

# Characterization of Extruded Plant Protein and Petroleum-Based Packaging Sheets

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ABSTRACT

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Extruded packaging sheets (EPS) were manufactured from wheat gluten (WG) or sorghum flour (SF) in combination with (10, 25, 50, 75, and 100%) low density polyethylene (LDPE) or metallocene-catalyzed ethylene-butene copolymer (MCEBC), and plasticized successfully with sorbitol at a weight ratio of 1:1. Physical analyses were used to characterize the extruded packaging materials. Tensile strengths and elongations of the sheets

significantly decreased as the WG or SF increased. Sheets formulated with ≈1:1:2 wheat gluten, sorbitol, and MCEBC exhibited similar elastic properties compared with a 100% MCEBC sheet. Young's modulus and percent elongation at break values decreased as WG-sorbitol or SF-sorbitol level increased in the EPS.

Generally, packaging material is disregarded and thus is one of the most inefficiently used portions of any product. Increasing the functionality of packaging material either by making it edible or reusable is a challenge to scientists. Currently, the United States Department of Defense, NASA, and consumers are requesting innovative packaging technologies that will be suitable for long-term space travel and reduce landfill waste. Thus, nontraditional sources of materials should be studied to meet the needs of the aforementioned market segments.

Many reports have been published on cast films using 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). The research has shown films cast with food proteins lack important barrier properties.

Combining a biological polymer (starch, protein, or lipids) and a petroleum polymer (low density polyethylene, ethylene coacrylic acid, or metallocene-catalyzed ethylene-butene copolymer) raises the issue of how biodegradation will proceed in the environment. Biological material can be metabolized by certain bacterium, whereas the petroleum polymer does not biodegrade but disintegrates. The presence of plasticizers, processing aids, stabilizers, and other additives are other factors that determine overall biodegradability of the end product (Koelsch and Labuza 1991).

Incorporation of starch (Otey et al 1987), protein, or fatty acids decreases flexibility and barrier properties of plastic films. Starch incorporation especially increases water sensitivity and decreases tensile strength and elongation of plastic films. These negative effects can be overcome by using hydrophobic derivatives of starch (Evangalista et al 1991) with compounds that increase compatibility such as oxidized polyethylene (Jane et al 1990) or with fatty acids (Griffin 1977). To increase the flexibility of biodegradable films, plasticizers have been added. Polyols such as sorbitol and glycerol plasticize effectively by reducing internal hydrogen bonding while increasing intermolecular spacing (Krochta and McHugh 1994). Plasticizers increase film flexibility while decreasing the barrier properties.

Sorghum flour (SF) is used mainly as a feed ingredient. The sorghum plant is a raw material for feed, food, fuel, and industry. Sorghum can be separated into a number of different kernel and straw fractions for various industrial applications such as particle

board, paper, adhesives, detergents, plastics, and sugars. The energy crisis in Europe and the United States, as well as large-scale production of grains in these countries, has resulted in new ideas for the use of renewable sources.

Neither SF nor wheat gluten (WG) has been reported in the literature regarding extruded films. Most work with biological materials has focused on small-scale casting of materials dissolved in solvents. Cast films are time-consuming because some parameters, such as film thickness, are difficult to control. Extrusion of packaging material is the next step in an attempt to develop and process plant-based packaging films and sheets for commercialization. The objectives of this study were to produce an extruded packaging sheet material containing SF or WG (biological material), a plasticizer in combination with a petroleum polymer, and to determine the physical properties of the extruded sheet.

## MATERIALS AND METHODS

### Materials

Commercial SF was donated by ADM Milling Co. (Dodge City, KS) and had a mass median diameter of 290 μm. The commercial WG (76% protein, dry basis) was obtained through Lortscher Agri Service (Bern, KS).

Sorbitol, palmitic, and stearic acids, and glycerin were investigated as plasticizing agents. Sorbitol, palmitic, and stearic acids were purchased from Ruger Chemical Co. (Irvington, NJ). Glycerin (99.5 % USP, Hydrite Chemical Co. (Waterloo, IA) and the low density polyethylene (LDPE) pellets (Lyondell Polymers, Houston, TX) were donated. Metallocene-catalyzed ethylene-butene copolymer (MCEBC) was supplied by Exxon Chemical Co. (Exact 3028 SLP-8-80-20, Baytown, TX).

### Preconditioning

The SF was pregelatinized in a corotating twin-screw Leistritz extruder with electric heating and air-cooling in the barrel assembly (Micro 18, Leistritz, Nuremberg, Germany) using a K-tron screw feeder (K2VT20, K-tron North America, Pitman, NJ). The extruder barrel had a length of 545 mm. Total feed rate was 163 g/min. Water flow was adjusted to 27.5 g/min with a K-tron pump. The SF was cooked to 72°C to gelatinize the starch.

Prior to sheet production, the gelatinized SF was dried at 100°C for 4 hr using a Wenger dryer (Sabetha, KS) to reduce the possibility of bubble formation as material emerges from the extruder die. After drying, all precooked SF was milled using a feed mill (Fitzmill) while WG was dried at 50°C in a laboratory oven for 24 hr.

### Plasticization

Either gelatinized SF or dried WG was plasticized with palmitic acid, stearic acid, or sorbitol at weight ratios of 25 and 50% and with glycerin at either 10 or 20%. Extrusion conditions for plasticizing

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process were total feed rate into the extruder, 36 g/min; die temperature measured at the die by thermocouples on the extruder, 174°C; and die pressure 1,350–3,625 kPa. Because the plasticized, extruded material (SF or WG with sorbitol) was in the shape of long ropes, the particle size of plasticized SF or WG was reduced by hand.

### Sheet Production

The Leistritz extruder used for EPS production was the same as for cooking and plasticization. The die used was a Leistritz slit die with a die gap of 1.4 mm and with a die width of 6 cm. The lengths of die and die adaptor were 160 and 20 mm, respectively. The extrusion rate was 21 g/min.

The plasticized SF or WG was combined at weight percentages of 10, 25, 50, and 75% with LDPE or MCEBC. The 100% plasticized WG or SF and pure MCEBC or LDPE sheets were also produced. The height of the die slit was 1.4 mm for all experiments. The slit height is a critical parameter because it determines final thickness of the extruded sheets. The extruder barrel had six heating zones (first two zones at 100 and 120°C, respectively) and was controlled thermally at the last four heating zones (220, 220, 220, and 190°C toward the die). Conveying was done in the first two zones. The following three consecutive zones were used to melt the material. The last zone was used for forming the extrudate. The die temperature was maintained between 185 and 195°C. The pressure at the die varied between 1,350 and 3,625 kPa depending on the extruded sheet formulation. The temperature profile was modified to have a satisfactory sheet product (determined by visual inspection of the extruded sheets).

The sheet out of the extruder was cooled with forced air before being stretched and rolled by a Buhler take-up system (Minneapolis, MN). The take-up speed was adjusted to have a satisfactory product depending on product formula. The product was extruded until a

steady state was reached. Steady state was achieved after 25 min and the samples were collected for tensile testing. The extruder was purged at the end of each treatment run for 5 min to ensure that no residual material from the previous run remained.

### Tensile Testing

All the specimens were tested according to standard D 882-91 (ASTM 1994). A dumb-bell shaped template was constructed of heat-treated stainless steel Type 17-4 and met ASTM standard D 638-94b. The specimens were conditioned at  $21 \pm 1^\circ\text{C}$  and  $65 \pm 2\%$  rh for 24 hr. Conditioning and measuring tensile properties were performed in the same room. The template was placed on top of the sample and struck with a hammer to cut out the sample. This method of template cutting reduced the micro fractures as compared with knife cutting.

Five specimens from each treatment were tested using a universal testing system (model 4466, Instron Corp., Canton, MA) equipped with a 50-kg load cell and pneumatic grips with rubber faces and interfaced to an IBM-compatible computer. Thickness and width of the specimens were measured to the nearest 10  $\mu\text{m}$  using a hand micrometer. Tensile strength, percent elongation at break, and Young's modulus were measured.

### Experimental Design

Completely randomized design was used in analysis of variance (ANOVA). All data were analyzed using SAS methods (SAS Institute, Cary, NC). All extruded sheets were produced in replicates. Least significant difference (LSD) was used to analyze the differences at 5% confidence level to compare mean tensile testing values across the treatments.

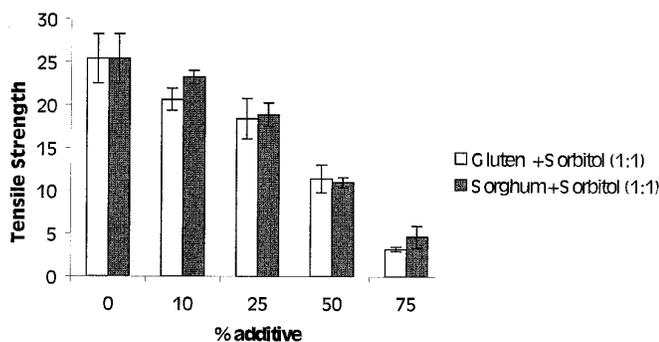


Fig. 1. Tensile strength (MPa) among extruded sheets with metallocene-catalyzed ethylene-butene copolymer (MCEBC) as a petroleum polymer.

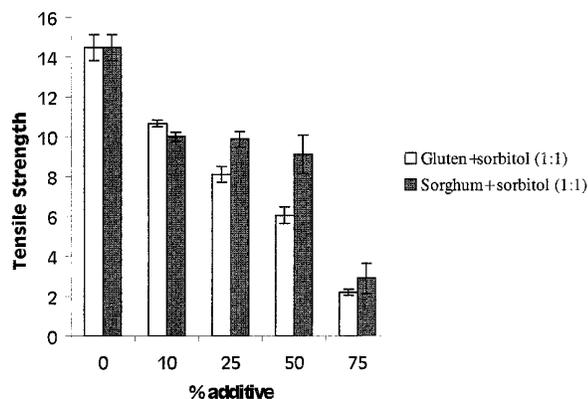


Fig. 2. Tensile strength (MPa) among extruded sheets with low density polyethylene (LDPE) as a petroleum polymer.

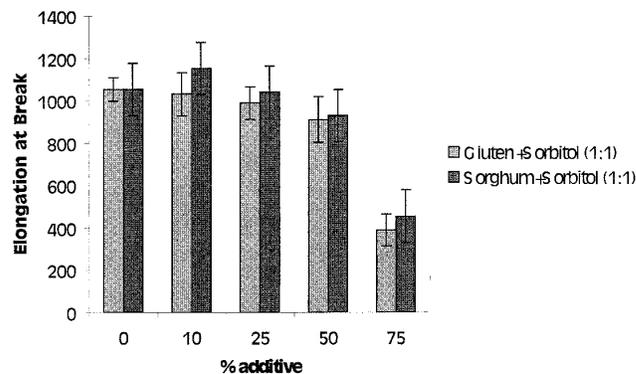


Fig. 3. Elongation at break (%) among extruded sheets with metallocene-catalyzed ethylene-butene copolymer (MCEBC) as a petroleum polymer.

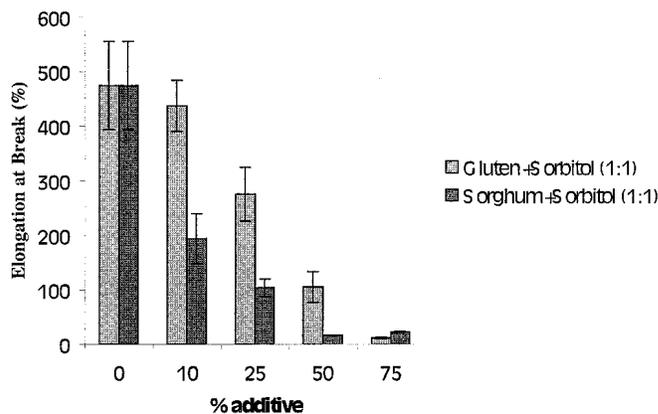


Fig. 4. Elongation at break (%) among extruded sheets with low density polyethylene (LDPE) as a petroleum polymer.

## RESULTS AND DISCUSSION

### Plasticization

During the processing of WG-glycerin and SF-glycerin mixtures, the extruder pressure reached up to 10,350 kPa, causing the extruder to shut down. Glycerin, which has a low melting temperature (20°C), softened in the extruder's feed section and produced a tacky surface, which caused bridging in the feed throat. Therefore, glycerin was eliminated from the experiment because it did not work within the confines of the process.

Palmitic acid (PA) or stearic acid (SA) gave similar results as glycerin. At 50% PA or SA, the mixtures of PA-WG, PA-SF, SA-WG, and SA-SF melted very quickly (visual inspection) and the extruder would not convey them. The PA or SA could not plasticize the SF or WG at 25% because of their poor ability to work within the extruder parameters. In these treatments, processing pressure went very high (10,350 kPa), causing the extruder to shut down. The mixtures (WG-PA, WG-SA, SF-PA, or SF-SA) had a tacky structure on the extruder and did not flow. Therefore, PA and SA were not considered in the experimental design.

Sorbitol was incorporated at the 25 and 50% levels. The 25% sorbitol level was not high enough to plasticize either WG or SF and also caused the extruder to shut down. However, 50% sorbitol did plasticize WG and SF effectively. The extruder ran smoothly and die pressure never exceeded 6,900 kPa. Visual inspection of the extrudate showed that the plasticization process was successful. Sorbitol at the 50% level was the only plasticizer that worked within the extrusion parameters.

### Sheet Production Step

Plasticized WG or SF was incorporated into LDPE or MCEBC up to 50% plasticized material content. However, as the concentration (w/w) of WG and sorbitol mixture reached  $\geq 50\%$  in the sheets, the incorporation of the mixture into LDPE or MCEBC became more difficult. This can be attributed to the burning of WG-sorbitol mixture in the extruder, resulting in poor material flow. A pure WG-sorbitol sheet was very difficult to produce because the extrudate burned and did not flow in the extruder. The extruded product was not flexible or stretchable (visual inspection). All plasticized SF sheets were produced successfully.

### Tensile Testing

The behavior of SF or WG in LDPE or MCEBC needs to be addressed before discussing tensile properties. The composites in this work behaved as a filled system where the filler (SF or WG) is embedded particles in the continuous phase. The properties of composite system greatly depend on the shape of filler phase, the morph-

ology of the system, and the nature of the interface between the phases. Fillers decrease the tensile strength of a composite (Nielsen and Landel 1994).

The 100% petroleum polymer films, MCEBC and LDPE, exhibited tensile strengths that averaged 25.4 and 14.5 MPa, respectively (Figs. 1 and 2). As the EPS WG ratio increased, tensile strength values decreased. As the WG ratio increased, flashing off of internal moisture and die swelling expanded the sheets. Plasticizer decreased the tensile strength of the dispersed SF-WG. Therefore, the tensile strength of blend is indirectly affected.

Statistically, the tensile strength of all WG sheets containing MCEBC was significantly lower than that of 100% MCEBC sheets. The same trend was observed for the WG sheets containing LDPE as a synthetic polymer. The tensile strength of all WG sheets except for the 10% WG-sorbitol-LDPE sheet was statistically lower than that of pure LDPE.

Our research suggested that starch or protein incorporation into LDPE or MCEBC decreased the tensile strength because starch or protein does not contribute much to tensile strength value. Genadios and Weller (1990) reported that tensile strength value of WG was 1.86 MPa, while the value for starch (24% amylose) films cast from water solutions conditioned at 30% rh and 22°C was 3.24 MPa (Wolff et al 1951). Whether a chemical reaction occurs between the filler (starch or protein) and synthetic polymer (LDPE or MCEBC) or not, the filler will have a reducing effect on tensile strength. If no adhesion between the matrix and filler is assumed, tensile strength will be reduced because the applied stress in the continuous regions increases due to lack of stress transfer across the matrix-filler interface. The filler particles can not carry any load efficiently, which decreases the load-carrying cross-sectional area of the sample. Therefore, the actual stress becomes greater than macroscopic stress (Willet and Westhoff 1994). The tensile strength invariably decreases with filler concentration because stress needs to be transferred from continuous phase to dispersed phase. Sorbitol used at the same level with biological material (WG or SF) decreased the tensile strength of the EPS, probably due to disturbed intermolecular interactions between synthetic polymer and biological material.

Researchers (Griffin 1977; Gage 1990; Evangelista et al 1991; Lim et al 1992) reported that tensile strength was reduced as a result of added starch. Starch causes discontinuity of starch-petroleum polymer matrix, which might reduce tensile strength (Lim et al 1992). Griffin (1994) reported that incorporation of starch increased film thickness but decreased the molecular orientation. The reduction in molecular orientation subsequently reduced the film's tensile strength.

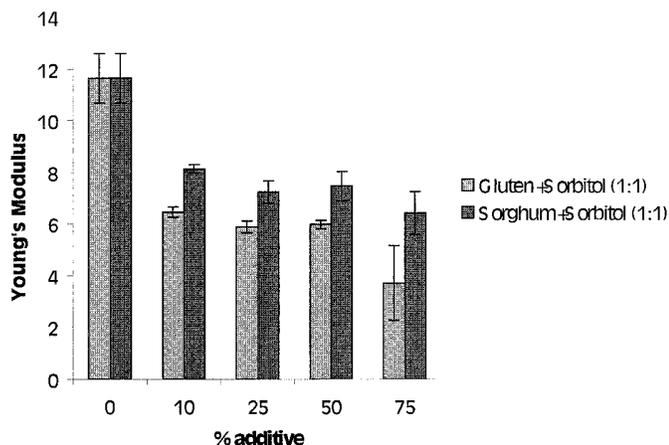


Fig. 5. Young's modulus (MPa) among extruded sheets with metallocene-catalyzed ethylene-butene copolymer (MCEBC) as a petroleum polymer.

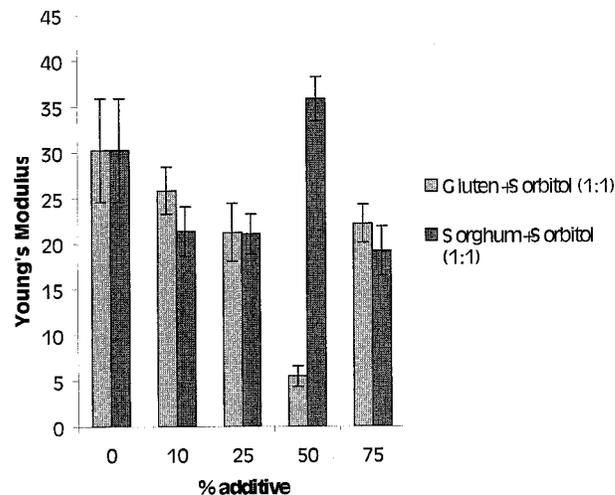


Fig. 6. Young's modulus (MPa) among extruded sheets with low density polyethylene (LDPE) as a petroleum polymer.

## Percent Elongation at Break

Values for percent elongation at break (PEB) of the EPS decreased significantly as the level of WG or SF in the polymer matrix increased (Figs. 3 and 4). PEB values ranged from 447 to 1,054% for the WG sheets containing MCEBC as a synthetic polymer and from 473 to 1,153% for the SF sheets. EPS formulated with LDPE had lower values than MCEBC sheets. PEB values of pure MCEBC sheets were not statistically different from those of MCEBC-based sheets containing 10, 25, 50% (1:1) SF-sorbitol. The same trend was observed for the WG sheets containing MCEBC as a synthetic polymer.

Reductions in PEB with the addition of starches (rice, corn, wheat, and potato) into extruded films have been observed by several researchers (Narayan et al 1990; Lim et al 1992). Raymond and Charles (1981) reported that fillers accumulate in adjacent polymeric chains, thus reducing the mobility of the chains and increasing the adhesion to one another through Van der Waals forces and hydrogen bonds. If perfect adhesion between the matrix and the filler particles is assumed, polymer matrix confined between two particles has to show a larger strain than the macroscopic strain. Then, this material will yield a lower macroscopic strain than the polymer containing no fillers. (Willett 1994; Willett and Westhoff 1994). PEB will always decrease with increasing filler concentration because stress has to be transferred from dispersed phase to continuous. PEB is not affected by the level of plasticizer because slippage or debonding occurs at critical stress level. After slippage or debonding, plasticizer has no further effect on deformation of the composite (Willett and Westhoff 1994).

## Young's Modulus (Elastic Modulus)

All the sheets containing MCEBC as a polymer and WG-sorbitol mixture (1:1) or SF-sorbitol mixture (1:1) as additives had Young's modulus values that were not statistically different from each other. The values were 5.98–11.67 MPa, with the highest Young's modulus for pure MCEBC sheet. In general, Young's modulus values decreased with higher SF or WG concentration (Figs. 5 and 6). Twombly (1998) manufactured extruded corn zein and LDPE films and noted a decreasing Young's modulus value with higher corn zein content.

Young's modulus decreased by  $\approx 50\%$  with the incorporation of 75% biological material (SF-sorbitol) into the EPS containing MCEBC as the petroleum polymer (Fig. 5). Obviously, adding more SF increased the starch level in the EPS, thus reducing Young's modulus. Arvanitoyannis et al (1997) concluded that extruded blends of LDPE-wheat starch with ethylene acrylic acid or polycaprolactone exhibited lower Young's modulus values with higher starch content.

Fillers modify the shape of stress-strain curves of ductile polymers, changing the yielding behavior of composite. This change is due to a crazing effect or dewetting effect. The adhesion between the filler and matrix is lost leading to a dramatic decrease in the modulus of composite (Nielsen and Landel 1994).

Plasticizers decrease H-H bonding in pure WG or SF. The function of plasticizers is not restricted to reducing H-H bonds. By diluting the polymer, plasticizers create "free volume", allowing for greater chain mobility. That is, without the steric hindrance of its neighbor, a polymer chain is less restricted in its range of motion. Greater mobility reduces chain entanglements likely reduce the overall strength (or Young's modulus). This effect has been seen in materials where hydrogen bonding is significant. The blend Young's modulus greatly depends on the physical state of the filler and will increase if the filler is rigid and decrease if the filler is soft. In this work, blend modulus decreased with increased filler concentration, confirming a plasticized, soft SF-WG phase.

## CONCLUSIONS

Extruded packaging sheets (EPS) containing wheat gluten (WG) or sorghum flour (SF) as filler in low density polyethylene (LDPE) or metallocene-catalyzed ethylene-butene copolymer (MCEBC) were manufactured. Sorbitol (plasticizer) decreased the tensile strength of dispersed SF-WG.

MCEBC-SF or MCEBF-WG sheets maintained tensile properties better than LDPE-SF or LDPE-WG sheets. All sheets containing WG or SF showed decreases in Young's modulus compared with the 100% polymer sheets used as controls. In addition to that, sheets containing MCEBC were stronger and exhibited greater PEB and higher Young's modulus compared with LDPE-based sheets. Although EPS were successfully extruded and showed reasonable tensile properties, additional work to increase the hydrophobicity of plant-based materials would be needed to improve the performance of EPS.

## ACKNOWLEDGMENTS

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