European Polymer Journal 72 (2015) 23–33

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Optimization of solvents for the encapsulation of a phase change material in polymeric matrices by electro-hydrodynamic processing of interest in temperature buffering food applications

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ARTICLE INFO

Article history:
Received 8 May 2015
Received in revised form 27 August 2015
Accepted 30 August 2015
Available online 5 September 2015

Keywords:
Electro-hydrodynamic processing
Phase change materials
Superchilling
Temperature buffers

ABSTRACT

In this work, a PCM with a phase transition temperature set at −1.5 °C 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 matrix.

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]. Specifically, in the food packaging area, PCM's are replacing dry ice containers used during the transport and

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http://dx.doi.org/10.1016/j.eurpolymj.2015.08.033
0014-3057/

storage of perishable foodstuffs with the additional advantages of reducing the weight of the containers in comparison with dry ice and, on the other hand, 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 500 °C [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 [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-hydrodynamic processing [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 [16–18].

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.) [19–22]. 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 [20,21]. 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 [23].

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 [21,23–25].

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 in order to be applied as a food packaging system. The PCM was obtained from a mixture of commercial paraffin's which presented a phase transition at around −1.5 °C. 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 0 °C 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 [26–29].

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 (−1.5 °C) 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 25 °C 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 −4 °C, 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.