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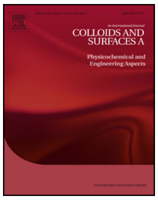

Nanoporous cellulose nanocomposite foams as high insulated food packaging materials

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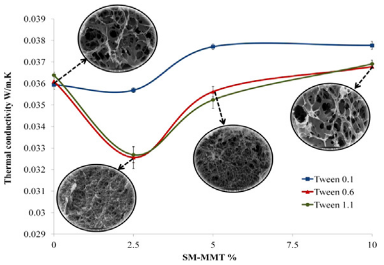
HIGHLIGHTS

- Nanocomposite foam-like materials were prepared based on cellulose/SM-MMT.
- The presence of SM-MMT improved the insulation performance of cellulose matrix by reducing the cell sizes.
- The dispersed SM-MMT particles cooperated on the improvement of thermal, mechanical and barrier properties of cellulose matrix.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, cellulose nanocomposite foams incorporated with surface-modified montmorillonite (SM-MMT) were developed using high shear homogenizer method which can substantially delaminate clay platelets. The goal of this study was to improve the properties of cellulose matrix as well as reducing the bubble sizes to prepare nanofoams in order to enhance mechanical and barrier properties, and thermal insulation performance. Several methods were used to characterize the prepared foam materials including scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal conductivity, mechanical and barrier analysis. Raman spectroscopy was also used to evaluate structural differences between microcrystalline cellulose and nanocomposite foams. The results of thermal conductivity and morphology indicated that presence of SM-MMT improved thermal insulating properties due to reduction of average cell size. Thermal, mechanical and barrier properties were significantly enhanced for the nanocomposites filled with low content of SM-MMT compared to pure cellulose foam. The properties of these materials allow their use as a possible alternative to expanded polystyrene (EPS) foam trays for dry food packaging. Additional studies would be needed to improve the properties to use these materials with moist foods. The thermal conductivity values obtained for cellulose foams make them suitable to use for chilled chains.

1. Introduction

Quality preservation of perishable products depends on a complex combination of both their physical and chemical characteristics and the external environment. Temperature variations during storage and distribution stages is one of the main extrinsic

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factors affecting the quality of perishable products [1]. The undeniable effect of temperature variation makes this necessity to control this parameter to extend products shelf-life. Temperature variation can be controlled in chilled distribution chains for products including beef, poultry, and vegetables [2]. In these cases, packaging has an important role because of chilled chains discontinuity from process to market. By utilization of insulators as packaging, heat transfer is limited and the temperature can be maintained within acceptable ranges.

Expanded polystyrene (EPS) boxes are currently used as insulator with porosity of almost 98%, low density and acceptable insulating performance [2,3]. Since the products based on polystyrene are not degradable, recently there has been much interest to replace this material with biodegradable ones. However it is necessary to use some additives to attain water resistance of biopolymers [4].

In the current method of foam production, a blowing agent is mixed under pressure with mixture of liquid polymer which ultimately makes macromolecular foam by a pressure release or proper temperature raising. An uncontrolled nucleation in this method causes growth and aging of cells [5]. The reduction of mean cell size in porous materials leads to less heat transfer and greater insulation. The novel insulating materials such as aerogels and nanofoams have been developed by using nanotechnology that achieve similar results to current products but with substantially lower thickness. Recently, Aerogel-like materials have been studied increasingly because of their unique properties that make them potentially attractive for various applications. The sol–gel method is an approach to prepare aerogel-like materials which has been widely investigated. In this method, aggregation of solid matter in a solution leads to gel formation. An effective drying process is then used to replace the liquid in the gel with gas [6]. Many studies on aerogel-like materials have been performed to prepare thermal insulation, mainly based on polyurethane, while natural products are concerned in only few works. In recent years, there is an increasing demand for petrol-based products alternatives. Cellulose as a sustainable source of natural, biodegradable and environmentally friendly polymer, has been drawn much attention in this field. Moreover, combining sol–gel science with cellulose could be of high interest. However, cellulose solvents are very limited and melting cellulose is also not possible because of the strong intra and intermolecular hydrogen bonding. Therefore, utilization of cellulose has more problems than the other kind of biopolymers. Recently, new cellulose solvents such as sodium hydroxide solution at low temperature have been discovered that make it possible to use this inexhaustible natural polymer to prepare materials with various functionalities [7].

Some important needs for an insulation packaging material are including resistance to heat transfer, low moisture susceptibility, mechanical strength, low cost and ease of fabrication and transportation [8]. The properties of packaging materials based on biopolymers such as mechanical, barrier and thermal properties are weak and should be improved. It has been reported that introducing nanoparticles into the biopolymer matrix reinforces its characteristics. According to the kind of nanoparticles, the aspect ratio is very different. The high improvement of properties in polymer nanocomposites depends on filler dispersion in polymer matrix that is affected by interactions between polymer and filler. Interactions are also related to the contact surface. Therefore, the aspect ratio impacts strongly on the dispersion quality [9]. Montmorillonite is one of the most widely used type of nanoparticles to produce nanocomposites which has high aspect ratio and some interesting properties such as naturally abundant, nontoxic, inexpensive and chemically and thermally stable [10]. Pierfrancesco et al. [11] have achieved to cellulose/clay composite films with superior thermal and mechanical properties.

Since the cell structure is one of the most important factors affecting foam properties, the major goal of this work was to investigate the effect of SM-MMT on cell sizes and morphological characteristics of composite foams, which subsequently influences mechanical, thermal and barrier properties. Surface-modified MMT was used as reinforcing material to improve the properties of cellulose matrix and to reduce the bubble sizes. According to our knowledge, there is no publication on the effect of SM-MMT on cellulose foam properties. In this work, we reported the influence of SM-MMT on cellulose foam properties to introduce cellulose composite foam as a possible alternative to EPS foam for food packaging application.

2. Materials and methods

2.1. Materials

Avicel PH-101 microcrystalline cellulose (MCC) was purchased from Sigma–Aldrich and was used as a raw material. The crystallinity index of MCC was 60%, based on the XRD patterns. Surface-modified MMT containing 25–30 wt% methyl dihydroxyethyl hydrogenated tallow ammonium was purchased from Sigma–Aldrich and was used as the MMT sample. Tween-80 surfactant was purchased from Sigma–Aldrich. All other chemicals with analytical grade were purchased from commercial sources without any pretreatment.

2.2. Sample preparation

Cellulose solution was prepared according to the procedure reported by Sescousse et al. [12]. Briefly, an aqueous solution of 8% wt NaOH was prepared. A desired amount of SM-MMT was dispersed in this solution, and then was stirred for 2 h at 25 °C. The SM-MMT dispersion was further homogenized at 15,000 rpm for 5 min using Ultra-turrax T25 model homogenizer (IKA, Germany) [13]. The suspension was then cooled down to −12 °C. Simultaneously, a certain amount of MCC was swollen in distilled water and was cooled to 5 °C. Afterwards, the swollen MCC was added to SM-MMT dispersion at −12 °C and then was mixed immediately at 3000 rpm for 10 min at ambient temperature to dissolve cellulose. Then, various concentrations of surfactant Tween-80 (0.1, 0.6, and 1.1%) were added as foaming agents to increase cellulose foam porosity and also to stabilize SM-MMT dispersion. The mixture was stirred at stirring rate of 4000 rpm for 5 min at ambient temperature. The solutions were then poured into Petri dishes in a 2 mm thick layer and also into cylindrical molds by the height of 5 cm. The gelation of cellulose solution was performed immediately at 60 °C for 1 h to stabilize the cells. In the next step, the coagulation was performed by immersing gels in water bath at 25 °C, and gels were then washed in water regenerating bath until all solvent were washed out (control of pH). Subsequently, the foams were soaked into the glycerin solution (8.0 wt%) as a plasticizer. Finally, after freezing gels at −80 °C, a freeze-dryer (Lyophilisateur ALPHA 1-2/LD, France) was used to dry the samples at −52 °C for 24 h before further characterization [12,14,15]. The weight ratios of cellulose and SM-MMT in the composite foams under investigation were 100:0, 97.5:2.5, 95:5 and 90:10, which are noted as CN0, CN2.5, CN5, and CN10, respectively. The foams were conditioned at 20 °C and 50% relative humidity for 48 h before conducting the experiments.

2.3. Field-emission scanning electron microscopy (FE-SEM)

Scanning electron microscopy (SEM) images were taken using a HITACHI S4160 (cold field emission-scanning electron microscopy)