

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Starch

The use of renewable resources in packaging allows non-degradable, petroleum based plastics to be substituted by environmentally friendly, biodegradable materials. In order to process starch into shaped foam articles, the method of thermopressing solidification in modified wafer baking equipment can be applied.

Shogren *et al.* (1998) prepared baked starch foams by baking process. In this process, a thin-walled object such as a plate is formed by heating a starch batter inside a closed mold. First, the starch paste must have sufficient elastic strength so that expanding steam bubbles are trapped in the paste rather than breaking with the consequent collapse of the foam. Secondly, the viscosity of the starch paste must increase rapidly after expansion to stabilize the foam structure and prevent collapse as water evaporates. In summary, foam containers of various shapes such as plates, cups, clamshells or package cushioning can be prepared by baking a starch batter inside a hot mould. These foams have a dense outer layer and a less dense core containing mostly open cells. Although starch crystallinity is mostly destroyed during baking, some swollen granules remain bound within a starch matrix. The density and mechanical properties of the foams can be controlled by changing the batter formulation. Batters which gelatinize rapidly (at low temperatures) such as those containing a starch with low amylose content, a low starch solids content or lower molecular weight, tend to give less dense foams with lower compression strength and higher flexibility. Compared to expanded polystyrene foam, starch foams have higher densities and lower strength, 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 some applications, such as plates or containers for dry foods, this is not a concern. For other applications, such as drink cups, a water resistant would be necessary.

The way to improve strength, flexibility, and water resistance of starch foams are addition synthetic biodegradable polymers to prepare composite foams and addition plasticizers.

## **2.2 Synthetic Biodegradable Polymers**

### **2.2.1 Poly(vinyl alcohol) (PVA)**

Poly(vinyl alcohol) (PVA) is a biodegradable synthetic polymer, which has excellent strength and flexibility. The tensile strength and elongation of PVA are approximately 80 MPa and several hundred percent, respectively, at 50% humidity. PVA can be dissolved in hot water and, hence, is used in applications such as textile sizing, paper coatings, and water-soluble film.

Young (1967) found that films cast from aqueous solutions of amylose or high amylose starch and PVA had higher strength and elongation to break at 23 and 50% humidity than films cast from starch alone.

Otey and Mark (1976) found improvement in mechanical properties for films cast from solution mixtures of normal (27% amylose) cornstarch and PVA and also incorporated formaldehyde as a cross-linking agent.

LaCourse and Altieri (1989) described the extrusion of modified high amylose starches, water, and up to 10% PVA into expanded foam.

Bastioli *et al.* (1990) described the extrusion of starch, PVA, and water into a homogeneous melt, followed by molding. Some improvement in dimensional stability at high humidities was claimed.

Shogren *et al.* (1998) studied potato and corn starch-poly(vinyl alcohol) 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 while strength at higher humidities improved most with fully (98%) 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 packaging containers over a wide range of humidity.

Liu *et al.* (1999) studied thermoplastic wheat starch/PVA compounds: preparation, processing, and properties. This study reported that a mixture of glycerine and water (50/50 wt%) is found to be the best one for the compounds in terms of rheological behavior, mechanical properties, and environmental stability. Incorporation of PVA into starch can enhance the mechanical properties, although the melt viscosity is increased as well.

Ishigaki *et al.* (1999) studied biodegradation of a poly(vinyl alcohol)-starch blend plastic film. A part of the starch fraction of this plastic was dissolved into an aqueous phase in a control test. Treatment with a PVA-degrading bacterium or enzyme gave a maximal weight loss of approximately 70% and film breakage occurred.

Tudorachi *et al.* (2000) studied testing of poly(vinyl alcohol) and starch mixtures as biodegradable polymeric materials. The weight loss after 18 days of inoculation with microorganisms is between 38 and 73% by weight and is influenced by the composition of the blend as well as by the nature of the microorganism used, During biodegradation, plasticizers (glycerine and urea) and starch are consumed together with some amorphous structures from poly(vinyl alcohol).

### 2.2.2 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is of considerable interest as biodegradable polymers in medical applications and also potentially for use as environmentally friendly packaging materials.

Sinclair (1996) studied the case for poly(lactic acid) as a commodity packaging plastic. Its general physical properties and melt processing ease are similar to conventional packing resins. PLA slowly degrades by hydrolysis in even a slightly moist environment over a period of several months to a year to environmentally-friendly products, which, in turn, biodegrade to carbon dioxide, methane, and water. When plasticized with its own monomers, PLA becomes increasingly flexible so that a continuous series of products can be prepared that can mimic PVA, LDPE, LLDPE, PP, and PS. Orientation also substantially improves tensile strength, modulus, and heat stability.

Wang and Shogren (1997) extruded regular corn starch blended with biodegradable polymers to make loose-fill foams and reported that addition of 10-15% PLA gave foams the lowest density and the highest resilience.

Yoon *et al.* (1998) blended PLA with poly(ethylene-vinyl acetate) (EVA) and found that the tensile strength and modulus of PLA-EVA85, that contained 85wt% of vinyl acetate, blended were dropped rapidly, followed by a more gradual decrease with the increase in the EVA content. Strain-at-break, however, was increased rather slowly up to 70wt% of EVA and then increasing quite rapidly around 90%wt of EVA85.

Fang and Hanna (2000) studied functional properties of poly(lactic acid) (PLA) starch-based loose-fill packaging foams. In this study, attempts were made to improve the characteristics of starch-based plastic foams by blending starch with PLA, a biodegradable polymer made from renewable sources. The addition of the PLA polymer to regular (25% amylose) and waxy corn starches significantly improved the physical and

mechanical properties of the extruded foams. Foams made from waxy starch had better radial expansions, higher WSI, higher compressibilities, and lower spring indices than those of regular starch foams. The formulation containing waxy starch, 40%PLA, and 19% moisture produced a loose fill foam with the best physical characteristics and mechanical properties.

### 2.2.3 Polycaprolactone (PCL)

Koenig and Huang (1995) blended polycaprolactone with starch derivatives. The properties of films of these blends were evaluated using differential scanning calorimetry, dynamic mechanical thermal analysis and Instron tensile testing. Blending granular starch or starch acetate with PCL increases the modulus and decrease the overall strength compared to the polymer before blending.

Vikman *et al.* (1999) studied morphology and enzymatic degradation of thermoplastic starch-polycaprolactone sheets. The thin layer of polycaprolactone formed on the surface of the thermoplastic starch-polycaprolactone blends during compression molding strongly reduced the rate of enzymatic hydrolysis.

Avella *et al.* (2000) studied preparation and characterization of compatibilised polycaprolactone/starch composites sheet and reported that the PCL, is a ductile polymer, able to undergo large deformations; unfortunately it possesses a relatively low modulus rendering it unable to be used for any applications where a high rigidity is required. Thus, the presence of starch phase in the mechanical blends can contribute to improve its modulus.

Kim *et al.* (2000) prepared starch/PCL/polyethylene glycol blends. The gelatinization of starch resulted in good dispersion of the starch in the PCL matrix and a higher modulus and strength of the blend. From the change of the 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.

Averous *et al* (2000) studied properties of thermoplastic blends sheet: starch-polycaprolactone. The thermal, thermo-mechanical and mechanical characteristics of the blend clearly indicate a phase separation in the blend, as is generally found for non-miscible polymers and found that the same behavior from mechanical characteristics. In most of the blends tested, it is possible to find the thermal transition of each component with only a minor shift of the characteristic temperatures. They have observed a significant improvement of the properties of thermoplastic starch based blend due to the presence of PCL. When the starch matrix has a glassy behavior, blending with PCL results in a decrease of the material modulus but the impact resistance is improved. On the other hand, when the starch has a rubbery behavior, PCL increase the modulus of the materials.

### 2.3 Plasticizers

Polymer-chemistry aspects, indispensable for the knowledge of, and hence the development of thermoplastic starches for industrial applications, have to be incorporated in the processing of these materials. From a polymer-chemistry perspective, several known concepts have shown to be applicable to starch. The effects of the amount of water and other plasticizers on the mechanical properties of thermoplastic starches have been determined by several researches.

Stein *et al.* (1997) studied amino acids as plasticizers of starch-based films. Plasticizers typically reflect the polarity of the polymers with which they are blended. Hydrophobic plasticizers are used extensively with petroleum-based polymers. In contrast, plasticizers used in starch-based plastics must be more polar allow better compatibility with the hydrophilic polysaccharide polymer. Common plasticizers for starch-based plastics including water, glycerol, sorbitol, sucrose, urea, polyethylene glycol and poly (vinyl alcohol). In addition, this paper found that urea was the best way to

increase the percent elongation at low and high humidity. Blending the starch with ammonium chloride produced a flexible ribbon at the lowest concentration.

Van Soest and Knooren (1997) studied effect of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. During aging the materials became less flexible with higher elastic modulus and tensile stress. The changes are related to changes in water content and glass transition temperature. The changes in stress-strain properties are explained by formation of helical structures and crystals, which results in a reinforcement of the starch network by physical crosslinking.

Lourdin *et al.* (1997) investigated the effect of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. In general, the starch-plasticizer-water systems studied in this work were more sensitive to ambient humidity when plasticizer content was high, owing to the creation of hydrogen bonds between the plasticizer and water.

Stephan *et al.* (1998) studied the role of water during plasticization of native starches. Varying the water content in the premixes led to large changes in strain and stress at break. This effect could be explained by a dependence of the polysaccharide mobility on the water content in the premix. The mechanical properties above  $T_g$  of compression molded corn, potato, waxy corn, and wheat starch were highly dependent on both water content during compression molding and starch type. Waxy corn starch gave the best strain at break while potato starch gave the best stress at break.

Jiugao *et al.* (1998) studied the properties of starch/glycerine blend. Glycerine is proved to be an excellent plasticizer for starch and can obviously improve the processing ability of starch.