

## CHAPTER II

### THEORETICAL BACKGROUND

The increased interest in the environmental safety and biodegradability of packing materials has led to a variety of new products, which dissolve harmlessly in water, rather than accumulate in landfills. For example, large volumes of packaging foam filler are produced and used to protect items in containers from damage during shipping. This high volume, foam filler has mainly been produced from polymers, such as polystyrene, which are not biodegradable. The accumulation of such polymers in landfills is of major concern because it occupies large volumes of space for the nominal weight of the product. Furthermore, these polymers do not readily degrade and therefore create long term difficulties for waste management. Attempts to burn these polymers generates noxious or toxic gases, further limiting disposal options. In addition to the adverse nature of the polystyrene polymers as a final product are the environmental hazards of their preparation. For example, chlorofluorocarbons (CFC's) used in the preparation of polystyrene foam, commonly called Styrofoam (registered trademark of Dow Chemical Co), are harmful to the earth's ozone layer.

Although these foamed polymers are useful in filling space as packing materials, their hydrophobic character tends to enhance electrostatic charge buildup. This is particularly true for the polystyrene materials, which are often used as shipping material for electronic components. It is well known that such electrostatic

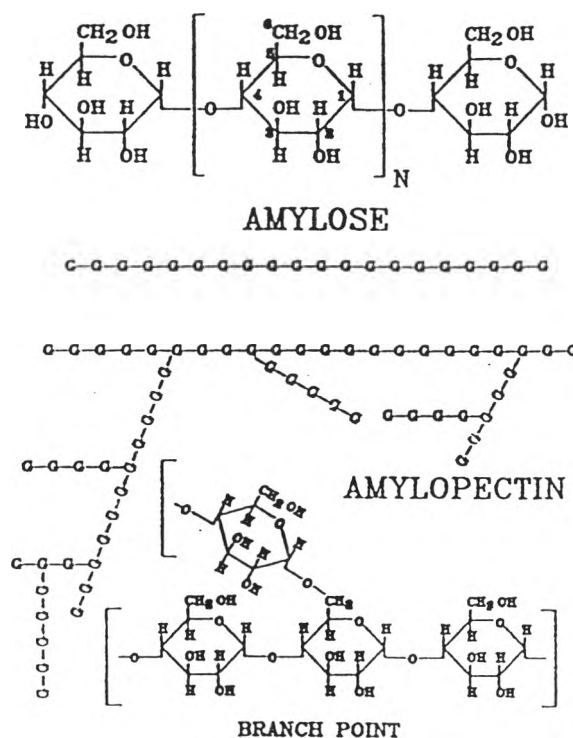
accumulation poses a risk to much of the electronic equipment and software, which may be affected by the presence of an electric field. It is not surprising, therefore, that substantial interest has developed in the use of starch composition as a substitute for polystyrene polymers, particularly in production of packing materials.

Starch offers several clear advantages over polymers previously used in this field. Starch is well known to be biodegradable and is a natural renewable resource that is produced in excess of the present market demand. Because starch is hydrophilic, it does not retain an electrostatic charge as occurred with hydrophobic polymers. Due to this hydrophilicity, packaging foam fillers prepared from starch can be readily dissolved in water as part of their natural decomposition. This obviously reduces their volume many times and allows them to be disposed in a normal waste water system [5].

## 2.1 General consideration of starch

Starch is an abundant, inexpensive, natural raw material, which permits the development of products recyclable to atmospheric CO<sub>2</sub> when biodegraded or incinerated. These characteristics have excited a renewed interest in starch-based plastics, as testified by an impressive literature in recent years [6].

Starch consists of two major components; amylose, a mostly linear alpha-D-(1-4)-glucan and amylopectin, an alpha-D-(1-4) glucan which has alpha-D-(1-6) linkages at the branch points (Fig. 2.1). The linear amylose molecules of starch have a molecular weight of 0.2-2 million, while the branched amylopectin molecules have molecular weights as high as 100-400 million [6,7].



**Fig. 2.1** Components of normal cornstarch (G is an anhydroglucosidic unit).

In nature, starch is found as crystalline beads of about 15-100  $\mu\text{m}$  in diameter, in three crystalline modifications designated A (cereal), B (tuber), and C (smooth pea and various beans), all characterized by double helices; almost perfect left-handed, six-fold structures, as elucidated by X-ray diffraction experiments. Crystalline starch beads in plastics can be used as fillers or can be transformed into thermoplastic starch, which can be processed alone or in combination with specific synthetic polymers. To make starch thermoplastic, its crystalline structure has to be destroyed by pressure, heat, mechanical work and plasticizers, such as, water, glycerine or other polyols [7,8].

### 2.1.1 Starch properties

Starch is stored in plants as granules or solid particles comprised of molecules of both amylose and amylopectin. The granules, which are isolated and sold in bulk by the wet milling industry, may vary in size from a few to 50 or more micrometers, depending on the source plant. Starch granules are hydrophilic since each starch monomer unit contains three free hydroxyl groups. Consequently, starch changes moisture content as relative humidity changes. Cornstarch granules retain about 6% moisture at 0% relative humidity (RH), but contain 20% moisture when in equilibrium with about 80% RH [6].

Granules are thermally stable when heated in an open atmosphere to about 250°C above that temperature the starch molecules begin to decompose. Dry granules absorb moisture when immersed in water, but retain their basic structure due to crystalline and hydrogen bonded structure within the granules. Native granular starch contains crystalline areas within the amylopectin (branched) component but the linear amylose is largely amorphous and can be mostly extracted in cold water. The granular structure is ruptured by heating in water or heating with aqueous solutions of reagents that disrupt crystalline areas and hydrogen bonding within the granules. The constituent molecules become completely soluble in water at 130 to 150°C and at lower temperatures in alkaline solutions. Starch granules that have been ruptured in aqueous media are said to have been gelatinized. Application of high pressure and shear to starch granules permits disruption of organized structure at lower water content than is possible at atmospheric pressure. Linear amylose component of starch is similar to cellulose but differs in molecular weight and the configuration of the

acetal linkage. Cellulose, a linear  $\beta$ -(1 $\rightarrow$ 4) glucan, is highly crystalline and insoluble in water [6].

### **2.1.2 Starch-plastic composite**

Use of granular starch as a filler in plastics began with the work of Griffin in the 1970's. Starch-containing polyethylene films and other consumer items based on this technology are currently being marketed. Since whole starch granules are used in this technology, the level of starch addition is generally limited to about 10% or less, by weight. Starch is dried to < 1% moisture to inhibit steam formation during extrusion processing, and starch granules have also been surface-treated (for example with silanes) to increase the compatibility of hydrophilic starch with the hydrophobic polymer matrix. Pro-oxidants can also be added to promote degradation of the synthetic polymer [9].

At about the same period as Griffin's research, Otey and coworkers at the National Center for Agricultural Utilization Research (NCAUR) were studying starch-plastic systems in which the starch granule structure was totally disrupted. For example, a process was developed to extrusion-blown films from mixtures of starch and poly(ethylene-co-acrylic acid) or EAA in the presence of aqueous ammonium hydroxide and urea. Polyethylene could be incorporated into these formulations as a partial replacement for EAA in order to reduce raw material costs and in some instances improve film properties. In these systems, starch can form a continuous phase rather than merely being present as a particulate filler. Starch loadings as high

as 50 % by weight can thus be obtained in these composites and acceptable properties of the blend can still be obtained [9].

Since starch can biodegrade to carbon dioxide and water in a relatively short time compared with most synthetic polymers, much of the research in recent years has centered on increasing the amount of starch in starch-plastic composites to the highest possible level. The ultimate goal of these research efforts is to prepare consumer items for one-time use from substantially pure starch and to exclude synthetic polymer from the formulation [9].

## **2.2 Natural Rubber (NR) Latex**

Natural rubber (NR) latex produced by *Hevea brasiliensis* tree consists of cis-1, 4-polyisoprene whose molecular weight is in the region of one million. A few percents of non-rubber substances such as proteins, fatty acid soaps, and inorganic salts are also presented in the latex. The rubber particles in NR latex are polydisperse having diameter from 0.01-5  $\mu\text{m}$  while their average size is usually ranged from 0.25 to 0.8  $\mu\text{m}$  [10].

### **2.2.1 Stabilisation of NR Latex**

It has been believed that the non-rubber constituents, *i.e.*, proteins and lipids are adsorbed on the natural rubber particles [10,11]. This complex layer has an important influence on the colloidal stability of NR latex particles. However, at present, the detailed information on the exact nature of adsorbed layer is not readily

available, because any attempt to remove the layer results in immediate coagulation of the latex.

Moreover, in the ammonia-preserved NR latex, the ammonia promotes hydrolysis of proteins to polypeptides and amino acids and of phospholipids to glycerol, fatty acid anions, phosphate anions and organic bases. The fatty acid anions are also adsorbed on the surface of rubber particles and contribute to colloidal stability of latex. The presence of bound charge on surface of rubber particles in the dispersion medium leads to electrostatic stabilisation.

### **2.2.2 Destabilisation of NR Latex**

NR latex can be destabilised in various ways such as acidification, addition of salts, mechanical agitation or freezing. In rubber product manufacture, the most important method of destabilisation is to produce gelation, which is an uniform destabilisation of the latex resulting in a three dimensional aggregate of rubber particles termed “gel”. Two methods of gelation widely used in industry are listed below [10].

#### **2.2.2.1 Gelation by Acids**

The addition of acids such as formic, acetic and sulphuric acids to NR latex provides a high electrolyte concentration. Consequently, the electrical double layer around the rubber particles is compressed and then the thickness of double layer

decreases. The interparticle repulsive potential is diminished and, hence, the aggregation of latex particles occurs.

#### **2.2.2.2 Gelation by salts**

The most important salts used for destabilisation of NR latex are based on calcium and zinc. Calcium salts, particularly calcium nitrate, are widely used because calcium ions form salts with all fatty acid soaps and with solutions of protein. High concentration of the ions can also reduce the colloidal stability by compressing the electrical double layer around the particle. Zinc salts destabilise latex in a similar way to calcium ions, but there are some significant differences. Zinc ions in latex react with ammonia to give complex amine cations. These cations also form insoluble salts with all fatty acid soaps but do not appear to react in the same way with proteins. This selective reaction of the ammoniated zinc ions appears to explain why zinc salts tend to have only a partial destabilising effect upon NR latex compared with the total destabilisation produced by calcium ions.

### **2.3 Stability of Natural Rubber Latex Dispersion in the blend**

Since natural rubber latex can be destabilised when raising the temperature in the blending process, natural rubber latex cannot be directly dispersed in gelatinized starch. In general, the surface-active agents are used to disperse fine particles of hydrophobic materials, including natural rubber latex, in aqueous solution. An



interfacial approach between lyophobic colloids and surface-active agents should be studied in order to further control the properties of natural rubber latex dispersion.

### 2.3.1 Theory of Stability of Lyophobic Colloids

Stability of lyophobic colloids is basically determined by the balance between repulsive and attractive potential energies of interaction as shown in the following equation [12,13];

$$V = V_R + V_A \quad (2.1)$$

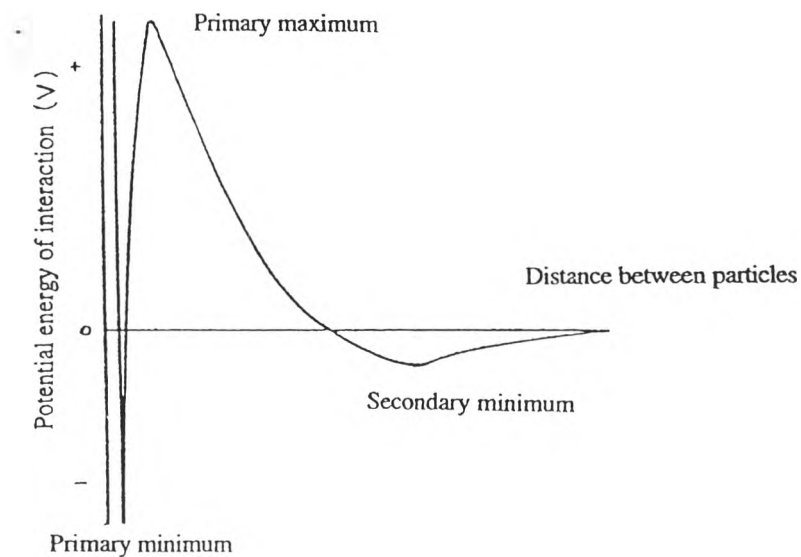
where,  $V$  : potential energy of interaction  
 $V_R$  : potential energy of repulsion  
 $V_A$  : potential energy of attraction

Typical potential energy curve is shown in Figure 2.2.

At a large distance, the flocculation may occur in secondary minimum because the value of  $V$  is reduced due to the exponential decay of electrical double layer around the particles. At intermediate distance, the repulsion force ( $V_R$ ) between two particles is greater than the attractive one ( $V_A$ ) providing the stable particles. At short distance, two particles are approached together and the attractive force is stronger than the repulsion. Therefore, the irreversible coagulation of particles takes place in

primary minimum. A number of circumstances lowering the potential energy maximum can be summarized into three main categories [13]:

- i) Increasing of ionic strength of the dispersion medium can decrease the repulsive potential energy.
- ii) For larger particles, the secondary minimum may become deeper than  $\sim 6kT$  and lead to flocculation of particles.
- iii) Addition of polyelectrolytes and hydrolysing inorganic ions, which act as crosslinking agents cause the flocculation of particles.

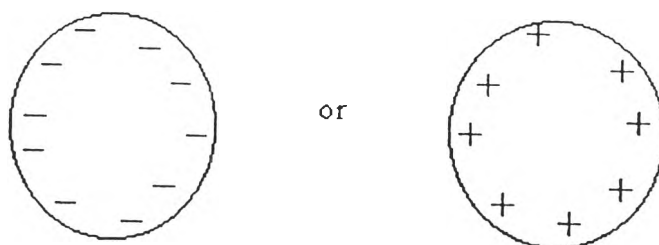


**Figure 2.2:** Potential energy of interaction as a function of distance between two spherical particles [13]

### 2.3.2 Adsorption of Surfactant on Spherical Colloids

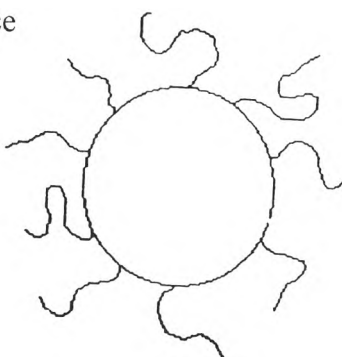
The adsorption of surfactant molecules on spherical particles can provide three types of particle structure surface [13]:

#### i) Smooth charged surface



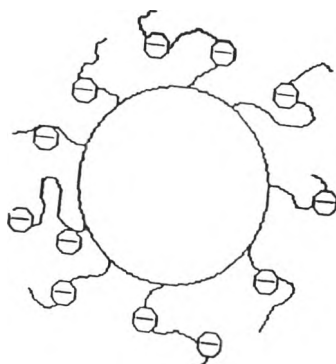
In this case, spherical colloids are adsorbed with ionic surfactant. The surface charge of colloids can be negative or positive depending on type of the ionic surfactants, *i.e.*, anionic or cationic surfactants. The stability of colloids is associated with electrostatic stabilisation.

#### ii) Hairly uncharged surface



This surface structure is due to the adsorption of non-ionic surfactant or polymer molecules on colloidal particles. The colloidal stability is governed by steric stabilisation.

### iii) Hairly charged surface



In this case, spherical colloidal particles are adsorbed with materials containing both non-ionic and ionic groups in molecules such as proteins and ammonium nonylphenyl ether sulphate. The colloidal stability concerns both electrostatic and steric stabilisations.

### 2.3.3 Adsorption of Non-ionic Surfactant on natural rubber latex particle

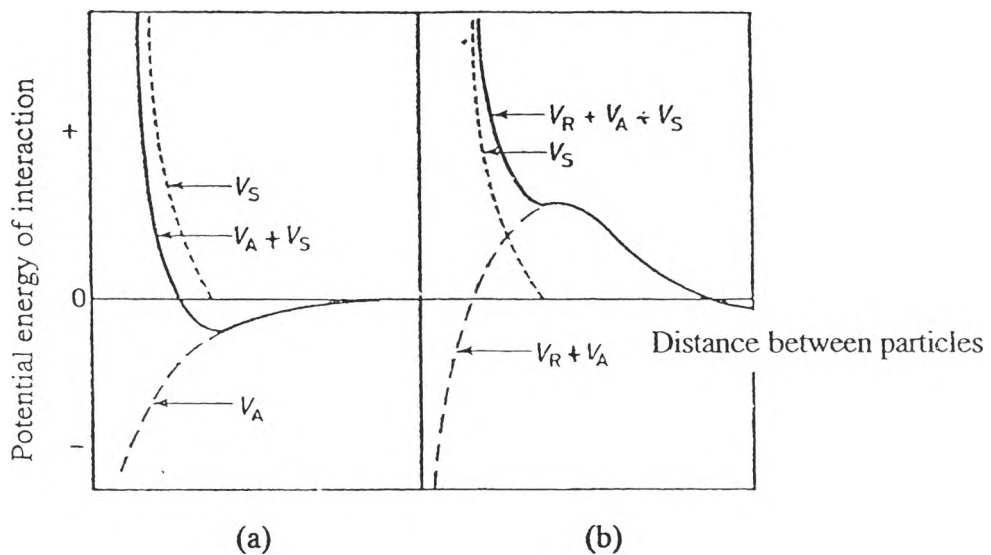
Most of non-ionic surfactants are basically composed of hydrophobic part (alkyl or nonylphenyl groups) and hydrophilic part (polyethylene oxide). The hydrophobic moiety adsorbs on particle surface while the polyethylene oxide (PEO) chains protruding in water from a layer around the particles. This configuration provides the stability of suspended particles with steric stabilisation. Therefore, the stability of particles adsorbed with non-ionic surfactant is not sensitive to the electrolyte concentration but it is a temperature sensitive system.

It is well known that the adsorption of non-ionic surfactant can affect the potential energy of interaction ( $V$ ) of smoothly charged surface particles as follows [13]:

$$V = V_R + V_A + V_S \quad (2.2)$$

Where  $V_S$  : potential energy caused by adsorbed non-ionic surfactant.

$V_S$  depends on the polymer-solvent interaction parameter ( $\chi$ ). In a good solvent, the positive value of  $V_S$  is obtained. The repulsive force between two particles increases and, hence, the particles are more stable. The potential energy curves of particles modified by the adsorption of non-ionic surfactant are shown in Figure 2.3.



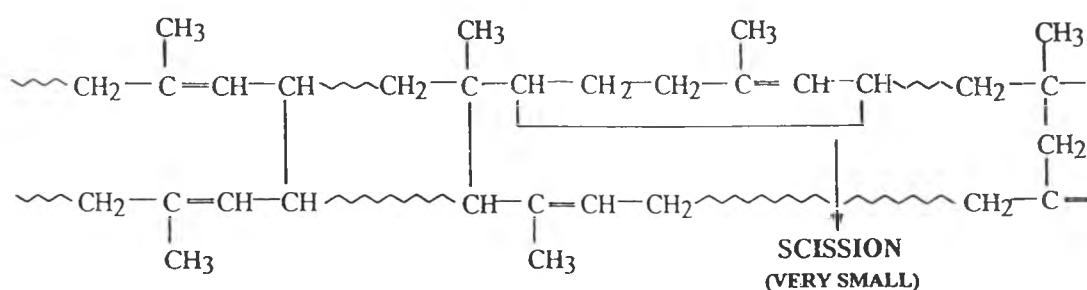
**Figure 2.3** : Potential energy curves of interaction against distance for interaction between two spherical particles adsorbed with non-ionic surfactant : (a) without potential energy of repulsion and (b) with potential energy of repulsion

## 2.4 Peroxide Vulcanisation

### 2.4.1 Characteristics of Peroxide Vulcanisation

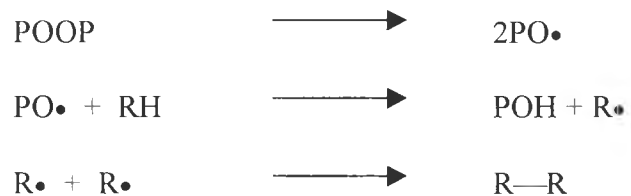
Peroxide vulcanisation is one of the systems of elastomer vulcanisation which use organic peroxide as crosslinking agents to form carbon-carbon crosslinks. It has several advantages over sulphur curing system. Peroxides can crosslink both saturated and unsaturated polymers. The vulcanisation has better heat-ageing resistance and lower compression set. In the case of white or transparent vulcanisates, peroxides give freedom from colour opacity and resistance to UV light discoloration. However, there are also some disadvantages compared with sulphur vulcanisation, for example, scorch times are short, cure times are long and less controllable. Many antioxidants also interfere with peroxide vulcanisation. In unaged vulcanisates, both tensile and tear strengths are inferior to conventional sulphur cured natural rubber vulcanisates and tension fatigue lifetimes are low [14].

The structure of peroxide vulcanised NR can be presented in Figure 2.4.



**Figure 2.4:** The simple representation of structure of peroxide vulcanised

The mechanism of rubber crosslinked by peroxide may be outlined as follows,



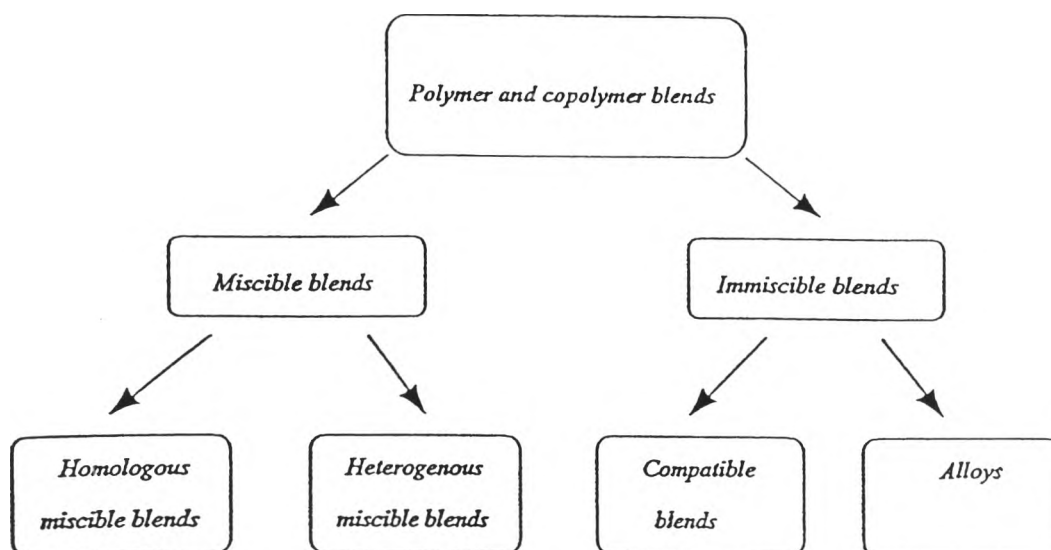
## 2.5 Blending Process

Different polymers when blended together may be miscible, partially miscible, or completely immiscible. General classification of polymer blends are given in Fig.

2.4. Preparation of polymer blends can be accomplished by [15]:

1. Mechanical mixing,
2. Dissolution in co-solvent then film casting, freeze or spray drying,
3. Latex blending (e.g. SAN + AB  $\rightarrow$  ABS),
4. Fine powder mixing,
5. Melt blending,
6. Use of monomer(s) as solvent for another blend component then polymerization as in IPN's or HIPS, manufacture
7. Diverse other methods of IPN technology

For economic reasons, mechanical blending predominates. The mechanical blending is employed in the present work, which the mixture is simply stirred at 70 °C for 15-20 min.



**Fig 2.4** Classification of polymer blends

## 2.6 Plastic foam

Cellular plastics or plastic foams, also referred to as expanded or sponge plastics, generally consist of a minimum of two phases, a solid polymer matrix and a gaseous phase derived from a blowing agent. There may be more than one solid phase present, as in case of a blend or alloy of polymers (generally heterogeneous) [16].

Plastic foams can be produced in a great variety of densities ranging from about  $1.6 \text{ kg/m}^3$  ( $0.1 \text{ lb/ft}^3$ ) to over  $960 \text{ kg/m}^3$  ( $60 \text{ lb/ft}^3$ ). Since the mechanical strength properties are generally proportional to the foam densities, the applications of these foams usually determine which range of foam densities should be produced. Thus, rigid foams for load-bearing applications require high density, fiber reinforcement, or both, while low densities are usually used for thermal insulation. Low-density flexible foams (around  $30 \text{ kg/m}^3$ ) are usually used in furniture and



automotive seating, while somewhat higher densities are used for carpet backing and energy-absorbing applications.

### **2.6.1 Methods of foaming**

The foaming of polymeric materials can be carried out by either mechanical, chemical, or physical means. Some of the most commonly used methods are the following [16,17].

1. Thermal decomposition of chemical blowing agents, generating either nitrogen or carbon dioxide or both, by application of heat or as a result of the exothermic heat of reaction during polymerization.
2. Mechanical whipping of gases (frothing) into a polymer system (melt, solution, or suspension), which hardens either by catalytic action or heat or both, thus entrapping the gas bubbles in the matrix.
3. Volatilization of low-boiling liquids (such as fluorocarbons or methylene chloride) within the polymer mass as a result of the exothermic heat of reaction or by application of heat.
4. Volatilization by the exothermic heat of reaction of gases produced during polymerization, such as occurs in the reaction of isocyanate with water to form carbon dioxide.
5. Expansion of gas dissolved in a polymer mass upon reduction of pressure in the system.
6. Incorporation of microspheres into a polymer mass. The hollow microspheres may consist of either glass or plastic beads.

7. Expansion of gas-filled beads by expansion of these beads in a polymer mass by heat of reaction (e.g. expansion of polystyrene beads in a polyurethane or epoxy resin system).

### **2.6.2 Properties of foam**

Foams may be flexible or rigid, depending upon whether their glass transition temperature is below or above room temperature, which in turn depends upon their chemical composition, the degree of crystallinity, and degree of cross-linking. Intermediate between flexible and rigid foams are semirigid or semiflexible foams. The cell geometry may be open-(tunnels between the cells), or closed-cell. In comparison with closed-cell foamed polymers, open-cell foamed plastics have a higher absorptive capacity for water and moisture, a higher permeability to gas and vapor, less effective insulation capabilities for either heat or electricity, and a better ability to absorb and damp sound [16].

### **2.7 Literature Reviews**

Altieri et al [1] studied a process to prepared a biodegradable shaped product comprising an expanded modified flour product preferably having at least 40% by weight amylose content and containing about 2% or more by weight of an inorganic water soluble salt, said expanded product having a low density, closed cell structure with good resilience and compressibility. Another embodiment provides a biodegradable packaging material comprising an expanded, low density, closed cell

modified flour product, the flour preferably having at least 40% by weight amylose content and containing about 2% or more by weight of an inorganic water soluble salt, and the expanded product having a bulk density of less than about 2.0 lb/ft.<sup>3</sup>, a resiliency of at least about 50%, and a compressibility of from about 100 to 800 g/cm<sup>2</sup>.

Lacourse et al. [2] studied a process to produce a biodegradable packaging material comprising an expanded high amylose starch product having at least 45% by weight amylose content, said expanded product having a low density, closed cell structure with good resilience and compressibility. Another embodiment provides a method of preparing a low density, biodegradable packaging material comprising extruding a starch having at least 45% by weight amylose content, in the presence of a total moisture content of 21% or less by weight, at a temperature from 150 to 250°C.

Shogren et al. [3] prepared composite foam plates by baking a mixture of granular starch and aqueous poly(vinyl alcohol)(PVOH) solution inside a hot mold. Foam strength, flexibility, and water resistance were markedly improved by addition of 10-30% PVOH to starch batters. The improvement in strength at low humidity was greater for partially hydrolyzed PVOH (88%) while strength at higher humidities improved most with fully hydrolyzed PVOH (98%). 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. The starch component was gelatinized (melted) during baking while the PVOH component crystallized to a high degree during baking. Baked foams prepared from starch and PVOH have mechanical properties that are adequate for use as packaging containers over a wide range of humidity.

Kakinoki et al. [4] prepared foam-expanded material by mixing starch, rubber latex and water. The proportion of rubber latex relative to starch is 3-60 weight %. The amount of water is 10-25 weight %. This mixture is extruded from the extruder in the form of rod, cut into pellets or shaped into granules. When these granules are introduced in a mold and heated to a temperature within the range 100 – 250 °C, this granule material foams within a few seconds and expands to fill the shape of the cavity of the mold. In the expansion process, the material expands to 3-40 times its original volume. The strength and resilience of the foam-expanded material obtained are not inferior to those of expanded polystyrene.

Hyrum et al. [5] reported a biodegradable closed cell light weight packaging material formed by extrusion of a modified starch. Non-modified starch is reacted in an extruder with certain mild acids in the presence of water and a carbonate compound to generate CO<sub>2</sub>. Resiliency of the product is said to be 60% to 85% with density less than 0.032 g/cm<sup>3</sup>.

Tomka et al. [18] studied a process for producing a substantially biologically degradable polymer foam, a thermoplastic or disaggregated starch or a polymer mixture of thermoplastic or disaggregated starch with at least one biologically degradable hydrophobic polymer. In addition, the material is mixed with a biologically degradable fibrous or capsular material capable of binding water by capillary action, said material being at least partially treated or saturated with water before being mixed with the polymer. The polymer/material mixture thus obtained is processed under controlled pressure and temperature so that the water bound by capillarity in the material is released and causes the polymer to foam. The polymer

foamed obtained is suitable as a packaging material, as thermal or acoustic insulation, or, in general, as absorbing material and for various uses in construction.

Boehmer et al. [19] studied a process to prepared an expanded foam materials having a high degree of biodegradability by combining a starch-graft copolymer (SGC) with grain based starch containing materials and 15-25% water and expanding the mixture either with or without blowing agents. The mixture of SGC and grain based material is directly expanded at elevated temperature with an extruder or other expansion means. The product may be customized for particular applications by manipulating the particular grafted monomer, manipulating the ratio of SGC to grain based material and/or by the addition of nucleators, blowing agents, plasticizers or other additives, and/or by varying moisture content and the conditions of expansion.

Akamatu et al. [20] studied a process for producing a biodegradable resin foam, having the steps of mixing a starch polymer containing from 5% by weight to 30% by weight of water, a vinyl alcohol resin containing from 5% by weight to 30% by weight of water, a nonionic surfactant, an inorganic filler, and optionally a thickening agent, optionally adjusting the water content of the mixture, to prepare a composition having from 5% by weight to 30% by weight of water on the whole, based on total weight of the composition; melting and expanding it to prepare a foam, which has a low density and fine closed cells, and shows a good surface condition in a molded body.

Kustner et al. [21] studied a process and device for producing a foamed product or foam made of unmodified starch. The starch is introduced through a feed opening into a treatment chamber containing a conveying device. The conveying device conveys the starch from the feed opening in an axial direction through the

treatment chamber. The conveying device has an increasing effective cross section so that by increasing the volume, or by expansion foaming and/or break down of the starch is achieved. An outlet is provided at the other end of the treatment chamber for extruding the product.

Franke et al. [22] provided a method for producing an improved high resiliency expanded starch product which comprises extrusion of a starch-containing mixture through an expansion die followed by subjecting the extrudate to pressure perpendicular to the direction of extrusion, for example by use of a rolling device. The rolled extrudate strand is then cut to desired length to suit the planned application. Preferably the pressure applied to the hot extrudate strand is sufficient to substantially crush the cell in the extrudate. Surprisingly, crushing the cells of the expanded product significantly improves the resiliency of the product. The rolled expanded starch product is biodegradable and has high resiliency and other properties attractive for use in packaging materials such as loose fill.

Neumann et al. [23] reports biodegradable, compressible and resilient starch-based packaging fillers with high volumes and low weights. The products are formed by extrusion of a blend of non-modified starch with poly(alkylene glycol) or certain derivatives thereof (up to 10% by weight) and a bubble-nucleating agent, such as silicon dioxide. The nucleating agent is said to enhance bulk resiliency and uniformity of cell structure of the extrudate products. The starch blends is “preconditioned” by steam injection prior to addition to the extruder. Bulk resiliency of the exemplified wheat starch products (shaped as small or large tube) ranged from a low of 56.8% (0.5% silicon dioxide, small tube) to a high of 69.9% (6.0% PEGC a poly(ethylene glycol) derivative with molecular weight 20,000, 1.0% silicon dioxide, large tube).

Bulk densities for these exemplary products was 1.69 lbs/ft.<sup>3</sup> and 1.22 lbs/ft.<sup>3</sup>, respectively.

Knight et al. [24] reported the production of shaped articles from high amylose starch. A hot melt is formed under pressure at elevated temperature from a mixture of high amylosic starch with water and with optional plasticizers and lubricants and extruded to form a shaped article. The hot melt is subjected to atmospheric or subatmospheric pressure just prior to extrusion or to subatmospheric pressure after extrusion to remove water from the hot melt. This first extrudate can then be subjected to a second extrusion to form a film or other shaped article. The film produced in the two-step process is said to be highly elastic with elongation before failure from about 80% to 240%.