

STARCH/PULP-FIBER BASED PACKAGING FOAMS AND CAST FILMS CONTAINING ALASKAN FISH BY-PRODUCTS (WASTE)

Syed H. Imam,^{a*} Bor-Sen Chiou,^a Delilah Woods,^a Justin Shey,^a Gregory M. Glenn,^a William J. Orts,^a Rajnesh Narayan,^a Robert J. Avena-Bustillos,^b Tara H. McHugh,^b Alberto Pantoja,^c and Peter J. Bechtel^c

Baked starch/pulp foams were prepared from formulations containing zero to 25 weight percent of processed Alaskan fish by-products that consisted mostly of salmon heads, pollock heads, and pollock frames (bones and associated remains produced in the filleting operation). Fish by-products thermoformed well along with starch and pulp fiber, and the foam product (panels) exhibited useful mechanical properties. Foams with all three fish by-products, ranging between 10 and 15 wt%, showed the highest flexural modulus (500-770 Mpa). Above 20% fiber content, the modulus dropped considerably in all foam samples. Foam panels with pollock frames had the highest flexural modulus, at about 15% fiber content (770 Mpa). Foams with salmon heads registered the lowest modulus, at 25% concentration. Attempts were also made to cast starch-glycerol-poly (vinyl alcohol) films containing 25% fish by-product (salmon heads). These films showed a tensile strength of 15 Mpa and elongation at break of 78.2%. All foams containing fish by-product degraded well in compost at ambient temperature (24°C), losing roughly between 75-80% of their weight within 7 weeks. The films degraded at a much higher rate initially. When left in water, foams prepared without fish by-product absorbed water much more quickly and deteriorated faster, whereas, water absorption in foams with fish by-product was initially delayed and/or slowed for about 24 h. After this period, water absorption was rapid.

Keywords: Fish-waste; Foam; Films; Biobased; Biodegradable; Poly(vinyl alcohol)

Contact information: a: Bioproduct Chemistry & Engineering Research, WRRRC-ARS-USDA, Albany, CA 94710; b: Processed Food Research, WRRRC-ARS-USDA, Albany, CA 94710; c: Subarctic Agricultural Research Unit, ARS-USDA, Fairbanks, AK 99775

**Corresponding author: simam@pw.usda.gov*

INTRODUCTION

The seafood industry produces large quantities of fish waste globally. Most of the fish waste, also known as fish by-product, is generated during large-scale fish processing operations carried out onboard by big trawlers (Bluhm and Bechtel 2003). According to the Food & Agricultural Organization of the United Nations, in approximate terms, over 100 million metric tons of fish waste or discard is generated worldwide annually resulting from both sea and land-based fishing operations, of which only a small portion is used in the production of fishmeal and fish oil (Kilpatrick 2003). In waters around Alaska, fish waste generally consisted mostly of pollock followed by salmon and cod in the form of heads, tail, viscera and backbones (frames) produced from filleting operations. Properties

of various fish processing by-products recovered from pollock, salmon and cod have been described in detail (Bechtel 2003).

More than 65% of the total wild fish harvest for consumers in the United States comes from Alaskan waters. In the year 2000 roughly 1.0 million metric tons of fish processing waste was produced in Alaskan waters in the Bering Sea-Aleutian Islands Area alone (Bluhm and Bechtel 2003), and about 85% of this waste was discharged offshore. Continued dumping of fish discards at one of the most productive seas in the world may cause multiple effects on organisms that influence the food chain dynamics on several trophic levels, thus posing a threat to the ecological balance of this ecosystem (Stevens and Haaga 1994; Williams et al. 1999). Periodic abundance of nutrients in seawaters is well known for producing toxic algal and plankton blooms, causing mass-scale fish mortality. In this regard, microbiological analysis of a fish waste dump site in Alaska showed the presence of substantially higher number of both aerobic and anaerobic bacteria in the water column, as well as in the sediments at the dumpsite compared to the control sites (Himelbloom and Stevens 1994).

Other investigators have also shown the impact of salmon cannery waste on the water quality and marine organisms. While the macro-fauna was not adversely affected by the discharge, increased turbidity and biochemical oxygen demand were observed in the immediate vicinity (Beyer et al. 1975). These authors predicted that the continued dumping may lead to undesirable changes in pH and dissolved oxygen levels in these waters. More recently, changes in the open-ocean pelagic fish community structure of the tropical Pacific Ocean has also been reported in areas coinciding with the commencement of commercial fishing (Ward and Myers 2005) where fish waste is routinely discarded overboard.

Fish waste is a source of many useful natural polymers, fuels, and other industrially important chemicals. It is critical that we seek new and novel ways to use this abundant resource of raw material (Blythe 1996; Bimbo 1987; Sada 1984; Miyazaki et al. 1996; Shahidi 1995) and at the same time prevent environmental degradation. Single-use packaging presents one of the most promising applications for inherently biodegradable natural polymers (Petersen et al. 1999).

In this regard, many investigators, including those participating in the work from our laboratory, have successfully shown that starch polymers, derived from a variety of botanical sources, can be expanded into foams via thermal treatment (extrusion, as well as baking processes) in the presence of other biopolymers such as cellulose, poly(vinyl alcohol) (PVOH), polylactic-acid (PLA) and polyhydroxybutyrate-co-valerate (PHBV) (Shogren et al. 1998a and 1998b; Lawton et al., 1999; Fang and Hanna 2000; Glenn et al. 2001; Shogren et al. 2002; Willett and Shogren 2002; Chen et al. 2004; Glenn et al. 2004; Lawton et al. 2004; Guan et al. 2005; Preechawong et al. 2005; Cinelli et al. 2006). However, fish waste, which mostly contains proteins (including collagen), CaCO₃, oil and water, has never been used in conjunction with starch and/or fiber for making foam packaging material. Thus, this is the first report which describes our efforts to use processed fish waste in baked starch/pulp foams and starch-PVOH cast film formulations. The foams and films were produced and evaluated to examine their properties for use in packaging applications.

EXPERIMENTAL

Materials

Native potato starch (PenCook 10) and potato pre-gelatinized starch (PenPlus UM) were purchased from Penford (Englewood, CO). Recycled fiber was pulped paper fiber (PL416) from Weyerhaeuser (Federal Way, WA). Magnesium stearate (905-G) was from Whittaker, Clark, and Daniels (South Plainfield, NJ). PVOH (99% hydrolyzed, M_w 89,000-98,000) was purchased from Sigma-Aldrich Inc., (St. Louis, MO).

The panel press (110 mm by 165 mm by 1.8 mm) from Hebenstreit GmbH (Mörfelden-Walldorf, Germany) was equipped with temperature controllers (Series 93) from Watlow (St. Louis, MO). The batter mixer was a 5 quart capacity Hobart Model-N50A (Hobart MFG Co., Troy, OH). For flexural strength, a three point bend flexural testing was done with an Instron Universal testing Machine-model 5500R (Canton, MA) with the aid of an Instron's Series IX software. Moisture content was determined on a Mettler Toledo Halogen Moisture Analyzer model HR73 (Columbus, OH).

Processing of Fish By-Products

Freshly frozen fish samples of salmon heads, pollock heads, and pollock frames were received in 5-gallon plastic buckets directly from Alaska and stored at -80°C until further use. The detailed procedure for by-product processing is outlined in Fig. 1. Briefly, frozen fish samples were fed into a meat grinder (Model A-200, Hobart MFG Co.) and coarsely ground (plate with pores of 4.5 mm in size). The frozen fish was much easier to grind and process compared to thawed fish samples. For fish heads too big to be fed into the grinder, a hammer and chisel were used to break them into usable chunks. The coarsely ground sample was fed to the grinder for a second time with a much finer screen (pores of approximately 2.0 mm diameter pore size) in place. A sample, resembling and having the consistency of pâté, was spread (5-7 cm in height) over a porcelain-coated pan and dried in the oven overnight at 60°C . The moisture content of the fish paste before drying was between 69-74%. Dried fish purée was collected and placed in a 50% RH chamber for 10 min to cool without condensation. The sample was further ground (2-3 cycles of 1 min each) in a BRAUN coffee-grinder, Model KSM2, (Lynnfield, MA) to generate a finer powder. The powder was then placed in zip lock bags and stored at room temperature (24°C) for subsequent use.

Preparation of Baked Foam Panels and Cast Films

The procedure for preparing the baked foam panels has been described in greater detail in earlier published reports (Glenn et al. 2001; Shey et al. 2006). Briefly, recycled fiber was first dispersed in water for 15 min with stirring in a beaker. Dispersed fibers were directly added to the pre-gelatinized starch, magnesium stearate and the processed fish powder in a Hobart mixer. The ingredients were mixed for about 5 min until a dough of good consistency was obtained. Since pre-gelatinized starch was used in formulations, pre-cooking of the starch was not necessary. The batter contained water with fiber (7.7 wt%), magnesium stearate (2.3 wt%), native starch (46 wt%), and pre-gelatinized starch (6.5 wt%). Native starch was substituted for fish content. All weight percent values are based on the amount of added water in the formulation. All batters prepared from fish content had the same final weight. The panel press was preheated to $190\text{-}200^{\circ}\text{C}$, and the batter was placed in the center of the mold. The mold was closed shut to spread the

material out and baked for 1 min. About 18 g of batter was required to fill the mold. The density of fish-containing foams typically ranged between 0.15 - 0.20 g/cm³. The Mg Stearate used in formulations is a filling agent and acts as a binder to some extent. Additionally, it also has lubricating properties and prevents sticking of materials to the mold during the baking process.

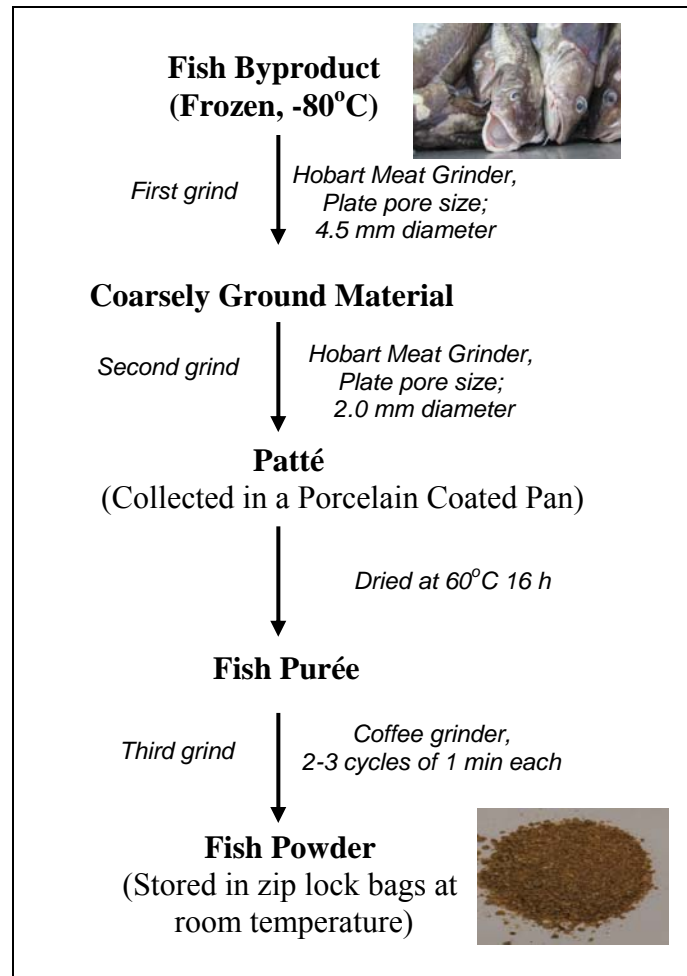


Fig. 1. Schematic diagram showing the steps involved in processing of fish by-products.

Starch-Polyvinyl Alcohol (PVOH) Films

An aqueous solution containing 15% starch (wt%), 10% PVOH (wt%), and 25% powdered fish (wt%), 10% glycerol (wt%), and 40 g of deionized water (40 mL) was used to cast films. In the presence of water, starch was gelatinized in a beaker by heating it in a boiling water-bath for 15-20 minutes with continuous mixing. PVOH and glycerol were added after starch gelatinization. Fish waste was added while stirring with moderate shearing until the powder completely dispersed in the solution. Water was added to compensate for any loss due to evaporation during heating. PVOH stock solution was prepared in advance by dissolving the PVOH in deionized water (in-house) and heating it in a boiling water bath with continuous stirring. Once PVOH was dissolved in water, the solution was cooled at the room temperature (23°C) for future use.

Cast films (about 100 μ m thick) were prepared by pouring the warm solution onto the glass plate (20 x 25 cm) between the doctors' blade (a device that allows the spread of viscous liquids at a predetermined thickness) and spreading it over the entire area of the plate. Any excess was wiped off with a paper towel. Plates were either dried in the preheated oven (60°C) for a 4-6 h or left at room temperature (23°C) over night.

Material Performance

For evaluation of mechanical properties, prepared materials were subjected to Instron testing. The starch foams were cut to 25.4 mm wide x 127 mm long strips using a Delta band saw (Jackson, TN) and equilibrated at ~50% relative humidity (saturated solution of calcium nitrate tetrahydrate) at ambient temperatures (24°C) for at least one week before testing. Data were analyzed by two- and one-way analysis of variance (ANOVA) using Minitab version 13.31 software (Minitab Inc., State College, PA). The Tukey test was used to determine the difference at 5% significance level.

To study biodegradation in compost, foam strips were cut from the panel as described above. Marked strips were weighed and placed on commercial compost (5-7 cm thick, 60% moisture content) in a Teflon-coated metal tray and covered with another 2-3 inches of compost on top of it. Trays were covered with aluminum foil and left in a room with controlled temperature and humidity conditions (23°C, 50% RH). The strips were recovered at the indicated time intervals and any dirt or debris was removed with a soft brush and the remaining strips weighed. For every data point, at least three strips were weighed, and the average weight-loss was recorded. Polystyrene foam strips was used as a control.

For moisture absorption, square-shaped pieces of foam (approximately, 2.54 cm²) of known weights were left in a beaker of water. At the designated time, the pieces were recovered, excess water was blotted, and sample was weighed. Any increase in weight was recorded. Each data point represents an average of quadruple samples.

Scanning Electron Microscopy (SEM)

The foam sample pieces of approximately 3-4 mm were cut and mounted onto aluminum specimen stubs using double adhesive-coated carbon tabs (Ted Pella, Inc, Redding, CA) and dried in a Tousimis Autosamdri 815 (Tousimis, Rockville, MD) critical point drier. The samples were then coated with gold-palladium in a Denton Desk II sputter coating unit (Denton Vacuum, Moorestown, NJ). Sample were viewed and photographed in a Hitachi S4700 field emission scanning electron microscope (Hitachi, Japan).

RESULTS AND DISCUSSION

Each foam sample had a maximum flexural modulus value over the filler concentration range studied. Table I shows the flexural properties of foams containing salmon heads, pollock heads, and pollock frames as filler. All foam samples with fish byproduct showed much improved flexural modulus compared to controls with no fish content. The pollock samples (both head and frame) had maximum modulus values at approximately 15% filler, whereas the salmon sample (head) had maximum modulus value at approximately 10% filler. Also, foams containing pollock heads had the largest

modulus values at lower filler concentrations. Foams containing salmon head had modulus values that decreased at a rapid rate at high filler concentrations. In contrast, in pollock foams, modulus values did not decrease as rapidly with higher filler content (Table I).

The flexural yield stress generally decreases in value for higher filler concentrations (Table I). The salmon head sample maintained a fairly constant stress value up to 20% filler, after which the stress dropped dramatically in value. In contrast, the pollock samples showed a decrease in stress at 5% filler and then a relatively constant stress thereafter.

The salmon and pollock samples had very different yield strain behavior. This is shown in Table I. The yield strain values for pollock foams decreased to approximately 0.5-0.6% at 15% filler concentration and remained constant for higher filler concentrations. In contrast, the salmon foam exhibited an initial decrease in yield strain, but then an increase between 15-20 % filler. The large increase in yield strain at 25% filler coincided with the large decrease in modulus value. This indicated that the 25% salmon head sample was more ductile and less stiff than the samples at low filler concentrations. In addition, the salmon foams had a higher percent yield strain values than the pollock foams over the entire filler concentration range.

The differences found in the flexural properties among three fish samples (Table I) were unexpected. Particularly, differences in the flexural modulus, yield stress and yield strain in foams with highest salmon content compared to pollock heads and pollock frame were surprising. Fish waste mostly consists of protein, calcium-carbonate, and small amounts of fish-oil, and about 66-77% water. For example, fish frames are mostly calcium with moderate amount of proteins containing little or no oil. On the other hand, fish heads have a lot more proteins than calcium followed by oil content. These proteins are mostly fish muscle proteins derived from cheeks, tongue, gills, and skin. The differences in flexural properties may be attributed to the proportion of these constituents in the final composition. The results of DSC and TGA analyses performed on these foams were inconclusive (data not shown).

When totally immersed in water, control starch foam samples without fish waste absorbed water quickly. About 50% weight gain due to water absorption was achieved within 12-13 h (Fig. 2). Starch polymer with three free hydroxyl units on each glucose monomer is extremely hydrophilic in nature, and rapid water absorption was not surprising. However, foams containing either salmon or pollack waste initially showed excellent moisture resistance. Compared to the control, salmon- and pollack-containing foams only gained 10 and 18% water, respectively, within 12-13 h of exposure in water. This clearly indicated initial water resistance in these foams due mostly to polypeptides and calcium in fish wastes. Interestingly, these differences were only apparent until 20 h of exposure. By 24 h of exposure, all foams had weight gains equivalent to 120% of their original weight (Fig. 2). Peptides, calcium, and starch all have ionic moieties, which may form inter- and intra-molecular cross-links. Possibly such cross-linking was responsible in providing the initial water resistance to fish-containing foams but deteriorated or become weaker after an extended exposure to water.

Table I. Flexural Properties of Fish-based Foams^{1,2}

Fish by-product filler (%)	Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)
Pollock frame			
0	265 ± 33 ^a	4.73 ± 0.42 ^b	2.27 ± 0.27 ^c
5	380 ± 86 ^{ab,A}	3.87 ± 0.78 ^{ab,NS}	1.08 ± 0.17 ^{b,B}
10	519 ± 66 ^{b,A}	3.48 ± 0.87 ^{a,A}	0.69 ± 0.09 ^{a,A}
15	770 ± 115 ^{c,B}	4.27 ± 0.72 ^{ab,NS}	0.58 ± 0.08 ^{a,A}
20	762 ± 134 ^{c,B}	3.68 ± 0.87 ^{ab,A}	0.52 ± 0.08 ^{a,A}
25	643 ± 104 ^{bc,B}	3.90 ± 0.67 ^{ab,B}	0.65 ± 0.10 ^{a,A}
Pollock head			
0	265 ± 33 ^a	4.73 ± 0.42 ^c	2.27 ± 0.27 ^c
5	494 ± 56 ^{b,B}	3.72 ± 0.67 ^{ab,NS}	0.77 ± 0.09 ^{b,A}
10	643 ± 55 ^{cd,B}	4.11 ± 1.02 ^{bc,AB}	0.66 ± 0.15 ^{ab,A}
15	698 ± 128 ^{d,B}	3.31 ± 0.53 ^{ab,NS}	0.49 ± 0.05 ^{a,A}
20	630 ± 57 ^{cd,B}	3.54 ± 0.30 ^{ab,AB}	0.56 ± 0.07 ^{ab,A}
25	530 ± 89 ^{bc,B}	3.04 ± 0.72 ^{a,AB}	0.62 ± 0.11 ^{ab,A}
Salmon head			
0	265 ± 33 ^b	4.73 ± 0.42 ^b	2.27 ± 0.27 ^c
5	321 ± 66 ^{b,A}	3.89 ± 0.55 ^{ab,NS}	1.47 ± 0.21 ^{b,C}
10	565 ± 101 ^{c,AB}	5.57 ± 1.67 ^{b,B}	1.04 ± 0.23 ^{a,B}
15	490 ± 136 ^{c,A}	4.56 ± 1.86 ^{b,NS}	1.03 ± 0.16 ^{a,B}
20	397 ± 47 ^{bc,A}	4.75 ± 0.89 ^{b,B}	1.56 ± 0.34 ^{b,B}
25	107 ± 29 ^{a,A}	2.27 ± 0.65 ^{a,A}	3.33 ± 0.33 ^{d,B}

¹ Different letter (^{a,b,c,d}) in same column at different concentrations for each fish by-product added indicate significant difference at p<0.05

² Different letter (^{A,B}) in same column at the same concentration for the three fish by-products added indicate significant difference at p<0.05

^{NS} No significant difference

Biodegradation of foams in compost (as measured by their respective weight-losses) initially showed a much slower rate of degradation in foams containing fish-waste compared to control without any fish content (Fig. 3). Little or no difference was observed among the three different fish wastes used. Again, starch foams degraded much more rapidly in first few weeks, achieving a 50% weight-loss within the first two weeks, and then reaching a plateau (Fig. 3). Interestingly, the extent of degradation was quite similar by the fifth week. In fact, by 6 weeks, all fish-containing foams showed much higher total degradation compared to the control. As expected, polystyrene, a petroleum-based commercial packaging foam, showed absolutely no sign of biological activity in compost during the six week period (Fig. 3). Initial rapid degradation of foams with starch is understandable, as starch is a much simpler molecule, and both linear and branched glucose polymers in starch are readily accessible to microbes and their hydrolytic enzymes for biological breakdown.

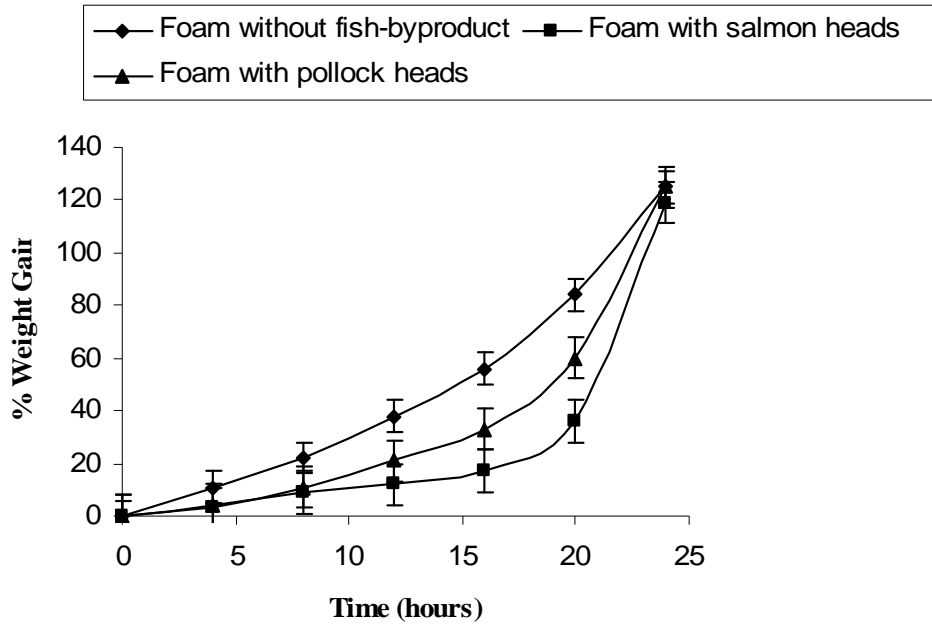


Fig. 2. Weight gain in foam samples containing salmon heads and pollock heads exposed to water along with control without any fish byproduct.

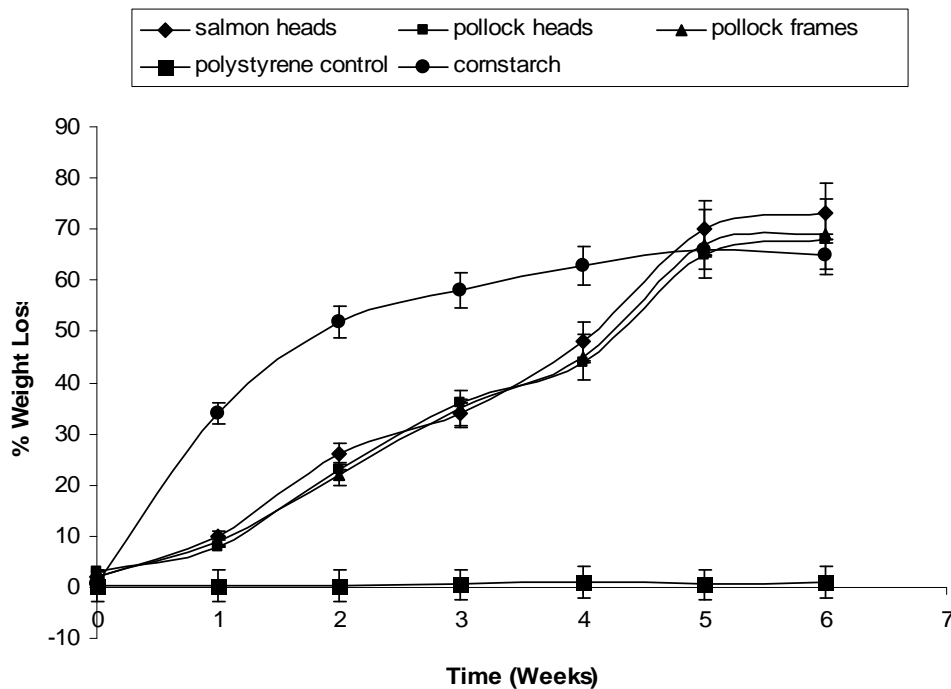


Fig. 3. Biodegradation (weight-losses) in foam samples buried in compost

In the hybrid foams with fish-byproducts, much of the starch polymer is complexed with polypeptides and calcium carbonate, perhaps forming ionic cross-links, thus, restricting its accessibility for microbial attack, which explains their initial slow

degradation. Once the starch is depleted, the matrix becomes loose, and microbes then start to use glucose as well as partially hydrolyzed peptides and polypeptides in the matrix accelerating its degradation. A similar degradation pattern has also been observed in starch-PHBV extruded composites, where enhanced degradation was observed in blended starch-PHBV composites compared to starch alone (Imam et al. 1999).

The morphology of the foams was examined using scanning electron microscopy (SEM). A scanning electron micrograph of typical starch-based baked foam is shown in Fig. 4. The surface appears to be rather smooth, with starch polymers agglomerating with other additives of the formulation (Fig. 4A). Figure 4B represents a cross-section showing open cells throughout the height of the foam. In particular, the edges of the starch foam have a characteristic thin wall. Starch foam with added pollock and salmon by-products are shown in Figs. 5 and 6, respectively. Foams with fish waste were morphologically distinct as viewed under the scanning electron microscope. The surface view showed a complex network of fibrous proteins and starch in foams with pollock and salmon waste, as depicted in Figs. 5A and 6A, respectively. Interestingly, in control foam samples containing starch and pulp without fish byproduct, such fibrous material was not visible on the surface (Fig 4A). Apparently, pulp fibers disperse and mix well with gelatinized starch and plasticizer that they are no longer in a recognizable form. Furthermore, cross-sections also indicated much larger cells in the interior of the foam and substantially thicker edges or walls compared to starch foam (Fig. 5B and 6B). The exterior walls of the foams were much thicker in salmon-based foams than pollock. Presumably, due to the salmon proteins being more fibrous than pollock, formation of starch-protein complex might have resulted in thicker exterior walls in salmon-based foams as seen in cross-section (Fig. 6B). The fibrous nature of the salmon proteins, however, needs to be evaluated. This would also explain the initial slow rate of water absorption and degradation in these foams. Thick walls may also indicate some interference on part of fish proteins with the foaming process in starch.

Self-assembly of proteins and peptides into unique fibrous nanostructures has recently been shown in a partially hydrolyzed α -lactalbumin, a whey protein (Graveland-Bikker 2005). This self-assembly required presence of Ca^{2+} ions. It is possible that the fibrous structures seen in fish-containing foams may also represent self-assembled hydrolyzed peptides. Interestingly, in processed fish samples (both salmon and pollock) before addition into formulations, no fibrous structures were visible under the SEM, and most proteins appeared to be globular in nature. This aspect, however, requires further evaluation under the experimental conditions described.

A possibility of preparing thin flexible packaging films based on fish-waste was also examined. Cast films (100 μm thickness) were prepared from formulations containing fish waste. Films stored at 50% RH for 2-weeks were strong and flexible, exhibiting a tensile strength of about 15.0 Mpa and an elongation at break of 78.2 % (Table II). Compared to controls (such as starch-glycerol or starch-PVOH-glycerol), films with added fish content exhibited both markedly improved tensile strength and elongation at break. Compared to starch-glycerol, starch-PVOH-glycerol films without fish content showed higher tensile strength, indicating that the PVOH improved film properties. But films containing starch-glycerol-PVOH and fish byproduct together had superior tensile properties, indicating a synergistic effect of PVOH and protein. These films were also strong and flexible compared to films without fish content.

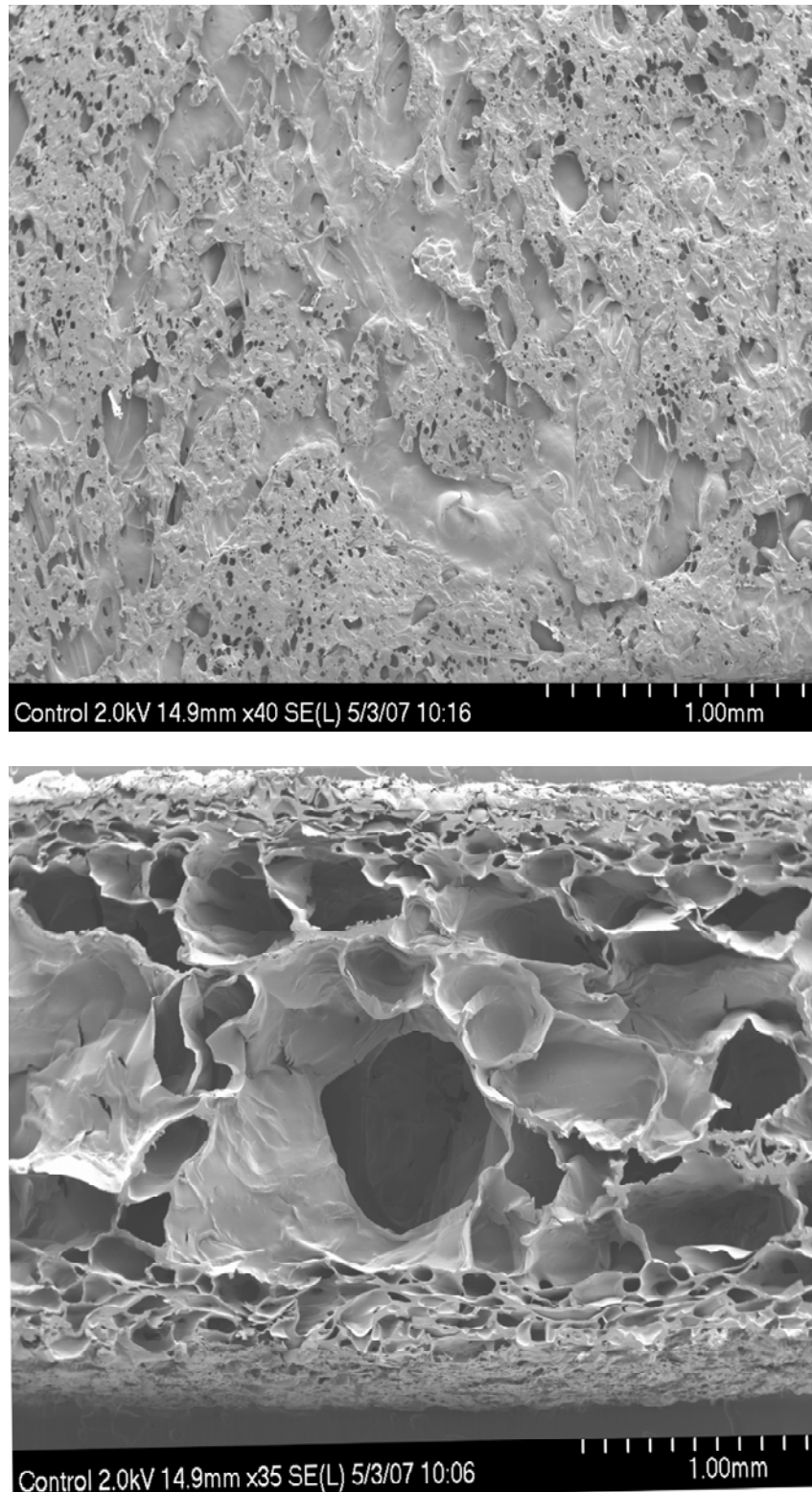


Fig. 4. Scanning electron micrographs showing the surface view [A] and a cross-section [B] of control starch foam containing pulp fiber without fish-byproduct.

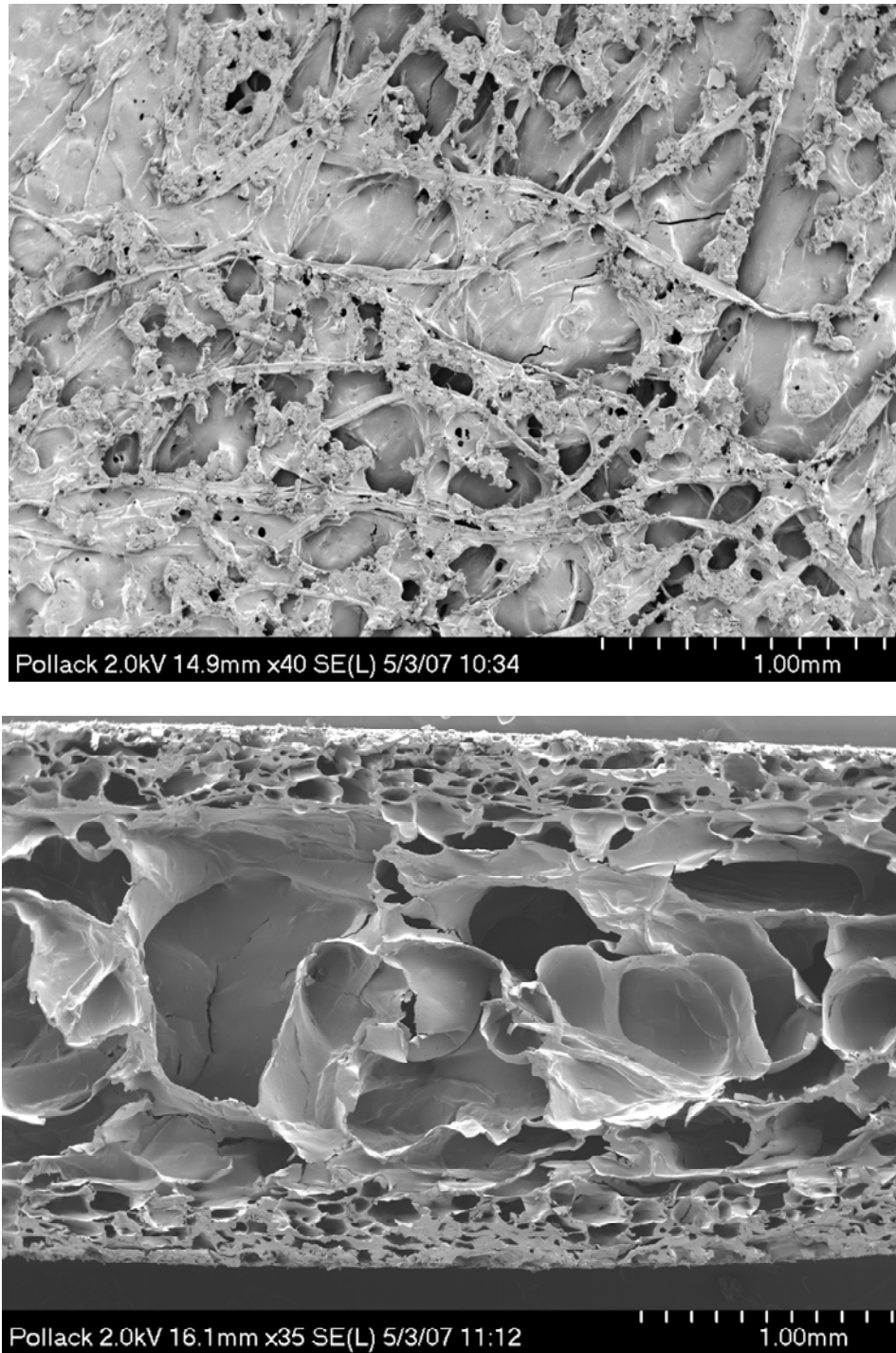


Fig. 5. Scanning electron micrographs showing the surface view [A] and a cross-section [B] of the starch foam containing pollock by-product (heads).

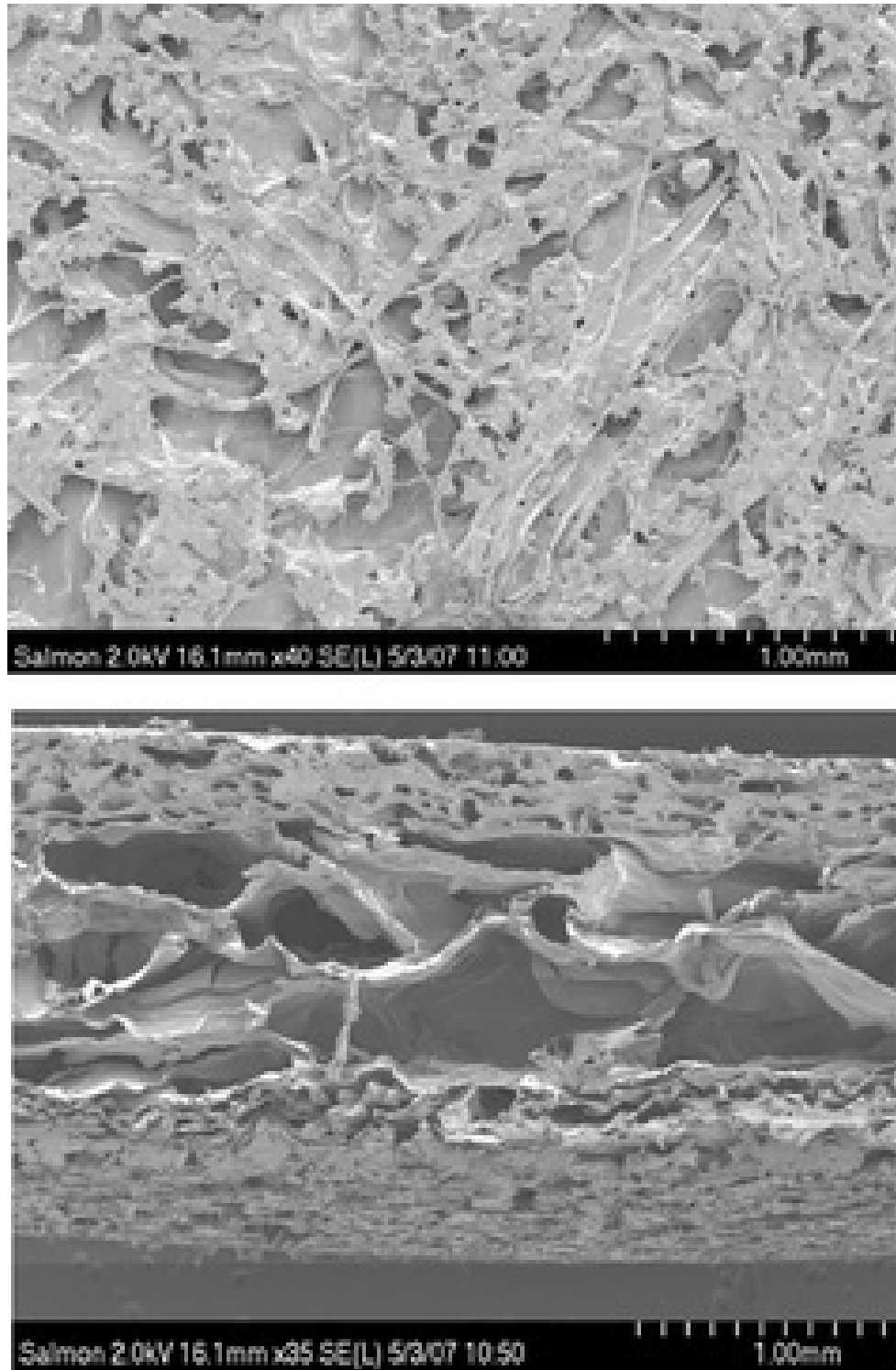


Fig. 6. Scanning electron micrographs showing the surface view [A] and a cross-section [B] of starch foam containing salmon by-product (heads).

Sample	Tensile strength (Mpa)	Elongation at break (%)
Starch-glycerol-PVOH film with fish byproduct*	15.0 ± 1.1 (4)	78.2 ± 2.7 (4)
Starch-PVOH-glycerol film without fish byproduct	10.2 ± 0.3 (4)	54.9 ± 1.7 (4)
Starch-glycerol film without PVOH or fish byproduct	8.1 ± 1.4 (4)	29.5 ± 2.0 (4)

* Fish byproduct used was salmon heads.

When tested for degradation in the compost environment, films with or without fish content degraded rapidly. Compared to control (starch-glycerol-PVOH with no fish), films containing fish content degraded at a much slower rate. After an initial period, the rate and extent of degradation in two films remained somewhat different, but by day 35 these differences had diminished, and both films achieved an overall weight-loss between 75-80% (Fig. 7). After 25 days, the rate at which the weight-loss occurred in films decreased considerably. It is not surprising that the films exhibited degradation rates twice as fast, compared to the foam samples, because the films had significantly larger surface areas that were exposed to the compost. Additionally, foamed starch may also have formed complexes or encapsulated some of the polypeptides in fish waste, thereby restricting their excess to microbes and/or their hydrolytic enzymes.

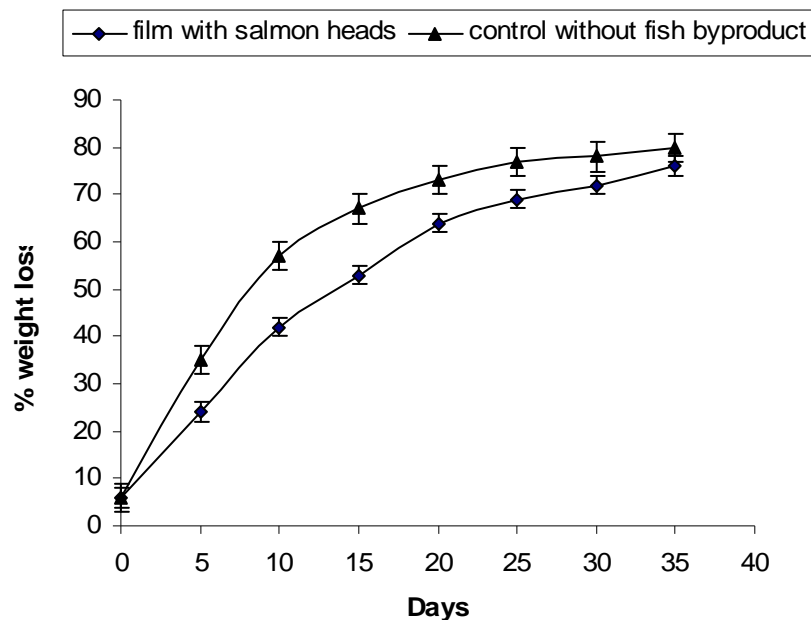


Fig. 7. Biodegradation (weight-losses) of cast films with or fish byproduct in compost environment.

Fish-waste represents a tremendous biomass resource as a raw material suitable for many applications. Currently, many consumer products, including fuel, oil, feed, fertilizer and several pharmaceuticals are derived from fish discard globally, but this only represents a small portion of the total fish waste, most of which is discarded in the environment. This report points to usefulness of such biomass resource in consumer packaging as an alternative to its disposal in ocean, which may have potentially damaging consequences for the environment. The intent was simply to show that upon processing into a specific form, protein rich streams could be used as filler in starch/pulp foams or films. No attempts were made to evaluate the economic feasibility of making packaging products from fish waste. However, utilization of such biomass available in huge quantities into packaging products offers an option that is worth exploring and may potentially translate into better revenues for fish industry and a more sensible use of this resource. Approaches like these provide an attractive economic alternative to dumping and would also help save the environment. A persistent minute fish odor in packaging films and foams made from fish by-product still existed. However, if the packaging is to be used for packing fish products, the odor might not be a major problem. For example, fresh fish fillets in supermarkets sold in packaging foam-trays containing fish by-product may not be an issue from the consumer stand point. Particularly, with excellent mechanical properties and better water resistance, these formulations would serve well for the intended application. Still, research is needed to further improve the moisture barrier property of such foams for wider applications and a longer shelf life. In this regard, a preliminary study at the USDA laboratory has already shown that incorporation of small amount of a natural polymer, guayule latex, in the formulation can add moisture barrier properties to starch/pulp foams (Shey et al. 2006). Additionally, further research is warranted to address any food safety concerns due to food contact with such packaging.

CONCLUSIONS

1. Fish byproducts can be processed and transformed in to starch-based packaging foams and film, indicating a usefulness of such a bioresource as an alternative to ocean dumping.
2. Both foams and films had useful mechanical properties, which can be exploited for certain packaging applications.
3. Current products offer reasonable moisture resistance. But for use in applications where packaging needs to be immersed in water or exposed to a high moisture environment for an extended period of time, improvement in water resistance is highly desirable.
4. Both products described in this article quickly biodegrade in compost.

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REFERENCES CITED

- Bechtel, P. J. (2003). "Properties of different fish by-products from pollock, cod and salmon," *J. Food Process. Preserv.* 27, 101-116.
- Beyer, D. L., Nakatani, R. E., and Staude, C. P. (1975). "Effects of salmon cannery wastes on water quality and marine organisms," *J. Water Pollu. Cont. Fed.* 47, 1857-1869.
- Bimbo, A. P. (1987). "The emerging marine oil industry," *J. Am. Oil Chem. Soc.* 69, 706-715.
- Bluhm, B. A., and Bechtel, P. J. (2003). "The potential fate and effects of seafood processing wastes dumped at sea: A review," P. J. Bechtel (ed.), In *Advances in Seafood Byproducts 2002*, Conference Proceedings. University of Alaska Sea Grant College Program (publisher), Fairbanks, Alaska, pp. 121-140.
- Blythe, N. X. (1966). "Fish oil as an alternative fuel for internal combustion engines," Fairbanks Morse Engine Division, BF Goodrich Company, Beloit, Wisconsin.
- Chen, L. G., and Imam, S. H. (2004). "Starch graft poly (methyl acrylate) loose-fill foam: Preparation, properties and degradation," *Biomacromol.* 5, 238-244.
- Cinelli, P., Chiellini, E., Lawton, J. W., and Imam, S. H. (2006). "Foamed articles based on potato starch, corn fibers and poly (vinyl alcohol)," *Polym. Degrad. Stabil.* 91, 1147-1155.
- Fang, Q., and Hanna, M. A. (2000). "Functional properties of polylactic acid starch-based loose-fill packaging foams," *Cer. Chem.* 77, 779-783.
- Glenn, G. M., Imam, S. H., Orts, W. J., and Klamczynski, A. K. (2004). "Fiber reinforced starch foams," *Ann. Tech. Conf. – ANTEC*, Conference Proceedings, 2, 2484-2488.
- Glenn, G. M., Orts, W. J., and Nobes, G. A. R. (2001). "Starch, fiber and CaCO₃ effects on the physical properties of foams made by a baking process," *Ind. Crops. Prod.* 14, 201-212.
- Graveland-Bikker, J. F. (2005) "Self-assembly of hydrolyzed α -lactalbumin into nanofibers," Ph.D. thesis, Utrecht University, Netherlands.
- Guan, J., Eskridge, K. M., and Hanna, M.A. (2005). "Acetylated starch-polylactic acid loose-fill packaging materials," *Ind. Crop. Prod.* 22, 109-123.
- Himelbloom, B. H., and Stevens, B. G. (1994). "Microbial analysis of a fish waste dump site in Alaska," *Bioresource Technol.* 47, 229-233.
- Imam, S. H., Gordon, S. H., Shogren, R. L., Tosteson, T. R., Govind, N. S., and Greene, R. V. (1999). "Degradation of starch-poly (β -hydroxybutyrate-Co- β -hydroxyvelerate) bioplastics in tropical coastal waters," *Appl. Environ. Microbiol.* 65, 431-437.
- Kilpatrick, J. S. (2003). "Fish processing waste: Opportunity or liability," P. J. Bechtel (ed.), *Advances in Seafood Byproducts*, 2002 Conference Proceedings. University of Alaska Sea Grant College Program (publisher), Alaska, pp. 1-10.
- Lawton, J. W., Shogren, R. L., and Tiefenbacher, K. F. (1999). "Effect of batter solids and starch type on the structure of baked starch foams," *Cer. Chem.* 76, 682-687.
- Lawton, J. W., Shogren, R. L., and Tiefenbacher, K. F. (2004). "Aspen fiber addition improves the mechanical properties of baked cornstarch foams," *Ind. Crop. Prod.* 19, 41-48.
- Miyazaki, S., Kawasaki, N., Serizawa, I., and Doi, K. (1996). "Pharmaceutical application of chitosan: Drug release from oral mucosal adhesive films of chitosan

- and alginate,” in Stevens, W. F., Rao, M.S., and Chandkrachang, S. (eds.), *Proceedings of the 2nd Asia Pacific Symposium on Chitin and Chitosan: Environmental Friendly and Versatile Biomaterials*. Asian Inst. Technol. (Publisher), Bangkok, Thailand, pp. 291-294.
- Preechawong, D., Peesan, M., Supaphol, P., and Rujiravanit, R. (2005). “Preparation and characterization of starch/poly(l-lactic acid) hybrid foams,” *Carbohydr. Polym.* 59, 329-337.
- Petersen, K., Væggemose, P., Bertelsen, G., Lawther, M., Olsen, B., Nilsson, H., and Mortensen, G. (1999). “Potential of biobased materials for food packaging,” *Trend Food Sci. Technol.* 10, 52-68.
- Sada, M. (1984). “Fish calcium,” *Infofish Marketing Digest* 3, 29-30.
- Shahidi, F. (1995). “Role of chemistry and biotechnology in value-added utilization of shellfish processing discards,” *Can. Chem. Neur.* 10, 25-29.
- Shey, J., Imam, S. H., Glenn, G. M., and Orts, W. J. (2006). “Properties of backed starch foam with natural rubber latex,” *Ind. Crops. Prod.* 24, 34-40.
- Shogren, R. L., Lawton, J. W., Doane, W. M., and Tiefenbacher, K. F. (1998a). “Structure and morphology of baked starch foams,” *Polym.* 39, 6649-6655.
- Shogren, R. L., Lawton, J. W., Tiefenbacher, K. F., and Chen, L. (1998b). “Starch-poly (vinyl alcohol) foamed articles prepared by a baking process,” *J. Appl. Polym. Sci.* 68, 2129-2140.
- Shogren, R. L., Lawton, J. W., and Tiefenbacher, K. F. (2002). “Baked starch foams: Starch modifications and additives improve process parameters, structure and properties,” *Ind. Crop. Prod.* 16, 69-79.
- Stevens, B. G., and Haaga, J. A. (1993). “Ocean dumping of sea-food processing wastes: Comparison of epibenthic macrofauna sampled by submersible in impacted and non-impacted Alaskan bays, and estimation of decomposition rate,” *National Marine Fishery Service Report*, Washington, DC.
- Ward, P., and Myers, R. A. (2005). “Shifts in open-ocean fish communities coinciding with the commencement of commercial fishing,” *Ecology* 86, 835-847.
- Willett, J. L., and Shogren, R. L. (2002). “Processing and properties of extruded starch/polymer foams,” *Polym.* 43, 5935-5947.
- Williams, K., Williams J., and Blanchard, A. (1999). “Pollution concerns of fish waste in Orca Inlet, Prince William Sound, Alaska,” Final technical/Performance report USEPA Assistance Agreement No. CP-980335-01-0. Native village of Eyak, Cordova, AK.

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