

CHAPTER II

LITERATURE REVIEW

The use of polymeric foam continues to grow rapidly throughout the world. Some of the reasons for this are the light, excellent strength to weight ratio, superior insulating abilities, energy absorbing performance, and comfort features of the foam (Cunningham *et al.*, 1998). However, foam articles made from non-degradable petroleum based that cannot be composted in the landfill give rise of environmental problem. Starch is one interesting alternative material for making foam because it is biodegradable, inexpensive and has a thermoplastic behavior for the performance of the classical technical processes such as extrusion, injection-molding, and thermal molding (Stenhouse *et al.*, 1997).

Expanded starch-based foams have been prepared since the 1970s by extrusion of grains or starch with water. High temperature and shear within extruder barrel cause the starch-water mixture to melt into a plastic-like consistency. Water serves as the blowing agent as it expands upon exiting the extruder. For example, expanded snack foods and cereals are prepared in this manner (Lacourse and Altieri, 1989; Glenn and Irving, 1995). Starch foams made by these methods have useful mechanical and thermal properties, but are difficult to form into containers such as clamshells (Glenn *et al.*, 2000) because the heat required to soften the foam and mold it into the desired shape will cause the starch to lose moisture and raise its glass transition temperature to levels above the decomposition temperature (~200°C) (Shogren *et al.*, 1997).

In 2000s, a compression/explosion molding process has been described for making molded foam products from starch (Glenn and Orts, 2000). However, the process is limited only to simple shapes and relatively thick (>1 cm) products.

Tiefenbacher (1993) and Haas *et al.*, (1996) demonstrated a baking process for making molded starch products as thin as 1.5 mm. The process is similar to the baking process used to make waffles and wafer cookies and involves placing a predetermined amount of a starch/water-based dough into a preheated (120–200°C) mold cavity. As the dough is heated, the starch component gelatinizes and the water component turns into steam that serves as the foaming agent.

The foaming process of a starch batter inside a hot mold can be divided into several steps. First, the temperature of the batter increases to the point at which the temperature is equal or above the gelatinization temperature of the starch. Upon gelatinization, the viscosity of the starch increases dramatically. This causes starch to turn from easy flowing slurry into a thick paste. The high temperature of the batter mixture leads to a rapid evaporation of the entrapped water to evaporate, which, in turn, causes the paste to expand dramatically. The starch paste must have sufficient strength in order to withstand the force of the rapid expansion without a permanent, structural damage. Once the starch paste fills up the mold (as a result of the rapid expansion), the viscosity of the starch paste further increase expeditiously to stabilize the foam structure and to prevent the molding to collapse as residual water further evaporates. The evaporated water vents out around the edge of the mold. In the final and longest step of the baking process, the starch foam gradually dries to obtain the foam having the residual moisture content of ca. 2–4% (Shogren, Lawton, Doane, & Tiefenbacher, 1998c).

In summary, the foams have a dense outer skin and a less dense interior with large, mostly open cell. Overall foam density and strength increase with increasing starch concentration, molecular weight and amylase content. Foam flexibility tends to increase with decreasing density. Thus, changing the batter formulation can control the density and mechanical properties of the foams. Compared to expanded polystyrene foam, starch foams have higher densities and lower strengths, especially at extremes of low and high humidities. The properties of the baked starch foams vary with the moisture content, starch type and additives used in the dough formulation (Andersen and Hodson, 1996; Shogren et al., 1998; Lawton *et al.*, 1999). Baked starch foam containers have many of the mechanical and aesthetic properties needed to function well in commercial applications but lack moisture resistance and flexibility (Glenn et al., 2001).

Flexibility and strength of baked starch foams are improved by incorporating a fiber in the dough formulation:

In 1999, Andersen and co-workers prepared highly inorganically filled starch based fiber reinforced foam composites for food packaging. Starch, obtained from potato, corn, or other sources, is used as binder to form net shape foam composite

substrates under hydrothermal conditions. The starch content is 25 to 60 wt.% of the product. Ground calcium carbonate is the principal inorganic material, being 25 to 60 wt.% of the product. The composite substrate is foamed by steam at temperatures between 160 and 220°C in a single 15 to 200 seconds step within heated moulds. The organic-inorganic composite is reinforced with 5 to 20 wt % wood or plant fiber. The substrate is rendered functional with food and beverages by thin overlay coatings that provide moisture barrier properties and additional mechanical flexibility. The final result provides a new class of materials that is low in cost, low in environmental impact, is biodegradable and compostable, and meets commercial performance criteria.

Lawton *et al.*, [2003] was added aspen fiber into baked cornstarch foams to improve its mechanical properties. Foam trays were made with fiber content of the batter ranging from 2.5 to 45%. The starch–fiber composite foam trays were formed by heating a starch-based batter inside a closed mold. The strength of the foam trays increased as fiber content of the trays increased, until fiber content reached about 15%. Trays containing between 15 and 30% fibers had no significant difference in tray strength. Trays containing more than 30% fiber had lower tray strength. The lower tray strength was thought to be due to the lack of uniform fiber distribution at high fiber content. Displacement of the trays at break was also affected by fiber content. The effect of fiber on displacement at break was greatest at extreme relative humidity. At low humidity (5%), displacement at break went from 2.2 to 5.4mm as fiber content increased from 2.5 to 40%. Displacement at break increased from 9 to 20mm as the fiber content increased from 2.5 to 40% for trays stored at 93% relative humidity. Fiber content did not effect displacement at break for trays stored at moderate relative humilities. Fiber content of 15% was adequate to increase the tray strength. Greater amounts of fiber (up to 30%) can be added without detrimental affects to strength, but increasing fiber above 15% increased baking time and increased the amount of batter needed to make a complete tray.

Soykeabkaew *et al.*, [2004] prepared starch-based composite foams (SCFs) by baking starch-based batters incorporating either jute or flax fibers inside a hot mold. Addition of jute or flax fibers to the starch-based foams resulted in the much improvement in the flexural strength and the flexural modulus of elasticity, at the

expense of the flexural strain at maximum force both the flexural strength and the flexural modulus of elasticity were found to increase with increasing aspect ratio of the fibers. The improvement in the mechanical properties of SCFs was attributable to the strong interaction between fibers and the starch matrix. Between jute- and flax-reinforced SCFs, jute fibers had a greater reinforcing effect than flax fibers did. The optimal moisture content which resulted in the maximum values of the flexural strength and the flexural strain at maximum force for both jute and flax-reinforced SCFs was observed between 8 and 10%, depending on the batter formulations.

Moisture resistance can be improved in baked starch products by adding a moisture resistant polymer:

Shogren *et al.*, [1998] studied potato and corn starch-poly(vinyl alcohol)(PVA) foamed articles prepared by a baking process. Foam strength, flexibility and water resistance were markedly improved by addition of 10-30%PVA to starch batters. The improvement in strength at low humidity was greater for partially (88%) hydrolyzed PVA. Foam flexibility increased with higher PVA molecular weight. Baked foams prepared from potato and corn starch-PVA have mechanical properties that are adequate for use as packing containers over a wide range of relative humidity.

Kim *et al.*, [2000] prepared starch/polycaprolactone /polyethylene glycol(PEG) blends. The gelatinization of starch resulted in good dispersion of starch in the PCL matrix and a higher modulus and strength of the blend. From the change of toughness of the blends with the PEG molecular weight, it was found that the blend containing PEG of molecular weight 3400 shows the highest tensile toughness.

Preechawong *et al.*, [2004] prepared starch/poly(L-lactic acid) (PLA) hybrid foams were prepared by baking a mixture of starch, PLA, and other ingredients in a hot mold. Addition of PLA helped improve the ultimate tensile strength and the percentage of elongation at break of the hybrid foams. Resistance to water absorption of the starch/PLA hybrid foams was superior to that of pure starch foams. Lastly, enzymatic degradation tests in an α -amylase solution showed that addition of PLA improved the resistance to enzymatic degradability of the hybrid foams.

Moisture resistance can also be improved by a post-processing step wherein a protective coating is applied to the containers following the baking process (Earth-Shell, 1998). The disadvantage of using post-processing steps in container production is that it increases the equipment needs and part handling and tends to reduce overall production rates.

Glenn *et al.*, [2000] described an in situ method of baking and laminating the starch-based foams in a single step. The procedure involves a dough formulation consisting of starch, fiber and magnesium stearate that is placed in a mold-heated to 160°C between two sheets of laminate. Sheets of laminate material tested included foil, tissue paper, weighing paper, polyvinyl alcohol film and polyvinyl chloride film. The laminated foams generally had a higher density, tensile strength, elongation to break and flexural strength than the non-laminated sample. All of the laminate materials decreased the water vapor permeance. Foam samples laminated with foil, polyvinyl alcohol (PVOH, processed at 130°C) or polyvinyl chloride sheets had the lowest permeance values and had mechanical properties in the same range as those of commercial containers made of EPS or coated paperboard.

A shortcoming of these starch foams is their lack of flexibility as well as moisture susceptibility (Glenn *et al.*, 2001b). To overcome these problems, the use of natural rubber latex in the batter formulation were interested. The solids in natural rubber latex are comprised mainly of *cis*-1,4-polyisoprene (Subramaniam, 1990). When this latex cures or dries, an elastic and hydrophobic material is produced. However, before the latex is cured, it is in an aqueous emulsion, which allows the rubber to be evenly distributed throughout the batter in the production of baked starch foams.

Carvalho *et al.*, [2002] prepared thermoplastic starch/natural rubber polymer blends by using directly natural latex and cornstarch. The blends were prepared in an intensive batch mixer at 150 °C, with natural rubber content varying from 2.5 to 20%. The results revealed a reduction in the modulus and in tensile strength, becoming the blends less brittle than thermoplastic starch alone. Phase separation was observed in some compositions and was dependent on rubber and on plasticizer content (glycerol). Increasing plasticizer content made possible the addition of higher amounts of rubber. The addition of rubber was, however, limited by phase separation

the appearance of which depended on the glycerol content. Scanning electron microscopy showed a good dispersion of the natural rubber in the continuous phase of thermoplastic starch matrix.

Shey *et al.*, [2006] incorporated natural rubber latex into baked starch foams based on wheat, potato, and waxy corn starches. While latex increases the density of the foam, it also improves the flexibility of the product. Stabilization of the latex with non-ionic additives helped prevent irregularities in the foam product. The flexural properties of these foams are comparable with commercial products and can be 'tuned' by varying the starch type and adjusting the latex concentration. Latex also decreases the equilibrium moisture content and decreases the effect of higher humidity on the foam products.