Effect of Corn-Zein Coating on the Mechanical Properties of Polypropylene Packaging Films

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ABSTRACT: In this study, a novel film structure of corn zein coated on polypropylene (PP) synthetic films for food packaging applications was developed, and the mechanical properties of the resulting coated film, as affected by the coating formulation, were investigated. Composite structures of PP films coated with corn zein were obtained through a simple solvent casting method. Different amounts of corn zein (5 and 15%) were dissolved in 70 and 95% aqueous ethanol solution at 50°C. Solutions of corn zein plasticized with poly(ethylene glycol) and glycerol (GLY) at various levels (20 and 50%) were applied on corona-discharge-treated PP. A statistical analysis based on full factorial design was performed to examine the influence of the coating formulation on the final properties of the corn-zein-coated PP films. A significant ($p < 0.05$) improvement in the coated film's mechanical properties was observed compared to those of the uncoated PP. The effect of the plasticization of the coating solutions was also quite significant. In general, GLY provided better improvements in the mechanical properties of the corn-zein-coated PP films. The statistical analysis of the results showed that the corn-zein and plasticizer concentrations and plasticizer type used in the coating formulations were more effective parameters and had significant effects on the mechanical behavior of the coated PP films. In conclusion, corn-zein coatings could have potential as alternatives to conventional synthetic polymers used in composite multilayer structures for food packaging applications. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 235–241, 2011

Key words: coatings; mechanical properties; poly(propylene) (PP); proteins

INTRODUCTION

Plastics are the preferred material for food packaging nowadays because of their low cost, durability, and structure, which results in a wide range of strengths and shapes.[1,2] These polymers are used in various combinations for their barrier and mechanical properties to preserve the quality and safety of packaged foods from processing through handling and storage and, finally, to consumer use. The mechanical properties are important for packaging materials as barrier properties. Having sufficient mechanical strength and being free of minor defects ensure the integrity of a packaging film. Among the many mechanical properties of plastic materials, the tensile properties are the most frequently considered, evaluated, and used throughout the industry. Tensile testing of films provides data also for the yield strength, tensile strength, modulus of elasticity (Young's modulus), and elongations at yield and break.[3,4] Quantitative information on the mechanical parameters of packaging films is essential for the packaging design process.

Conventional coatings on food packaging materials typically consist of expensive and synthetic polymers, such as ethylene vinyl alcohol, poly(vinylidene chloride), and polyesters.[5] Despite the availability of a variety of excellent synthetic coatings, the disadvantage is the difficulty entailed in their recycling. Existing coatings containing layers of different synthetic plastic materials may not be recycled because, typically, only single-component plastics can be recycled.[6] Therefore, the replacement of nondegradable polymer coatings by biodegradable coatings is of major interest to the plastic packaging industry. Biodegradable coating materials include films made from polysaccharides (e.g., starch, cellulose, chitosan/chitin), proteins (e.g., whey protein, corn zein, wheat gluten, soy protein), or lipids (e.g., animal and plant-derived lipids). To date, many research studies on polysaccharide and whey protein coatings for food packaging applications have been done.[7–9] To the best of our knowledge, however, there has been no study on the effect of corn-zein coatings on the mechanical properties of synthetic monolayer polymeric films. Existing studies have been limited

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to only freestanding films of corn zein.[10–12] Zein is the alcohol-soluble protein found in corn endosperm, and it is a byproduct of the corn wet-milling industry. Zein is a relatively hydrophobic and thermoplastic material, and this hydrophobicity is related to its high content of nonpolar amino acids. In a previous study, we showed that corn-zein-coated synthetic films have better water-barrier and thermal properties. Corn-zein and plasticizer concentrations and plasticizer type in coating formulations had significant effects on the water-vapor-barrier properties of corn-zein-coated polypropylene (PP) films.[13,14] Therefore, the replacement of common synthetic layers with corn-zein protein coatings provides a new path to the improvement of the properties of base films for packaging applications by allowing higher recyclability of a base film at the end of their useful life.[15,16]

The purpose of this study was to develop a novel film structure of coated synthetic films for food packaging applications with good mechanical properties. The feasibility of plasticized corn-zein coatings on PP films was examined as affected by the coating formulation (solvent, corn-zein, and plasticizer concentrations and also plasticizer type). Statistical analysis based on full factorial design was also performed to examine the influence of the three variables (ethanol, corn-zein, and plasticizer concentrations) on the mechanical properties of the corn-zein-coated PP films.

EXPERIMENTAL

Materials

The corn zein used in this study was obtained from Sigma-Aldrich (Seelze, Germany). Ethanol (99.5%), which was used as a solvent, was supplied from Panreac, and it was diluted with distilled water to prepare two different solvent concentrations, which were 70 and 95%. Poly(ethylene glycol) (PEG) and glycerol (GLY), which were used as plasticizers to overcome film brittleness, were obtained from Merck and Sigma, respectively.

Preparation of the corn-zein-coated PP films

Corn-zein film solutions were prepared by the dissolution of zein to different concentrations between 5 and 15% (w/v) in an aqueous ethanol solution, in which its concentration ranged from 70 to 95% (v/v), respectively, and were stirred with a magnetic stirrer for 2 h at 50°C. The solutions of corn zein were plasticized with both PEG and GLY with various levels, 20 and 50% on the basis of the corn-zein weight. After the addition of plasticizers, stirring was continued for a further period of 2 h. After the corn-zein coating solutions were stirred, film solutions were cast with an automatic film applicator (Sheen 1133N, Kingston, England) on corona discharge-treated PP with a wet coating thickness of 30 μm. Corn-zein-coated PP films were dried at 50°C for 2 h *in vacuo* at 200 mbar. Then, the temperature of the vacuum oven was increased to 120°C to allow further evaporation of the solvent.

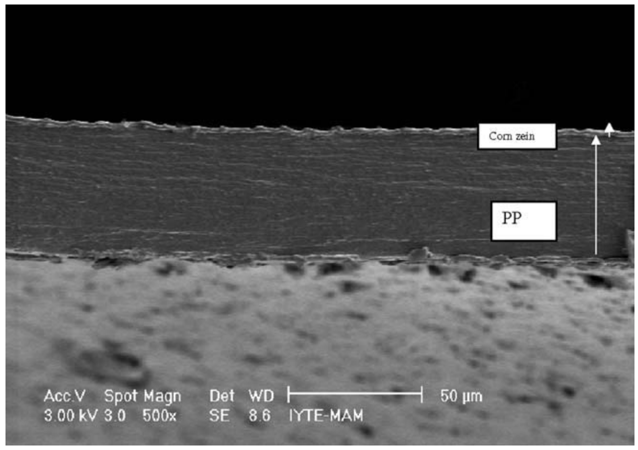

Figure 1 SEM micrograph of the corn-zein-coated PP film for thickness determination.

The thickness of the PP base film was 40 μm. The total thicknesses of the films were in the range 42.6–43.9 μm, depending on the coating formulation. Figure 1 shows a scanning electron microscopy (SEM) image of the corn-zein-coated PP films as an example for the determination of the thickness of the coating. The total thicknesses of all of the coated PP films were determined by SEM analysis and are tabulated in Table I.

Mechanical properties

A universal testing machine (Shimadzu AG-I 5 kN, Tokyo, Japan) was used to perform mechanical testing of the coated PP films according to ASTM D 882. Specimens were prepared at 10 mm in width and 100 mm in length and preconditioned at 23°C and 50% RH for 24 h before testing. The initial gauge length and crosshead speed were set at 50 mm and 10 mm/min, respectively. A total of five samples were tested for each film sample.

Design of the experiments

Statistical analysis based on full factorial design was performed to examine the influence of the three variables on the final properties of the corn-zein-coated PP films. The model included factors of two replications at a center point for corn-zein concentration (5 and 15 wt %), ethanol concentration (70 and 95 wt %), and plasticizer concentration (20 and 50%) for

TABLE I
Thickness of the Corn-Zein-Coated PP Films

PEG plasticization		GLY plasticization	
Coated film number	Thickness (μm)	Coated film number	Thickness (μm)
1	42.8 ± 0.72	12	42.9 ± 0.84
2	42.6 ± 0.45	13	43.1 ± 0.82
3	43.3 ± 0.19	14	43.2 ± 0.59
4	43.5 ± 0.98	15	43.5 ± 0.64
5	43.5 ± 0.49	16	42.8 ± 0.73
6	43.8 ± 0.36	17	43.4 ± 0.96
7	43.8 ± 0.26	18	43.2 ± 0.38
8	43.9 ± 0.58	19	43.4 ± 0.15
9	43.8 ± 0.84	20	43.8 ± 0.17
10	43.3 ± 0.88	21	43.2 ± 0.14
11	43.3 ± 0.75	22	43.1 ± 0.16

TABLE II
Experiments Performed According to the Experimental Design for a Certain Plasticizer Type

Coated film number	Ethanol concentration (% v/v)	Corn-zein concentration (% w/v)	Plasticizer concentration (% w/w)
1	70	5	20
2	95	5	20
3	70	15	20
4	95	15	20
5	70	5	50
6	95	5	50
7	70	15	50
8	95	15	50
9	82.5	10	35
10	82.5	10	35
11	82.5	10	35

each plasticizer-containing film, where GLY and PEG were used as a plasticizer. These variables were examined at three levels: upper, midpoint, and lower limits. Testing of all three factors (ethanol, corn-zein, and plasticizer concentrations) simultaneously involved factorial design with 11 experiments for a single plasticizer containing different coating solutions (Table II) determined by the statistical analysis system MODDE version 7.0 (Umetrics, Malmö, Sweden).

RESULTS AND DISCUSSION

The mechanical properties of the corn-zein-coated PP films that are important for packaging applications were determined in this study to investigate the effect of the coating formulation on the resulting PP films. Several factors were hypothesized to affect the properties of the corn-zein-coated PP films, and a full factorial design was set to examine the relationship among these different factors. Quantitative information on the mechanical parameters of the coated PP films is necessary for the packaging design process. Although the mechanical properties of the coated or laminated films in multilayer structures generally depend strongly on the substrate rather than on the coating, the tensile properties can be influenced by coating materials having different molecular characteristics than PP. Interactions between the zein protein and plasticizers dispersed in the space of the polymer matrix and the coating solvent concentration could have contributed to the mechanical behavior of the final coated PP films.

The mechanical behavior of coated films generally depends on the coating formulation. The results indicate that these properties were influenced by the nature of the coating composition. Table III shows the tensile strength and elongation break values of all of the coated PP films obtained from the tensile testing measurements.

The tensile strength of the commercial corona-discharge-treated PP film used in this study was 9.65 MPa without corn-zein coating. Therefore, it was

TABLE III
Tensile Strengths of the Corn-Zein-Coated PP Films Prepared According to Experimental Design

PEG plasticization			GLY plasticization		
Coated film number	Tensile strength (MPa)	Elongation at break (%)	Coated film number	Tensile strength (MPa)	Elongation at break (%)
1	12.94 ± 0.45	150.98 ± 12.9	12	11.65 ± 0.39	169.48 ± 13.6
2	10.86 ± 0.68	131.74 ± 9.22	13	12.24 ± 0.60	167.90 ± 17.7
3	11.17 ± 0.28	138.11 ± 6.87	14	12.65 ± 0.58	142.88 ± 7.41
4	11.27 ± 0.95	148.23 ± 17.6	15	13.13 ± 1.03	150.52 ± 16.7
5	10.31 ± 1.00	148.52 ± 17.6	16	10.93 ± 0.17	166.88 ± 11.1
6	10.69 ± 1.95	165.53 ± 7.71	17	11.17 ± 0.39	147.61 ± 8.58
7	10.38 ± 1.68	152.77 ± 8.53	18	13.27 ± 0.85	162.63 ± 9.20
8	12.20 ± 0.95	147.43 ± 4.81	19	11.58 ± 0.26	147.48 ± 6.76
9	10.42 ± 1.21	143.91 ± 2.18	20	13.37 ± 1.35	149.15 ± 5.08
10	10.59 ± 1.28	147.48 ± 2.10	21	14.66 ± 0.48	147.49 ± 3.02
11	10.36 ± 0.59	148.36 ± 2.31	22	14.09 ± 1.71	155.01 ± 12.3

TABLE IV
Effects of the Plasticizer Type and Concentration on the Tensile Strength of the Coated PP Films[a]

Plasticizer type	Plasticizer concentration (% w/w on the basis of the corn-zein content)	Tensile strength (MPa)
PEG	20	10.86 ± 0.68
PEG	50	10.69 ± 1.95
GLY	20	13.13 ± 1.03
GLY	50	11.17 ± 0.39

[a] Where the ethanol and corn-zein concentrations were constant at 95 and 5%, respectively.

clearly observed from experimental results that the maximum amount of tensile stress of the PP films before failure was improved with corn-zein coating. The tensile strength values of all of the coated films were in the range 10.31–14.66 MPa (Table III).

The plasticizing of the corn-zein-coating solutions with GLY and PEG caused differences in the mechanical properties of the coated PP films. The increasing plasticizer concentration in the corn-zein-coating solutions generally decreased the tensile properties of the resulting PP films. GLY and PEG could form numerous hydrogen bonds with the zein polypeptide chain because of the carbonyl of protein and hydroxyl groups of these plasticizers. Thus, these plasticizers introduced between the polypeptide chains affected the polymer–polymer interaction and caused a decrease in the tensile strength of the coated films. Therefore, as the plasticizer content increased, the tensile strength had a tendency to decrease because of weak polymer–polymer interaction. The plasticizing efficiencies of each PEG and GLY strongly depended on their concentrations.

PP films coated with corn zein containing high amounts of GLY and PEG in the coating formulation showed the lowest values for tensile stress. Therefore, a low level of plasticizer was enough to increase association within the zein polymer chains in the coating,; otherwise, a further increase in the plasticizer content negatively affected the mechanical properties. The effect of the plasticizers PEG and GLY and also their concentrations used in the zein coating solution on the tensile strength of the resulting films are tabulated in Table IV.

Similar results were obtained for freestanding zein films by several authors.[11,17,18] Lai and Padua[11] reported that 25% stearic acid used as a plasticizer for zein films increased the tensile strength of zein sheets substantially, but above this concentration, the tensile strength decreased. In the study of Gioia et al.,[17] GLY was used as a plasticizer for zein-based films. An increase in the GLY content resulted in a decrease of the tensile strength, which was also consistent with our results.

In comparison, the coating solution plasticized with PEG showed a relatively lower tensile strength in the resulting PP films compared to films prepared with coatings containing GLY. This could have been due to the more hygroscopic nature of the zein coating solution including PEG (the ability to attract water molecules) compared to those containing GLY. This showed that PEG was a more hydrophilic plasticizer than GLY, which was in agreement with the results obtained on the water-vapor permeability of coated PP films in our previous study.[13,14]

Furthermore, the results show that high corn-zein concentrations in the coating formulations induced the formation of coated PP films with higher mechanical strengths because of the stiffness of the corn zein. Also, the increase in the percentage of aqueous ethanol solution in the coatings resulted in a slight increase in the tensile properties, as shown in Table V.

However, statistical analysis of the data revealed that none of the parameters investigated had any significant effect on the tensile strength of the coated films, regardless of the plasticizer type.

An increase in the film flexibility was indicated with a higher value in elongation to break, that is, the maximum elongation of the sample (before failure occurred) divided by its original length and usually indicated as a percentage. The plasticizers, both PEG and GLY, were used to make the coating solutions more flexible. They worked as spacers between the zein protein chains, decreasing the intermolecular forces, and this resulted in an improvement in the flexibility of the corn-zein coating and, finally, the coated PP films. The elongations at break (%) of the coated PP film are presented in Table VI as a function of the coating parameters.

The elongation at break of the base PP film was found to be 121.69%. When the base PP film was coated with corn-zein solution, improvements in elongation at break of the films were obtained. As

TABLE V
Effects of the Ethanol and Corn-Zein Concentrations on the Tensile Strength of the Coated PP Films[a]

Ethanol concentration (%)	Corn-zein concentration (g/100 mL of ethanol)	Tensile strength (MPa)
70	5	11.65 ± 0.39
70	15	12.65 ± 0.58
95	5	12.24 ± 0.60
95	15	13.13 ± 1.03

[a] Where the plasticizer was GLY, with its concentration constant at 20% (w/w) on the basis of the corn-zein content.

TABLE VI
Effects of the Plasticizer Type and Concentration on the Elongation at Break of the Coated PP Films[a]

Plasticizer type	Plasticizer concentration (% w/w on the basis of the corn-zein content)	Elongation at break (%)
PEG	20	131.74 ± 9.22
PEG	50	165.53 ± 7.71
GLY	20	147.61 ± 8.58
GLY	50	167.90 ± 17.6

[a] Where the ethanol and corn-zein concentrations were constant at 95 and 5%, respectively.

shown in Table III, a significant increase in the elongation at break in all of the corn-zein-coated PP films was obtained.

These mechanical behaviors of the coated films were related to the structural modifications of the zein network with changing coating formulation parameters. Zein is a storage protein of corn. Proteins are generally known to undergo conformational and chemical changes, particularly changes in ionic, hydrogen, and hydrophobic bonding and crosslinking by disulfide or nondisulfide covalent bonds.[19] Zein aggregation after solvent evaporation due to the formation of disulfide bonds was also demonstrated by Batterman-Azcona et al.[20] Zein–plasticizer interaction effect could have also been important in the structural changes of the zein. The separation of zein protein chains by breakage of the bonds that held the polymer chains together and then the covering of the centers of forces resulted in the plasticizer–zein interaction because of the plasticization effect.

Fracture modes of the PEG- and GLY-plasticized coated PP films were examined with the surface-fractured tensile film surfaces with SEM (Fig. 2). Both samples showed a similar failure mechanism. With a plasticizer in the coating formulation, the films became more ductile.

The statistical models developed for the elongation at break for PEG- and GLY-plasticized coatings were significant ($p < 0.05$). Significant factors affecting the elongation at break were the plasticizer concentration and corn–plasticizer interaction for the coatings plasticized with both plasticizers. The elongations at break of the coated PP films increased with increasing plasticizer levels for all of the coating formulations, as shown in Table VI. The coating solution plasticized with GLY contributed to the relatively higher elongation of the resulting PP films compared to films coated by zein containing PEG. The PEG-based coated films were less flexible than the GLY-based coated PP film.

In addition, because GLY had a lower molecular mass compared to PEG, the number of moles of GLY incorporated into the coating solution was higher than the PEG ones, and this certainly was more important to the plasticizing effect. More reasons for the more flexible structure of the coatings produced with GLY were the easy fitting of this plasticizer into the zein protein chains and the establishment of hydrogen bonds with the reactive groups of proteins.

Because an increasing amount of corn zein present in the coating solution caused a more hydrophobic nature and also because of the brittleness of corn zein, the elongation of the coated PP films decreased. The effects of the corn-zein and ethanol concentrations on elongations of the resulting films are shown in Table VII.

Furthermore, the elongation results of the coated PP films were also in agreement with the study of Parris and Coffin,.[21] where zein films were plasticized with PEG and GLY. Films plasticized with

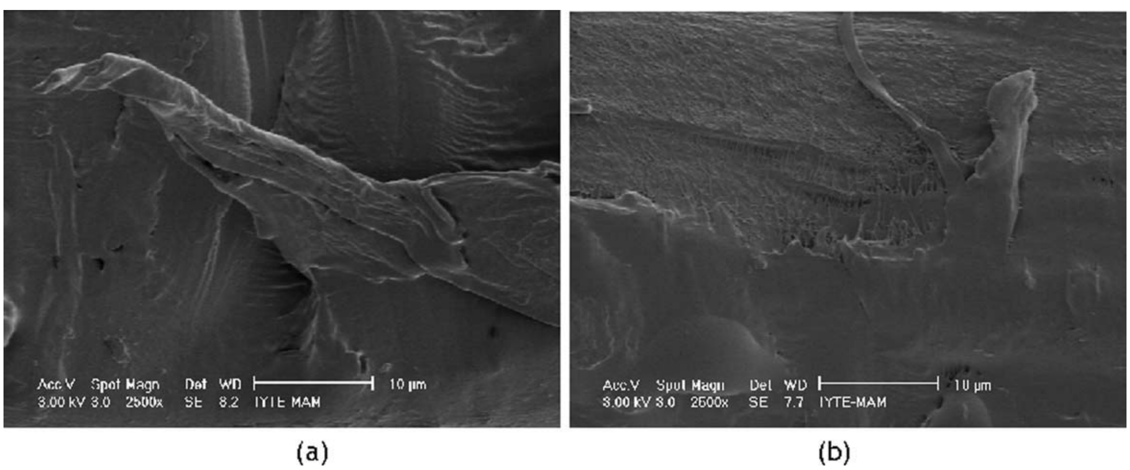

Figure 2 SEM micrographs of (a) PEG- and (b) GLY-plasticized corn-zein-coated PP films, where the ethanol and corn-zein concentrations were constant at 95 and 5%, respectively.

TABLE VII
Effects of the Ethanol and Corn-Zein Concentrations on the Elongation at Break of the Coated PP Films[a]

Ethanol concentration (%)	Corn-zein concentration (g/100 mL of ethanol)	Elongation at break (%)
70	5	169.48 ± 13.60
70	15	142.88 ± 7.413
95	5	167.90 ± 17.70
95	15	150.52 ± 16.77

[a] Where the plasticizer was GLY, with its concentration constant at 20% (w/w) on the basis of the corn-zein content.

GLY were found to be more flexible. Furthermore, they showed a significant improvement in the zein film flexibility when a mixture of GLY and poly(propylene glycol) (PPG) was used as the plasticizer. Films containing GLY and PPG at a ratio of 1 : 3 exhibited elongation at break values almost 50 times greater than GLY-plasticized zein films. However, a similar increase in the elongation was not observed when PEG replaced with PPG in the plasticizer mixture.

The Young's modulus (modulus of elasticity) is the measure of the force that is required to deform a film by a given amount of tension. It is also a measure of the intrinsic stiffness of a film and is related to the rigidity of the film: a higher Young's modulus means a higher stiffness of a material. Young's modulus was determined from the slope of the stress–strain curve at the elastic limit. The modulus of the zein-coated PP films as affected by the coating formulation are presented in Figure 3, and the numerical values are tabulated in Table VIII. Significant improvements in the stiffness of the coated PP films were achieved, whereas the value was 842.82 MPa for the PP base film without zein coating. In this study, the coating of PP with zein led to a significant increase in the stiffness values, as shown in Table VIII. All of the modulus values of the coated films were higher those of the PP base film without coating. Increasing the plasticizer content of the coating solution resulted in a lower Young's modulus and a higher flexibility in the coated films. The results show that the PP films coated with zein solution plasticized with PEG were much stiffer than the films coated with zein solution plasticized with GLY. It is concluded that the incorporation of the same amount of GLY into corn zein increased the chain flexibility more compared to PEG.

The statistical results show that model was significant for both plasticizers. The most effective parameters on the Young's modulus of the coated PP films were determined as the corn zein–plasticizer and ethanol–plasticizer interactions.

Finally, we realize that the development of corn-zein-coated PP films with desirable mechanical properties represents a rather challenging multidisciplinary problem. The results show that the mechanical behaviors of corn-zein PP films strongly depend on the formulation of the coating solution, which depends among other factors, such as polymer–polymer and polymer–plasticizer interactions. Many studies have shown that films become weak in

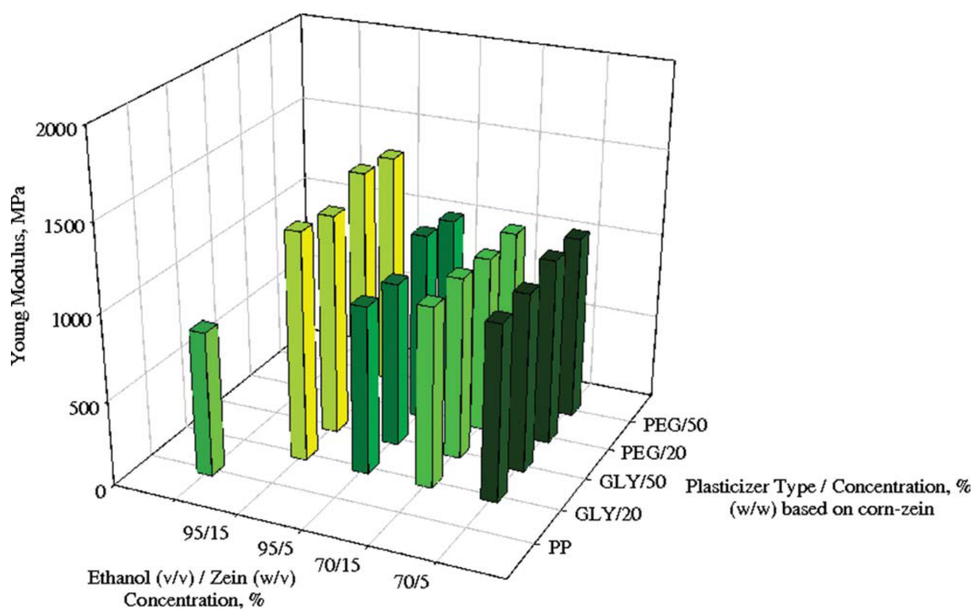

Figure 3 Young's modulus values of corn-zein-coated PP films as affected by the coating formulation. (PEG, polyethylene glycol; GLY, glycerol % w/w on the basis of the corn zein). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VIII
Young's Modulus of the Corn-Zein Coated PP Films Prepared According to Experimental Design

PEG plasticization		GLY plasticization	
Coated film number	Young's modulus (MPa)	Coated film number	Young's modulus (MPa)
1	1086.01 ± 65.16	12	1028.28 ± 134.1
2	1100.67 ± 48.44	13	977.24 ± 64.301
3	1030.24 ± 173.7	14	1046.68 ± 100.3
4	1404.69 ± 112.9	15	1331.31 ± 80.49
5	1074.50 ± 122.4	16	1101.34 ± 31.77
6	1056.48 ± 21.94	17	958.62 ± 25.06
7	1043.44 ± 30.98	18	1159.26 ± 154.3
8	1372.32 ± 269.3	19	1287.07 ± 55.83
9	982.64 ± 6.325	20	1050.68 ± 82.07
10	991.38 ± 33.10	21	1057.56 ± 90.19
11	982.42 ± 40.84	22	1099.73 ± 75.47

tensile strength and elongation at break increases at high plasticizer contents. The incorporation of plasticizers into coating solutions also induces the formation of protein–plasticizer interactions and, consequently, a loss of protein–protein interactions. These observations were also in agreement with our results obtained in this study. The elongation and tensile strength showed a stronger effect of plasticizer content. Also, the smaller size of GLY present in the coating solution influenced the mechanical properties of the coated PP films, giving more elongation to the film compared to PEG. Similar changes in the mechanical properties of films, as affected by different plasticizers, have been observed previously for various freestanding zein films.[11,17,22]

Statistical differences were observed for all mechanical properties between coated and uncoated PP films by hypothesis testing. Statistical analysis results show that the plasticizer and corn-zein concentrations in the coating formulations were the most effective parameters in the final properties of the resulting PP films.

CONCLUSIONS

In this study, corn-zein coatings on PP films were examined as an alternative to commercial coatings on films that consist of expensive and nondegradable polymers. The plasticized corn-zein coatings for the PP films were prepared to investigate their mechanical properties as affected by the corn-zein, ethanol, and plasticizer concentrations and plasticizer type. Thus, a novel film structure for food packaging applications, which provides a better possibility for recycling processes because of the easy separation of the coating from the base plastic, was proposed by the optimization of the coating formulation. The mechanical behavior of the PP films (tensile strength and elongation at break) was significantly improved at different levels by all coating formulations of the corn zein. The plasticization degree of the coating solutions increased considerably with elongation of the coated PP films, and the tensile strength decreased with increasing plasticizer content used in the coating formulations. GLY worked well as a plasticizer in the corn-zein solution, and better improvements were obtained in the mechanical properties of the corn-zein-coated PP films. The statistical analysis of the results showed that the corn-zein and plasticizer concentrations and plasticizer type used in the coating formulation were more effective parameters and had a significant effect on the mechanical behavior of the coated PP films.

The results suggest that the corn-zein-coated PP films showed a tendency to be able to provide packaging criteria with proper coating formulations, especially high-corn-zein-content films plasticized with low levels 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 alternatives to synthetic coating materials with appropriate formulations.

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