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PVP/PVA blended hydrogels as a biofilm for use in food packaging applications

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ABSTRACT

Bio-films have been produced that attract attention with their functional behavior among conventional food packaging materials of bio-based polymer blends. The physical and morphological properties of copolymeric biofilms have been extensively investigated. Biodegradable polymer and copolymer films were produced by in situ polymerization technique and prepared as solution casting. The strong water absorbency of polyvinyl alcohol and the antimicrobial property of polyvinylpyrrolidone are combined in a single material. Structural and morphological properties of the films were characterized by Fourier-Transform Infrared Spectroscopy and Scanning Electron Microscope analysis. These results show that the films obtained can be used as an environmentally friendly bio-based polymer blend packaging material to extend the shelf life of food products.

Keywords: Food packaging, Bio-film, Hydrogel, Polymer

Introduction

Hydrogels can offer new opportunities for the design of efficient packaging materials with desirable properties (i.e. durability, biodegradability, and mechanical strength). It is a promising and emerging concept, as most biopolymer-based hydrogels must be biodegradable so they can be considered alternative eco-friendly packaging materials. In food packaging systems, hydrogels have a great potential to be used as covering and carrier materials. Nowadays, biopolymer-based hydrogels have been preferred for food packaging. Hydrogels that can adsorb more than 100% and up to thousands of times their dry weight in water are called superabsorbent hydrogels (Batista et al., 2019; Feng et al., 2014). The main role of hydrogels in the food packaging system is humidity control inside of a packaging container. The activity of hydrogels in these systems can be given as mechanical resistance, swelling behavior potential, and moisture-holding capacity (Chen et al., 2016; Guilherme et al., 2015; Gulrez et al., 2021; Sro et al., 2016). Because of these properties, hydrogels are interesting for various industrial fields. They contribute to the development of common applications such as cosmetics, wastewater treatment, tissue engineering, drug release, biosensing, agriculture, and biomedicine, generally, hydrogels are produced from synthetic compounds and their polymer matrices are linked predominantly by chemically crosslinking. Compounds commonly used in the literature; polyacrylamide, poly (sodium acrylate), poly (acrylic acid), polyvinylpyrrolidone (Kabiri et al., 2011; Ullah et al, 2015), and bio-based and biodegradable polymers. In most of the studies on food packaging, hydrogels have been prepared and used in film-shaped forms. While producing hydrogel films, the most important feature desired in food packaging applications is the absence of chemical crosslinkers (Kalia, 2016). Chemical crosslinkers may show toxic properties in their nutritional value. Generally, hydrogels obtained using PVP (polyvinylpyrrolidone) and PVA are transparent, biodegradable, flexible, hydrophilic, and permeable. The most important active application of hydrogels in food packaging systems is to control the moisture generated by meat products, fresh fruits, vegetables, and other food products with higher water content (Bodbodak & Rafiee, 2016). Among various polymers, Poly Vinyl Alcohol (PVA) is widely used as a film-forming polymer with highly flexible, emulsive, and adhesive properties. It has been reported in previous studies that PVA improves its mechanical and antimicrobial properties to take advantage of its wide applications (Jayakumar et al., 2019). Polyvinyl alcohol (PVA) is a hydrophilic and non-toxic polymer with excellent film-forming, emulsifying, and adhesion properties along with high tensile strength and flexibility (Yuan et al., 2015). However, the major disadvantage of PVA is the moisture-related mechanical property changes that greatly limit its application (Jayakumar et al., 2019). Because of that, in this study, the physical properties of PVP were used to eliminate the disadvantage. Due to the chemical nature of each type of food, undesirable effects of ambient change require pH change indicators to be included in food packaging. This also increases consumer trust as it ensures the safety of the product (Park, 2016). At this point, hydrogels also act as smart materials, due to their responses in different pH environments. To examine the food packaging system in terms of waste management, biodegradable food packaging provides an advantage for existing packaging that cannot be recycled and degraded (Dilkes-Hoffman et al., 2018). The biodegradability problem of common plastic food packaging is a global environmental problem (Bergmann, 2015). This problem will continue to increase as urbanization and dietary change in developing countries lead to an increasing global dependence on packaged foods (Dilkes-Hoffman et al., 2018). Another attractive aspect of biodegradable food packaging is that it can expand waste management options for materials that cannot be easily recycled (Brine & Thompson, 2010; Volova et al., 2010). The desired improvement in food packaging systems is the replacement of non-biodegradable petroleum-based polymers with environmentally friendly bio-based polymeric hydrogels materials that also have a longer food shelf life (Haghighi et al., 2020; Kanatt et al., 2012). PVA is a synthetic, low-cost, non-toxic, and water-soluble polymer with the excellent film-forming ability, which has been commercially obtained from the hydrolysis of polyvinyl acetate. Although PVA is a synthetic material, it has been reported to be biodegradable. This defines PVA as a biodegradable polymer. High tensile strength, flexibility, gas barrier properties, and good resistance to acid/alkali environments are among the specific features of PVA (Aloui et al., 2021). PVA can easily form mixtures with hydrophilic polymers. Since PVP also has excellent physiological compatibility, when these two polymers are mixed, the easy interaction between PVA and PVP is expected to occur through intermolecular hydrogen bonding between the hydroxyl group of PVA and the carbonyl group of PVP (Mahdavinia et al., 2009; Sunitha & Jeba, 2017). Copolymer films resulting from the high compatibility of PVP and PVA show a homogeneous structure. In addition, with the PVA/PVP blend, the single film production cost is reduced and the mechanical properties and stability of the blend are improved (Haghighi et al., 2020). On the other hand, in 2003, PVA has been evaluated for safety by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (Haghighi et al., 2021; WHO, 2004) and it has also been confirmed for packaging of the meat and poultry products by the

USDA (Bellelli et al., 2018; Kanatt et al., 2012). Polyvinylpyrrolidone (PVP) as a hydrophilic synthetic polymer was discovered in 1939 (Fischer, 2009; Gregorova et al., 2015). PVP has been used as a binder and stabilizer in the cosmetic, pharmaceutical, and food industries (Keipert & Voigt, 1979). It is a water-soluble polymer with good biomedical properties but exhibits poor mechanical properties (Saha, 2014; Shkolnik, 1992). Due to its water solubility and film-forming ability, PVP can be mixed with other polymeric or cellulosic materials and form films with new improved mechanical properties (Wang et al., 2007). However, the water-soluble nature of PVP makes it impossible to use PVP directly as a packaging material (Li et al., 2020). This study includes the production of PVP/PVA blends as a bio-film with desired properties in different ratios (0:100; 25:75; 50:50; 75:25 and 100:0) for food packaging applications. Among the study, physicochemical, microstructural, physical, mechanical, and water barrier properties for food packaging applications were evaluated. PVP and PVA polymers have interacted with each other through hydrogen bonding. This article reports the production of synthetic biopolymer-based (polyvinylpyrrolidone (PVP)) and PVA as a novel copolymeric hydrogel biofilm and its physicochemical property under controlled environmental conditions.

Materials and Methods

Method

The composite biofilms were produced by mixing PVA and PVP solutions in different amounts by the solution casting method. Dry hydrogel films were prepared by solution casting method and named "PVP/PVA composite biofilms".

Materials

Polyvinylpyrrolidone (PVP) average molecular weight of 40,000 was purchased from Merck. Powder Poly (vinyl alcohol) PVA with an average molecular weight of 89,000-98,000 was purchased from Sigma-Aldrich. Both polymer solutions produced in this study were prepared using distilled water.

Preparation of the PVP/PVA Composite Biofilms

10% PVA solution was stirred at 80°C for 4 hours. For the 10% PVP solution, the temperature was 60°C and the mixing time was 2 hours. 10% polymer solutions were blended in certain amounts (0:100; 25:75; 50:50; 75:25 and 100:0) and stirred for more 1 hour at 60°C. PVP/PVA blend was poured into 60x15 mm glass petri dishes in equal volumes. The solutions were left to dry for a week under room conditions. After, the film-formed polymers were separated from the glass petri dishes with the help of a micro spatula and forceps without any damage. The mechanism of these interactions is given in Figure 1.

Characterization

Chemical bond properties of PVP/PVA composite biofilms obtained at different ratios were elucidated by FTIR analysis. Spectrums were taken in ATR mode with Perkin Elmer, Spectrum 100 device in the range of 4000-400 cm^{-1} wavenumber at $4cm^{-1}$ resolution. The morphological properties of the films were investigated in Carl Zeiss, Supra 40 VP FESEM device at 15 kV voltage value at different magnifications. The conductivity of the films was achieved by platinum coating with the Qourum DC Sputter device. The transparency properties of the films are demonstrated by photographing the text under the film.

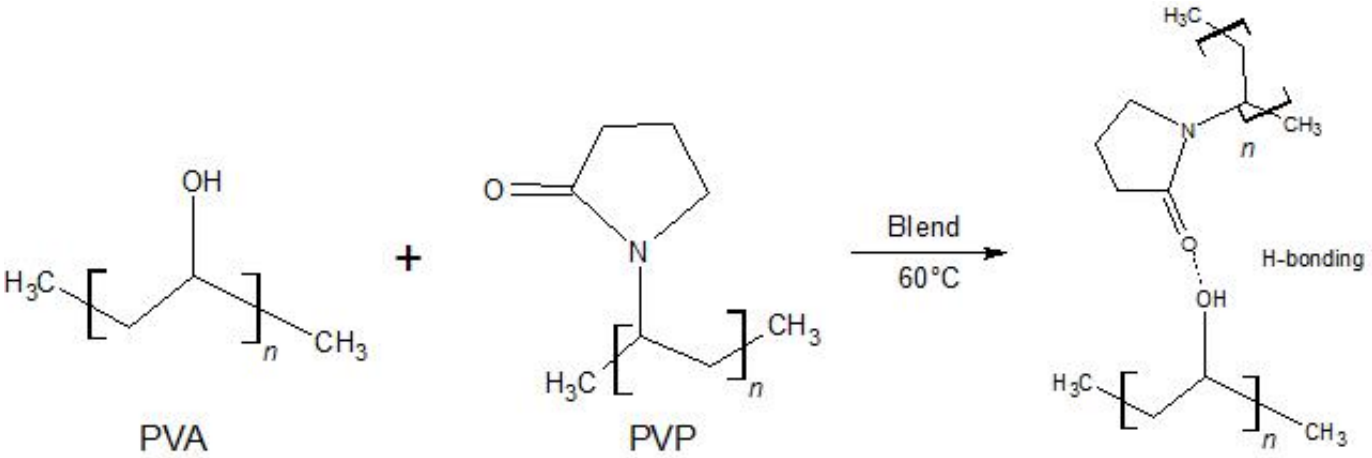

Figure 1. Schematic illustration of the PVP/PVA mechanism

Results and Discussion

FTIR Analysis

The Fourier transform infrared (FTIR) spectra were characterized to confirm the presence or absence of the various vibrational bands in PVP/PVA blended biofilms. The results obtained are given in Figure 2. In the samples with high PVA content (75% and 50%), the hydroxyl groups (O-H) of PVA were seen as wide and broadband in the 3270cm^{-1} region (Portillo-Rodríguez et al., 2021). Wide flat peaks were observed in PVP/PVA (25:75%wt) (black line) and PVP/PVA (50:50%wt) at 3267 cm^{-1} and 3278 cm^{-1}, respectively, and PVP/PVA (75:25%wt) (red line) was seen as a narrow peak at 3356 cm^{-1}. While the asymmetric stretch bands of the C-H groups were observed at 2943 cm^{-1} in the black and blue lines (Portillo-Rodríguez et al., 2021), they lost their intensity in the region enclosed in the circle which the blend containing 75% PVP shown in the red line. When the amount of PVP in the mixture increased to 75%, the strong peak at 2943 cm^{-1} disappeared. The short-intensity peak PVP/PVA (75:25 %wt) observed at approximately 2158 cm^{-1} in the region between 1900 cm^{-1} - 2250 cm^{-1}, which is enclosed in the circle, is not seen in the (red line). In the region marked with a rectangle in the range of 863 cm^{-1} – 1007 cm^{-1}, the moderate-intensity 920 cm^{-1} band completely disappeared in PVP/PVA (75:25 % wt) (red line). In all three samples, plane bending of CH-OH groups and CH_2 bending vibrations were observed at 1640 cm^{-1} and 1420 cm^{-1}, respectively. The band at 1079 cm^{-1} corresponds to the C–O stretching vibration at all 3 samples (Portillo-Rodríguez et al., 2021). In addition, characteristic peaks of PVP, carbonyl, and –CN groups were observed at 1650 cm^{-1} and 1300 cm^{-1}, respectively (Bandatang et al., 2021).

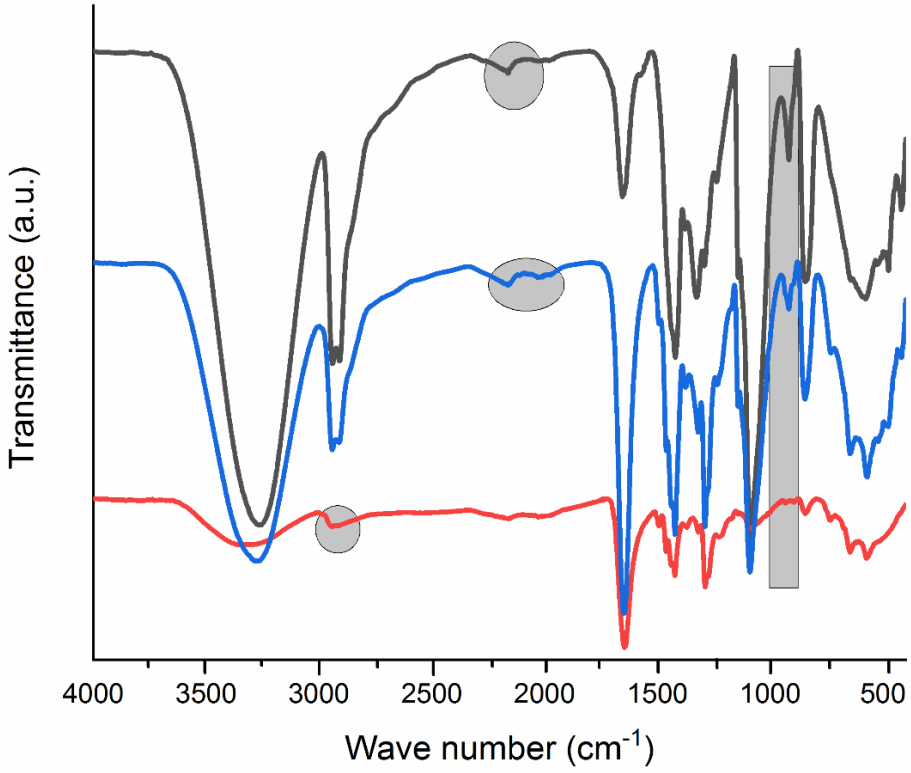

Figure 2. FTIR spectrums of PVP/PVA (25:75 % wt) (black line); PVP/PVA (50:50 % wt) (blue line); PVP/PVA (75:25 % wt) (red line).

SEM Results

As the PVP ratio in the blends increased, the surface morphology of the films changed from homogeneous to heterogeneous. The porosity on the film surfaces was increased through the PVP additive. With increasing porosity, the mechanical strength of the films decreased and the transparent property of the films was lost. The film-forming ability of PVA decreased with increasing PVP amount in composites. Figure 3 shows SEM images of plain PVA and plain PVP was n at 500x and 2000x magnification, respectively. As seen in Figure 3(a2 and b2), plain PVP which was obtained without the use of crosslinkers did not show film properties. While the homogeneous surface of PVA was evident in both magnifications, the film features of plain PVP were not observed.

In Figure 4, the morphological differences were seen with the amount of PVP in the blend increasing from left to right. In Figure 4(c), heterogeneous pore distribution on the surface of the film obtained by 75% PVP and 25% PVA blend is seen.

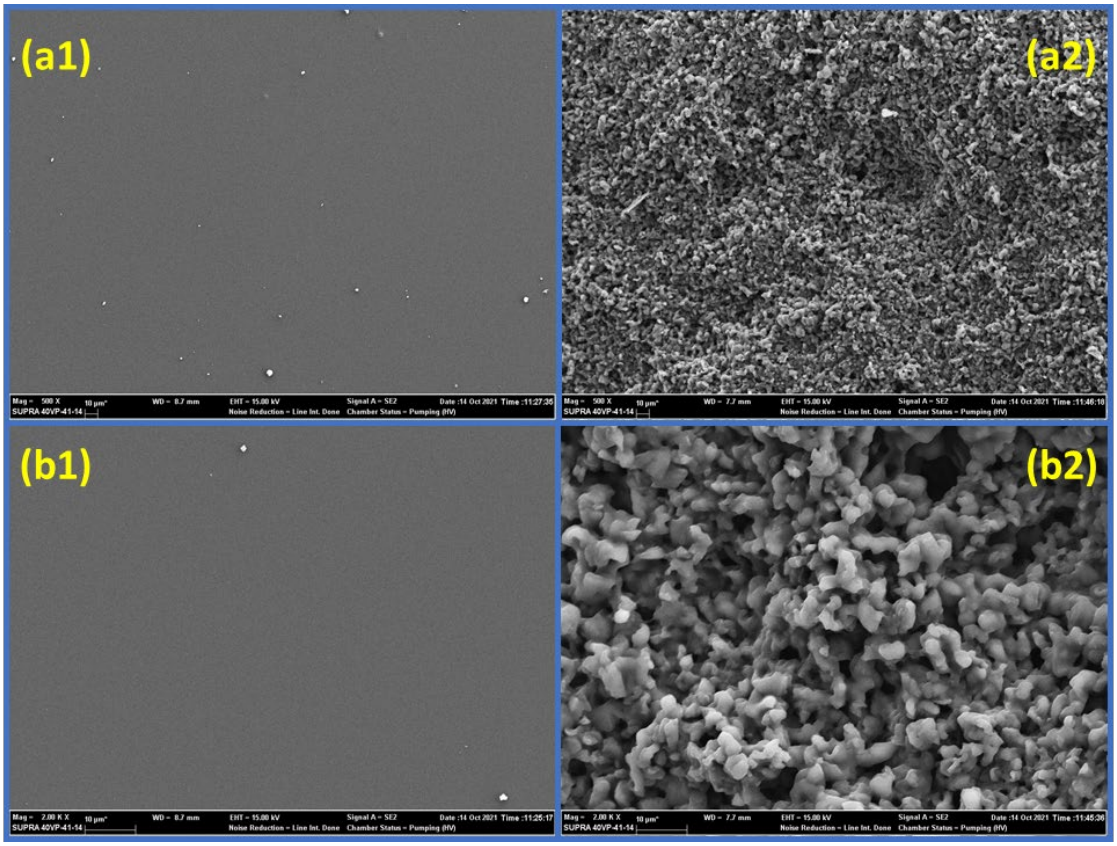

Figure 3. SEM images of plain PVA and PVP film at 500x magnification (a1 and b1, respectively); at 2000x magnification (a2 and b2, respectively).

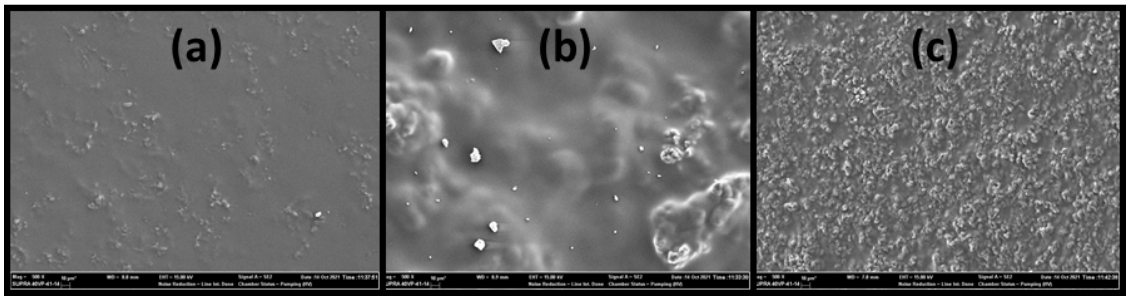

Figure 4. SEM images of (a) PVP/PVA (25:75 %wt); (b) PVP/PVA (50:50 %wt); (c) PVP/PVA (75:25 %wt) at 500x magnification.

Transparency Tests

As seen in Figure 5, the visibility of the text placed under the obtained films was photographed to determine the transparency. It is seen in Figure 5(a) that the 100% PVA film is completely transparent. On the other hand, increased PVP additive in the blends engendered opacity in the films. Fig. 5(d) showed that the PVP/PVA with 75% PVP additive has lost its film form. As the amount of PVP increased in the films, the surface morphology lost its elasticity due to the increased heterogeneous porosity, as seen in the SEM images (Fig.4).

Conclusion

PVA / PVP hydrogel films are transparent, flexible, and exhibit good mechanical properties. These biopolymer-based hydrogel films were produced without the use of toxic cross-linking agents. Significant differences of functional groups in FTIR spectra, and morphological evaluations of films obtained by SEM analysis. Composite biofilm with 25:75 ratios of PVP and PVA shows the best mechanical properties among all test specimens (i.e. 0:100; 25:75; 50:50; 75:25 and 100:0). Therefore, 25:75 %wt. PVP/PVA composite biofilm has been recognized as a useful food packaging material and further experiments with this particular composite biofilm are targeted.

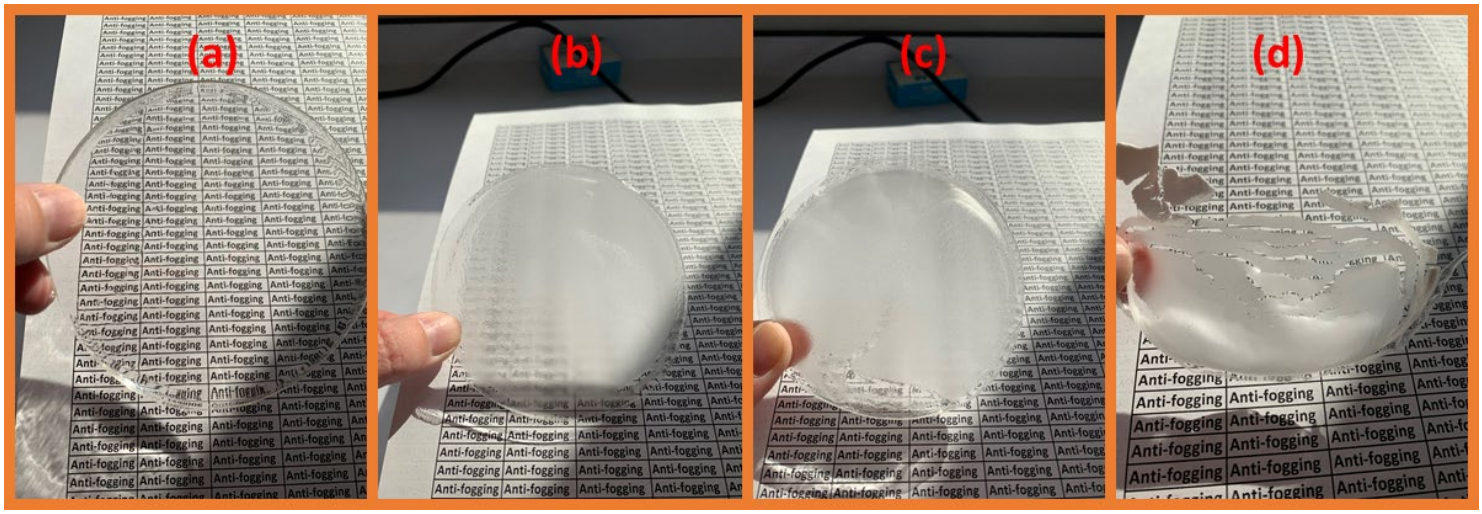

Figure 5. Photograph of (a) plain PVA film (b) PVP/PVA (25:75 %wt.); (b) PVP/PVA (50:50 %wt.); (c) PVP/PVA (75:25 %wt.)

Compliance with Ethical Standard

Conflict of interests: The author declares that for this article they have no actual, potential, or perceived conflict of interests.

Ethics committee approval: The author declares that this study does not include any experiments with human or animal subjects; therefore, no ethics committee approval is needed.

Funding disclosure: -

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Disclosure: -

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