CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Multicomponent Polymers

2.1.1 Scope of multicomponent polymer

<u>Block and Graft Copolymers</u>[3]

Block copolymers are linear chains with alternating long sequences of one repeating unit. There are 3 major types of block copolymer, AB type(1), ABA type(2) and $(AB)_n$ type(3).

~AAAAAAABBBBBBB~   ~AAAAAABBBBBBAAAAAA~

(1)   (2)

AB type   ABA type

~AAAAABBBBBAAAAABBBBB~

(3)

$(AB)_n$ type

The long sequences usually are homopolymers but can also be random or alternating copolymers. Examples of block copolymers are polystyrene-polybutadiene simple block copolymers, polystyrene-polybutadiene-polystyrene ABA type(2) block copolymers.

Graft copolymers are branched chains with a continuous backbone of one structural type and side chains of another.

BBBBBBBBBB~
|
~AAAAAAAAAAAAAAAAAAAAAA~

(4)

simple graft copolymer

Backbone and pendant branches can be either homopolymers, alternating copolymers , or random copolymers. A maleic anhydride is an example of simple graft copolymers.
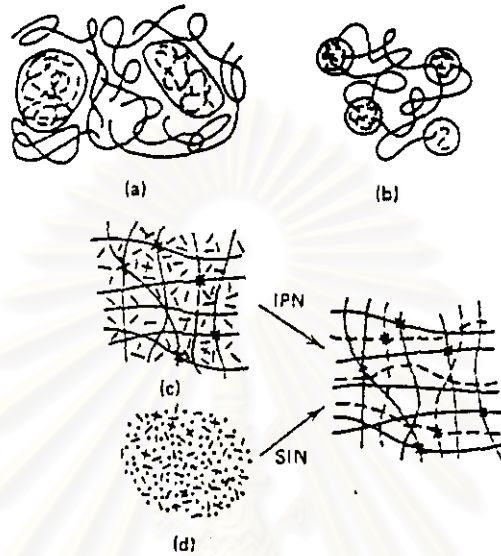

Figure 2.1 Schematic illustration of molecular and phase domain morphologies in various types of polymer blends: polymer A, —; polymer B   ; crosslinks, (a) Mechanical blend. Particles of A dispersed in B. (b) A-B-A block copolymer. Blocks between domains formed by end blocks of A. (c) and (d) Interpenetrating polymer networks (IPN). In (c), monomer A and crosslinking agent swelled into crosslinked polymer B. A is polymerized to produce an interpenetrating polymer network. In (d), monomers A and B and crosslinking agents are mixed and simultaneously polymerized to produce a similar result, designated as simultaneous interpenetrating network (SIN).

Polymer blends

A polymer blends is defined as a combination of two or more polymers resulting from common processing step, e.g. mixing of two polymers in the molten state, in latex, casting from common solvent, etc. these preparation methods do not usually lend to chemical bonding between the components.

Interpenetrating Network (IPN)[4]

An interpenetrating network (IPN) from a particular class of multicomponent polymeric systems, consist of two separate crosslinked polymers with no covalent bonds between network. However, binary polymer systems with only one polymer crosslinked are also classified as a type of IPN but are more commonly known as semi-IPN

2.1.2 Comparison of various types of multicomponent polymers

Preparation

Block and graft copolymers, by virtue of covalent bonding between polymeric structures of difference compositions, are prepared in a two-step process. For block copolymers, the first polymer is formed under suitable conditions so that chain ends contain reactive species such as alcohol, amines, halides or cations, anions, and radical. A second monomer is then polymerized through the activation of end groups. The preparation of graft copolymers differs from that of block copolymers only in that activation is restricted to polymer's backbone.

Polymer blends are prepared by mixing different homopolymers or copolymers. The mixing process is aided by high temperatures, diluents or suspending media. Interpenetrating networks can be prepared by swelling a crosslinked polymer A with a second monomer B containing appropriate crosslinking agents, followed by polymerization of the second monomer.

Structure

Since different polymers are usually thermodynamically incompatible, multicomponent polymers commonly exhibit a two-phase morphology with the minor component forming a dispersed phase or domain, and the major component forming a matrix. Thus block and graft copolymers, polymer blends or interpenetrating network polymers are formed into multiphase structures if their

different compositions of size of domains, depend on the nature and composition of constituted polymers and on the method of preparation.

On the other hand, if the polymers concerned are compatible, which is rarely, the resulting multicomponent polymers will have homogeneous structures. In any case, molecular homogeneity or true solution cannot be achieved for polymer systems and a certain degree of in homogeneity still exists.

Properties

Properties of multicomponent polymers, whether they be block or graft copolymers, polymer blends or IPNs, depend primarily on whether they are homogeneous or heterogeneous polymers.

Homogeneous multicomponent polymers show properties that are intermediate between those of the polymers in a manner which depends on composition. Heterogeneous polymers, on the other hand, possess both properties and characteristics of their constituents, thus allowing the realization of property reinforcement in a single product. Properties of heterogeneous polymers are also complicatedly determined by their structures which can assume a variety of forms depending on chemical compositions and methods of preparation. Heterophase copolymers, and IPN generally exhibit similar properties; the major differences lie in the strength of adhesion between phases.

2.2 Polymer Blends

2.2.1 Reason for blending[5]

- Extending engineering resin performance by diluting it with a low cost polymer

- Developing materials with a full set of desired properties

- Forming a high performance blend from synergistically interacting polymers.

- Adjusting composition of the blend to customer specifications

- Recycling industrial waste

2.2.2 Method of preparation of polymer blends

Polymer blends are prepared by mixing polymers in a mixing process, which is aided by high temperatures and diluents or suspending media. Melt mixing, solution blends, and latex mixing are the principal commercial methods for preparing polymer blends[3].

Melt Mixing

Melt mixing of polymer avoids the contamination and removal problems of diluents and assures that a system will not change in molding operations. Because of the amount of heat necessary to maintain a low viscosity and the shearing rates needed for through mixing, a degradation of either or both polymers can occur. Melt mixing is used for systems in which thermal degradation does not ordinarily occur. The shearing forces required to blend high molecular weight elastomers are provided only by open-roll mills, internal mixers (e.g. Banbury) and extruders. Mixing equipment for melting blending is described below[6] :

1) Open-roll mill : A two-roll mill consists of two opposite rotating parallel rollers placed close to another with the rolls lying in a horizontal plane so that a small gap or " nip" exits between the cylindrical surfaces. The nip is adjustable by moving the rollers. The rollers are run cold for rubber mixing and hot for plastic mixing. The rollers have different speeds, the front rolls are usually slower and the back roll is faster. Material reaching the nip is deformed by frictional forces between itself and the rolls and is made to flow through the nip in the direction of roll motion.

2) Internal mixer : An internal mixer consists of a feed hopper standing above a mixing chamber. A floating ram that forces the material into the mixing chamber contains rotors of complex shape, moving at different speeds. In the design of internal mixer, these developments include increase the number of wings,

on the mixer rotors to increase the quantity of high shear areas inside the mixer, and allowing the rotors to intermesh so that dispersive shearing occurs not only between the rotor tip and walls, but also between the rotor themselves. Dispersive mixing requires high shear stress. It is often important to efficiently cool the rubber in an internal mixer in order to maintain a high viscosity. Of course, precise temperature control in general requires the capability for efficient removal of heat. The most effective cooling method is to drill passages that allow flow of the cooling close to the inner surface of the mixing chamber.

3) Extruder : Along with the use of extruder in the transfer and forming of rubber stocks, they can also contribute to distributive mixing. Increasing demands for the screw and barrel of the extruder to not only convey the materials to a die but also its mixing have led to modification of the mix by exchange of materials between planes. Representative approaches include the use of pins in the barrel to divert and divide the flow of materials and the use of the cavity transfer mixer (CTM); it has hemisphere cavities in the screw and barrel to promote exchange of materials. The resulting diversion and reorientation of the flow stream improves the efficient distributive blending of the extruder. For an extruder to perform the dispersive functions of an internal mixer, special mixing screws must be employed. These can contain dams so that the material is forced through a tight clearance with the wall and is thereby subjected to large shearing stress. Twin-screw extruders can also be used where shearing force is developed by employing various mixing elements.

Solution Blending

In solution blending, a diluent is added to lower the temperature and shear-force requirements for a satisfactory mixing, without degradation. However, attempts to remove the diluent can often lead to changes in the domain sizes of the blend and in severe cases cause a complete polymer separation. As solvent is

moved from a one- phase mixed polymer solution, contacts of dissimilar solvated polymers will bring about phase separation.

Latex Mixing

Latex Mixing is one of the most important techniques for the preparation of commercial polymer blends. In a latex, polymers are present as suspended microspheres. Interactions of neighboring spheres are prevented by the suspending medium (soap). After through blending, a mixture of two latices with different polymers contains a random suspension of dissimilar particles, each is unaffected by the other. Coagulation is also random because the rate of flocculation is dependent entirely on the soap concentration and not on polymer characteristics. Coagulated material contains an intimate mixture of the polymers. Melt mixing is often employed for compounding and pelletizing the latex-blend material, and necessary precaution in this stage must be taken to avoid degradation.

2.2.3 Category of polymer blends

The combination of two or more polymers has been frequently not satisfied to the required application yet, due to the majority of polymers do not readily mix with one another. The mixing level can be classified into 3 categories[5]:

1) Miscible polymer blend: The miscible polymer blend is a class of materials, which is found to be homogeneous down to the molecular level. It is associated with the negative value of free energy of mixing; $\Delta Gm = \Delta Hm < 0$, e.g., polystrene-poly (2,6-dimethyl 1,4 phenylene oxide).

2) Immiscible polymer blend: The polymer blend shows a positive value of the free energy of mixing; $\Delta Gm = \Delta Hm > 0$, e.g., polyethylene-poly(methyl methacrylate).

3) Partially miscible polymer blend: The mixture always forms two separated phases comprising A and B alone plus an additional phase containing a mixture of A and B, e.g., polystyrene-poly(vinyl methyl ether). The different characteristics of the above polymer blends can be distinguished by observing the transition temperature which is shown in Figure 2.2.
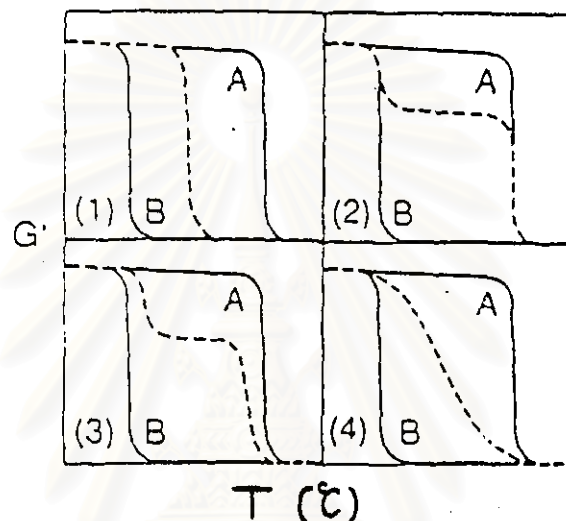

Figure 2.2 Schematic representation of temperature dependence of storage shear modulus for polymers A and B (solid line) and their 50:50 mixture (broken line). (1) Miscible blend, (2) Immiscible, (3) Partially miscible, (4) Immiscible blend with fine dispersion and broad glass transition region.

Figure 2.2 shows the relationship between storage modulus and temperature. The solid lines represent the behaviors of neat polymers and the broken line of their 50:50 blend. The sudden drop of a modulus is associated with the onset of molecular thermal motion in the region of glass transition temperature (T_g). The four schematics illustrate typical traces of (1) miscible blend, (2) immiscible, (3) partially miscible, and (4) immiscible blend with fine dispersion, respectively. The first characteristic traces represent the miscible blend which has only one T_g. The following picture (2) is the traces of immiscible blend which shows two T_g peaks. Both T_g peaks are similar to their individual materials. The third

feature shows the partially miscible blend. It has two Tg peaks but both are shiftily. The last picture shows an immiscible blend with fine dispersion. Thus the broad glass transition temperature is obtained.

Since miscible blend is rarely observed. The miscibility of a polymer mixture can be done by addition of a compatibiliser. Compatibiliser is used for modification of interfacial properties of immiscible polymer blend leading to the formation of a polymer alloy as shown in Figure 2.3.
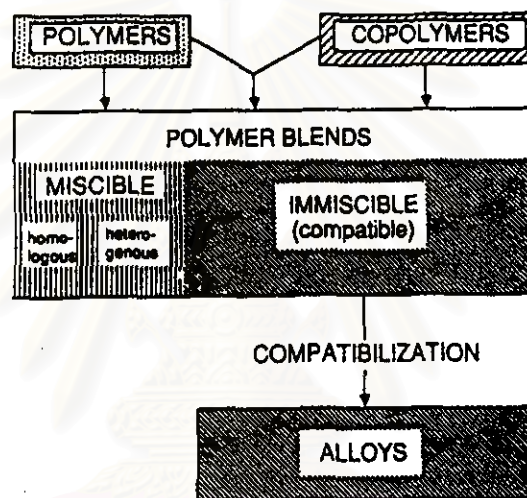

Figure 2.3 Interrelation in polymer blend nomenclature.

2.2.4 Blend Morphology

Although many miscible polymer pairs have been identified, most combinations of polymers are immiscible. In many instances, phase-separated blends are preferred for achieving useful results[7]. For example, such polymer-polymer composites yield materials whose stiffness can be adjusted, in principle, to any value between those of the component polymers. However, tailoring blends to achieve this or other characteristics requires, among other things, control over the spatial arrangement or morphology of the phases and some degree of stability once formed. These arrangements may consist of one phase dispersed as simple
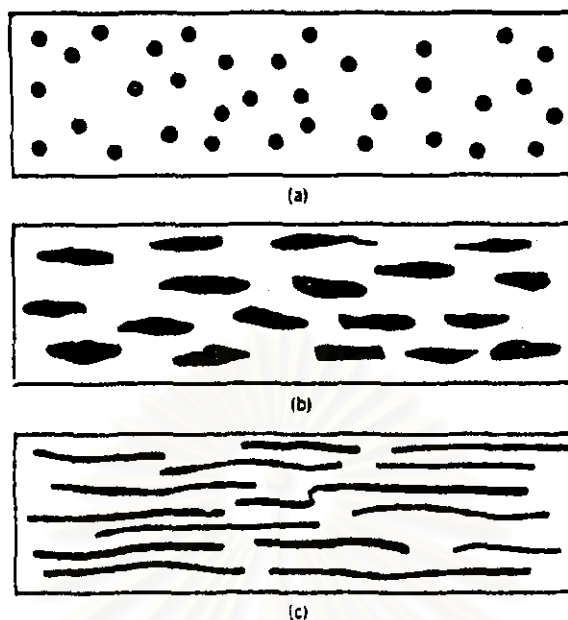
Figure 2.4 Different types of dispersion of a polymer (dark regions) in the matrix of an immiscible polymer. The spherical droplets (a) are progressively extended into platelets, (b) (biaxial) or fibrils, and (c) (uniaxial) by deformation.
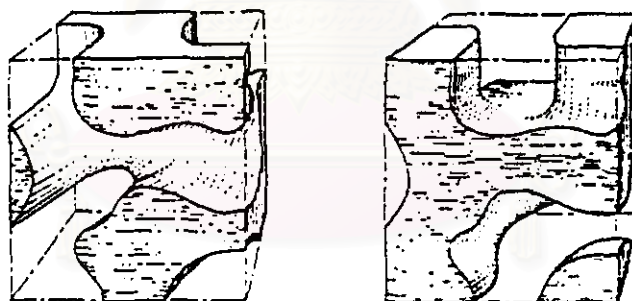

Figure 2.5 Conceptual illustration of an interpenetrating network of phases by showing the two interlocking materials separated from one another.

spheres in a matrix of the other polymer, as shown in Figure 2.4a. On the other hand, the dispersed phase may take the form of fibrils or platelets with varying aspect ratios, as shown in Figures 2.4c and 2.4b, respectively. Another distinct morphology consists of both phases simultaneously having a continuous character

or an interpenetrating network of phases (Figure 2.5). The typical dimensions of the phases are important in all these morphologies.

2.3 Expanded solid polymers

Expanded polymer is the cellular polymer which has predominantly closed cells and is prepared from polymers.

2.3.1 Theory of the expansion process

The most important process for preparation cellular polymer consists of expanding a fluid polymer phase to a low-density cellular state and then preserving this state. The expansion process may be divided into three steps[8]:

      i) creating small discontinuities or cells in a fluid or plastic phase.

      ii) causing these cells to grow to a desired volume.

      iii) stabilizing this cellular structure by physical or chemical means.

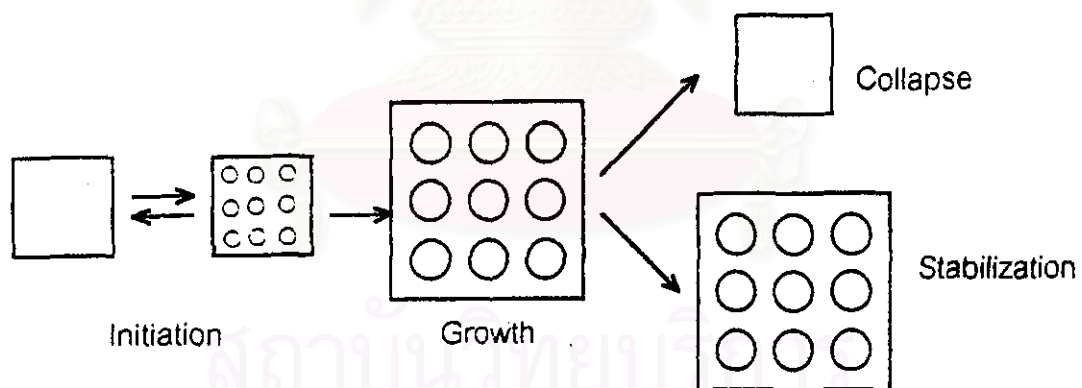These steps are shown in Figure 2.6.

Figure 2.6 Steps in preparation of cellular polymers.

Bubble Initiation

The development of bubbles is called nucleation. The process has several sources:

1) dissolved gases that are normally present in the liquid or polymer solution and forced into supersaturation by increased temperature.

2) low boiling liquids that are incorporated into the system as blowing agents and forced into the gas phase by increased temperature or decreased pressure.

3) gas produced as blowing agents, e.g., the aqueous isocyanate reaction is used for CO_2 production in polyurethane foams.

4) chemical blowing agents that decompose thermally to form a gas.

Bubble Growth

The growth of a hole or cell in a fluid medium is controlled by the pressure difference, P, between the inside and the outside of the cell, the surface tension of the fluid phase, γ, and the radius, r, of the hole, according to equation 2.1.

$$P = 2\gamma/r \tag{2.1}$$

The pressure outside the cell is the pressure imposed on the fluid surface by its surroundings. The pressure inside the cell is the pressure generated by the blowing agents (qv) which is dispersed or dissolved in the fluid.

Coalesence of cells

Growth of cells

$$P_2 - P_1 = \Delta P = 2\gamma\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$
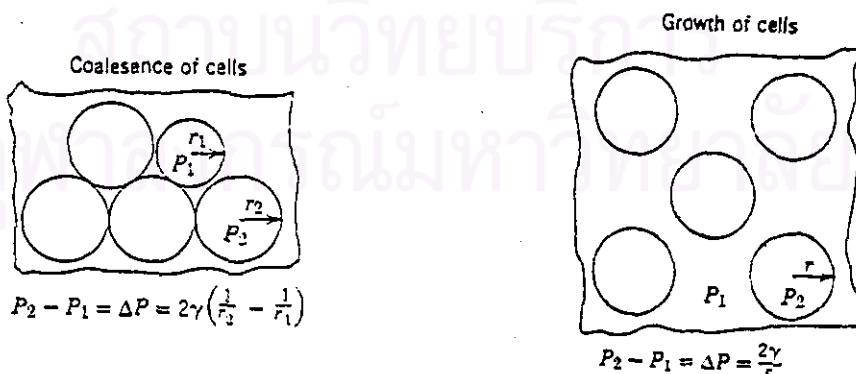
$$P_2 - P_1 = \Delta P = \frac{2\gamma}{r}$$

Figure 2.7 Relations governing cell growth and collapse.

During the time of cell growth in a foam, there are a number of properties of the system which are greatly changed. Cell growth can therefore be treated only qualitatively; the following considerations are of primary importance:

(a) the fluid viscosity is changing considerably, which tends to influence both the cell growth rate and the flow of polymer from cell walls to intersections leading to collapse;

(b) the pressure of the blowing agent (qv) decreases, falling off less rapidly than an inverse volume relationship because new blowing agent diffuses into the cells as the pressure falls off according to equation 2.1;

(c) the rate of growth of the cell depends on the viscoelastic nature of the polymer phase, the blowing agent pressure, the external pressure on the foam, and the permeation rate of blowing agent through the polymer phase; and

(d) as a consequence of equation 2.1, the pressure in the cell of smaller radius, r_2, is greater than that in the cell of larger radius, r_1. There will thus be a tendency to equalize these pressures either by breaking the wall separating the cells or by diffusion of the blowing agent from the small to the large cells. The pressure difference ΔP between cells of radii r_1 and r_2 is shown in equation 2.2 and Figure 2.7.

$$\Delta P = 2\gamma(1/r_1 - 1/r_2) \tag{2.2}$$

Bubble Stabilization

The increase in surface area corresponding to the formation of many cells in the plastic phase is accompanied by an increase in the free energy of the system, and hence the foamed state is inherently unstable. Methods of stabilizing this foamed state can be generally classified as chemical, i.e., the polymerization of a fluid resin into a three-dimensional thermoset, by cooling the expanded polymer to a temperature below its second-order transition temperature, or its crystalline melting point to prevent polymer flow.

The factors which merit important consideration where the chemical method of dimensional stabilization is utilized are:

1. Chemical of the system. This determines both the rate at which the polymer phase is formed and the rate at which it changes from a viscous fluid to a dimensionally stable thermoset phase. It also governs the rate at which the blowing agent is activated, whether it can be due to temperature rise or to insolubilization in the liquid phase.

2. Type and amount of blowing agent. These factors govern the amount of gas generated, the rate of generation, and the pressure which can be developed to expand the polymer phase. They also determine the amount of gas lost from the system relative to the amount retained in the cells.

3. Additives to the foaming system. Additives can influence greatly nucleation of foam cells, either through their effect on the surface tension of the system, or by acting as nucleating sites from which cells may grow. They can influence the mechanical stability of the foam structure considerably, either by changing the physical properties of the plastic phase or by providing discontinuities in the plastic phase which allow blowing agent to diffuse from the cells to the surroundings.

4. Environmental factors such as temperature, geometry of foam expansion, and pressure also influence the behavior of thermoset foaming systems.

The factors to be considered in physically stabilized foaming systems are essentially the same as for chemically stabilized systems, but for somewhat different reasons. Such factors are:

1. Chemical composition of the polymer phase. The type of polymer determines the temperature at which foam must be produced, the type of blowing agent required, and the type of cooling of the foam necessary for dimensional stabilization.

2. Blowing agent composition and concentration. These control the rate at which gas is released, the amount of gas released, the pressure generated by the gas, escape or retention of gas from the foam cells for a given polymer, and heat absorption or release due to blowing agent activation.

3. Additive. Additives have the same effect on thermoplastic foaming processes as upon thermoset foaming processes.

4. Environmental conditions. Environmental conditions are important in this case because of the necessity of removing heat from the foamed structure in order to stabilize it. The dimensions and size of the foamed structure are also important for the same reason.
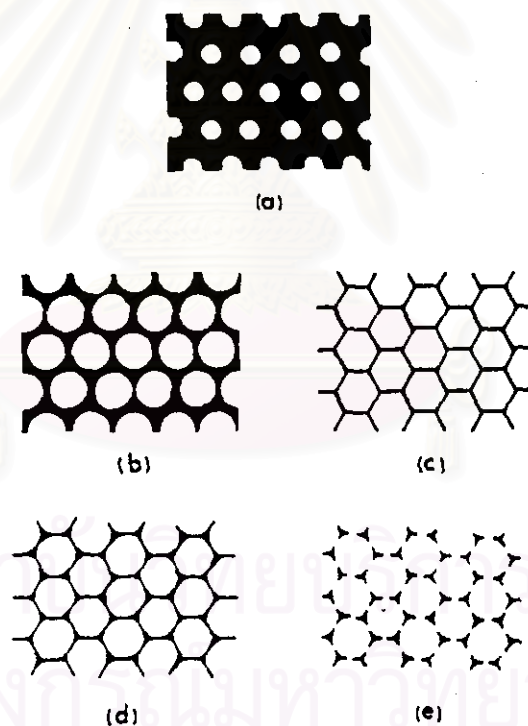

Figure 2.8 Idealized two-dimensional cellular structures at different stages of foam expansion.

Representations of idealized structure at different stages of the expansion process[9] are given in Figure 2.8. In the first instance the bubbles are dispersed

throughout the liquid and if stabilized at this stage the foam would have high density, Figure 2.8 (a). For spherical bubbles of uniform size, the lowest value of density is when the bubbles are close packed, Figure 2.8 (b). If the expansion process is allowed to continue the bubbles touch and distort to fill the interstices, forming, in the three-dimensional case, polyhedral structures which are often represented in the literature by idealized form of a pentagonal dodecahedron (Figure 2.8 (c)). Depending on the physical states of the liquid system, such as viscosity and surface energy, gravitational and other forces may cause the liquid material to concentrate at the intersection of the elements of the repeating cells to form Plateau borders which are usually tricuspid in cross-sectional shape, Figure 2.8 (d). At this stage the foam is of low density and is closed cell. However, the membranes between the cell struts which result from the intersection of the spherical bubbles (the 'windows') may be ruptured. In the case of polyurethane foams this can be achieved by means of a chemically based cell-opening mechanism or by post-processing treatment (reticulation). These procedures give open cell foams with varying degrees of connectivity (Figure 2.8 (e)). Even with the same generic type of polymer, this can depend on the starting formulation and process conditions.

2.3.2 Production methods of expanded polymers

The techniques for production of expanded polymers can be divided into 4 techniques depending upon the final shape of products

Extrusion process[10]

1) Direct extrusion process

A block diagram of the general extrusion process is shown in Figure 2.9 Commercially, the steps of the extrusion process may be expected on equipment of several different configurations, single screw extruder, twin screw extruders, and tandem extruder lines. The tandem extruder can prepare expanded polymers which

have small cross section and low extrusion rate as depicted in Figure 2.10 The primary extruder has a two-stage screw for pumping and melting in the first stage and mixing the melt with solid additives and blowing agent in the second stage. The second extruder cools the mixture to the optimum foaming temperature.
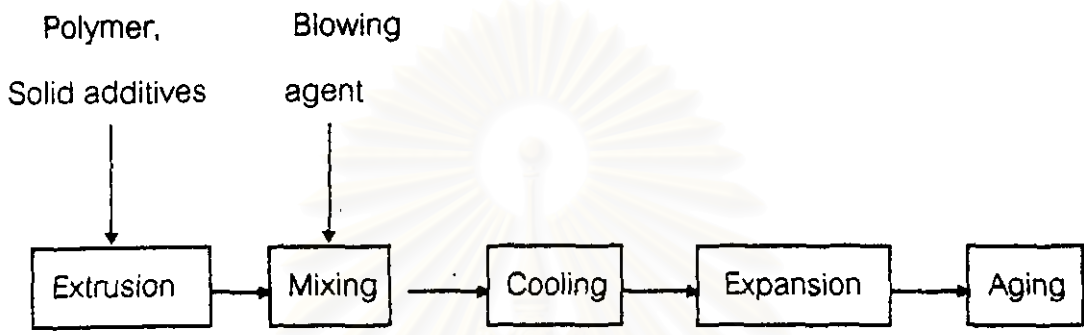
Polymer,
Solid additives

Blowing
agent

Extrusion → Mixing — Cooling → Expansion — Aging

Figure 2.9 Flow diagram of extrusion process

Polymer,
Solid additive
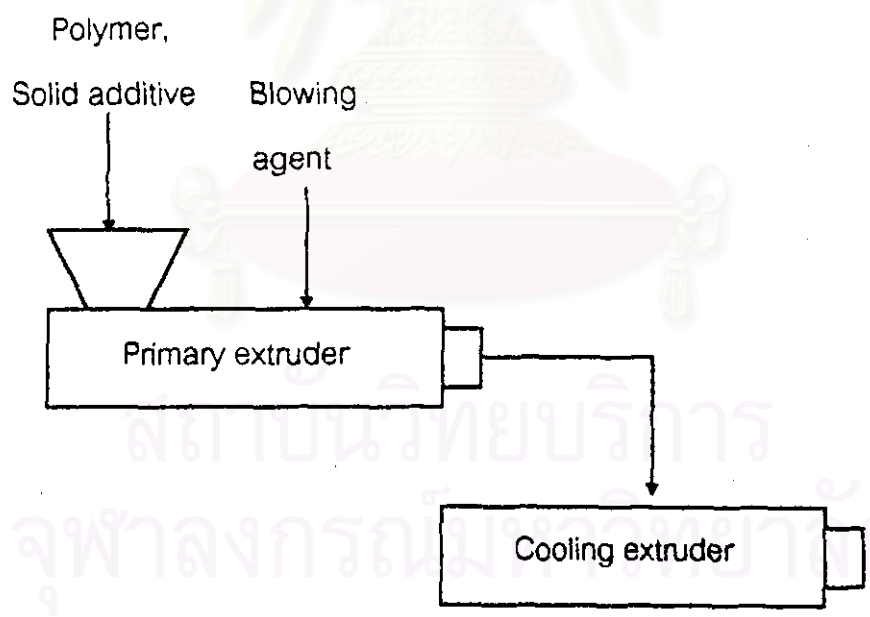
Blowing
agent

Primary extruder

Cooling extruder

Figure 2.10 Schematic diagram of tandem extruder

2) Accumulating extrusion

An accumulating extrusion system is used for the production of large plant products. As shown in Figure 2.11, the foamable melt is fed into an accumulator by a single screw extruder and rammed out through a die orifice.
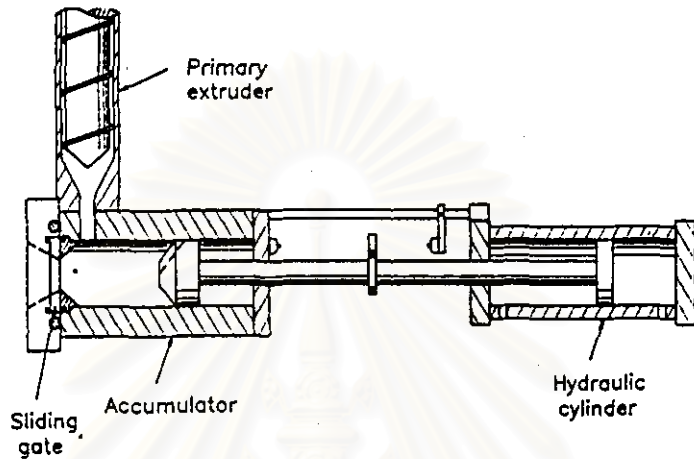

Figure 2.11 Accumulation extrusion system

3) Flash extrusion

The flash extrusion process is used to prepare thin expanded sheet, such as ultra-low density PP foam sheet. The sheet line consists of tandem extruder, and accumulating vessel and annular die.

Compression moulding process[10, 11]

This process can be classified into sub-groups, one-step expansion and two-step expansion processes, as shown in Figure.2.12. In the one-step expansion process, a homogeneous mixture of the polymer, crosslinking and blowing agents are formed into a slab, heated in the mould on a press so that the crosslinking agent can crosslink the polymer and blowing agent can decompose, and expanded by a release of pressure. In the two-step expansion process, the mixture is expanded only partially by quenching. Foam expansion is subsequently

completed by heating the partially expanded polymer in a mould or hot oven at atmospheric pressure.
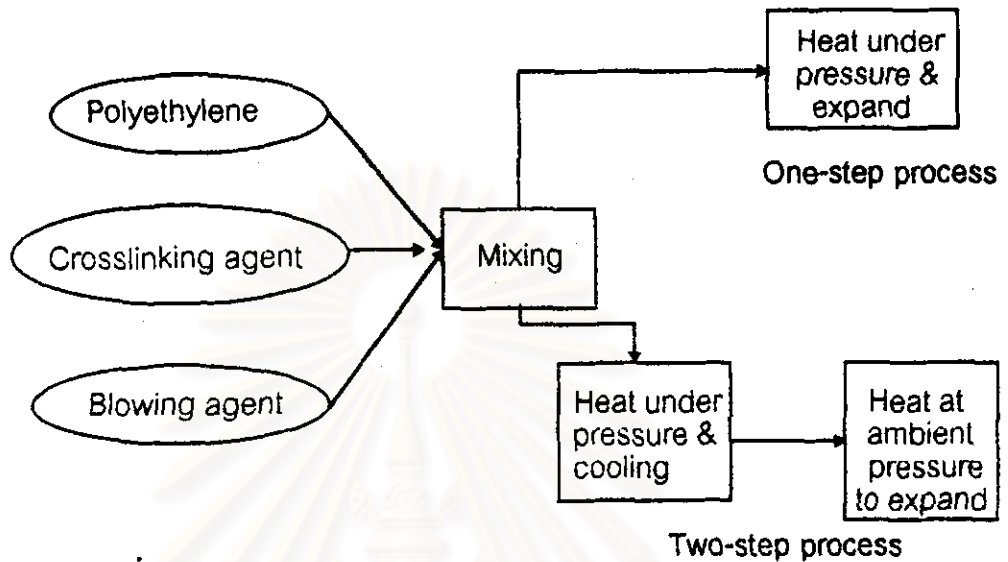

Figure 2.12 Compression moulding technique

Injection moulding process[11]

The injection moulding technique is based upon the simultaneous crosslinking and expansion of the mixture in a heated mold cavity. It is used in the production of complex shape products and reducing problems of scrap. The suitable screw and mould design are necessary, otherwise the expansion systems or the crosslinking agent may be decomposed prior to injection.

Radiation crosslinking process[10, 12]

The flow diagram of the radiation crosslinking process is shown in Figure 2.13. The process has four steps, mixing the polymer with the blowing agent, extruding the mixture into a solid sheet of the desired thickness, crosslinking the sheet by irradiation with a high energy ray and expanding the sheet in an oven.
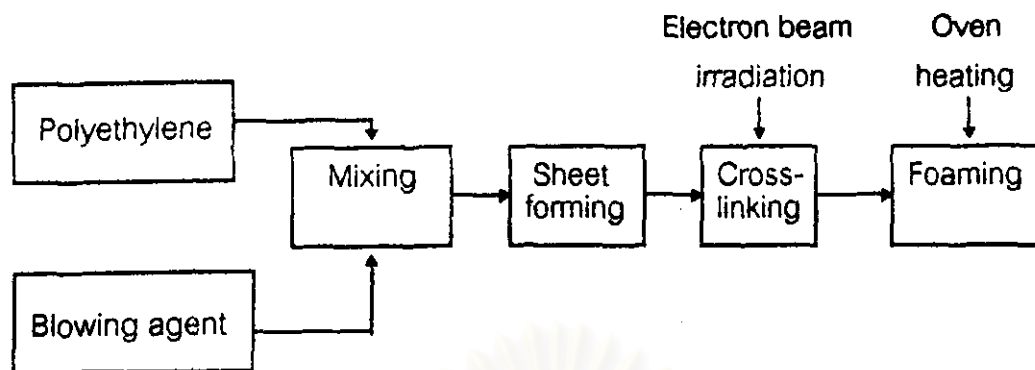
Figure 2.13 Flow diagram of radiation crosslink process

The present thesis will concern only with the cellular polymer which is obtained from a single-stage process of compression moulding.

2.3.3 Chemical composition of expanded polymers

1) Polymer matrix[1]

The properties of expanded polymer directly depend upon original properties of base polymer. Base polymer include thermosets (e.g. polyurethane, phenolic, polyphosphazene, malamine formaldehyde, and polymethacrylamide), thermoplastics (e.g. polystyrene, polypropylene, poly(vinyl chloride) and polyethersulphone), and rubbers (e.g. ethylene-propylene terpolymer, silicone, natural rubber, and ethylene vinyl acetate). In this thesis, polymer matrix is polyolefins (high-density polyethylene). Polyolefin are polyethylene and polypropylene. Polyethylene is produced in two basic forms. High-density polyethylene (HDPE) consists of linear molecules which can crystallize quite readily. Low-density polyethylene (LDPE) has a highly branched structure and, therefore, does not crystallize as much. The mechanical properties of polyolefins lie usually between the rigid and flexible classifications. These foams have excellent chemical and abrasion resistance as well as good electrical and thermal insulation properties.

2) Blowing agents[13]

The functions of blowing agents are to generate gas during foaming process and to expand the polymer and thereby create a cellular structure or foam. The blowing agents are divided into two groups, i.e., physical and chemical blowing agents. The former liberates gases as a result of physical processes at elevated temperatures or reduced pressures. Examples of this type are low-boiling volatile liquids, such as aliphatic (butane, pentane, neopentane, hexane and heptane) and halogenated hydrocarbons (freons, CFC compounds), low-boiling alcohols, ethers, aromatic hydrocarbons (xylene, toluene and benzene) and water. The latter is popularly used in the preparation of expanded polymer. The chemical blowing agents produce gases by a chemical reaction. The reaction may be a thermal decomposition or reaction between chemicals. The choice of a blowing agent is determined by its thermal decomposition properties, i.e., the rate at which the blowing agent decomposes must be compatible with the polymer processing. The chemical blowing agents can be classified into organic and inorganic blowing agents. Both inorganic and organic blowing agents are currently being manufactured. Ammonium bicarbonate and sodium bicarbonate are examples of inorganic blowing agents. These blowing agents which release carbon dioxide are used extensively in the production of open cell sponge, as shown by the reactions (2.3) and (2.4) as below:

$$NH_4HCO_3 \longrightarrow NH_3 + CO_2 + H_2O \qquad (2.3)$$
$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O \qquad (2.4)$$
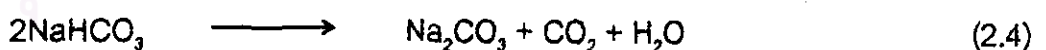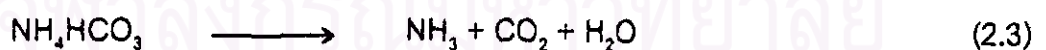
Ammonium bicarbonate slowly decomposes at $60°C$ and releases the gas products of 850 ml/g. Sodium bicarbonate decomposes slowly at approximately $100 °C$ and releases the gas products of 276 ml/g. However, these blowing agents poorly disperse in polymeric compositions, have low decomposition temperatures, give

out ammonia odor and cause rusting of steel part from water products. Therefore, they are not extensively used in production of expanded polymers.

The organic blowing agents release gas mixture that contains predominantly nitrogen and small quantities of other gases like carbon dioxide and ammonia, and therefore, are generally used for the production of closed-cell cellular polymers. The organic class of blowing agents includes many types, differing in their chemical composition, decomposition temperature and physical appearance, as shown in Table 2.1. The most popular blowing agents for closed cell expanded rubbers and plastics is azodicarbonamide, as described below.

Azodicarbonamide (AZD) is one of the most effective high temperature nondiscoloring, nonstaining and odorless chemical blowing agent. Its chemical structure is shown in Figure 2.14.

$$H_2N-\overset{\overset{\text{O}}{\|}}{C}-N=N-\overset{\overset{\text{O}}{\|}}{C}-NH_2$$
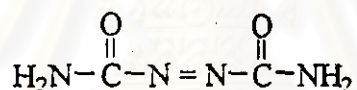
Figure 2.14 Chemical structure of azodicarbonamide (AZD)

When AZD decomposes, gas is evolved (predominantly nitrogen) and sublimate is formed. Its decomposition reactions are complex and there are several reported pathways[14], as shown in Figure 2.15. This leads to the possibility of a number of different decomposition routes with differing proportions of decomposition products. The decomposition of AZD can be adjusted by the use of variety of chemicals, such as acid, base, metal oxide, metal organic salt, urea and amine. The degree to which the decomposition temperature is reduced depends on which additive is chosen and the amount used. Zinc oxide and zinc stearate are very strong activators for the decomposition of AZD[15], while urea is a moderate activator. The measured gas evolution rates for these activators at $170^{\circ}C$ are shown

in Figure 2.16. Barium stearate, and calcium stearate are also strong activators, as shown in Figures 2.17.

Table 2.1 Characteristics of chemical blowing agents

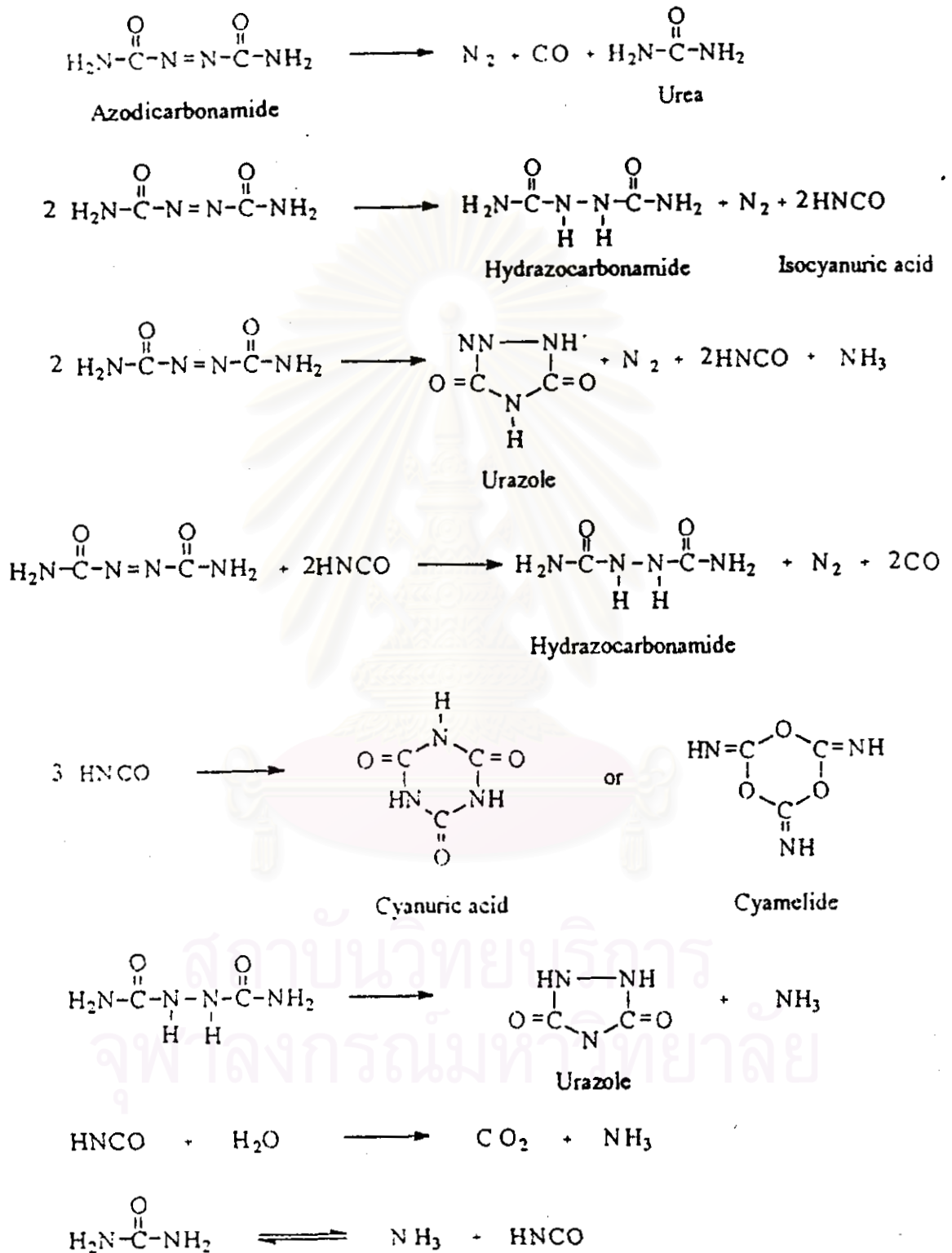| Chemicals	Decomposition temperature in air (°C)	Decomposition range in plastic (°C)	Gas yield (ml/g)
A. Azo compounds			
1. Azodicarbonamide	195-200	160-200	220
2. Azobis(isobutyronitrile)	115	90-115	130
3. Diazoaminobenzene	103	95-100	115
B. N-Nitroso compounds			
1. N,N'-Dimethyl-N,N'-dinitrosoterephthalamide	105	90-105	126
2. N,N'-Dinitrosopentamethylenetetramine	195	130-190	265
C. Sulfonyl hydrazides			
1. Benzene sulfonylhydrazide	>95	95-100	130
2. Toluene-4-sulfonylhydrazide	103	100-106	120
3. Benzene-1,3-disulfonylhydrazide	146	115-130	110
4. 4,4'-Oxybis(benzene-sulfonylhydrazide)	150	120-140	125

$$H_2N-\overset{O}{\underset{\|}{C}}-N=N-\overset{O}{\underset{\|}{C}}-NH_2 \longrightarrow N_2 + CO + H_2N-\overset{O}{\underset{\|}{C}}-NH_2$$

Azodicarbonamide   Urea

$$2\ H_2N-\overset{O}{\underset{\|}{C}}-N=N-\overset{O}{\underset{\|}{C}}-NH_2 \longrightarrow H_2N-\overset{O}{\underset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{O}{\underset{\|}{C}}-NH_2 + N_2 + 2HNCO$$

Hydrazocarbonamide   Isocyanuric acid

$$2\ H_2N-\overset{O}{\underset{\|}{C}}-N=N-\overset{O}{\underset{\|}{C}}-NH_2 \longrightarrow [\text{Urazole}] + N_2 + 2HNCO + NH_3$$

Urazole

$$H_2N-\overset{O}{\underset{\|}{C}}-N=N-\overset{O}{\underset{\|}{C}}-NH_2 + 2HNCO \longrightarrow H_2N-\overset{O}{\underset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{O}{\underset{\|}{C}}-NH_2 + N_2 + 2CO$$

Hydrazocarbonamide

$$3\ HNCO \longrightarrow [\text{Cyanuric acid}] \quad or \quad [\text{Cyamelide}]$$

Cyanuric acid   Cyamelide

$$H_2N-\overset{O}{\underset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{O}{\underset{\|}{C}}-NH_2 \longrightarrow [\text{Urazole}] + NH_3$$

Urazole

$$HNCO + H_2O \longrightarrow CO_2 + NH_3$$

$$H_2N-\overset{O}{\underset{\|}{C}}-NH_2 \rightleftharpoons NH_3 + HNCO$$

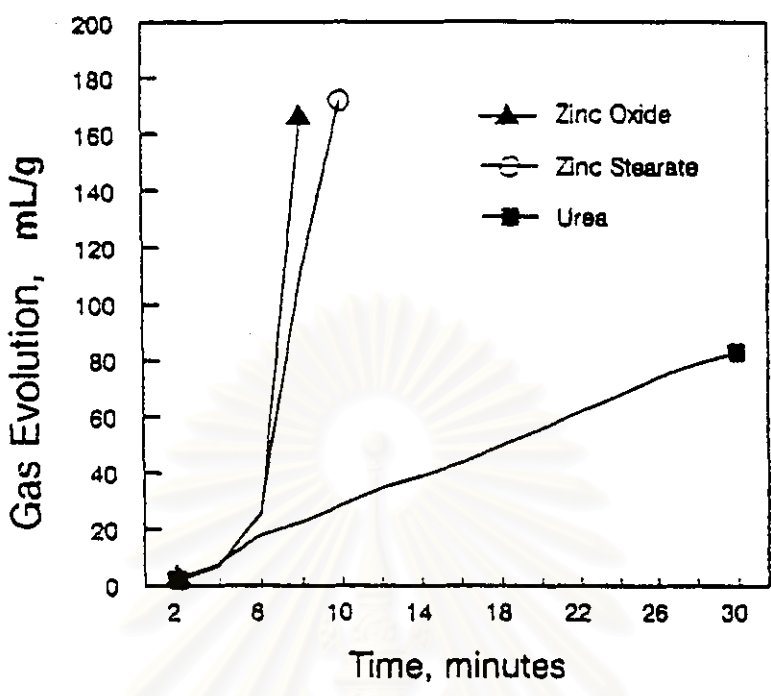Figure 2.15 Decomposition reactions of azodicarbonamide (AZD)

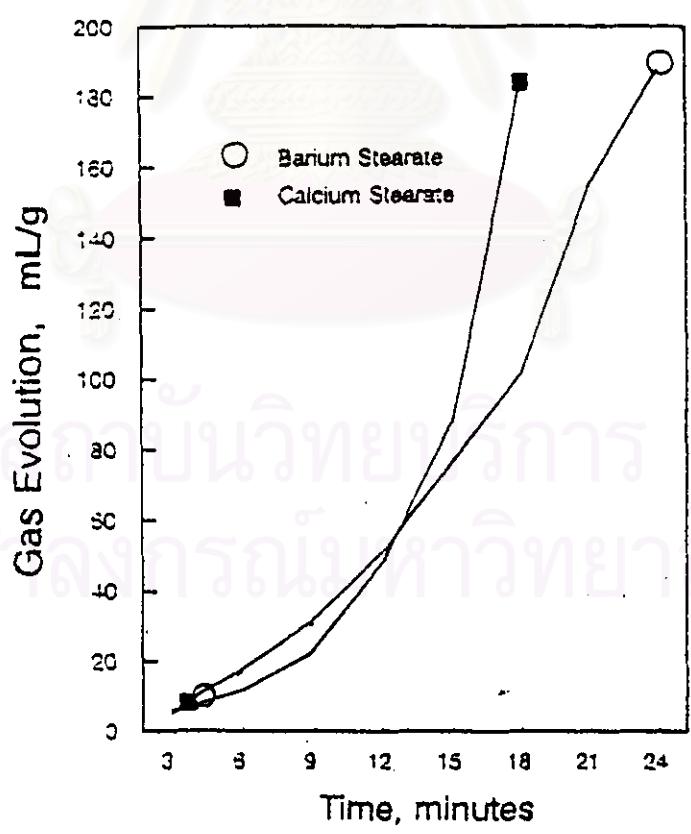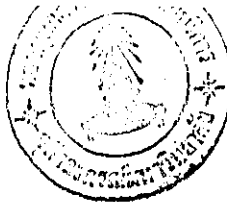Figure 2.16 Isothermal gas evolution test data of activators for AZD at 170 $^{\circ}$C

Figure 2.17 Isothermal gas evolution test data of moderate activators for AZD at 185 $^{\circ}$C

2.3.4 Relationship between cell structure and properties of expanded polymers

The properties of expanded polymers are generally believed to depend upon the structure of both the polymer network. The cell is formed at the end of expansion process. Also, the study of foam structures is required for understanding the relationship between the structures and their properties. Among the structure variables, density, open- versus closed-cell structure, cell size and cell shape are discussed [1, 16, 17].

1) Density

The effect of density has been investigated more than any other structural variables with regard to its effect on the physical properties of polymer systems. Modulus of foam generally increases with increasing density. This can be seen from the data of Figure 2.18 where a straight line relationship between flexural modulus and density of the foam is presented.
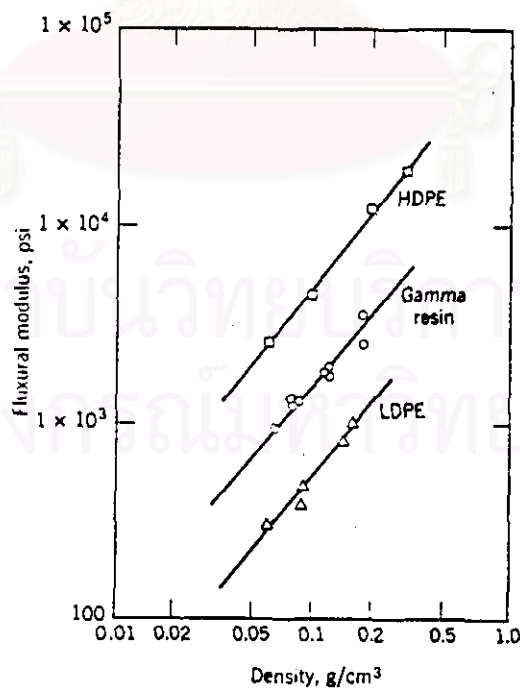

Figure 2.18 Effect of density on flexural modulus of LDPE and HDPE foams.

Table 2.2 Properties of expanded polyethylene at various densities.

Properties	Density, kg/m^3			
	100.8	62.4	30.4	14.4
Compression-deflection load,kg/cm^2				
At 10% compression	1.36	0.66	0.22	0.07
At 20% compression	1.75	0.91	0.34	0.12
At 50% compression	2.87	1.82	0.98	0.51
Tensile strength, kg/cm^2	14.7	10.5	5.74	3.22
Elongation at break, %	130	98	78	65
Tear strength, N/m	5600	3150	1277	525
Permanent compression set, %	1	4	8	12
Resiliency, %	31	37	47	56
Thermal conductivity, W/(m K)	0.053	0.049	0.045	0.043

The data in Table 2.2 show that tensile strength, elongation at break, tear strength increase with increasing density. Permanent set, resilience and thermal conductivity, on the other hand, decrease with increasing density.

2) Open- versus closed-cell structures

Converting a closed-cell structure into an open-cell structure without changing the polymer phase can convert a rather a semiflexible foam to a more flexible composites with a lower modulus. Figures 2.19 and 2.20 show that compressive load and compressive strength increase with the decreasing fraction of open-cells.
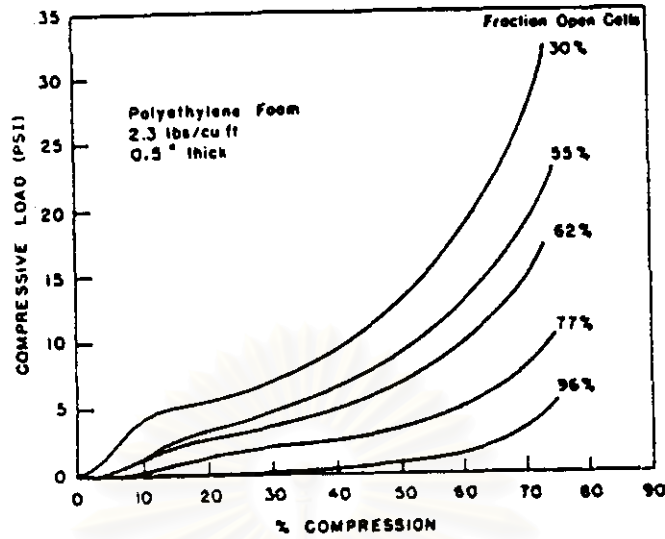
Figure 2.19 Compressive stress-strain curves of polyethylene foams with various fractions of open cells.
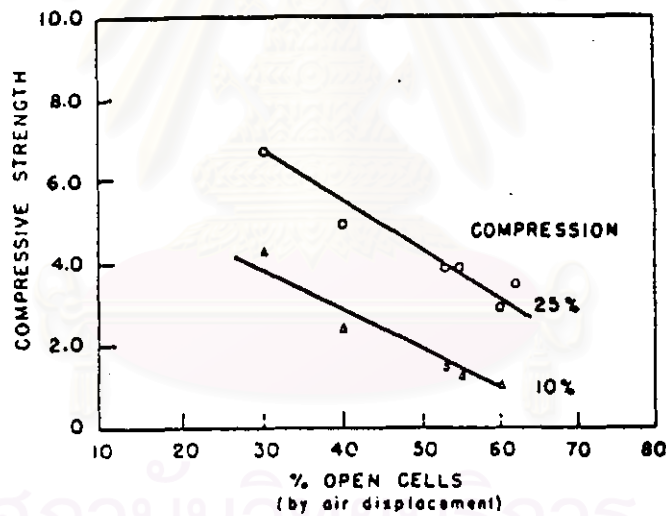

Figure 2.20 Compressive strength VS. percentage open cells for polyethylene foams.

Foams produced originally as closed-cell foams, which subsequently crushed to produce an opened-celled foam have lower strength than foams produced originally as open-celled foams. This is presumably because the polymer in the broken cell walls of crushed foam does not contribute significantly to the properties, whereas the original open-celled foams are prepared in such a manner

that the cell walls have retracted back into the rib structure and contribute to the physical properties. The closed-cell structure has low thermal conductivity and low water absorption, whereas open-celled structure has better acoustic insulation properties and cushioning characteristics. In some cases both rigid and flexible foams may be obtained with open and closed cell.
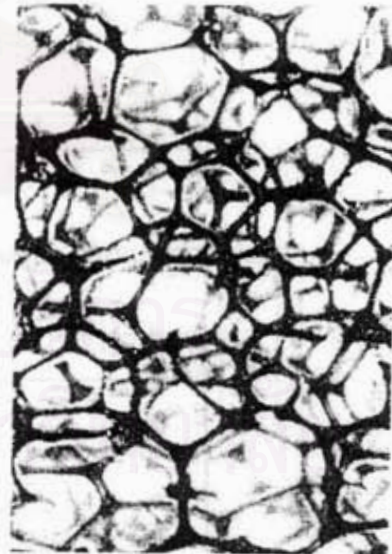
3) Cell size
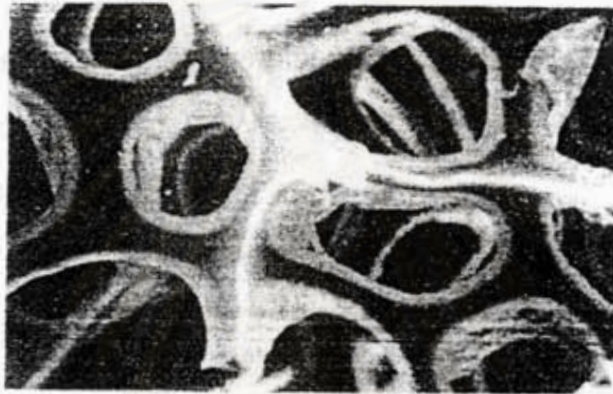
(1)

(2)   (3)

Figure 2.21 Typical structure of (1) open, (2) closed, and (3) reticulate cell foams

Three basic types of cells can be formed: open, closed, and reticulated. They are depicted in Figure 2.21. A membrane of variable thickness covers each face of the cell. In an open cell foam, most of these membranes are perforated, and in reticulated materials the membranes have been removed by chemical means or with the help of heat treatments. Open, closed and reticulated cell structures of varying sizes can be produced with the help of different technologies.

As the cell size of a given composite increases, the flexural modulus increases as well. An increase in cell size detracts from the insulation efficiency of the foam because of the increased thermal conductivity caused by radiation and convection. As cells become smaller, tensile strength increases and resistance to compression increases.
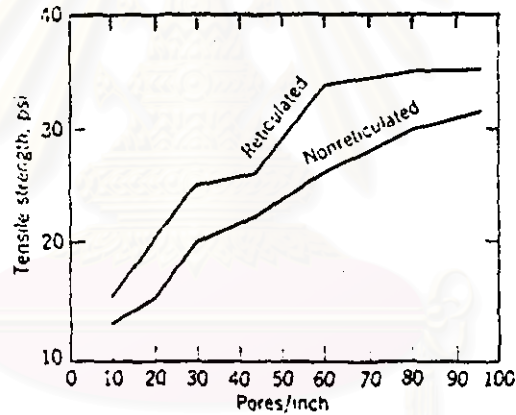

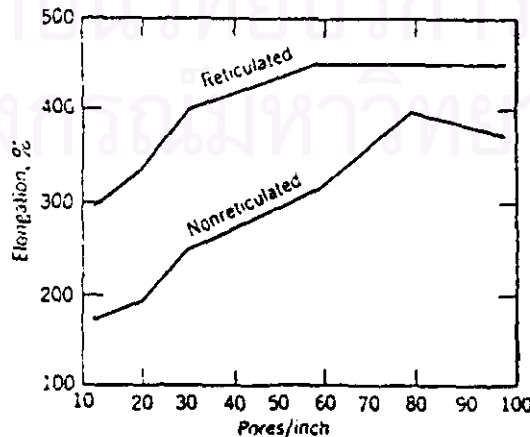Figure 2.22 Tensile strength versus cell size.

Figure 2.23 Elongation versus cell size

Figures 2.22 and 2.23 show tensile strength and elongation for both reticulated and nonreticulated foams, versus cell size (pores/inch). The smaller cell size produces the stronger foams. Figure 2.24 shows the relationship between tear strength and pore size, since tear strength depends on tensile strength and elongation. The reticulated foam has higher tear strength. In a reticulated foam, the cell size has little or no effect.
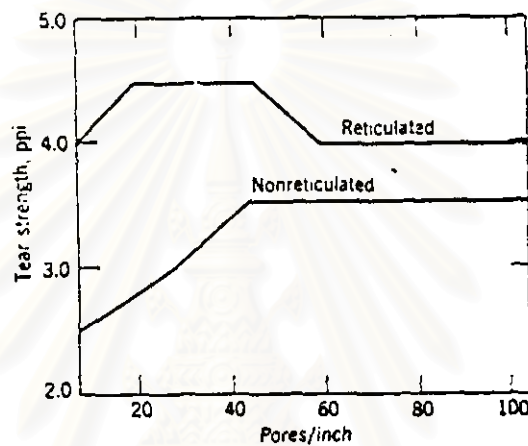

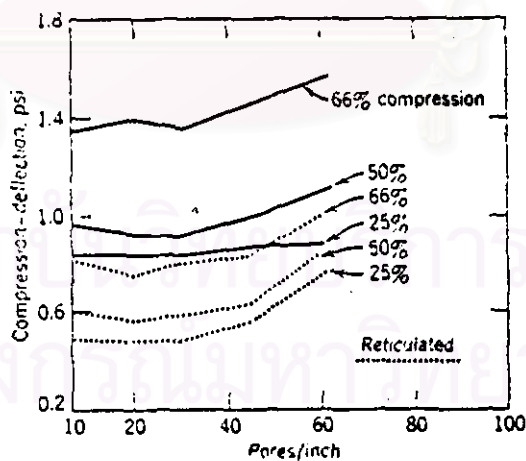Figure 2.24 Tear strength versus cell size.

Figure 2.25 Compression-deflection versus cell size.

Figure 2.25 shows that the force for any given deflection, which is greatly decreased by reticulation. The explanation for this is shown in Figure 2.26, where the effect of compression along the plane of the side of cell is shown. When a cell

having a window is compressed, the membrane must be stretched as well as the strands being bent, if the elongation of the break is not propagated through the strand. If no window is present; hence less force is needed for a given deflection. Figure 2.27 shows compress-deflection between large cell size and small cell size of foams.
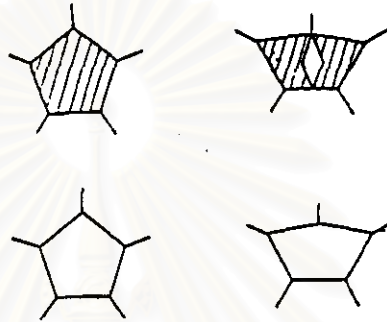

Figure 2.26 Role of window in compression.
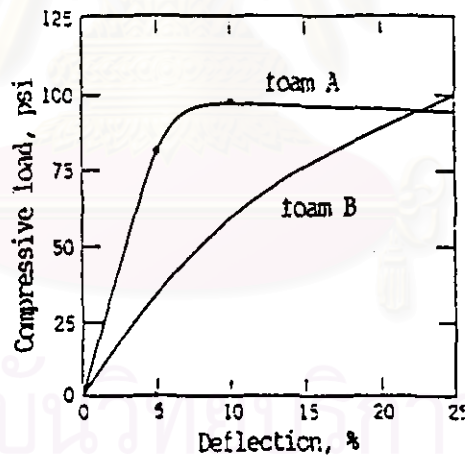
Figure 2.27 Effect of cell size on compression properties foam A-large cells and foam B-smaller cells.

4) Cell shape

Mechanical restraints can distort cell shape, regulating the rate of expansion and crosslinking can also modify cell shape and unidirectional expansion in the

mould can produce oriented structure. In the process, cell shape depends mainly on the inherent rise and flow properties of the system.

Figure 2.28 Compression-deflection properties of unbalanced foam

Figure 2.29 Typical effect of cell structure on rigid foam strength.

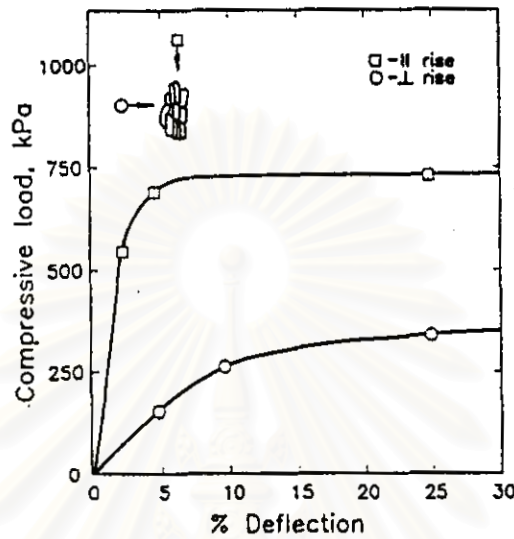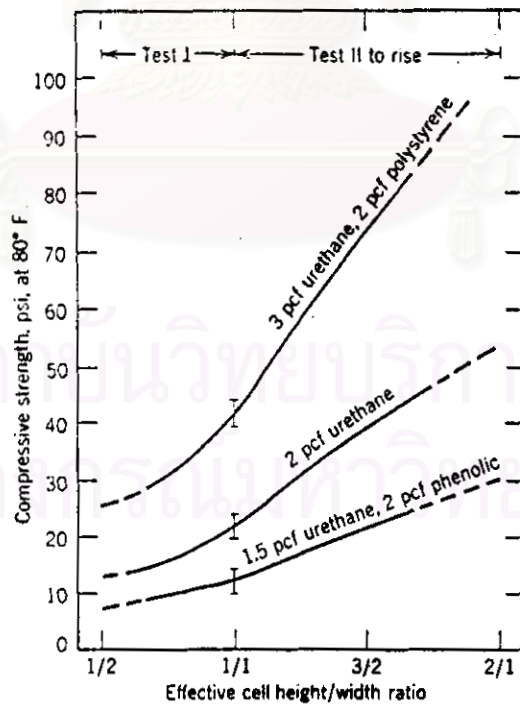Figure 2.28 shows the type of compressive behavior and Figure 2.29 describes low density foam strength primarily as functions of cell shape and test orientation. The elastic moduli of base polymers are similar, 32 kg/m^3 styrene foam behaved like 48 kg/m^3 urethanes. Perhaps polymer distribution with the cell walls (lamellae) and struts (veins) is different in each case. For example, polystyrene foam has very thin lamellae; phenolic foams have thicker lamellae and a different degree of open-cell content; the urethanes have a cell wall thickness intermediate between these two.

2.3.5 Application for cellular materials[18]

1) Polymer foams for construction and thermal insulation

Foams have entered construction by direct replacement of conventional materials. Improved technology has set the stage for future growth. Rigid foam polymers compete successfully in the thermal insulation market because they are good insulators and are also lightweight, strong, buoyant, water-resistant, easy to fabricate and resistant to rot and fungus.

2) Polymer foams for packaging

Foam materials have many properties that make them suitable as packing materials. These are low weight per unit volume (density), moisture resistance, low cost, non-dusting surface (so as not to foul delicate switches and components), chemical inertness (to eliminate corrosion or secondary effects), wide temperature range (so the package can function at night, in summer or winter, in the Arctic or equatorial area), and thermal insulation. The lowest cost expanded plastics that fulfills most of these requirements is the rigid polystyrene foam. Polyethylene foams, although quite expensive, possess the best shock-absorbing properties and are chemically inert.

Polystyrene foam

Polystyrene foam is the lowest-cost and largest-volume rigid expanded plastic on the market. A rapidly expanding field of application is in the manufacture of disposable containers (cups, trays, etc.). The advantage of expanded polystyrene in these applications is freedom from staining or "tainting".

Super light polystyrene foam

It has rather low strength and rigidity, which makes it unsuitable for packaging large and heavy objects. In applications where softness and flexibility are required, ordination polystyrene foam is too hard and rigid, so that at present other materials are being used in its place. Super light foam is much better in this respect and has already been employed successfully in the packaging of light and fragile articles.

Polyurethane foam

It cannot be used as an outer case or shell; its main function is that of a cushion or space filler. Polyurethane foam also suffers from high creep under vibration, some water absorption, poor aging and some staining to adjacent materials. The greatest potentials of polyurethane lies in low-cost foamed-in-place applications.

Polyethylene foam

Polyethylene foam has outstanding performance in respect to high energy absorption and low rebound. The foam is more expensive, but it outperforms such products as rubberized hair and expanded rubber. Polyethylene foam can be vacuum-formed with virtually no change in density. There is a further potential use in the cushioning of very low weight articles.

Poly(vinyl chloride) foam

It has a relatively minor role in the packaging industry. The reason is that these foams are more dense than polystyrene and polyurethane foams and therefore becoming more expensive. Nevertheless they are used in two areas of application in the packaging industry: as protective coating for parts during shipment and as bottle crow and jar closure seals. Foamable plastisols are sprayed on metal parts and expanded in oven. The expanded coating protects the metal part in transit and is easily stripped off before use.

Phenolic foam

Phenolic foam finds application in the packaging of fission materials. Although designed principally for transporting uranium hexafluoride cylinders, the phenolic foam is adaptable as a protective linear for all enclosures of fissile material.

3) Plastic foams for marine application

Plastic foams have a major application in buoyancy market as supports for floating structures, buoyancy inserts in vessels, life jackets, fishing floats, floating harbor devices, to restrict oil slicks from spreading and fouling marine life and the shore, harbor buoys, and also as a floatation material for deep submergence vehicles. Ideally, all foams used in buoyancy applications are closed-cell types for the life of the composite. Each cell acts as an individual float. Two essential properties of foams are the buoyancy factor, which must remain constant throughout, the service life, and the foam must be unaffected by water. Polystyrene, polyethylene, and poly(vinyl chloride) are the outstanding foams in these respects found in harbors, that are oil and gasoline slicks, etc. The foams that perform well in these environments are polyethylene, styrene-acrylonitrile and PVC foams.

Table 2.3 Application for polyolefin foams

Application	Key properties	Examples
Cushion packaging	Energy absorption	corner pads, pads and saddles, encapsulation, case inserts, overlap sheeting, bracing and blocking, dunnage
Construction	Low thermal conductivity Low water vapor transmission Sound absorption	sealant backer, expansion joint filler, closure strips, curing blankets, floor underlayment, roofing underlayment
Insulation Industrial uses	Low thermal conductivity Compressibility Oil resistance Buoyancy	insulation of pipe, storage tanks, tunnels gaskets, grommets, vibration pads, tape backing, buoys, oil booms, flotation collars, ship fenders
Automotive uses	Light weight Thermoformability Energy absorption	headliner, instrument panel, door trim, quarter panel, wheel house cover, trunk liner, seat back garnish, sun visor, bumper inserts, air conditioner liner
Sports and leisure	Buoyancy Low water pick-up Energy absorption	life vests, ski belts, surfboards, swim aids, pool covers, gym mats, wall pads, athletic padding, camping mats
Agriculture	Insulation Cushioning	insulation blankets for greenhourse, produce packages
Miscellaneous	Thermoformability Fabricability	toys, luggage liner, desk pads, shoe soles

4) Flexible foams in cushioning

The foams used extensively in this overall market are latex foam rubber (cushions, bedding, furniture), polyurethane foam (cushions, bedding, furniture rug underlays), vinyl foam (top coatings, seat covers, sheet goods, clothing) and polyethylene foam (gasket, rug underlays in cars, inner liners in clothing). Rubber foams are used in textile coating, carpet backing, carpet underlay, padded undergarment.

5) Refrigerators, freezers and heaters

Refrigerators and freezers require good insulation and styling and efficient storage space. In recent years manufactures have used three insulants: glass fiber blankets, expanded polystyrene blocks and boards and expanded polyurethane slab or foamed-in-place foam. The plastic foams also have a lower moisture vapor permeability. Foamed-in-place urethane makes a good metal-foam bond and the rigidity of the core provides a stronger, metal cabinet. The pyranyl foam system is a new insulating material competitive with polyurethane. Freezer cabinets varying in storage capacity from 1 to 30 ft^3 have been the insulation efficiency of the foam.

This thesis concerns polyolefin foams, which major application in various market segments are summarized in Table 2.3[10].

2.4 Literature review

A comparison of mechanical properties, structure and morphology of NR/LDPE blends in varying compositions was studied by Qin et al.[18] Change in mechanical properties during the course of dynamic vulcanization (expressed in terms of the number of consecutive extrusions) was also examined. Blends were prepared by unvulcanized, static vulcanization, and dynamic vulcanization of the NR component in the blends. Morphological studies with TEM and SEM showed that, in unvulcanized NR/LDPE blends, phase inversion occurred between

NR/LDPE = 40/60 to 60/40; for dynamically vulcanized blends, LDPE remained as a continuous phase even at NR/LDPE = 70/30. Change in morphology of dynamically vulcanized blends of specified composition (NR/LDPE = 70/30) with vulcanization time as observed by SEM indicated that phase inversion occurred with progress of vulcanization, followed by fracture of the vulcanized phase inversion into small particles. The models were proposed as shown in Figures 2.16 and 2.17. Mechanical properties of dynamically vulcanized blends were higher than those of unvulcanized blends but lower than those of statically vulcanized blends.
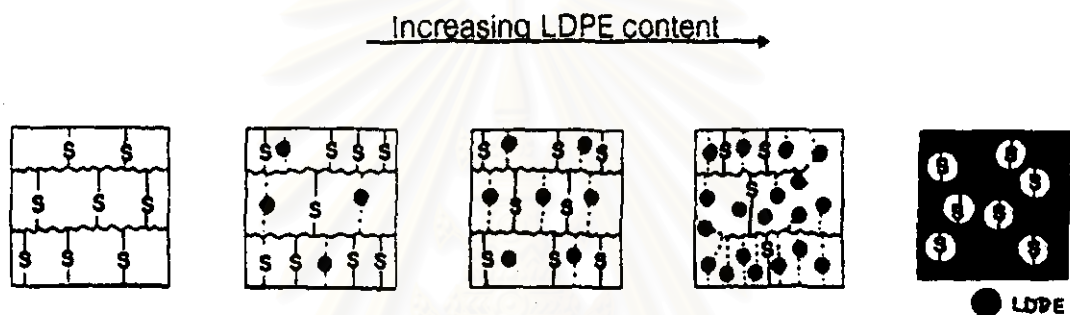
Increasing LDPE content

Figure 2.30 Model describing the static vulcanization process in NR/LDPE blends.

Increasing LDPE content
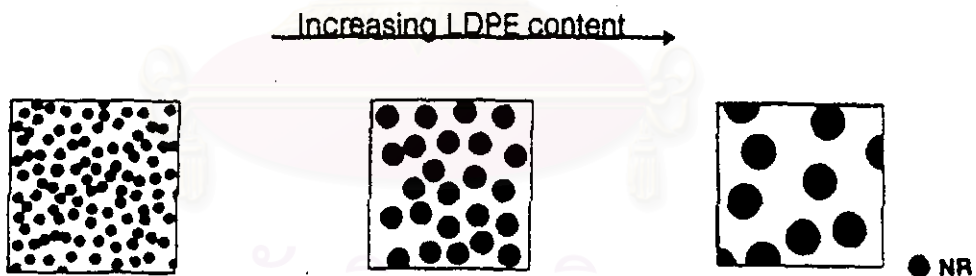
Figure 2.31 Model describing the dynamic vulcanization process in NR/LDPE blends.

The other physical properties of blends are mainly dependent on the properties of the plastic phase, such as tear strength, 300% modulus, hardness and permanent set; all increased with increasing LDPE in different processing methods.

Ahmad et al. discussed the preparation of new thermoplastic natural rubber using NR-HDPE blends with liquid natural rubber (LNR) as a compatibilizer.[19] LNR

with active terminals and molecular weight, Mw, of 50,000 has been prepared in the laboratory using a photodegradation technique. The blend compositions varied between 20 and 55% HDPE and 45 and 80% NR with 13% LNR. Two compositions of NR/HDPE blend had been prepared, known as Blend 1 (60/40) and Blend 2 (70/30), with various percentages of LNR. These blends were studied for their physical properties. The tensile properties and hardness of thermoplastic natural rubber improve significantly with the addition of LNR to the blends. The degree of cross-linking also increased with increasing amounts of the LNR added. The LNR promotes cross-linking within the rubber phase and grafting of the polyethylene chains onto the rubber matrix system. The maximum stress and strain of the blends measured are about 7.5 MPa and 1000%, respectively. Dynamic mechanical analysis results indicate a single Tg on a tanδ trace at about -50 and 55 $^{\circ}$C for Blend 1 and Blend 2, respectively.

Morphology and physical properties of thin films of thermoplastic elastomers from blends of natural rubber and polyethylene have been discussed by Akhtar.[20] Formulations of NR/HDPE blends were 0/100, 30/70, 50/50, and 70/30. Each formulation of the films was prepared by quenching in ice (-10°C), cooled in water (25°C), cooled in air (30°C), and cooled in the press under pressure, consecutively. Press-cooled blends exhibit very poor properties, while ice-cooled blends have good tear and tensile strength. Water-cooled blends also have reasonably good properties. These results can be ascribed to changes in the crystallite morphology of PE. Since the 30% PE content is lowest, the properties of the blends are less influenced by the method of preparation. Further, NR/HDPE 30/70 shows higher strength values and elongation at break on cooling in water compared to that on cooling in air, because for the latter, it is prone to thermo-oxidative aging.

Akhtar and Bhagawan reported dynamic mechanical properties of NR-HDPE blends.[21] The effects of blend ratio, dynamic crosslink, and carbon black filler on the storage, loss moduli, and loss tangent are examined. It was observed that

above room temperature, both storage and loss moduli increased and loss tangent decreased as the HDPE content in the blend increased. The effects of dynamic crosslink and carbon black filler on dynamic mechanical behavior of 70/30 NR/HPPE blend were also examined. Carbon black increased the storage and loss moduli but lowered and broadened the tanδ peak. On the other hand, crosslinking increased storage modulus and decreased the loss modulus and loss tangent, particularly after the NR's Tg. The tanδ peak area which appeared at Tg for NR was proportional to the rubber content in the blends.

An experimental study of the relationships between foaming variables and foamed structures of expanded ethylene-propylene terpolymer (EPDM) is reported by Wang.[22] The study was carried out using EPDM compositions containing azobisformamide blowing agent. The compositions were expanded and cured in hot air into a foamed structure consisting of a dense skin and a foamed core. The results show that the foam density, skin thickness, average cell size, and number of cells of the expanded rubbers can be controlled closely by the foaming variables, such as, residence time, foaming temperature, and blowing agent concentration.

Mukhopadhyay et al. report the results of their studies on mechanical properties of microcellular EVA rubber with a specific reference to the effects of concentration of blowing agent and precipitated silica filler on its failure properties.[23] They found that increase in the blowing agent concentration causes decrease in average pore size, increase in largest pore diameter, and decrease in foam density. Physical properties like modulus, tensile strength, elongation at break, hardness, and tear resistance decrease, while hysteresis and set properties improve with an increase in blowing agent concentration. Incorporation of silica filler causes a decrease in both average pore size and largest pore diameter along with improvement in physical properties. Theoretically, calculated values of the flaw size in tensile rupture are found to be in reasonable agreement with the values of largest pore lengths measured from SEM photomicrographs of razor cut foam samples.

This suggests that the tensile rupture of foam samples occurs by catastrophic tearing from a flaw in the form of the largest pore diameter. SEM fractograph studies of tensile and tear fracture surfaces of foam vulcanizates suggest that the mechanism of rupture is dependent on the concentration of blowing agent and silica filler.

Dynamic viscoelastic properties of carbon black loaded closed-cell microcellular ethylene-propylene-diene rubber vulcanizates in terms of the effect of blowing agent, temperature, frequency, and strain were studied by Guriya and Tripathy.[24] A plot of the log of the storage modulus bears a linear relationship with the log of density for the solid as well as the closed-cell microcellular rubber. The slope of the line is found to be temperature-dependence. The relative storage modulus decreases with decreases in the relative density. It was also observed that the storage modulus and tanδ are both frequency- and temperature-dependence. The storage modulus results are superposed to form master curves of the modulus vs. log temperature-reduced frequency, using shift factors calculated by the Arrhenius equation. Strain-dependent isothermal dynamic mechanical analysis was carried out for DSA (double-strain amplitude) varying from 0.07 to 5%. The effect of blowing agent loading on the storage modulus (E') and loss tangent (tanδ) were also studied. Cole-Cole plots of microcellular rubber shows a circular arc relationship with the density. Plots of tanδ against E' were found to exhibit a linear relationship.

Guriya and Tripathy studied the morphology and physical properties of the microcellular ethylene-propylene-diene terpolymer (EPDM) rubber with a special reference to the variation of blowing agents and carbon black loadings.[25] The morphologies of the microcellular EPDM vulcanizes of both an unfilled and filled compound were studied from SEM photomicrographs. Carbon black adversely affects the average cell size, maximum cell size, and cell density. Enclosed gas pressure in a closed cell increases the relative modulus at higher strain. Tensile

strength decreases more steeply than the expected value obeying the additive rule. At higher temperatures, tensile strength, elongation at break, and modulus values decrease. The stress-relaxation behavior is independent of blowing agent loading, i.e., the density of closed-cell microcellular rubber. The elastic nature of the closed cell, i.e., the gas bubbles in the microcellular rubber, reduce the hysteresis loss compared to solid rubber vulcanizates. Theoretically calculated flaw sizes are found to be about 3.4 times larger than the maximum cell sizes observed from SEM photomicrographs. It reveals that tear path deviates from the linear front and gives an effectively larger depth of the flaws.

Various foam formulations based on polyethylene and ethylene-vinyl acetate copolymers were investigated by Sims and Khunniteekool.[26] Interactions between crosslinking and blowing agent concentrations were systematically studied for each base polymer using a two-stage compression moulding technique to manufacture the foams and their effects on physical properties were determined. Progressively increased blowing agent concentration, whilst maintaining a fixed crosslinking agent level, results in density and relative density reduction as expected. However, it was observed that at any specific blowing agent concentration, foam density increased with increasing chain branching in polyethylene and with increasing vinyl acetate content in the copolymers. This phenomenon was satisfactorily explained in terms of increasing crosslinking efficiency with increasing tertiary hydrogen concentration in the base polymer by comprehensive studies on gel content, melt strength at the expansion temperature and cell size trends. Surprisingly, cell size increased with vinyl acetate content at any particular gel content suggesting that an absolute cell size is a function of nucleation in the first stage of the process.

Compression moulded ethylene homopolymer and copolymer foams in terms of the effects of processing conditions and crystallinity on cell structure development was studied Sims and Khunniteekool.[27] Crosslinked polyethylene and ethylene-vinyl acetate copolymer foams were produced by a single-stage heating

and the two-stage heat and chill compression moulding techniques. At a fixed blowing agent concentration, crosslinking agent concentrations were adjusted to give similar gel contents independent of the base polymer. Relative densities of fully-expanded foams produced by either the single stage or heat and chill process did not show significant variation. However, relative densities of partially expanded material after the first stage of the heat and chill process showed a considerable decrease at higher vinyl acetate contents resulting in a consequent reduction in further expansion in the second stage. Cell structures of foams from the single-stage expansion and after each stage of the heat and chill process were observed by scanning electron microscopy. Micrographs were analysed to give mean cell sizes and cell size distributions. The studies showed a reasonable regularity of cell structure for all foams expanded by the single stage process and for high vinyl acetate content foams produced by the heat and chill process. However, heat and chill processed foams from polyethylene and low vinyl acetate content base polymers showed a pronounced bimodal cell size distribution. This was attributed to possible crystallinity, solubility and diffusion effects. It was concluded that cell structure regularity was adversely affected if the cooling cycle after the first stage allowed crystallisation of the polymer to take place.

Structure characterisation of extruded foam profile made from polypropylene and polypropylene/polyethylene blends containing chemical blowing agents was studied by Shishesaz and Hornsby.[28] Emphasis will be given to the influence of blowing agent concentration on the melt rheology of foamable compositions combined with the effects of die geometry and processing conditions on the resulting density in the foamed state, before and after cooling of the melt. Cellular structure will be discussed in terms of the relative levels of open and closed cell content, the uniformity of cell distribution, determination by mercury penetration, porosimetry and microscopic techniques, and microstructural characterisation of the semi-crystalline polymeric phase.

Foam extusion of a series of dynamically vulcanized polypropylene (PP)/ethylene-propylene-diene terpolymer (EPDM) blends (commercially available Santoprene) by using chemical blowing agents have been studied by Dutta and Cakmak.[29] Results suggest that foaming occurs only within the thermoplastic phase and for each composition there exists a limiting density which controls the maximum volume expansion. This limiting density is controlled only by the composition and is independent of the blowing agent concentration, extrusion conditions, and the geometry. For the softest and the hardest blends, maximum volume expansion was found to be about 20 and 100%, respectively. Considerable differences in cell structure were also observed with change in the blend composition. As the rubber content increases, bubbles change their shapes from spherical to highly elongated channels where long axes are primarily along the extrusion direction. When the shapes of the bubbles are viewed by cutting the specimen, the bubbles were found to become highly irregular as the rubber content was increased. The fractal dimension of the perimeter profiles revealed that increases in rubber content give increases in the characteristic fractal dimension. Additionally, wide angle x-ray pole figure analysis, which gives an average orientation behavior of the material, indicates that low levels of preferential crystalline chain orientation develop in the extrudates. This preferential orientation was found to vary from skin to core.

Using two different types of chemical blowing agents, foaming behavior of partially vulcanized PP/EPDM blends with high EPDM ratio was studied by Dutta and Cakmak.[2] The objective was to induce foaming within the EPDM phase prior to complete curing. The results suggest that with a proper choice of blowing agents and by an optimum balance of curative loading, foams with densities as low as 0.55 g/cm^3 could be obtained. This corresponds to nearly 90 percent density reduction which is significantly greater than the 15 to 20% afforded by similar fully-vulcanized dynamically cured blends. The degree of cure in the rubber phase was determined

to play a key role in determining the overall foamability. In particular, the foamability of the blend was found to decrease linearly with increase in the gel content. In addition, the compounding technique also plays a major role in controlling foamability of these blends. Attempts at extrusion foaming of these blends, however, were successful only for blends with a rather low degree of cure.