



# Preparation and characterization of active emulsified films based on chitosan-carboxymethyl cellulose containing zinc oxide nano particles



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## ABSTRACT

Active nanocomposites based on carboxymethyl cellulose-chitosan-oleic acid (CMC-CH-OL) incorporated with different concentrations (0.5–2 wt.%) of zinc oxide nanoparticles (ZnO NPs) were produced by casting method. The effects of ZnO NPs on the morphological, mechanical, thermal, physical and antifungal properties of the films were studied. New interaction between ZnO NPs and polymer matrix were confirmed by Fourier Transform infrared. After addition of ZnO NPs, tensile strength, lightness ( $L^*$ ) and thermal stability decreased however, elongation at break, contact angle,  $a^*$  (greenness) and  $b^*$  (yellowness) of the nanocomposite films increased in comparison to the films without nano-filler. UV transmittance at 280 nm decreased from 17.3% to 0.2, 0.1 and 0.1 for the nanocomposite films containing 0.5, 1 and 2 wt.% ZnO NPs, respectively, suggesting higher UV blocking properties. Disc diffusion test showed considerable antifungal properties of the active nanocomposite films against *Aspergillus niger*, especially in CMC-CH-OL-ZnO 2 wt.% by more than 40% fungal growth inhibition.

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## 1. Introduction

Microbial contamination of food is a serious problem which causes health problems for consumers and decreases food shelf life [1]. Mostly, synthetic preservatives are added into the food for controlling microbial growth. However, due to probable problems of synthetic preservatives to human health, consumers are looking for bio-based and generally recognized as safe (GRAS) preservatives to control the microbial growth of food [2]. Antimicrobial active packaging is a new method to increase the shelf life of food without direct addition of antimicrobial agents into the food. Active food packaging includes interaction between food and packaging material, which inhibits microbial growth of food and increases its shelf life [3].

Nanotechnology provides comprehensive opportunity to improve food packaging, and can increase the shelf life of food as well as improve the properties of packaging material. There

has been much interest in the use of metal nanoparticles in this type of packaging, due to fact that metal oxide nanoparticles show excellent antimicrobial properties [4]. Among them, application of gold and silver as antimicrobial agent, is limited due to their high price [5]. Zinc oxide is an interesting agent in food and pharmacy fields due to its nutritional properties, effective antimicrobial properties at low concentrations, high stability against high temperatures, non-toxicity, and good UV absorbance properties. Also, it is known as a GRAS compound by Food and Drug Administration [6]. It is worth noting that because ZnO NPs use as a nutrient agent, thus addition of it to the film packaging and its probable diffusion to the food products are not harmful to human health [7]. The effective antimicrobial properties of ZnO NPs in active films have been reported for starch films against *Staphylococcus aureus* [8]; polylactic acid-ZnO NPs nanocomposite films against *Escherichia coli* and *Staphylococcus aureus* [5]; chitosan-neem oil based film against *E. coli* [9]; and sodium alginate-gum acacia hydrogels versus *Pseudomonas aeruginosa* and *Bacillus cereus* [10]. The main reason for superior antimicrobial properties of metal nanoparticles is connected to their high surface area [11]. *Aspergillus* and *Penicillium* species are among the major spoiler fungal strains, which limit the shelf life of food products by

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production of toxic mycotoxins, off flavor, bad appearance etc. Thus, it is important to study the antifungal effects of ZnO NPs [12], while few studies have been done on it. Incorporation of ZnO NPs in biopolymer matrix is not only for its antimicrobial effects, but also for enhancing the mechanical and barrier properties of the bio nanocomposites as filler [13]. Previous studies have shown that the ZnO NPs can improve the mechanical [6,13], barrier [5,8,14,15]; and thermal properties [9,14] of nanocomposite films.

Biopolymers including polysaccharides and proteins have been increasingly paid attention in food packaging application due to their low cost and good film forming properties [16–18]. Chitosan is a linear cationic carbohydrate polymer, which derives from chitin [19]. Due to its superior film forming properties, antimicrobial properties, and biodegradability, chitosan is a promising biopolymer for active packaging. Reactive amino and hydroxyl functional groups in chitosan, capable it to blend with other polymers to improve the properties of them, as well as chelating metal ions such as  $Zn^{+2}$  [20]. Chitosan film is a good barrier to oxygen and  $CO_2$  at low relative humidity, due to its ordered and packed structure and high hydrophilicity [21]. However, low water barrier properties is one of the disadvantages of polysaccharide films like chitosan [22], which can be improved by blending chitosan with other polymers. Carboxymethyl cellulose (CMC) is a linear water soluble derivative of cellulose, which is inexpensive, nontoxic and non-allergenic and frequently used in foods, cosmetics, pharma etc. [1,23]. In addition, CMC films are transparent, thus blending of chitosan with CMC decrease the yellow appearance of chitosan films. In addition, a reduction in water barrier properties of chitosan in chitosan/methylcellulose blend films have been observed [24]. Despite to the improvement in barrier properties of blend films compared to single films, they still show high sensitivity to water, hence incorporation of lipid compounds or other hydrophobic compounds is a promising way to overcome this problem [22]. Up to now, few studies have been reported on the CMC-CH based films [13,25,26]. As far as we know, there is no study with CMC-CH-OL-ZnO NPs formulation. Thus, the aim of the present study is to produce active emulsified packaging film based on carboxymethyl cellulose-chitosan-oleic acid incorporated by ZnO NPs by the solution casting method and then, to study their physical and antifungal properties.

## 2. Material and methods

### 2.1. Materials

Chitosan (low molecular weight, 20–300 cP, 50–190 kDa, deacetylation degree 75–85%) and sodium carboxymethyl cellulose (high viscosity, 1500–3000 cP) were purchased from Sigma Aldrich (USA) and Caragum Parsian (Tehran, Iran), respectively. Analytical grade glycerol, oleic acid and tween 80 were obtained from Merck (Darmstadt, Germany), potato dextrose agar (PDA) from Merck Milipore (Darmstadt, Germany). All other products were of analytical grade. Zinc oxide NPs with average size of <25 nm was purchased from Sigma Aldrich (USA).

### 2.2. Preparation of films

Films were elaborated by solution casting method. At first, 0.2 g of chitosan dispersed in acidic distilled water (0.5% v/v acetic acid) and stirred overnight. Afterwards, the pH was adjusted to around 6.8 by pouring drop by drop of NaOH solution (3 M). ZnO NPs powder at different concentrations (0.5, 1 and 2 wt.%) was solubilized in water and sonicated for 30 min. Then, CMC (0.4 g) was dissolved in distilled water (50 mL) contain ZnO NPs suspension and were mixed by magnetic stirrer for 1 h. Then, both solutions were mixed;

tween 80 (0.2 mL) was added as an emulsifier and stirred again for 15 min. Oleic acid (0.3 mL) was then added, and the mixture, was homogenized by probe ultrasound (Bandelin Sonopuls, Germany) for 15 min (31 KJ). Glycerol (0.3 mL) as the plasticizer of the film was added to the dispersions and stirred for 15 min and degassed under vacuum for 30 min in order to remove air bubbles from the dispersions. Then, about 50 mL of each dispersion was poured into the polystyrene petri-dishes (9 cm diameter) and dried at 25 °C for 72 h. Dried films were peeled and conditioned at 25 °C and 55% relative humidity before analysis.

### 2.3. X-ray diffractometry (XRD)

X-ray diffraction patterns of the film samples was analyzed using an APD 2001 X-ray diffractometer (Ital Structures, Italy). The spectra were recorded using Cu-K $\alpha$  radiation at a voltage of 40 kV and a current of 50 mA with scanning at ambient temperature from 2 $\theta$  values from 2.5 to 60°, where  $\theta$  is the angle of incidence of the X-ray beam on the sample. The size of the crystals was calculated according to the Scherrer equation (Eq. (1)):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, D is the crystal size,  $\lambda$  is the X-ray wavelength; K is Scherrer constant is 0.9;  $\beta$  is width at half maximum (FWHM), and  $\theta$  is the Bragg diffraction angle [27].

Determination of Crystallinity index (%) was calculated according to the Segal Equation (Eq. (2)):

$$\text{Crystallinity index} = \frac{I_t - I_a}{I_t} \times 100 \quad (2)$$

Where,  $I_t$  is the height of the (200) peak, represents both crystalline and amorphous regions; and  $I_a$  is the lowest height between the (200) and (110) peaks, which represents the amorphous region [27].

### 2.4. Scanning electron microscopy (SEM)

Microstructure analysis of surfaces of the films was carried out using SEM technique in a (SEM) (TOPCON SM-200 SEM). The films deposited onto a copper holder with conductive carbon paint and coated with gold under vacuum before observation. All samples were examined using low vacuum at a voltage of 20 KV.

### 2.5. Attenuated total reflectance-Fourier transforms infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra of the films were obtained using a FTIR spectrometer (PIKE technologies/Gladi Atrvertex 70, Bruker, France). Spectra were recorded at the absorbance mode from 4000 to 400  $cm^{-1}$  with automatic signal gain (32 scans) at a resolution of 4  $cm^{-1}$ .

### 2.6. Film thickness

Film thickness was measured using a micrometer (Mitutoyo, 293-766-30, Tokyo, Japan). Reported values were the average of ten random locations for each film.

### 2.7. Mechanical tests

Films were cut in dumbbells forms (5 mm width  $\times$  60 mm long), later conditioned in a desiccator containing a saturated calcium nitrite solution at a relative humidity (RH) of 55% for 72 h at ambient temperature before measurements. Tensile strength (TS, MPa), Elongation-at-break (EB, %) and Young modulus (YM, MPa)

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