Journal of Food Engineering xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Food Engineering

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

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

Wilson Chalco-Sandoval, María José Fabra, Amparo López-Rubio, Jose M. Lagaron *

*Novel Materials and Nanotechnology Group, IATA-CSIC, Avda. Agustin Escardino 7, 46980 Paterna, Valencia, Spain*

ARTICLE INFO

*Article history:*
Received 9 July 2014
Received in revised form 20 January 2015
Accepted 28 January 2015
Available online xxxx

*Keywords:*
Phase change material
Electrohydrodynamic processing
Heat management materials
Food packaging
Encapsulation

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 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:

* Corresponding author. Tel.: +34 96 390 00 22x2512; fax: +34 96 363 63 01.
*E-mail address:* lagaron@iata.csic.es (J.M. Lagaron).

http://dx.doi.org/10.1016/j.jfoodeng.2015.01.019
0260-8774/

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 PCMs 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, PCMs (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.

Electrohydrodynamic 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, PCMs and others substances within polymer matrices (Goldberg et al., 2007; Lopez-Rubio et al., 2012; Pérez-Masiá et al., 2013a,b,c). 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 electrohydrodynamic 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 5 °C (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 $m^{-3}$, 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 electrohydrodynamic 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 Pérez-Masiá et al. (2013a,b,c), 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 h 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 (~50 g) was deposited onto the PS trays and was annealed at 145 °C 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 25 °C 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

Please cite this article in press as: Chalco-Sandoval, W., et al. Use of phase change materials to develop electrospun coatings of interest in food packaging applications. Journal of Food Engineering (2015), http://dx.doi.org/10.1016/j.jfoodeng.2015.01.019