Review

Nanocomposites for food packaging applications

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ABSTRACT

Most materials currently used for food packaging are non-degradable, generating environmental problems. Several biopolymers have been exploited to develop materials for eco-friendly food packaging. However, the use of biopolymers has been limited because of their usually poor mechanical and barrier properties, which may be improved by adding reinforcing compounds (fillers), forming composites. Most reinforced materials present poor matrix–filler interactions, which tend to improve with decreasing filler dimensions. The use of fillers with at least one nanoscale dimension (nanoparticles) produces nanocomposites. Nanoparticles have proportionally larger surface area than their microscale counterparts, which favors the filler–matrix interactions and the performance of the resulting material. Besides nanoreinforcements, nanoparticles can have other functions when added to a polymer, such as antimicrobial activity, enzyme immobilization, biosensing, etc. The main kinds of nanoparticles which have been studied for use in food packaging systems are overviewed, as well as their effects and applications.

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1. Introduction

"Nano-" denotes nanometer (10^{-9} m). The concept of nanotechnology was introduced by Richard Feynman in 1959 at a meeting of the American Physical Society (Khademhosseini & Langer, 2006). Since then, nanotechnology has developed into a multidisciplinary field of applied science and technology. Nanotechnology is the ability to work on a scale of about 1–100 nm in order to understand, create, characterize and use material structures, devices and systems with new properties derived from their nanostructures (Roco, 2003). Because of their size, nanoparticles have proportionally larger surface area and consequently more surface atoms than their microscale counterpart. In the nanoscale range, materials may present different electronic properties, which in turn affects its optical, catalytic and other reactive properties (Boccuni, Rondinone, Petyx, & Iavicoli, 2008; Kahn, 2006).

All biological and man-made systems have the first level of organization at the nanoscale. By using nanotechnology techniques, it is possible to assemble molecules into objects, along several length scales, and to disassemble objects into molecules, as nature already does (Roco, 2003).

Two building strategies are currently used in nanotechnology: a "top-down" approach and the "bottom-up" approach. The commercial scale production of nanomaterials currently involves basically the "top-down" approach, in which nanometric structures are obtained by size reduction of bulk materials, by using milling, nanolithography, or precision engineering. Size usually relates to functionality of food materials, smaller sizes meaning a bigger surface area, desirable for several purposes. The newer "bottom-up" approach, on the other hand, allows nanostructures to be built from individual atoms or molecules capable of self-assembling (Föster & Konrad, 2003; Moraru et al., 2003). Self-assembly relies on balancing attraction and repulsion forces between a pair of molecules as building blocks to form more functional supramolecular structures (Sanguansri & Augustin, 2006).

Nowadays, most materials used for food packaging are practically undegradable, representing a serious global environmental problem. New bio-based materials have been exploited to develop edible and biodegradable films as a big effort to extend shelf life and improve quality of food while reducing packaging waste (Tharanathan, 2003). However, the use of edible and biodegradable polymers has been limited because of problems related to performance (such as brittleness, poor gas and moisture barrier), processing (such as low heat distortion temperature), and cost. Starch, as an example, has received considerable attention as a biodegradable thermoplastic polymer. However, it has a poor performance by itself because of its water sensitivity and limited mechanical properties (Vaidya & Bhattacharya, 1994) with high brittleness, which is related to the anarchical growth of amylose crystals with time (Dufresne & Vignon, 1998). The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the cost-price-efficiency (Sorrentino, Gorrasi, & Vittoria, 2007).

Several composites have been developed by adding reinforcing compounds to polymers to enhance their thermal, mechanical and barrier properties. Most of these reinforced materials present poor interactions at the interface of both components. Macroscopic reinforcing components usually contain defects, which become less important as the particles of the reinforcing component are smaller (Ludueña, Alvarez, & Vasquez, 2007).

Polymer composites are mixtures of polymers with inorganic or organic fillers with certain geometries (fibers, flakes, spheres, particulates). The use of fillers which have at least one dimension in the nanometric range (nanoparticles) produces polymer nanocomposites (Alexandre & Dubois, 2000). Three types of fillers can be distinguished, depending on how many dimensions are in the nanometric range. Isodimensional nanoparticles, such as spherical silica nanoparticles or semiconductor nanoclusters, have three nanometric dimensions. Nanotubes or whiskers are elongated structures in which two dimensions are in the nanometer scale and the third is larger. When only one dimension is in the nanometer range, the composites are known as polymer-layered crystal nanocomposites, almost exclusively obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layered host crystals (Alexandre & Dubois, 2000).

A uniform dispersion of nanoparticles leads to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior and the consequent thermal and mechanical properties of the material. Fillers with a high ratio of the largest to the smallest dimension (i.e., aspect ratio) are particularly interesting because of their high specific surface area, providing better reinforcing effects (Azizi Samir, Alloin, & Dufresne, 2005; Dalmas, Cavaillé, Gauthier, Chazeau, & Dendievel, 2007; Dubief, Samain, & Dufresne, 1999). In addition to the effects of the nanoreinforcements themselves, an interphase region of altered mobility surrounding each nanoparticle is induced by well dispersed nanoparticles, resulting in a percolating interphase network in the composite and playing an important role in improving the nanocomposite properties (Qiao & Brinson, 2009). According to Jordan, Jacob, Tannenbaum, Sharaf, and Jasiuk (2005), for a constant filler content, a reduction in particle size increases the number of filler particles, bringing them closer to one another; thus, the interface layers from adjacent particles overlap, altering the bulk properties significantly.

Besides reinforcing nanoparticles, whose main role is to improve mechanical and barrier properties of the packaging materials, there are several types of nanostructures responsible for other functions, sometimes providing active or "smart" properties to the packaging system such as antimicrobial activity, enzyme immobilization, biosensing, etc. The most studied nanoparticles will be presented according to their primary functions/applications in food packaging systems. Some particles can have multiple applications, and sometimes the applications can overlap, such as some immobilized enzymes which can act as antimicrobial components, oxygen scavengers and/or biosensors.

2. Nanoreinforcements

2.1. Clays and silicates

2.1.1. Structure, properties and types of composites

Although several nanoparticles have been recognized as possible additives to enhance polymer performance, the packaging
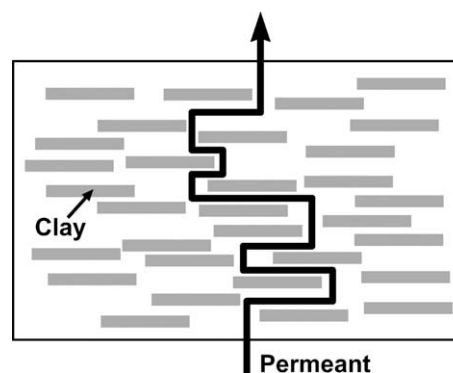

Fig. 1. Tortuous path of a permeant in a clay nanocomposite. (Adapted from Adame & Beall, 2009).