

CHAPTER II LITERATURE SURVEY



2.1 Starch Foams

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 composed in the landfill give raise 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 temperatures and shear within the 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. It is, however, difficult to prepare shaped objects such as a plate from starch foam because the heat required softens the foam and mould it into the desired shape will cause the starch to lose moisture and raise its glass temperature to levels above the decomposition temperature (Shogren *et al.*, 1998c).

Shogren *et al.* (1998c) prepared starch foams by baking a starch-water batter in a hot mould. A starch-formed article is fashioned as starch gelatinizes, expands, and dries. This involves mixing starch, guar (1% based on starch weight) and magnesium stearate (2% based on starch weight) in the dry state. Guar was added to increase batter viscosity and therefore prevent starch from settling during preparation. Magnesium stearate was added to facilitate release of baked starch foams from the mould surface. Distilled water was then added to give a batter with the desired solids content. Then starch foam trays were prepared using a lab model-baking machine at mould temperature of 175-235 °C.

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 amylose 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. Containers made from starch foams will be inherently sensitive to water since starch is a very hydrophilic polymer. For applications, such as drink cups, a water-resistant coating would be necessary.

In order to improve the strength, flexibility, and water resistance of starch foam, composite foam plates were prepared by baking a mixture of granular starch and aqueous poly(vinyl alcohol) (PVOH) solution inside a hot mould (Shogren *et al.*, 1998b). The improvement in strength at low humidity was greater for partially (88%) hydrolyzed PVOH while strength at higher humidities improved most with fully (98%) hydrolyzed PVOH. Foam flexibility increased with higher PVOH molecular weight. Scanning electron micrographs of the surface of the foams revealed a phase-separated morphology in which swollen starch granules were embedded in a matrix of PVOH. In summary, the desired strength, flexibility, or stiffness can be tailored by formulating with different PVOH level, PVOH type, starch type, batter solids level, and crosslinking agent. Water resistance can be increased by addition of crosslinking agents or by applying an outer coating of a hydrophobic, biodegradable polymer.

Respirometry studies in soil showed that the starch component of starch-PVOH foams biodegraded relatively rapidly (weeks) while the PVOH component degraded more slowly (months). Baked foams prepared from starch and PVOH have mechanical properties that are adequate for use as packaging containers over a wide range of humidity.

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.

Glenn *et al.* (2001b) baked foams made of starch or starch composites containing fiber and/or CaCO_3 to study their functional properties. Baked foams made of formulations containing only starch had a lower flexural strain to break and tensile elongation to break than expanded polystyrene and coated paperboard. The flexural strain to break was increased by lowering the starch concentration in the formulations, using potato starch versus wheat, corn or tapioca starch and by increasing the moisture content. Nevertheless, the flexural strain to break and the tensile elongation to break values remained lower than in the expanded polystyrene and coated paperboard. Foam density decreased and the flexural strain to break markedly increased by including softwood fiber in the dough formulations. Formulations with a starch/fiber ratio of approximately 5:1 or less made baked foams with the flexural strain to break greater than 5% and the tensile elongation to break nearly double those of foams containing only starch. The addition of CaCO_3 to starch/fiber foam composites did not improve foam properties. The CaCO_3 increased density and decrease the flexural strain to break and the tensile elongation to break compared to foam made of starch and fiber. However, starch/fiber foams have good flexibility, degradability and with the appropriate coating material should function adequately in single-use food containers.

In 2002, Shogren and co-workers used various modified starches and additives in baked foam plates formulations to improve strength and water resistance properties in lieu of coating. Foam plates made from chemically modified starches had shorter baking times, lighter weights and higher elongation at break than unmodified starch. Plates made from genetically modified (waxy) starches and poly (vinyl alcohol) had elongation to break at low humidities, which were much higher

than those made from normal starches and poly(vinyl alcohol). Addition of softwood fibers increased starch foam plate strengths at low and high humidities. Addition of monostearyl citrate to starch batter formulations gave the best improvement in water resistance among the compounds tested. Baked foams made from potato amylopectin, poly(vinyl alcohol), aspen fiber, and monostearyl citrate appeared to have adequate flexibility and water resistance to function as clamshell-type hot sandwich containers.

2.2 Natural Fiber Composites

The interest in using different plant and wood fibers as reinforcement in plastics has increased dramatically during the last few years. Environmental concern is one driving force. However, the use of cellulose fibers has not been widely spread because of the poor compatibility between the fibers and the thermoplastic matrix. These factors lead to less satisfactory mechanical properties (Albano *et al.*, 2001; Oksman *et al.*, 2002).

Lee *et al.* (2001) successfully formed natural fiber reinforced polypropylene sheets from a practical method of blending to form a mat and then consolidated into a sheet by hot pressing. The natural fibers assessed were *Pinus radiata* and *Eucalyptus regnan* pulps and sisal (*Agave sisalana*) fibers. The tensile and flexural strengths were shown to decrease with an increase in fiber content, while the tensile and flexural modulus were shown to increase. The tensile and flexural strengths and modulus were positively influenced by fiber length. The water performance tests of the sheets generally showed approximately 3% thickness swell at 30% fiber content. The natural fiber surface chemical composition was determined by X-ray photoelectron spectroscopy and shown to be primarily covered with partially hydrophobic material such as lignin and extractives, which helped in the compatibility with polypropylene.

An important technique to improve the compatibility is surface modification of fibers to make it more hydrophobic, which improve its compatibility with non-polar thermoplastics (Karnani *et al.*, 1997). In 2001, Albano and co-workers were prepared composites from waste wood flour, sisal fiber and polypropylene (PP). The

surface of the filler was modified to enhance the chemical affinity between hydrophilic cellulose and hydrophobic polymer. The treatments studied were: a) The addition of a coupling agent; b) chemical treatment with NaOH; and c) the addition of functionalized polypropylene (Polybond 3150 and 3200). After treatment, mixtures of PP with 40% and 20% of the filler, wood flour and sisal fiber respectively, were extruded and injection molded. In the case of wood flour, a mixture of two particle sizes (mesh 20 and 40, 50% each) was used, and in the case of sisal, 10 mm long fibers were selected. Results showed that, the tensile strength of wood flour and sisal fiber reinforced polypropylene composites is strongly dependent on the degree of adhesion between filler and matrix. However, the results also show that both tensile strength and modulus increased, irrespective of the treatment to which the filler was submitted, whereas elongation at break decreased for the treated cellulosic filled composites in comparison to the original ones (PP and untreated filler). They concluded that the improvement of some mechanical properties is result of the decrease in the hydrophilicity of the fillers due to the treatments applied. Based on these studies on the tensile and impact properties, treated sisal has a greater reinforcing effect on treated wood flour, which implies better adhesion and/or dispersion of sisal fiber due to the treatment.

From the main bottlenecks, poor compatibility between the natural fiber and the matrix, a natural fiber would be a much better choice as reinforcement for starch, which also has inherent polar and hydrophilic nature (Dufresne *et al.*, 1999). To preserve renewable raw materials, biodegradability and to improve the mechanical resistance of the final products, associations between cellulose fibers and thermoplastic starch have been tested (Averous *et al.*, 2001). Plasticized starch composites are produced by introduction of leaf wood cellulose fibers into a matrix obtained from water/glycerol plasticization of wheat starch. From the dynamic thermo-mechanical analyzer (DMTA), the main transition temperature about 30 °C increase by the introduction of fibers which could be related to fiber-matrix interactions and a decrease of starch chain mobility. These interactions have influence on the mechanical behavior. They showed that the strength and modulus ratio of composite to matrix and the dimension stability increases dramatically with

fiber length and fiber content while elongation at break ratio decrease especially with fiber content effect.

Clemons *et al.* (1999) investigated the microstructure of injection-molded polypropylene reinforced with cellulose fiber. Scanning electron microscopy of the fracture surfaces and X-ray diffraction were used to investigate fiber orientation. The results showed that at low fiber contents, there was little fiber orientation and at high fiber contents, a layered structure arose. Furthermore, dynamic fracture toughness, which accompanied in both strength and modulus, increased with increasing cellulose content and orientation of fibers perpendicular to the crack direction.