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Nano-clays from natural and modified montmorillonite with and without added blueberry extract for active and intelligent food nanopackaging materials

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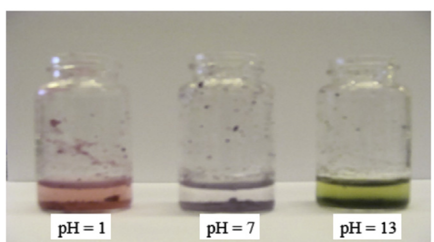
HIGHLIGHTS

- Food nano-packaging were obtained from natural and modified montmorillonite (Mnt).
- XRD, TGA and FTIR results suggests the blueberry extract nano-packaging.
- Intelligent nanocomposites were obtained.
- Greater interlayer spacing of the nano-Mnt allows greater nano-packaging.

GRAPHICAL ABSTRACT

Active and intelligent food nanopackaging materials



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ABSTRACT

The aim of this study was to evaluate the potential of nano-clays as active and intelligent (A&I) food nanopackaging materials. Nanopackaging is a structured system that allows the storage of certain compounds in a stable form. Nano-clays were prepared from natural and modified montmorillonite (Mnt) with and without added blueberry extract, and characterized in terms of their: X-ray diffraction (XRD) patterns, thermogravimetric (TGA) properties, microstructure, moisture content, water activity (a_w), infrared spectra (FTIR), Raman spectra, color parameters, response to pH changes, and antioxidant and antimicrobial activity. Mnt prepared with added blueberry extract showed antioxidant activity and intelligent behavior under different pH conditions. Modifying the Mnt increased the interlayer spacing, thus allowing more blueberry extract to be incorporated within the system. In conclusion, natural and modified Mnt are eco-friendly resources with potential applications for nano-packaging. The addition of blueberry extract imparted intelligent properties to the nano-clays as regards their responses to changes in pH.

1. Introduction

Montmorillonite (Mnt), a member of the smectite group, is one of the clay minerals most commonly utilized as nanocomposites

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and accounts for nearly 70% of the clay market volume [1,2]. Clay is a naturally abundant, toxin-free mineral used in foods, medicines, cosmetics, and healthcare products [3] as well as being environmentally friendly and inexpensive.

Clays and clay minerals are technologically important materials mainly composed of hydrated aluminosilicate with neutral or negative charged layers [4]. Layered silicates typically have a stacked arrangement of silicate layers (platelets) held apart principally by electrostatic forces. Platelets are only 1 nm thick but have a huge surface area (over 750 m^2/g) and aspect ratios ranging from 100 to 500 [1,5,6]. Each layer is characterized by a 2:1 structure with a central octahedral sheet of alumina attached to two external tetrahedral sheets of silica [7–9]. The net negative charge of the layers, generated due to isomorphic substitutions of Al^{+3} with Fe^{+2} or Mg^{+2} in the octahedral sites and of Si^{+4} with Al^{+3} in the tetrahedral sites, is compensated by the presence of cations, mainly Na^{+} and Ca^{+2}, situated in the interlayer space [10]. The presence of inorganic cations between the planar surfaces of the Mnt layers is what gives these clays their hydrophilic character.

Clays have been modified for different purposes by replacing these inorganic cations with organic ones through cation exchange reactions. Organic cations employed in this way are mostly surfactants, such as ammonium salts, which increase the interlayer spacing and surface hydrophobicity [5,11]. Modified clays prepared by cation exchange with long-chain quaternary alkylammonium or phosphonium salts have been widely studied and the resulting organoclays used in the preparation of nanocomposites, mainly for industrial applications [12,13]. In recent years, however, the use of these clays has been extended to other fields including drug delivery systems [14–17], the production of excipient and active substances in pharmaceutical products [18,19] and antithrombogenic materials [20], and the immobilization of hosts for biological species such as enzymes, amino acids, proteins, nucleic acids, and phospholipids [12,21–26]. Nonetheless, organoclays have been little studied as food nano-packaging materials compared to other nano-encapsulation systems [27].

According to Bracone et al. [27], the term nano-packaging refers to nanostructured materials that package certain compounds of interest. In this context, clay minerals have been developed and used especially in food and drug nanopackaging. These clay mineral-based systems, as mentioned above, allow the controlled release of drugs and prevent oxidative damage in foods, thus reducing food loss. Despite their importance, however, clay mineral systems have been poorly studied.

With this in mind, a nano-packaging system could be developed by incorporating blueberry extract in the silicate interlayer spaces of clay, i.e. between the silicate layers [6,28]. Blueberries contain anthocyanins which change color under different pH due to a shift in their molecular structure from a quinoidal to a flavylium form [29]. The addition of blueberry extract could thus transform these clays into active and intelligent nanocomposites that respond to changes in pH.

These active and intelligent materials derived from eco-friendly resources could be used to produce food nano-packaging that provides consumers with information about the quality and safety of food products. Changes in the coloration of the packaging could be associated with the fraudulent modification of foods, non-compliance of the cold chain, or simply alert consumers to the freshness of the food [30,31]. In this regard, the FAO [32] has estimated that approximately a third of the food produced annually for human consumption is wasted. This represents a loss of about 1.3 billion tons of food, valued at over USD 750 billion, which could feed the more than 842 million of people that still suffer from chronic hunger globally [33]. The incorporation of blueberry extract could, furthermore, enable the production of bioactive compounds that have a favorable impact on the prevention of diseases such as cancer [34] and kidney infections [35].

The goal of this research was to develop nano-clays with potential uses for active and intelligent food nanopackaging. In order to achieve this the physical and chemical properties of two nano-clays derived from Mnt, one natural, and the other modified with a quaternary ammonium salt (dimethyl dehydrogenated tallow ammonium), were analyzed. Nanocomposites prepared from the clays plus blueberry extract were also investigated.

2. Experimental

2.1. Materials

The clays evaluated in this study were natural and modified montmorillonites (Mnt) supplied by Laviosa Chimica Mineraria S.p.A. (Livorno, Italy), and were used as received. According to the manufacturer's instructions, the modified Mnt is a nanoclay derived from a naturally occurring Mnt, purified and modified with a quaternary ammonium salt (dimethyl dehydrogenated tallow ammonium). This modification was selected based on the fact that it has been well known in the literature for years, and the resulting modified clay is nontoxic with no risk to human health [36–38]. The cation exchange capacity (CEC) of natural Mnt, measured by the methylene blue method, gave a CEC of 105 meq/100 g clay. Blueberry (*Vaccinium corymbosum*) extract was obtained according to the methodology proposed by Dai et al. [39] using ethanol as a solvent, since it maintains the properties of blueberries. According to Dai et al. [39] the chemical composition of blueberry extract is 100% anthocyanin. Ripe fruits were purchased from a local market in Mar del Plata, Buenos Aires, Argentina. The fruits were selected, discarding any diseased or stained specimens, before weighing out 170 g, crushing and filtering. The residue obtained, mainly the fruit skin, was then washed with 100 mL of ethanol (Aldrich: product code: 34923). Interestingly, this type of waste is normally produced by manufacturing processes during the preparation of filtered blueberry juices. The blueberry extract was prepared the same day the clays were developed, and maintained refrigerated at 5 °C in a dark container until further processing in order to avoid oxidative damages.

2.2. Formation of the nano-clays

The nano-clays were prepared by mixing 2 g of clay and 40 mL of blueberry extract. The mixture was then frozen at −20 °C for 48 h after which it was lyophilized at 100 mTorr and −50 °C for 72 h using a Gland type Vacuum Freeze Dryer, Columbia International, Model FD-1B-50 (Shaan Xi, China) in order to obtain a free flowing product. Lyophilization also preserves the active compounds of the blueberry extract and ensures a size of clay particle in the nanometer range. The resultant clays were conditioned in containers with a saturated solution of NaBr (a_w ~0.575 at 25 °C) for seven days prior to each test. During this period the containers were protected from light in a dark room to avoid photodegradation of the antioxidant compounds and pigments. Samples used to determine the water activity (a_w) of the clays were not conditioned. Four types of clay samples were prepared as follows: natural montmorillonite (NMnt), natural montmorillonite with added blueberry extract (NMnt+BE), modified montmorillonite (MMnt) and modified montmorillonite with added blueberry extract (MMnt+BE).

2.3. Characterization of clays

2.3.1. X-ray diffraction (XRD)

The X-ray diffraction patterns of the clay powders were