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New nanocomposite design from zeolite and poly(lactic acid)

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ABSTRACT

We studied the effect of zeolites ($NaAlO_2$, SiO_2) and their dispersion in biopolymer poly(lactic acid) (PLA), with a particular interest in the improvement of antibacterial properties, permeability to water vapor, oxygen permeability and mechanical properties. Using two zeolite particles of a different size: micrometric (zeolites) and nanometric (Nanozeolites) sizes, we prepared these composites using the melt mixing process/technique by means of a Brabender mixer. We started by characterizing the morphology of these composite materials using a scanning electronic microscope (SEM) and NanoSIMS microscopies. A good dispersion of nanozeolites is ensured only when a stabilizer (polyethylene glycol (PEG) with $M = 1000$ g/mol) is used. Then a comparative study on the physical (gas barrier properties) and mechanical properties (high strain mechanical properties) of these two families of composites has been conducted. It was shown that these two families present almost similar barrier and anti-bacterial properties. The strong point of the nanocomposites is their good mechanical properties (high young modulus and high tensile strength). These mechanical and physical properties of the nanocomposites are ensured only when a PEG of $M = 1000$ g/mol is used as stabilizer.

1. Introduction

The plastics industry is one of the most important chemical industrial activities in terms of quantity and diversity of business applications. Plastics are used in multiple areas; in the automobile industry, in toys for children, but more particularly in the field of packaging.

Petrochemical plastics used primarily for their lightness of weight, their low cost and ease of implementation have a major and significant drawback nowadays: their environmental impact. Today, plastics from fossil resources have a life of about 400 years, a period of 1 year use to the maximum, for a classic packaging. On the other hand the fossil resource (oil), is not renewable, and has begun to run out, oil resources could be completely exhausted within 40 years (Babusiaux and Bauquis, 2015).

In recent years, many research projects have emerged to develop polymers from renewable resources in order to replace synthetic plastics. These 'biopolymers' are of interest because they are renewable and sometimes biodegradable.

In the field of everyday life, the packaging sector is an important niche for the biodegradable polymer market. They provide a solution to the problems of waste, however, they require the setup of a suitable polymer for this type of product waste management sector. Thus the organization of a composting sector is essential to ensure an optimal recovery of this biodegradable packaging waste (David, 2003; Klauss and Bidlingmaier, 2003).

Active packaging is one of the innovative food packaging concepts. It has been introduced as a response to the continuous changes in current consumer demands and market trends (Vermeiren et al., 1999a). Properties and potential applications of edible films and coatings have been extensively reviewed (Bravin et al., 2006; Jagannath et al., 2006; Min et al., 2005; Serrano et al., 2006). Many studies have demonstrated that antimicrobial agents when incorporated into film packaging could be effective for reducing the levels of foodborne organisms (Cutter, 2006; Ojagh et al., 2010; Quintavalla and Vincini, 2002).Active packaging is currently one of the most dynamic technologies used to preserve the quality of food via the release of active agents from the packaging film. Release of the active agents can be controlled over an extended period of time to maintain or extend the quality and shelf-life of products, without the need for direct addition of any substances to the foodstuffs (Lee, 2010a).

Some studies have evaluated how antioxidants (such as butylated hydroxytoluene (BHT), butylhydroxyanisole (BHA),

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alpha-tocopherol and natural extracts) incorporated in packaging film migrate out of the film and delay lipid oxidation in the stored foodstuff (Barbosa-Pereira et al., 2013; Moore et al., 2000). The incorporation of rosemary extract in active packaging film has been described by Nerín et al. (2006), with promising results in relation to extending the shelf life of beef.

Another concept in active packaging is the addition of bioactive substances by a coating process. The development of coatings with an antimicrobial capacity has been studied in relation to the preservation of meat products (Bonilla et al., 2012; Kerry et al., 2006; Lee, 2010b; Zhou et al., 2010). Antioxidant additives can also be incorporated by coating them onto food packaging materials to control spoilage by oxidation and to preserve food quality (Vermeiren et al., 1999b; Lee et al., 2003).

In this article, we concentrate exclusively on food packaging (the bio-packaging). In agri-food most foods are packed with plastic because the plastic is a stable, light, material having good properties such as impermeability to gases which enables a good conservation of the food. The final purpose of packaging is to maximally prolong the life of food.

Today packaging represents approximately 30% of the weight of our trash. The majority of this packaging is plastic containers, this represents millions of tons of plastic waste per year. In addition, almost all of this packaging is synthetic polymers and most of them have very long life before being completely exhausted. This raises the concept of waste. Recycling is very small (only 30% of household waste is recycled). A solution would be to replace non-degradable plastics from renewable resources and biodegradable polymers. This would on the one hand, reduce the carbon footprint by fixing carbon (dioxide CO_2) during photosynthesis (check with a life cycle assessment (ISO 14044)). On the other hand, the use of these plastics offers a new alternative for the end of the life of our materials: composting.

In addition to their biodegradability, biopolymers have other interesting properties for applications in the field of packaging. Apart from their primary function of protecting products, biopolymers offer packaging with other functions owing to their intrinsic properties, for example, their permeability to water vapor useful for packing fresh products such as fruit and vegetables (Petersen et al., 1999).

Three types of biopolymers, poly(lactic acid) (PLA), starch-based polymers and cellulose-based polymers, are experiencing an industrial development in the manufacture of packaging. These biopolymers can cover a wide range of applications in the packaging sector.

Biopolymers (from biomass) are made up of three families (Gabor and Tita, 2012): biopolymers fauna or flora, such as cellulose, starch..., biopolymers produced by chemical polymerization such as the PLA and biopolymers produced by microorganisms, such as polyhydroxybutyrate (PHB) or the poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV).

Poly(lactic acid) (PLA) is a thermoplastic aliphatic polyester, compostable in the sense of the EN13432 European standard. It is synthesized from sugar extracted from corn or sugar cane. Bacterial fermentation of this sugar leads to the production of lactic acid, dimerized in cyclic lactide, ring-opening polymerization synthesizes the PLA. The PLA is a semi-crystalline polymer, its mechanical and optical properties (transparency) are similar to those of polyethylene terephthalate (PET).

Zeolites are highly crystalline microporous alumino-silicates containing alkaline metal ions and water molecules and are explored greatly in drug delivery (Shams and Ahi, 2013). They are biocompatible and have an ion exchange capacity (Malekian et al., 2011). They are used for encapsulating anticancer drugs (Vilaça et al., 2013), antibacterial agents (Fox et al., 2010), anthelmintic drugs (Dyer et al., 2000) and anti-inflammatory drugs (Climent et al., 2005).

The negatively charged zeolite framework is balanced by divalent copper ions (Ninan et al., 2013). These copper ions impart antibacterial properties by causing in vitro bacterial inactivation after binding to the microbial DNA, thereby preventing bacterial replication (Kim et al., 2012). They are vital angio-genic factors and can promote wound healing (Wu et al., 2013).

In the literature, Gregorova et al. (2012) studied the relationships between the viscoelastic damping behavior of filled PLA composites and the three mineral fillers Mica, Zeolite, and Vansil distribution in the PLA matrix. Yuzay et al. (2010a) also reported the preparation of PLA (94% L-lactide)/synthetic zeolite (Type 4A, Si/Al 1:1, pore size of 3.8–4 Å) composites using a melt compounding process and the effects of zeolites loading (0–5 wt%) on PLA physical-mechanical properties. Yuzay et al. (2010b) tested PLA composites containing 5 wt% synthetic (type 4A) and natural (chabazite) zeolites that were prepared using extrusion/injection molding. Morphological, structural, and thermal properties of composites have been investigated. Marçal et al. (2015) developed PLA zeolite-composites which were produced by melt-blending using three different commercially available zeolites (4A, 13X and Ag-exchanged). Following the evaluation of molecular, rheological and thermal parameters, the zeolites 13X and Ag-exchanged are selected between most efficient fillers to produce PLA-zeolite composites. Fernández et al. (2010) investigated silver ion migration and antimicrobial activity of PLA/silver zeolite composite films. In conclusion, no work has been published yet on PLA-zeolite bioactivity and permeability.

In this paper, our aim was to develop biodegradable plastics for the active packaging of fresh produce. The purpose of this article is to design new composite materials based on poly(lactic acid) (PLA) with zeolites that can be innovative packaging solutions to increase the shelf life of fresh products and explore the morphological, structural, biological,mechanical properties and permeability of the resulting nanocomposite materials.

2. Materials and methods

2.1. Materials

The polymer used in the study is the poly(lactic acid) PLA L9000® marketed by Biomer (Biomer®, Krailling, Germany) and has a density of 1.25 $g\,cm^{-3}$.

Zeolites ($NaAlO_2$, SiO_2) (Zs) and nanozeolites (NZs) were obtained from our industrial IRMA (Lorient-France). These zeolites and nanozeolites were activated by copper metal. Nanozeolites are supplied as dispersion in water.

PEG (polyethylene glycol) polymers of a different molecular weight (400; 1000; 4000; 10,000 in $g\,mol^{-1}$) were supplied by Sigma–Aldrich. These polymers were used as stabilizer for the nanozeolites particles.

All chemicals were used without further purification.

2.2. Preparation of stabilized nanozeolites

An amount of PEG is dissolved in a minimum of water. The nanozeolite dispersion is then added drop by drop under magnetic stirring for two hours to ensure effective encapsulation and dispersion of the NZs particles. The weight ratio NZs/PEG used is 50 wt%/50 wt% regardless of the PEG molecular weight. The mixture was then dried at 40 °C overnight to obtain a powder of NZs encapsulated by PEG.

2.3. Preparation of composites and nanocomposites

The materials processing and working parameters (temperature, screw speed, thickness of film...) influence their final