Applied Clay Science 161 (2018) 464–473

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Poly(vinyl alcohol): Montmorillonite: Boiled rice water (starch) blend film reinforced with silver nanoparticles; characterization and antibacterial properties

Shiji Mathew[a], Snigdha S.[b], Jyothis Mathew[a], Radhakrishnan E.K.[a,*]

[a] School of Biosciences, Mahatma Gandhi University, P.D Hills (P.O), Kottayam, Kerala 686 560, India
[b] International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, P.D Hills (P.O), Kottayam, Kerala 686 560, India

ARTICLE INFO

Keywords:
Nanocomposite blend
Clay mineral
Active packaging material
Boiled rice starch
Foodborne pathogens

ABSTRACT

Poly(vinyl alcohol) (PVA) is an excellent film forming polymer used for packaging applications, but it has weak barrier and mechanical properties. Hence improvement in material properties of PVA is expected to enhance its suitability as an ideal food packaging material. For the first time, this study reports the use of boiled rice starch as a blending agent to modify the physicochemical properties of PVA. The aim of the work was to develop montmorillonite (Mt)/PVA/boiled rice starch blend material reinforced with silver nanoparticles (AgNPs) for food packaging application. Highly cost effective method was used for the generation of AgNPs from $AgNO_3$ by using rice starch as a reducing agent. The rapid *in situ* generation of AgNPs within the polymer matrix, under the influence of direct sunlight, as conducted in this study is a novel approach. The nanocomposite films prepared by solvent casting method were characterized by SEM, XRD, FT-IR and UV–vis spectroscopy analysis. Mechanical, optical, and barrier properties of the nanocomposite films further showed its excellent properties when compared to the neat PVA film. The nanocomposite also showed promising antimicrobial activity against foodborne pathogens *Salmonella typhimurium* and *Staphylococcus aureus*. Hence the results suggest the nanocomposite blend developed in the study to be an ideal material for food packaging application.

1. Introduction

Proper packaging is in high demand to maintain the quality of food and its microbiological safety. This is highly challenging as the industry is moving towards distribution of highly processed and ready-to-eat food (Issa et al., 2017). Conventional food packaging materials have serious concern with respect to its recycling, renewability and biocompatibility (Taghizadeh et al., 2013). To tackle this, there is in need of biodegradable, low cost and eco- friendly polymer based materials.

Poly(vinyl alcohol), (PVA) is an artificial, semi-crystalline, water soluble, film forming polymer with wide range of applications. PVA has a low rate of biodegradability, poor mechanical and moisture barrier properties (Tang & Alavi, 2011). Hence many studies have been focused on the material engineering of PVA to improve its properties. One of the effective approaches for achieving this involves the incorporation of layered silicates into the polymer matrix (Purwar et al., 2015; Saha et al., 2016). Silicates such as smectite, hectorite, saponite, kaolinite, mica and montmorillonite have been used for this purpose. Among these, montmorillonite (Mt) is most commonly employed for the development of PVA based nanocomposite films (Junqueira-Gonçalves et al., 2017; Saha et al., 2016; Yadav & Ahmad, 2015). Here, the Mt layers are considered to create a tortuous pathway (Junqueira-Gonçalves et al., 2017) for the controlled release of antimicrobial agents incorporated within the nanocomposites (Lavorgna et al., 2014). Blending of PVA with natural polymers such as starch has also been employed to get the desired properties (Guaras et al., 2016; Liu et al., 2017). Starch has been used as a better alternative for non-biodegradable and non-renewable materials in packaging industry (Pineros-Hernandez et al., 2017) due to its biocompatible (Huo et al., 2016) and excellent film forming properties (Liu et al., 2017). Starch from various sources like rice (Vargas et al., 2017), potato (Choi et al., 2017), cassava (Pineros-Hernandez et al., 2017), wheat (Bonilla et al., 2013), yam (Mali et al., 2005) and corn (Chang-Bravo et al., 2014) has been studied for film forming properties.

Nanocomposites with antimicrobial surfaces can have superior performance as packaging material. For this, different metallic nanoparticles such as silver (Ag) (Gautam & Ram, 2010), zinc oxide (ZnO) (Akhavan et al., 2017) and copper oxide (CuO) (Rao et al., 2015) have been used. Among these, silver nanoparticle (AgNPs) is the primary choice due to its broad spectrum antimicrobial effects and easiness with

* Corresponding author.
E-mail address: radhakrishnanek@mgu.ac.in (E.K. Radhakrishnan).

https://doi.org/10.1016/j.clay.2018.05.009
Received 25 October 2017; Received in revised form 9 February 2018; Accepted 10 May 2018

incorporation into polymer matrices. Various biopolymers such as gelatin (Kanmani & Rhim, 2014), lignin (Shankar & Rhim, 2017), chitosan (Huang & Yang, 2004), and banana starch powder (Orsuwan et al., 2016) have been used for the green synthesis of AgNPs. In the current study, boiled rice starch was chosen as the biopolymer for blending and for *in situ* AgNP production within the polymer matrix. Generally, it takes 18 to 20 h for the generation of brown coloration in the nanocomposite film solutions, if the AgNP formation occurs under the influence of fluorescent light. However, in this study, the *in situ* reduction of $AgNO_3$ to AgNPs by boiled rice starch was found to take place within minutes under the influence of direct sunlight. This ensured green, rapid, and cost effective generation of AgNPs (Mathew et al., 2017) with the combination of sunlight and rice starch.

In the present study, PVA based nanocomposite blend films incorporated with rice starch, Mt and AgNPs were developed by solvent casting method. The nanocomposite blends were further characterized and its mechanical, UV light barrier, water barrier and antimicrobial properties were evaluated. This study is the first report on use of boiled rice water for the preparation of blends films with PVA.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA) with average MW of 92,500 was purchased from HiMedia (India). Silver nitrate (99% purity) from Merck (Worli, Mumbai), and Montmorillonite K 10 (Mt) powder (69866) from Sigma Aldrich, India were also used. Brown rice (*Oryza sativa L.*) was obtained from local market of Kottayam District, Kerala, India.

2.2. Methods

2.2.1. Preparation of boiled rice starch water

For this, 175 g of brown rice was cooked in a pressure cooker (5 whistles) in 500 mL of distilled water and the cooked rice water obtained (100 mL) was stored in sterile conical flasks. The rice water/starch obtained was soluble in hot water.

2.2.2. Preparation of nanocomposite blend films

2.2.2.1. Preparation of PVA (P) film. For the preparation of P film, 1.2 g of PVA was dissolved in 40 mL of distilled water at 80 °C under magnetic stirring for 4 h (Usman et al., 2016). The transparent solution obtained was then casted on sterile glass petri dish and kept in hot air oven (KEMI, KOMS-5, India) at 60 °C for 8 h. The dried film was then peeled off from the petri dish and was stored safely for further characterization.

2.2.2.2. Preparation of PVA/boiled rice starch (PS) blend films. For PS film, 1.2 g PVA was dissolved in 30 mL of distilled water under continuous stirring for 2 h at 80 °C. Then 10 mL of freshly prepared boiled rice starch water was added to the PVA solution and again mixed for 2 h. The solution was poured onto sterile glass petri dish and thin film was prepared.

2.2.2.3. Preparation of Mt/PVA (PM) films. To 30 mL of PVA solution, 10 mL of 0.3 g Mt was added and was mixed using magnetic stirrer for 4 h. Further, this was used for thin film preparation.

2.2.2.4. Preparation of Mt/PVA/boiled rice starch (PSM) blend films. Here, 1.2 g of PVA was dissolved in 20 mL of distilled water under stirring, then 10 mL of sterile boiled rice starch water was added to the PVA solution and again mixed for 2 h. Then, 10 mL of Mt dispersion (0.3 g/10 mL distilled water) was added into 30 mL of PS solution under stirring for 2 h. The resulting solution (40 mL) was casted onto sterile glass petri dish as described above.

2.2.2.5. Preparation of Mt/PVA/AgNP/boiled rice starch (PASM) blend films. Here, PSM film solution (40 mL) was prepared as described above. Then, 40 µL of 1 M $AgNO_3$ solution was added into this. The solution was further kept under direct sunlight for 15 mins. The resulting brown coloured solution was then mixed in magnetic stirrer for 30 mins and then casted onto petri plates, dried in hot air oven and were peeled off.

2.2.3. Film characterization

2.2.3.1. Mechanical properties. The mechanical properties of thin film such as tensile strength, elongation at break and modulus were measured using Tinius OlsenH50 KT Universal Testing machine according to ASTM D 882 standard by applying a 500-N load cell at a crosshead speed of 5 mm/min. All the samples were cut into 5 × 1 cm^2 rectangle pieces and vertically mounted in between two mechanical gripping units of the tester, leaving a 3 cm gauge length for mechanical loading. The sample thickness was measured using an electronic micrometer having a precision of 1 µm. The average values of tensile property were obtained from the results of five tests and expressed as the mean ± standard deviation (SD).

2.2.3.2. SEM, FTIR, XRD and UV–vis absorption analysis. The surface morphology of prepared films was studied using Scanning Electron Microscopy (SEM, model JSM-6390). For this, small pieces of all film samples were placed on copper grid and sputtered with platinum for making the sample conductive. Then photographs were taken at a magnification of 6000×, with an accelerating voltage of 6 kV. FTIR analysis of the films was performed using Shimazdu IR Prestige 2 FTIR Spectroscopy in attenuated total reflectance mode (ATR). The measurements were recorded in the range of 4000–450 cm^{-1} with a scan rate of 4 cm^{-1}.

Powder X-ray diffraction patterns of the samples were recorded using Xpert^3 PANalytical X-ray diffractometer. The machine was equipped with Ni filtered Cuα radiation (λ = 1.540 Å) under the conditions of 45 kV and 30 mA at a step scan size of 2θ = 0.02°. The data was collected in the 2θ range of 10–80°.

The UV–vis absorption spectra of all the nanocomposite films were carried out using UV–vis spectrophotometer (Shimazdu UV 2600). The measurements were collected from wavelength ranging from 200 to 800 nm.

2.2.3.3. Water absorption capacity (WAC %). Here, 2 × 2 cm^2 pieces of film samples were cut and initial dry weight was recorded (m_{dry}). Then the samples were placed in separate tubes containing 5 mL distilled water according to the previous methodology (Taghizadeh et al., 2013). After 1, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 h, samples were taken out and excess water was wiped off with filter paper and final weight was noted (m_{wet}). The water absorption capacity of the films was calculated using Eq. (1)

$$\mathrm{WAC}\ (\%) = \left[\frac{(m_{wet} - m_{dry})}{m_{dry}}\right] \times 100 \quad (1)$$

2.2.3.4. Film solubility. Film solubility of the samples was determined as the percentage of dissolved dry matter after immersion in water according to the previous methodology (Orsuwan et al., 2016). For this, film samples of 3 cm × 3 cm size were cut and dried at 60 °C for 24 h and the initial dry weight was determined (M_i). Then, the film samples were immersed in 30 mL distilled water with mild shaking for 24 h. Then the samples were removed and dried at 100 °C for 24 h to determine the undissolved final dry weight (M_f). The film solubility was calculated using Eq. (2)

$$FS = \left[\frac{(M_i - M_f)}{M_i}\right] \mathrm{X}\ 100 \quad (2)$$