



CHAPTER II

LITERATURE REVIEW

2.1 Polybenzoxazine

Douglas *et al.* (2006) Over the past decade, the research community has focused considerable effort on developing polybenzoxazines as a class of thermosetting material to overcome many of the shortcomings associated with traditional resole and novolac-type phenolic resins. Benzoxazine monomers are readily synthesized, either in solution or by a patented melt-state process, through the Mannich condensation of a phenolic derivative, formaldehyde, and a primary amine, as generalized in Scheme 1. Benzoxazines can be thermally activated and do not require acid or base catalysts for ring-opening polymerization; see Scheme 1. The unique chemistry provides tremendous opportunities for molecular design and offers a number of inherent processing benefits, including low melt viscosity, no volatile release upon cure, rapid property development, and low overall shrinkage. The polymerization of multifunctional monomers produces thermosetting polybenzoxazines that have excellent thermal, mechanical, and dielectric properties, as well as low water absorption. Polybenzoxazines are typically bisphenol based and, therefore, possess a rigid aromatic core in their backbone structure. Yet, despite the numerous advantages highlighted earlier, polybenzoxazines still suffer to a certain extent from the brittleness that plagues conventional thermosetting resins. As a result, much of the published benzoxazine research has targeted improvement in the toughness of these thermosetting materials. Phase-separated, physical blends of polybenzoxazine with amine-terminated (ATBN) or carboxyl-terminated (CTBN) butadiene-acrylonitrile rubber have improved fracture toughness. As much as 12% ATBN rubber has also been covalently bonded to the benzoxazine matrix at the amine functionality during synthesis. Physically interacting thermoplastic polymer modification has been achieved with polycaprolactone (PCL), which is compatibilized by hydrogen bonding between the phenolic group of the polybenzoxazine and the carbonyl group of PCL. Copolymerization has improved mechanical performance by taking advantage of the reactivity at the phenolic

hydroxyl group to chemically incorporate a flexible chain into the polybenzoxazine matrix. Epoxy and polyurethane each contain functionalities that have been coreacted with benzoxazine to form homogeneous, single-phase copolymer systems with improved mechanical properties. Poly (imide-siloxane) has also been blended with benzoxazines to improve toughness, either as a reactive comonomer when the poly (imide-siloxane) contains phenolic hydroxyl groups, or as a semi-interpenetrating network when it does not.

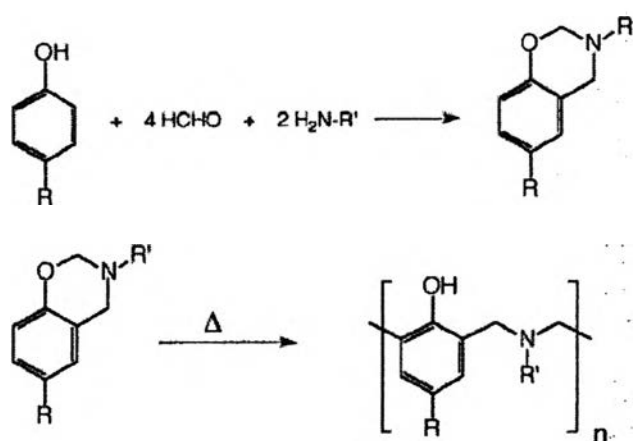


Figure 2.1 Synthesis (top) and thermal polymerization (bottom) of a benzoxazine monomer.

The majority of published benzoxazine research has focused almost exclusively on materials in which the phenolic compound, typically a bisphenol, provides the multifunctionality necessary to achieve an infinite network. This limits benzoxazines to materials with a rigid, aromatic core as the backbone of the crosslinked network. All of the previous attempts at improving the toughness of polybenzoxazines have involved the addition of a flexible component, often reactive, into the thermosetting matrix. This study, however, seeks to take advantage of the rich molecular design opportunities of benzoxazines to develop a matrix material with an inherently flexible molecular structure that is less brittle than typical benzoxazines. By switching multifunctionality of the benzoxazine to the amine portion of the structure, the limitations of the bisphenolic linkage can be eliminated, and less brittle materials can be specifically designed at the molecular level by

incorporating a flexible difunctional amine as the central core. (Fig. 2.1) In this study, a series of linear, aliphatic diaminebased benzoxazines, shown in Figure 2.2, will be synthesized and characterized to demonstrate the feasibility of increasing the inherent flexibility of the polybenzoxazine network structure itself. The effect of aliphatic chain length on the polybenzoxazine structure and properties is probed by systematic variation of the diamine compound.

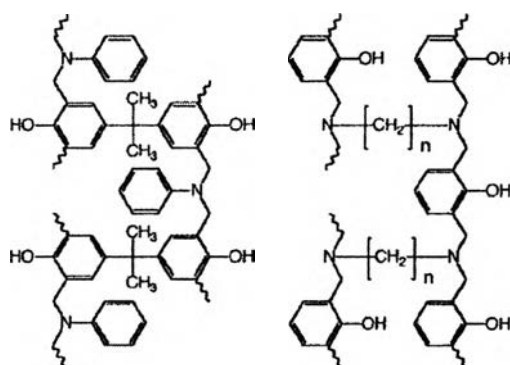


Figure 2.2 Comparison of the network structure of a bisphenol-A based polybenzoxazine and a linear aliphatic diamine-based polybenzoxazine.

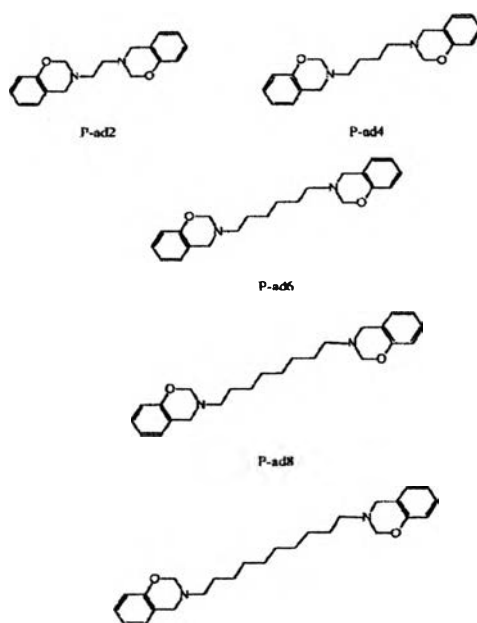


Figure 2.3 Structure and nomenclature used for the series of linear aliphatic diamine-based benzoxazine monomers.

2.2 Blowing agents

2.2.1 Physical blowing Agents (PBAs)

Pentrakoon *et al.* (2005) PBAs are gases or compounds that produce gases as result of physical processes such as a result of physical processes such as evaporation, desorption at elevated temperatures, or reduced pressures.

2.2.2 Chemical blowing Agents (CBAs)

CBAs are individual compounds or mixtures of compounds that produce gas as a result of a chemical reaction. The chemical change is usually brought about by thermal decomposition or as a result of chemical reaction with other components of the formulation.

Both PBAs and CBAs should posses the following qualities :

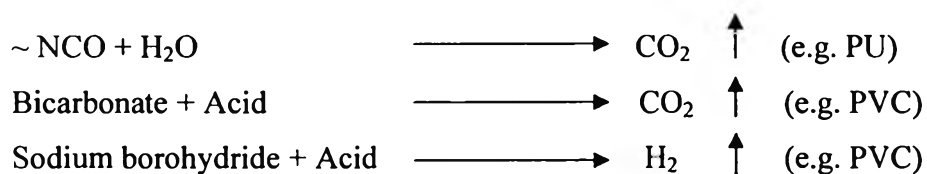
- (a) Long-term storage stability (shelf life) under ordinary conditions.
- (b) Gas release over a controlled time and temperature range.
- (c) The gas liberated and the products must be noncorrosive, nonflammable, and incombustible; compounds that liberate N_2 and CO_2 are preferable.
- (d) Low toxicity, odor, and color of both the blowing agent and its decomposition products.
- (e) No deleterious effects on the stability and processing characteristics of the polymer.
- (f) The liberated gas must have a low rate of diffusion through the polymer.
- (g) The ability to produce cells of uniform size.
- (h) The ability to produce a stable foam. The stability of the foam depend on the solubility and diffusivity of the gas in the polymer matrix.
- (i) Good cost-performance relation and availability.
- (j) Environmentally acceptable.

Two principle advantages of using CBAs are (i) they are easy to introduce into the composition to be foamed and (ii) they are easily processed with ordinary equipment. There are additional requirements to be taken into account when selecting a CBA.

- (a) The decomposition temperature of the CBA must be compatible with the processing temperature of the polymer, i.e. be close to the melting point or the hardening temperature of the polymer.
- (b) Gas must be liberated within a certain narrow temperature range.
- (c) The rate of gas liberated must be adequately high (but not violently), and controllable by temperature, pressure, and the decomposition of activators (kickers).
- (d) The CBA and gas(es) liberated must readily disperse or dissolve in the molten polymer compound.
- (e) The decomposition of CBA must not be accompanied by the release of so much heat that the polymer matrix will be thermally destroyed.
- (f) The CBA and the products of its decomposition must not affect the rate of polymerization (hardening) or cause destruction of the matrix.
- (g) The rate of gas liberation must not decrease appreciably during the process of thermal decomposition of the CBA as the internal pressure in the system increases.

To minimize mixing and homogenization problems and to obtain greater uniformity of the finished product (in terms of density and cell size) it is usual to use the blowing agent in masterbatch form.

- (i) Preblending the CBA into the polymer. Finely powdered solid Bas, such as azodicarbonamide (ADC) or carbonates, are normally processed this way, Thermal decomposition over a limited temperature range in the evolution of gas, primarily N_2 or CO_2 .
- (ii) The interaction between two reactive chemicals, e.g.,



Benning investigated the chemical blowing agent method and showed that when properly compounded into the polymer the particles of blowing agent are completely dispersed in the polymer phase. Thus, cell size is partially dependent on the particle size of the blowing agent and degree of dispersion of the blowing agent in the polymer.

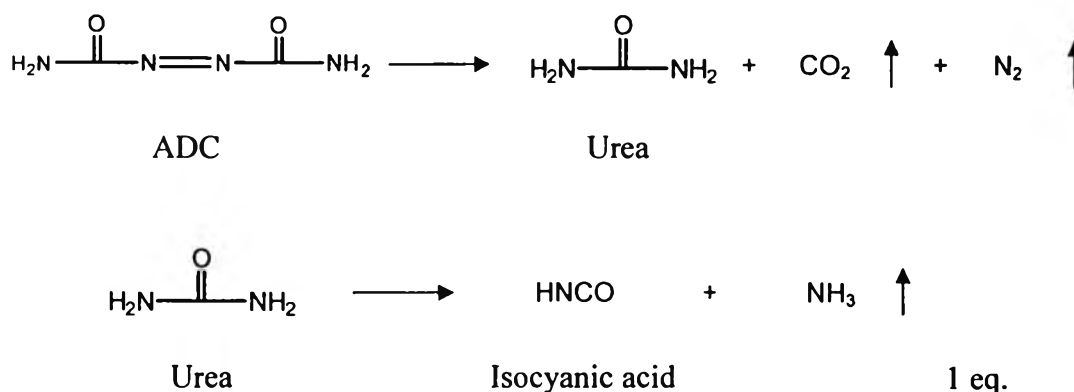
2.2.2.1 Inorganic Blowing Agents

These types of BA liberate gaseous products as a result of reversible equilibrium thermal decomposition. The reversible character of the reaction may result in a decrease in the gas content in the system, which can lead to a pressure drop in the foam cells causing shrinking of the material. Examples of these compounds are carbonates of alkali metals (such as sodium carbonate and bicarbonate, $(\text{NH}_4)_2\text{CO}_3$). These CBAs are not suited for producing flexing cellular material, but can be used successfully to produce microcellular rigid foams such as PVC and PC foams.

2.2.2.2 Organic Blowing Agents

In contrast to inorganic Bas these compounds liberate gaseous products as a result of Irreversible thermal decomposition reactions. The advantages of these organic CBAs are (i) the reaction is irreversible (ii) they can easily be mixed uniformly with the polymer and other compounding ingredients. Their main disadvantage is their high cost, and in some their toxicity. Most of the known organic CBAs fall into one of the following classes: azo and diazo compounds, N-nitro compounds, sulfonylhydrazides, azides, triazines, triazoles and tetrazoles, sulfonyl semicarbazides, urea derivatives, guanidine derivatives, and esters. The two most widely used organic Bas are azodicarbonamide and 4,4'-oxybis(benzenesulfonyl hydrazide). Azodicarbonamide (ADC or AZD) is one of the most effective high temperature CBAs and consequently the most widely used. It is a yellow powder that decomposes at 195-216°C depending on its method of

preparation. It evolves $220 \text{ cm}^3 \text{ g}^{-1}$ of gas (Eq.1) and leaves a white residue that is odourless, nontoxic, and nondiscolouring.



Note : Several other reaction take place during thermal decomposition of the ADC, but overall CO, CO₂, N₂, and NH₃ are the main gases liberated.

Unlike many other organic blowing agents, ADC does not support combustion and is self-extinguishing. The decomposition rate of ADC can be adjusted by using activators, or 'kicker', and a wide range of lower temperatures and high gas efficiency are the main advantages of ADC. Suitable activators include transition metal salts (especially those of lead, cadmium, and zinc), polyols, urea, alcohol amines, and some organic acids. The solids, which are not decomposed under the decomposition conditions, consists of urazole, hydrazodicarbonamide, cyanuric acid, etc. ADC is generally used for the foaming of thermoplastic polymers such as PE, PS, PVC, and ABS (acrylonitrile-butadiene-styrene terpolymer). It is also used for foaming certain. Rubber compositions.

2.3 Foams

Foamed plastics have been important ever since man began to use wood, it self a cellular form of the polymer cellulose. Cellulose is the most abundant of all naturally occurring organic compounds.

The word cellular is derived from the latin word cellula, meaning 'very small cell or room', and most of the polymer in a foam material does indeed exist in cellular form, e.g. in wood, natural straw, and seed husks. The combination of high

strength/weight ratio of wood, the good insulating properties of cork and balsa, and the cushioning properties of cork and straw have all contributed to the development of a broad range of cellular synthetic polymers in use to day. The first commercial man-made cellular polymer was sponge rubber, introduced between 1910 and 1920.

2.3.1 Classification of Cellular Polymers.

A cellular polymer is defined as 'a polymer the apparent density of which is decreased substantially by the presence of numerous cells disposed throughout its mass. Cellular polymers, or polymeric foams, are multi-phase materials consisting of a minimum of two phases—a continuous polymer matrix phase and a gaseous phase. There may be more than one solid phase present, as in the case of a blend or alloy of polymers. Other solid phases may be present in the form of fillers, either fibrous or other shapes, e.g. glass, ceramic, metal, or other polymers. Syntactic foams are specialized types of foam which are true composite three phase systems comprising hollow polymeric, ceramic, or glass microspheres dispersed in the continuous polymer matrix phase. The density of syntactic foam is generally lower than the solid polymer but not to the same degree as traditional foam materials. Their specialized market niche is in submarine applications—deep-sea diving equipment, diving bells, and submersibles where weight is reduced yet the foam composite can withstand the high hydrostatic two phase foams. In view of the limited packing density, Syntactic foams tend to have high densities of $\sim 600 \text{ kg m}^{-3}$ or higher. According to their complex nature, cellular polymers have been classified in a variety of ways, usually in terms of either the cellular morphology, mechanical behavior or composition. With respect to the cell structure, cellular polymers can be divided into two general classes:

2.3.1.1 *Closed Cell Foams*

The gas is dispersed in the form of discrete gas bubbles (Figure 2.4) and the polymer matrix exists as the only continuous phase. Gas transport take place by diffusion through the cell wall. Closed cell foams are generally formed by high-pressure techniques.

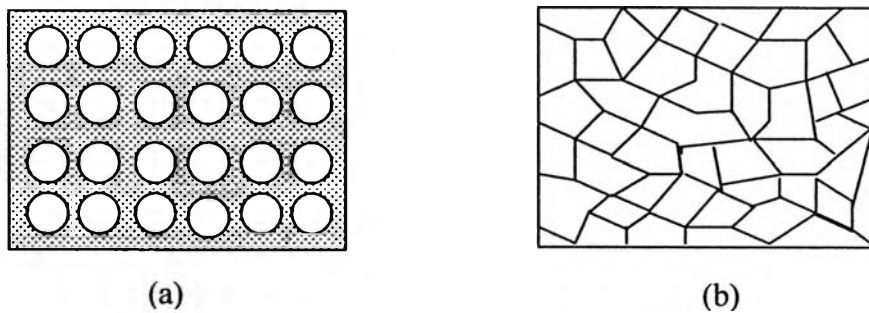


Figure 2.4 Closed cell foam structures 2.4(a) discrete cells dispersed in foam, e.g. syntactic foam 2.4(b) cells in contact with each other, e.g. expanded polystyrene foam.

2.3.1.2 Open Cell Foams

The voids (gas cells) coalesce so that the combined solid and gaseous phases are continuous (Figure 2.5) Therefore, the gas is able to flow through the polymer matrix under the action of some driving force. Open cell foams are generally formed during processing under ambient, i.e. low-pressure, atmospheric conditions.

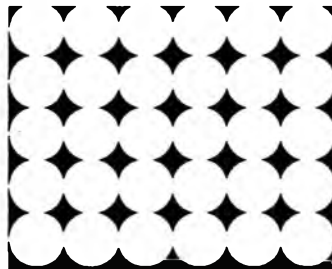
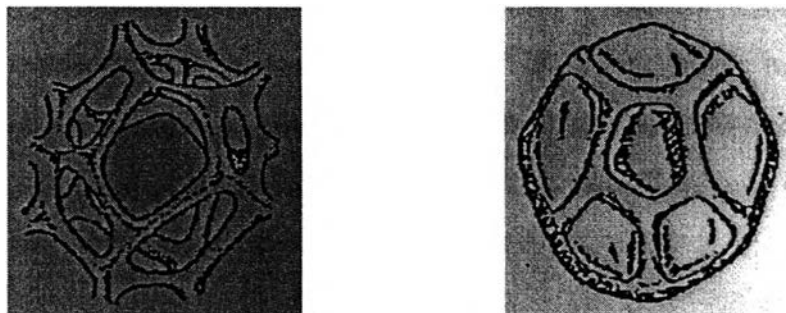


Figure 2.5 Idealised representation of open cell foam structure.

In practice, the two cellular morphological forms co-exist so that a polymer foam does not always have completely open or completely closed cells. The volume fraction of closed cells has a considerable influence on the mechanical behavior of these system, i.e. a high volume fraction of closed cells (low volume fraction of open cells) will lead to higher stiffness and strength. The main physical difference between the two types of cells, i.e. open and closed cells, is depicted in Figure 2.6



(b) Opened gas structural element (a) Closed gas structural element

Figure 2.6 Schematic representation of the gas structural element.

The open cell structure, Figure 2.6(a), consists of a lattice of struts, whereas for the closed cell structure, Figure 2.6(b), in addition to the struts there are windows or membranes of base polymer between the strut faces. These membranes are usually significantly thinner than the dimensions of the struts themselves but provide additional support and therefore stiffness and strength to the cell. Cellular polymers can also be classified according to their stiffness, the two extremes being rigid and flexible depending on the chemical composition, the rigidity of the polymer backbone, the degree of crosslinking (if any). Skochdopole and Rubens have defined each term as follows:

1. Rigid foams

The polymer matrix exists in the crystalline state, or if amorphous, below its glass transition temperature (T_g). Typical examples include most polyolefins, polystyrene (PS), phenolics (PFs), polycarbonate (PC), and some polyurethane (PU) foam, and plasticized poly(vinyl chloride) (pPVC) foam.

2. Flexible foams

The polymer matrix is always above its T_g . Typical examples include rubber foams, flexible PU foam, and plasticized poly(vinyl chloride) (pPVC) foam.

Intermediate between these two extremes is a class of cellular polymer known as semi-rigid. Although these materials have an elastic modulus higher than that of flexible foams, the stress-strain behavior is nevertheless closer to that of flexible systems than that exhibited by rigid foams.

2.3.2 Principle of Foam Formation

The most widely used system of producing foamed polymers involves (i) the nucleation of gas bubbles in a liquid polymer, (ii) the growth and stabilization of these bubbles, and (iii) the solidification of the polymeric phase by crosslinking or cooling to give a structurally stable cellular system.

2.3.2.1 *Bubble Formation*

In the general case described above, the first step in producing foam is the initiation of gas bubbles in a liquid system. This process is known as nucleation. In many cases, it is necessary to add nucleating agents such as talc and chemical silica to control cells size and cell distribution. Several techniques are used to entrain the gas in the liquid polymer before expansion.

(a) Thermal decomposition of a chemical blowing agent (CBA)

The solid blowing agent (BA) is intimately mixed with the polymer, preferably in the liquid state, and the mixture heated to a temperature at which the BA decomposes to give off an inert gas such as carbon dioxide (CO₂) or nitrogen (N₂). The polymer is then hardened either by gelation at this temperature (thermosetting plastics) or by cooling to room temperature (thermoplastics).

(b) Blowing due to an 'in situ' chemical reaction

Gas is formed by reaction of two chemicals and evolution occurs simultaneously with polymerization and crosslinking. This is an important process for the manufacture of PU foams.

(c) Low pressure release of a gas

Gas is dissolved in molten polymer under high pressure. On release of the pressure, expansion of the gas causes the formation of a cellular material which is then hardened. The extrusion of expanded polystyrene (EPS) sheet is an example of this foaming technique.

(d) Blowing by vapour from a volatile liquid

The liquid BA is incorporated into the polymer at atmospheric pressure and is converted into vapour by heat which may be externally applied or by exothermic heat from a crosslinking reaction. EPS beads and PU foams blown with chlorofluorocarbons (CFCs) are two examples of this method.

(e) Use of a temporary filler

Gases are not produced in this method. Particles of solid material are mixed with the polymer and processed to give a filled solid plastic. The filler is subsequently removed by leaching with a suitable solvent to give an open cell product. This method is used for foaming polytetrafluoroethylene (PTFE), which is difficult to expand by other methods.

(f) Mechanical entrapment of gas

Air is beaten into the liquid polymer to give a stable liquid foam, which is then cured either chemically or by heating. An open cell structure is foamed. It is probably the oldest method for forming cellular polymers-it was used to make foamed rubber latex as far back as 1920. However, this method gives a poor, coarse cell structure.

(g) Use of microspheres

Hollow spheres (micro-balloons) are stirred into a liquid polymer, which is then allowed to harden. The product is called 'syntactic foam' and the most common type is made by mixing phenolic spheres into liquid unsaturated polyester resin, then curing the resin.

Where the BA is incorporated into the molten polymer at high pressure, the melt becomes supersaturated with the BA.

Bubble nucleation is affected by a number of conditions. Physically, the effects of temperature, pressure, and in some cases humidity are fairly obvious. Other important parameters are surface smoothness of the substrate, surface characteristics of filler particles, presence and concentration of certain surfactants or nucleators, size and amount of second-phase liquid bubbles, and the rate of gas generation.

2.3.2.2 Bubble Growth

Lowering of the melt pressure relieves the supersaturation of the material, after which no new bubbles are formed. The solubilized gas then diffuses into the existing bubbles, causing them to expand. The initial bubble is spherical in shape and grows as a result of the differential pressure (ΔP) between the inside and outside of the cell. At equilibrium, ΔP , the interfacial surface tension (γ), and radius (r) of the bubble are related as follows,

$$\Delta P = 2\gamma/r \quad [1]$$

The differential pressure is larger for a smaller bubble than a larger bubble at a given surface tension. Consequently, smaller bubbles tend to equalize the pressure by growing faster and either break the walls separating the cells or the gas from the blowing agent diffuses from the smaller cells to larger cells according to equation [2].

$$\Delta P_d = 2\gamma \left[\frac{1}{r_1} - \frac{1}{r_2} \right] \quad [2]$$

Where ΔP_d is the difference in pressure between cells of radius r_1 and r_2 . The rate of growth of the cell depends on the viscoelastic nature of the polymeric material, the internal gas pressure, the external pressure on the foam, the cell size, and the permeation rate of blowing agent through the polymer membrane.

Saunders reported that a better bubble stability, a small average cell size, and a more even bubble size distribution is produced at low interfacial surface tension. Schematic representations of idealized cellular structures at different stages of bubble expansion are shown in Figure 4. The foam depicted in Figure 2.7(a) shows the bubbles uniformly dispersed throughout the liquid medium and if stabilized in this condition the foam would clearly have a high density. As the gas volume fraction increases, Figure 2.7(b), the foam density decreases. For spherical bubbles of uniform size, the lowest density is achieved when the bubbles are close packed.

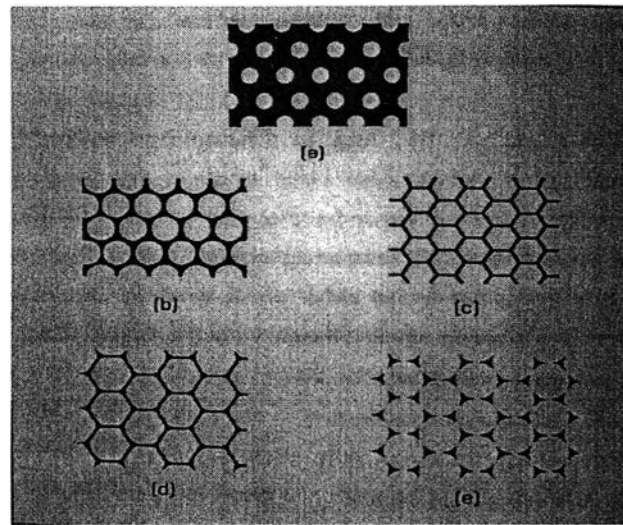


Figure 2.7 Schematic representation of cellular structures at different stages of foam expansion.

On further expansion, the bubbles eventually touch each other and the internal gas pressure presses the cells together causing the polymer to fill the interstices (available spaces). Thus, the cells become bounded by polyhedral, often represented in an idealized form as a pentagonal dodecahedron with plane surfaces of uniform thickness, but simplistically shown in two dimensions as a hexagonal honeycomb (Figure 2.7(c)). Depending on the physical state of the liquid system, i.e. its viscosity and surface energy, gravitational and other forces may cause the liquid material to concentrate at the intersection of the elements of the associated cells as depicted in Figure 2.7(d). At this stage the foam is of low density and is closed cell. However, the membranes between the cell struts, which represent the interface between the gas bubbles, may become ruptured and give varying degrees of connectivity between the cells. This gives rise to an open cell structure as represented in Figure 2.7(e).

Bubble stability during growth is a function of the type and concentration of surfactant present, the rate of bubble growth, the viscosity of the fluid medium, any differential gas pressure variations, and the presence of cell disrupting agents such as solid particles, liquid, or gases. As the cell walls are squeezed into polyhedral, a wall-thinning effect takes place, and liquid is drained

from cell wall faces into the cell intersection regions to form ribs or struts, which are typically triangular in cross section. If allowed to, this cell walls collapse and the cells become interconnecting. This mode of cell formation and development is a very important characteristic of most plastic foams and will affect thermal conductivity, moisture absorption, breathability, and load bearing properties.

The extent of drainage of liquid polymer from the membrane into the struts will be influenced by capillary action and gravity. Capillary drainage is proportional to the square of the distance between rib junctions. Increasing the viscosity of the fluid reduces the drainage effect. Viscosity increase may be brought about by (i) chemical reactions to increase molecular weight through polymerization or crosslinking or (ii) temperature reduction (thermoplastics).

2.3.2.3 Bubble Stabilisation

Ultimate stabilization is due to either chemical reaction continuing to complete gelation or the physical effect of cooling below a melting point or softening point to prevent polymer flow. As complete solidification is approached the previously formed spherical bubbles may become distorted by the flow of foam or by gravity, with resultant anisotropy of cellular structure. This effect must be considered when evaluating the physical properties of polymeric foams. Also, there is a tendency for the gas within the cell to equilibrate over a period of time at ambient temperature and pressure. This can result in changing properties with time as the balance between gas diffusion out of the cell and air diffusion into the cell takes place as the foam ages. For obvious "ageing" stage is minimized when nitrogen blown foams have no apparent ageing problems whereas hydrocarbon blown foams present significant ageing difficulties due to the diffusion rate of gas out of the cell being significantly greater than the diffusion rate of air into the cell. Consequently the foam is prone to collapse after manufacture, recovering slowly with ageing as air diffuse back into the cells. This problem is overcome in the manufacture of expanded polystyrene (EPS) moulding by first preparing pre-expanded beads. These beads are equilibrated before being charged into a steam chest for moulding.

2.3.3 Cellular Structure

A typical foam structure contains cells of many shapes and sizes. Two dimensional cell representations are assemblies of triangles, squares and, more commonly, pentagons or hexagons, whereas there are a wide variety of cell shapes in three dimensions, most commonly pentagonal dodecahedrons (twelve pentagonal faces per cell) as illustrated in Figure 2.8

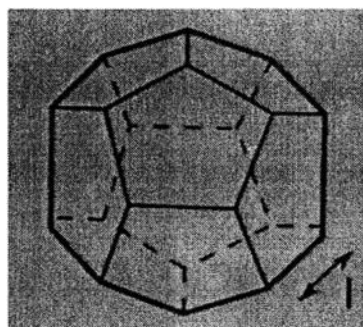


Figure 2.8 A pentagonal dodecahedron cell structure.

From a fundamental point of view, a liquid foam is most stable when the gas bubbles are perfectly spherical in shape because the interfacial area and the capillary pressure are at their minimum values. For a monodispersed spherical cellular structure, the closest packing pattern is obtained when each sphere contacts 12 neighbours; the gas then occupies 74% of the total volume of the foam. If the gas volume ratio is further increased, the spheres have to deform to accommodate the higher gas volume and cells become polyhedral in shape.

It is commonly found that cellular polymer are anisotropic, that is, the cells are elongated in the direction of foaming as shown in Figure 2.9

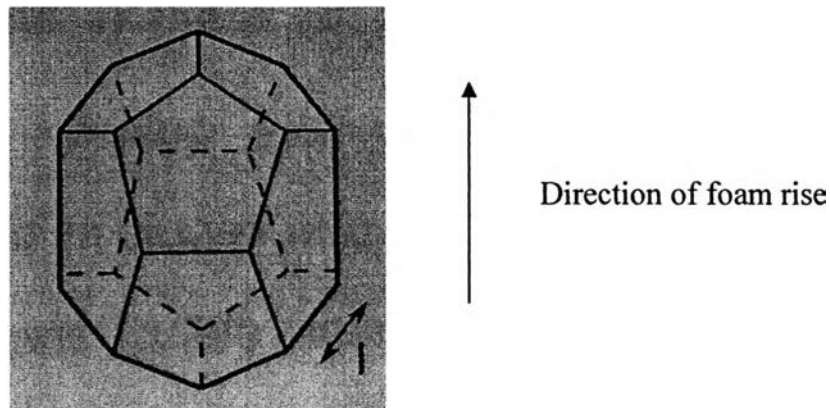


Figure 2.9 Representation of cell elongation during foam rise.

The mechanical stresses generated during foaming are not distributed uniformly throughout the volume of foam, hence the gas bubbles tend to expand along the directions of minimum local stress. In free-rise PU foaming, the extent of elongation of the cells decreases from the bottom to the top layers of the block, with the cells in the uppermost layers being substantially spherical. When foam expands in a closed space, the cellular anisotropy is always lower than for free-rise foaming, and cell elongation occurs only near the mould walls. The higher the pressure developed in the mould, the closer the cells approach a spherical shape. However, the outermost layers of the foam article usually contain very small cells, and under high pressure the surface layer of a block of foam is relatively smooth. Usually, where a foam contacts a mould surface the cells collapse to give a solid, smooth skin on the surface of the foam.

Anisotropy is commonly found in PU foams whereas thermoplastic foams such as polyethylene (PE), polypropylene (PP), PS, and PVC tend to be more isotropic.

2.3.4 General Properties of Cellular Polymers

Foaming dramatically alters the range of physical and mechanical properties of the base material. The mechanical properties of the solid polymer exert a strong influence on the properties of the foam, which are also affected by processing techniques and conditions, molecular orientation, crosslink density(if applicable), additives and blowing agents(s) used-or more strictly the gas in the cells of the newly formed foam.

The tendency of the gas within the cell to equilibrate with the ambient atmosphere over a period of time can result in changes in properties with time as the balance between gas diffusion out of the cell and air diffusion into the cell takes place during the ageing process. Nitrogen blown foam ages best as the cell contains a gas mixture similar to the environment, i.e. air. On the other hand, butane blown foams suffer from gas diffusing out of the cells at a much faster rate than air can enter the cells and replace the butane. This results in cell, i.e. foam, collapse and slow thickness recovery, which may never attain 100%.

However, most marked changes in the properties of foams are found by changing the gas/polymer ratio, i.e. the foam density. Density particularly affects the following parameters: (i) modulus, (ii) strength (in tension and compression), and (iii) thermal conductivity. The term 'foam density' can be defined as follows,

$$\text{Foam density} = \text{Mass/Volume} \quad (\text{can change during the ageing process})$$

Foam typically have the following density ranges :

$$\begin{aligned} > 600 \text{ kg m}^{-3} &= \text{High density} \\ 100\text{-}600 \text{ kg m}^{-3} &= \text{Intermediate density} \\ < 100 \text{ kg m}^{-3} &= \text{Low density} \end{aligned}$$

The mechanical properties of rigid foams differ markedly from those of flexible foams. The tests used to characterize both types of foam therefore differ, as do their application areas. Compressive properties are perhaps the most important mechanical properties for cellular polymers. Compressive energy absorption characteristics and deformation characteristics of a foam depend mainly on density, type of base polymer, and the predominance of either open or closed cells.

In simple terms, open cell foam (invariably flexible) relies on cell walls bending and buckling, which is essentially a reversible process (Figure 2.10)

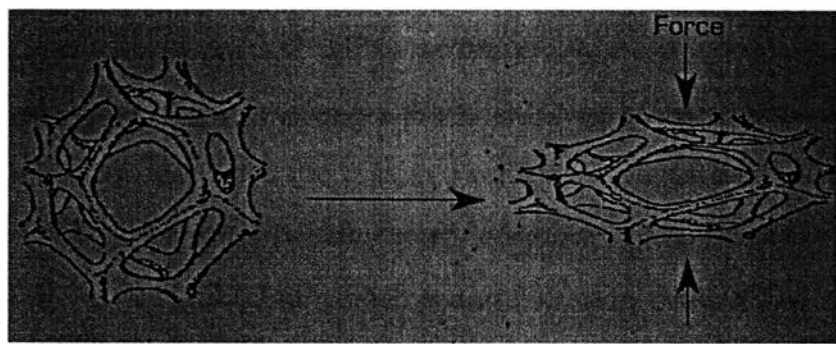


Figure 2.10 Schematic representation of open cell deformation.

In addition, as the cells become more compacted during compression, the escape of air through and out of the foam will become increasingly more difficult. The entrapped air will therefore offer some resistance to foam deformation during the final stages of compression.

On the other hand, air flow is not a consideration with closed cell foams. In this case (Figure 2.11) deformation involves cell wall bending/buckling (reversible), gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rupture.

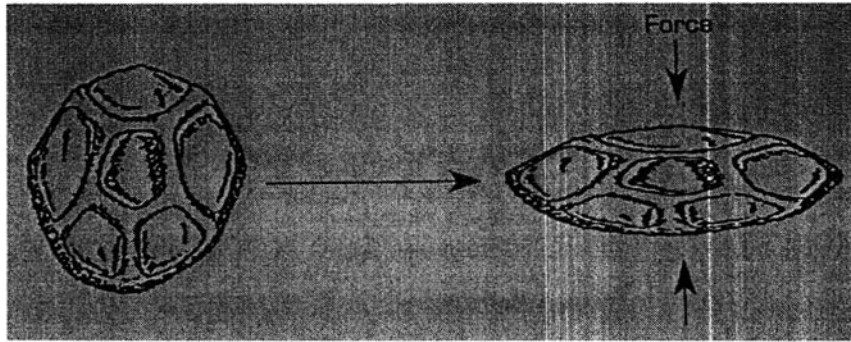


Figure 2.11 Schematic representation of closed cell deformation.

Closed cell rigid foams (e.g. PS and PU foams) exhibit from very limited to no yielding behavior. Consequently, gas compression and matrix strength play important roles during the mechanical deformation of rigid foams. In addition, cell rupture often occurs during the energy absorption process.

The energy absorbing characteristics of foam can be represented in terms of compression stress-strain curves of flexible and rigid cellular polymers, respectively.

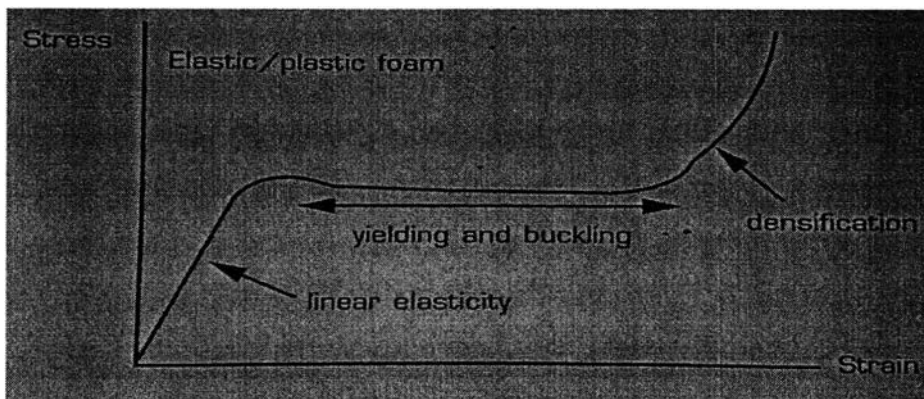


Figure 2.12 Typical compressive stress-strain curve for flexible foams.

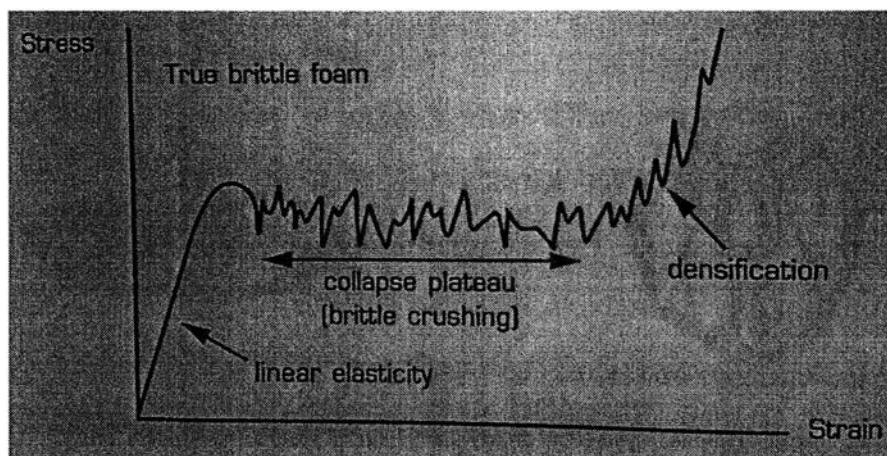


Figure 2.13 Typical compressive stress-strain curve for rigid foams.

In the case of an elastic/plastic foam, e.g. a flexible closed cell foam, deformation at small strains shows classical elastic response corresponding to cell wall stretching. A long collapse plateau follows this as gas compression occurs accompanied by cell wall yielding and buckling. When the cells have almost completely collapsed, opposing cell walls start to touch each other and further strain results in densification of the base polymer as the material approaches a completely solid state. Open cell foams exhibits a more gradual increase in the stress-strain curve until the onset of the collapse plateau; moreover, densification occurs at lower stress values than for closed cell foams. For rigid foams, elements of true brittle crushing are superimposed on the elastic/plastic response. The erratic nature of the collapse plateau corresponds to intermittent rupturing of individual cells. Due to cell rupture in rigid foams, resilience is dramatically affected. Foams can generally withstand only single impacts, for example the liners used inside riding or cycle helmets.

Rigid Cellular Polymers : The compressive strength of rigid cellular polymers is usually reported at some definite deformation (5 or 10%). The modulus is then extrapolated to 0% deformation unless otherwise stated. Structural variables that affect the compressive strength and modulus of these foams are, in order of decreasing importance, plastic phase composition, density, cell structure, and gas composition.

Tensile strength and modulus, flexural strength and modulus, and shear strength and modulus of rigid foams vary with density in much the same way as for compressive properties. The structural variables most important to the tensile, flexible and shear properties are polymer composition, density and cell shape.

Structural Foams : Structural foams are usually produced as fabricated articles by injection moulding or extrusion processes. The most important structural variables are polymer composition, density, and cell size and shape. Structural foams have relatively high densities, e.g. 700 kg m^{-3} , and they generally do not have uniform cell structure, which means there is considerable variation in properties with part geometry.

Flexible Cellular Polymers : The compressive nature of flexible foams, under both static and dynamic deformation modes, is their most significant mechanical property giving rise to their wide use in comfort cushioning, packaging, and wrapping apparel. The load-deflection curve between 0 and 75% deflection and its return to 0% deflection at the speed experienced in the anticipated application characterizes the compressive behavior of a flexible foam. The most important variables affecting compressive behavior is also influenced by part geometry. Figure 2.14 shows the effect of polymer composition on compressive behavior.

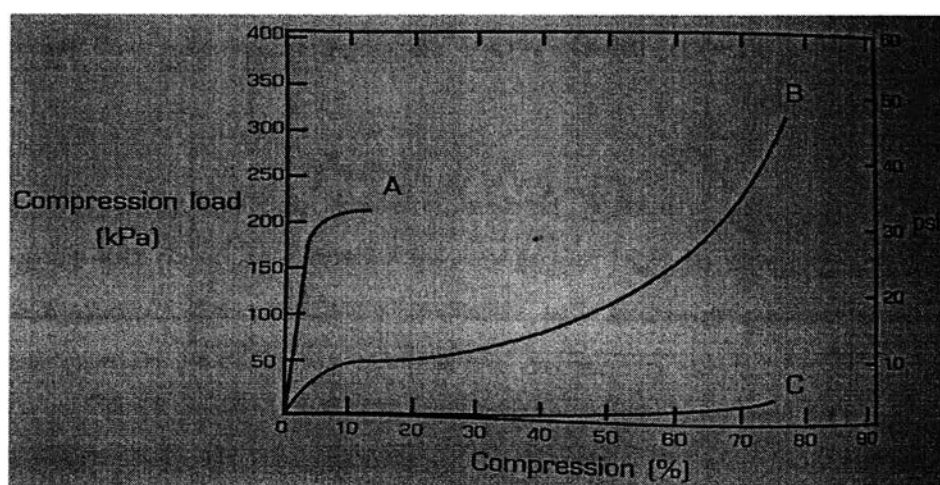


Figure 2.14 Effect of polymer composition on the compressive behaviour of some polymeric foams with densities of 32 kg m^{-3} (A) PS foam; (B) PE foam; (C) latex rubber foam.

2.4 Carbon Foams

Montserrat *et al* (2008), carbon foams are lightweight ($0.2-0.8 \text{ g cm}^{-3}$) and exceptionally strong cellular materials, with high-temperature resistance (up to $3000 \text{ }^{\circ}\text{C}$ under reducing or inert atmosphere) and thermal and electrical conductivity adjustable by the foaming thermal treatment. Their low production costs and flexible physical properties make them ideal for a wide range of applications in such diverse areas as thermal management, electromagnetic interference, acoustic shielding, energy absorption and storage, catalysts supports, filtration, etc. Carbon foams were first developed as reticulated carbons from thermosetting organic polymer foams through a thermal treatment that rendered macroporous refractory materials with a uniform cell size and moderate mechanical strength, especially intended for thermal insulating applications or as lightweight construction materials for the aerospace industry.