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 effectively encapsulated. 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 behaviour 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 2, 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.

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 1D) and even to those previously observed at the same relative humidity (*cf.* Figure 2A). This aspect limits the practical application of the developed hybrid structures since even at low relative humidity (~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[11-12] although this solution provided a handling problem under environmental conditions.

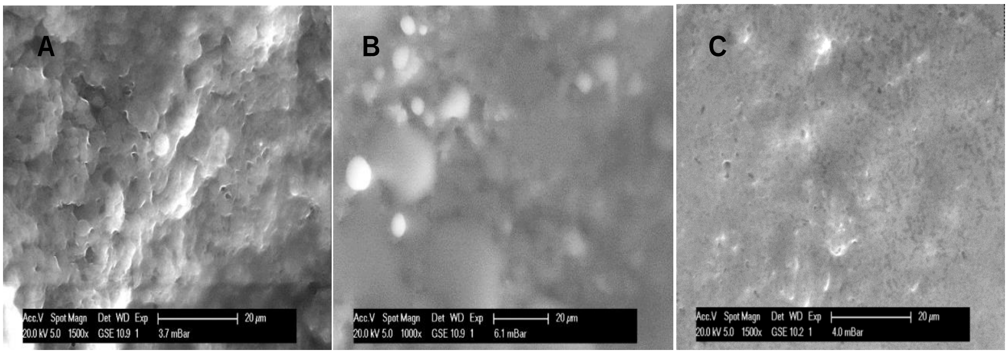

Figure 2. ESEM images of the PVOH/PCM emulsion-electrospun structures prepared with 7% (wt. %) of PCM and 0.32% of surfactant conditioned at different relative humidities as follows: (A) 28 % RH, (B) 46% RH (C) 31% RH.

3.2. Encapsulation of the PCM by coaxial electrospinning

In order 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 in order 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 4 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 exudation phenomena, 15.9 wt.-% of PCM was selected to develop the coaxial electrospun structures.

Table 4. Melting enthalpy values of PVOH/PCM emulsion electrospun structures prepared with 0.32 wt.-% of Tween 20 and different PVOH/PCM ratios. Mean value (standard deviation).

wt.-% polymer/100 g of sample	wt.-% PCM/100 g of sample	ΔHm	
		(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}

a-c: Different superscripts within the same column indicate significant differences ($p < 0.05$).

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 fibres 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 1G).

Table 3 displays the thermal properties of the PVOH/PCM electrospun fibres prepared with 15.9 wt.-% of PCM containing or not PCL as a shell material. The thermal behaviour 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 fibres, 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 3B). This was confirmed by decreasing the relative humidity to the initial conditions (*cf.* Figure 3C), indicating that the PCL was able to protect the electrospun structures from swelling.

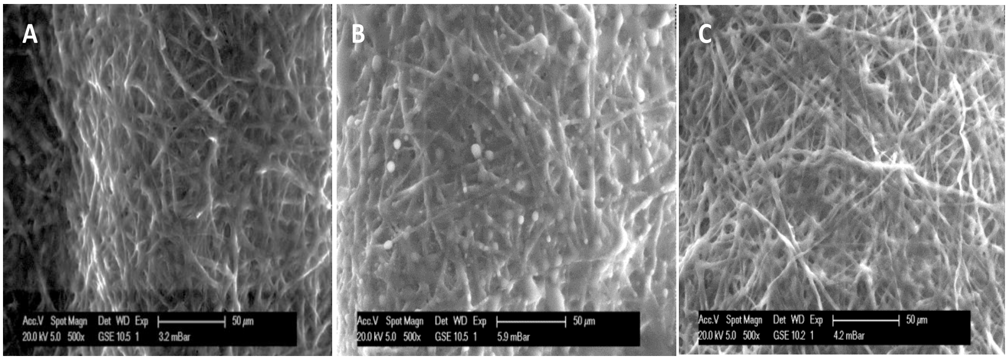

Figure 3. ESEM images of the coaxial hybrid structures prepared with PVOH/PCM emulsion (core material) and PCL (shell material) conditioned at different relative humidity conditions as follows: (A) 28 % RH, (B) 46% RH (C) 31% RH.

4. 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 favour 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 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.

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IV. GENERAL DISCUSSION

The use of phase change materials (PCM's) for the preservation of perishable products, such as food, beverages and biomedical substances I s gaining a great deal of attention because of the advantages that these materials can have on product quality preservation and also from the environmental viewpoint, related to their ability to reduce temperature fluctuations along the cold chain, reduce the energy consumption of refrigeration equipment and facilities, reduce the use of environmentally harmful refrigerants (such as chlorofluorocarbons and hydrochlorofluorocarbons) and provide high energy storage density in a reduced temperature range, among others. In this line, the main aim of the current thesis work was to develop different heat management materials of interest in refrigerated and superchilled foods. The strategy followed to develop the heat management materials was to encapsulate phase change materials (PCM's), specifically paraffin's, using the electrohydrodynamic processing, as this encapsulation method can be adjusted to modify the morphology and size of the electrospun structures. Moreover, it does not require the use of extreme conditions in terms of temperature, pH, pressure, etc. for structure formation. As an additional advantage of the electrospinning technique for encapsulation, it is worth mentioning that there is no limitation in terms of the substance to encapsulate due to the possibility of using different processing configurations, thus allowing the preparation of structures containing substances of different chemical nature and affinity.

Phase change materials (PCM's), specifically paraffin's, were encapsulated within different polymer and biopolymer matrices (various polyesters and polyvinyl alcohol) in order to obtain novel heat management materials to be incorporated either in food packaging structures or in refrigeration equipments. Specifically, commercial paraffin's with phase transitions at refrigeration temperatures (about 5ºC) and superchilling temperatures (about -1.5ºC) were used.

With a focus on application in refrigeration equipment, slabs with heat management capacity based on the encapsulation of a PCM which melted at 5ºC (RT5-core material) inside two different polymeric matrices (polycaprolactone (PCL) and polystyrene (PS)) (shell material) by means of the electrohydrodynamic processing were developed. The performance of these materials was studied during storage as a function of temperature (4ºC vs. 25ºC) and storage time and the results are compiled in Chapter 1. According to the thermal properties it was observed that melting temperature of the encapsulated RT5 was very similar to that of pure RT5. However, a multiple crystallization profile was observed for the encapsulated PCM, probably because of the reduction of the PCM particle size. Furthermore, it was noted that PCL/PCM slabs were able to encapsulate a greater amount of the RT5 than those obtained with PS. However, when the PS/PCM and PCL/PCM slabs were stored at 25ºC the encapsulation efficiency decreased, fact that was attributed to the progressive diffusion out of the PCM from the capsules during ageing (as the PCM was in liquid state at this temperature). However, in the case of slabs stored at 4ºC no significant changes during ageing were observed due to solid state of PCM at this temperature, showing that PCL/PCM slabs stored at 4ºC had the greatest encapsulation efficiency (98.56%). These materials were especially designed for applications in refrigeration equipments, in order to counteract temperature fluctuations and to increase the energy efficiency of the devices.

The second explored incorporation method of these novel heat management materials was as an ultrathin fiber-structured polystyrene/PCM coating onto PS foam trays. This type of application might be extremely useful for refrigerated food products packaged in trays, such as fresh meat and fish products. As for the slabs and multilayer structures, the effects of storage temperature and ageing on the behavior of the structures were studied. Results showed a greater supercooling degree, mainly ascribed to the reduced PCM drop sizes inside the electrospun fibers. Furthermore, PS/PCM fibers showed an encapsulation efficiency of ca. 78%, thus providing a heat storage capacity equivalent to ~34 wt.-% of PCM (107 J/g PCM). However, it was observed that when the fibers were stored for 3 months, a decrease in their heat management properties of ~56–58% and 30–40% was observed for the materials stored at 25ºC and 4ºC, respectively.

Another possible application of encapsulated PCM’s is their incorporation in packaging structures in order to increase the thermal energy storage capacity of the packaging for their application in refrigerated foods. To this end, multilayer heat management structures were developed based on a polystyrene (PS) film coated with a PCL/PCM electrospun layer. In a similar way as what it was done with the slabs, the effects of storage temperature and ageing on the behavior of the polystyrene (PS)-based multilayer structures were studied. Results, compiled in Chapter 2, showed that the melting behavior of the encapsulated PCM was similar to that of the pure PCM (5.3ºC), but again a multiple crystallization profile was observed for the encapsulated PCM. Furthermore, a greater supercooling degree was observed in all PS-multilayer structures, which was attributed to the reduction of the PCM particle size. However, it was observed that the heat storage capacity of these PS multilayer structures was affected not only by the film multilayer structure, but also by the storage time and temperature. As in the case of slabs of PCL/RT5 and PS/RT5, the heat storage capacity significantly decreased in PS-multilayer systems stored at 25ºC. As a strategy to counteract the loss of PCM during storage, an additional PCL external electrospun layer was incorporated in the multilayer structures, which was seen to improve the temperature buffering capacity along storage. It was observed that the greatest efficiency (65%) was achieved for PS-based multilayer structures prepared with both layers (PCL/PCM and PCL) and stored at 4ºC, while the thermal energy storage capacity was of about 88-119 J/g.

From the previous works it was observed that, in general, microencapsulation of the PCM's altered the thermal properties of the paraffin's, generating multiple crystallization profiles and increasing the supercooling degree. Therefore, a further aim of this thesis work was to optimize the electrospinning conditions so as to improve the heat management properties of the developed structures. As solution properties are known to have a great influence in the electrospinning process, the optimization of the process was based on modifying them by adjusting the solvent composition with the aim of obtaining hybrid fibers with thermal properties similar to those of the neat PCM. On the one hand, the effect of different solvents on the electrospinning capacity, the morphology and the heat management properties of the electrospun structures was studied and, on the other hand, the effect of different electrospinning solutions using mixed solvent systems with different physicochemical properties (dielectric constant, viscosity and solubility, among others) on the electrospinning capacity, the morphology and the heat management properties of the electrospun structures we evaluated. The starting points for the optimization of the polymer solutions were the results obtained in the first part of this chapter and the solvent properties. In the case of PCL/PCM solution, dimethylformamide (TCM) was mixed with both trichloromethane (TCM) and toluene (T). The DMF was selected because it provided high dielectric constant value, more uniform and smooth fibers, a single melting and crystallization peak and a supercooling degree similar to that of the neat PCM, has although it showed lower encapsulation efficiency. To counteract this drawback the best strategy was to add solvents which provided complementary properties in terms of viscosity and component solubility. In the case of PS and HIPS, DMF was mixed with THF to counteract the low solubility of PCM. THF was also a good solvent for both polymers, providing good encapsulation efficiency when used alone. All the materials were optimized for superchilling applications and, for this purpose, a PCM based on a mixture of commercial paraffin's which presented a phase transition at around -1.5ºC (core material) was encapsulated inside three different polymeric matrices: polycaprolactone (PCL), polystyrene (PS) and high-impact polystyrene(HIPS) (shell material) by means of the electrohydrodynamic processing. Results showed that the physical chemical properties of the solvents (mainly viscosity and dielectric constant) played an important role in the final properties of the solutions and, consequently, on the morphology and diameter of the electrospun fibers obtained thereof. Moreover, it has been demonstrated that the solubility of the fiber components (in this case the polymer and the paraffin) in the solvents is crucial in determining the thermal properties (enthalpy values, melting and crystallization temperatures and supercooling degree) of the electrospun hybrid fibers. The results obtained in this first part of the study showed that the thermal properties of the structures obtained from the polymer solutions prepared with pure solvents significantly differed from the ideal behavior desirable for a heat management material, since the encapsulation efficiency, the melting and crystallization temperatures and the supercooling degree of the hybrid structures were significantly affected by the polymer (shell material) and by the solvent used to prepare the electrospinning solutions. However, the use of polymer solutions prepared with solvent mixtures resulted in more homogeneous electrospun fiber morphologies, improved thermal properties of the hybrid heat management materials, which showed melting and crystallization temperatures and a supercooling degree similar to that obtained for the bulk PCM. The greater encapsulation efficiency was achieved for PCL-based structures, which showed that with the optimized conditions used, around 92 wt.-% of the PCM was effectively encapsulated.

The other drawback of the heat management structures developed for practical applications was related to the loss of PCM from the structures during storage and, thus, the last work presented in this thesis was focused on improving PCM retention in the structures. With the aim of preventing or minimizing the partial diffusion out of the paraffin from the electrospun structures during ageing, whatever the temperature used during the storage period, a hydrophilic material, specifically polyvinyl alcohol (PVOH) was used as encapsulation matrix, as from the literature it is well-known that hydrophilic matrices are more adequate to retain and encapsulate hydrophobic compounds since they are immiscible with the core material, favouring a phase separation between the core and the shell. However, PVOH is water soluble and very sensitive to humidity, meaning that at high relative humidity, the PCM could be released from these hydrophilic structures. Therefore, to improve the stability of the developed structures under different relative humidity (RH) conditions, addition of an extra encapsulation layer of a hydrophobic compound through coaxial electrospinning was considered. Consequently, this work was carried out in two stages. The first one was centred in the optimization of electrospun structures through an emulsion electrospinning technique using a hydrophilic shell material (polyvinylalcohol –PVOH-) to encapsulate the PCM mostly used along this thesis work which melted around 5ºC (RT5). In order to guarantee the incorporation of the water insoluble PCM, a surfactant was incorporated to the polymer-PCM emulsion. The amount of surfactant was optimized to reach the highest encapsulation efficiency. Once the optimum conditions were found, the second step consisted on the development of coaxial electrospun structures based in PVOH/PCM emulsion as core materials and a polycaprolactone (PCL) solution in TCM/DMF as shell material in order to hydrophobize the developed structures. This biopolymer was chosen as shell material of the emulsion electrospun structures, because apart from being a biodegradable hydrophobic polymer, it has good spinnability properties and it has been previously demonstrated to have good encapsulation yields. The morphology of the PVOH/PCM emulsion electrospun structures was affected by surfactant addition, which stabilized the emulsions, generating more uniform fibres and beaded areas. According to the thermal properties it was observed that the melting temperature of the PVOH/PCM electrospun hybrid structures prepared without the surfactant (Tween 20) did not differ from that of the neat PCM, indicating that similar PCM crystals were formed in the encapsulation structures probably due to the low compatibility between the paraffin and the hydrophilic polymer. However, 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 paraffin's when their particle size is reduced. 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. In the case of coaxial electrospun structures, about 82% of PCM was effectively encapsulated. However, the use of a coaxial configuration was a good strategy to preserve the morphology of the electrospun structures when exposed to high relative humidity as inferred from ESEM experiments. This confirms that using the PCL as shell material, it is possible to hydrophobize the developed structures.

V. CONCLUSIONS

- Novel temperature buffering materials were developed by means of the electrohydrodynamic processing by encapsulating two different phase change materials with transition temperatures at -1.5 and 5ºC, respectively within different polymeric matrices.

- The electrospinning conditions were optimized to develop encapsulation structures based on biopolyester matrices containing either a commercial paraffin (Rubitherm RT5) which a transition temperature around 5ºC or a PCM which melted at -1.5ºC.

- Electrospun temperature buffering materials were developed with different purposes of interest in food packaging applications. Firstly, slabs based on PCL and PS containing RT5 were developed to be introduced in refrigeration equipments. Secondly, PS foam trays containing nanostructured PS/PCM coatings were developed. Finally, PS-based multilayer heat storage structures were developed to be used in food packaging applications.

- The crystallization profile and supercooling degree of the developed electrospun heat management materials differed from the ideal behavior desirable for a heat management material.

- In all cases, the storage temperature was the determining factor in the reduction of heat management capacity over storage time, showing a lower decrease when the materials were stored at 4ºC.

- Through the optimization of the electrospinning solutions based on using mixtures of different solvents, encapsulation structures with a crystallization profile and supercooling degree similar to those from the neat PCM were obtained, thus, counteracting one of the drawbacks observed during the first research works.

- Moreover, in the last case, novel temperature buffering materials of interest in superchilling applications based on polyester matrices containing a PCM obtained from a mixture of commercial paraffin's with a transition temperature around -1.5ºC were developed.

- Amongst all the polymers studied for PCM encapsulation, PCL showed the best performance in terms of encapsulation efficiency and, thus, temperature buffering capacity. Moreover, PCL/PCM fibers also kept this heat management ability to a greater extent during storage time

- PVOH/PCM emulsion electrospun structures were developed to improve the retention of PCM and a surfactant (Tween 20) was added to the emulsion electrospinning to favor the encapsulation process.

- The surfactant (Tween 20) addition successfully increased the heat storage capacity of the PVOH/PCM emulsion electrospun structures.

- PVOH/PCM emulsion electrospun structures showed hydrophilic character and they were successfully hydrophobized by using a PCL outer layer by means of a coaxial electrospinning.

- The morphology of the electrospun structures prepared by the coaxial configuration (PCL/PVOH-PCM) remained when they were exposed at high relative humidity.

VI. ANNEXES

ANNEX 1. List of publications

This thesis compiles information from the following papers, patents and book chapters:

- Chalco-Sandoval, W., Fabra, M. J., López-Rubio, A., & Lagaron, J. M. (2014). Electrospun heat management polymeric materials of interest in food refrigeration and packaging. *Journal of Applied Polymer Science,* 131(16).

- Chalco-Sandoval, W., Fabra, M. J., López-Rubio, A., & Lagaron, J. M. (2015). Use of Phase Change Materials to develop Electrospun Coatings of interest in Food Packaging Applications. *Journal of Food Engineering*, in press.

- Chalco-Sandoval, W., Fabra, M.J., López-Rubio, A., Lagaron, J.M., (2015). Development of polystyrene-based films with temperature buffering capacity for smart food packaging. *Journal of Food Engineering* 164, 55-62.

- Chalco-Sandoval, W., Fabra, M. J., López-Rubio, A., & Lagaron, J. M. Optimization of solution composition for the encapsulation of a phase change material in polymeric matrices by electro-hydrodynamic processing. In preparation.

- Chalco-Sandoval, W., Fabra, M. J., López-Rubio, A., & Lagaron, J. M. Development of temperature buffering encapsulated phase change material in polyvinyl alcohol (PVOH) and polycaprolactone (PCL) via emulsion and coaxial electrospinning of interest in the food cold chain. In preparation.

- R. Pérez-Masiá, M.J. Fabra, W. Chalco-Sandoval, A. López-Rubio & J.M. Lagaron. Development by electrohydrodynamic processing of heat storage materials for multisectorial applications in "Electrospinning for high performance sensors" (Chapter 11). Eds. Springer International Publishing, 2015, p 281.

- E. Indergård, T. S. Nordtvedt, M. Bantle, I. C. Claussen, W. Chalco-Sandoval, J.M. Lagaron, 2014. Use of phase change materials (PCM) to keep superchilled temperatures in consumer packages through the cold chain, *International Conference on Sustainability and the Cold Chain*, 24-25 June 2014, London.

- P201431738 Patent Application (2014). Inyector multisalida. Inventors: Lagarón, J.M., Chalco-Sandoval, W., Fabra, M. J., López-Rubio, A. Holder entity: CSIC.

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Electrospun Heat Management Polymeric Materials of Interest in Food Refrigeration and Packaging

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ABSTRACT: The use of latent heat storage materials using phase change materials (PCMs) is an effective way of buffering thermal fluctuations and has the advantages of high-energy storage density and the isothermal nature of the storage process. The aim of this work was to develop slabs with energy storage capacity for their application in refrigerated foods. To this end, polycaprolactone (PCL) and polystyrene (PS) were used as encapsulating matrices of a PCM, specifically RT5 (a paraffin which has a transition temperature at 5°C), by using electrohydrodynamic processing. The effect of storage temperature (4°C and 25°C) and time on the morphology and thermal characteristics of the PCL/RT5 and PS/RT5 slabs was evaluated. Results showed that RT5 can be properly encapsulated inside both polymers, although PCL provided better encapsulation efficiency. Encapsulation efficiency was affected not only by the polymer matrix but also by storage time at 25°C. The greatest encapsulation efficiency (98.6%) and optimum heat management performance was achieved for PCL/PCM slabs stored at 4°C, corresponding to materials composed of ~44 wt % of PCM (core material) and ~56 wt % of the PCL shell material. These temperature buffering materials can be of great interest to preserve the quality of packaged foods and to increase efficiency and reduce energy consumption in refrigeration equipment. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40661.

KEYWORDS: biopolymers and renewable polymers; polystyrene; crystallization; differential scanning calorimetry (DSC); fibers

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INTRODUCTION

Refrigeration systems have been used during the last decades as a main method of food preservation. In fact, it is well-known that frozen and freezing temperatures are required during transport and storage in order to maintain the quality and safety of many foodstuffs. It is worth to note that food quality is often compromised by temperature fluctuations during food commercialization which, amongst others, contributes to the formation of heterogeneous crystal growth.

However, refrigeration is one of the heavy energy consumers. Furthermore, the ozone layer depletion and greenhouse gases emission associated to the use of air conditioners and refrigerators that make use of chlorofluorocarbons and hydrochlorofluorocarbons (CFCs and HCFCs) as refrigerants represent great environmental concerns. The phase-out of CFCs and HCFCs according to the Montreal Protocol urges the researchers to find out environmentally friendly new substitutes for refrigerants or novel technologies to reduce the amount of refrigerant used in these systems as well as to reduce the energy consuption of these.

As a result, researchers are focused on developing technical options for improving the energy performance of household refrigerators and one of the most innovative options is the use of phase change materials (PCMs).

PCMs are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release the latent heat when isothermal conditions are altered.[1] PCMs could be used during transport or storage, for the protection of solid foods, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products, and many others.[2] The most commonly used PCMs are paraffin waxes, fatty acids, eutectics, and hydrated salts.[3] The paraffin compounds fulfil most of the requirements for being used as PCMs, as they are reliable, predictable, nontoxic, chemically inert, and stable below 500°C. They also show little volume changes on melting and have low vapour pressure in the molten form.[4] On the other hand, the inorganic substances, like salt hydrates, usually suffer from supercooling and phase separation during their applications which often compromises the temperature buffering behavior of these materials and cause random variations or progressive drifting of the transition zone over repeated phase change cycles. Furthermore, corrosion is another shortcoming of these materials.[5]

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Use of phase change materials to develop electrospun coatings of interest in food packaging applications

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A B S T R A C T

In the present study, a heat management PS foam tray containing an ultrathin fiber-structured PS/PCM coating was prepared by using high throughput electrohydrodynamic processing. To this end, polystyrene (PS) was used as the encapsulating matrix of a commercial phase change material (PCM) called RT5 (a blend of paraffins with a transition temperature at 5 °C), by using the electrospinning technique. With the aim of imparting heat management capacity to the trays, the PS tray was coated by the PS/PCM ultrathin fiber mats and a soft heat treatment was applied to improve the adhesion between the layers. Results showed that RT5 could be properly encapsulated inside the PS matrix, with a good encapsulation efficiency (ca. 78%) and the developed PS fibers had a heat storage capacity equivalent to ~34 wt.% of the neat PCM. The effect of storage time and temperature was evaluated on the heat storage capacity of the developed PS-trays with the ultrathin fiber-structured PS/PCM layer. The heat storage capacity was affected not only by the storage time, but also by the temperature. This work adds a new insight on the development of heat management polymeric materials of interest in food packaging applications, in order to preserve the quality of refrigerated packaged food products. Although the electrohydrodynamic processing seems to be a promising alternative to develop heat management materials, further works will be focused on the improvement of heat storage capacity and efficiency of the developed packaging materials along storage time.

1. Introduction

Maintaining the cold chain during the commercialization of certain food products is one of the key aspects to ensure food safety and food quality. Refrigeration temperatures (from 2° to 8 °C) are used for preventing or slowing down microbial, physiological and chemical changes in food produced by microbial, chemical and/or enzymatic activity. Along the cold chain there can be temperature variations which will consequently have negative effects on food due to crystal ice growth, acceleration of chemical reactions and/or microorganism growth, which could result in a reduction of quality and may shorten the shelf-life of the food products. Therefore, there is a great interest on finding new strategies to reduce temperature fluctuations along the cold chain. In this sense, the packaging can be designed to play an active role to maintain the food temperature within desired limits and, thus, to ensure the quality, safety and increase the shelf-life of the products (James et al., 2006). However, traditional commercial packages such as low-density polyethylene and polystyrene. do not provide any protection for maintaining the cold chain.

Phase change materials (PCMs) are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release latent heat with a very small variation in temperature (Jin et al., 2010). PCMs could be used during transport, storage and distribution stages to maintain the cold chain of solid food, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products and many others (Alkan et al., 2011; Azzouz et al., 2009; Oró et al., 2012; Salunkhe and Shembekar, 2012; Zalba et al., 2003). The most commonly used phase change materials are paraffin waxes, fatty acids, eutectics and hydrated salts (Farid et al., 2004). Paraffin compounds fulfill most of the requirements for being used as PCMs, as they are reliable, predictable, non-toxic, chemically inert and stable below 500 °C. They also show little volume changes on melting and have low vapor pressure in the melt form (Sharma et al., 2009).

For the correct use of PCMs, as they experiment a phase change from solid to liquid at the target temperature, they must be encapsulated. In this context, there are two main encapsulation types:

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Development of polystyrene-based films with temperature buffering capacity for smart food packaging

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Smart food packaging

A B S T R A C T

One of the main factors affecting the quality of perishable products is represented by temperature variations during storage and distribution stages. This can be attained through the incorporation of phase change materials (PCMs) into the packaging structures. PCMs are able to absorb or release a great amount of energy during their melting/crystallization process and, thus, they could provide thermal protection to the packaged food. Thus, the objective of this research was to develop polystyrene (PS)-based multilayer heat storage structures with energy storage and hence temperature buffering capacity for their application in refrigerated foods. To this end, polycaprolactone (PCL) was used as the encapsulating matrix of a phase change material (PCM) called RT5 (a commercial blend of paraffins with a transition temperature at 5 °C), by using high throughput electrohydrodynamic processing. The PCL/PCM fibrous mats were directly electrospun onto PS films and an additional PCL electrospun layer (without PCM) was also deposited in some experiments to improve the overall functionality of the PCM. The attained morphology, thickness, deposition time, temperature and multilayer structure played an important role on the energy storage capacity of the developed PS-based multilayer structures. Results obtained from a differential scanning calorimeter (DSC) show that RT5 can be properly encapsulated inside the PCL matrix and the encapsulation efficiency and, thus, the heat storage capacity was affected not only by the multilayer structure, but also by the storage time and temperature. The thermal energy storage/release capacity was of about 88–119 J/g. As a result, this work demonstrates the potential of these materials for an efficient temperature buffering effect of relevance in food packaging applications, in order to preserve the quality of refrigerated packaged food products.

1. Introduction

Refrigeration plays an important role in food preservation, as low temperatures aid in preventing or slowing microbial, physiological and chemical changes in food produced by microbial and/or enzymatic activity. Temperature fluctuations in the cold chain during the storage and distribution stages have negative effects on food due to crystal ice growth, acceleration of chemical reactions and/or microorganisms growth, which could result in a reduction of quality and may shorten the shelf-life of the food products. Therefore, strategies to buffer potential temperature fluctuations during the commercialization of foods are highly desirable. Packaging can be designed to play an active role to maintain the food temperature within desired limits and, thus, to ensure the quality, safety and increase the shelf-life of the products (James et al., 2006). Usually, the limited thermal insulation and poor thermal buffering capacity of standard packaging do not provide any protection for maintaining the cold chain. But there are different strategies that could contribute to improving the thermal buffering capacity of a package, being one of them the development of thermal energy storage (TES) structures through the addition of phase change materials (PCMs) (Gin and Farid, 2010; Oró et al., 2012) within the polymeric structures (Oró et al., 2013). This strategy has been recognized as one of the most preferred forms of energy storage, mainly due to the high energy storage density provided by the PCMs and the nearly isothermal heat storage characteristics that can be attained (Melone et al., 2012). Phase change materials (PCMs) are substances that undergo a phase transition at a specific temperature and, as a result, they are able to absorb and release the latent heat with a very small variation in temperature (Jin et al., 2010). PCMs could be used during transport, storage and distribution stages to maintain the cold chain of solid food, beverages, pharmaceutical products, textile industry, blood derivatives, electronic circuits, cooked food, biomedical products and many others (Oró et al., 2012). The most commonly used phase

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