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Properties of Plasticized-Zein Film as Affected by Plasticizer Treatments

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Corn-zein is a protein polymer promising as a biodegradable food packaging film to overcome environmental pollution caused by the use of non-degradable petroleum-derived plastics. However, the brittleness of pure zein film requires that plasticizers be added. The effects of the proportion of polyethylene glycol (PEG) and lauric acid (LA) used as composite plasticizer on mechanical and barrier properties of zein-based film were observed. Flexibility of plasticized-zein films increased as the portion of PEG was increased, as shown by the trend of decreasing elastic modulus (EM) and increasing elongation to break (ETB). Tensile and puncture strength values were also affected by increase in the PEG portion, although they were not as consistent as EM and ETB values. Water vapor permeability values rose with PEG while values for oxygen permeability were more erratic.

Keywords: zein, biodegradable film, mechanical properties, barrier properties

Severe environmental pollution as a consequence of plastics-packaging waste has recently become a major issue of interest. There is growing concern over nondegradable petroleum-derived plastics used for food packaging, and research has begun to focus more on renewable and biodegradable polymers of agricultural origin. Interest in biodegradable materials for food packaging film is centered mostly on three major types of agricultural components: polysaccharides, lipids, and proteins or polypeptides. A good film must have the following properties: flexibility, moldability, be odorless, moisture resistant, thermoplastic and transparent. Proteins generally have excellent barriers to transport of gas and moderate barriers to the transport of moisture (Krochta, 1992), and are also moldable and transparent when used as a film sheet. Zein is one protein material promising as a food packaging film.

Zein, a prolamin fraction of corn, has been defined as an alcohol-soluble protein that occurs principally in protein bodies of maize endosperm (Wilson, 1991). Interest in the industrial utilization of zein is due mostly to its film-forming ability when cast from appropriate solvent systems. The film-forming ability of the molecules can be explained by glutamine interactions resulting in stacked zein molecular planes (Argos *et al.*, 1982). Film formed after solvent evaporation is tasteless, but it is glossy, scuff-resistant, and grease-resistant (Pomes, 1971; Gennadios & Weller, 1990). Zein sheets without plasticizer, however, resulted in a very brittle film (Lai *et al.*, 1997), and the addition of plasticizers increases flexibility (Andres, 1984).

Studies have been made on plasticizers added to zein when it is used as a film for food packaging (Herald *et al.*, 1996; Lai *et al.*, 1997; Di Gioia & Guilbert, 1999; Santosa & Padua, 1999). However, the real mechanism of plasticized action upon the film has not yet been explained. Plasticizers are theorized to decrease the intermolecular forces along polymer chains, imparting increased film flexibility while decreasing barrier abilities of film (Banker, 1966). When chain mobility increases, the coefficient of diffusion also increases thus enhancing the gas and water vapor permeabilities. In this experiment, polyethylene glycol exhibited excellent film flexibility but poor barrier ability and tensile strength, while lauric acid showed good performance in both properties although it did not enhance the film's flexibility. For that reason, the use of polyethylene glycol and lauric acid as composite plasticizers was suggested to improve flexibility of film without altering the important aspects of its properties.

The objective of this study was to evaluate characteristic changes in tensile and barrier properties of zein-based film as affected by the composition of polyethylene glycol and lauric acid.

Materials and Methods

Materials Pure zein powders for the films were provided by Showa Sangyo Co., Ltd., Tokyo. The plasticizers, lauric acid and polyethylene glycol were obtained from Wako Pure Chemical Ind., Ltd., Osaka. Potassium nitrate (Wako Pure Chem. Co) as a saturated salt solution at 40°C was used to equilibrate film at 90% relative humidity prior to water vapor permeability testing. Ethanol (Wako Pure Chem. Co) was used to dissolve pure zein powder.

Film formation

Single plasticized-zein film One gram of pure zein powder was dissolved in 10 ml of 80% ethanol, followed by 20% (w/w) of plasticizer, either polyethylene glycol or lauric acid. The mixture was heated with stirring at 60 to 70°C for 15 min.

Multiple plasticized-zein film One of gram pure zein powder and lauric acid (10% w/w of zein) were dissolved in 10 ml of 80% ethanol, followed by polyethylene glycol (10, 20, 30 and 40% w/w of zein). The mixture was stirred and heated at 65–70°C for 15 min (Fine Hot Stirrer F-101H Scientific Instruments

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and Utensils, Tokyo). The solution was then cooled to 40–50°C before being cast at 35–45°C and 20–30% relative humidity (RH) for 2–4 h. The mixture was pipetted onto a smooth 200 cm^2 polyethylene sheet on the board of automatic casting machine (Toyoseiki Co., Tokyo). The film was allowed to dry for approximately 18 h at 30°C and 20–30% RH. Dried films were peeled intact from the polyethylene sheet surface and stored at ambient temperature with ambient RH.

Mechanical properties Mechanical property testing was carried out on a Rheo meter NRM-3002D (Fudoh Kogyo Co., Ltd., Tokyo). 48 h after sample preparation. For tensile strength and elongation to break tests, samples were cut from the films using an industrial sample cutter (JIS Z 1702, Rheotech, Tokyo). For the puncture strength test, 3×3 cm^2 samples were used. Data on tensile properties were obtained from 8 replicates and measured at ambient temperature (15–20°C) with a 30–50% RH. Elastic modulus (Young's modulus) was measured by Dynamic Load Thermomechanical Analyzers (TMA/SS 150C, Seiko Instrument Inc., Tokyo). Samples were cut 3×20 mm^2 and measured in at least three replications at ambient temperature (15–20°C) and RH (30–50%).

Water vapor permeability Water vapor permeability (WVP) of each type of film was determined based on the WVP apparatus and method as described by the American Society of Testing Materials (ASTM) standard method E96-66. Three test cups were tested at 40°C, placed in a desiccator cabinet at 90% RH and maintained using saturated potassium nitrate solution. WVP (g/m.s.Pa) was calculated as the product of the permeance and average thickness of the film.

Oxygen permeability Oxygen permeability coefficient ($P_{(O_2)}$; cm^3.cm/cm^2.s.cmHg) was measured by gas permeability tester (Gasperm-100, JASCO Corporation, Tokyo). Oxygen transmission rates were determined at 25°C under 0.5–1 kgf/cm^2 pressure. The value of $P_{(O_2)}$ was calculated by dividing the rate of oxygen transmission (G, in 0.2 μl) by oxygen pressure (p, in kgf), square area of film (s, in cm^2) and time (t, in min.), and then multiplying by thickness of the film (d, in cm), $P_{(O_2)}=1/228.\ G.d.p^{-1}.s^{-1}.t^{-1}\times10^{-9}$.

Results and Discussion

The 20% polyethylene glycol (PEG) or 20% lauric acid (LA) used increased the flexibility of zein-based films when each of them was added singly (Table 1). In this experiment, it was noted that PEG and LA decreased the elastic modulus (EM) value by 75% and 45%, respectively. The EM values were 0.37 GPa in PEG and 0.82 GPa in LA compared to 1.88 GPa in unplasticized film. An increase in film flexibility was also indicated with a higher value in elongation to break (ETB). Addition of 20% LA to zein-based film caused a 12% increase while PEG improved ETB by 11% (Table 1).

Table 1. Effect of plasticizer on mechanical property parameters of zein-based film

Type of Plasticizer	EM[1] (G Pa)	ETB[2] (%)	TS[3] (MPa)	PS[4] (MPa)
Lauric acid	0.82^c	25.25^b	41.63^b	0.25^b
Polyethylene glycol	0.37^b	25.00^b	27.48^a	0.17^{a,b}
No plasticizer	1.88^a	22.50^a	27.00^a	0.14^a

[1]EM, elastic modulus; [2]ETB, elongation to break; [3]TS, tensile strength; [4]PS, puncture strength. Values followed by different letters are significantly different at $p<0.05$ using Duncan's Multiple Range Tests.

Table 2. Mechanical properties of various PEG/LA-zein film

Portion of PEG/LA (%, w/w of zein)	EM[1] (G Pa)	ETB[2] (%)	TS[3] (MPa)	PS[4] (M Pa)
10/10	1.01^b	19.89^a	26.74^b	0.18^a
20/10	0.39^a	32.03^{a,b}	33.75^c	0.35^b
30/10	0.37^a	41.41^b	23.49^b	0.42^b
40/10	0.29^a	74.06^c	7.51^a	0.37^b

[1]EM, elastic modulus; [2]ETB, period to breakage; [3]TS, tensile strength; [4]PS, puncture strength. Values followed by different letters are significantly different at $p<0.05$ using Duncan's Multiple Range Tests.

Table 2 shows that an increase in concentration of PEG from 10 to 40% added to 10%LA-zein films decreased EM values but increased ETB values. For PEG, only the 10% concentration gave a significantly (0.05 level, test) different result than higher concentrations. Whether PEG was added at 20, 30 or 40% did not matter as the values obtained did not significantly differ. That result indicates that addition of PEG above 20% did not further affect EM value, and it also suggested the limited capacity of a zein structure to absorb and make a linkage with PEG. The addition of PEG produced different results in ETB values. Increasing PEG caused an increase in ETB, however, by statistical analysis there was no significant difference between the addition of 10 to 20% and 20 to 30% PEG. Moreover, 40% PEG gave the highest and the best ETB at 74.06% which was also significantly different from others.

Theoretically, zein-protein is insoluble in water, however, it is not a totally hydrophobic polymer. Hydrophobic interactions are an important aspect of zein film formation. PEG provided good linkages through hydrophobic interaction between corn-zein protein molecules (Park *et al.*, 1994). This also indicates that lauric acid as an absolutely non-polar plasticizer might only play a secondary role in forming a film matrix. According to Santosa and Padua (1999), excessive heat treatment and stirring during initial dispersion of zein and fatty acid promoted gelation, which might lead to non-formation of protein-fatty acid associations.

In general, plasticizers reduce polymer chain associations in sheet matrix which usually might cause a decrease in tensile strength (TS) value. However, Table 2 shows that an increase in the ratio of PEG/LA to zein film was not as consistent as the values obtained for both EM and ETB. The TS value of 10 and 30% PEG film were not significantly different, and PEG added at 20% resulted in TS even above 30%. PEG at 40% of the film gave the lowest TS value and this was significantly different from other values obtained. The highest TS value of 33.75 MPa was recorded when 20% PEG was added, while the lowest, 7.51 MPa was noted at 40% PEG.

Puncture strength (PS) values followed the trend of EM values. Only 0.18 MPa in 10% PEG was significantly different from other values of 0.35, 0.42 and 0.42 MPa, for PEG added at 20, 30 and 40%, respectively. This might relate to the limited capacity of zein to absorb and make linkages with PEG. For mechanical parameters, the best concentration of PEG added to lauric acid-zein film was 20% because this gave the highest TS value (33.75 MPa), which was significantly different from the rest. It also gave 0.39 GPa (EM) –0.35 Mpa (PS) which were not significantly different from the higher values of EM and PS recorded in

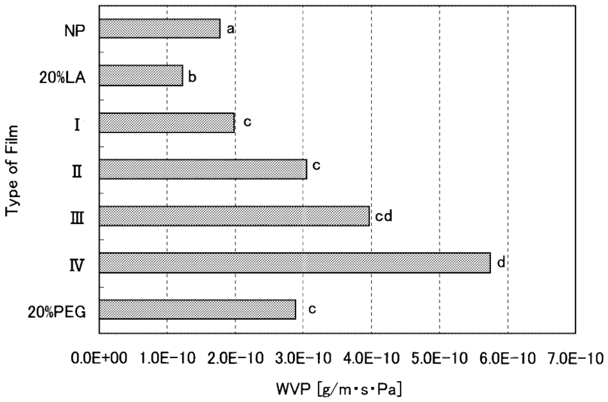

Fig. 1. WVP of zein-based film as affected by plasticizer treatment.
NP: unplasticized-zein film; I: 10% PEG+10% LA-zein film; II: 20% PEG+10%LA-zein film; III: 30% PEG+10% LA-zein film and IV: 40% PEG/10%-LA-zein film, 20% La: 20% Lauric Acid. 20% PEG: 20% Polyethylene Glycol. Values followed by different letters are significantly different at $p<0.05$ using Duncan's Multiple Range Tests.

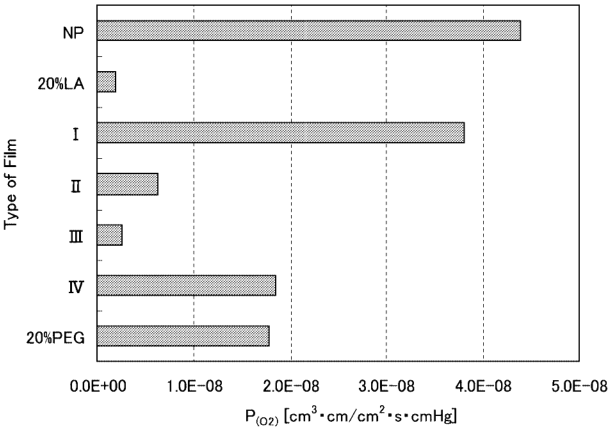

Fig. 2. $P_{(O_2)}$ of Zein-based films as affected by plasticizer treatment.
NP: unplasticized-zein film; I: 10% PEG+10% LA-zein film; II: 20% PEG+10% LA-zein film; III: 30% PEG+10% LA-zein film and IV: 40% PEG/10% LA-zein film. 20% La: 20% Lauric Acid. 20% PEG: 20% Polyethylene Glycol.

30 and 40% PEG.

Increasing amounts of PEG added to the zein-based film also affected the water vapor permeability (WVP) of the film (Fig. 1), although the presence of LA prevented this. The WVP of zein-based film plasticized with 20% of PEG added alone was 2.88×10^{-10} (Fig. 1), but this increased to 3.05×10^{-10} [g/m.s.Pa] when plasticized with a composite of 20% PEG/10% LA. Although LA might have played a secondary role in film matrix building, LA is important in preventing water absorption. Santosa and Padua (1999) reported in their studies that LA during polymerization may have filled pores and gaps in the structure which prevented the film from swelling. Based on their functional group, LA is less hydrophilic than PEG, thus WVPs of films containing only LA were expected to be lower than those for 10% PEG/10% LA, 20% PEG/10% LA, 30% PEG /10% LA and 40% PEG/10% LA. The WVP increased in all films as the concentration of PEG increased. However, zein film added with 10% PEG /10% LA, 20% PEG/10% LA and 30% PEG/10% LA did not significantly differ. The highest WVP, 5.74×10^{-10} [g/m.s.Pa] was noted with 40% PEG/10% LA, but this result was not significantly different from 3.96×10^{-10} [g/m.s.Pa], which was noted with 30% PEG/10% LA.

Lauric acid (20%, w/w of zein weight) added alone to zein-based film greatly decreased oxygen permeability coefficient ($P_{(O_2)}$) from 4.38×10^{-8} (unplasticized-zein film) to 1.95×10^{-10} [cm^3.cm/cm^2.s.cmHg] (Fig. 2). $P_{(O_2)}$ seems highly dependent on the porous structure of the film. As mentioned above, LA might have filled pores and gaps in the structure, and thus zein-based film plasticized with LA decreases $P_{(O_2)}$. In contrast, high hydrogen bonding between polymer is theorized form an excellent barrier to oxygen. PEG has some hydrophilic zones that can make hydrogen bonding. Through this ability PEG also was shown to decrease $P_{(O_2)}$ of zein-based film.

Figure 2 shows the effects of PEG and LA as composite plasticizers on $P_{(O_2)}$ of zein-based film. By different mechanisms PEG and LA seem to decrease $P_{(O_2)}$ as their amounts increase. The $P_{(O_2)}$ of zein-based film plasticized with 10% PEG/10% LA was 3.80×10^{-8}, then decreased to 6.23×10^{-9} and 2.48×10^{-8} [cm^3.cm/cm^2.s.cmHg] when PEG increased to 20% PEG/10% LA and 30% PEG/10% LA, respectively. Furthermore, when plasticizer was added in abundance to be 40% PEG/10% LA increased $P_{(O_2)}$ to 1.84×10^{-8} [cm^3.cm/cm^2.s.cmHg]. However, statistical analysis did not show a significant difference in $P_{(O_2)}$ among composite plasticizers treatments as experimental data distributions. The results of barrier properties suggest that the composite plasticizers have the potential to control barrier properties of zein film.

Conclusions

The use of individual degradable plasiticizer on zein-based film has improved film flexibility by significantly decreasing elastic modulus. Lauric acid exhibited improved tensile and puncture strengths as well as barrier properties. The use of polyethylene glycol did not affect existing performance in either tensile or barrier properties, but it was exhibited excellent in increasing film flexibility.

Overall, this result indicated the need for use of composite plasticizers on zein-based film for use in biodegradable food packaging. Further studies are necessary to learsn the effect of composite plasticizers and different conditions in the film forming process to develop a good formula for plasticized zein-based film.

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