

## CHAPTER I

### INTRODUCTION

Nowadays, expanded polystyrene (EPS) foams are used extensively in single-use packaging applications, due largely to their low bulk density, good thermal insulation property, reasonable strength, and low cost. In spite of these favored properties, there have been continual concerns about the impact of the manufacturing and the disposal of EPS foams on the environment (Soykeabkaew *et al.*, 2004) so a great deal of interest has arisen on the manufacturing of single-use articles such as plates, packaging foams, cups, and containers made from biodegradable materials as an alternative to non-biodegradable petroleum-based materials. Although many biodegradable synthetics have excellent mechanical properties, they are currently expensive when compared with their non-biodegradable counter parts (Lawton *et al.*, 2004). Bio-based materials such as starch and cellulose are receiving a great deal of attention as ingredients due to their low initial cost and their advantage of being biodegraded into useful compost. One of the commodities that researchers have studied extensively is starch. Starch is not only renewable and biodegradable, it is also inexpensive and abundant (Whistler *et al.*, 1984). Starch is an alternative material for making foams. Previous work (Tiefenbacher *et al.*, 1993) showed that batters of starch and water can readily be baked in a closed, heated mold where the starch granules gelatinize and the evaporation of water causes the starch to foam out and take up the shape of the mold.

Due to its hydrophilicity of starch, foams made from pure starch have major drawbacks on their brittleness and sensitivity to moisture and water so further treatments are necessary to attain the strength, flexibility and water resistance needed for applications such as foam plates or clamshells intended for moist food (Shogren *et al.*, 2002). Mineral fillers and wood fibers were added to improve strength, while surface coating with waxes or other materials was carried out to improve water resistance, of starch foam products (Andersen *et al.*, 1999). It was shown that water resistance and strength of the starch-based foams could be improved by coating with polyesters (Shogren & Lawton, 1998a) or by adding poly(vinyl alcohol) to the batters before baking (Shogren, Lawton, Tiefenbacher, & Chen, 1998b). The strength of

foam plates measuring under low and high humidity levels was shown to be improved by addition of soft wood fibers (Shogren, Lawton, & Tiefenbacher, 2002). Glenn, Orts, and Nobes (2001b) showed that starch/fiber composite foams could be prepared by baking process, and they found that the properties of the composite foams were within the range attainable in commercial EPS and coated paperboard food containers. The major drawbacks for these composite foams were lower tensile strength and lower elongation at break than were the commercial containers.

In order to overcome these problems, we investigated the use of natural rubber latex in the batter formulation. The solids in natural rubber latex are comprised mainly of *cis*-1,4-polyisoprene (Subramaniam *et al.*, 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.

Since, the incorporated natural rubber was improving the flexibility. Not surprisingly, the foam rigidity as indicated by specific flexural strength and specific flexural modulus also decreased with increased natural rubber content. In order to improve the foam rigidity, the cellulose pulp was selected as reinforcing filler.

In the present contribution, cellulose pulp reinforced natural rubber/tapioca starch composite foams were prepared by baking process. The effects of storage relative humidity, natural rubber content, starch type and cellulose pulp content on the physical and mechanical properties of foams products were thoroughly investigated. Morphology of the cross-sectional surface of cellulose pulp reinforced natural rubber/tapioca starch composite foams was assessed by scanning electron microscopy (SEM) technique. Finally, the degradability of composite foams were investigated by hydrolysis via  $\alpha$ -amylase.

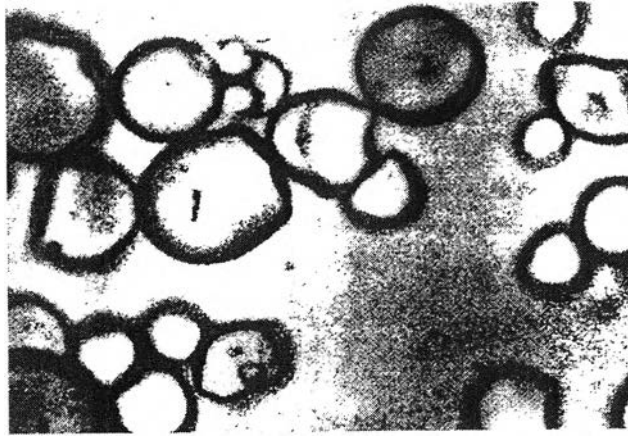
## THEORETICAL BACKGROUND

### 1.1 Starch

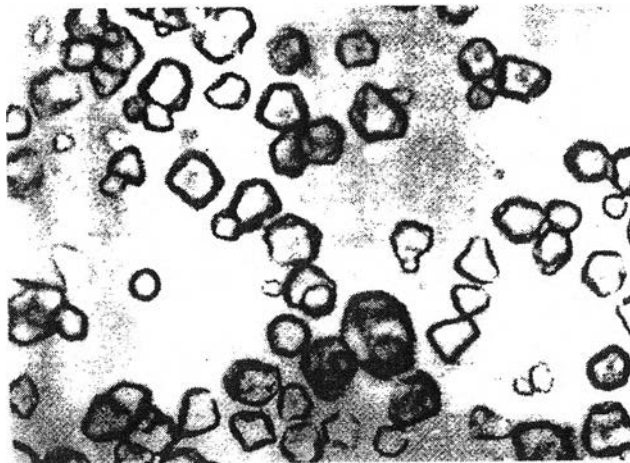
#### 1.1.1 Starch Sources and Granule Appearance

Starch is the reserve carbohydrate of the plant kingdom, where it generally is deposited in the form of minute granules or cells ranging from 1 up to 100  $\mu\text{m}$  or more in diameter. These granules are mainly deposited in the seeds, tubers, or roots of plants.

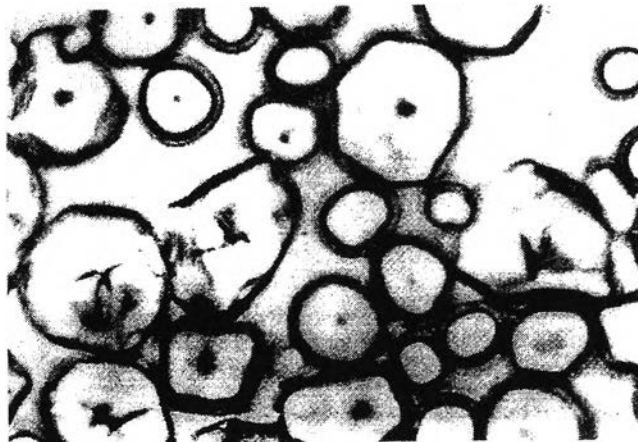
Various types of processes are used in the manufacture of starch, depending upon the plant source. In general, they involve freeing starch granules from the other constituents such as the fiber, germ, protein, and extraneous materials: purifying it, usually by screening, washing, utilization of centrifugal separators, then dewatering and drying. Starch granules are insoluble in water. They vary in size and shape, depending upon the plant source. Tapioca starch granules (Figure 1.1), the most abundant source in Thailand, usually have rounded shapes, which are truncated at one end. They average about 20  $\mu\text{m}$  in diameter, but may range from 5 to 35  $\mu\text{m}$  in diameter. Granules of rice starch (Figure 1.2) are polygonal in shape and mostly run about 3 to 8  $\mu\text{m}$  in diameter. They tend to aggregate in clusters. Corn or maize starch (Figure 1.3) has polygonal and some round granules which range from about 5 to 25  $\mu\text{m}$  in diameter, with about a 15  $\mu\text{m}$  average. Wheat starch (Figure 1.4) has flat, round, or elliptical granules, which tend to cluster in two size ranges: 2 to 10 and 20 to 35  $\mu\text{m}$ . Potato starch (Figure 1.5) has the largest granules of any commercial starch. They are oval or egg-shaped and range from 15 to 100  $\mu\text{m}$ .



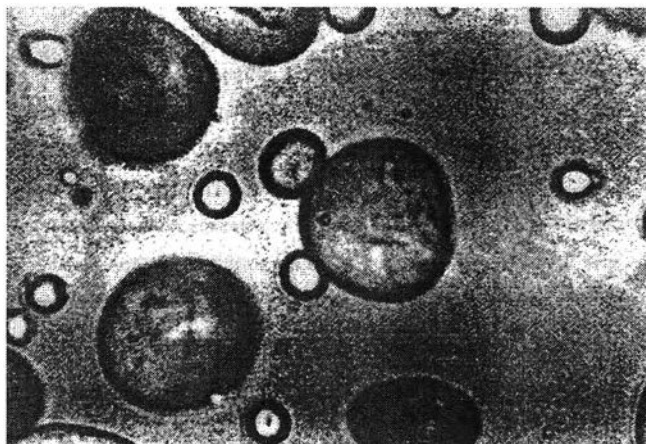
**Figure 1.1** Photomicrograph of cassava starch granules (magnification  $\times 788$ ).



**Figure 1.2** Photomicrograph of rice starch granules (magnification  $\times 788$ ).



**Figure 1.3** Photomicrograph of corn starch granules (magnification  $\times 788$ ).



**Figure 1.4** Photomicrograph of wheat starch granules (magnification  $\times 788$ ).



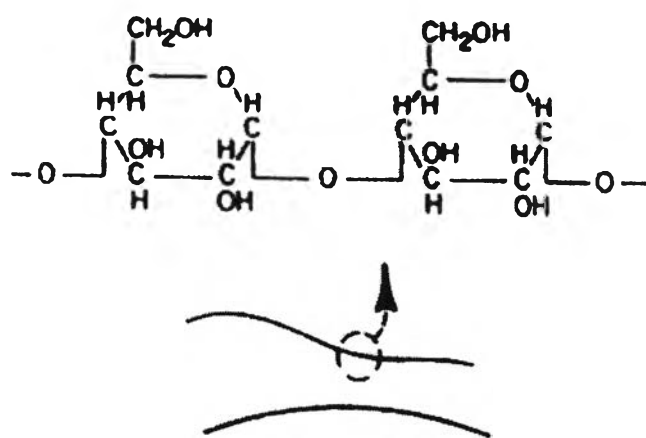
**Figure 1.5** Photomicrograph of potato starch granules (magnification  $\times 788$ ).

### 1.1.2 Chemical Structure of Starch

Chemically, starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through  $\alpha$ -D-(1 $\rightarrow$ 4) glucosidic bonds. While the detailed fine structure has not been fully elucidated, it has been established that starch is a heterogeneous material consisting at the extremes of two major types of polymers—amylose and amylopectin.

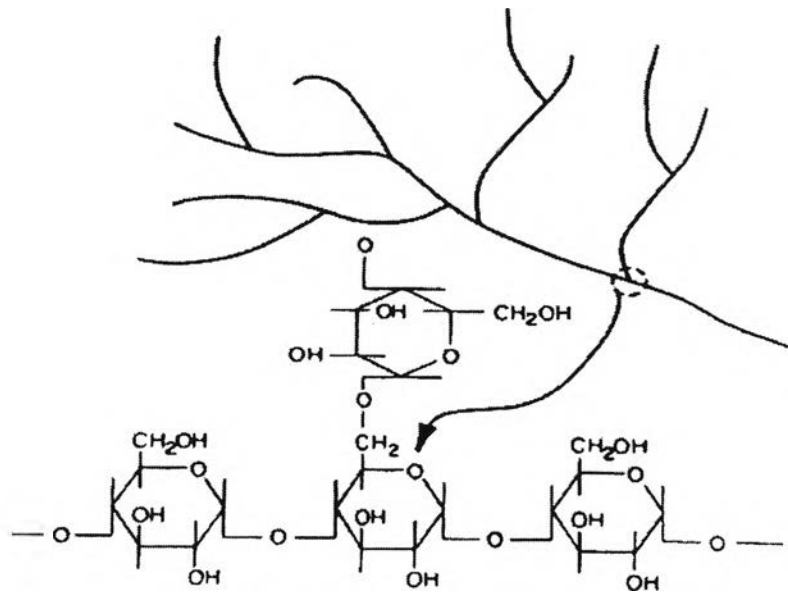
Amylose is essentially a linear polymer in which the anhydroglucose units are predominantly linked through  $\alpha$ -D-(1 $\rightarrow$ 4) glucosidic bonds

(Figure 1.6). Its molecular size varies depending upon the plant source and processing conditions employed in extracting of the starch. It may contain about 200 to 2000 anhydroglucose units. It has molecular weights varying from  $10^5$  to  $10^6$ . At one end of the polymeric molecule, the anhydroglucose unit contains one primary and two secondary hydroxyls as well as an aldehydic reducing group in the form of an inner hemiacetal. This is called the reducing end of the molecule. The opposite end, or nonreducing end, contains an anhydroglucose unit containing one primary and two secondary hydroxyls. The abundance of hydroxyls imparts hydrophilic properties to the polymer, giving it an affinity for moisture and dispersibility in water.



**Figure 1.6** Amylose schematic.

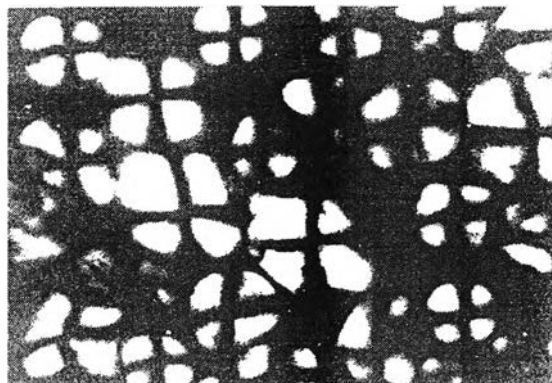
Amylopectin, on the other hand, is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through  $\alpha$ -D-(1 $\rightarrow$ 4) glucosidic bonds, periodic branches at the carbon-6 position. These branches are linked to the 6 carbon by  $\alpha$ -D-(1 $\rightarrow$ 6) glucosidic bonds. Each branch contains about 20 to 30 anhydroglucose units. The overall structure is thought to be tree-like. Molecular weights range from  $10^7$  to  $10^8$  with the average over  $10^8$ . A schematic diagram of the amylopectin molecule is shown in Figure 1.7.



**Figure 1.7** Amylopectin schematic.

The level of amylase found in starch varies depending upon the starch source. Most starches such as regular corn, wheat, and potato contain about 18 to 28% amylase. For tapioca, it has amylase content around 17%

The amylose and amylopectin fractions are oriented in the starch granule in a radial fashion. Wherever the linear segments of the amylopectin or amylose molecules run closely parallel, hydrogen bonding between adjacent segments may occur, forming micellar crystallites which are responsible for the granule integrity and for imparting properties. These polarization cross which are characteristics of intact starch granules are illustrated for starch in Figure 1.8.



**Figure 1.8** Photomicrograph of corn starch under polarized light (magnification  $\times$  788).

### 1.1.3 Gelatinization Phenomena

As noted earlier, starch granules are insoluble in cold water. When examined microscopically under polarized light, they show polarization crosses reflecting crystalline organization. The granules absorb water to a limited extent when exposed to high humidities or when suspended in water. When equilibrated under normal atmospheric conditions, starches usually contain 10 to 20 % moisture depending upon the starch source.

When a slurry of starch in water is heated above a critical temperature which varies with the type of starch and other factors, the hydrogen bonds responsible for the structure integrity of the granule weaken, allowing the penetration of water and hydration of the linear segments of starch. As this occurs, the molecules start to form helices or coils, creating tangential pressures causing the granules to imbibe water and swell to many times of their original volume.

During the swelling, the amylose tends to leach out of the granule and, along with the amylopectin, become highly hydrated. The suspension begins to clarify and the viscosity of the suspension rises and continues to rise until it approaches a peak where the granules have approached their maximum hydration. As heating is continued, the granules, and fragment, releasing the polymeric molecules and aggregates. The viscosity drops. However,

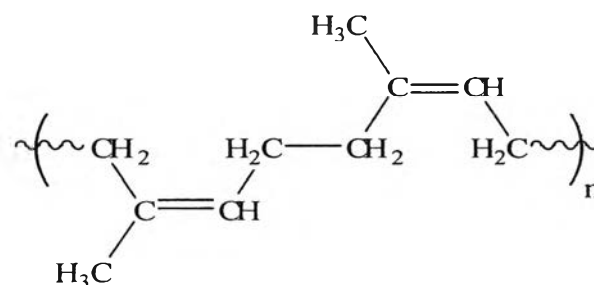


the swelling is reversible and the polarization crosses are retained when the humidity is reduced or the starch is dried.

As a general rule, root or tuber starches swell more rapidly in a narrower temperature range than the common cereal starches. For tapioca, its gelatinization temperature is about 67° C.

## 1.2 Natural Rubber

Natural rubber is discovered from the plants at least 2000 species the entire world. The most significant species is the para rubber tree, *Heavea brasiliensis*. Figure 1.9 illustrates the structure of this rubber, which is cis1-4-polyisoprene.



**Figure 1.9** Typical structure of NR latex form *Heavea brasiliensis*.

In general, natural rubber is known as the natural rubber (NR) latex. The latex appears in the bark outside the cambium layer in ducts spiraling from the left to right as the latex ascends the tree. These ducts are found in concentric rings around the cambium and are really more concentrated near the cambium (Cole O.D., 1958 and Margin G., 1961.).

The procedure to obtain the latex called tapping is to make a spiral cut that is made downwards from left to right through the bark of the tree. This cut is manipulated to promote the latex to flow into the receptacle such as a plastic, glass, or earthenware cup. The fresh latex coagulates rapidly after tapping, especially in the ambient temperature. The fresh latex has pH of 7.0. Bacteria decompose the sugar substances of latex, therefore the stability the latex decreases continually as the

pH decreases. Bacteria come from various places such as the atmosphere, the bark and the tapping. The preservation of NR latex was first introduced by Johnson and Norris (1853). They suggested using ammonia as the anticoagulant to the latex. The ammonia acts as an alkali to increase the pH of the fresh latex, thus the bacteria remains inactive and the stability of latex improves. In addition, the electrophoresis mobility of rubber tends to be negatively charged in the base environment. Fresh NR latex exuded from tree has dry rubber content 33%wt. In industry, the latex is concentrated to about 60%wt, which is economical and uniform in quality. There are several processes to concentrate latex: (1) evaporation, (2) creaming, (3) centrifuging.

The freshly-tapped NR latex is a whitish fluid of density between 0.975 and 0.980 g.m<sup>-1</sup>, and pH from 6.5 to 7.0.

The composition of latex is defined below:

Total solids content	36 %
Dry rubber content	33 %
Proteinous substances	1-1.5 %
Resinous substances	1-2.5 %
Ash	up to 1 %
Sugars	1 %
Water	add.100 %

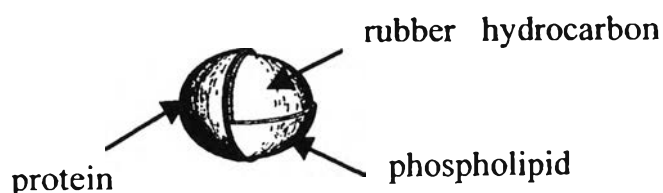
Hauser (1962) found that rubber particles were quite pear shaped rather than spherical, and consisted of a tough, hard elastic shell which enclosed a viscous liquid. However, many literatures have reported that the rubber particles were spherical in shape, especially the latex from young trees. There are also suggestions that the shape of the latex depends on the age and type of tree.

The structure of the *Heavea brasiliensis*. Latex is:

Rubber hydrocarbon	86 %
Water (dispersed in the Rubber hydrocarbon)	10 %
Proteinous substances	1 %
Lipid substances	3 %

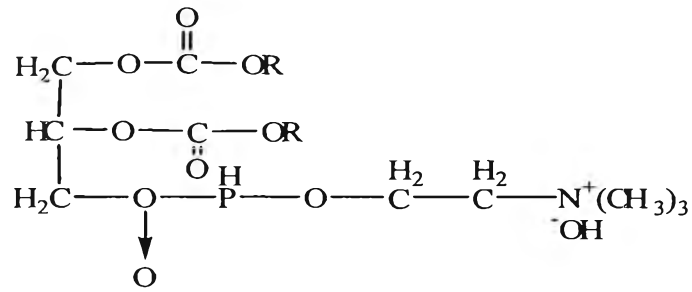
Trace metals such as magnesium, potassium and copper are included with the rubber particles about 0.05%.

Figure 1.10 shows the structure of the NR latex particle. The NR consists of the protein structure at the outer layer of the surface. The adsorbed layer of protein determines the charge on the particle, electrophoretic mobility, and coacervation characteristics. The lipids associated with rubber particles are sterols and sterol esters, fats and waxes, such as eicosyl alcohol and phospholipids. They are found in the bulk of latex particle. They may be dissolved in rubber hydrocarbon. The phospholipids are adsorbed on the particle and are associated with the protein which is anchored on to the rubber.



**Figure 1.10** Schematic representation of structure of NR latex particle.

The structures of phospholipids mostly found are lecithin. Figure 1.11 shows the example of one of lecithin structures whose R groups are hydrocarbon radicals of the heptadecyl ( $C_{17}H_{35}$ ) or heptadecenyl ( $C_{17}H_{33}$ ) types. The ammonia is used for hydrolysis of protein and phospholipid. The protein is degraded to polypeptide and amino acid and phospholipid is displaced by glycerol, fatty acid anion, organic bases and inorganic phosphate. The fatty acid anions are adsorbed at the particle interfaces. Therefore, the rubber particles of the ammonia-preserved latex consist of proteinate ions and the fatty acid anions to improve the stability of the latex.



**Figure 1.11** The lecithin structure of phospholipid.

### 1.3 Foamed Plastics

Foamed plastics, also known as cellular plastics, are 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 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 are characterized by techniques, which 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, remains. The solidified bubble containing material is thought of as a cellular structure. The products made by these processes are referred to as foams or cellular plastics (Ronald and David, 1986).

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

Plastic foam has some physical characteristics that are valuable for several important applications because their structures have a lot of the space, which filled with air or some other gas. The low thermal conductivity of gases means that these foams are very good thermal insulators.

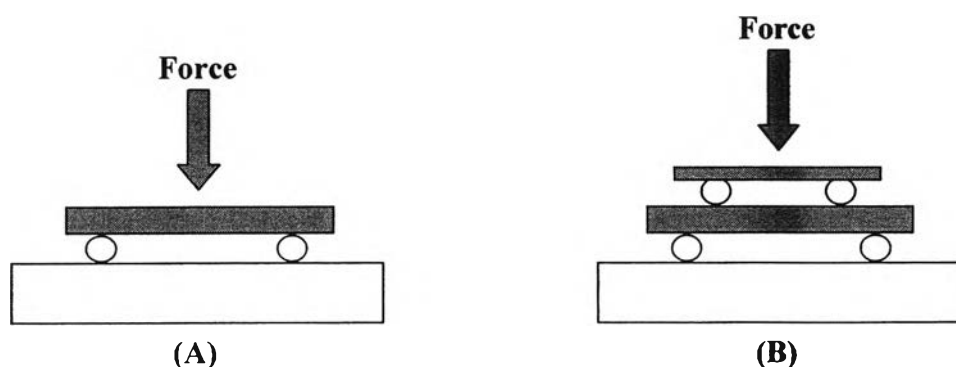
The advantages and disadvantages of foams are outlined in table 1.1

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

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>● Light weight</li> <li>● Low thermal conductivity</li> <li>● High support per unit weight</li> <li>● Low cost moulds</li> <li>● Many methods available to create forms</li> </ul>	<ul style="list-style-type: none"> <li>● Slowness of most processed</li> <li>● Evolution of gases in some process</li> <li>● Variable density with some parts</li> <li>● Loss of some mechanical properties</li> </ul>

#### 1.4 Flexural Properties Testing

Flexural properties are the ability of the material to withstand bending force applied perpendicular to its longitudinal axis. There are two basic methods that cover the determination properties of plastics. Method I is a three-point loading system utilizing center loading on a simply supported beam. While method II is a four-point loading system utilizing two load points equally spaced from their adjacent support points, with a distance between load point of either one-third or one-half of the support span. The pictures of both three-point and four-point loading systems are shown in figure 1.12



**Figure 1.12** Types of flexural testing method. (A) three-point and (B) four-point loading systems.

Flexural properties are usually reported and calculated in term of the flexural strength, maximum strain, and modulus of elasticity that occur at the outside surface of the test beam. Flexural strength (S) is equal to the maximum stress in the outer surface that occurs at the midspan. It is calculated in accordance with the following expression:

$$S = 3PL/2bd^2$$

Where:

S = stress in the outside at midspan, MPa (psi),

P = load at a given point on the load-deflection curve, N (lbf),

L = support span, mm (in.),

b = width of the beam tested, mm (in.), and

d = depth of beam tested, mm (in.).

The maximum strain in the outer surface also occurs at midspan, and it may be calculated as follow:

$$r = 6Dd/L^2$$

Where:

r = maximum strain in the outside at midspan, mm/mm (in./in.),

D = maximum deflection of the center of the beam, mm (in.).

And the tangent modulus of elasticity, often called the “modulus of elasticity” is the ratio of stress and strain. It is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve and using the following expression:

$$E_B = L^3m/4db^3$$

Where:

$E_B$  = modulus of elasticity in bending, MPa (psi),

$M$  = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm (lbf/in.) of deflection.

### **1.5 Morphology**

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