Comparative analysis of bacterial cellulose based polymeric films for food packaging

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Abstract. The excessive use of petroleum based packaging material has done enough harm to this planet. Largely to deal with this catastrophic cause, the scientific community has shifted towards the biopolymer based packaging resources. Bacterial cellulose (BC) is an edible packaging material but lacks the thermoplastic nature for wider application. In our present study we have integrated BC with carboxymethyl cellulose (CMC) and polyvinylpyrrolidone (PVP) to prepare polymeric films: PVP-BC and PVP-CMC-BC. The biopolymer, BC is hydrolyzed using an ultrasound treatment and used as an additive. Morphological, structural, rheological and water vapor permeability analysis were performed for the films. PVP-CMC-BC films has better thermal stability than PVP-BC films. Results from water vapor permeability analysis also suggest lesser penetration of oxidative degradation causing gasses like oxygen through PVP-CMC-BC films. Thus, it can be concluded that the polymeric film PVP-CMC-BC is appropriate for fresh fruits and vegetables for enhancing their shelf life. Further, PVP-CMC-BC can be recommended for its use as a food packaging biomaterial/film.

INTRODUCTION

The environmental concern for the soil and water pollution in the last few decades has raised interest of the scientific community for an alternative eco-friendly packaging material. Biopolymers has emerged as an important alternative material to the conventional plastic due to their abundancy in nature, low material cost, eco-friendly, biodegradability and bio compatibility. Packages composed of biopolymers also have an excellent selective barrier properties which prohibits the entry and growth of microbial contamination in the packaging environment. Apart from extending the food shelf life, biopolymers are also good integrating agent with different other active packaging copolymers and additives like antimicrobial agent, antioxidants, nutrients, color components, oxygen scavengers, lubricants, nucleating agents, light stabilizers, blowing agents, plasticizers, antifogs, slips and antistats (1).

Cellulose from microbial origin has already been established as a multifunctional biopolymer for its purity, water holding capacity, biocompatibility and biodegradability. Bacterial cellulose (BC) is secreted by the bacteria as an extracellular polysaccharide protective layer, which after treatment has also been utilized as an edible package. BC has also been applied in the production of paper and paper products, apart from using as wound dressing material. Since BC lacks the sealing ability, in our study we have to added thermoplasticity to BC filmswith the integration of other biodegradable and biocompatible copolymers PVP and CMC (Fig. 1). The evaluation is done on the basis of their morphological, rheological and barrier properties.

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MATERIALS AND METHODS

Materials

PVP was procured from Sigma Aldrich, USA and CMC was purchased from Sinopharm Chemical Reagent Co. Ltd. Polyethylene glycol (PEG) and Agar were provided by Fluka, CZ. Glycerine (Gly) was purchased from Lach-Ner, CZ. Sodium hydroxide (NaOH) were bought from VWR chemicals, CZ.

Methods

Production and cleaning of Bacterial Cellulose (BC)

The BC was produced as per the protocol followed in our previous work (2). To mention in brief, 100 mL H.S culture medium was inoculated with 5 mL H.S inoculum having 5 loops of bacterial culture, incubated for 3 days at 30°C. The 100 mL cultures were in turn incubated for 15 days at 30°C. The BC produced after 15 days were collected and treated with 0.5N NaOH, followed by repeated wash with distilled water until neutral pH.

Hydrolysis of BC

The BC was hydrolyzed using ultrasound treatment as per the method mentioned by Bandyopadhyay et al. (2). The hydrolyzed BC particles were measured in a Zetasizer of average size of 209 ± 18 nm.

Preparation of neat BC film and hydrogels (using hydrolysed BC)

The BC film was casted utilizing 100 g of hydrolyzed BC in a silicone tray for 2 days at 50°C. The PVP-BC hydrogels were prepared by mixing the hydrolyzed BC with PVP, PEG, Agar and Glycerin in the percent ratio 0.66: 0.66: 1: 1: 1 (dry weights) in 150 mL water. PVP-CMC-BC hydrogels were also prepared in a similar fashion by mixing PVP, CMC, BC, PEG, Agar and Glycerin in the percent ratio 0.66: 0.33: 0.33: 1: 1: 1 (dry weights) in 150 mL water. The physical cross linkage in the hydrogel (PVP-BC) is formed by exposing the mixture to 15 bar pressure and 121°C for 35 minutes. After the treatment the mixtures are poured in polyvinyl alcohol plates (with a dimension of 25 cm x 25 cm) and allowed to cool, then incubated for 48h at room temperature to dry.

SEM study

The morphological studies of the transverse-section of the samples were analyzed under a field emission scanning electron microscope (Nova NanoSEM™ by FEI™, CZ s.r.o, Brno). The samples were gold coated for 60 sec at 30 mA in SC7620 Mini Sputter Coater**(**Quorum Technologies Ltd, UK**).** The micrographs were taken under 1000x, magnification. The operating voltage was 5 kV.

IR analysis

Fourier transfer infrared spectra analysis was done using Nicolet iS5 (Thermo Scientific,USA) in ATR mode. The scans were performed between infrared regions of 2000 to 800 cm^{-1}, with an average from 64 scans.

DMA quantification

The DMA analysis was performed in dynamic oscillatory mode using DMA Q-800 (TA instruments, USA). The films were cut in a dimension of 30 mm length and 7 mm width. The thickness of BC film and PVP-BC hydrogel film were 0.02 mm and 0.12 mm respectively. The temperature range was between -25 °C to 100 °C with a heating rate of 3 °C/min. The frequency and the oscillatory amplitude for the experiments were maintained at 1 Hz and 10 um respectively.

Analysis of water vapour permeability

The water vapour permeability (WVP) was measured according to ASTM E96-00 method. The cup was filled with silica gel within 6 mm of the samples. The orifice of the cup or the test area of the samples was 9.42 cm^2. The set up was placed inside a climate chamber for 24 hrs with air velocity of 0.25 ms^{-1}, 20 °C temperature and 90 ± 2 % relative humidity.

RESULTS AND DISCUSSION

Morphological analysis

In contrast to the PVP-BC hydrogels, PVP-CMC-BC film is more translucent (Fig. 1). This blurriness of the PVP-CMC-BC film has its advantages over the other two films. The lower transmittance of light will protect the food from photo oxidation. PVP-CMC-BC films are more see through than the pure BC films but more yellowish than the PVP-BC.

Figure 1 (d-f) depicts the detail surface view of the samples under scanning electron microscope. It is evident from Figure 2 that all the samples have different topologicalarrangement. Thus, it is also apparent that the addition of other co-polymers to BC has resulted in diverse morphological features. These structural differences may attribute to the varied mechanical properties of the films and hydrogels.

Structural analysis

Fig. 2d shows the FTIR spectra of BC films and BC based hydrogels. The characteristic peaks assigned to BC found in all the samples can be ascribed as follows: 1146-1160 cm^{-1} for asymmetric stretching of (C-O-C) bond or CH deformation, 1111 cm^{-1} for stretching of (C-C) ring in polysaccharides or cellulose and 1059 cm^{-1} for C-O bond stretching (2). Moreover the distinguishing peaks for PVP – CMC based hydrogels can be seen in spectrum for PVP-BC and PVP-CMC-BC: 1285 cm^{-1} for C-N stretching vibration, 1654 cm^{-1} for C=O vibration and 1062 cm^{-1} for 1,4-β-D-glucoside stretching vibration (2).

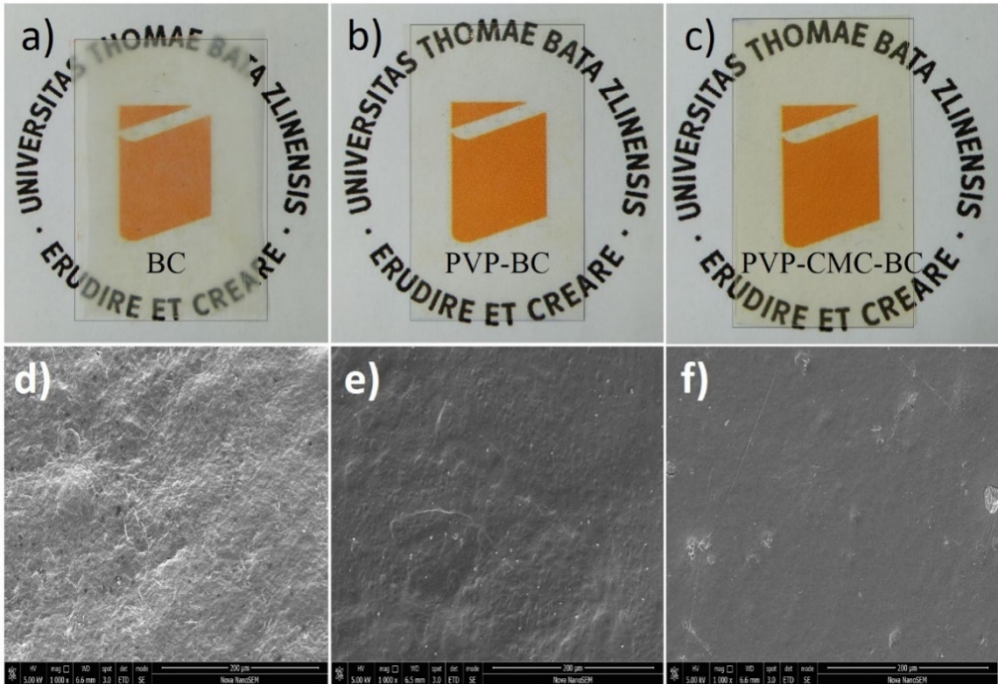

FIGURE 1. Physical appearance (a-c) and SEM (d-f) surface images of films a) BC b) PVP-BC c) PVP-CMC-BC d) BC films SEM e) PVP-BC SEM films and f) PVP-CMC-BC films SEM

Rheological properties

The viscoelasticity of the films was compared under varying temperatures and carried out by dynamic oscillatory experiments at 1 Hz. The temperature dependent curves for elasticity (storage modulus); viscosity (loss modulus) and damping properties (tan δ) are showed in Fig. 2 (a-c). It is evident from the graphs that PVP-BC has a wider deformation range than PVP-CMC-BC (Fig 2a). During the final use of the PVP-BC films the temperature region ranging from 15-35 °C (and higher) is not suitable for larger deformation, since tan delta raise lies in that region. The higher tan δ values for PVP-CMC-BC signifies it ability to dissipate more absorbed energy and giving more cushioning effect to the packed items (Fig 2c). The reason behind the loss of elasticity in the BC film with incorporation of the PVP and CMC may be due to the blocking of the intramolecular hydrogen bonds, the bonds which mainly attributes to the elastic nature of the BC (3).

Barrier properties

The water vapor permeability (WVP) is an indirect assessment of the porosity in the films. Figure 2e presents the water vapor permeability of the two films. Water vapor passes through the micro pores present in the structure of the films. The PVP-CMC-BC film has less micro pores than the PVP-BC film. The addition of additives to the BC has resulted in the formation of cross linking structure with bigger pores in surface than BC film. Since, the transmission of water vapor across the film occurs by the process of absorption and de-absorption of water molecules by the hydrophilic groups in the films, depending on a vapor pressure difference on either side of the film. Thus the presence of hydrophilic components in the hydrogel can also increase its WVP values in comparison to BC film. Based on the result PVP-CMC-BC film is more suitable for food packaging since less oxygen will pass through the pores thereby curbing the oxidative degradation and microbial spoilage of the vegetables packed inside.

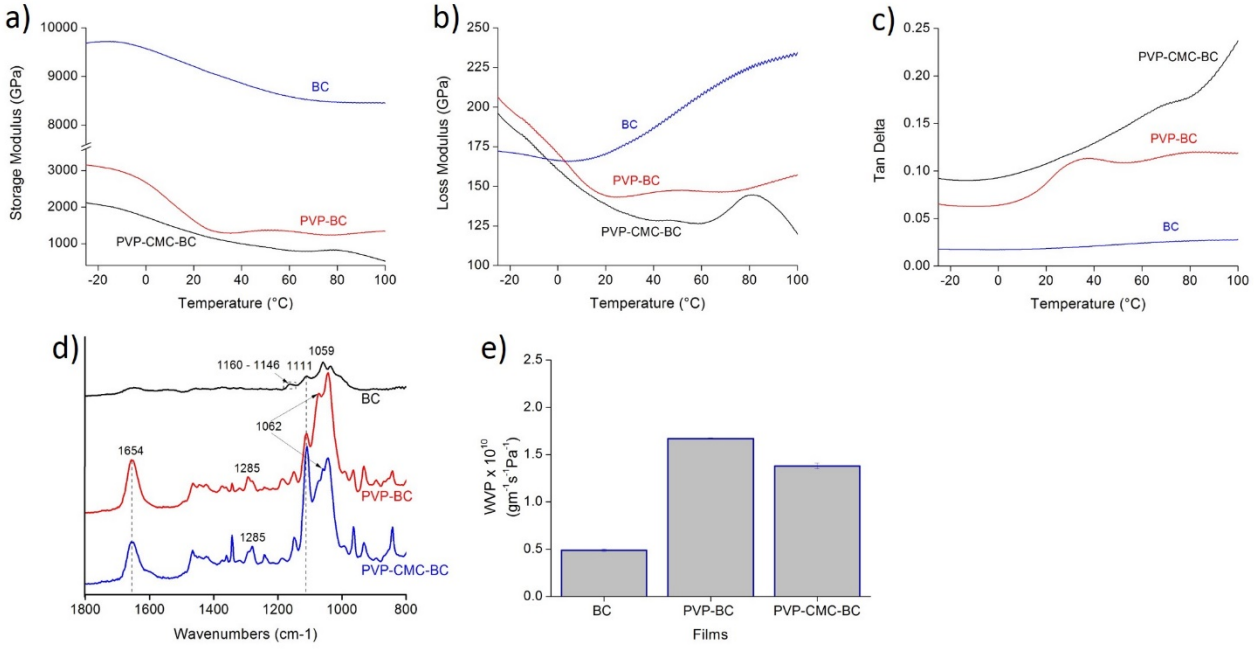

FIGURE 2. Effect of temperature (a-c) on storage modulus (a) loss modulus (b) and tan delta (c); FTIR spectra (d) and Water vapor permeability of the films (e)

CONCLUSIONS

The DMA and WVP analysis of the films suggest that PVP-CMC-BC film is best suited for food packaging application due to its better damping and barrier properties. It is also important to note that further analysis of color, chroma, lightness and resist to direct pull are important aspects of these packaging materials, to be done in future.

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