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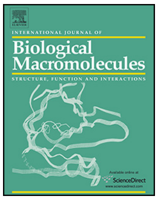

Physical and mechanical properties of hybrid montmorillonite/zinc oxide reinforced carboxymethyl cellulose nanocomposites

Younes Zahedi[a,*], Bahram Fathi-Achachlouei[a], Ali Reza Yousefi[b]

[a] Department of Food Science and Technology, Faculty of Agriculture and Natural resources, University of Mohaghegh Ardabili, Ardabil, Iran
[b] Department of Chemical Engineering, Faculty of Engineering, University of Bonab, Bonab, Iran

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ABSTRACT

In this research, a novel carboxymethyl cellulose (CMC)-based nanocomposite films containing sodium montmorillonite (MMT) (5% wt) and zinc oxide (ZnO) (1, 2, 3 and 4% wt) nanoparticles (NPs) were fabricated via casting method. The results revealed that addition of NPs decreased water vapor permeability of the films by about 53%, while moisture content, density and glass transition temperature increased. The nanomaterials enhanced resistance of the nanocomposites against tensile stress at the expense of elongation at break. Nano-ZnO was very effective than nanoclay in UV–light blocking (99% vs. 60%) associated with sacrificing the films transparency. Formation of hydrogen bonds between the hydroxyl groups of CMC and MMT was evidenced by FTIR spectroscopy. According to the XRD analysis, clay nanolayers formed an exfoliated structure in the nanocomposites, whereas ZnO NPs raised crystallinity. SEM micrographs showed well-dispersed MMT and ZnO NPs through the films surface. Antibacterial test showed that vulnerability of Gram-positive *S. aureus* toward ZnO NPs was more than that of Gram-negative *E. Coli*. In conclusion, simultaneous incorporation of MMT and ZnO NPs improved the functional characteristics of CMC film and extended the potential for food packaging applications.

1. Introduction

The increasing concern regarding environmental pollutions by oil-based packaging materials has created serious challenges in the past decades. Biopolymers have the advantage over synthetic polymers in that they are biocompatible, renewable, and can be easily degraded in natural environments during several weeks. They exhibit many potential applications particularly in packaging fields as edible films and food packaging. Biopolymers include carbohydrates and proteins derived from plant and animal origins, and also microbial products such as polyhydroxybutyrate and poly lactic acid [1–4].

Carboxymethyl cellulose (CMC) is an ether derivative of cellulose, having wide applications in the pharmaceutical, cosmetics and food industries. Also, CMC exhibits excellent film-making properties, providing efficient barriers to lipids, gases and aromatic compounds [2,5]. In the first try, Bifani et al. [6] succeeded to fabricate a stand-alone edible film from CMC. From that date onwards, many edible or biodegradable films have been prepared from CMC and/or combination of CMC with other carbohydrates, proteins, lipids and different functional ingredients. Although, the CMC-based films present high barrier and relatively good mechanical properties, but they are very susceptible to water vapor transmission. Hydrophobic substances reduce to some extent water vapor permeability (WVP) of the CMC films, most probably leading to opaque, brittle films with unacceptable organoleptic characteristics.

One of the most effective strategies to solve the deficiencies of the synthetic and natural packaging films is to incorporate nanoscale materials into the films matrix. The produced nanocomposites represent noteworthy improvement in mechanical, thermal and barrier properties in comparison with conventional composites and unmodified biopolymers [7–9]. Layered silicate clays have been received much attention for use as nanomaterial due to their more availability, low cost and biocompatibility. Montmorillonite (MMT) is the most well-known used layered silicate. It is a hydrophilic nanofiller with a high aspect ratio (about 100). In order to achieve the desired performance as well as increased interaction, the clay aggregates must be exfoliated in the polymeric matrix [10,11]. In the recent years, MMT was used to improve the mechanical

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* Corresponding author at: Department of Food Science and Technology, Faculty of Agriculture and Natural resources, University of Mohaghegh Ardabili, Ardabil, Iran.
E-mail addresses: Y_zahedi@uma.ac.ir, Younes.zahedi@gmail.com (Y. Zahedi), bahram1356@yahoo.com, b_fathi@uma.ac.ir (B. Fathi-Achachlouei), a_yousefi@bonabu.ac.ir (A.R. Yousefi).

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and barrier properties of the films made from many hydrophilic biopolymers such as starch, chitosan, CMC and gelatin. In one study, Shin et al. [10] reported that the incorporation of different types of nanoclay into the films prepared from apple peel powder and CMC led to a significant decrease in water vapor and oxygen permeability as well as a great increase in elongation at break, with a limited weakening of ultimate tensile strength (UTS). In other study, addition of MMT to CMC films decreased permeability to water vapor, oxygen and carbon dioxide, while increased UTS and elastic modulus of the CMC films [3]. Also, based on the findings of some researchers, increasing sodium montmorillonite clay content in the starch/CMC blend films resulted in increment of UTS, and decrement of WVP and strain to break [5,7,8].

Zinc oxide (ZnO) is an eco-friendly, non-toxic to human cells with noble properties such as optical transparency, chemical and photochemical stability, high thermal conductivity, photo-oxidizing against biological species and chemical [9,12–16]. It has been widely utilized in solar cells, semiconductor diodes, sensors, ceramics, UV light emitting device, varistors, catalysts, etc. Furthermore, a new application of ZnO has been identified with discovering its antimicrobial activities in 1995. Antimicrobial effect, UV-blocking property and capability to reinforce the nanocomposites have resulted in the growing application of ZnO as a multifunctional component of packaging films for food application [17–24]. In the recent years, several scientific studies have been conducted on development of composite films by combination of different biopolymers and nano-ZnO. For instance, Mohammadi-Nafchi et al. [20,21] employed nanorod-rich ZnO to improve the films properties made from gelatin and starch biopolymers. Furthermore, in some studies using nano-ZnO was proposed as a way for amending chitosan films and enhancing antimicrobial efficiency [17,19,25]. Some efforts have also been done to evaluate the performance of the edible films carrying ZnO in food packaging; Koushesh-Saba and Amini [26] extended the shelf life of ready-to-use pomegranate by controlling fungal and mesophilic bacteria growth using ZnO-loaded CMC coatings. In addition, the growth of yeasts and molds on wheat bread was noticeably retarded by ZnO NPs dispersed in CMC/chitosan/oleic acid films [27].

As above-mentioned, miscellaneous nanocomposites were prepared via addition of either MMT or ZnO NPs to many bio-based films. However, there are no published data about the simultaneous incorporation of MMT and ZnO nanomaterials into CMC film. Given the functional properties of each NPs, it would be expected that the incorporation of two or more types of nano-sized filler manifold improves the properties of films compared with the films having only one type of NPs [12,18,28,29]. Considering antimicrobial and UV shielding effects of ZnO, and with attention to the fact that montmorillonite could be beneficial only for mechanical reinforcement, the aims of this study were to fabricate ternary CMC-MMT-ZnO nanocomposites with promoted performance, and to evaluate their physical, mechanical and thermal properties.

2. Materials and methods

2.1. Materials

Anhydrous calcium chloride, potassium sulfate, glycerol and calcium nitrate tetrahydrate were purchased from Merck (Darmstadt, Germany), ZnO nanopowder (average size of <50 nm) and carboxymethyl cellulose sodium salt (CMC, 400–800 cP, 2% in H_2O (25 °C)) with an average molecular weight of 90 kDa from Sigma-Aldrich ChemieGmbh (Schnelldorf, Germany), and sodium montmorillonite (Cloisite® Na+) with a cation exchange capacity (CEC) of 92.6 mequiv/100 g clay from Nanocor Inc. (Arlington Heights, IL).

2.2. Film preparation

Most previous experiments have been indicated that the properties of nanocomposites containing 5% MMT were better than higher or lower concentrations; therefore, this value was kept fixed in all nanocomposites [5,7,8,28]. In the most literatures, the recommended ZnO concentration is placed in the range of 0–5% w/w of biopolymers. Additionally, pilot experiments proved that mechanical and optical properties of the nanocomposites were dramatically diminished at ZnO content of higher than 4% w/w of CMC. To prepare ZnO nanodispersion, ZnO NPs was dispersed in distilled water at different concentrations (1, 2, 3 and 4% w/w of CMC), stirred for 30 min in 1200 rpm, and then sonicated in an ultrasonic bath (Bandelin Sonorex Digitec Ultrasonic Bath, Germany) under 35 kHz frequency for 30 min. MMT solution (5% w/w of CMC) was prepared at the same manner.

Fabrication of CMC-based films was carried out by the casting method. First, amount of 1.5 g CMC was added to 100 mL distilled water (95 °C), mixed at 1200 rpm for 1 h. Then, the MMT and ZnO sonicated solutions were added drop wise into the CMC film solution, respectively, mixed for a further 30 min at 1200 rpm and 95 °C. Next, glycerol (50% w/w of CMC) was incorporated as the plasticizer of the film, stirred for 15 min without heating. Finally, the solutions were then cooled at room temperature, and 27 g of the filmogenic solutions were cast onto a polystyrene petri-dish. The films were dried at 50 °C for 30 h in an oven. Dried films were peeled and stored at laboratory conditions in polyethylene bags.

2.3. Film conditioning and thickness measurements

All of the films were equilibrated at 23 ± 1 °C and 50 ± 2% RH, inside a chamber containing saturated solution of calcium nitrate tetrahydrate for 48 h before WVP, mechanical properties and moisture content tests. Film thickness was measured with an electronic micrometer (QLR digit-IP54, China). Measurements were taken at the center of the film and at four positions around the perimeter for the WVP and at eight positions along the rectangular strips for the mechanical properties. The mean measurements were used to calculate the properties of the films.

2.4. Water vapor permeability (WVP)

The WVP was measured gravimetrically according to the ASTM E 96-00 method [30] at 22 ± 1 °C. The circular glass cups containing 6 g anhydrous calcium chloride (0% RH) were sealed by films without pinholes or defects (1.76 cm^2 film area) and then placed in a desiccator containing a saturated K_2SO_4 solution (97% RH). The permeability cups with the films were weighted at intervals of 2 h during the first 12 h and finally after 24, 48 and 72 h. When the relationship between the weight loss and time was linear, the slope of the plots was calculated by linear regression. Regression coefficients were greater than 0.99. The WVP was calculated using Eq. (1) as follows:

$$\mathrm{WVP} = \frac{\mathrm{Slope.x}}{\mathrm{A.S}\,(\mathrm{R}_1 - \mathrm{R}_2)} \tag{1}$$

where A is the area of the exposed film surface (m^2), S is the saturation vapor pressure at the test temperature (kPa), R_1 is the relative humidity inside the desiccator, R_2 is the relative humidity inside the glass cups, and x is the average film thickness (mm).

2.5. Moisture uptake

Moisture uptake of the films was measured by method of Angles and Dufresne [31] with minor modifications. The square cut of film

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