



Preparation and characterization of agar-based nanocomposite films reinforced with bimetallic (Ag-Cu) alloy nanoparticles



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ABSTRACT

Agar-based active nanocomposite films were prepared by incorporating silver-copper (Ag-Cu) alloy nanoparticles (NPs) (0.5–4 wt%) into glycerol plasticized agar solution. Thermo-mechanical, morphological, structural, and optical properties of the nanocomposite films were characterized by texture analyzer, differential scanning calorimetry (DSC), scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy, and surface color measurement. Tensile strength and the melting temperature of the film increased linearly with NPs loading concentration. Color, transparency and UV barrier properties of agar films were influenced by the reinforcement of Ag-Cu NPs. XRD analysis confirmed the crystalline structure of the Agar/Ag-Cu nanocomposite films, whereas the smoothness and the homogeneity of film surface strongly reduced as observed through the SEM. The nanocomposite films exhibited a profound antibacterial activity against both Gram-positive (*Listeria monocytogenes*) and Gram-negative (*Salmonella enterica sv typhimurium*) bacteria. Overall, the agar nanocomposite films could be used as packaging material for food preservation by controlling foodborne pathogens and spoilage bacteria.

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1. Introduction

Since, conventional petroleum-based packaging materials (e.g. polyethylene, low-density polyethylene, high-density polyethylene, polyethylene terephthalate, and polypropylene) have adverse impact on the ecosystem and environment, and to counter those issues, bio-based materials emerged as an alternative in the area of food packaging with unprecedented growth. Biopolymer based films not only act as barriers to oxygen, carbon dioxide and volatile compounds, but also serve as a carrier for a wide range of additives, such as antioxidants, antimicrobial agents, antifungal compounds, colorants, and other nutrients (Rhim & Ng, 2007; Arfat, Benjakul, Prodpran, Sumpavapol, & Songtipya, 2014). Biopolymers produced from various natural resources such as starch, proteins, agar and cellulose. They have been considered as fascinating alternatives for conventional polymers since they are renewable, abundant, inexpensive, environment friendly and biodegradable. Furthermore, researchers find a new resource other than food and feed for generation of bio-based and biodegradable plastics produced from algae and/or algae components (Rosenthal, 2013).

Agar is a fibrous carbohydrate extracted from a group of marine algae of the class Rhodophyceae, and one of the most attractive materials since it is abundant, thermoplastic, biocompatible and biodegradable (Rhim, 2011; Atef, Rezaei, & Behrooz, 2014). Agar has been impressively used as an alternative source for the non-renewable and non-biodegradable plastic based packaging materials since it has excellent film-forming capability with reasonable mechanical properties (Atef et al., 2014; Rhim, 2011, 2012;). However, low thermal stability, limited oxygen barrier, and low water barrier properties are some of the limitations observed in agar based packaging films that hinder their applications in food packaging (Rhim, 2012; Yoo & Krochta 2011).

Recently, a novel nanotechnology approach has been extensively employed to enhance the material properties of agar-based films by incorporating NPs either individually or in a combination. Such NPs offer several advantages over microparticles due to their interfacial interactions on polymer branches, increased surface area and aspect ratio, high surface energy, and therefore, improve mechanical, thermal and barrier properties of polymers (Rouhi, Mahmud, Naderi, Ooi, & Mahmood, 2013). A number of researchers have reported development of agar-based films by incorporating single metallic NPs including ZnO, Ag and Cu (Kanmani & Rhim, 2014a; Rhim, Wang, Lee and Hong, 2014; Shankar, Teng, & Rhim, 2014). However, contrary to single metallic NPs, bimetallic NPs have improved optical, interfacial and catalytic properties. For

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instance, silver (Ag) NPs have been alloyed with Copper (Cu) NPs to enhance their interfacial and catalytic activity (Tan & Cheong, 2013). Additionally, silver–copper (Ag–Cu) alloy NPs exhibited excellent antibacterial activity against food-borne pathogens and spoilage bacteria even at a lower concentration over individual Ag or Cu NPs (Ahmed, Hiremath et al., 2016; Taner, Sayar, Yulug, & Suzer, 2011; Valodkar, Modi, Pal, & Thakore, 2011), and, therefore, bimetallic Ag–Cu NPs have been approved by the United States Food and Drug Administration (FDA) for use in food packaging (Ahmed, Hiremath et al., 2016; Duncan, 2011). Ag–Cu NPs has intensive ultraviolet absorption capacity, so it could be potential filler for the improvement of optical, antimicrobial and thermo-mechanical properties of the biopolymer films. No report is available on the incorporation of bimetallic Ag–Cu NPs into an agar matrix, and resultant packaging. Therefore, the main objectives of the present study were to develop agar/Ag–Cu nanocomposite films, and characterize their mechanical, thermal, structural and morphological properties. Finally, the antimicrobial properties of the developed films were tested against Gram-positive *Listeria monocytogenes* and Gram-negative *Salmonella enterica* sv *typhimurium*, respectively. This information could be useful for commercial development of agar/Ag–Cu nanocomposites films, and their possible applications in active food packaging.

2. Materials and methods

2.1. Chemicals

Food grade agar was obtained from Quelab Laboratories Inc. (Montreal, Canada) and Ag–Cu NPs (Ag/Cu ratio of 9:1) (particle size: <100 nm) from Sigma–Aldrich (St. Louis, MO, USA). All chemicals were of analytical grade. Lyfo Disk pellets® of *Listeria monocytogenes* (ATCC 19114) strain was purchased from Medi-Mark Europe (Grenoble, CEDEX, France). Culti-loops® of *Salmonella enterica* sv *typhimurium* (ATCC 14028) was obtained from Remel Europe Ltd. (Dartford, Kent, UK). Brain heart infusion agar (BHIA) was procured from Conda Laboratories (Torrejón de Ardoz, MD, Spain). Muller Hinton agar (MHA) and Tryptic soya broth (TSB) were purchased from TM Media (Bhiwadi, India).

2.2. Preparation of agar/Ag–Cu nanocomposite film

Control agar and agar/Ag–Cu nanocomposite films were prepared via solution casting method following the method of Shankar et al., 2014. Ag–Cu alloy NPs at selected concentration [0 (control), 0.5% (15 mg), 1% (30 mg), 2% (60 mg) and 4% (120 mg) of agar, w/w] were mixed well in a beaker containing 150 mL distilled water, and sonicated for 5 min. Then, glycerol (0.9 g) was added as a plasticizer into the NPs solution with a constant stirring for 20 min. Thereafter, 3 g of agar was added gradually into the NPs solution with stirring and boiling until dissolved completely. The film-forming solutions were degassed for 10 min using a sonicating bath, and casted evenly onto a rimmed silicone resin plate (6 × 6 cm²). The casted films were air-blown for 10 h at 25 °C followed by drying in an environmental chamber (Binder GmbH, Tuttlingen, Germany) at 25 ± 0.5 °C with a relative humidity of 50 ± 5% for 48 h. Conditioned films were manually peeled off and used for tensile, oxygen transmission rate, and optical property measurement. For XRD, FTIR, DSC, and SEM analyses, films were dried in a desiccator containing dried silica gel for 2 week at room temperature (25–28 °C) to minimize the plasticization effect.

2.3. Characterization of films

2.3.1. Film thickness and tensile properties

The thickness of films was measured using a digital hand-held micrometer (Mitutoyo, Model MCD-1“PXF” Mitutoyo Corp., Kawasaki-shi, Japan) with a precision of 0.001 mm. Eight random locations around each film sample were used for average thickness determination.

Tensile strength (TS) and elongation at break (EAB) of films were measured using the Texture Analyzer TA.XT plus (Stable Micro Systems, UK) equipped with tensile grips (A/TG model) following the standard method D882 (ASTM, 2001). The films were cut into rectangular forms (size of 70 mm × 20 mm) and were fixed on the grip device with a gap of 40 mm. They were then pulled apart at crosshead speed of 30 mm/min and preload of 50 N. TS and EAB were determined from the stress-strain curve. Results of TS and EAB were average of ten determinations from each type of film, and were expressed as MPa and%, respectively.

2.3.2. Color and optical properties

Colour values of film were determined using a CIE colourimeter (Hunter associates laboratory, Inc., Reston, VA, USA). Colour of the film was expressed as L^* – (lightness), a^* – (redness/greenness) and b^* – (yellowness/blueness) values. Total difference in colour (ΔE^*) was calculated according to the following equation (Gennadios et al., 1996):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where ΔL^* , Δa^* and Δb^* are the differences between the corresponding colour parameter of the samples and that of white standard ($L^* = 93.51$, $a^* = -1.32$, $b^* = 0.18$).

The light transmittance of films was measured at the ultraviolet and visible range (200, 280, 350, 400, 500, 600, 700 and 800 nm) using a UV–visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) according to the method of Fang, Tung, Britt, Yada, & Dalgleish (2002). The transparency value of film was calculated using the following equation (Han & Floros 1997):

$$\text{Transparency value} = \frac{\log T_{600}}{x}$$

where T_{600} is the fractional transmittance at 600 nm and x is the film thickness (mm). The greater transparency value represents the lower transparency of film.

2.3.3. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) analysis

The FTIR spectra of film samples were determined in the wave number of 500–4000 cm⁻¹ using a Nicolet iS5 FT-IR Spectrometer (Thermo Scientific, Madison, WI, USA). Film samples were placed on the surface in contact with attenuated total reflectance (ATR) on a multi-bounce plate of Zn–Se crystal at 25 °C. Each spectrum collected from an average of 32 scans at a resolution of 4 cm⁻¹ was ratioed against a background recorded from the air spectrum at 25 °C. The results were reported as mean values.

X-ray diffraction analysis of the selected films was performed using a diffractometer Bruker D8 Advance (Bruker AXS, Germany) equipped with monochromatic Cu–K α radiation ($\lambda = 0.154$ nm) under a voltage of 40 kV and a current of 40 mA. All samples were measured in continuous scan mode with the 2θ varied from 5 to 80°.

2.3.4. Differential scanning calorimetry (DSC)

Thermal properties of film samples were determined using a TA Q2000 differential scanning calorimeter (DSC) under a nitrogen atmosphere. Film samples (≈ 10 mg) were precisely weighed into

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