

WATER VAPOUR BARRIER PERFORMANCE OF CORN-ZEIN COATED POLYPROPYLENE (PP) PACKAGING FILMS

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The novel film structure of corn-zein coated on polypropylene (PP) synthetic film for packaging industry was developed to examine the feasibility of resulting coated films as an alternative water barrier performance for food packaging. The effects of coating formulation (solvent, corn-zein, plasticizer concentration and plasticizer type) on final properties of films were observed. Corn-zein is the most important protein of corn and has good film forming property. Composites structures of PP films coated with corn-zein were obtained through a simple solvent casting method. Polyethylene glycol (PEG) and glycerol (GLY) were used as plasticizer to increase film flexibility. Statistical analysis based on full factorial design was performed to observe coating formulation effects. The high water vapour barriers were obtained for films coated with coating formulation consisting of higher amounts of corn-zein plasticized by GLY. The lower glass transition temperatures (T_g) of films were obtained by plasticization of films and T_g decreased by increasing plasticizer content. The statistical analysis defined the key parameters of coating formulation that had major effects on the final properties of coated PP films as corn-zein, plasticizer concentration and plasticizer type. In conclusion, corn-zein coatings could have potential as an alternative to conventional synthetic polymers used in composite multilayer structures for food packaging applications.

Keywords: coating, corn zein, packaging, polypropylene, water vapor barrier

Introduction

The plastics, polypropylene (PP) and polyethylene (PE) used for food packaging today consist of petroleum-derived (non-degradable) polymers because of their low cost, durability and structures that resulted in wide ranges of strengths and shapes [1, 2]. The purpose of food packaging is to preserve the quality and safety of the food it contains from their manufacture to consumer use [3]. The polymers used for food packaging should have combination of moisture and gas barrier, mechanical and also thermal properties [4]. The protection of packaged food against water and oxygen is one of the most important requirements and they can be blocked by the use of coatings on the packaging materials. Conventional barrier coatings on packaging materials typically consist of expensive and synthetic polymers such as ethylene vinyl alcohol (EVOH), polyvinylidene chloride (PVDC) and polyesters [5].

Despite the availability of a variety of excellent synthetic coatings, the disadvantage is the difficulty entailed in their recycling. The coating films containing layers of different plastic materials may not be recycled, because typically only recycling of single component plastics is feasible. Furthermore, the growing reliance on these coated packaging films has raised a number of environmental concerns. The increased consumption of these laminated packaging films has resulted in increased environmental waste [2, 6, 7].

Therefore, biodegradable polymers are now being considered for packaging materials because of their film-forming abilities and also their favorable environmental advantages in terms of recyclability and reutilization compared with conventional synthetic polymeric films [8]. However, biopolymer films have a susceptibility to drying, brittleness and lower mechanical properties. In an attempt to overcome this problem, a novel approach can be explored for the use of biopolymer coatings on conventional synthetic plastic films (e.g. polyethylene and polypropylene) to produce a multilayer film structure. One advantage of these multilayer films is an easy separation of the films in solvent, which provides a higher possibility for recycling. Another advantage is to improve the barrier and mechanical properties of synthetic monolayer films [9].

To date, many studies based on biodegradable polymers as a free film [10] or coatings have been studied. Hong *et al.* studied (2005) the properties of PP coated with polysaccharides [11]. Whey protein, one of the animal based proteins, is another important research area and new studies have been focusing on this topic [12]. To our knowledge, however, there is no study about corn-zein coated synthetic monolayer polymeric films. Existing studies are limited only with free-standing films of corn-zein which have excellent film forming properties [13]. Zein is the most important protein in corn. It is a prolamine protein and therefore, it

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can be dissolved in ethanol. Zein is a relatively hydrophobic and thermoplastic material [14].

In this work, the surface of the polypropylene film was coated with a biodegradable corn-zein polymer for food packaging applications. These films were prepared as an alternative to multilayer packaging films which consist of non-degradable polymers. The effectiveness of these films for food packaging applications was evaluated in terms of water vapour barrier and thermal properties of the resulting coated film.

Experimental

Materials

Corn-zein (regular grade) was obtained from Sigma-Aldrich. Ethyl alcohol (99.5%) used as a solvent was supplied from Panreac and it was diluted with distilled water to prepare two different solvent concentrations (70 and 95 v%). Polyethyleneglycol (PEG) ($M_w=400 \text{ g mol}^{-1}$) and glycerol (GLY) ($M_w=92 \text{ g mol}^{-1}$) used as plasticizer to overcome film brittleness was obtained from Merck and Sigma, respectively. Commercial corona discharge-treated PP cast film of 40 μm thickness (C11/40 μm) obtained from Polinas Company (Manisa, Turkey) was used as a substrate for corn-zein coatings.

Preparation of corn-zein coated PP films

Corn-zein film solutions were prepared by dissolving zein with two different concentrations (5 and 15% (mass/v)) in 70 and 95 v% aqueous ethanol solution, respectively. The solution was stirred on a magnetic stirrer for 2 h at 50°C. Zein solutions were plasticized by both PEG and GLY with various concentration levels, which were 20 and 50%, based on corn-zein mass. Following the addition of plasticizer, stirring was continued for a further period of 2 h. Then, film solutions were cast by using automatic film applicator (Sheen 1133N, England) on corona discharge-treated PP film with wet coating thickness of 30 μm . Corn-zein coated PP films were dried at 50°C for 2 h under vacuum of 200 mbar (1 mbar=0.1 kPa). Then, the temperature of the vacuum oven was increased to 120°C to allow further evaporation of solvent.

Water vapor permeability

Water vapor permeability (WVP) of coated films was determined with the standard method of ASTM E96. The method was performed by sealing a film to the open mouth of a test cup containing silica gel (20 g)

and placing the assembly into the controlled environmental chamber at 60% relative humidity (RH) and 25°C. This allows the conditions with low humidity on one side of the film and high humidity on the other side. The water vapour transferred through the film and absorbed by the silica gel was detected by weighing the cups periodically until a stationary state was reached. Initially, masses of the cups were recorded at 30 min intervals for a period of 8 h. The final measurement was done after 24 h. Then, WVP was determined from mass differences of test cups at the end of test duration by following equation.

$$\text{WVP} = \frac{\Delta W}{A \Delta t} \frac{L}{\Delta p} \quad (1)$$

WVP results were reported as an average of three replicated samples for each film.

Thermal analysis

Differential scanning calorimetry measurements were carried out in Shimadzu DSC-50 (Japan) equipment. Film samples were scanned at a rate of 10°C min⁻¹ between temperature ranges of 20 and 500°C. Glass transition temperatures of the plasticized corn-zein films were determined from resulting thermograms as the midpoint between onset and end temperatures of step changes in heat flow observed during heating. The melting and degradation temperatures of the coated PP samples were also determined by using DSC.

Statistical planning of experiments

Statistical analysis based on full factorial design was performed with the analysis of variance (ANOVA) to examine the influence of the three variables on the final properties of corn-zein coated PP films. The model included factors of two replications at centre point, for corn-zein concentration (5 and 15 mass%), ethanol concentration (70 and 95 mass%) and plasticizer concentration (20 and 50%) for each plasticizer containing films; GLY and PEG. These variables were examined at three levels: upper, midpoint and lower limits. Testing of all three factors (ethanol, corn-zein and plasticizer concentrations) simultaneously would involve factorial design with eleven experiments for a single plasticizer containing coating solution determined by statistical analysis system, MODDE version 7.0 (Umetrics, Sweden).

Table 1 WVP of corn-zein coated PP films prepared according to experimental design^a

Corn-zein/ mass/v%	Ethanol/ v/v%	Plasticizer content/ g(g zein) ⁻¹	PEG plasticization	GLY plasticization
			WVP·10 ⁴ / g mm kPa ⁻¹ min ⁻¹ m ⁻²	WVP·10 ⁴ / g mm kPa ⁻¹ min ⁻¹ m ⁻²
5	70	0.2	1.51±0.41	0.95±0.14
5	95	0.2	0.92±0.05	0.44±0.02
15	70	0.2	1.62±0.39	0.93±0.11
15	95	0.2	4.55±0.48	0.23±0.03
5	70	0.5	6.60±3.20	2.15±0.53
5	95	0.5	4.08±1.39	3.89±1.06
15	70	0.5	1.50±0.36	2.32±0.38
15	95	0.5	3.51±0.67	0.12±0.05
10	82.5	0.35	3.04±0.82	0.31±0.04
10	82.5	0.35	2.70±1.38	0.29±0.04
10	82.5	0.35	0.60±0.15	0.31±0.06

^avalues are average of three samples±standard deviation

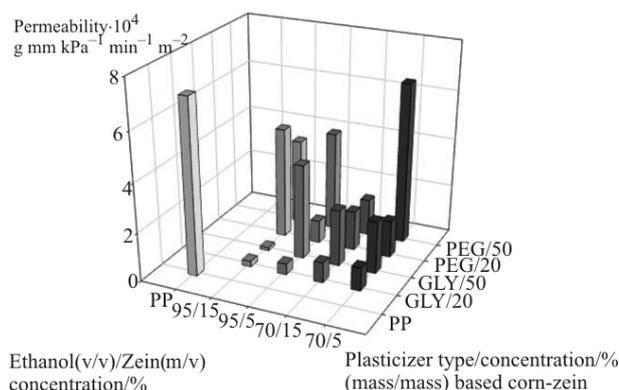


Fig. 1 Effects of coating composition on WVP of corn-zein coated PP films

Results and discussion

Water vapour barrier performances

The WVP values of the PP films coated with different coating formulation are illustrated in Fig. 1. The corn-zein, ethanol and plasticizer concentration and plasticizer type in coating solution produced statistically significant differences ($p < 0.05$) in water barrier properties of coated PP films. The considerable effects on WVP of coated PP films can be easily observed from Fig. 1. The significant improvement in water vapour barrier of PP base films was obtained and these results were also tabulated in Table 1. The improvement in WVP was observed in all formulations compared with uncoated PP film having WVP value of $7.140 \cdot 10^{-4} \text{ g mm kPa}^{-1} \text{ min}^{-1} \text{ m}^{-2}$.

Generally plasticizers increase permeability of the films depending on the concentration of plasticizer used.

Table 2 Effects of plasticizer type and concentration on the WVP of coated PP films^{a,b}

Plasticizer type	Plasticizer concentration/ mass% (based on corn-zein content)	WVP·10 ⁴ / g mm kPa ⁻¹ min ⁻¹ m ⁻²
PEG	20	0.92±0.05
PEG	50	4.08±0.39
GLY	20	0.44±0.02
GLY	50	3.89±0.06

^awhere ethanol and corn-zein concentrations are constant at 95 and 5%, respectively

^bvalues are average of three samples±standard deviation

Plasticizer was used to increase the flexibility of corn-zein films. They work as spacers between protein chains resulting in a less dense structure where chain ends became more mobile and increase permeability. The effect of different plasticizers, PEG and GLY and also their concentrations used in zein coating solution on WVP of resulted films are tabulated in Table 2. In comparison, among the films coated by zein solutions containing two different plasticizers, the coating solution plasticized by GLY had the highest water vapour barrier properties. The both plasticizers, PEG and GLY, have polar and hydrophilic character. However, it was seen that PEG has more the ability to attract water molecules through either absorption or adsorption and also strong affinity for moisture, thus PEG plasticized zein coating on PP films resulted in relatively large amounts of water sorption and higher permeability values.

Furthermore, the higher WVP of corn-zein plasticized by PEG coated PP films as compared with GLY plasticized films may be related to the hydration of the plasticizers in which water molecules associated by PEG

were more than GLY for the same concentration. Thus, the concentration of hydrophilicity becomes the key factor for the barrier efficiency, so, the more hydrophilic nature of PEG than GLY increased the WVP.

Several authors studied the influence of the plasticizer content on barrier properties of zein films and they showed that the increase in WVP of films was caused by the increase of plasticizer content [13–16]. The results from these studies were similar to those reported in this study. Parris and Coffin (1997) studied the effect of some of plasticizers on the WVP of the free-standing zein films. Water vapour barrier properties were the best for unplasticized zein films and incorporation of plasticizers, PEG and GLY, into the zein films resulted in almost doubled WVP values. The increase in WVP was more pronounced for films plasticized with PEG which is similar to our results [15]. Lawton (2004) studied the relationship between plasticizer type and water sorption of zein films and reported that films increasingly absorbed water depending on the plasticizers used in the film in the order of GLY>PEG and found that plasticizing efficiency increased with the molecular mass of the plasticizer used. Thus, PEG plasticized films had higher plasticizing efficiency than GLY plasticized films. So, their results confirm our permeability results that the films plasticized with PEG have higher values than GLY plasticized films [14].

Furthermore, most of the published work in the literature deals with water vapour transfer properties of other biodegradable based films. The results showed that plasticizers generally increase permeability when high ratio of plasticizer was used in polymer [17–19]. As seen from Fig. 1, ethanol and zein concentrations in coating formulation were important and affect the WVP coated PP films. Corn-zein coated films were expected to have variable behaviour against water vapour depending on zein concentration because of major hydrophobic character of zein. In addition, the ethanol concentration affects the solubility of corn-zein that resulted in different permeability properties of coated films. The effects of ethanol and

corn-zein concentration on WVP values of coated PP films are summarized in Table 3.

The corn-zein films having zein concentration of 5 and 15 g/100 cm³ ethanol were prepared to coat PP films at the same ethanol concentration and then the effect of ethanol concentration of 70 and 95 v% used in preparation of film-forming solution was also investigated. As the corn-zein concentration in the coating formulations increased, the water vapour barrier of coated PP films was also increased.

Corn-zein and ethanol concentrations in coating film-forming solutions strongly affected film structure and high water vapour permeability properties of coated PP films were obtained at low concentrations of ethanol. Since the amount of corn-zein present in the coating formulations affects the hydrophobicity of coated PP films, which was the key factor for the barrier efficiency, the WVP of films was influenced by corn-zein concentration. The films coated with solutions included higher amount of zein created the more hydrophobic nature than the coated PP films containing low corn-zein in the coating solutions; thus the improvement of water barrier was observed for high concentrations of zein. In addition, results showed that WVP decreased significantly when the ethanol concentration increased. Although an increase in concentration of zein decreased WVP, for film solutions plasticized with 20 mass/mass% of PEG in an increase in WVP resulted at both low and high ethanol concentrations whereas it was expected to cause a decrease in WVP of coated films. This can be explained by non-homogeneous distribution of corn-zein in the coating solution, therefore, the effect of corn-zein may not be observed for these films. The general linear models procedure was used for ANOVA; results showed that model is significant for WVP results using both experimental methods. The statistical analysis also defined the key parameters that had dominant effect on WVP of coated PP films as corn-zein, plasticizer concentration and plasticizer types. Finally, the corn-zein coatings could work successfully as a water vapour barrier and have a potential to be used as an alternative to existing packaging materials under optimum levels of these coating parameters mentioned above.

Table 3 Effects of ethanol and corn-zein concentration on the WVP of coated PP films^{a,b}

Ethanol/ v/v%	Corn-zein concentration (g/100 mL ethanol)	WVP·10 ⁴ /g mm kPa ⁻¹ min ⁻¹ m ⁻²
70	5	0.95±0.14
70	15	0.93±0.11
95	5	0.44±0.02
95	15	0.23±0.03

^awhere plasticizer is GLY and its concentration is constant as 20 mass/mass%

^bvalues are average of three samples±standard deviation

Thermal analysis

To investigate the effect of plasticizer on the thermal behaviour of zein films, DSC was carried out using the film formulation with constant plasticizer content of 20 mass/mass% (based on corn-zein amount). The addition of plasticizers affected the thermal behaviour of zein films. The effective plasticization induces the change in thermal properties of polymer/plasticizer

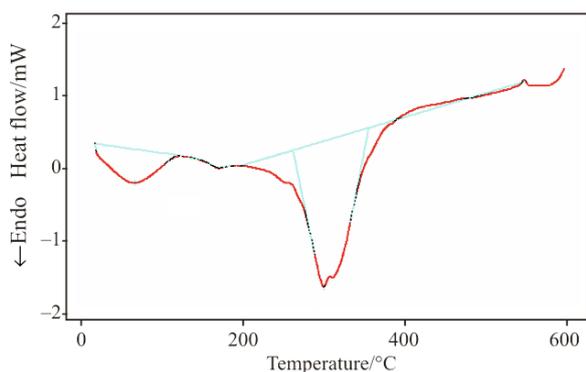


Fig. 2 DSC curve of unplasticized corn-zein films

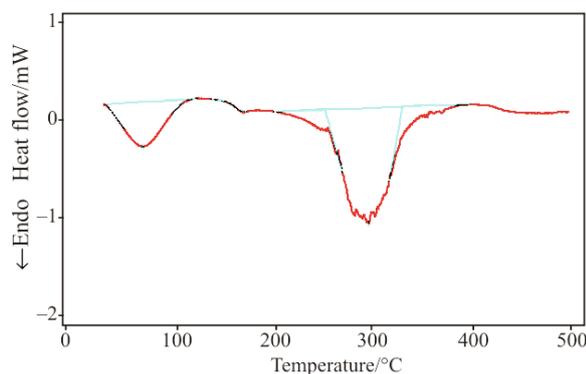


Fig. 3 DSC curve of corn-zein films plasticized with GLY

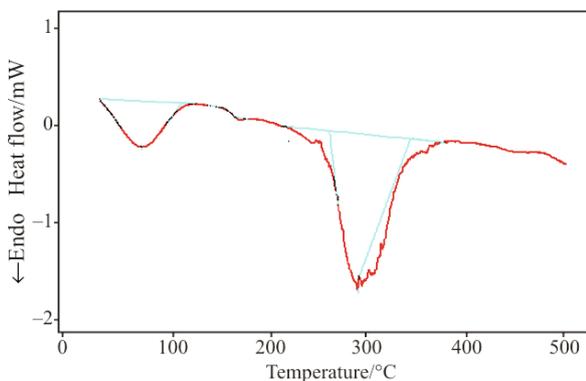


Fig. 4 DSC curve of corn-zein films plasticized with PEG

systems. The corn-zein films without plasticizer was initially analyzed to examine plasticizer effect on T_g of coating solution and T_g was found as approximately 160°C for unplasticized zein films as shown in Fig. 2. Since T_g is the function of polymer chain flexibility, the decrease in T_g of the zein coating was expected to decrease by increasing plasticizer content. A DSC curve of unplasticized zein film (Fig. 2) showed an endothermic peaks centered at 65 and 301°C, respectively. These endothermic peaks could be interpreted as the result of break-down of hydrogen bonds within this temperature range and other molecular associations and also protein unfolding [20].

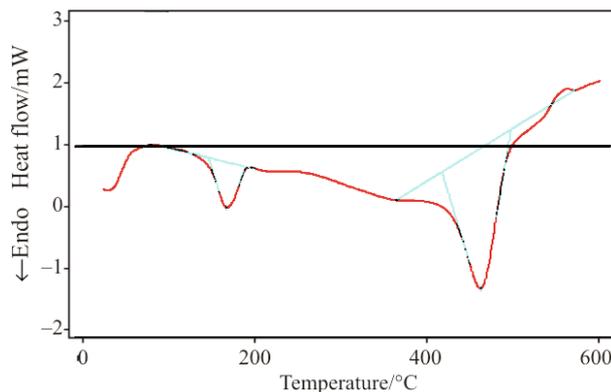


Fig. 5 DSC curve of PEG plasticized corn-zein coated polypropylene film (plasticizer concentration: 20 mass/mass%, ethanol concentration: 70 v/v%)

The curves between DSC thermograms (Figs 3 and 4) from unplasticized zein and plasticized zein were believed to be due to the effects of plasticization applied to zein during preparation. Plasticizers are expected to decrease intermolecular forces between zein polymer chains. The incorporation of plasticizer into corn-zein solution resulted in a decrease in T_g value from 160.5 to 157.7 and 157.9°C for GLY and PEG, respectively. The endothermic peaks observed for unplasticized corn-zein films shifted to 66 and 296°C for GLY plasticization (Fig. 3), respectively.

Furthermore, these observations were similar to previous studies based on plasticizer effects on thermal behaviour of zein films [21–23]. Kokini and coworkers (1996) investigated the plasticizing effect of water on cereal proteins. They reported that the first few percentages of water resulted in a decrease in T_g of zein. Then, they measured T_g of zein at various moisture contents and reported its decrease from 139 to 47°C when water content increased [21]. Tillekeratne and Eastale (2000) studied thermal properties of corn films plasticized with PEG. They measured T_g of unplasticized zein films between 162–165°C [22]. Furthermore, Magoshi *et al.* (2000) investigated the thermal behaviour of corn-zein films and T_g was observed at 165°C. The results from these studies are comparable and in agreement with our results [23]. Also endothermic peak observed at 287–301°C for plasticized and unplasticized corn-zein films is attributed to thermal degradation of prolamine [24].

In addition, two major endothermic peaks were observed from DSC curves of PEG plasticized zein coated PP films, which were attributed to melting and degradation of bilayer films (Fig. 5). T_m and T_d of PP base film without coating were 170.0 and 457.8°C, respectively. The thermograms showed that the melting and degradation peaks of the coated PP film were similar to uncoated PP film (Table 4), however shift in melting (T_m) and

Table 4 Melting (T_m) and degradation temperatures (T_d) of corn-zein coated PP films

Corn-zein conc./ m/v%	Ethanol conc./ v/v%	Plasticizer/ (g/g zein)	PEG Plasticization		GLY Plasticization	
			Melting temp., $T_m/^\circ\text{C}$	Degrad. temp., $T_d/^\circ\text{C}$	Melting temp., $T_m/^\circ\text{C}$	Degrad. temp., $T_d/^\circ\text{C}$
5	70	0.2	164.9	459.8	167.3	461.1
5	95	0.2	166.6	460.1	169.1	460.2
15	70	0.2	168.2	462.9	169.7	462.5
15	95	0.2	169.1	463.4	169.3	463.4
5	70	0.5	168.6	461.6	168.7	463.0
5	95	0.5	165.5	463.9	168.9	463.4
15	70	0.5	169.3	462.7	167.8	461.3
15	95	0.5	168.9	462.3	169.2	464.7
10	82.5	0.35	167.2	460.7	165.1	459.2
10	82.5	0.35	166.9	461.2	165.9	458.9
10	82.5	0.35	166.6	460.6	166.9	459.6

degradation temperatures (T_d) were observed. The peaks related to corn-zein were not seen in the thermogram due to PP base film thickness and also small amount of plasticizers present in the whole film structure.

The coating of corn-zein on PP films increased their degradation temperature while decreased melting temperature, which can allow wide service temperature range of coated PP films without losing mechanical property such as strength, stiffness and toughness. The melting temperature of coated PP films decreased slightly due to increase in mobility of polymeric chains in coating by plasticization.

Conclusions

The plasticized corn-zein coatings on PP films were prepared as an alternative to commercial coated films, which consist of expensive and non-degradable polymers. The water vapour barrier and thermal properties of resulting films affected by corn-zein, ethanol and plasticizer concentration and plasticizer types were examined. Thus, the novel film structure for food packaging applications, which provide better possibility in recycling processes because of easy separation of coating from the base plastic, was proposed by optimizing coating formulation.

The final corn-zein coated PP films showed good appearance, flexibility and adhesion between the coating and the base film. WVP of PP films significantly decreased by corn-zein coating, depending on coating formulation. The improvement of water vapour barrier properties of coated PP films was obtained for high concentrations of both corn-zein and ethanol in coating solutions. In addition, the WVP of coated PP films increased with increased concentrations of PEG and

GLY used as plasticizers. The higher water barrier of corn-zein coated PP films was observed by plasticization of GLY as compared to PEG due to higher hydrophilicity of PEG. The coating of corn-zein on PP films increased their degradation temperature which can allow higher service temperature. Due to increase in mobility of polymeric chains in coating by plasticization, melting temperature of coated PP films decreased which allow high processability of films even at low temperatures. The statistical analysis of the results showed that corn zein, plasticizer concentrations and plasticizer type used in coating formulation were more effective parameters and had significant effects on barrier and thermal behaviour of coated PP films.

In summary, results suggested that the corn-zein coated PP films showed tendency to provide packaging criteria with proper coating formulations especially high corn-zein content films plasticized with low level of GLY. Furthermore, the film coating formulation can be changed depending on property required. In conclusion, corn-zein coatings on PP films could have potential as an alternative to synthetic coating materials with appropriate formulation.

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