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Use of electrohydrodynamic processing to develop nanostructured materials for the preservation of the cold chain

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ABSTRACT

In this study Rubitherm-RT5®, a PCM with a phase transition temperature around 5 °C, was encapsulated inside PCL, PLA and PS by means of electrohydrodynamic processing in order to develop thermal energy storage systems for refrigeration applications. The effect of the morphology of the encapsulation structures (fibrillar or spherical) on thermal properties and encapsulation efficiency was evaluated. The morphology of the structures played an important role on the energy storage capacity, since PCM was better encapsulated in fibrillar structures, providing higher energy storage capacity. The greater encapsulation efficiency was achieved for the fibers, which showed that ~80–90 wt.% of the incorporated PCM, effectively remained within the polymeric matrices. These hybrid structures are of great interest for the development of active packaging systems aimed at improving food quality preservation under refrigeration conditions.

Industrial relevance: As a response to the consumers for more safety foodstuffs and low environmental impact technologies, this work presents a novel methodology to develop energy storage materials. These materials buffer thermal variations and, thus, could be used in packaging systems to better preserve the cold chain. Furthermore, the incorporation of these materials in refrigeration equipment could reduce energy consumption of existing refrigeration technologies.

1. Introduction

Conventional food packaging has been used to enable marketing of products and to provide passive protection against environmental contaminations or influences that affect the shelf life of foodstuffs (de Abreu, Cruz, & Losada, 2012). However, consumers are claiming higher quality, safer and fresher products and, thus, new functions are demanded to the packaging structures. Therefore, over the last decade, there has been an increased research interest in the development of different active packaging systems, such as oxygen scavengers, moisture absorbers, flavor and odor absorbers/releasers or antimicrobials systems, which have an active role in food preservation, extending the shelf life or improving the conditions of packaged food through the retention or release of compounds from/to the food or package headspace. A more recent concept of packaging structure having an active role in food preservation is packaging with heat management properties. It is well-known that temperature is a critical parameter which activates chemical reactions and microorganisms' growth. In this sense, refrigeration temperatures have preservative effects on perishable products and thus, by controlling the temperature along the different stages of the food production, a great number of deteriorative processes could be avoided and the shelf life of products could be increased. However, temperature fluctuations during storage and commercialization of foods can result in a number of quality drawbacks, such as crystal ice growth in products like meat or ice-cream. A possible approach to control thermal variations during storage and distribution of food, maintaining the preservation temperature constant and thus, preventing temperature fluctuations which can derive in food quality loss is through packaging structures with thermal energy storage capacity. 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, as a consequence, they are able to buffer the thermal variations of the environment, and thus, they could provide thermal protection to the packaged food. The use of PCMs 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 and biomedical systems (Sarier, Onder, Ozay, & Ozkilic, 2011). Specifically in the food packaging area, PCMs are replacing dry ice containers used during the transport and storage of perishable foodstuffs. Some of the advantages of using PCMs include the weight reduction of the containers in comparison with dry ice and, their reusability during many thermal cycles.

Among all the compounds available as phase change materials, paraffins are one of the most studied, since they are chemically stable and do not degrade after repeated cycling. Paraffins are highly compatible with a wide variety of materials and have a latent heat of fusion of

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around 200 kJ/kg depending on the particular paraffin selected (Ehid & Fleischer, 2012). However, the use of paraffins for thermal energy storage applications also presents some drawbacks. On one hand, paraffins have a low thermal conductivity, which limits the energy that can be extracted from them. Another 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. Some strategies to overcome these difficulties are the reduction of the PCM particles' diameter in order to achieve a very high surface area to volume ratio, thus increasing their heat flow rate due to a higher exchange area per unit of volume (Alkan, Sari, & Karaipekli, 2011). Furthermore, the encapsulation of these particles in a solid matrix can solve the handling problems of the PCMs. The most common paraffin encapsulation techniques are interfacial polymerization (Chu et al., 2003), emulsion polymerization (McDonald & Devon, 2002), in situ polymerization (Yang, Xu, & Zhang, 2003), layer by layer deposition of polyelectrolytes (Sukhorukov et al., 2004), spray drying and coacervation (Hawlader, Uddin, & Khin, 2003). However, only small amounts of PCM can be effectively encapsulated by some of these techniques, and they render too large particle sizes for some applications (Sánchez-Silva et al., 2010). Therefore, a rather novel route for PCM encapsulation, based on the electrospinning process (Lagaron, Perez-Masia, & Lopez-Rubio, 2011), is proposed in this work. The electrospinning process uses 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 (Li & Xia, 2004). This technique has recently proven to encapsulate different materials with significant yielding and flexibility in design, obtaining submicron sized structures (Torres-Giner, Gimenez, & Lagaron, 2008; Fernandez, Torres-Giner, & Lagaron, 2009; López-Rubio & Lagaron, 2012). Although there are a few works using electrospinning to develop PCM-containing materials, most of them deal with room and human comfort range temperatures (Alay, Göde, & Alkan, 2010; Arecchi, Mannino, & Weiss, 2010; Cai et al., 2012; Chen, Wang, & Huang, 2007; McCann, Marquez, & Xia, 2006; Seifpoor, Nouri, & Mokhtari, 2011).

The aim of this work was to use the electrospinning technology to obtain novel food packaging energy storage systems of interest in refrigeration applications. Two biopolyesters, polylactic acid (PLA) and polycaprolactone (PCL), were used as shell materials since they have attracted great interest among the existing biodegradable matrices because of their good physical properties (when compared to other biodegradable and renewable polymers), excellent biocompatibility and commercial availability (Cohn & Hotovely Salomon, 2005; Garkhal, Verma, Jonnalagadda, & Kumar, 2007; Huang, Günther, Doetsch, & Mehling, 2010; Pamula & Menaszek, 2008). Furthermore, the encapsulation systems based on these biodegradable materials were compared with others obtained with polystyrene (PS), since this petro-based polymer is currently used in refrigerating equipments and food packaging. Regarding the PCM, Rubitherm-RT5® (RT5) was encapsulated in the different polymers. RT5 is a commercial mixture of paraffins, specifically $C_{14}H_{30}$ (33 wt.%), $C_{15}H_{32}$ (47 wt.%), $C_{16}H_{34}$ (16 wt.%), $C_{17}H_{36}$ (3 wt.%) and $C_{18}H_{38}$ (1 wt.%), which presents a phase transition at around 5 °C. This temperature is commonly used to keep the refrigerating conditions of foodstuffs in retail and display cabinets at supermarkets or in household refrigerators. For each material, the effect of encapsulation morphology (fibrillar or spherical) on the molecular organization and on the thermal properties of the capsules was evaluated.

2. Materials and methods

2.1. Materials

Rubitherm-RT5® (RT5) was purchased from Rubitherm (Germany). A semicrystalline extrusion grade of polylactide (PLA) (Natureworks) with a D-isomer content of approximately 2 wt.% was used. It had a weight-average molecular weight (Mw) of 150,000 g/mol and a number average molecular weight (Mn) of ca. 130,000 g/mol. The polycaprolactone (PCL) grade FB100 was kindly supplied in pellet form by Solvay Chemicals (Belgium). This grade had a density of 1.1 g/cm^3 and a mean molecular weight of 100,000 g/mol. Polystyrene (PS) commercial grade foam was supplied by NBM (Spain). N,N-dimethylformamide (DMF) with 99% purity and trichloromethane were purchased from Sigma-Aldrich (Spain) and Panreac Quimica S.A. (Spain), respectively.

2.2. Preparation of polymer/RT5 solutions

Based on previous studies, the different polymers and RT5 were dissolved under magnetic stirring, in a solvent prepared with a mixture of trichloromethane:N,N-dimethylformamide (85:15 w/w) in order to produce fibrillar (fibers) or spherical (beads) capsules according to the conditions presented in Table 1.

2.3. Characterization of the solution properties

The viscosity and surface tension of the pure RT5, the solvent mixture used and all the biopolymeric solutions were characterized before the electrospinning process. The viscosity of the solutions was measured using a rotational viscosity meter Visco Basic Plus L from Fungilab S.A. (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, Germany). Both measurements were done, in triplicate, at 25 °C.

2.4. Preparation of the polymer-PCM fibers or beads through electrospinning

Fibers and beads were obtained using the electrospinning technique. The electrospinning apparatus, equipped with a variable high-voltage 0–30 kV power supply, was a FluidNatek® basic setup assembled and supplied by BioInicia S.L. (Spain). The polymer/PCM solutions were electrospun under a steady flow-rate using a stainless-steel needle situated toward a metallic grid used as collector. The needle was connected through a PTFE wire to the polymer solution kept in a 5 mL plastic syringe which was disposed horizontally lying on a digitally controlled syringe pump. The electrospinning conditions were the following: 1 mL/h flow-rate, 12.5 kV voltage and 10 cm tip-to-collector distance for all the solutions.

2.5. Scanning electron microscopy (SEM)

The morphology of the electrospun structures was examined using scanning electron microscopy (SEM; Hitachi S-4100) after having been sputtered with a gold–palladium mixture under vacuum. All SEM experiments were carried out at 10 kV. Fibers and bead diameters were measured by means of the Adobe Photoshop CS4 software from the SEM micrographs in their original magnification.

Table 1
Polymers and PCM loadings.

Type of Polymer	Polymer concentration (wt.%)	Polymer: PCM weight ratio	Morphology
PCL	13	55:45	Fibers
PLA	5	80:20	Fibers
PS	10	55:45	Fibers
PCL	1.5	55:45	Beads
PLA	2.5	55:45	Beads
PS	2.5	55:45	Beads