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Original Article

Preparation and Study of Physical Properties of Zein Based Composite Films as Food Coatings

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ABSTRACT

Background: Demand for degradable and biocompatible polymers is rapidly increasing, especially in the food packaging sector where it is highly encouraged by environmental management policies.
Methods: This study aimed to prepare zein/Montmorillonite (MMT) and zein/Poly (vinyl alcohol) (PVA) composite films by a high-power ultrasonic probe method for use as a food coating. The film was produced through solvent casting method. In all the films, glycerol and Polyethylene glycol were used to improve the fragility properties. The biodegradability, color characteristics and surface roughness of the films were evaluated.
Results: Based on the results of the statistical analysis, the clay dispersion method a, MMT and PVA content significantly affected the mechanical and properties of the composite films. The results showed that mechanical properties of the nanocomposites were improved in the presence of small amounts (up to 3%) of MMT, while increased MMT percentage in the micro composite films weakened the mechanical properties of these films. It was also found that the addition of MMT and PVA increased the porosity of the film. Therefore, the use of high-power sonication is a suitable method for producing protein-based nanocomposites with an exfoliated structure.

Conclusions: as the nanocomposite films of zein, zein-PVA and zein-MMT are highly biodegradable, natural and non-toxic, they are highly efficient in this field and can be used in food packaging.

Keywords: Composite, Food coating, Montmorillonite, poly vinyl alcohol, Zein.

1. Introduction

Natural Polymers, such as proteins, cellulose derivatives, starches and other gums have potential as packaging materials. Research on such edible film materials has been mostly related to using them for auxiliary packaging, such as moisture barriers between dough and toppings in foods (pizza and pies) [1]. zein is a Generally Recognized as Safe (GRAS) polymer approved by the U.S. Food and Drug Administration (FDA) for human applications such as Food coating [2]. Zein is a prolamine-rich protein that contains a high proportion of hydrophobic amino acids, proline, and glutamine. It is a protein found in proteinaceous bodies from the endosperm of corn kernels. This hydrophobic protein is widely used for films and coatings [3]. Corn zein protein coatings are used as oxygen and moisture barriers for nuts, candies and other foods. Corn zein films and coatings have relative insolubility in water, and they form strong, glossy films resistant to grease and oxygen permeation [1]. Reported zein films had oxygen permeability coefficients, under dry conditions (0% relative humidity), much lower than many commercial polymer films including low- and high-density polyethylene, polypropylene, and nylon-6. Reported zein films cast from a commercial zein solution had lower bursting strength but greater tear strength than commercial cellophane films [1].

Chen *et al.* [4] showed that the boosted bulk quality of zein films, particularly for thermal stability and flexibility, can be completed compositing with chitosan. Additionally, chitosan can suggestion potential antibacterial attributes for zein films to be used as antibacterial packaging materials, zein films were changed by a two-phase technique containing of combination with chitosan, performed via contact to cold plasma.

In a recent study, a simple antisolvent precipitation technique was used to fabricate zein colloidal FX-loaded zein-Cas nanoparticles at neutral pH. These results proved that nanoparticles could enable the application of FX in functional foods and pharmaceutical products [4]. In another study, release of lysozyme via the pliable zein–wax combination and the zein–fatty acid blend films were controlled by modification of hydrophobicity and morphology of zein films using combination and blend film making techniques [5]. Another review demonstrated that zein/SSPS nanoparticles have high potential to be used as nano delivery systems for bioactive combination [6].

Introduction of MMT combine with zein, zein/MMT nanocomposite nanofiber mats resulted in the improvement of the thermal stability and hydrophilicity for the zein [7]. Composites have better properties than pure materials, which is why MMT and PVA have been used in this study to improve the properties of zein.

2. Experimental

2.1. Materials

Zein, Glycerol, Polyethylene Glycol from Sigma, MMT from Zarin Dane, Ethanol 96% from Razi, PVA from Merck and other materials were provided from reputable companies.

2.2. Preparation of zein film

2 g of zein was poured into 10 ml of 75% ethanol solution at 50 °C. After homogenization of the solution, 0.03 g of glycerol and polyethylene glycol were added and stirred for 30 min. To make 10% MMT solution, 2 g of that material was poured into 30 ml of 75% ethanol solution and stirred for 15 min. The solution was then placed in an ultrasonic device for 5 minutes. To make PVA solution, two grams of this material was poured into 30 ml of 75% ethanol solution and mixed for 90 minutes. To prepare the final solution, some of the MMT or PVA solutions were poured into the zein solution and mixed for 5 min. They were then placed in an ultrasonic device for 2 minutes. Likewise, 0, 3, 5, 7 and 10% solutions of MMT and PVA were prepared [8].

2.3. Biodegradability

The films were cut to 2*2 cm and after weighing, they were immersed in 25 ml of

3% α-amylase (Bacillus sp. KR 8104) solution. α-amylase solution of Bacillus sp. KR-8104 was prepared using wheat bran by SSF (Solid-State Fermentation) method. In this method, fermentation was performed in a glass column reactor at 37 °C, air flow rate was 0.1(L/min) and initial bed moisture was 64% (w/w) [9]. The container containing the solution was incubated in a shaker incubator (120 rpm, 30 °C) for 36 hours. Finally, the enzyme digestibility was evaluated [10].

2.4. Color features

Composite films of zein, zein-PVA and zein-MMT were exposed to light and the results were qualitatively evaluated.

2.5. Surface morphology

The surface morphology of the film was studied using confocal microscopy. A 2 x 2 piece of zein, zein-PVA and zine-MMT films were mounted on a stand and the surface of the films was imaged using a 20X lens and the results were reported.

3. Results

3.1. Biodegradability

The test showed that the films were highly degradable in α-amylase solution. Zein and zein-PVA films were completely degraded and zein-MMT films degraded about 70-80 percent. As MMT increased, the degradability decreased because ceramic materials such as MMT were not biodegradable.

3.2. Color features

Color and transparency are two of the most important features of a film or cover that play an important role in attracting customer opinion. Generally, the more transparent a biopolymer film is and the more similar it is to synthetic polymer films, the easier it will be to commercialize [11].

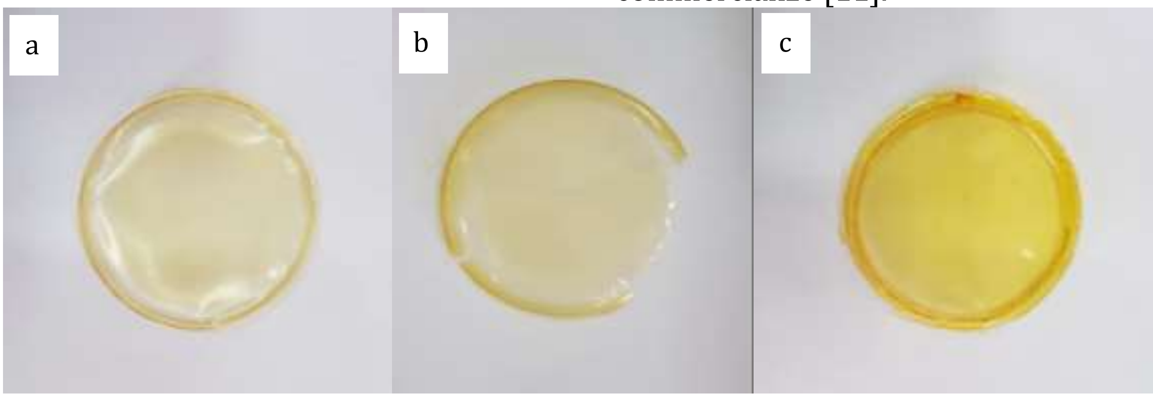

Figure 1. (a): zein-MMT film, (b): zein- PVA film (c): pure zein film

Figure 1 shows that the zein-PVA (b) and zein-MMT (a) films have lower color value but have greater transparency or in other words, they are more colorless .The saturation criterion of difference is a color of gray color and is defined as the criterion of purity. The highest color saturation was observed in pure zein film. It can be concluded that zine composite with PVA and MMT is more similar to synthetic polymer films and is able to cover food because of its greater transparency and lightness than pure zein(c).

3.3. Surface morphology

The surface morphology of the pure zein, zein-MMT 5% and zein-PVA 5% films was investigated by confocal microscopy (Fig. 2-7). In this study, we used a confocal microscope to analysis the surface morphology of the films, which has the advantage of using this method to create high-contrast images [12]. The confocal results showed that zein composite films have higher thickness than pure zein film. This observation can explain higher porosity of zein composite films compared with pure zein film porosity. Figure 1 shows that the pure zein film has a uniform, roughly smooth surface (Sq=0.438 μm). Figures 2 and 3 also show that the zein-PVA (Sq=2.73 μm) and zein-MMT (Sq=3.76 μm) films have non-uniform and uneven surface networks. This test showed that the morphology of the nanocomposite films was affected by PVA and MMT (Table 1). Surface roughness increased with increasing MMT and PVA content. The non-uniform distribution of the zein particles is due to an increase of MMT and PVA. This phenomenon may be related to the degree of dispersion of additives in the zein network and the inhibition of the adhesion of the zein nanoparticles; This resulted in the formation of a non-uniform plate.

Figure 2. Confocal image on Pure zine film surface

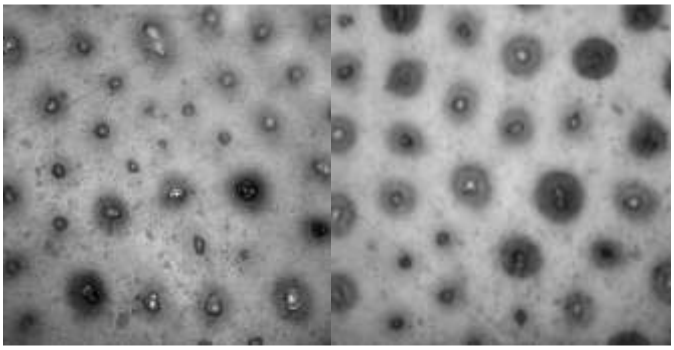

Figure 3. Confocal image on zein-MMT (5%) film surface

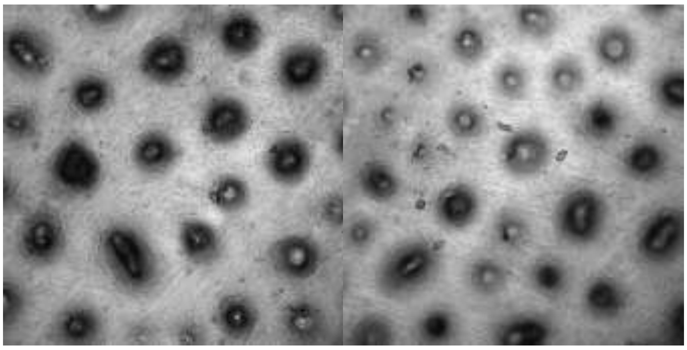

Figure 4. Confocal image on zein-PVA (5%) film surface

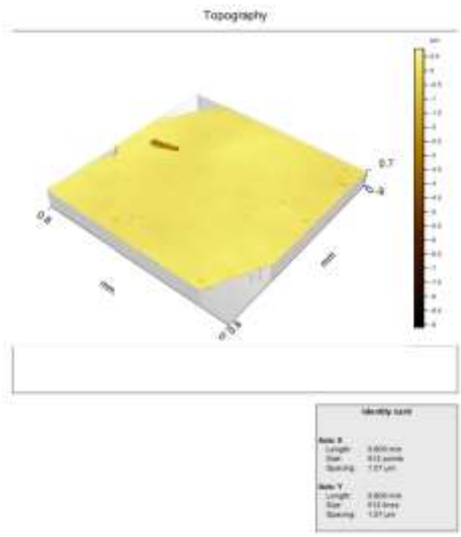

Figure 5. Confocal analytical image on pure zein film surface

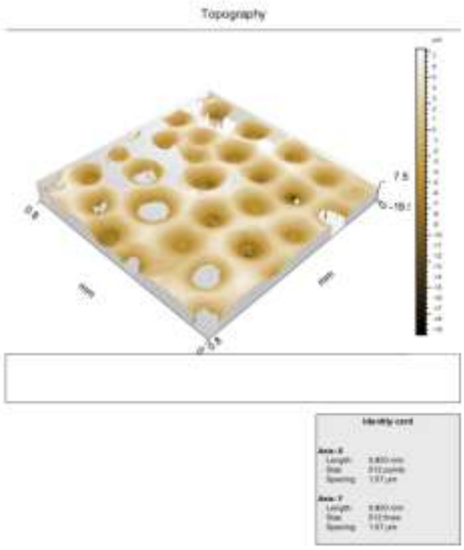

Figure 6. Confocal analytical image on zein-MMT (5%) film surface

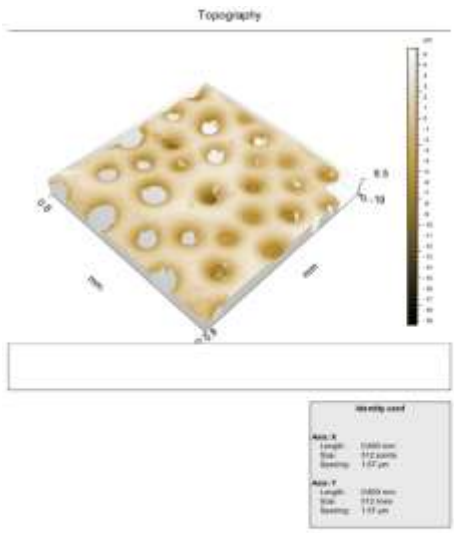

Figure 7. Confocal analytical image on zein- PVA (5%) film surface

Table 1. Surface roughness of the films

Property (mµ)	zein-PVA (5%)	pure zein	zein-MMT (5%)
Surface roughness	2.73	0.438	**3.76**
Maximum peaks	6.56	0.768	**7.73**
Maximum depth	19.4	9.10	**19.5**
maximum thick	26.0	9.87	**27.2**

Table 2. Other studies

No.	Material	Preparation of sample/solution	Conclusions	References
1	Zein-chitosan	zein films modified by a two-step method consisting of compositing with chitosan, followed by exposure to cold plasma.	notable increase in their elongation at break, the composite film exhibited an optimum tensile strength, enhanced water vapor, improved thermal stability.	[13]
2	Zein	Preparation and ACP treatment of zein films.	Increased surface roughness with the treatment time extending, enhanced tensile strength.	[14]
3	Zein-chitosan nanoparticles - pomegranate peel extract	Ultrasonic treatment was employed to enhance the polyphenols extraction from pomegranate peel & the ionic gelation method was employed to prepare the chitosan nanoparticles / pomegranate peel nanocomposite	zein/ chitosan nanoparticles/ pomegranate peel nanocomposite film had better thermal stability than the neat zein film, addition of plant extract to biopolymers can be projected as a hopeful ecofriendly food wrapping material to replace synthetic polymers.	[15]
4	Zein-chitosan-nanoTiO2	zein/chitosan films were prepared through a process involving blending, solution casting and evaporation	addition of nanoscale TiO2 remarkably improved the mechanical properties and thermal stability. The tensile strength of	[16]

			the films significantly increased.	
5	Zein	zein films obtained by electro spraying	possibility to produce homogeneous films, without electrical arc formation,development of more homogeneous films, without affecting the water vapor barrier capacity, but with a different structure as compared to the casting method, with the advantage of shorter processing times.	[17]
6	Zein-chitosan-rosemary oil	all the solutions were prepared separately and afterwards layer by layer coating was applied.	a high thermal stability, especially those coated with chitosan, zein and rosemary oil layer by layer, Uncoated paper has poor water and oil barrier properties due to its porous structure.	[18]

4. Discussion

According to the biodegradability part, it can be said that zein, as a base polymer in the production of polymer films, has good biodegradability properties, which has led to the use of this polymer in various applications. Zein is a hydrophobic material. Therefore, zein film is not easily hydrolyzed in water [19]. In this study for biodegradation test, the zein film was placed in a amylase solution for long time. Due to the high hydrophobicity of zein-containing films, we exposed them to a solution containing α-amylase for 36 hours for complete degradation. This hydrophobicity, makes zein based composites suitable for food packaging and maintains the degradability of films in an optimal range. Other studies have been performed on the evaluation of zein bio-polymer in food coatings. Takahashi et al., by examining zein/CMS films in α-amylase solution, confirmed the biodegradability of these films and concluded that by increasing the concentration of zein in the films, their hydrophobicity improves, which is an important factor in food packaging. In this study, hydrolysis of films in α-amylase solution was also observed [20]. Wang et al., After examining the contact angle of pure KGM and zein films as well as their composites, concluded that pure zein has the highest hydrophobic properties. This hydrophobicity confirms the low solubility of zein-containing films [19].

Also, in the color properties of polymer films, it can be noted that increasing the purity of zein in the polymer film increases the purity of the yellow color in it and improves the appearance of the film. But if we look at the films in terms of transparency, the other two films, which are compounds of zein-MMT and zein-PVA, have better clarity due to the reduction of yellow color. Soliman et al. Showed that the value of yellow in zein films was higher than other samples [21]. Vahedikia et al. Also attributed the pale-yellow color of the films to the presence of zein in zein/CNP films, which increases the transparency of the films by increasing the amount of CNP to the zein films [22]. In the present study, the amount of yellow color in pure zein films was higher than other samples, which increased the transparency of the films by adding PVA and MMT compounds.

In this study, the pure zein film surface was, smooth, but the zein/MMT and zein/PVA film surfaces were porous and rough. Examination of film morphology shows that most porosity of zein composite films compared to pure zein films is due to the increase in thickness of composite films and the addition of MMT and PVA causes roughness on the surface. Vahedikia et al. Showed that films containing pure zein and the zein/CNP combination had a smooth and uniform surface, while zein/CEO and zein/CEO/CNP composite films had a rough surface with cavities [22]. Other studies are listed in Table 2.

5. Conclusions

In addition to the use of corn zein in food packaging, it is used to make multilayer films (Protein and polysaccharide films). Because films made of biological polymers such as protein and polysaccharide films have poor performance in terms of mechanical properties and water vapor barrier, research has shown that their composition with zein film is due to its good mechanical properties (high tensile strength) and a low permeability to water vapor would be a good solution to improve the properties of these films [23, 24]. In the biodegradability test, zein and zein-PVA films were completely degraded and zein-MMT films degraded About 70-80 percent. The zein-PVA and zein-MMT films have lower color value or in other words, they are more colorless and the highest color saturation was observed in pure zein film. The pure zein film has a uniform, roughly smooth surface and it was observed that the zein-PVA and zein-MMT films have non-uniform and uneven surface networks. The high porosity in the nanocomposite films of zein-PVA and zein-MMT show that the addition of MMT and PVA results in high porosity in the final films, which has a great effect on the increase of adsorption on the surface. It can be used to increase the absorption of the material. One of the effective ways to reduce environmental pollution is the use of biodegradable films in food packaging. As the nanocomposite films of zein, zein-PVA and zein/MMT are highly biodegradable, they are highly efficient in this field and can be used in food packaging.

Abbreviations

MMT: Montmorillonite; GRAS: Generally Recognized as Safe; FDA: Food and Drug Administration; PVA: poly (vinyl alcohol); sq: Square Micrometer; SSPS: soluble soybean polysaccharide; U.S.: United States; ACP: atmospheric cold plasma; CMS: carboxymethyl starch; KGM: konjac glucomannan; CNP: Chitosan nano particle; CEO: Cinnamon essential oil.

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Conflict of interests

We have no competing interests.

Consent for publications

All authors have read and approved the final manuscript for publication.

Availability of data and materials

Authors declare that all data are embedded in the manuscript.

Authors' contributions

S.K., Z.B.M.H., M.S., S.A.Y., R.S. and A.A.A., designed the study, carry out experiments, drafted the initial manuscript, and analyzed the data; A.H.Z, supervised the study, performed the statistical analysis and revised the manuscript before submission. M.H., Edited and submitted to the journal. All authors read the revised manuscript and approved it for final submission.

Ethics approval and consent to participate

This does not apply to this study.

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