



Solvent strength and biopolymer blending effects on physicochemical properties of zein-chitosan-polyvinyl alcohol composite films

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ABSTRACT

The aim of this research was to optimise and develop edible films made from zein (ZN), chitosan (CS), poly(vinyl alcohol) (PVOH) and poly(ethylene glycol) (PEG400) using Box Behnken Design (BBD). Four factors *viz.* ZN:CS ratio (w/w) (1:3, 1:1, 3:1), PVOH wt.% (in dry film) (0, 0.25, and 0.5), PEG400 wt% (0.13, 0.21, 0.31) and ethanol (40–80% v/v in water), were investigated. The effects on tensile strength (TS), Young's modulus of elasticity (EM), elongation at break (%EAB), water vapour permeability (WVP), solubility in water (Ws), and optical properties were evaluated. The films were further characterised using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), x-ray diffraction (XRD) and swelling behaviour. SEM micrographs showed that high levels of ZN and PEG400 resulted in rough surfaces with major film defects, but these were minimised at high levels of CS or PVOH. XRD analysis indicated potential interactions through hydrogen bonding between the polar groups of ZN and hydroxyl moieties of PVOH and CS. Stress-strain curves showed that ZN and CS composite films possessed high TS but were brittle. Incorporation of PVOH increased the ductility of the composite films. Optimum films were obtained using ZN/CS/PVOH/PEG400 ratio of 0.35/0.29/0.13/0.23 (wt.%) and 60% ethanol, giving dry state properties of TS, EM, and EAB as 24.21 MPa, 356.62 MPa and 84.23%, respectively. This study demonstrated the influence of critical interactions between solvent features (polarity) and interfacial properties of ZN, CS, PVOH and PEG400. The observed crosslinking behaviour suggested the effectiveness of blending technique in improving the compatibility of biopolymers and overall functionality of edible films.

1. Introduction

Protein-polysaccharide blends or combinations with biosynthetic polymers have increasingly attracted attention for biomaterial applications (Escamilla-García et al., 2013; Sun, Dai, & Gao, 2017a; Yuan et al., 2016). The functionality and cross-linking mechanisms for proteins-polysaccharides composite films have been reviewed (Azeredo & Waldron, 2016). Among the proteins used in the formation of edible films, zein (ZN), a prolamin protein from the corn endosperm is an interesting material due to its amphiphilicity and self-assembly capabilities through hydrophobic/hydrophilic interactions (Shukla & Cheryan, 2001). Owing to the high proportion (50%) of non-polar amino acid residues, zein does not dissolve in water but can be solubilised in acetone, ethanol, anionic detergents and high concentration of urea or alkali (pH ≥ 11) (Shukla & Cheryan, 2001). It is highly regarded for its potential in film formation (Wang & Padua, 2010), development of delivery systems (Liang et al., 2015) and fabrication of

fibres and fabrics (Selling, Woods, & Biswas, 2011). Compared to other proteins, zein films present better water vapour barrier properties (Ghanbarzadeh & Oromiehi, 2008). However, they are constrained by fragility and poor extensibility (Argüello-García et al., 2014), limiting their use in tension-based applications.

Chitosan (CS), a copolymer of α -(1 → 4) glucosamine, (C₆H₁₁O₄N)_n, is a cationic polysaccharide obtained by alkaline deacetylation of chitin. Besides biodegradability and renewability, its biocompatibility and non-toxic features permit applications in the food industry, particularly in the formulation of food materials, films and coatings (Escamilla-García et al., 2013). The presence of amino groups on the structure of chitosan enables it to undergo ionic or hydrophobic modifications under varying pH (Sun, Zhang, & Chu, 2007). As a widely investigated material for edible film production, notable properties of its products include clear, flexible and robust film materials with an adequate oxygen barrier and may possess antimicrobial properties. Like zein films, chitosan films lack flexibility due to high brittleness and

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exhibit weak water resistance characteristics (Suyatma, Tighzert, & Copinet, 2005).

The weak structural integrity and poor functionality of ZN and CS have challenged the development of edible and biodegradable films. Modification approaches, including chemical and physical techniques, continue to remedy the shortcomings of the food contact materials through various crosslinking mechanisms (Azeredo & Waldron, 2016). Attempts by previous studies to involve ZN/CS blends in the formulation of edible films (Cheng, Wang, & Weng, 2015; Escamilla-García et al., 2013) or delivery systems involving nanoparticles (Liang et al., 2015) showed that additional cross-linking techniques such as the use of dicarboxylic acids or heat were required for improvement of mechanical and functional properties. However, the continued use of chemicals and energy inefficient modification techniques render these materials less attractive for food applications (Ashogbon & Akintayo, 2014). A major drawback to the use of chemicals is the occurrence of undesired changes and potential toxic effects (Sun et al., 2007). In addition, the majority of chemically and physically modified films and coating still exhibit poor mechanical and barrier properties (Azeredo & Waldron, 2016).

Poly(vinyl alcohol) (PVOH) is a biodegradable and non-toxic biosynthetic polymer (Chiellini, Corti, D'Antone, & Solaro, 2003) used as an ingredient in the food and pharmaceutical applications, for example, in the production of coatings and films (Nakano et al., 2007; Wright, Andrews, McCoy, & Jones, 2013). The linear carbon backbone of PVOH is rich in hydroxyl (-OH) groups making it highly hydrophilic and dispersible in water. The chemical structure of PVOH permits various reactions through cross-linking between the -OH groups and other polar molecules to form entanglements and aggregates (Bercea, Morariu, & Teodorescu, 2016). Its excellent film forming ability has been used in combination with numerous biopolymers to enhance their mechanical properties and chemical resistance (Senna, Salmieri, El-naggar, Safrany, & Lacroix, 2010; Srinivasa, Ramesh, Kumar, & Tharanathan, 2003).

Although there have been wide applications of ZN/CS blends in the formulation of delivery systems and nanoparticles (Luo, Zhang, Cheng, & Wang, 2010; Müller et al., 2011), applications in edible film formulations have only recently emerged (Cheng et al., 2015; Escamilla-García et al., 2013, 2017). Available literature shows that these materials are characterised by low TS and elastic modulus (5.4–5.6 MPa and 65 to 7 MPa respectively) (Escamilla-García et al., 2013), which may pose a challenge in food applications. Similarly, investigations involving ZN/PVOH suggested that unmodified blends could not be handled for food applications (Lacroix et al., 2014; Senna et al., 2010). Blending is a promising technique for improvement of functional properties of protein-polysaccharide edible films. The main advantages of the technique are the utilisation of distinct functional properties of each component to improve the overall functionality of the final product (Senna et al., 2010). Additionally, plasticization of biomacromolecules is an established and acceptable approach to alter their physicochemical properties and functionality during application. PEG400 is a widely investigated plasticizer for various food and pharmaceutical applications. It is a water-soluble, non-toxic and biodegradable synthetic polymer known for its colloidal stability and plasticising effects (Tillekeratne & Easteal, 2000).

To date, little is known concerning the functionality of ZN/CS/PVOH blends in composite film formulations or whether the use of plasticizers such as polyethylene glycol (PEG) 400 can mitigate incompatibility and general weaknesses of these materials for food applications (Escamilla-García et al., 2017; Senna et al., 2010). Initially, understanding the solvent properties of these combinations is essential since the solvent determines the unfolding and dispersion of macromolecular chains, whereas its removal accelerates molecular aggregation into ordered microphases (Wang & Padua, 2010). The phase behaviour properties of macromolecules during self-assembly are determined by the solution properties including ionic strength, pH and

the proportions of various compounds (Gaona-Sánchez et al., 2015). Therefore, varying the type and strength of the solvent can influence the microstructure and functionality of the formed aggregates (Wang & Padua, 2010).

The aim of this study was to evaluate the effect of blending using ZN:CS ratio, PVOH, PEG400 and the concentration of ethanol on mechanical and physicochemical properties of composite films. The optimisation approach used in this study enabled the understanding of the effects of individual factors on the physical characteristics of the films using scanning electron microscopy, which were then related to the tensile, water interaction and permeability properties. Changes due to cross-linking and inherent interactions were evaluated using differential scanning calorimetry, thermogravimetric analysis and X-ray diffraction.

2. Materials and methods

2.1. Materials

Corn zein (ZN) (Z 3625, molecular weight (M_w) 22–24 kDa) and 98% (w/w) protein, poly(vinyl alcohol) (PVOH) (M_w 89,000–98,000 Da, 99+ % hydrolysed) and polyethylene glycol (PEG400) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Chitosan (CS) (M_w 890 kDa, 91% degree of deacetylation (DD)) was obtained from Waseta Int'l trading company (Shanghai, China). Glacial acetic acid (Univar, USA) and ethanol (99.5%) (Anchor ethanol limited, Auckland, NZ) were of analytical grade. The biopolymer/biosynthetic polymers used in the study are Generally Recognized as Safe (GRAS) (U.S. code of federal regulations) (USFDA, 2018) under the sections; ZN (part 184.1984), CS (GRN 443) (FDA, 2013), PVOH (part 177). All reagents and chemicals were used as received.

2.2. Experimental design and optimisation

Film formulations were optimised to verify the synergistic influence of the variables using Box-Behnken experimental design (BBD). Four independent variables were fixed at three equidistant levels; ZN:CS ratio (X_1), (1:3, 1:1, 3:1), ethanol (X_2) (40, 60, 80% v/v), PVOH (X_3) (0, 25, 50% w/v), and PEG400 (X_4) (15, 30, 45% w/w of total solids). The number of experiments ($N = 27$) (Table 1) was determined by $N = 2k(k - 1) + C_0$ (where k is the number of factors and C_0 is the number of central points) (Yetilmezsoy, Demirel, & Vanderbei, 2009). The response variables were taken as the average values of tensile strength (TS) (Y_1), (MPa), Young's modulus of elasticity (EM) (Y_2) (MPa), elongation at break (%EAB) (Y_3), water vapour permeability (WVP) ($g \cdot mm/h \cdot m^2 \cdot kPa$) (Y_4), water contact angle (WCA) (Y_5) and solubility in water (Ws) (Y_6). Optical properties including; overall colour change (ΔE) (Y_7) and opacity (Op) (AU nm/mm) (Y_8) were also determined. Film preparation and response characterisation for each formulation type was independently repeated three times.

2.3. Preparation of film-forming solutions

Stock solution of CS (1.5%) (w/v) in 2% (v/v) acetic acid was prepared by stirring at 22 °C and 400 rpm for 12 h. PVOH, 10% (w/v) in deionised (DI) water was stirred (400 rpm) for 2 h at 75 ± 3 °C. ZN solution 1.2% (w/v) in 80% (v/v) ethanol-water solution was prepared by stirring (400 rpm) for 1 h at 22 °C. The solutions were equilibrated at 4 °C for 6 h then centrifuged (Beckman J-1, Beckman, USA) at $10,000 \times g$ and 4 °C for 15 min.

2.4. Film casting

Film forming solutions (FFS) were prepared by mixing the stock solutions as shown in Table 1. This was followed by stirring for 20 min and homogenisation at 8000 rpm for 2 min (IKA® T 50 ULTRA-

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