

Investigation of Water Vapour Permeability, Hydrophobicity and Morphology of Zein Films Plasticized by Polyols

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ABSTRACT

Zein (prolamin of corn) has good film forming properties. The pure zein film is very brittle and plasticizers can improve its mechanical and film making properties and represses its permeability to gases. Polyols are natural plasticizers for food biopolymers. In this research, three types of polyols (sorbitol, manitol, and glycerol) were used as plasticizers and the water vapour permeability (WVP), contact angle and microstructure of different zein films were studied. The pure zein film had high WVP and adding glycerol and sorbitol by 0.7 g/g zein lowered WVP but this effect was not observed in films containing manitol. The films containing glycerol had the lowest WVP. The zein films containing glycerol had the highest water contact angle compared with the plasticized films. The pure zein films and the films containing manitol had the higher critical surface tension of wetting (γ_c) than the films containing glycerol and sorbitol. Adding polyols to zein films increased the surface tension of the zein films. In the unplasticized zein films and those plasticized by manitol, loose structural integrity and a lot of cavities and voids have been detected. The films plasticized by glycerol had smooth glassy surface.

Key Words:

zein films;
polyols;
water vapour permeability;
surface hydrophobicity.

INTRODUCTION

The use of plastics for packaging has grown extensively in recent years. In this context, biodegradable films can be a source of saving energy and important issue for environmental protection. Edible and biodegradable films and coatings, by acting as barriers to control the transfer of moisture, oxygen, carbon dioxide, lipids, and flavour-

ing compounds, can prevent deterioration quality and increase the shelf life of food products [1,2]. For example, the coatings and edible films placed between adjacent foodlayers can prevent undesirable migration of moisture, oxygen or food components between these layers. In addition, edible films or coatings may provide mechanical

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integrity and improve the handling characteristics of the food and can be effective carriers of many functional ingredients, such as antimicrobial agents to improve safety and stability of foods and antioxidants to prevent lipids oxidation and flavourings and pigments to improve the quality of food. Materials that can be used for film making include polysaccharides, proteins, lipids and polyesters or combination of them [1-3]. Polysaccharides and proteins are good film-forming materials, but they are poor moisture barriers [13]. Zein is the most important protein in corn. It is a prolamin protein and so that dissolves in ethanol 70-80% [4-7]. Zein is a relatively hydrophobic and thermoplastic material. The hydrophobic nature of zein is related to its high content of non-polar amino acids [8]. Zein has excellent film forming properties and can be used for fabrication of biodegradable films. The zein biofilm is formed through the development of hydrophobic, hydrogen and limited disulphide bonds between zein chains [2,9]. The zein films are brittle, and thus the plasticizers are needed for improving their flexibility [10-13]. Plasticizers are low molecular mass organic compounds which are added to soften rigid polymers. In general, the protein films are poor moisture barriers due to the hydrophilic nature of proteins, but they are good barriers to gases such as oxygen and carbon dioxide [1,2].

The water vapour permeability (WVP) values of the protein films are normally 2-4 orders of magnitude higher than that of LDPE [3]. Cross-linking of some proteins by lactic acid, tannic acid, ionized calcium or transglutaminase has been shown to increase resistance to water vapour and gas transport. In addition, preparation of films from aqueous emulsions of proteins and lipids or lamination of the protein films by lipid films causes WVP to be decreased. Thermal denaturation of some proteins and use of long chain fatty acid or alcohol can improve the film's water vapour barrier properties [14,15].

The alcohol-soluble proteins, such as zein, wheat gluten, and the fish myofibrillar proteins form films which have relatively low WVP when they are compared to other proteins [3]. Moisture has a plasticizing or swelling effect on polymers, resulting in increased gas permeability [16]. Relative humidity (RH) markedly affects WVP and oxygen permeability of protein films. Lai and Padua [17] have observed an

increase in WVP values as RH of the test environment increased from 53% to 98%. This was attributed to the plasticization effect of water on the protein films. Water is a strong plasticizer for biopolymers, although it is not necessarily a good solvent. The mechanism of water plasticization was believed to be governed by the free volume theory. Water increases the polymer free volume, allowing the segments of polymeric chains to increase their mobility [18-20]. Higher segment mobility resulted in higher WVP. Rakotonirainy and Padua [21] studied the effects of lamination and coatings with drying oils on water vapour barrier properties of the zein films. The WVP did not drop appreciably with lamination and the number of laminated sheets had no significant effects on water barrier property but coatings with drying oils substantially improved the water barrier properties of films, because coating formed more hydrophobic surface that prevented film wetting.

Commonly used plasticizers for zein are liquid organic compounds such as polyols, sugars, lipids, and lipid derivatives. Park et al. (1994c) used a mixture of glycerol and PEG (average molecular weight of 400). They have observed that migration rates of glycerol-PEG mixtures in zein-based films were slower than that of glycerol alone and such mixtures could slow down the deterioration of mechanical properties during film storage. Fatty acids have been used to plasticize zein films [10,17,31]. Unsaturated fatty acids remain effective plasticizers at temperatures below freezing and in low RH environments. However, it was reported that oleic acid-plasticized zein films became brittle and almost colourless over a storage period of six weeks in a light stability chamber. Property changes were attributed to oleic acid oxidation [10].

The objectives of this study are to determine the effects of different polyolic plasticizers on the water vapour permeability, hydrophobicity and microstructure of the zein films produced from zein resins.

EXPERIMENTAL

Materials

Zein, regular grade, was obtained from Freeman Industries Inc. (Tuckahoe, NY). Other Materials: sor-

bitol, manitol, glycerol, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were purchased from Merck. Ethanol 95% was obtained from Razi Corporation and it was used to prepare ethanol 80%.

Preparation of Zein Films

Zein dispersions were obtained by dissolving zein (20% w/v) in warm (80°C) aqueous ethanol 80%. Polyols were added to the solution at 0.5 g, 0.7 g, and 1 g/g of zein and stirred in mixer at 300 rpm for 10 min. Zein-plasticizer dispersions precipitated by the addition of cold water (5°C) as result of hydrophobic aggregation. Resins were collected as soft solids and kneaded in a mixer for separation of remained alcohol and water to obtain cohesive mouldable resins. Resins were rolled and then pressed by a hot press (80°C, 25 MPa) between two metal surfaces to form zein films. Films were dried at room condition for 48 h.

Water Vapour Permeability

Water vapour permeability (WVP) was determined gravimetrically according to the standard method E96-95 (ASTM, 1994) [22] by water vapour permeability tester (L80-5000, Switzerland). The films were inserted between the lower chamber containing distilled deionized water and upper chamber containing sensor for controlling of temperature and relative humidity (23°C and 15% RH). Air velocities were approximately 750 m/min across the films. Silica gel (desiccant) was used for the absorption of air water. The moisture adsorbed by the silica gel was detected by weighing periodically until a stationary state was reached. For each measurement, at least five repetitions were made. The final measurement was done after incubation for 1 day.

The slope of the weight vs time plot was divided by the effective film area to obtain the water vapour transmission rate (WVTR). This was multiplied by the thickness of the film and divided by the pressure difference to obtain the water vapour permeability (WVP).

$$\text{WVTR} = \text{slope/film area}$$

$$\text{WVP} = \text{WVTR} \times \text{thickness}/\Delta\text{Vapour pressure}$$

$$\text{WVPC} = \frac{\Delta W}{A \cdot \Delta T} \cdot \frac{X}{\Delta p}$$

where ΔW =weight gain by desiccant (g), X =film thickness (mm), A = area of the exposed film surface (m^2), ΔT = incubation period (h), and Δp = difference of partial pressure (kPa).

Contact Angle and Critical Surface Tension

Contact angle measurements were carried out with ethanol, ethylene glycol, water, and using a goniometer (Kruss G10, Germany). To perform the measurements of the contact angles, a syringe was filled with 5 μL of a particular test solution after it had been cleaned a few times with the same solution, and a drop was placed on top of the film surface. For each film type, at least 10 measurements were made and the average value was taken.

Estimation of the critical surface tension (γ_c) of zein films was attained by contact angle measurements followed by extrapolation from Zisman plots technique. Zisman plots were obtained by plotting the cosine of the contact angles of a series of liquids on the surface of films against the surface tension of the same series of liquids. The critical surface tension values of zein films are the mean of the extrapolation product obtained from five independent plots.

Morphology

Scanning electron microscopy (SEM) was used to examine the surface of zein-plasticizer films. Pieces of 5 mm \times 1 mm were cut from films and were mounted directly on stubs with double-coated carbon-conductive tabs and coated with gold. Samples were observed with a SEM (Cambridge-S360) equipped with image analyzing system with an accelerating voltage of 10 kV.

Statistical Planning of Experiments

WVP Values were measurements of three replicated samples for each type of film. Statistics on a completely randomized design were performed with the analysis of variance (ANOVA) procedure in SPSS (Version 10.0 for windows) software. Duncan's multiple range test ($P < 0.05$) was used to detect differences among film WVP properties mean values.

RESULTS AND DISCUSSION

Water Vapour Permeability

The water vapour permeability values of different zein films are given in Table 1. The pure zein film had the highest WVP probably due to not well chains association and formation of a lot of void spaces and cavities in films, although films without polyolic plasticizers had more hydrophobic nature than the films containing plasticizer. Permeability is influenced by the hydrophobic or hydrophilic nature of the material, by the presence of voids or cracks, and by the stearic hindrance and tortuosity in the structure [23]. Water sorption by biopolymers often results in swelling and conformational changes. The absorbed water plasticizes the film matrix, leading to a less dense structure where chain ends are more mobile, thus increasing permeability. Manitol and sorbitol have similar chemical structures and both of them have six carbons in their structure and they are available as solid powder, but glycerol is liquid and has three carbons in its structure. In comparison, among the films containing different plasticizers, the films plasticized by glycerol and manitol had the highest and lowest barrier properties, respectively. This could be attributed to lower ability of manitol in increasing zein chain association. Decrease of chain association enhances the voids in film structure. Manitol had probably very low compatibility with zein and did not solve in zein solution completely. Increasing plasticizer content from 0.5 to 0.7 g/g of zein, decreased WVP in the specimens containing glycerol and sorbitol but this phenomena was not observed in films plasticized by manitol. It was probably due to increasing chain association at low level of plasticizer content. However, when plasticizers content increased to 1 g/g of zein, WVP increased in all samples. This was probably due to increase in chain mobility and enhancement of the void spaces between polymer chains. Generally plasticizers increase permeability at high ratio of plasticizer to polymer. Parris and Coffin [24] studied the effect of some of plasticizers and cross-linking compounds on the WVP of the casting zein films. Water vapour barrier properties were best for unplasticized zein films cross-linked with 20% polymeric dialdehyde starch and incorporation of plasticizer into the zein films resulted in an almost doubled WVP values.

Table 1. Water vapour permeability of zein films^a.

Film type	Plasticizer content (g/g zein)	WVP (g.mm/kpa.h.m ²)
Zein	0.0	1.9516 ±0.0015 a
Zein + sorbitol	0.5	1.7290±0.0052 b
Zein + sorbitol	0.7	1.7126±0.0030 c
Zein + sorbitol	1.0	1.8223±0.0051 d
Zein + manitol	0.5	1.8253±0.0032 d
Zein + manitol	0.7	1.8483±0.0028 e
Zein + manitol	1.0	1.9043±0.0060 f
Zein + glycerol	0.5	1.4356±0.0051 g
Zein + glycerol	0.7	1.4323±0.0035 g
Zein + glycerol	1.0	1.5721±0.0054 h

(a) Values are average of five samples ±standard deviation.

(b) Means with the same letter are not significantly different (P<0.05).

Contact Angle and Critical Surface Tension

One of the primary characteristics of any immiscible, two- or three-phase system containing two condensed phases, at least one of which is a liquid, is the contact angle of the liquid on the other condensed phases (solid or liquid surface). These phases can be as follows:

- Liquid-vapour-solid: for example water on the edible film.
- Liquid-liquid-solid: for example water-oil-protein in the emulsion.
- Liquid-liquid-vapour: for example oil drop on the top of water.

Of more practical and widespread importance is the contact angle of a liquid on a solid. The contact angle was defined as the angle formed by the intersection of two tangential lines to the liquid and solid surfaces at the perimeter of contact between the two phases and the third surrounding phase (mostly air or vapour) [25]. Protein and carbohydrate films are known to possess hydrophilic character. Water contact

angles of films can be good indicator for determining their degree of hydrophilic nature.

When a drop of liquid is placed on a solid surface, the liquid spread across the surface to form a thin, approximately uniform film (duplex film) or spread to a limited extent but remain as a discrete drop on the surface. The final condition of the applied liquid on the surface is taken as an indication of the wettability of the surface by the liquid or the wetting ability of the liquid on the surface, depending on one's appropriate choice. Wetting process is evaluated by measuring the contact angle, θ , which the drop makes with the solid [26].

In the case of a liquid that forms a uniform film (i.e., where $\theta=0$), the solid is said to be completely wetted by liquid, or that the liquid wets the solid. If a finite contact angle is formed ($\theta>0$), some investigators describe the system as being partially wetted. Others prefer to make a distinction based on the size of the contact angle. For example, a given worker may define as wetting any liquid that produces a contact angle of 30° or less on a solid. Between 30° and 89° the system would be partially wetting, and 90° and above non-wetting [26]. In our works, the contact angles of the zein films (plasticized by polyols) with ethanol, ethylene glycol, and water were measured. All samples had minimum contact angle with ethanol and maximum angle with water (Table 2). It is well-known that the water contact angle increases with increasing surface hydrophobicity. According to the obtained results, the pure zein films had higher contact angle than the films containing plasticizers and polyols diminished the water contact angle of films. Plasticization, therefore, resulted in decreasing hydrophobicity of the zein films. The higher

hydrophilicity of the samples is attributable to the hygroscopicity (the water binding capacity) of plasticizers. Among the plasticized zein films, those containing glycerol and manitol had the highest and lowest water contact angle, respectively. It appears that the water contact angles of the films increase during the storage (for example it increased in films plasticized by glycerol from 52° to 61° during one week), indicating films becoming more hydrophobic, which may be due to the loss or migration of plasticizer and moisture content. Sanchese et al. [27] have studied the effect of different polyolic plasticizers from the ethylene glycol series on the surface properties of wheat gliadin (a glycoprotein) films. Protein films similar to polysaccharide films are known for their hydrophilic character, but the gliadin films exhibited contact angles between 85° and 105° . The angle increased with the number of carbons in the ethylene glycol series. Nevertheless, the contact angles of the pea protein films were in the range of $14-40^\circ$ [9] and angles of the sunflower protein films with different plasticizers were in the range of $12-30^\circ$ [28]. This means that the gliadin films were less readily wetted, suggesting a higher surface hydrophobicity, which can be related to the water insolubility of gluten proteins. Their values of contact angle were similar to those observed currently with polystyrene or poly(tetrafluoroethylene) [29]. In contrast with synthetic polymer films, contact angles on the gliadin films decreased rapidly with contact time, suggesting a rapid change of the surface properties. The zein protein is similar to wheat gliadin and both of them are prolamin proteins and have a high ratio of hydrophobic amino acids. So that, the zein film without any plasticizer had a relatively high contact angle (62.30°).

Table 2. Contact angles of zein films with different solvents.

Sample	Contact angle(deg)	Contact angle(deg)	Contact angle(deg)
	with water	with ethylene glycol	with ethanol
Zein	62.30	40	16.26
Zein + sorbitol	48.62	34.41	21.25
Zein + manitol	45.41	38.37	15.42
Zein + glycerol	52.48	42.44	19.61

Zisman et al. have developed a useful and practical systematic method for characterizing the wettability of solid surfaces [30]. The system is based on the observation that for solid surfaces having a surface tension (γ_{s-v}) < 100 mN.m⁻¹ (generally classified as low-energy surfaces), the contact angle formed by a drop of liquid on the solid surface will be primarily a function of the surface tension of the liquid (γ_{l-v}). They found that for a given solid surface and a homologous series of related liquids, $\cos\theta$ was an approximately linear function of γ_{l-v} . For several non-polar liquids, the relationship holds very well, while for high-surface-tension, polar liquids, the correlation begins to break down somewhat and the line begins to curve. From a plot of $\cos\theta$ vs. γ_{l-v} one can obtain the value of the liquid surface tension at which $\cos\theta=1$, a value that has been termed the *critical surface tension of wetting* (γ_c) (Figure 1). It is defined as the surface tension of a liquid that would just spread on the surface of the solid to give complete wetting [26]. In other words, if, $\gamma_{l-v} < \gamma_c$ the liquid will spread; if, $\gamma_{l-v} > \gamma_c$ the liquid will form a drop with a non-zero contact angle. The surface tensions of some liquids (water, ethanol and ethylene glycol) and their polar and disperse sections are presented in Table 3. The critical surface tension of different zein films are presented in Table 4. It should be noted that critical surface-tension values had been reported to be lower than the surface tension values of the same tested surfaces. Only the surface tension of ethanol was near to γ_c of the zein films. So that ethanol can spread rather completely on the surface of films. The pure zein films and the films containing manitol had higher γ_c than films containing glycerol and sorbitol.

The interfacial tension between film and liquid (γ_{s-l}), depends on the surface tension of the solid film (γ_{s-v}), the surface tension of the liquid (γ_{l-v}), and the

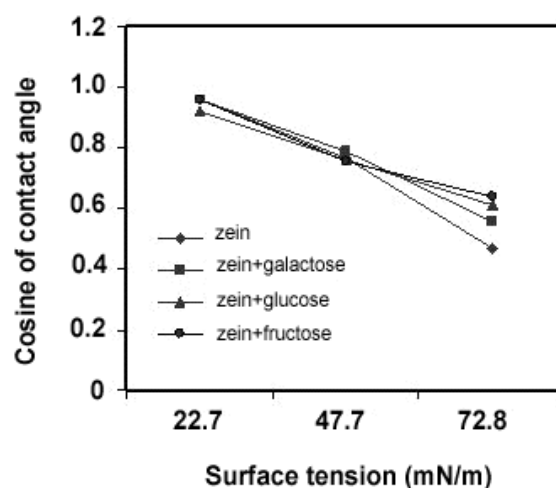


Figure 1. Zisman plot for zein films.

contact angle (θ) of liquid on a solid surface according to the Young equation:

$$\cos\theta = \gamma_{s-v} - \gamma_{s-l} / \gamma_{l-v}$$

where γ denotes surface tension and subscripts l, v, and s denote liquid, vapour, and solid, respectively. Surface tension is composed of dispersive and polar components according to following equation:

$$\gamma_{l-v} = \gamma_{l-v}^d + \gamma_{l-v}^p$$

where d refers to the non-polar component (dispersive forces) and p to the polar one. Dispersive forces are apolar, weak attractions that operate at a relatively long range, in excess of 100 Å. The polar interactions are much stronger than the dispersive interactions and can act over ranges as short as 5 Å and require an intimate contact between the liquid and the solid surface [23]. The similarity between the liquid and the solid film in values of dispersive and polar components has

Table 3. Surface tension of different solvents.

Liquid	Surface tension (mN/m)	Disperse part (mN/m)	Polar part (mN/m)
Water	72.8	26	46.8
Ethylene glycol	47.7	26.4	21.3
Ethanol	22.7	15.8	6.9

Table 4. Critical surface tension and surface tension of different zein films.

Sample	Critical surface tension (mN/m)	Surface tension (mN/m)	Disperse part (mN/m)	Polar part (mN/m)
Zein	20.4	43.7	10.5	33.2
Zein + sorbitol	11.9	55.2	10.1	45.1
Zein + manitol	12.7	61.3	7.8	53.5
Zein + glycerol	12.1	53.7	8.1	45.46

influence on the spreadability of the liquid [30]. The surface tension of the pure and plasticized zein films and their polar and disperse sections are presented in Table 4. Adding polyolic plasticizer to zein films increased surface tension of zein films. The results showed that polyols caused to decrease in non-polar interactions and increase in polar interactions in zein films matrix.

The zein films containing manitol had the highest surface tension (66.2 mN/m). Similarity between surface tension component of water and films containing manitol can be an important reason for higher hydrophilicity of those films. As well as the films plasticized with sorbitol had not a great effect on non-polar interaction in zein films

Morphology

Differences in the film morphology of the zein films were investigated by SEM. Zein has been described as a globular protein in many systems but Lai and Padua [17,31] have suggested that after precipitation from alcohol solution and mechanical treatment, zein particles merge with each other to form fibrillar structures. We have not been able to observe fibrillar structure in all samples. It could have been due to different mechanical treatments on the zein resin because we used rolling and hot press and Lai and Padua have used rolling and drawing for film making. Lai and Padua [17] studied the morphology of the zein resin films and the zein casting films plasticized with oleic acid and observed three types of morphology in the resin films (in the same sample): (1) aligned protein fibrils embedded in a continuous material, (2) arrangements of oriented ribbon-like structures of zein, and (3) entanglements of ribbon-like strands of

zein. Oriented ribbon-like morphology was observed in the middle region of films along the direction of drawing. They have suggested that orientation is induced by applied stress and the entangled morphology may be the result of non-homogeneous stretching toward the rim of films.

In our works, we observed three different morphologies in different samples. In the unplasticized zein films and the films containing manitol, loose structures with a lot of cavities and voids were detected (Figure 2a,c). These micrographes showed continuous even matrix was not formed in the pure zein film because there was not plasticizer for increasing association within protein polymer chains. In addition, manitol was not suitable plasticizer for the zein films. Manitol was not dissolved in alcoholic solution well and the films containing manitol had chalky appearance due to crystallization of manitol on the surface of films. This type of microstructure can be another reason for high WVP of films containing manitol. The films matrix containing sorbitol and glycerol (Figure 2b,d) had compact and dense microstructure. The morphology of the films containing sorbitol and glycerol were similar together, although it seemed to be different in the surface contour. The films plasticized by sorbitol were clearly uneven and had rougher surface than the films containing glycerol but the phase separation between protein matrix and plasticizers in both of films was not observable. The films plasticized by glycerol had smooth glassy surface. Solid particles on the surface of films containing glycerol probably related to contamination of films by the surface of hot press (in Figure 2b,d dark areas represent the protein matrix and the white areas show plasticizer particles).

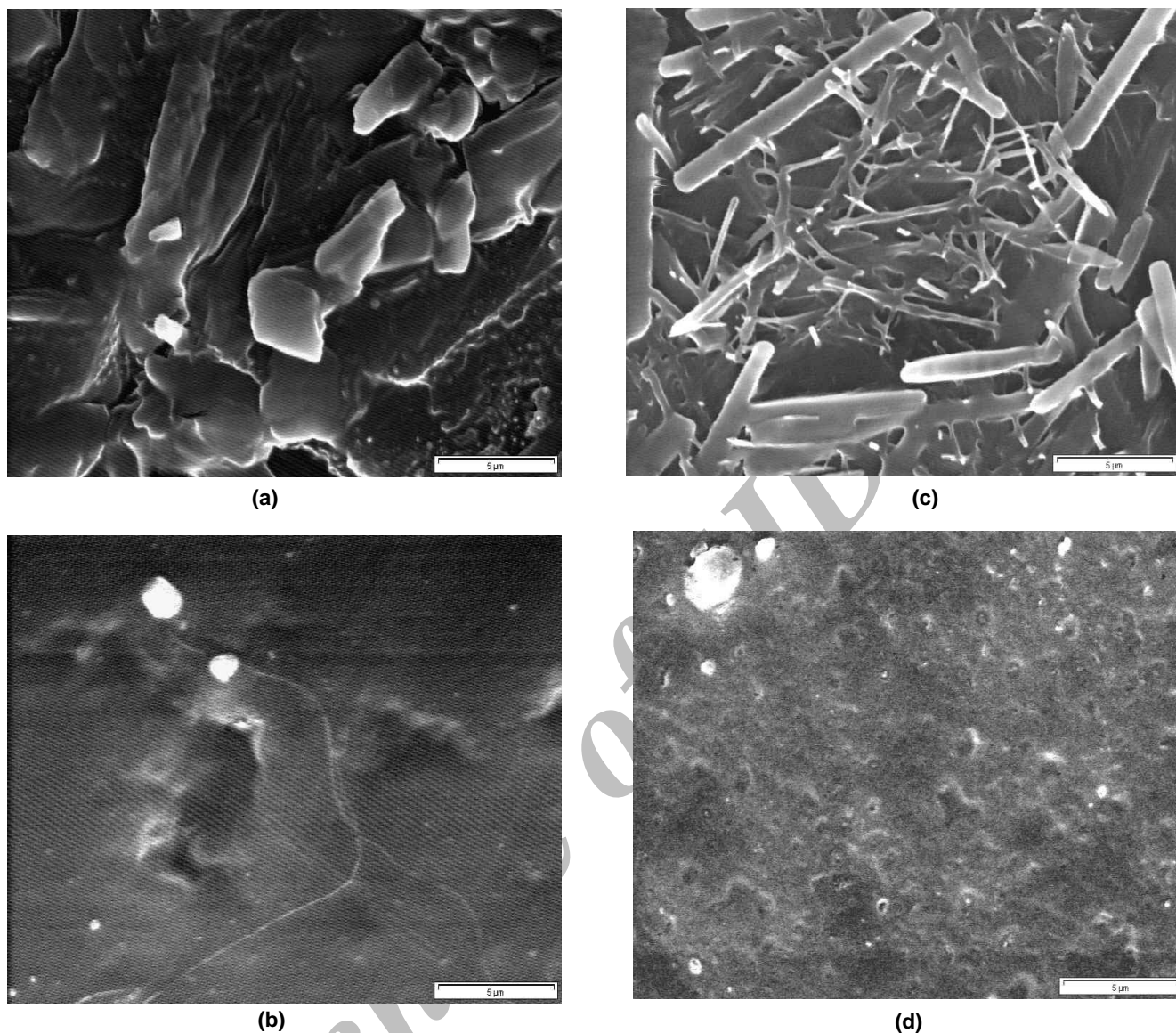


Figure 2. Scanning electron micrographs of zein films prepared from resins: (a) pure zein, (b) sorbitol, (c) manitol, (d) glycerol.

CONCLUSION

Polyols are natural compounds in fruits and foods. This compound can act as plasticizer in edible films. Utilization of these compounds decreases the WVP of zein films to a certain level (0.7 g/g of zein) and increases WVP at higher levels (1 g/g of zein). Incorporation of polyols has caused to diminish contact angle and to increase surface tension. It means that polyols can decrease the surface hydrophobicity. SEM Micrographs have shown manitol is not a good plasticizer for the zein films and the films containing manitol give loose structure.

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