



## CHAPTER I INTRODUCTION

The use of polymeric foam continues to grow rapidly throughout the world. Some of the reasons for this are the light weight, excellent strength/weight ratio, superior insulating abilities, energy absorbing performance, and comfort features of the foams (Cunningham *et al.*, 1998). However, foam articles made from petroleum-derived plastics which can not be composted in the landfill give raise of environmental problem. The development of biodegradable thermoplastic starch is considered important for reducing the total amount of plastic waste (Stenhouse *et al.*, 1997a).

Starch consists of a mixture of about 25% amylose, a nearly linear polymer of  $\alpha$ -1,4 anhydroglucose units, and 75% amylopectin, a highly branched polymer consisting of short  $\alpha$ -1,4 chains linked by  $\alpha$ -1,6 bonds. In the native state, starch exists as 5-60  $\mu$ m diameter granules with amylopectin providing a crystalline framework (Shogren *et al.*, 1998a). Starch is widely available and is less expensive than polyethylene and polystyrene. Starch is a particularly interesting candidate of non-degradable petroleum-based plastics because it is biodegradable, inexpensive and has a thermoplastic behavior for the performance of classical technical processes (extrusion, injection-molding, thermal molding) (Stenhouse *et al.*, 1997a).

Expanded starch-based foams have been prepared since the 1970s by extrusion of starch with water. Water serves as a 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 transition temperature to levels above the decomposition temperature (Shogren *et al.*, 1998a).

Tiefenbacher (1993) described a process for preparing shaped foam articles from starch by baking process. This involved baking a starch-water batter in a hot mould. A starch-formed article is fashioned as starch gelatinizes, expands, and dries.

However, foam packaging materials made from pure starch usually do not have satisfactory physical and mechanical properties and they are highly water-soluble. To improve the physical and mechanical properties and the resistance to water of the starch-based foams, Bhatnagar and Hanna (1995) extruded 25% amylose corn starch with polystyrene and polymethyl methacrylate at a ratio of 70:30. Water solubility indices (WSI) were reduced to 4-13% compared with 97% for the pure commercial starch loose-fill foam material. However, the use of polystyrene lowered the biodegradability of the foam as well.

One attractive strategy in order to improve strength, flexibility, water resistance, and biodegradability of baked starch foams is to prepare composite foams made from starch and other synthetic biodegradable polymers, such as poly(vinyl alcohol), poly(caprolactone), and poly(lactic acid). These synthetic polymers have good mechanical properties and are commercially available biodegradable polymers.

Poly(vinyl alcohol) (PVA) is a biodegradable synthetic polymer, which has excellent strength and flexibility. It has been reported that addition of PVA improves the strength and flexibility of gelatinized starch (Shogren *et al.*, 1998). Young (1967) found that films cast from aqueous solutions of amylose or high amylose starch and PVA had higher strength and elongation at break at 23 and 50% humidity than films cast from starch alone. Otey and Mark (1976) found similar improvement in mechanical properties for films cast from solution mixtures of normal cornstarch and PVA. Shogren *et al.* (1998b) prepared starch-PVA foam articles by a baking process and found that

foam strength, flexibility, and water resistance were markedly improved by addition of 10-30% poly(vinyl alcohol) to starch batters.

Poly lactide, sometimes called polylactic acid (PLA), is a thermoplastic, high strength, high modulus polymer which can be made from renewable resources to yield articles for use in either the industrial packaging or the biocompatible/bioabsorbable medical device market (Kaplan, 1998). Yoon *et al.* (1998) blended PLA with poly(ethylene-co-vinyl acetate) and found that stress at break increased and strain at break decreased with increasing the amount of PLA. Wang and Shogren (1997) extruded regular corn starch blended with biodegradable polymers to make loose-fill foams and found that addition of 10-15% PLA gave foams the lowest density and the highest resilience. Fang and Hanna (2000) improved the characteristics of starch-based plastic foams by blending starch with PLA and reported that the formulation containing waxy starch, 40% PLA, and 19% moisture produced a loose fill foam with the best physical characteristics and mechanical properties.

Polycaprolactone (PCL) is an environmentally friendly, biodegradable polymer which is generally prepared from the ring-opening polymerization of  $\epsilon$ -caprolactone. The blend of starch and aliphatic polyester, especially PCL, have been considered as completely biodegradable plastics (Tokiwa and Iwamoto, 1990; Koenig and Huang, 1992; Bastioli and Cerutti, 1995). PCL was chosen because of its good mechanical properties such as tensile strength and elongation and also its good compatibility with many types of polymers. Averous *et al.* (2000) studied the properties of starch/polycaprolactone blends and found that blending starch with polycaprolactone is an interesting way to overcome the most important weaknesses of thermoplastic starch: low resilience, high moisture sensitivity and high shrinkage, even at low PCL concentration, e.g. 10 wt %. Change-Hyeon *et al.* (1999) investigated the blend of a gelatinized starch and polycaprolactone (PCL) and found that

the gelatinization of starch resulted in good dispersion of the starch in the PCL matrix and a higher modulus and strength of the blend.

This study was conducted to develop tapioca starch-based composite foam by blending starch with synthetic biodegradable polymers such as poly(vinyl alcohol), polylactic acid, and polycaprolactone in order to compare their mechanical properties and morphology. The effects of humidity and storage time on its mechanical properties of the composite foams were investigated. In addition, the effect of plasticizers such as glycerol, ammonium chloride, and urea on the mechanical properties of starch-based composite foam was also studied.

## **Theoretical Background**

### **1.1 Foamed Plastics**

Foamed plastics, also known as cellular plastics or plastic foams, have been important since primitive man began to use wood, a cellular form of the polymer cellulose. Cellulose is the most abundant of all naturally occurring organic compounds, comprising approximately one-third of all vegetable matter in the world (Ott *et al.*, 1954). Its name is derived from the Latin word *cellula*, meaning very small cell or room, and most of the polymer does indeed exist in cellular form as in wood, straws, seed husks, etc.

A cellular plastic is defined as a plastic the apparent density of which is decreased substantially by the presence of numerous cells disposed throughout its mass (ASTM D 883-80C, 1982). The gas phase in a cellular polymer is usually distributed in voids or pockets called cells. If these cells are interconnected, the material is termed open-celled. If the cells are discrete and the gas phase of each is independent of that of the other cells, the material is termed closed-cell.

Foaming processes (Ronald and David, 1986) are characterized by techniques that cause tiny bubbles to form within the plastic material such that when the plastic solidifies the bubbles, or at least the holes created by the bubbles, remain, the solidified bubble-containing material thought of as a cellular structure. The products made by these processes are referred to as foams or cellular plastics.

Plastic foams can also be classified on the basis of wall stiffness, if the walls are stiff, the foam is called a rigid foam. If the walls collapse when pressed, the foam is called a flexible foam. Both open and closed cell foams can have either flexible walls or rigid walls.

Plastic foams have some physical characteristics that are valuable for several important applications. The cellular structure means that much of the space in the plastic foam is filled with air or some other gas. The low thermal conductivity of gases means that these foams are very good thermal insulators. Some applications that utilize this insulating property are hot and cold cups, building insulation slabs, and pipe insulation.

The advantages and disadvantages of foams are outlined in Table 1.1

**Table 1.1** Advantages and disadvantages of foamed versus non-foamed plastics.

Advantages	Disadvantages
Light weight Low thermal conductivity High support per unit weight Low cost molds Many methods available to create forms	Slowness of most processed Evolution of gases in some processes Variable density with some parts Loss of some mechanical properties

## 1.2 Biodegradable Polymers

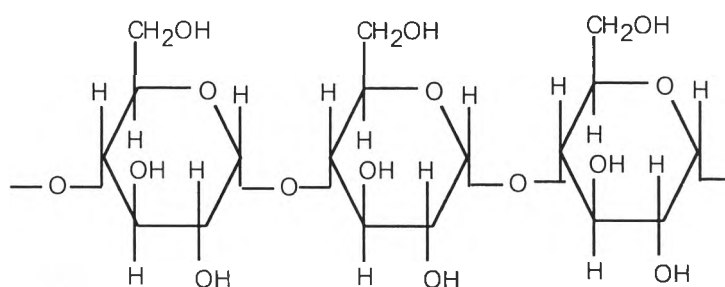
Traditional applications of synthetic polymers are mostly based on their relative inertness to biodegradation compared with natural macromolecules such as cellulose and proteins. Concerns about preventing or retarding attack on polymers by bacteria, fungi, insects, rodents, and other animals provided the early incentive for the study of the biodegradation of polymers. Now the use of synthetic polymers has accelerated to the extent that the disposal of the polymer products currently in use, most of them bioresistant, has become increasingly difficult. One of the important current incentives for the study of biodegradable polymers is their easier disposal. Moreover, biodegradable polymers are useful for applications such as sutures, surgical implants, controlled-release formulations of drugs and agricultural chemicals, agricultural mulch, etc, and interest in them continues to increase.

### 1.2.1 Starch

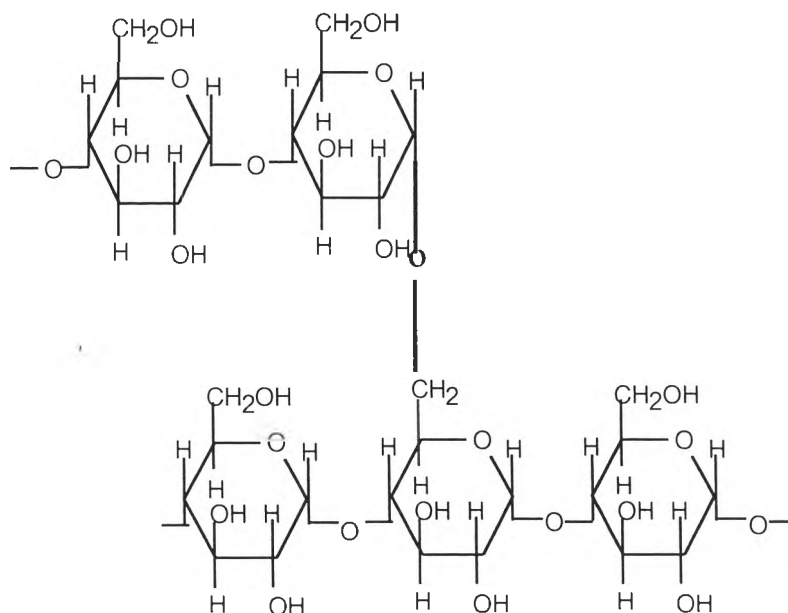
Starch is one of the major components of cereal grains. Commercially important starches come from corn, waxy corn, high amylose corn, wheat, rice, potato, tapioca, and pea. The major sources of commercial starch here in Thailand are tapioca and rice. The starches are readily obtained from these plant source as a fine powder (granular starch) consisting of spherical or ellipsoidal grains ranging in particle size from 3 to 100 $\mu$ m. Among these, rice starch (3-9 $\mu$ m) has among the smallest granule size and potato starch (15-100 $\mu$ m) the largest of all starch types.( Kirk and Othmer, 1997)

Starch (David, 1998) is predominantly composed of two polymers of D-glucose, amylose and amylopectin. Amylose is a lightly branched polymer comprised of  $\alpha$ -1,4 linked anhydroglucose units and has molecular weights which vary from  $10^5$  to  $10^6$ . Amylose from different sources contains, on average, two to eight  $\alpha$ -1,6 branch points per molecule. Amylopectin is a

highly branched molecule consisting of short (15-45 residues)  $\alpha$ -1,4 oligomers linked by  $\alpha$ -1,6 bonds. The overall structure is thought to be tree-like. Molecular weights range from  $10^7$  to  $10^9$  with the average over  $10^8$ . Within the native starch granule, amylopectin is partially crystalline while amylose is amorphous (non-crystalline). The native crystalline structure of amylopectin consists of parallel-stranded double helices with six glucose units per 2.1 nm. rise in each individual strand.



**Figure 1.1** Structure of amylose.



**Figure 1.2** Structure of amylopectin.

The physical properties of starch reflect the rigidity of the starch backbone and the tendency of the hydroxyl groups of starch to form intermolecular hydrogen bonds. Although the overall configuration of an amylose molecule is that of a random coil, local rigidity of the starch backbone results from steric hindrance of the bulky glucose residues during rotation.

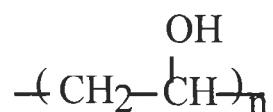
**Table 1.2** Effect of starch type on mechanical properties of films cast from aqueous solution (Kaplan, 1998).

Starch type	Amylose content (%)	Tensile strength (MPa)	Elongation at break (%)
Waxy maize	0	34	1.7
Normal corn	27	45	2.5-3.3
Corn amylase, degree of polymerization 820	27	48	4.9

Starches are used primarily as a food ingredient, in sizing of paper and textile, and in the adhesive industry. Their uses can be dated back to 3500-4000 BC when the Egyptians used wheat starch modified by boiling in vinegar to produce a smooth surface of papyrus documents (Kirk and Othmer, 1997). What makes them an attractive materials are low cost, readily available, renewable resource, and biodegradable materials.



### 1.2.2 Poly(vinyl alcohol)



**Figure 1.3** Structure of poly(vinyl alcohol).

Poly(vinyl alcohol) (PVA), a polyhydroxyl polymer, is the largest-volume synthetic, water-soluble resin produced in the world. It is commercially manufactured by the hydrolysis of poly(vinyl acetate), because monomeric vinyl alcohol cannot be obtained in quantities and purity that makes polymerization to poly(vinyl alcohol) feasible (Hay and Lyon, 1967, Capon and Watson, 1987, Novak and Cederstav, 1994).

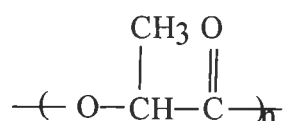
Poly(vinyl alcohol) is the most readily biodegradable of vinyl polymers. It is readily degraded in waste water-activated sludges (Casey and Manly, 1976). The microbial degradation of PVA has been studied, as well as its enzymatic degradation by secondary alcohol peroxidase isolated from soil bacteria of the *Pseudomonas* strain (Suzuki, 1979, Watanabe *et al.*, 1975, Morita and Watanabe, 1977, Watanabe *et al.*, 1976). It was concluded that the initial biodegradation step involves the enzymatic oxidation of the secondary alcohol groups in PVA to ketone groups.

The excellent chemical resistant and physical properties of PVA resins have resulted in broad industrial use.

**Table 1.3** Physical properties of poly(vinyl alcohol) (Wiley, 1992).

Properties	Value	Comments
Tensile strength (MPa)	67-110	Increasing with degree of crystallinity and molecular weight
Elongation (%)	0-300	Increase with increasing humidity
T <sub>g</sub> (K)	358	98-99 % hydrolyzed
T <sub>m</sub> (K)	503	98-99% hydrolyzed

### 1.2.3 Poly(lactic acid)

**Figure 1.4** Structure of poly(lactic acid).

Poly(lactic acid) (PLA) degrade biologically into acid, a product of the carbohydrate metabolism, and its importance as a substitute for the non-degradable thermoplastics has attracted a lot of attention in recent years.

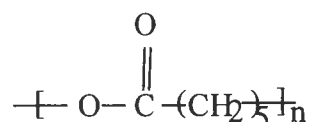
PLA are of considerable interest as biodegradable polymers in medical applications and also potentially for use as environmentally friendly packaging materials. PLA is a thermoplastic, high strength, high modulus polymer which can be made from annually renewable resources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market (Migliaresi *et al.*, 1988).

PLA exists in L- and D- form, which are optical isomers. PLA with large amount of L- form isomer is highly crystalline. In general, the crystallinity and biodegradability depend on the content of D- form isomer (Zhang *et al.*, 1993).

**Table 1.4** Effects of stereochemistry and crystallinity on mechanical properties of poly(lactic acid) (Kaplan, 1998).

Properties	D-PLA	L-PLA	D,L-PLA
Yield strength (MPa)	70	70	53
Tensile strength (MPa)	59	66	44
Flexural strength (MPa)	106	119	88
Notched izod impact (J/m)	26	66	18

#### 1.2.4 Polycaprolactone



**Figure 1.5** Structure of polycaprolactone.

Polycaprolactone (PCL) has been thoroughly studied as a substrate for biodegradation (Potts, 1984) and as a matrix in controlled-release systems for drugs (Pitt *et al.*, 1980). Its degradation *in vivo* is much slower than that of poly( $\alpha$ -hydroxy acid) (Pitt *et al.*, 1980). Thus, it is most suitable for controlled-release devices with long *in vivo* lifetimes. PCL is generally prepared from the ring-opening polymerization of  $\epsilon$ -caprolactone.

PCL was chosen because of its good mechanical properties and its compatibility with many types of polymers, and because it is one of the more

hydrophobic of the commercially available biodegradable polymer (Koleske, 1978).

**Table 1.5** Physical properties of PCL (Avella *et al.*, 2000).

Properties	Value
T <sub>g</sub> (K)	206
T <sub>m</sub> (K)	335
Tensile modulus (MPa)	280
Strength at yielding (Mpa)	13.3
Strength at break (MPa)	33
Elongation at break (%)	1328

### 1.3 Plasticizers

In most applications in which plasticizers are incorporated into plastics, their purpose is to convert an otherwise hard and rigid plastic to a flexible or semiflexible tough part. In some instances the same or similar conversions are obtainable by copolymerizing certain flexibility imparting monomers or by blending or grafting elastomers with those rigid plastics. Some of them are specifically made for use as polymeric-type plasticizers (Gaechter and Mueller, 1990).

The low-molecular-weight plasticizers show the best plasticizing performance but have the disadvantage of being more prone to migration when in contact with other plastics and of being somewhat more volatile. The plasticizing power is proportional to the viscosity of the plasticizer or mixture of plasticizers, with the lowest viscosity resulting in the best flexibility. Evaporation loss of plasticizers render plastics less flexible in time. The plasticizer vapors may cause windshield fogging in automobiles because they condense on the interior glass surfaces.

The effectiveness of any plasticizer in regard to imparted mechanical properties is very much temperature dependent. That is why most plastics are not compounded with plasticizers. At elevated temperature they would become too soft and at the low temperature range they would be too hard and brittle. The cellulose and polyvinyl chloride represent notable exceptions.

## 1.4 Mechanical Properties

The mechanical properties, among all the properties of plastic materials, are of ten the most important properties because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. In this study, tensile and flexural are mentioned.

### 1.4.1 Tensile Property Testing

Testing of tensile properties is probably the most widely used short-term mechanical test of all. This is because it is relatively easy to perform, gives reasonably reproducible results and yields a great deal of information. From this test one can obtain not only tensile strength, but also elongation and modulus.

Tensile properties are determined by stretching a test specimen at a constant rate. The resulting stress (or load applied) is measured and recorded as a function of strain (or elongation). The stress and strain are defined mathematically by:

$$\text{Stress} = \frac{\text{Load applied on specimen}}{\text{Cross-section area of specimen}} \quad (1.1)$$

$$\text{Strain} = \frac{\text{Increase in length of specimen}}{\text{Original length of specimen}} \quad (1.2)$$

$$\text{Modulus} = \frac{\text{Stress}}{\text{Strain}} \quad (1.3)$$

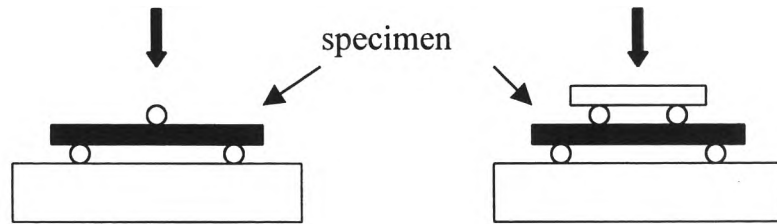
Tensile strength is the maximum tensile stress which a material is capable of supporting. It is calculated from the maximum load carried during the tensile test and the original cross-sectional area of the specimen. If the tensile strength occurs at the sample's yield point, this stress is designated as the tensile strength at yield. If it occurs at the sample's break point, it is then designated the tensile strength at break.

The percentage of elongation at break is the ratio, expressed in percentage, of the extension (change in gauge length) at break point to the original gauge length multiplied by 100.

#### 1.4.2 Flexural Properties Testing

Flexural properties are the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis.

Flexural properties are reported and calculated in term of the maximum stress and strain that occur at the outside surface of the test bar. There are two basic methods that cover the determination of flexural properties of plastics. Method I is a three-point loading system utilizing center loading on a sample supported beam. While method II is a four-point loading system utilizing two load points of one-third of the support span. The pictures of both three-point and four-point bending are shown in Figure 1.6



**Figure 1.6** Types of flexural testing equipment.

Flexural strength is the maximum stress developed when a rectangular bar test piece is subjected to a bending force perpendicular to the bar. The flexural strength ( $S$ ) is calculated from the following expression:

$$S = \frac{3PL}{2bd^2} \quad (1.4)$$

where  $P$  is the load at a given point (N)

$L$  is the length of support span (mm)

$b$  is the width of the bar (mm)

$d$  is the depth of the bar (mm).

The following expression can be used to obtain the maximum strain ( $r$ ) of the specimen under test:

$$r = \frac{6Dd}{L^2} \quad (1.5)$$

Where  $D$  is the deflection under load  $P$  (mm).

## **1.5 Morphology**

Microstructure of materials must be understood in order to develop relationships between the structure and properties of materials. The morphology of polymer blends is determined by a wide range of electron microscope techniques. In foam system, The micrographs can illustrate the interior of the foam.