Biopolymer Films and Potential Applications to Meat and Poultry Products

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Introduction

Large amounts of packaging waste are discarded into the U.S. municipal waste system each year. Over 23 million tons of plastic packaging waste was generated in 1998 (EPA 1999). To reduce the amount of synthetic polymer waste, a considerable amount of research has been devoted to the production of bio-based polymer films derived from natural sources. The use of plant material to form films is an active research topic (Jane et al., 1996). As new applications for such materials are still emerging, characterization of renewable biopolymers is very important if these materials are to be used for packaging applications.

A question concerning the use of biopolymers as packaging materials is why should these materials be used instead of petroleum-based materials that are highly functional and relatively inexpensive. The advantages of using biopolymers for food packaging include: reduction of dependence on petroleum-based packaging, use of a renewable agricultural resource that can be mass-produced in the U.S., the biopolymers can act as carriers to deliver shelf-life extenders such as antimicrobials or antioxidants, and biodegradability. Biopolymers can originate from a variety of sources that include plant and animal material. Since the forming of a film requires cross-linking of molecular units to impart strength and flexibility, proteins and carbohydrates are often the best candidates for biopolymer films.

Biopolymer Film Research

Proteins investigated include wheat gluten, corn zein, whey, pea protein, meat proteins, egg proteins, and soy. Starches studied in the literature include alginate, polysaccharides, cellulose, carrageenans, microbial polysaccharides, and chitosan. There has been research activity on developing bio-based packaging in Europe and some U.S. companies are utilizing modified starch materials. Commercial raw materials include polylactate produced by Cargill Dow (trade name NatureWorks PLA) and by Mitsui under the trade name LACEA. Other starch-based raw packaging materials include Novamont (Mater Bi), Biotec (Bioplast), and Earth (Earth Shell). These materials require chemical modification of native starch materials and have been tested as molded containers (Salvage, 2001). Much of the research on biopolymer films has involved the production of films from the method of solvent casting. In contrast, thermal processing methods such as compression molding and extrusion have received limited attention. Jane and Wang (1996) and Huang et al. (1995) reported on an extrusion/molding technique, whereas Paetau et al. (1994), Jane et al. (1994), and Paulk et al. (1995) used compression molding to produce films from soy protein isolates. Other studies discuss the compression molding of starch and corn zein films. Some of these films were reported to be rigid and brittle due to the absence of a plasticizer in the preprocessed mixture. The reducing agents in the Jane and Wang (1996) patent break the disulfide bonds in protein fractions to enable processing of the soy protein isolates. The disadvantage of the chemically modified protein is that the individual molecules are not structurally bonded, and water-resistance decreases drastically. Cross-linking has been found to stabilize polymer chains and decrease vapor and gas permeability in protein-derived films (Kumins, 1965). Guilbert (1986) improved the barrier characteristics of films from various proteins (dried gelatin, casein, albumin, and ovalbumin) by the addition of organic acids. Various cross-linking agents and treatments that have been used in cast films include formaldehyde, glutaraldehyde, cysteine, transglutaminase, ultraviolet radiation, and glyoxal. Qualitative comparisons have been made between cast and heat-pressed protein 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).

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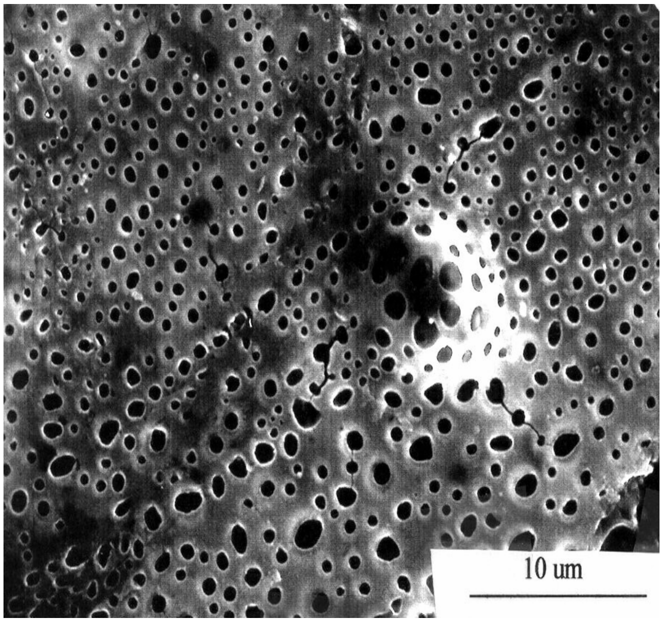


Figure 1. Cast corn zein film

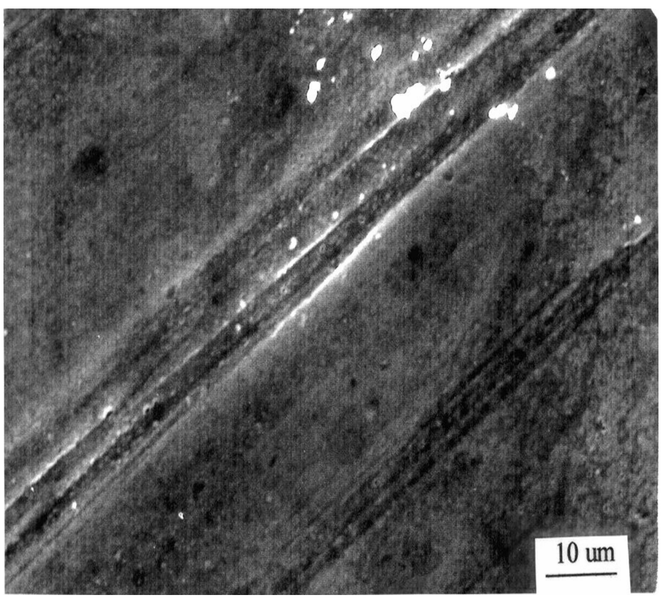


Figure 2. Thermally-compacted corn zein film

Batch Processing of Films

Research at Clemson University has shown that soy protein/glycerol, wheat/glycerol, and corn zein/glycerol mixtures can be thermally compacted using a Carver Laboratory Press (Fred S. Carver Inc., Menomonee Falls, WI). The procedure consists 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 150ºC for soy mixtures. To reduce water permeability, soy film has been laminated with the corn zein/glycerol mixture at 125ºC.

Continuous Film Extrusion

Clemson University has also investigated using a twin-screw extruder to mix the soy/glycerol and then place the mixture into a heated (135ºC) 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
Cast corn zein*	.089	.4	<1
Cellophane	0.36	114	20
High density PE	.025	17.3-34.6	300
Low density PE	.025	8.6-17.3	500

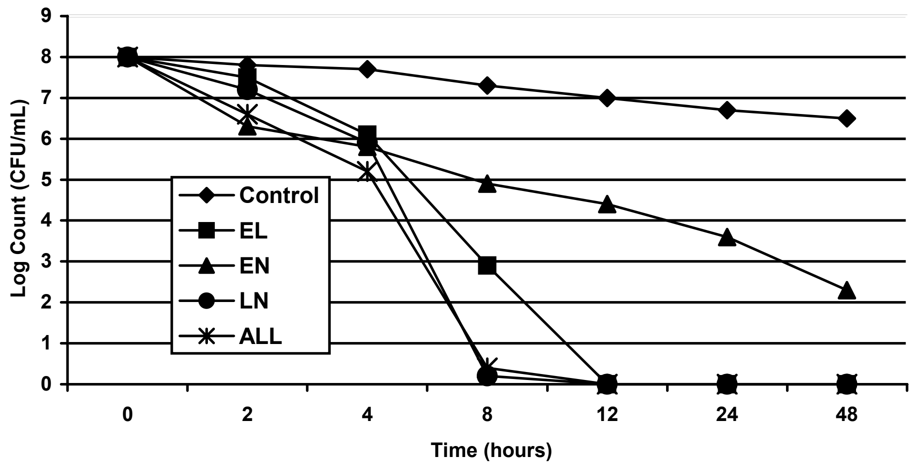
Applications

Research on the formation of bio-polymeric films has been ongoing since 1940s with increased research activity in recent years. Pearce and Lavers (1949) reported using carrageenan to protect frozen poultry and Klose et al. (1952) incorporated an antioxidant into a gelatin coating to slow the development of oxidative rancidity in cut poultry meat prior to freezing. Edible film applications to meat include the film functioning as a moisture barrier, oxygen barrier, texture modifier, breading adhesion aid, mold suppressor, bacterial inhibitor, physical protectant, oil barrier, antimicrobial carrier and antioxidant carrier (Table 2). 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 its antimicrobial activity (Hoffman et al., 2000). Three to four log reductions in *L. monocytogenes* (Dawson, 1998) and two to three log reductions in *E. coli* (Padgett et al., 1998) were found when the bacteria were exposed directly to the film.

Table 2. Biopolymer film and coatings applications tested for meat and poultry products

Material	Meat Product	Application	Reference
methyl cellulose	pork and poultry	breading adhesion	Bauer et al., 1967
carboxy-methyl cellulose	sausage	mold suppression	Luck, 1968
alginates	beef,pork,chicken	texture modifier, moisture barrier	Allen et al., 1963
alginates	lamb carcass	inhibit microbial growth	Lazarus et al., 1976
alginates	beef	moisture/oxygen barrier	Williams et al., 1978
carrageenan	poultry	moisture/oxygen barrier	Pearce & Lavers, 1949
microbial pullulon	diced meat	oxygen barrier	Yuen, 1974
chitosan	chicken	inhibit microbial growth	Acton et al, 2000
gelatin	meats	mold reduction, barrier	Kiel, 1961; Kiel et al., 1960
gelatin	frozen chicken	oxygen barrier, antioxidant carrier	Klose et al., 1952
gelatin	smoked chicken	moisture barrier	Moorjami et al, 1974
gelatin	breaded meat	oil barrier	Olson and Zoss, 1985
gelatin	meat cuts	moisture/oxygen barrier	Whitman & Rosenthal, 1971
corn zein	cooked turkey	oxygen barrier, antioxidant carrier	Wong et al, 1996
corn zein	sausage	moisture/oxygen barrier	Turbak, 1972
wheat gluten	sausage	moisture/oxygen barrier	Turbak, 1972; Mullen, 1971
wheat gluten	turkey	antimicrobial carrier	Schilling and Burchill, 1972
wheat gluten	bologna	antimicrobial carrier	Dawson et al, 2002
whey protein	frozen chicken	physical protection	Alcantara et al., 1997
collagen	beef steak	moisture/oxygen barrier	Farouk et al., 1990
collagen	beef cubes	moisture/oxygen barrier	Conea and Yang, 1993; Conean, 1994; Rice, 1994
soy protein	sausage	moisture/oxygen barrier	Turbak, 1972
soy protein	chicken	antimicrobial carrier	Dawson, 1998
albumen/gelatin	chicken parts	breading adhesion	Suderman et al., 1981
albumen/soy/wheat protein	meat parts	batter/breading adhesion	Baker et al., 1972

The addition of combinations of antimicrobial compounds to packaging films was shown to provide inhibition against *Listeria* and *Escherichia coli* species (Figure 3A and 3B) (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. 3B) while EDTA with lauric acid or EDTA/lauric acid/nisin also effectively inhibited *Salmonella enteriditis* (not shown). *L. monocytogenes* (Fig. 3A) was completely eliminated when exposed to films containing any combination of biocides that included lauric acid.



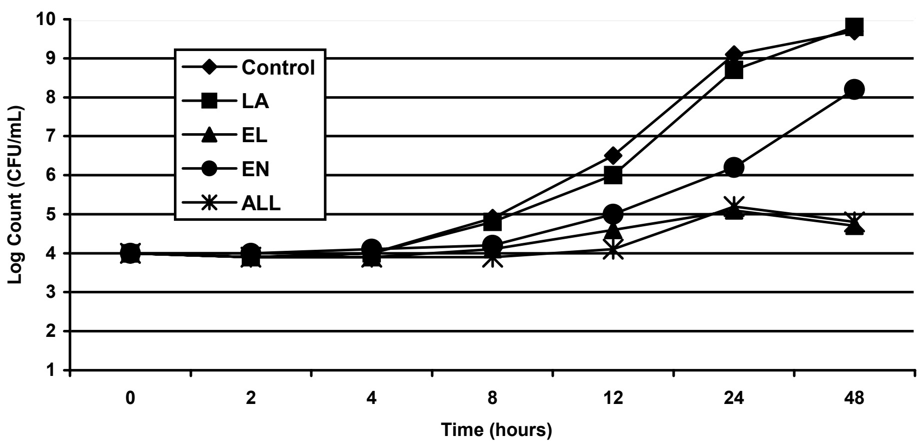


Figure 3. Effects of lauric acid (LA), EDTA/lauric acid (EL), EDTA/nisin (EN), lauric acid/nisin (LN) and EDTA/lauric acid/nisin (ALL) in corn zein films on [A] *Listeria monocytogenes* and [B] *Esherichia coli* n=6.

The application of thermally-compacted soy films containing 2.5% pure nisin (4%, wt/wt) to *Listeria monocytogenes* in a liquid medium suppressed cell numbers 1 log CFU/mL after 2 hours however cell numbers increased to 10^8 after 24 and 48 hours at 22 C (Dawson et al., 2002). Films containing lauric acid (8%) and nisin completely eliminated detectable cells from a 10^6 culture after 8-h exposure to the liquid medium (22 C). Refrigerated bologna exposed to control films increased by 0.5 log from 10^6 after 21 d at 4ºC (Figure 4) while nisin films reduced cell numbers on turkey bologna from 10^6 to 10^5 after 21 d as did films containing both nisin and lauric acid. Films with lauric acid alone reduced *L. monocytogenes* culture from 106 to <102 after 48 h and by 1 log on turkey bologna after 21 d.

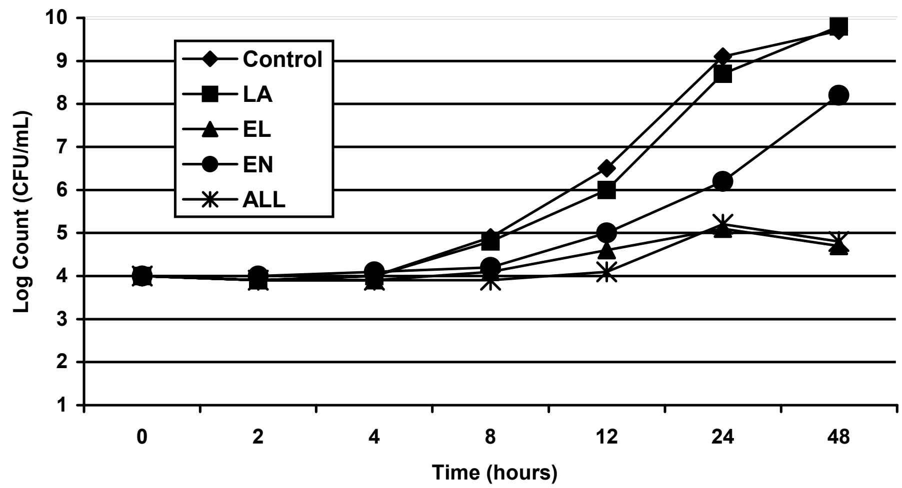


Figure 4. *Listeria monocytogenes* (cfu/mL) on turkey bologna during exposure to biocide-impregnated packaging films at 4 C ±2. N + L = nisin and lauric acid.

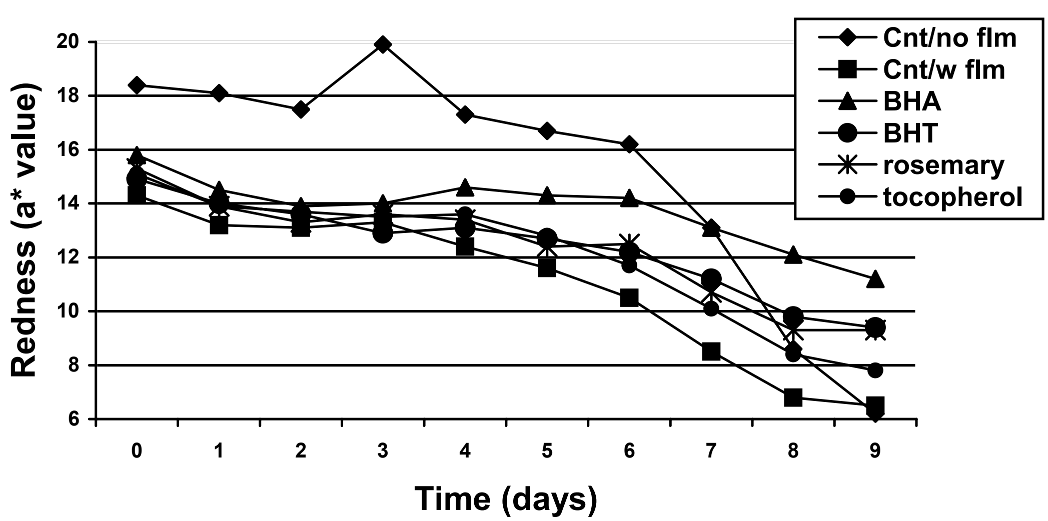


Figure 5. Effect of antioxidant impregnated corn zein films on the color stability of freshly-cut beef tissue. Cnt/no film = control with no corn zein film; Cnt/w film = control with a corn zein film; BHA = butylated hydroxy anisole added to corn zein; BHT = butylated hydroxy toluene added to corn zein;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

Another biopolymer under development is based on chitosan, a carbohydrate derived from chitin found in 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 were shown to reduce the total bacterial population on chicken drumsticks by 1 log (90%) compared to non-coated chicken drumsticks (Acton et al., 2000).

In a recent study (Moore et al., 2002), 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.

Future applications of biopolymers packaging are likely to be divided into coatings that are closely associated with the meat products and may in fact be consumed with the food or flexible films/composites that partially replace current petroleum-based flexible films and containers. Containers produced from potato processing waste are currently being tested

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