THE STATUS AND POTENTIAL FOR EDIBLE BIODEGRADABLE PACKAGING FILMS

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Background

Increasing amounts of packaging waste are discarded into the municipal waste system each year. Approximately 8.28 million tons of plastic packaging waste was generated in 1993 (EPA, 1994). A considerable amount of research is focused on the production of edible or biodegradable polymer films derived from natural sources. Two main incentives exist for the production of reliable, cost effective, biodegradable packaging films. The first incentive is environmental. Biodegradable films can be composted and eventually converted into natural elements by the enzymatic attack from micro-organisms such as bacteria and fungi. The second incentive is economic. The supply of petroleum feedstock will eventually limit the production of synthetic polymers. By developing biodegradable polymer films from natural sources, packaging films would be produced from renewable resources, thus increasing market demand for biopolymer materials such as protein isolates.

Much of the research on biodegradable films has involved the production of films using methods based on solvent casting, which is not a commercially viable production process. Roy et al. (1999) and Gennadios et al. (1993) solvent cast films made from wheat gluten and soy protein isolate. Debeaufort and Voilley (1994) solvent cast films made from cellulose-based materials. More practical thermal processing methods such as compression molding and extrusion have yet to be investigated thoroughly. However, Paetau et al. (1994) used compression molding to produce films from soy protein and others have compression molded dialdehyde starch and corn zein films. These films were reported to be rigid and brittle due to the absence of a plasticizer in the pre-processed mixture. The main objectives of the Food Packaging Films Group at Clemson University were to investigate thermal processing methods and to characterize the resulting biodegradable films.

One of the first and principal objectives was to develop a heat-pressed film that could be utilized in a heat extrusion system without casting. This would closely mimic the large-scale production of polymer "plastics" in the film industry. Nylon and protein were chosen due to similarities in their chemical structure. Proteins and nylon have the peptide bond in common which joins repeating units within their respective polymer structures.

Thus, a food protein with a similar "melt" temperature to a nylon was needed. Thermogravimetric analysis was used to determine which nylons and proteins would be good matches. It was expected that the nylon would have to have a very low melt point compared to most nylons since book values for food proteins show denaturation temperatures near 100°C. It was not known if the proteins would even melt or if they would burn without forming a film. Proteins were found to melt but matching a nylon source was difficult. A dehydrated protein mix from beef bone actually formed the best material when mixed with nylon 6. After a food protein was found to melt it was tested alone for film forming ability. Since then other food proteins have also been found to form films including a type of soy protein isolate and corn zein. The work branched out to include potential addition of compounds (antimicrobial and others) to the protein films, measuring and altering the physical properties of the films through various additives and processing treatments, and determination of the bioavailability of the films through both *in vitro* and *in vivo* studies.

Qualitative comparisons have been made between cast protein films and heat-pressed films using scanning electron microscopy (Dawson, 1998). Casting films involves the evaporation of an organic solvent, ethanol in the case of corn zein, which results in a very porous material (Figure 1). The use of heat to form the films using corn zein or soy protein results in a more homogenous structure with fewer voids seen at 1000X magnification (Figure 2).

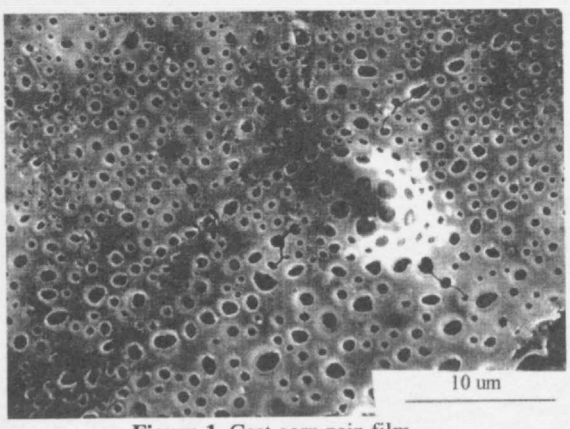

Figure 1. Cast corn zein film

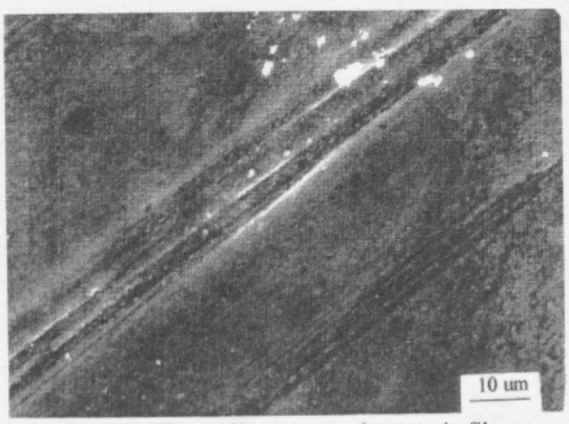

Figure 2. Thermally-compacted corn zein films

Materials

Soy protein isolate (PC 9000z) with molecular weight of 230,000 and initial moisture content of 10-12% was provided by Protein Technologies International, St. Louis, MO. The protein was freeze dried 24 hours to obtain a final moisture content of 5-7% using a Virtis Freeze Dryer (The Virtis Company, Inc., Gardiner, NY). Glycerol (Fisher Scientific, Fair Lawn, NJ) was used as a plasticizer in the protein films. Corn zein (Freeman Industries, Inc. NY) was also utilized to form a separate plant-based film material. Both batch processing (compression molding) and continuous extrusion (chill-roll) have been developed using the biodegradable film materials. Optimal film properties have been found on compounding or vigorously mixing the dry film components prior to compression or extrusion.

Compounding

Soy protein was compounded with glycerol in amounts of 20, 25, 30, 35, and 40 wt.% glycerol using a Brabender Plastic-Corder PL 2000 with a roller type mixing head. Compounding was done at a temperature of 62°C using a mixing speed of 42 rpm. Mixing time varied with the amount of plasticizer in a mixture. Mixing times used were 5, 10, 20, 25, and 30 minutes for mixtures containing 20, 25, 30, 35, and 40 wt.% glycerol, respectively.

In addition to the compounded protein/glycerol mixtures, several uncompounded mixtures were also investigated. These uncompounded mixtures were manually blended in a mortar and pestle for a period of approximately 10 min. The uncompounded mixtures were either processed immediately (the mixture referred to as "unaged") or were aged for several time intervals (the mixture being referred to as "aged" mixture) before being processed into films.

Batch Processing of Films

Soy protein/glycerol and corn zein/glycerol mixtures were thermally compacted using a Carver Laboratory Press (Fred S. Carver Inc., Menomonee Falls, WI). The procedure consisted of placing 3 g of mixture between two sheets of aluminum and then inserting the aluminum sheeting between the heated platens of the press. The press applied a pressure of approximately 10 MPa for 2 minutes using a processing temperature of 150°C for soy mixtures. To reduce water permeability, soy film was laminated with the corn zein/glycerol mixture at 125°C. Next, the aluminum sheeting was removed from the press and allowed to cool for 3 minutes. The protein film could be easily removed from the aluminum sheeting.

Continuous Film Extrusion

First a twin-screw extruder was used to compound (mix) the soy/glycerol and then this mixture was placed into a heated (135°C) single screw extruder set at 70 RPM. Adding some water during the compounding step was found to facilitate extrusion during the next step. The extruding sheet was fed onto chilled rolls to rapidly cool the film.

Film Properties

Tensile strength (TS) values for the soy films ranged from 0.8 to 5.0 MPa for soy protein/glycerol/water films depending upon the concentration of the components and the percentage of elongation (%E) ranged from 6 to 123% (Cunningham et al., 2000). These values TS and %E compare favorably to those made with other biopolymers but do not yet equal the physical properties of most polyethylene films (Table 1).

Table 1. Comparison of the physical properties of thermally compacted, solvent cast and synthetic commercial films.

Film type	Thickness (mm)	TS (MPa)	%E)
Heat-set soy protein	.38	5.0	123
Cast wheat gluten*	.101	2.6	276
Cast whey protein/glycerol*	.11	13.9	31
Cast soy protein isolate*	NA	37	4.0
Cast corn zein*	.089	.4	<1.0
Cellophane	0.36	114	20
High density PE	.025	17.3-34.6	300
Low density PE	.025	8.6-17.3	500

*values taken from references Cunningham et al., 2000, J. Food Sci. (Accepted, in press).

Applications

Antimicrobial and Antioxidant Meat Packaging

Nearly all commercial over-wrap and vacuum-skin films are produced by a heat-extrusion method. The exceptions are some meat casings produced from collagen. Films using soy and corn materials have been formed by heat extrusion to carry antimicrobials within their structure (Padgett et al., 1998). Creating films from natural plant materials by the heat extrusion method is a new technology and will enable the films to act as a carrier to deliver the antimicrobial to the food product (Dawson, 1998). Nisin and lysozyme, in combination with EDTA, when incorporated into the structure of soy and corn protein films inhibit the growth of selected strains of gram-positive and gram-negative bacteria (Padgett et al., 1995). Nisin has also been incorporated into protein films and polyethylene films and found to retain it's antimicrobial activity

(Figure 3) (Hoffman et al., 2000).

Further testing of these films has proven their effectiveness against *Listeria monocytogenes* and *E. coli*. Three to 4 log reductions in *L. monocytogenes* (Dawson et al. 1998) and 2-3 log reductions in *E. coli* (Padgett et al., 1998) were found when the bacteria were exposed directly to the films.

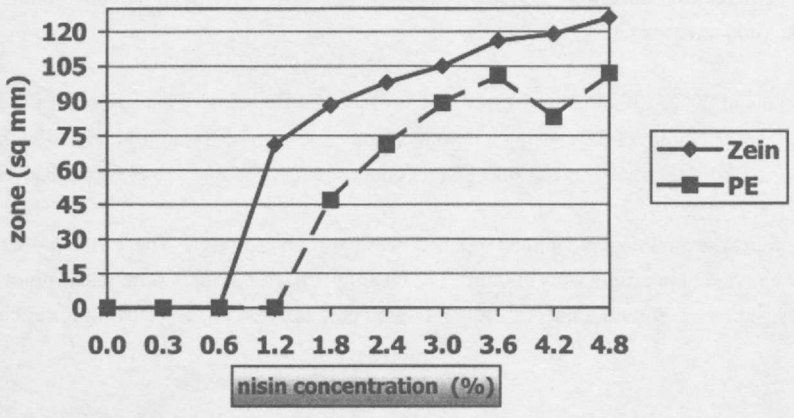

Figure 3. Bacterial zone of inhibition (area) for corn zein and polyethylene (PE) films formed with different levels of added nisin.

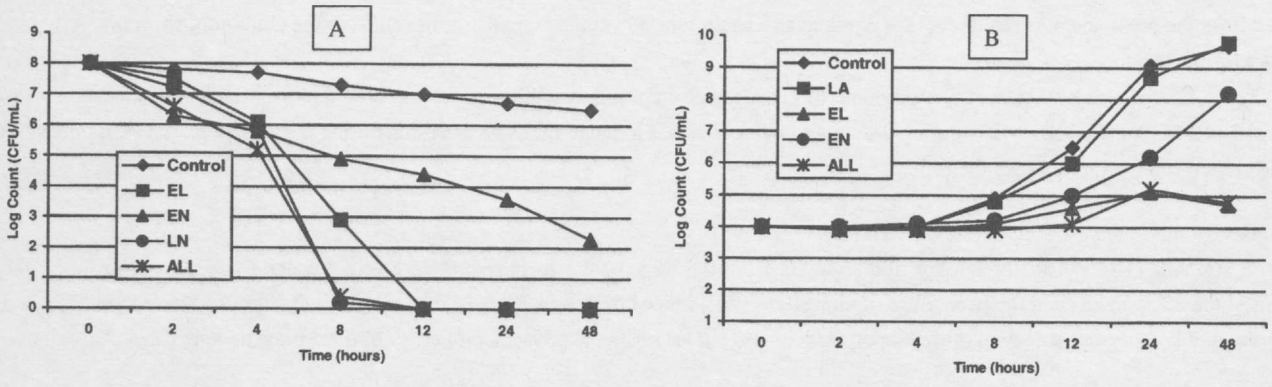

Figure 4. Effects of lauric acid (LA), EDTA/lauric acid (EL), EDTA/nisin (EN), lauric acid/nisin (LN) and EDTA/lauric acid/nisin (ALL) in corn zein films on [A] *Listeria monocytogenes* and [B] *Esherichia coli* n=6.

The addition of combinations of antimicrobial compounds to packaging films was shown to provide inhibition against *Listeria* and *Escherichia coli* species (Figure 4A and 4B) (Hoffman et al. 2000). The combinations of EDTA with nisin or with lauric acid or EDTA/lauric acid/nisin inhibited the growth of *E. coli* (Fig. 4A) while EDTA with lauric acid or EDTA/lauric acid/nisin also effectively inhibited *Salmonella enteriditis* (not shown). *L. monocytogenes* (Fig. 4B) was completely eliminated when exposed to films containing any combination of biocides that included lauric acid.

Another meat coating under development is based on chitosan, a carbohydrate derived from the skeleton of shellfish. This is a waste product of commercial shellfishing and can be processed to form a coating that has anti-fungal and anti-bacterial properties. Chitosan coatings

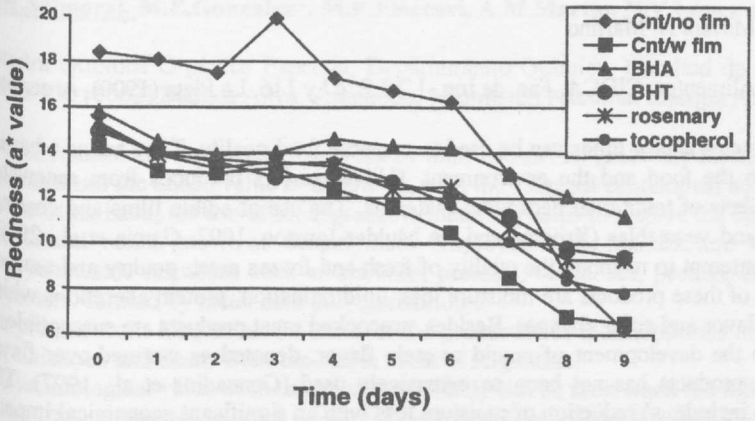

Figure 5. Effect of antioxidant impregnated corn zein films on the color stability of freshly-cut beef tissue. Cnt/no film = control with no corn zein film; Cnt/w film = control with a corn zein film; BHA = butylated hydroxy anisole added to corn zein; BHT = butylated hydroxy toluene added to corn zein; rosemary = rosemary extract added to corn zein; tocopherol = α-tocopherol added to corn zein

were shown to reduce the total bacterial population on chicken drumsticks by 1 log (90%) compared to non-coated drumsticks (Dawson et al. 1998).

In a most recent study (Finkle et al., 2000), the color stability of freshly-cut beef surfaces has been improved by exposing the meat surface to antioxidant-impregnated corn zein films. Commercial preparations of BHA, BHT, rosemary extract and tocopherol were incorporated into the films. The films were then placed on the fresh cut surface of beef and then held in close contact with an aerobic over-wrap synthetic film. The meat exposed to any film containing an antioxidant retained a redder color compared to meat not exposed to the protein-antioxidant film (Figure 5). The BHA impregnated corn zein film maintained color stability to the greatest extent compared to the other antioxidants tested. Subsequent migration tests revealed that BHA migrated at a faster rate than BHT in water and ethanol simulants and this may theoretically explain the greater color stability provided by the BHA treated film.

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