Tensile Properties of Extruded Corn Protein Low-Density Polyethylene Films[1]

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ABSTRACT

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The strength of films extruded from powder blends of corn zein or corn gluten meal (CGM) with low-density polyethylene was investigated. Tensile strength, percent elongation at break, and elastic modulus of the extruded films were measured. The tensile strength decreased from 13 MPa to ≈10.5 MPa with zein addition, while CGM addition resulted in tensile strength of ≈6 MPa. The higher the level of biological material (CGM or zein) in the films the lower the tensile properties. Films containing CGM exhibited significantly lower tensile properties than those containing zein. Extrusion processing of biological films is a step toward commercial viability.

Researchers have developed degradable films over the past few decades as possible replacements for petroleum-derived films. The efforts have varied from films entirely composed of biological materials to combinations of biological materials and petroleum products. Justifications for research in this area have included production of value-added biological products, petroleum conservation, and conservation of landfill space.

Research in protein films has focused on the production of solvent-cast films. Corn and wheat protein (Aydt et al 1991; Herald et al 1995), whey protein (Krochta and McHugh 1994), and soy protein isolate (Gennadios et al 1993) were cast from solution. However, these films require a multistep protocol to dissolve protein and plasticizer, then remove the solvent, which is usually more costly than single-step extrusion.

Extrusion is the process of forcing material through a die under controlled conditions. Extrusion technology offers advantages over traditional industrial processes. Crucial operations such as dehydration, expansion, homogenization, pasteurization, and thermal cooking can be done in one pass using an extruder. The extruder uses less space per unit of operation than traditional multistep processes. Moreover, extrusion is a continuous process and can be used to produce immense quantities of product (Riaz 2000).

The first successful degradable extruded films were manufactured from starch and petroleum-derived products (Otey et al 1980, 1987). Lim et al (1992) extruded films with linear low-density polyethylene (LLDPE) and a variety of starch fillers. The tensile strength and percent elongation of extruded films significantly decreased with increased starch concentration. Obuz et al (2001) manufactured extruded packaging sheets formulated from sorghum flour or wheat gluten, low-density polyethylene (LDPE), or metallocene-catalyzed ethylene butene copolymer and a plasticizer (sorbitol). They reported a decrease in tensile strength, percent elongation, and Young's modulus of extruded packaging sheets with increased concentration of either sorghum flour or wheat gluten.

Zein is a corn protein with an average molecular weight of 22,000 and is mainly used in the formulation of edible coatings for pharmaceutical and confectionery products. Zein has a high content of nonpolar hydrophobic amino acids such as leucine (17–20%), alanine (8–10%), and proline (5–9%). Zein is reported to be a possible candidate for food and nonfood uses due to inherent hydrohobictity and ability for film formation (Wu et al 1997). However, zein is expensive ($10/lb) compared with commonly used LDPE (<$1.00/lb). Spence et al (1995) and Lai et al (1997) cast biodegradable sheets of zein. The researchers reported that addition of palmitic or stearic acid (plasticizers) increased the tensile strength of these films.

CGM is mainly composed of protein (60%) and has a high percentage of hydrophobic amino acids (10% leucine) with the remaining components mainly being moisture, fiber, and lipids (Watson and Ramstad 1987). CGM lacks the purity of zein but is cheaper ($0.20/lb). Thus, blending petroleum-based plastics with compatible biodegradables may provide an alternative packaging material that is inexpensive and friendly to the environment.

Neither zein nor CGM has been reported in the literature on extruded films. Most work with zein or CGM has focused on solvent-cast films (Aydt et al 1991; Lai et al 1997).

Single step extrusion is potentially faster for the production of protein-based packaging films. Therefore, the objectives of this study were to extrude films from zein or CGM in combination with LDPE and to evaluate the film's tensile properties.

MATERIALS AND METHODS

Raw Materials

The LDPE was donated by Lyondell Polymers (Houston, TX); zein (88–96% protein, db) was purchased from Freeman Industries (product F-4000, Tuckahoe, NY), and CGM (64.7% protein, wb) was purchased from Lortscher Agri Service (Bern, KS).

Extrusion Parameters

Preliminary data were collected on a melt extruder (CSI 194, Custom Scientific Instruments, Whippany, NJ). This extruder is an extremely small plastics extruder with a feed rate of ≈100 g/hr. At this small scale, the LDPE pellets were ground using a Wiley mill (Philadelphia, PA) before blending. Zein was mixed into the LDPE at 0, 5, 10, and 15%, w/w.

The CGM was ground using a hammer mill (Bliss Industries, Ponca City, OK) equipped with a 0.508-mm screen to aid in the dispersion within LDPE. Zein was not ground. A calibration curve was created for a feeder to allow rapid determination of LDPE feed rate at a given total rate to the extruder. The LDPE-zein or LDPE-CGM blends were fed into the extruder (Micro 18, Leistritz, Nuremberg, Germany) using a feeder (model K2VT20, K-tron, North America, Pitman, NJ). Feed rate to the extruder was 3.6 kg/hr. The extruder had six thermally controlled heating zones (100, 135, 220, 220, 205, and 190°C, toward the die). The die temperature was maintained at 165–175°C. The slit die was set at 1.0 mm. The film was collected using a take-up system immediately after the extruder outlet. Each treatment was extruded for 15 min before sample collection to allow enough time for the extruder to purge the previous treatment.

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Tensile Testing

A template was constructed (standard D 882-91, ASTM 1994) and used to cut a dog-bone shape from the extruded film specimen. The blade was replaced after every 20 specimens to minimize surface defects due to a dull blade. Five specimens from each replicate of each treatment were tested on a universal testing system (UTM model 4466, Instron Corp., Canton, MA). Samples were allowed to equilibrate in the testing room with controlled conditions of 21.1°C and 65 ± 2% rh for 24 hr before testing. Tensile strength, percent elongation at break (PEB), and Young's modulus were measured.

Experimental Design

The film compositions used were 0, 5, 10, and 15% zein, and 0, 5, 10, and 15% CGM, combined with LDPE. All treatments were extruded three times. The formulated protein levels did not correlate simply with analytical results. Because of this, regression analysis using analytical protein levels was used to determine the relationship between the added protein and physical properties of the film.

RESULTS AND DISCUSSION

Tensile Strength

Tensile strength of zein-LDPE or CGM-LDPE films decreased with increased zein or CGM concentration (Figs. 1 and 2). The relationship between zein content and average tensile strength of the film was quadratic: Tensile strength (MPa) = 13.15 + 0.16 (zein content) – 0.05 (zein content)^2 (R^2 = 0.82). According to the regression model, the maximum tensile strength occurs at ≈1.6% zein. After this maximum value, both measured and predicted data indicated that tensile strength decreased with increased zein. The zein may cause discontinuity of zein-LDPE polymer matrix, which

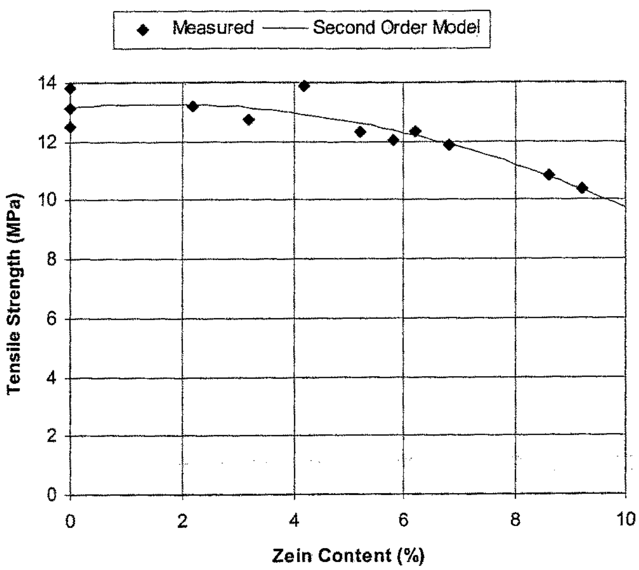

Fig. 1. Tensile strength comparisons between experimental and predicted values for extruded zein and low-density polyethylene films. Tensile strength (MPa) = 13.15 + 0.1559 (zein content) – 0.0499 (zein content)^2 R^2 = 0.82.

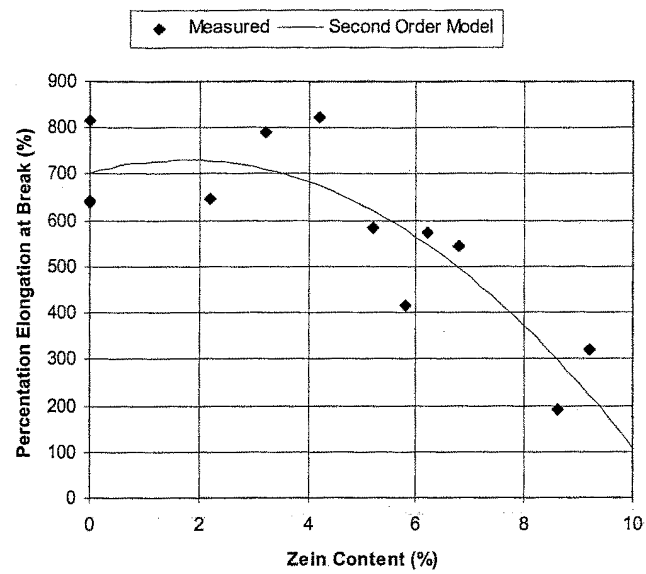

Fig. 3. Percent elongation at break comparisons between experimental and predicted values for extruded zein and low-density polyethylene films. Percent elongation at break = 702 – 31.7 (zein content) – 9.14 (zein content)^2 R^2 = 0.75.

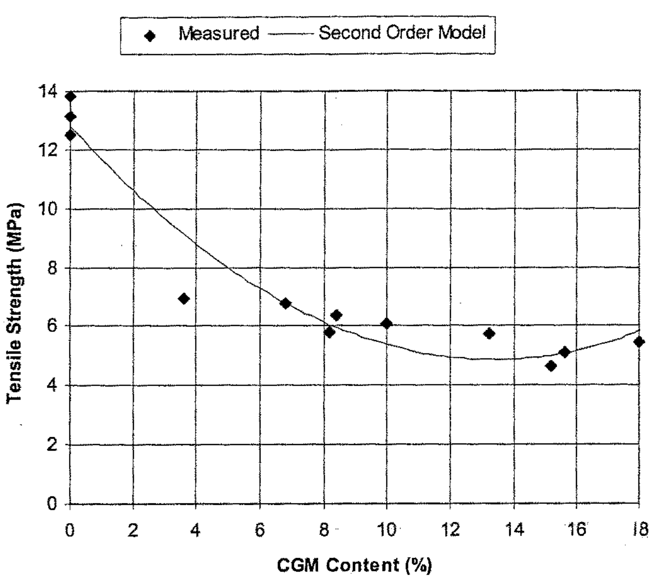

Fig. 2. Tensile strength comparisons between experimental and predicted values for extruded corn gluten meal (CGM) and low-density polyethylene films. Tensile strength (MPa) = 12.80 – 1.188 (CGM content) – 0.0445 (CGM content)^3 R^2 = 0.94.

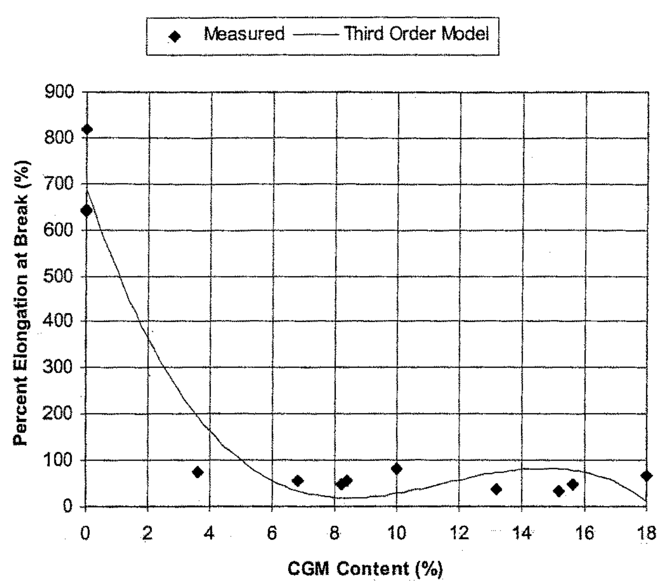

Fig. 4. Percent elongation at break comparisons between experimental and predicted values for extruded corn gluten meal (CGM) and low-density polyethylene films. Percent elongation at break = 685 – 195.8 (CGM content) + 18.11 (CGM content)^2 – 0.524 (CGM content)^3 R^2 = 0.95.

will reduce tensile strength. Lim et al (1992) observed a similar trend with a starch-petroleum polymer matrix. Obuz et al (2001) reported a maximum tensile strength at 12.5% sorghum flour in LDPE.

A quadratic relationship between CGM content and average tensile strength of the film is given as: tensile strength (MPa) = 12.80 – 1.19 (CGM content) + 0.04 (CGM content)^2 (R^2 = 0.94). The regression model suggests that the maximum tensile strength occurred at 13% CGM; thereafter, tensile strength decreased with increased CGM.

The decrease in tensile strength of a composite system with increasing content of a filler (zein or CGM) can be attributed to increased stress in the continuous phase due to lack of stress transfer across the LDPE-filler interface. The zein or CGM in combination with LDPE may form a composite system in which the filler (zein or CGM) was embedded in the continuous phase. Fillers such as zein or CGM may decrease the tensile strength of composite by changing the morphology of the system and the nature of the interface between the phases (Nielsen and Landel 1994). Willet and Westhoff (1994) reported that filler particles in a composite system were not able to carry any load efficiently, resulting in decreased load-carrying cross-sectional area of the film.

Percent Elongation at Break

The PEB values for zein-LDPE films ranged from 800% (100% LDPE) to 200% (8.5:91.5% zein to LDPE) (Fig. 3). A regression analysis determined a quadratic model for predicting PEB at specific concentrations: PEB (%) = 702 – 31.7 (zein content) – 9.14 (zein content)^2 (R^2 = 0.75). Maximum PEB was at ≈1.7% zein content.

PEB for CGM-LDPE films ranged from 800% (100% LDPE) to ≈50% (15:85% CGM to LDPE) (Fig. 4). Regression analysis produced a cubic model for PEB: PEB (%) = 685 – 195.8 (CGM content) + 18.1 (CGM content)^2 + 0.5 (CGM content)^3 (R^2 = 0.95). The maximum predicted PEB value occurred at 5.4% CGM; thereafter, PEB decreased with increased CGM. The CGM film PEB failed at <25% of the minimum average zein film PEB. This may suggest that CGM had a more profound decreasing effect on film PEB than zein. This effect may be explained by the higher compatibility of zein with LDPE compared with CGM, which contains other nonprotein constituents.

Researchers reported decreased PEB with filler addition (rice, corn, wheat, and potato starch, wheat gluten, or sorghum flour) (Narayan 1990; Lim et al 1992; Obuz et al 2001). Raymond and Charles (1981) concluded that the fillers accumulate in adjacent polymeric chains, thus reducing the mobility of the chains. Subsequently, the fillers increase adhesion to one another through Van der Waals forces and hydrogen bonds. These researchers further suggested that if perfect adhesion between the filler and polymer matrix is assumed, the polymer matrix confined between two particles would undergo a larger strain than the macroscopic strain. This would be due to the fact that rigid filler particles do not elongate. Thus, this material will give a higher macroscopic strain than the polymer with no fillers (Willett 1994; Willett and Westhoff 1994).

Elastic Modulus (Young's Modulus)

The best model from regression of measured elastic modulus and zein content was cubic with R^2 = 0.35. A plot of measured elastic modulus versus zein content can be seen in Fig. 5. Elastic modulus for the zein films decreased slightly with increased zein content; however, the decrease was relatively small, with a large difference between observed data and the regression value.

Regression analysis showed a linear relationship between the CGM level in the film and the measured elastic modulus (Fig. 6): Elastic modulus (MPa) = 17.7 – 0.6 (CGM content) (R^2 = 0.73). The data suggested that an increase in CGM content would result in a decreased elastic modulus for the film. While the regression produced a good fit, the observed data points can be divided into two groups, those at ≤10% CGM and those at >10% CGM. In both groups, higher CGM content decreased the elastic modulus. Other researchers observed a similar decrease in the elastic modulus of film with increased biological polymer content. Arvanitoyannis et al (1997), reported lower elastic modulus values of LDPE-wheat starch extruded films with increased starch concentration. Obuz et al (2001) reported reduced elastic modulus with LDPE-sorghum flour or LDPE-wheat gluten extruded sheets with increased sorghum flour or wheat gluten level.

The decrease in elastic modulus with filler addition can be explained by changes in composite yielding behavior. Fillers modify the shape of stress-strain curves of ductile polymers due to a crazing or dewetting effect. The adhesion between the filler and matrix was probably lost, which leads to a significant decrease in the elastic modulus of composite (Nielsen and Landell 1994).

CONCLUSIONS

The CGM or zein behaved as fillers in a composite system. As was the case with other fillers, CGM or zein addition decreased tensile properties of extruded films. Zein maintained the tensile

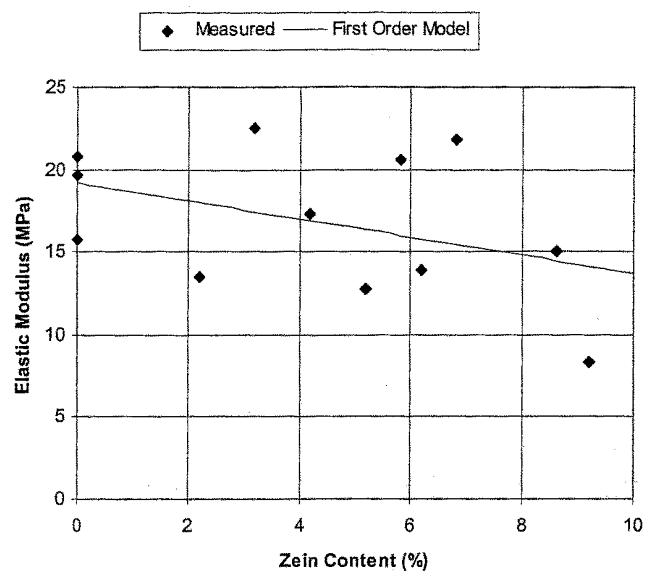

Fig. 5. Elastic modulus comparisons between experimental and predicted values for extruded zein and low-density polyethylene films.

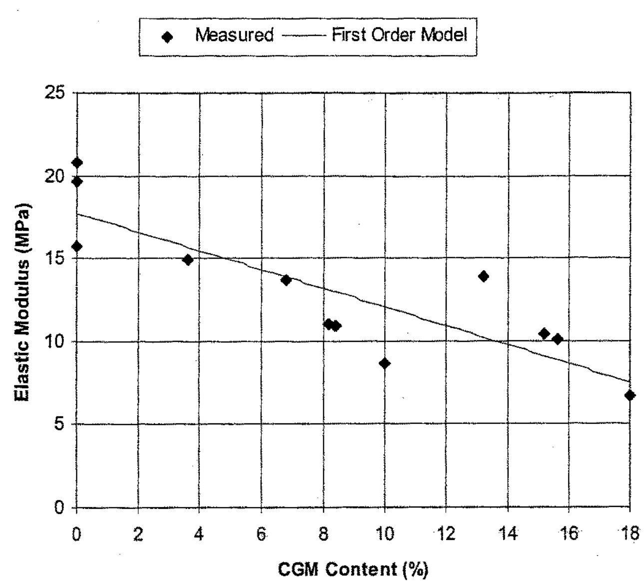

Fig. 6. Elastic modulus comparisons between experimental and predicted values for extruded corn gluten meal (CGM) and low-density polyethylene films. Elastic modulus (MPa) = 17.74 – 0.570 (CGM content) R^2 = 0.73.

properties of film better than CGM, indicating zein may be more compatible with LDPE. This may be due to the high hydrophobic amino acid content of zein. CGM has ≈35% (wb) zein (Wu et al 1997) but still in the form of protein bodies. The zein used in our study was purer and somewhat degraded in the extraction process (by use of alkaline-alcohol solution). Although zein or CGM could be incorporated into LDPE, compatibility issues between biological material (zein or CGM) and petroleum polymer (LDPE) remain a challenge for scientists. As far as packaging disposal issues are concerned, extrusion of renewable sources with petroleum-derived packaging material is a move in an environmentally friendly direction only if the price and property of the product fulfill the function of the LDPE film.

LITERATURE CITED

ASTM. 1994. Standard Test Methods for Tensile Properties of Thin Plastic Sheeting, Method ASTM D 882-91. Standard Test Methods for Tensile Properties of Plastics. American Society for Testing and Material: Philadelphia, PA.

Arvanitoyannis, I., Psomiadou, E., Biliaderis, C. G., Ogawa, H., Kawasaki, N., and Nakayama, A. 1997. Biodegradable films made from low density polyethylene, ethylene acrylic acid, polycaprolactone and wheat starch for food packaging applications. 3. Starch 49:306-322.

Aydt, T. P., Weller, C. L., and Testin, R. F. 1991. Mechanical and barrier properties of edible corn and wheat protein films. Trans. ASAE. 34:207-212.

Gennadios, A., Brandenburg, A. H., Weller, C. L., and Testin, R. F. 1993. Effect of pH on properties of wheat gluten and soy protein isolate films. J. Agric. Food Chem. 41:1835-1839.

Herald, T. J., Gnanasambandam, R., McGuire, B. H., and Hachmeister, K. A. 1995. Degradable wheat gluten films: Preparation, properties, and applications. J. Food Sci. 60:1147-1150.

Krochta, J. M., and McHugh, T. J. 1994. Sorbitol vs. glycerol plasticized whey protein films: Integrated oxygen permeability. J. Agric. Food Chem. 42:841-845.

Lai, H., Padua, G. W., and Wei, L. S. 1997. Properties of microstructure of zein sheets plasticized with palmitic and stearic acids. Cereal Chem. 74:83-90.

Lim, S., Jane, J., Rajagopalan, S., and Seib, P. 1992. Effects of starch granule size on physical properties of starch-filled polyethylene film, Biotechnol. Prog. 8:51-57.

Narayan, R. 1990. Introduction. Pages 1-10 in: Degradable Materials: Perspectives, Issues, and Opportunities. S. A. Barenberg, R. Narayan, and E. Redpath, eds. CRC Press: Boston.

Nielsen, L. E., and Landel R. F. 1994. Mechanical Properties of Polymers and Composites, 2nd Ed. Marcel Dekker: New York.

Obuz, E., Herald, T. J., and Rausch, K. D. 2001. Characterization of extruded plant protein and petroleum based packaging films. Cereal Chem. 78:97-100.

Otey, F. H., Westhoff, R. P., and Doane, W. 1980. Starch-based blown films. Ind. Eng. Chem. Prod. Res. Dev. 19:592-595 .

Otey, F. H., Westhoff, R. P., and Doane, W. M. 1987. Starch-based blown films. II. Ind. Eng. Chem. Prod. Res. Dev. 26:1659.

Raymond, B. S., and Charles, E. C. 1981. Polymer Chemistry: An Introduction. Marcel Dekker: New York.

Riaz, M. N. 2000. Extruders in Food Applications. Technomic Publishing: Lancaster, PA.

Spence, K. E., Kane, J. L., and Pometto, A. L., III. 1995. Dialdehyde starch and zein plastic: mechanical properties and biodegradability. J. Environ. Polym. Degrad. 3:69-74.

Twombly, W. W. 1998. Preparation and properties of an extruded corn protein film. MS thesis. Kansas State University: Manhattan, KS.

Watson, S. A., and Ramstad, P. E., eds. 1987. Corn Chemistry and Technology. Am. Assoc. Cereal Chem.: St. Paul, MN.

Willett, J. L. 1994. Mechanical properties of polymers and composites. J. Appl. Polym. Sci. 54:1654-1695.

Willett, J. L., and Westhoff, R. P. 1994. Tensile properties of starch/polyethylene blends: A composite theory analysis. ANTEC: 1572-1576.

Wu, S., Myers, D. J., and Johnson, L. A. 1997. Factors affecting yield and composition of zein extracted from commercial corn gluten meal. Cereal Chem. 74:258-263.

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