CHAPTER I

INTRODUCTION

In recent years, much progress has been achieved in the development of biodegradable products using agricultural materials as basis. Various approaches have used starch for the production of functional materials. For examples, native starch has been chemically transformed into the easier-to-process thermoplastic starch. Unfortunately, properties of products derived from such a material still do not meet requirements for certain applications, such as in packaging (Averous et al., 2001). 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. These concerns have led to an interest in developing alternative foam materials from renewable resources which are readily degradable (Glenn and Orts, 2001a).

Starch is an alternative material for making foams. Previous work (Tiefenbacher, 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. Foams made from pure starch have major drawbacks on their brittleness and sensitivity to moisture and water. Further treatments are, therefore, necessary to impart the required properties (i.e., reasonable strength, good flexibility, and water resistance) to the products. 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). Such improvements led to the commercialization of hinged-lid food containers for the fast-food industries.

Clamshell hinges with sufficient bending flexibility were developed by spraying the hinges with glycerol or poly(vinyl alcohol) solutions (Andersen and Hodson, 1998). It was shown that water resistance and strength of the starch-based foams could be improved by coating with polyesters (Shogren and Lawton, 1998a) or by adding poly(vinyl alcohol) to the batters before baking (Shogren et al., 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 *et al.*, 2002). Glenn *et al.* (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.

Due to concerns on the environment, the interest in using different types of plant and wood fibers as reinforcing fillers in plastics has increased dramatically during the last few years. Cellulose fibers, however, have not received much attention, because of the poor compatibility between the fibers and the thermoplastic matrix, which, in turn, resulted in poor mechanical properties of the composites. An important technique to improve the compatibility is chemical modification on the fiber surface by making it more hydrophobic in order to improve compatibility between the fibers with non-polar thermoplastics (Karnani *et al.*, 1997; Albano *et al.*, 2001; Oksman *et al.*, 2002). Such a compatibility problem between these natural fibers and starch should be minimized as compared to natural fibers and non-polar thermoplastics, since starch molecules are naturally polar and hydrophilic (Dufresne *et al.*, 1999).

In the present contribution, cellulose fiber-reinforced starch-based composite foams (SCFs) were prepared by baking process. The cellulose fibers used were jute and flax fibers. Since both the fibers and the starch matrix were naturally polar and hydrophilic, strong interaction between them was expected. The effects of moisture content, fiber content, fiber aspect ratio, fiber type, and fiber orientation on the physical and mechanical properties of SCFs were thoroughly investigated. Morphology of the fracture surface of SCFs was assessed by scanning electron microscopy (SEM) technique.

Theoretical Background

1.1 Starch

1.1.1 <u>Starch Sources and Granule Appearance</u>

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 μm 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 cold 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 μm in diameter, but may range from 5 to 35 μm in diameter. Granules of rice starch (Figure 1.2) are polygonal in shape and mostly run about 3 to 8 μm 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 μm in diameter, with about a 15 μm 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 μm. 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 μm.
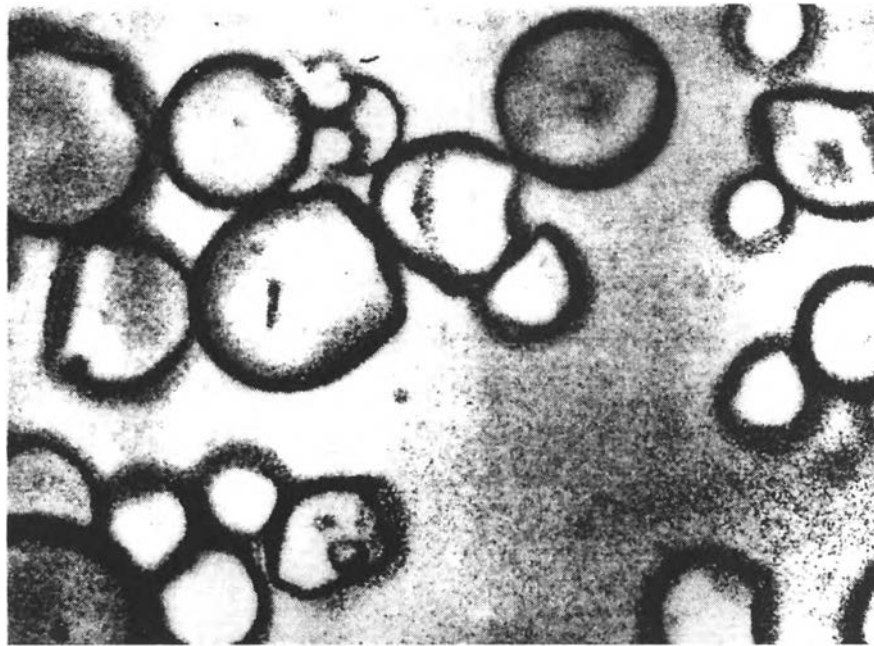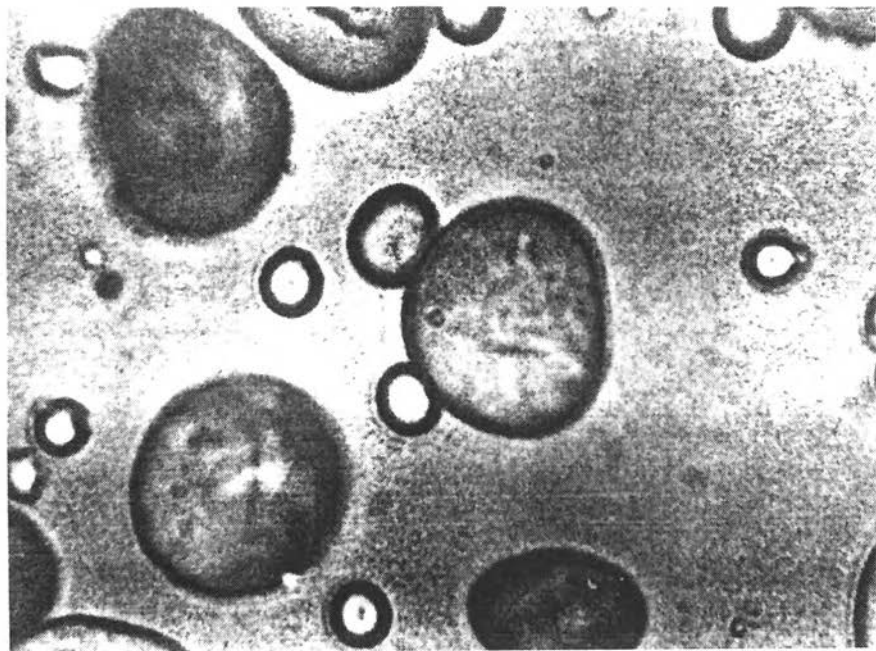
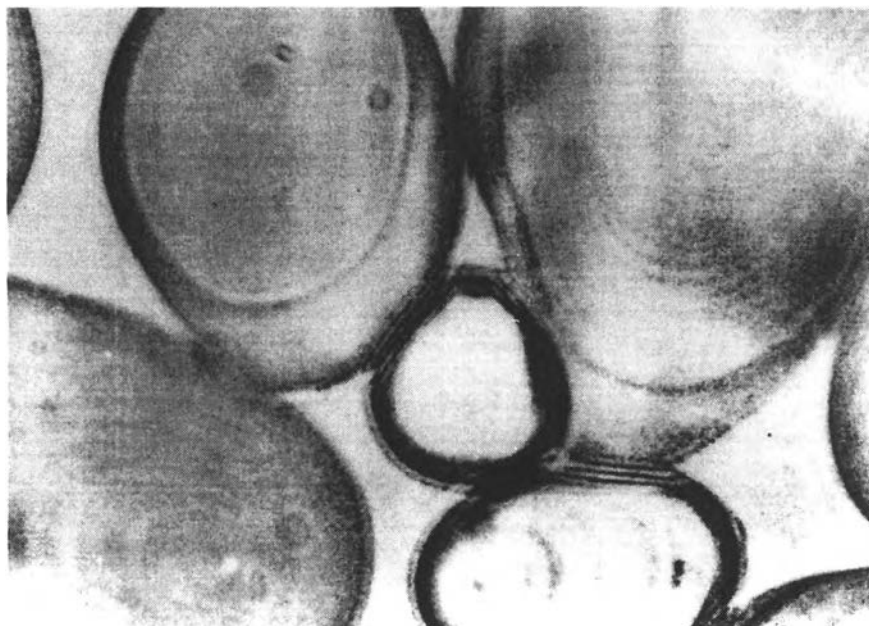**Figure 1.1** Photomicrograph of tapioca starch granules (magnification × 788).
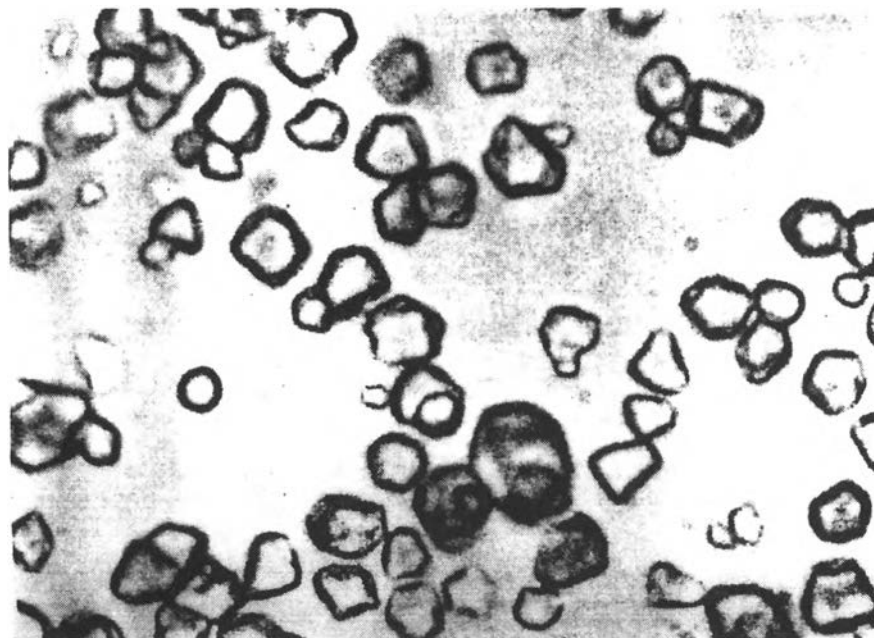
Figure 1.2 Photomicrograph of rice starch granules (magnification × 788).
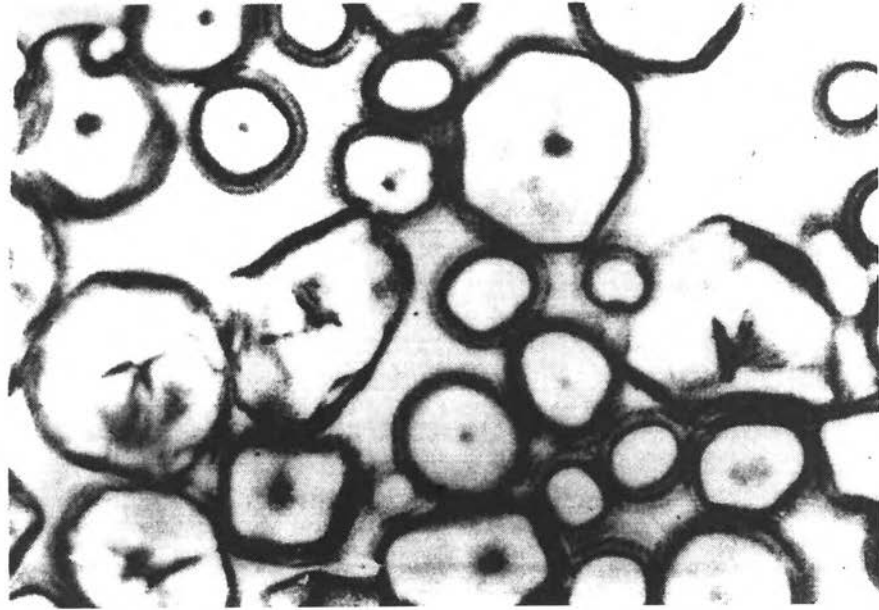
Figure 1.3 Photomicrograph of corn starch granules (magnification × 788).

**Figure 1.4** Photomicrograph of wheat starch granules (magnification × 788).

Figure 1.5 Photomicrograph of potato starch granules (magnification × 788).

1.1.2 Chemical Structure of Starch

Chemically, starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-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 α-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 anywhere from 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.
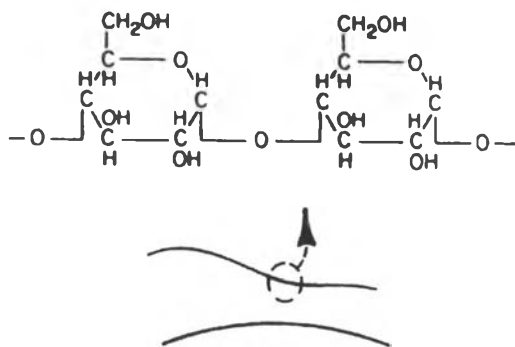
Figure 1.6 Amylose schematic.

Amylopectin, on the other hand, is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through α-D-(1$\rightarrow$4) glucosidic bonds, periodic branches at the carbon-6 position. These branches are linked to the 6 carbon by α-D-(1$\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 schematics diagram of the amylopectin molecule is shown in Figure 1.7.
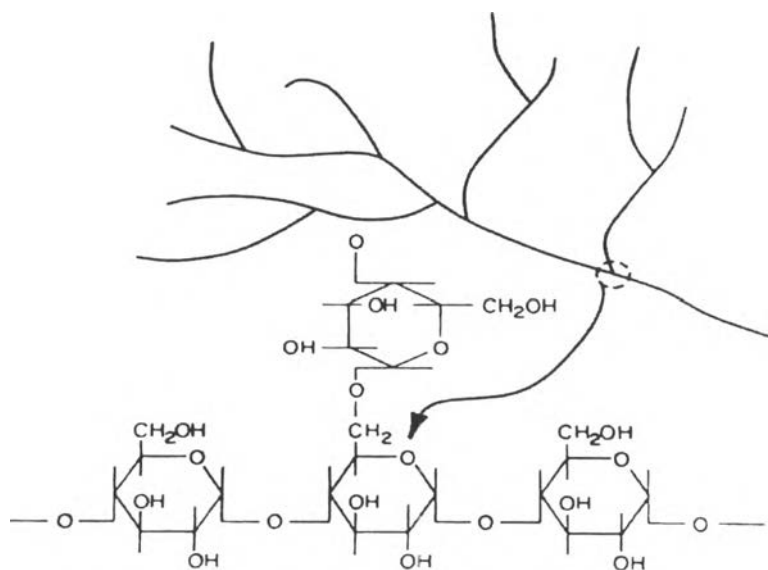
Figure 1.7 Amylopectin schematic.

The level of amylose found in starch varies depending upon the starch source. Most starches such as regular corn, wheat, and potato contain about 18 to 28 % amylose. For tapioca, it has amylose 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 birefringent properties. These polarization cross which are characteristics of intact starch granules are illustrated for starch in Figure 1.8.
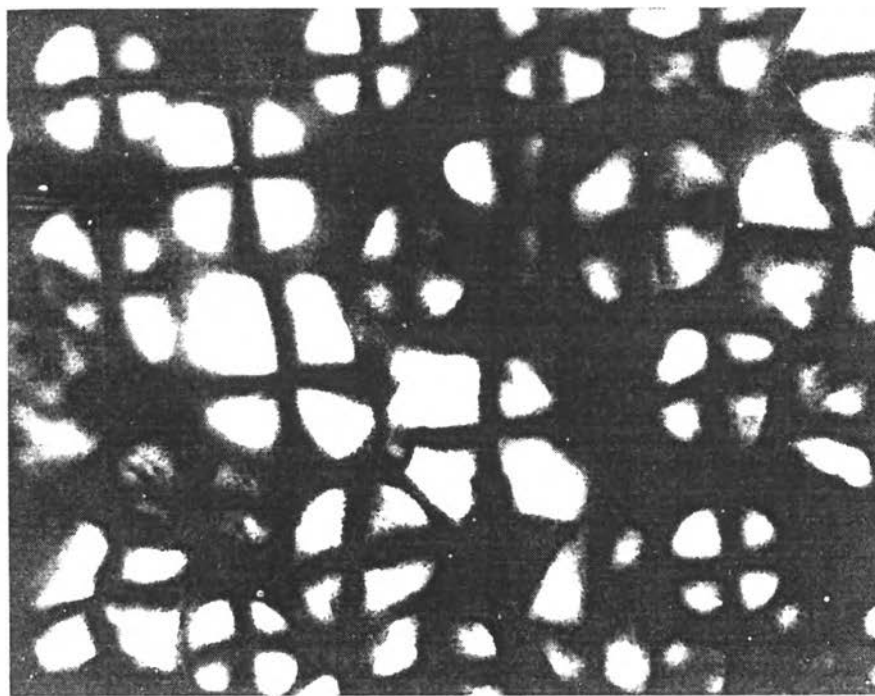
Figure 1.8 Photomicrograph of corn starch under polarized light (magnification × 788).

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 extend

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 tend to rupture, collapse, 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 Fiber and Starch

Cellulose is the basic structural component of all plant fibers. The isomeric polysaccharides amylose (a component of starch) and cellulose show the significance of stereoisomerism on polymer properties. Cellulose and amylose have the structures shown in Figure 1.9. Both are polymers of glucose in which the glucose units are jointed together by glucoside linkages at carbons 1 and 4. The two polysaccharides differ only in the configuration at carbon 1.

(A)

(B)
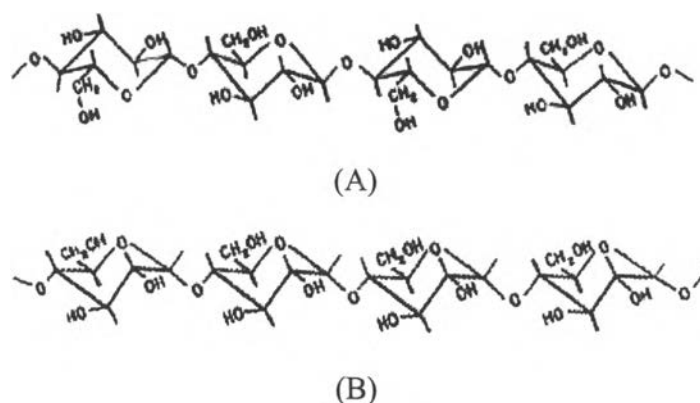
Figure 1.9 Chemical structure of (A) cellulose and (B) amylose (linear segment of starch).

In terms of the nomenclature used for stereoregular polymers, cellulose has a threodisyndiotactic structure while amylose is erythrodiisotactic. In the nomenclature of carbohydrate chemistry, cellulose consists of β-1,4-linked D-glucopyranose chains and amylose of α-1,4- linked D-glucopyranose chains. The 1,4-linkage is trans (diequatorial) in cellulose and cis (equatorial-axial) in amylose. The difference in structure results in amylose existing in random-coil conformation while cellulose exists in an extended-chain conformation. This leads to closer packing of polymer molecules with much greater intermolecular attractive force and crystallinity in cellulose relative to amylose (and also amylopectin). Cellulose, compared to amylose, has good physical strength and mechanical properties, decreased solubility, and increased stability to hydrolysis. The result is that cellulose is used as a structural material both in nature (plants) and by people. Although starch is not useful as a structural material, it does serve important functions as a food source and storage form of energy for both plants and animals. The structure of each polysaccharide is uniquely fitted to its biological function in nature.

1.3 Composite Materials

1.3.1 Definition of composite materials

A composite material consists of two or more physically and/or chemically distinct, suitably arranged or distributed phases, with an interface separating them. It has characteristics that are not depicted by any of the components

in isolation. Most commonly, composite materials have a bulk phase, which is continuous, called the matrix, and one dispersed, non-continuous, phase called the reinforcement, which is usually harder and stronger.

The concept of composite materials is ancient: to combine different materials to produce a new material with performance unattainable by the individual constituents. An example is adding straw to mud for building stronger mud walls. Some more recent examples, but before engineered materials became prominent, are carbon black in rubber, steel rods in concrete, cement/asphalt mixed with sand, fiberglass in resin etc. In nature, examples abound a coconut palm leaf, cellulose fibers in a lignin matrix (wood), collagen fiber in an apatite matrix (bone) etc.

The essence of the concept of composites is this: the bulk phase accepts the load over a large surface area, and transfers it to the reinforcement, which being stiffer, increases the strength of the composite. The significance here lies in that there are numerous matrix materials and as many fiber types, which can be combined in countless ways to produce just the desired properties.

Most research in engineered composite materials has been done since 1965. Today, given the most efficient design, of say an aerospace structure, a boat or a motor, we can make a composite material that meets or exceeds the performance requirements. Most of the savings are in weight and cost. These are measured in terms of ratios such as stiffness to weight, strength to weight, etc.

1.3.2 Components of Composite Materials

- Bulk phase: matrix materials (polymers, metals, and ceramic)
- Reinforcement: fibers and particulate
- Interface

a. Reinforcement

Reinforcements are not necessarily in the form of long fibers. They can be particles, whiskers, discontinuous fibers, sheets etc. A great majority of materials is stronger and stiffer in the fibrous form than in any other form. This explains the emphasis on using fibers in composite materials design. There are many

naturally occurring fibers: cotton, flax, jute, hemp, ramie, wood, straw, hair, wool, silk etc., but these have varying properties, and present many processing challenges. Fibers used in advanced composites have very high strength and stiffness but low density. They also should be very flexible (to allow a variety of methods for processing) and have high aspect ratio (length/diameter) that allows a large fraction of the applied to be transferred via the matrix to the fiber. Fibers are added to a ductile matrix (like polymers and metals) usually to make it stiffer, while fibers are added to a brittle matrix (like ceramics) to increase toughness.

b. Interface

1) The interface is a bounding surface or zone where a discontinuity occurs, whether physical, mechanical, chemical etc.

2) More often than not, the interface between fiber and matrix is rather rough, instead of ideal planar.

3) The matrix material must "wet" the fiber. Coupling agents are frequently used to improve wettability. Well "wetted" fibers increase the interface surface area.

4) To obtain desirable properties in a composite, the applied load should be effectively transferred from the matrix to the fibers via the interface. This means that the interface must be large and exhibit strong adhesion between fibers and matrix.

5) Bonding with the matrix can be either weak Van der Waals forces or strong covalent bonds.

6) Interfacial strength is measured by simple tests that induce adhesive failure between the fibers and the matrix. The most common is the Three-point bend test or ILSS (interlaminar shear stress test).

1.3.3 Fabrication of Composites

Polymer Matrix Composites:
1) Filament winding
2) Pultrusion
3) Compression molding

4) Laminate stacking/Vacuum Bagging/ Autoclaving

5) Wet flow methods (injection molding and resin transfer molding)

1.3.4 Properties of Composites

The matrix, besides holding the fibers together, has the important function of transferring the applied load to the fibers. It is of great importance to be able to predict the properties of a composite, given the component properties and their geometric arrangement.

a. Isotropic vs. anisotropic

1) Fiber reinforced composite materials typically exhibit anisotropy. That is, some properties vary depending upon which geometric axis or plane they are measured along.

2) For a composite to be isotropic in a specific property, such as Young's modulus or the coefficient of thermal expansion (CTE), all reinforcing elements, whether fibers or particles have to be randomly oriented. This is not easily achieved for discontinuous fibers, since most processing methods tend to impart a certain orientation to the fibers.

3) Continuous fibers in the form of sheets are usually used to deliberately make the composite anisotropic in a particular direction that is known to be the principally loaded axis or plane.

b. Interface, fracture propagation and toughness

1) In a ductile matrix, like most polymers and metals, a strong interfacial bond is important, since the fibers carry most of the load in such matrices. Fibers tend to fail first, usually by cohesive failure through the fiber cross-section. This is because the fibers cannot strain as much as the matrix (e.g. carbon in epoxy). Cracks are few, and tend to propagate slowly. When the cracks hit the interface, strong interfacial bonds stop them.

2) In a brittle matrix, like ceramics, the matrix carries most of the load, which is usually compressive (like in teeth or bone), and fibers are added only to increase toughness. That is, to increase the time to catastrophic failure by holding

the matrix together after cracking. Fibers here are more ductile than the matrix (e.g. glass in alumina) and the matrix fails first. As the cracks propagate and reach the interface, a weak interfacial bond is desired. This enhances debonding, and the cracks are not stopped, but deflected along the length of the fibers. This effectively delays the time it takes the cracks to propagate through the entire matrix, and thus increases toughness.

1.4 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 a 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 foams have 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
▪ Light weight ▪ Low thermal conductivity ▪ High support per unit weight ▪ Low cost moulds ▪ 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

1.5 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. Methods 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 1.9
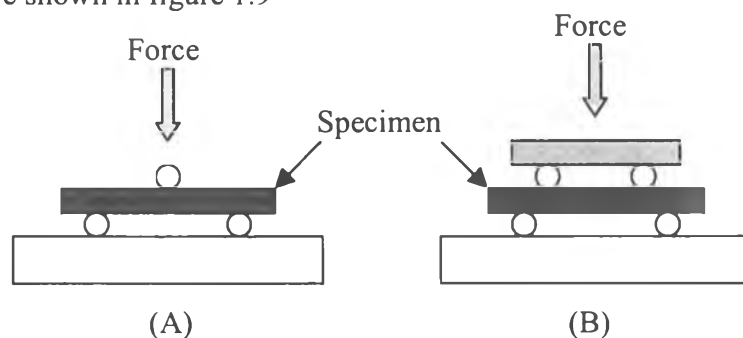
Figure 1.10 Types of flexural testing method. (A) three-point and (B) four-point loading systems.

Flexural properties are usually reported and calculated in term of the flexural strength, maximum strain, and modulus of elasticity that occur at the outside

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 deflction.

1.6 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.