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Evaluation of zein/halloysite nano-containers as reservoirs of active molecules for packaging applications: Preparation and analysis of physical properties

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A B S T R A C T

This work aims to evaluate the possibility to introduce natural nano-containers for active molecules, such as halloysite nanotubes (HNTs), into an environmentally friendly material: natural zein. Composites were prepared in a wide range of HNTs composition (i.e. 1–10 wt%) and structural and physical properties were analyzed. HNTs were also filled with an active molecule commonly used as preservative in food packaging, such as potassium sorbate (KS), and the diffusion of such molecule was evaluated. The zein thermal degradation resulted significantly improved with the filler content. Mechanical properties showed a reinforcement of zein matrix. HNTs were filled with potassium sorbate and dispersed into the zein matrix.

1. Introduction

In the last few years environmental concerns on the use of *undegradable* plastics for packaging foodstuff, like any other short-term storage packaging material, led to intensified research on the development of biodegradable packaging materials. A big effort to extend the shelf life and enhance food quality, while reducing packaging waste, has encouraged the exploration of new bio-based packaging materials, such as edible and biodegradable films from renewable resources (Zeng et al., 2011; Liang et al., 2015; Soltani and Madadlou, 2016). Edible biodegradable materials, by acting as barriers to control the transfer of gases, moisture, lipids, and flavor components, can increase the shelf-life of food products preventing the quality deterioration (Sinha Ray and Bousmina, 2005; Singh et al., 2012). Unfortunately, the use of biodegradable films for food packaging has been strongly limited because of the poor physical properties shown by natural polymers. For this reason natural polymers were frequently blended with other synthetic polymers or, less frequently, chemically modified with the aim of extending their applications in more special or severe circumstances. Nanotechnology is a truly promising strategy for improving physical properties of natural polymers. The introduction of nanofillers into biopolymers has been shown to be a good strategy to overcome some critical issues, such as a poor barrier to water vapor and low mechanical properties (Panchapakesan et al., 2012; Gorrasi and Sorrentino, 2015). The development of polymer nanocomposites allows to expand the use of edible and biodegradable films (Pomes, 1971; Joshi et al., 2012). In addition, inorganic fillers may be used to introduce multiple functionalities, like act as reservoirs for the controlled release of active molecules (Joshi et al., 2012; Lvov and Abdullayev, 2013). In the last few years zein has been examined as a possible raw material for polymer application (Arcudi et al., 2014). It is a highly important industrial and environmentally friendly corn storage protein with extensive food applications. It is clear, odorless, tasteless, edible, and hence used in processed foods and pharmaceuticals. It contains high proportions of non-polar amino acid residues (such as leucine, alanine, and proline) which render it water insoluble (Pomes, 1971). Since zein is completely safe to ingest, it is used for perfect coating of foods and pharmaceutical ingredients, and hence it interacts with other proteins upon its way to ingestion. In the food and confectionary industries, it is used for coating bakery products, candies and chocolates as well as for packaging of frozen and ready-to-eat foods. Zein is a predominantly hydrophobic protein and possesses a highly robust structure which is made up of nine homologous repeat units arranged in an anti-parallel distorted cylindrical form and stabilized by the hydrogen bonds (Argos et al., 1982; Deo et al., 2003; Liang et al., 2015). Very

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recently a new class of inorganic fillers, halloysite nanotubes (HNTs), has attracted considerable interest. HNTs are green materials, not hazardous for the environment, cheap, and available in thousands of tons from natural deposits They belong to the alumosilicate clays with a length of about 1000 nm, external diameter of about 50–80 nm, an internal one (lumen) of 10–15 nm. Chemically, halloysite is two-layered aluminosilicate clay, $Al_2Si_2O_5(OH)_4 \times nH_2O$, which exhibits a predominant form of hollow tubes, and it is similar to kaolin, but its alumosilicate sheets are rolled into tubes (Lvov and Abdullayev, 2013; Yuan et al., 2015). The HNT external surface is composed of Si–O–Si groups, whereas the internal surface consists of a gibbsite-like array of Al–OH groups (Lvov and Abdullayev, 2013). HNTs can be easily dispersed in polymers without any need for exfoliation, as required for a good dispersion of platy clays, due to the tubular shape and less abundant –OH groups on the surface. Polymeric materials can be filled with these tiny tubular containers (Lvov et al., 2008; Arcudi et al., 2014; Gorrasi et al., 2014a; Gorrasi et al., 2014b; Liu et al., 2014) that release specific active molecules (antimicrobial, drugs, flame retardant, self-healing, anticorrosion, etc …) in specific environments (Veerabadran et al., 2007; Lvov and Price, 2008; Abdullayev et al., 2008; Abdullayev et al., 2009). The combination of zein and halloysite nanotubes may allow to generate novel materials with unique properties, combining the advantages of materials from renewable resources, and nanoparticles, environmentally friendly. Both components being available at low cost. The objective of this work was to design and prepare and characterize novel zein/HNTs nanocomposites that, to our best knowledge, have been never produced. Main part of the paper is related to the demonstration of the possibility to disperse HNTs nano-containers into a zein matrix up to 10 wt% of filler. The analysis of structural organization and physical properties was conducted and correlated to the filler amount. HNTs were also loaded with potassium sorbate (KS), as preservative antimicrobial molecule used in food packaging, and dispersed into zein. Preliminary studies of in-vitro release of KS were then carried out.

2. Experimental

2.1. Materials

Halloysite nanoclay (CAS 1332-58-7), corn zein powder (CAS 9010-66-6, Mw = 25,000 Da), poly(ethylene glycol), PEG (CAS 25322-68-3, Mw = 400 Da) used as plasticizer, 1,4 dioxane (CAS 123-91-1) and potassium sorbate (CAS- 24634-61-5) were purchased from Sigma-Aldrich (Italy). All the materials were used as received from the supplier.

2.2. Composites preparation

Halloysite and zein powders were mixed in 1,4 dioxane solution, using PEG as plasticizer. 1 g of milled powder of pure zein and composites at different HNTs loading were dissolved in 20 ml of 1,4 dioxane and 3 ml of PEG. The temperature was fixed to 70 °C for 20 min. After filtration the plasticized samples were kept in vacuum oven at 40 °C for 48 h. Halloysite amount in the composites was 1; 3; 5; 10 wt%. In the following, composites will be coded as Zein_Y_HNT, where Y is the amount of the halloysite into the composites.

2.3. Film preparation

Plasticized zein and its composites with HNTs were molded in a Carver laboratory press between two teflon sheets, at 80 °C, followed by cooling at ambient temperature. Films about 300 ± 0.5 μm thick were obtained. Samples were stored at 50% of RH in a desiccator for one week, and analyzed.

2.4. Incorporation of KS into HNTs

Empty lumen of halloysite nanotubes is a good nano-container for loading active molecules allowing smart functions of plastic composites filled with HNTs. We loaded HNTs with a common used preservative molecule, potassium sorbate, following a previously reported procedure (Joshi et al., 2012; Gorrasi et al., 2016). HNTs (2 g) were mixed, as dry powder, to a saturated (highly concentrated) solution (25 ml) of potassium sorbate in water. Once halloysite was added to the solution, the suspension was stirred for 1 h at ambient temperature, and then transferred to a jar evacuated with vacuum pump. Suspension was kept under vacuum for 15 min and allowed to atmospheric pressure. Slight fizzling of the solution under vacuum indicated that air being removed from the tubes. Once the vacuum was broken, solution enters into lumen and loaded compound condensates within the tube. This was repeated 3 times to increase the loading efficiency. After loading, tubes were washed once with distilled water to remove loosely attached substance from the external walls, filtered, and dried in vacuum oven at 40 °C for 24 h.

The amount of the benzoate molecules in the nano-hybrid was determined by the thermogravimetric analysis in according to the equation (1)

$$X = \frac{R_{mix} - R_H}{R_s - R_H} \times 100 \quad (1)$$

where X is the loaded potassium sorbate, R_{mix} is the weight loss percentage of the mixture, R_H and R_s are the weight loss percentages of the halloysite and sorbate component, respectively. Obviously, with this equation it is assumed that the total weight loss of the single component is not affected by the other components present in mixture. The KS amount detected with this method was ≅ 25%.

2.4.1. Active composites preparation and release analysis

In order to evaluate the controlled release of KS, either from the HNTs-KS hybrid, or as free molecule into zein, preliminary tests were conducted on two composites: i) film at 10 wt% of HNTs-KS (i.e. 2.5 wt% of active molecule) and ii) film at 2.5 wt% of KS directly mixed into the zein matrix. Both were prepared by mixing the zein with HNTs-KS, and zein with free KS, following the procedure described in the Sections 2.2 and 2.3. It is worth noticing that the use of 1,4 dioxane for the preparation of all the composites films was due to the fact that such solvent is able to dissolve the zein, but not the KS. Films (approximately 100 mg), having thickness of 300 ± 0.5 μm were immersed into beaker containing 25 ml of distilled water. The beaker was placed in a controlled temperature room at 25 ± 0.5 °C. The solution was well-stirred with a magnetic stirring bar to minimize boundary layer formation around the film. Potassium sorbate concentrations, at different contact times, were measured at 254 nm. To model of KS diffusion mechanism, it was assumed that the process occurred in a thin sheet of film, with an initially homogeneous KS concentration distribution. Solvent absorption and solute diffusion occurred simultaneously. The thickness was considered very small in comparison with the width of film, so that the diffusivity was considered unidirectional and perpendicular to the surface of the sheet. The KS concentration inside the film was a function of x, the distance from the surface. The following one-dimensional linear partial differential equation is derived from Fick's second law of diffusion (Crank, 1975)