



Effects of montmorillonite on properties of methyl cellulose/carvacrol based active antimicrobial nanocomposites



Sibel Tunç*, Osman Duman, Tülin Gürkan Polat

Akdeniz University, Faculty of Science, Department of Chemistry, 07058 Antalya, Turkey

ARTICLE INFO

Article history:

Received 26 February 2016
Received in revised form 5 May 2016
Accepted 7 May 2016
Available online 10 May 2016

Keywords:

Methyl cellulose
Montmorillonite
Carvacrol
Nanocomposite film
Mechanical properties
Permeability

ABSTRACT

The effect of montmorillonite and carvacrol (as an antimicrobial agent) on the wettability, mechanical, gas barrier, thermal and color properties of methyl cellulose-based nanocomposite films was investigated. To make a comparison among the film samples, methyl cellulose (MC) film and methyl cellulose/montmorillonite (MC/MMT) and methyl cellulose/carvacrol/montmorillonite (MC/CRV/MMT) nanocomposite films with different clay concentration were prepared. The interactions among MMT, CRV and film matrix were characterized by FTIR spectroscopy. The contact angle value of MC film showed an increase of 2.5 fold with the incorporation of 60 wt.% MMT into the film matrix. The addition of clay into the film matrix increased the melting point of MC film and improved the mechanical properties of film material. The tensile stress of pure MC film exhibited an increase of 9.2 MPa in the presence of 60 wt.% MMT. With the addition of MMT into the film matrixes, water vapor permeability values of MC film and MC/CRV film were decreased by 28% and 13%, respectively. The incorporation of 60 wt.% MMT into the film matrix caused to a decrease of 47 fold for MC film and 16 fold for MC/CRV film in the oxygen permeability of film sample. The addition of CRV into MC film and MC/MMT nanocomposite films with different clay concentration reduced the mechanical strengths of film materials. Oxygen permeability values of MC film and MC/MMT nanocomposite films decreased with the inclusion of CRV into the film matrix.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

An increase in consumer sensitivity about food safety and awareness toward environmental concerns led to an increment in demand for renewable and bio-based food packaging materials (Scarfato, Di Maio, & Incarnato, 2015). These materials have the advantage of being biodegradable, renewable and often edible and are obtained from natural raw materials such as polysaccharide and protein. In spite of these advantages, their commercial usage has been limited because they have lower mechanical, thermal and gas barrier properties compared to synthetic polymers (Mondal et al., 2013). The addition of nanofillers, e.g. clays, results in an improvement in the properties of biodegradable polymers including enhanced mechanical, thermal and barrier properties (Tunc et al., 2007; Yu, Wang, Hu, & Wang, 2014).

Antimicrobial active packaging has been used to delay or inhibit microbial growth and improve the safety of food materials by incorporating antimicrobial agents into packaging films (Appendini

& Hotchkiss, 2002). Bio-based nanocomposite food packaging materials have the potential to be useful in active antimicrobial food packaging applications (Abdollahi, Rezaei, & Farzi, 2012; Madusanka, Nalin de Silva, & Amaratunga, 2015). In the preparation of active antimicrobial food packaging materials, antimicrobial agents based on natural substances are more preferable to synthetic chemicals due to their potential toxic effects (Ruiz-Cabello et al., 2015). Essential oils and their components are natural and safety agents. They have been incorporated into different food packaging materials to develop antimicrobial active food packaging. Cinnamaldehyde and eugenol were used in the preparation of cellulose based films (Sanla-Ead, Jangchud, Chonhenchob, & Suppakul, 2012). Carvacrol (CRV), a monoterpene phenolic constituent of essential oil produced by some aromatic plants and spices such as black cumin (*Nigella sativa* L.), marjoram (*Origanum majorana* L.), oregano (*Origanum vulgare* L.), summer savory (*Satureja hortensis* L.) and thymine (*Thymus vulgaris* L.) (Landa, Kokoska, Pribylova, Vanek, & Marsik, 2009), was successfully employed in the development of antimicrobial methyl cellulose-based nanocomposite films (Tunç & Duman, 2011). Ben Arfa, Preziosi-Belloy, Chalier, and Gontard (2007) prepared the antimicrobial papers based on a soy protein isolate or modified starch coating including CRV and cinnamaldehyde.

* Corresponding author.

E-mail addresses: stunc@akdeniz.edu.tr (S. Tunç), osmanduman@akdeniz.edu.tr (O. Duman).

One of the desired properties of antimicrobial packaging films is the controlled release of antimicrobial agent through the film matrix (Tunç & Duman 2011). When the release of an antimicrobial compound occurs too quickly, the minimum inhibition concentration is not sustained for long periods of time. When this release occurs too slowly, a sufficient concentration of the antimicrobial agent at an early stage is not achieved, and spoilage is not controlled (Campos-Requena, Rivas, Perez, Garrido-Miranda, & Pereira, 2015). In literature, the studies about the preparation of polymer/clay nanocomposite materials with the improved mechanical, thermal and barrier properties have been focused on the controlled release of antimicrobial agents from active packaging materials (Mascheroni, Guillard, Gastaldi, Gontard, & Chalier, 2011; Tunç & Duman, 2011). In these studies, nanoclay is spread on the polymer matrix resulting in a homogeneous layer dispersion creating tortuous pathways which provides controlled release of antimicrobial agents (Campos-Requena et al., 2015).

The present study is a continuation of a series of works on the development and characterization of methyl cellulose-based active antimicrobial nanocomposite films carried out in our laboratories. In our previous paper (Tunç & Duman, 2010), the effect of mixing types, mixing speeds and mixing times on the preparation of methyl cellulose/montmorillonite (MC/MMT) nanocomposite films was studied and the most suitable nanocomposite film preparation method was determined from XRD and TEM analyses. Furthermore, the effect of MMT concentration on the thickness, opacity, water adsorption and water solubility properties of nanocomposite films was investigated. This study showed that water adsorption and water solubility values of MC/MMT nanocomposite films exhibited a decrease with increasing MMT concentration within film matrix (Tunç & Duman, 2010). In addition, methyl cellulose/carvacrol/montmorillonite (MC/CRV/MMT) nanocomposite films were prepared to obtain active antimicrobial food packaging materials and the release of CRV from nanocomposite films with different MMT concentration was studied (Tunç & Duman, 2011). Antimicrobial activities of these films were also tested against *Escherichia coli* and *Staphylococcus aureus* (Tunç & Duman, 2011). Moreover, the antibacterial effect of MC/CRV film and MC/CRV/MMT-60% nanocomposite film for the growth of *Escherichia coli* and *Staphylococcus aureus* on sausage was determined.

In this study, the mechanical, barrier, thermal and physicochemical properties of MC/MMT and MC/CRV/MMT nanocomposite films were studied. The effect of MMT concentration and CRV on the nanocomposite film properties was investigated.

2. Materials and methods

2.1. Materials

Chemicals used in the methyl cellulose (MC) film preparation are MC with an average molecular weight of 41 000 (viscosity of its 20 g/L aqueous solution at 25 °C is 400 cP) supplied from Sigma (St. Louis, MO, USA), polyethylene glycol with an average molecular weight of 400 (PEG 400) and carvacrol (CRV) purchased from Aldrich (St. Louis, MO, USA) and ethyl alcohol (C₂H₅OH) bought from Merck (Darmstadt, Germany). Montmorillonite (MMT) without organic modification was supplied by Süd-Chemie AG (München, Germany) under the name Nanofil 116.

An acrylic desiccator cabinet with gas port including hygrometer (Plas-Labs) was used for conditioning film samples at a constant relative humidity (RH) and temperature. RH value of the cabinet was adjusted by saturated salt solution of Mg(NO₃)₂·6H₂O (Merck, Darmstadt, Germany). Sanyo MIR 553 incubator was used to control the temperature.

2.2. Preparation of films

In the preparation of MC film, a mass of 3 g MC was dissolved in a solvent mixture of 33 mL H₂O and 66 mL C₂H₅OH. After addition of 0.9 g PEG 400, the solution was homogenized with an Ultra Turrax T18 model homogenizer (Staufen, Germany) at 13 500 rpm for 5 min. The final film solution was kept in a Nüve EV 018 vacuum oven (Ankara, Turkey) at 60 °C for 30 min to remove air bubbles or dissolved air. The solution was then spread on 20 × 20 cm glass plates by adjusting the hand operated CAMAG thin layer chromatography plate coater (Muttentz, Switzerland) to 500 μm thickness. The spread film was dried at 60 °C in an oven for 30 min and then at room temperature for one day (Ayrancı & Tunç, 1997; Ayrancı, Tunç, & Etcı, 1999).

MC/CRV films were prepared with the similar method used in the preparation of MC films. Only one difference is that the inclusion of 1.5 g CRV into film solution with PEG 400 at the same time before homogenization step.

Active nanocomposite films including CRV and MMT were prepared according to the method described by Tunç and Duman (2010, 2011). 3 g MC, 0.9 g PEG 400 and 1.5 g CRV (it should be noted that CRV was not added into the film matrix to prepare the MC or MC/MMT films) were dissolved in a solvent mixture of 33 mL H₂O and 66 mL C₂H₅OH. The solution was homogenized with an Ultra Turrax T18 model homogenizer at 13 500 rpm for 5 min. MMT in varying amounts (MMT-MC ratios are 10, 20, 40 and 60 wt.% in these films) was dispersed separately in 25 mL water and mixed by magnetic stirrer at 600 rpm for 2 h. Then, an ultrasonic mixing at 35 Hz for 10 min was applied to increase the dispersion of clay in water. After that MC film solution and MMT dispersion were mixed and re-homogenized with homogenizer at 20 500 rpm for 10 min. The final solution was kept under vacuum in a vacuum oven at 60 °C for 30 min to remove air bubbles or dissolved air. The solution was then spread on 20 × 20 cm glass plates using a hand operated plate coater of CAMAG thin layer chromatography by adjusting its thickness to 500 μm. The spread film was dried at 60 °C in an oven for 30 min and then at room temperature for one day as mentioned above. The film name-percent MMT concentration was used as an abbreviation to define the MMT concentration within film matrix.

2.3. Characterization of MC/MMT and MC/CRV/MMT nanocomposite films

2.3.1. FTIR spectroscopy

FTIR measurements were carried out to realize the interactions between MMT and MC film matrix due to the addition of MMT into film matrix. Film samples were cut into 5 × 5 cm sizes and placed into the cabinet at 25 °C and 52% RH for 48 h to perform the condition of film samples. Scimitar 1000 model FTIR spectrometer (Varian, Australia) was used to obtain the IR spectra of samples in the range of 400–4000 cm⁻¹. The FTIR spectrum of MMT was recorded by KBr pellet technique.

2.3.2. Contact angle measurements

The surface hydrophobic or hydrophilic character of nanocomposite films containing 0, 10, 20, 40 and 60 wt.% MMT was determined using the Rame-Hart Goniometer (Mountain Lakes, NJ, USA). One drop of water was dropped on the surface of the film samples using a micro syringe to measure the contact angle values of samples. Data presented are the means of ten independent determinations at different sites. When a water drop was dropped on the films including CRV, immediately a white zone occurred on the film surfaces in contact with water and approximately 30–45 s later, a hole formed in the film samples with CRV. On the other hand, this situation was not observed in other film samples without CRV. For

Download English Version:

<https://daneshyari.com/en/article/1384837>

Download Persian Version:

<https://daneshyari.com/article/1384837>

[Daneshyari.com](https://daneshyari.com)