CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Background on polymer science

2.1.1 Polymer crystallinity

Polymers are organic macromolecules that comprised of several thousand repeating segments which are linked together in a chain-like form. They have been considered as an inexpensive alternative to more common materials such as metal, wood, and glass. The polymeric molecular weight is depended on the degree of polymerization (n). Polymers are classified into two major categories; thermosetting and thermoplastic polymers [18]. Thermosets have three-dimensional organic structure that cannot be reprocessed once the products are formed. They were processed ably set or crosslinked upon heating. The crosslinking process actually is the formation of chemical bonds between the long chains [18] as shown in Figure 2.1 (a) and (b) [19].

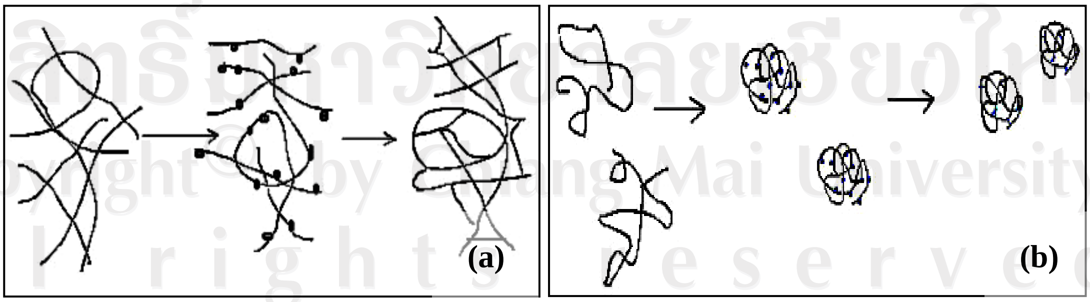
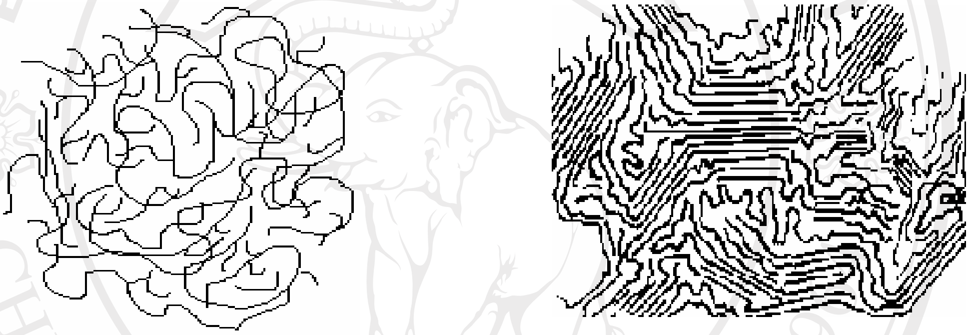


Figure 2.1 Crosslinking process (a) Intermolecular crosslinking due to the fixation of entanglement in concentrated polymer solution and (b) Intramolecular crosslinking in diluted solution [19].

The terms used to refer to the crosslinking process are set, cure, or vulcanize [18]. These thermosetting polymers are rigid materials and network polymers, in which chain motion is greatly restricted by a high degree of crosslinking [20]. The additional chemical bonds of the crosslinked thermosetting polymer allow it to absorb more thermal energy (heat) before the carbon chain is broken. This is the reason they usually are able to perform at higher temperatures [18]. These polymers such as epoxy, polyurethane (PU), and tires are counted as the thermosets. On the other hand, thermoplastic polymers or thermoplastics can be reprocessed many times. They soften upon heating and harden upon cooling. Unlike thermosets, there are no chemical bonds between the long chain molecules, but the way the thermoplastic molecules position themselves next to each other and the intermolecular forces that hold them together further affects their properties and classification. Random entanglement of the thermoplastic molecules, much like the long spaghetti on the end of the fork, is called amorphous structure (see Figure 2.2 (a)). Amorphous means without a logical order. Amorphous thermoplastics can be clear, have uniform (isotropic) properties in all direction, and have a wide range of melting temperature. Typical amorphous thermoplastics are polystyrene, acrylics, polycarbonate, and polyvinyl chloride, etc [18]. They are glassy brittle at room temperature. As the amorphous polymer is heated, the molecular chains become mobile until the polymer structure becomes rubbery. The brittle glass-to-ductile rubbery transition is the glass transition, which occurs over a few degree of temperature. This temperature is called the glass transition temperature (T_g). As the polymer continues to heat, there is no further transition. Instead, the polymer becomes more and more fluid and less and less rubbery until it is a truly pumpable liquid. A polymer becomes glassy again only by cooling it through this transition region. Characteristically, amorphous polymers have substantial free space around the polymer chains. This space is commonly called free volume. Free volume account for 10 to 15% of the total bulk volumes of amorphous polymers. This free volume can be occupied by small molecules such as foaming agent gases and organic additives [21].

In the other words, molecules that have an order in the solid state are referred to as semicrystalline. Micron-size crystallites are the common crystalline structure. A crystallite is usually spherical and is sometimes called a spherulite. A spherulite is comprised of ribbon-like elements called lamellae. In addition, a lamella is comprised of molecules that are fold back and forth across its width. Because polymer molecules are very long and somewhat bulky, usually only a portion of the molecular chain folds into the crystallite. The remaining portion has no regular molecular order and is therefore amorphous. At low temperature, the amorphous portion is glassy and brittle. The extent of free volume depends on the degree of crystallinity. When a crystalline polymer is heated, the molecular chains in the amorphous portion of the polymer become increasingly mobile until the polymer becomes rubbery and the amorphous portion of the semicrystalline polymer passes through the glass transition temperature. However, those portions of the polymer chains that are embedded in the crystallites act to maintain the rigidity of the bulk polymer. But the crystalline phase that is above its glass transition temperature remains a solid. All semicrystalline polymers have melting temperature. Since not all crystallites are perfectly formed, imperfect ones melt at lower temperatures than perfect ones. Most semicrystalline thermoplastics have melting temperature ranges of a few degrees. Convention again defines the melt temperature as that temperature where most of the crystallites melt. Typically, crystalline polymers are quite fluid above their melt temperatures. Unlike crystal structure in salt or metals, semicrystalline in thermoplastics refers to an occasional order where molecules may line up next to one another (see Figure 2.2 (b)). This semicrystalline thermoplastic is characterized by its opacity, non uniform (anisotropic) properties, and distinct or narrow melting range. Typical semicrystalline thermoplastics are polyethylene (PE), polypropylene (PP), nylon, and thermoplastic polyesters [18].



(a) Amorphous structure (b) Semicrystalline structure

Figure 2.2 Structure of long plastic molecules [22].

However, commercialization of thermoplastics required high levels of monomer purity and high pressure and temperature equipment, conditions that were not achieved until the early to mid-twentieth century. By the end of the World War II, thermoplastics were competing commercially with thermosets. Thermoplastics now represent more than 80 % of all polymers commercially produced worldwide [21].

For such normal hydrocarbons, it is well known that crystallization will take place very rapidly on lowering the temperature only infinitesimally below the equilibrium melting temperature. On the other hand, the polymer can be crystallized by reducing the temperature well below the melting temperature even for a low molecular weight fraction. In the former case, the chains are completely extended and molecular crystals are found since each molecule is of exactly the same length. The crystallization of long-chain molecules will occur at finite or reasonable rates only at large under the cooling (i.e., 20-40 °C) below the melting temperature. Consequently, polymer with polycrystalline system that is only partially crystalline or semicrystalline is formed. As Figure 2.2 (b), high molecular weight polymers usually form folded structures. The crystallite structure is form as a complex morphology. The crystallite structure is resulted from the polycrystalline nature of the system, which involves a description of the structure of the actual crystallite. The supermolecular structure is concerned with organization of the crystallites into larger structures. Now, the attention is directed to the crystalline structure. It is well established and accepted that a lamellar-like crystallite is developed crystallization from the pure melt. These crystallites possess some important features. The lamellar thickness is of the order of 100-200 angstroms (dilute-solution-formed crystals) depending on the crystallizing solvent and temperature. Since the thickness of crystallites in the chain direction is only of the order of 100-200 angstroms, a single chain must traverse the crystallite from which it originates many times [23].

Polymer crystallinity is one of the important properties of all polymers. Polymer exists both in crystalline and amorphous form. It is well known that the part of molecules are arranged in regular order, these regions are called crystalline regions. Between these ordered regions molecules are arranged in random disorganized state and these are called amorphous regions. Crystallinity is indication of amount of crystalline region in polymer with respect to amorphous content. Crystallinity influences many of the polymer properties some of them are; hardness, modulus, tensile, stiffness, crease, and melting point. Therefore, selecting polymer for required application its crystallinity plays foremost role [24]. Modern techniques such as infrared spectroscopy and neutron scattering suggest that the fold perfection in such crystals is about 75 percent. In fact, polymer single crystals are not of great commercial importance, although strong mats resembling a sheet of paper can be prepared from them. The importance is that they are started a whole new line of thought concerning the morphology and basic character of crystalline polymers and provided new insights into structure-property relationships for crystalline and semicrystalline polymer materials. The most of polymers of commerce are potentially crystallizable, and in practice do frequently exhibit crystalline, or more often semicrystalline, properties. Depending on intended use, the crystallinity can be either useful or detrimental. More frequently, the crystalline regions are relatively effective barrier to diffusion of gases and small molecules. Hence, the use of semicrystalline polymers (i.e., PE, PP) in applications such as plastic foams, food packaging is not much. This is because the crystalline regions may act as physical, rather than chemical as a stiff phase of the polymer which imparts mechanical stability and processability [25].

2.1.2 Comparison of semicrystalline and amorphous polymers

There are some unique differences between semicrystalline and amorphous polymers. Table 2.1 compares polymer characteristics for semicrystalline and amorphous polymers. The uniformly packed molecules present in semicrystalline polymers are not found in amorphous polymers [26].

Table 2.1 Comparison of semicrystalline and amorphous polymers [26].

Characteristics	Semicrystalline	Amorphous
Uniformly packed molecules	Yes	No
Randomly packed molecules	Yes	Yes
Sharp melting point	Yes	No
Clarity	Opaque/Translucent	Transparent
Shrinkage	High	Low
Chemical resistance	Good	Poor
Hardness	Hard	Soft
Easy to melt	High	Low

Generally, in the extrusion process, it is required to be started at low temperature with an amorphous material than with a semicrystalline resin. Above the melting point, semicrystalline polymers flow very easily with low viscosity. Amorphous resin viscosity in normal tends to be more temperature sensitive with the viscosity decreasing more rapidly as the resin temperature is increased. Close to their T_g, amorphous polymers are more apt to be very thick and require higher motor load to process. In addition, semicrystalline polymers require more energy to melt than amorphous material. This is because semicrystalline polymers have a very sharp melting point, while amorphous polymers soften slowly above their T_g until the polymers start to flow. More energy requirement of melting with a semicrystalline resin is to provide the additional heat for fusion the crystal phase. During the melting of semicrystalline polymer, the additional heat must be added until the crystalline phase is melted and the added energy is called the heat of fusion.

Starting up an extruder with a semicrystalline polymer in the barrel or die, it is necessary to heat soak the barrel to ensure the temperature is above the polymer melting point and the polymer is molten. If the polymer is become solid and the die is blocked by the solid polymer then the extruder head pressure builds up very rapidly and it can blow the die off the machine or blow the rupture disk or cause polymer to flow back out the vent. Thus it is necessary to preheat the die prior to the extruder barrels because the die needs extra time to come to equilibrium. Amorphous materials do not have a sharp melting point; instead of the equipment can be started with the screw generating the shear heat required to soften the material sufficiently for processing [26].

Another characteristic shown in Table 2.1 is that amorphous polymers are transparent. This is due to the effect of its structure which packed in a random configuration take up more volume than orderly, closely packed molecular chains as good as the structure of semicrystalline polymers. This results amorphous polymers in generally tend to be softer than semicrystalline polymer. Semicrystalline polymers tend to be more resistant to chemical attack than amorphous polymers. While a certain amorphous polymer may be susceptible to chemical attack by solvent, that solvent may not attack a crystalline polymer. The orderly structures in semicrystalline resins in general are more thermodynamically stable and tighter packed, making chemical attack more difficult. Moreover, due to the uniformly closely packed of atoms in crystalline regions of semicrystalline polymers, their densities are higher than those of the amorphous polymers. The density of semicrystalline polymer is a weighted average of the amorphous and the crystalline regions [26].

2.1.3 Crystallinity determination

In the molten state of polymer, the crystallized polymer is never completing crystalline. This is because there are an enormous number of chain entanglements in the melt and it is impossible for the amount of organization required to form a 100 % crystalline polymer to take place during crystallization. The degree of crystallinity is of great technological and practical importance and several methods, which do not always produce precisely the same results, have been devised to measure it. There are many powerful methods for determining the degree of crystallinity, such as wide-angle X-ray scattering (WAXS), nuclear magnetic resonance spectroscopy (NMR), infra-red spectroscopy, and differential scanning calorimetry (DSC) [20].

DSC is a technique in which the difference in energy inputs into a substance (the sample) and a thermally inert reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. DSC has many useful applications in both qualitative and quantitative such as glass transition temperature (T_g), melting studies (T_m and ΔH_m), crystallization studies (ΔT_c and ΔH_c), and % crystallinity. The principle of crystallinity determination using DSC is an investigation of the enthalpy change (ΔH_m) during the melting of semicrystalline polymer. The degree of crystallinity of a semicrystalline polymer can be determined compared to the heat of melting of the theoretical 100 % crystalline polymer (ΔH_m^*) as Equation 2.1 [27].

$$\frac{\Delta H_m}{\Delta H_m^*} \times 100 = \%crystallinity \tag{2.1}$$

It should be understood that the value of the % crystallinity calculated from ΔH_m in the previous equation is the pre-melt %crystallinity after crystallization has already taken place. However, if melting is proceeded by crystallization, then the initial % crystallinity before crystallization occurred will obviously be less than after. If the melting and crystallization are energetically equation but they are the opposite processes. Thus, in order to calculate the initial % crystallinity of the sample before crystallization, it is necessary to modify the above equation to Equation 2.2 [27].

$$\frac{\Delta H_m - \Delta H_c}{\Delta H_m^*} \times 100 = initial\,\%crystallinity \qquad (2.2)$$

2.1.4 Thermal properties of polymers

2.1.4.1 Glass transition temperature

The glass transition temperature (T_g) is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. Since cooling cause the polymer to freeze into an unordered solid, this process is also referred to as vitrification. T_g is a secondary thermodynamic transition related to the flexibility of a polymer backbone, the secondary interchain forces acting on it, and the free volume of the system. These same parameters determine the crystalline transition temperature (T_m); therefore, it is reasonable that T_m by T_g vary similarly from polymer to polymer. In general, T_m exceeds T_g by a factor of 1.4-1.7 on an absolute temperature scale. The more able a chain or chain segment is to move, the less energy is required and therefore the lower the temperature at which movement occurs. This motion is now thought to be a segmental jump-rope rotation. There are some factors which contributing to T_g such as bond type, bond length, bond polarity, rotational freedom, type of functional group, type of secondary bonds, regularity of backbone, type, size, number, and substituted group, etc. The relationship of mechanical properties to temperature can be determined by monitoring almost any physical property while gradually changing the temperature because the properties change so drastically from the rubbery to the glassy state. Some of these properties are hardness, volume, strength, percent elongation-to-break, modulus, and permeability. The temperature at which a relaxation occurs produces a change in the effect of the property with temperature. It is a secondary change and not a discontinuity as in the case with T_m. The T_g is important for end users of a polymeric product in that most application demand that no significant property changes occur over the temperature range of its use. The T_g is closely related to other mechanical property changes with temperature which are important for use by engineers in design criteria. Because the T_g can be affected externally or internally on a molecular level as regards the chain backbone. It can be lowered by the addition of plasticizers which allow a greater molecular freedom in the polymeric matrix. This could be considered an external modification which almost always lowers the T_g. However, some fillers or additives can serve to form secondary bonds to flexible portions of the backbone and thereby raise the T_g. Internal processes can also affect the T_g in either direction. Internal refers to a chemical modification rather than a physical one. While anything which will decrease the flexibility (stiffer functional groups in the backbone, crosslinking, etc.) will increase T_g, and these factors which increase backbone flexibility (primarily bonding) will lower T_g [28].

2.1.4.2 Crystalline transition (melting) temperature

The crystalline transition temperature (T_m) is a primary thermodynamic transition which exhibits a discontinuity in the property and temperature curve rather than a change in slope. It is the temperature at which the crystallites lose their intermolecular bonding and go to the amorphous or rubbery state. This transition can be observed and accurately determined by use of a polarizing microscope and hot stage. Since these types of intermolecular bond forces are much stronger than those in the amorphous glass, the T_m always occurs at a value higher than T_g. The ratio of T_m/T_g on an absolute temperature scale is generally found to be in the region of 1.4-1.7. For this reason little change in property is seen at the T_m for polymers with low crystallinity; i.e., the polymer is largely already rubbery (the continuous phase of the system is rubbery), and the bulk properties are determined primarily by the continuous phase which does not experience the T_m [28]. When allowance the polymer to be melted by heating to the T_m, the polymer crystals begin to fall apart. Then the chains come out of their ordered arrangements, and begin to move around freely [20].

2.1.5 Thermal analytical techniques

Thermal analysis is a term used to cover a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature. Many techniques and instruments are known to those involved in thermal analysis such as differential thermal analysis (DTA), differential scanning calorimetry (DSC); which used for determining T_g and T_m, and thermogravimetric analysis (TGA). The last method measures the weight comparing to the temperature. While DSC and DTA are the common methods in the laboratory of the polymer chemist to determine both the T_g and T_m. Briefly, DTA is a measure of the difference in temperature between the sample and the inert reference material as the temperature of the common chamber is raised. Thus, if a material experiences a T_g or T_m, energy is consumed and its temperature lags behind that of the reference, hence a negative slope. In DSC the measured data is not temperature differential, but rather a measure of power input required to maintain equal temperatures between sample and reference as both are raised in temperature according to a predetermined program. Therefore, in this situation the current required for the individual heaters is measured and this differential is plotted. DSC can be used to conduct quantitative experiments regarding a thermal process with 1-2% accuracy. This device consists of two pans. In one pan, the polymer sample is loaded. The other pan is the reference pan and is normally left empty. These two pans are located on top of a heater [29] as shown in Figure 2.3 [27]. The computer assembly will turn on the heaters and the heating rates of the two pans are accurately controlled (about 10 °C per minute). The computer programs the heating rate to stay exactly the same through out the experiment. It is also important to note that the two separate pans, with their heaters are heated at the same rate as each other. The presence of polymer material in the sample pan results in an uptake of more heat in order to keep the temperature of the sample pan increasing at the same rate as the reference pan. This means that the heater underneath the sample pan will provide more heat energy than the heater under the reference pan. The DSC experiment is all about the measurement of heat amount that the sample pan heater has to put out as compared to the reference pan heater.

In DSC experiments the data of temperature increase are plotted against the difference in heat output of the two heaters at a given temperature. It is important to recognize that not all polymers will show the crystallization temperature (T_c) and T_m. T_m and T_c will only show up for polymers that can form crystals. Completely amorphous polymers exhibit only T_g. However, polymers with both crystalline and amorphous domains will show all the features [29] as shown in Figure 2.4 [27].

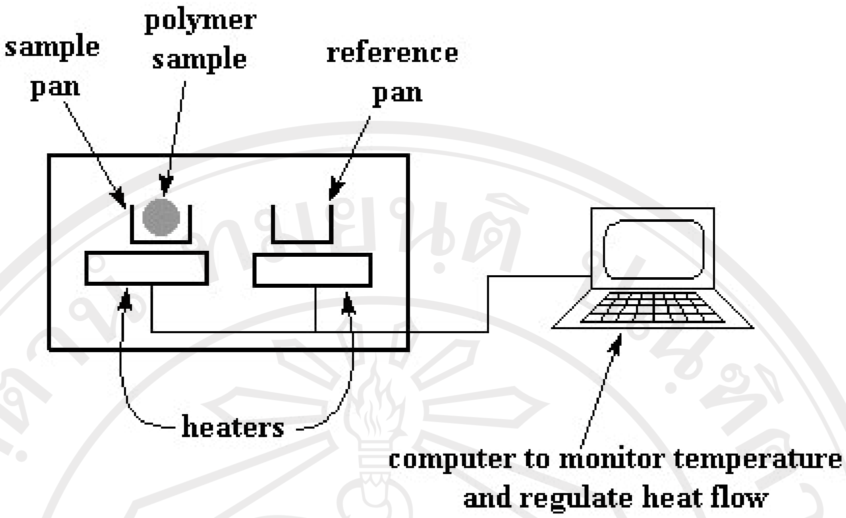


Figure 2.3 Schematic of differential scanning calorimeter (DSC) [27].

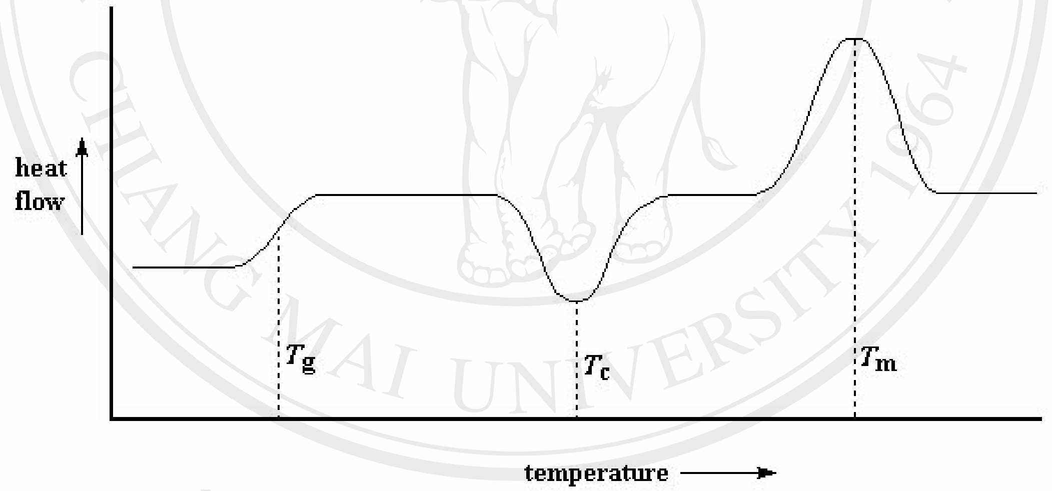


Figure 2.4 Typical DSC thermogram of completely amorphous polymer [27].

2.1.6 Mechanical properties of polymers

The mechanical properties, among all properties of plastic materials, are the most important properties because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. Mechanical property data are used regularly to preselect materials, estimate part performance, and predict deformation and stresses from applied loads. The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength. Although these values are normally derived from the technical literature provided by the material supplier, but in practically plastics are seldom and steady deformation without the presence of other adverse factors such as environment and temperature. Therefore, a thorough understanding of mechanical properties, tests employed to determine such properties, and the effect of adverse conditions on mechanical properties over a long period and short-term is extremely important. In this research, the experiment has focused on the mechanical properties (i.e., tensile properties and impact strength) of the foams based upon testing done over a shot period of time, does not account for long-term phenomena, such as creep or stress relaxation. This information should be used only when loading or other stress is applied for such a short period of time that the long-term effects are insignificant. All mechanical properties are tested at room temperature unless otherwise stated [30-31].

The basic understanding of stress-strain behavior of plastic materials is of utmost importance to design engineers. A typical stress-strain diagram is illustrated in Figure 2.5 [30].

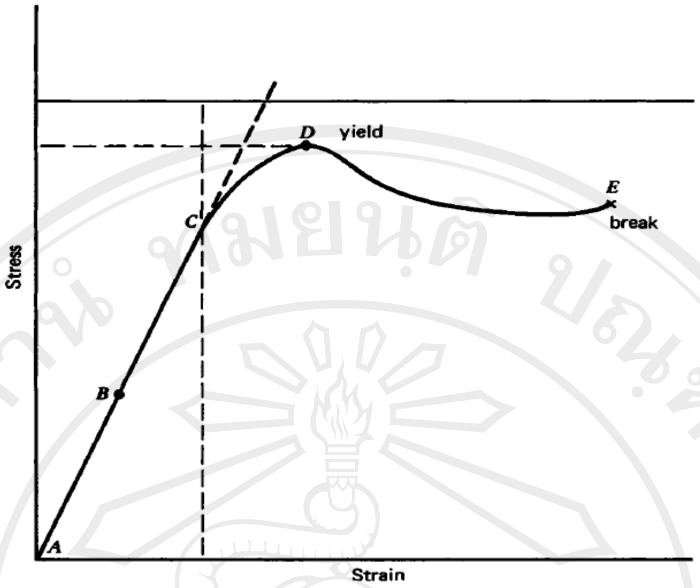


Figure 2.5 A typical stress-strain diagram [30].

This diagram is typically obtained in tension for a constant rate of loading. However, the curves which obtained from other loading conditions such as compression or shear are quite similar in appearance. The initial portion of the stress-strain curve between point A and C is linear which states that for an elastic material the stress is proportional to the strain. The point C at which the actual curve deviates from the straight line is called the proportional limit, meaning that only up to this point is stress proportional to strain. The behavior of plastic material below the proportional limit is elastic in nature and therefore the deformations are recoverable. The deformations up to point B are relatively small and have been associated with the bending and stretching of the inter-atomic bonds between atoms of plastic molecule. This type of deformation is instantaneous and recoverable. The deformation that occurs beyond point C is similar to a straightening out of a coiled portion of the molecular chains. There is no intermolecular slippage and the deformations may be recoverable ultimate, but not instantaneously. The extensions that occur beyond the yield point or the elastic limit of the material are not recoverable [30]. At point D, the yield point marks the beginning of the region in which ductile plastic continues to deform without a corresponding increase in stress. Elongation at yield gives the upper limit for applications that can tolerate the small permanent deformations that occur between the elastic limit and yield point, but not the larger deformations occurring during yield. Point E, the break point, shows the strain value at which the test bar breaks. These five transitional points, important in plastics part design, are the basis for several common tensile properties [31]. The polymeric materials can be broadly classified in terms of their relative softness, brittleness, hardness, and toughness. The tensile stress-strain diagrams serve as a basis for such a classification. The area under the stress-strain curve is considered as the toughness of the polymer. Figure 2.6 shows typical tensile stress-strain curves for several types of polymers.

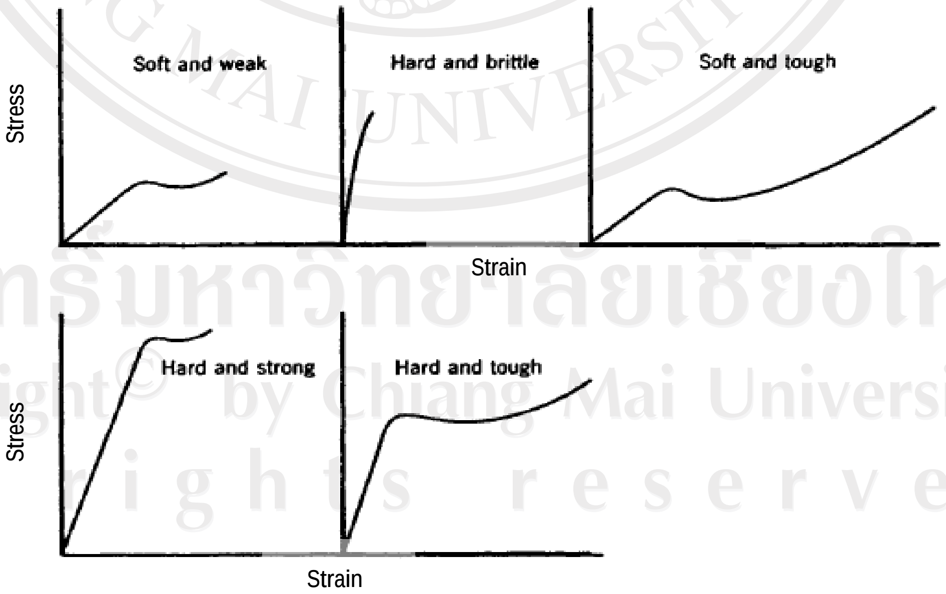


Figure 2.6 Typical tensile stress-strain curves for general polymers [30].

2.1.6.1 Tensile properties

Tensile properties are important in structure design and used to compare the relative strength and stiffness of plastics. The standard tensile test for plastics is ASTM D638 and the procedure is performed by involve clamping a standard molded tensile bar into the test device as shown in Figure 2.7. The device's jaw then moves at a constant rate of separation between the clamps [31]. The result usually expressed as a curve illustrating the relationship between stress, or the force per original cross-sectional area, and the strain, defined as percentage change in length as can be seen in Figure 2.5).

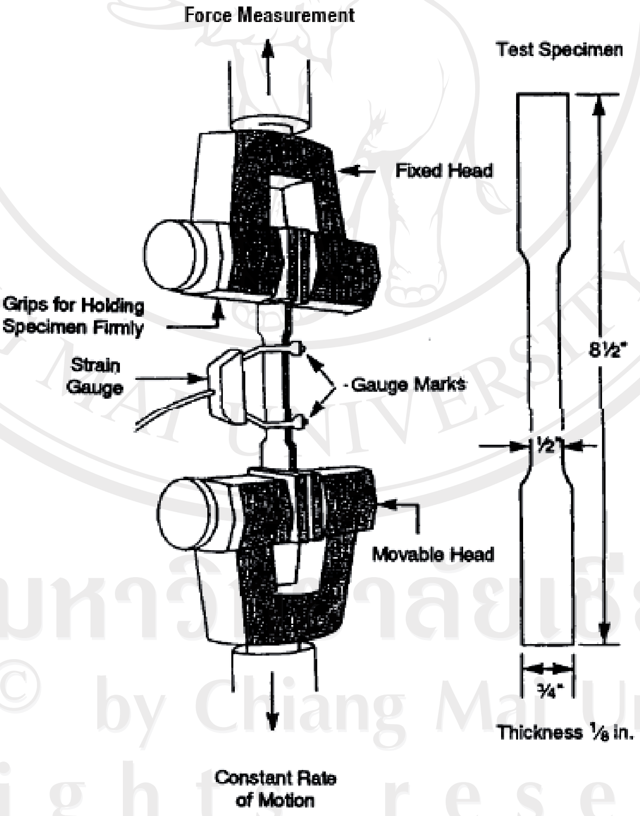


Figure 2.7 Typical test setup and specimen [31].

Tensile test is a measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Different types of plastic materials are often compared on the basis of tensile strength, elongation, and tensile modulus. The tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a movable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and the movable member prevent alignment problem. A controlled velocity drive mechanism is used. Some of the commercially available machines use a closed-loop-served-controlled drive mechanism to provide a high degree of speed accuracy. A load indicating mechanism capable of indicating total tensile load with an accuracy of ± 1 percent of the indicated value or better is used [30].

Test specimens for tensile tests are prepared many different ways. Most often, they are either injection molded or compression molded. The specimens may also be prepared by machining operations from materials in sheet, plate, slab, or similar form. Test specimen dimensions vary considerably depending upon the requirements and are described in detail in the ASTM book of standard. Since the tensile properties of some plastics change rapidly with small changed in temperature, it is recommended that tests be conducted in the standard laboratory atmosphere of 23 ± 2 °C and 50 ± 5 percent relatively humidity [30].

For a better understanding of the tensile properties of the material and the stress-strain curve, it is necessary to define a few basic terms that are associated with the diagram.

1) Tensile strength

The point at which a stress causes a material to deform beyond its elastic region is called the tensile strength at yield. The force required to break the test sample is called the ultimate strength or the tensile strength at break. Ultimate strength measures the highest stress value during the tensile test. This value should be used in general strength comparisons, rather than in actual calculations. Ultimate strength is usually the stress level at the breaking point in brittle materials. For ductile materials, it is often the value at yield or a value slightly before the breaking point. The strength is calculated by dividing the force (at yield or break) by the original cross-sectional area as Equation 2.3. Tensile strength at yield generally establishes the upper limit for application that can only tolerate small permanent deformation. At this value, the stress corresponding to the point of zero slope on the stress-strain curve and can only be measured for materials that yield under testing conditions. While tensile strength at break defined as the stress applied to the tensile bar at the time of fracture during the steady-deflection-rate tensile test, data for tensile stress at break establishes upper limits for two types of applications; one-time-use applications, which normally fail because of fractures; and those parts that can still function with the large deformations that occur beyond the elastic limit. These tensile values can be calculated as the following equations [30].

$$\text{Tensile strength (psi)} = \frac{Force\,(load)\,(lb)}{Cross\,\sec tion\;area\,(sq.in.)} \qquad (2.3)$$

$$\text{Tensile strength at yield (psi)} = \frac{Maximum\,load\;recorded\,(lb)}{Cross\,\sec tion\;area\,(sq.in.)} \qquad (2.4)$$

$$\text{Tensile strength at break (psi)} = \frac{Load\;recorded\;atbreak\,(lb)}{Cross\,\sec tion\;area\,(sq.in.)} \qquad (2.5)$$

2) Tensile modulus

The modulus of elasticity (Young's modulus or tensile modulus) is the ratio between stress and strain in the reversible region (or below the proportional limit on the stress-strain curve). Higher modulus values indicate greater stiffness. Because of plastic's viscoelastic tensile behavior, determining tensile modulus is more subjective and less precise for plastics than it is for metals or other materials. When dealing with materials with no clear linear region, the modulus can be calculated at some specified strain value, typically at 0.1 % (secant modulus). For some applications, it may be more appropriate to derive a tensile modulus from the slope of a straight line drawn tangent to the curve at a point on the stress-strain diagram (tangent modulus) [30].

$$\text{Tensile modulus} = \frac{Difference\;in\;stress}{Difference\;in\;corresponding\;strain} \qquad (2.6)$$

3) Elongation

Elongation is a type of deformation. Deformation is simply a change in shape that anything undergoes under stress. Elongation at yield, the strain value at the yield point, determines the upper limit for applications that can tolerate the small permanent deformations that occur before yield. Elongation at break measures the strain at fracture as a percentage of elongation. Brittle materials break at low strain levels; ductile and elastic materials attain high strain levels before breaking. While ultimate elongation is often shown for highly elastic resins such as polyurethane. The test for ultimate elongation uses narrower test bars and faster deflection speeds than the elongation at break test. Elongation can be calculated through the strain as the following equation [30].

$$\text{Strain} = \frac{Change\,in\,length\,(elongation)}{Original\,length\,(guage\,length)} \tag{2.7}$$

2.1.6.2 Impact properties

Impact properties are important in a variety of applications. Impact strength measures the amount of energy that a material can absorb without breaking. The ability of plastic part to absorb energy is a function of its shape, thickness, temperature and the molecular character of the resin. While impact properties can be critical in some applications, test results are among the most difficult to relate to actual part performance. Variable such as part geometry, temperature, stress concentration points, molding stresses, and impact speed reduce the accuracy of general impact data for quantitative calculations. The complex and dynamic nature of resin performance during impact has led to the development of a variety of tests that more closely represent different in use conditions. The test results from these impact tests can only be used to rank the toughness or the notch sensitivity of similar materials [31].

There are several types of impact tests that are used today. The tests are performed as the standard test methods for impact resistance of plastics and electrical insulating material (ASTM D 256). The most common one is the notched Izod test. Izod specimens are tested as cantilever beams. The pendulum arm strikes the specimen and continuous to travel in the same direction, but with less energy due to impact with the specimen. This loss of energy is called the Izod impact strength, measured in foot-pounds per inch of notch of beam thickness (ft-lb/in). The specimens can be un-notched or with the notch reversed with the results reports as un-notched or reverse notch Izod impact strength. The impact test specimen is usually notched in order to have a controlled failure point. In Charpy impact test, the specimen is a supported beam, which is then struck with a pendulum. The loss of energy is measured in the same unit as in Izod impact test. The specimen can be either notched or un-notched. Figure 2.8 shows the Izod and Charpy impact tests [31].

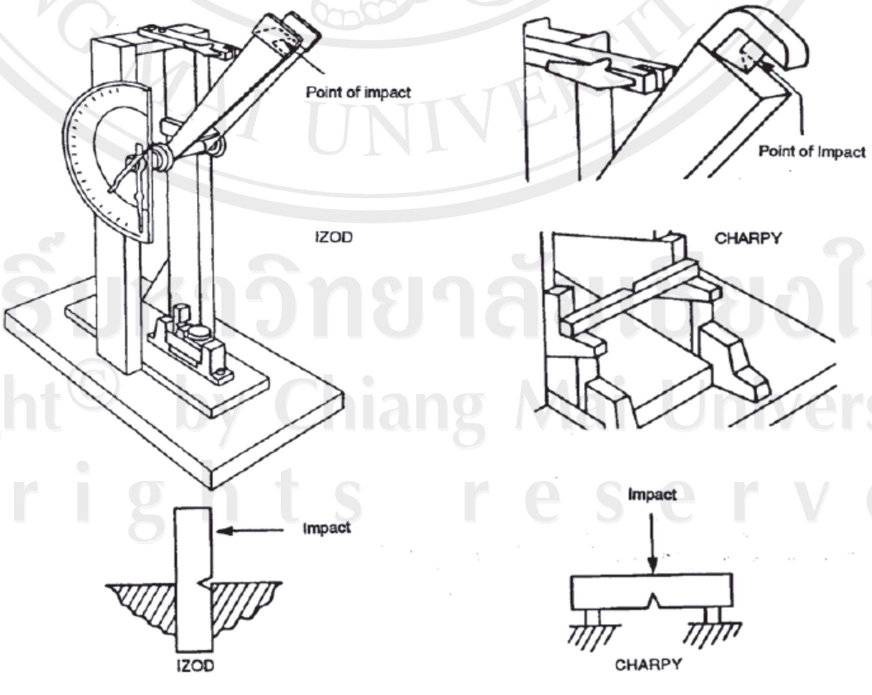


Figure 2.8 Impact test setups [31].

2.1.7 Swelling of polymer in a solvent

Using solvents to dissolve a polymer, some very important issues are applicable to develop a process that is industrially suitable and process able. Another importance in using solvents is due to the large molecular structures of polymeric materials, the thermodynamics begin to play a very important role in solubility. In order to understanding of polymeric solubility, there are three main factors which control the thermodynamics of the polymeric solubility within solvent. All of these factors are a function of the thermodynamics behind the mixing of two species. The first factor is the combinational entropy of mixing. This comes from the entropic effect of mixing the two species together and relates to the fact that the amount of disorder in the system must increase when it is dissolved. The next important factor in polymeric solubility is the enthalpy effect arising from the mixing of the two species. This change can be either positive (the components prefer to be with themselves) or it can be a negative (the polymer likes the solvent more than itself). And the last one is the free volume effects between the polymer and the solvent. This factor deals with the solvent's ability to surround and contain the polymeric molecule in solution. The combination of the first two factors is the basis for an important thermodynamic relationship [32].

In order to dissolve the polymer material, the Gibb's free energy of mixing must be zero or negative as can be seen in Equation 2.8 [32]. Since the total Gibb's free energy of mixing (ΔG_{mix}) needs to be negative, then the enthalpy of mixing (ΔH_{mix}) must to be negative and the entropy of mixing (ΔS_{mix}) needs to be positive;

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2.8}$$

For the polymer/solution system, the entropy of mixing is not substantially large in comparison to equivalent masses or volume. This is due to the nature of polymer and their ability to move and get into different configurations. Small molecules can pack tightly together and can rotate around, whereas polymer chains are confined to a lower number of conformations. A good representation of this phenomenon is the lattice model of solubility as shown in Figure 2.9 [33]. A solution is treated as a volume that consists of a number of small volumes that make up a total volume [32].

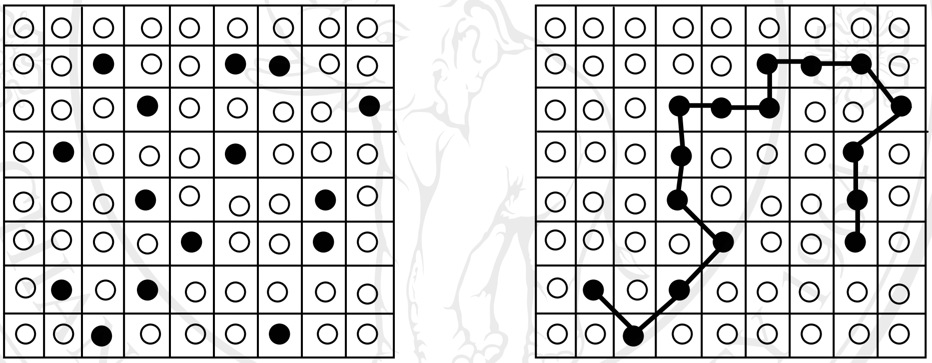

(a) **(b)**

Figure 2.9 The Lattices model of solubility of (a) small molecules (•) and (b) large polymeric molecules (•–•) [33].

From this model, each molecule can only occupy one cell at a time, but they can distribute themselves in any number of ways. However, due to the rigid conformational mobility of a polymer chain, there exists only a few ways in which the polymer can pack itself into the lattice. As seen in Figure 2.9, the smaller molecules have more choices of where they reside than does the polymer chain. It is this confined nature that generates a lower difference in the value for the entropy of mixing for polymeric solutions as compared to traditional, small molecule solutions.

With this being the case, the temperature and the entropy of mixing become very important when dealing with polymer solubility.

In regular solution theory, the enthalpy of mixing may be estimated by assuming that there are specific interactions between the polymer and the solvent, and therefore it can be equated to the change in internal energy per unit volume of solution. The form of this equation can be seen in Equation 2.9 [32] and it is used for determination the change in internal energy for the solution through the solubility parameter (δ) and the volume fraction (ϕ).

$$\Delta H_{mix} \approx \Delta E_{mix} = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \tag{2.9}$$

The subscripts 1 and 2 represent the solvent and the polymer. As Equation 2.9, it should be understood that the enthalpy of mixing is equated to the internal energy when the system is under the zero pressure. Namely, ΔE_{mix} is defined as the energy change upon isothermal evaporation of the saturated liquid to the ideal gas state at infinite dilution. Therefore, the energy change of vaporization is approximately related to the enthalpy of vaporization as Equation 2.10 [32].

$$\Delta E_{mix} \approx \Delta H_{mix} - RT \tag{2.10}$$

From Equation 2.9, to increase the possibility of solubility, the internal energy of mixing must be minimized by picking a solvent with a solubility parameter that is very close or equivalent to the solubility parameter of the polymer. A good guideline for polymer solubility is for the absolute value of the difference between the solubility parameters to be around 1.0 (cal/cm^3)$^{1/2}$ [32].

However, the regular solution theory does not deal with the difference in size between the polymer and the solvent molecules. This becomes important when dealing with solvents that consist of long chain molecules themselves, and therefore have a better chance at dissolving the polymer molecules. The most recognizable theory that deals with these interactions is the Flory-Huggins theory [32]. Based on Equation 2.8 and 2.9, in order to generate a low enthalpy of mixing, the difference in solubility parameters must be closed to zero and the molar volume must be very small. In order to maximize solubility, a polymer solvent must either be very small, and therefore the larger difference in solubility parameters does not matter, or the polymer solvent must be very large and have an equivalent solubility parameter to the polymer. If a solvent can be found that has a low molar volume and one that has a solubility parameter that is closed to the solubility parameter of the polymer, then conditions could be reached for solubility. Polymer solubility has been shown to be a function of density or molar volume, temperature, and molecular weight. An old rule of solubility is that "like dissolves like". This stems from the chemical structure of solvent, in relation to the chemical structure of the polymer. Solvents that are similar in chemical structure to polymers will have a better chance in dissolving a polymeric molecule.

$$\Delta H_{mix} = RT\chi\phi_2 n_1 x_1 \tag{2.11}$$

Where χ is the Flory-Huggins interaction parameter, n_1 is the number of moles of solvent, ϕ_2 is the volume fraction of the polymer, x_1 is the number of segment in the solvent molecule, and R is the ideal gas constant. The value of the interaction parameter comes from the solubility parameters and the molar volume of the solvent (v) [32];

$$\chi = \frac{v(\delta_1 - \delta_2)^2}{RT} \tag{2.12}$$

Any solvent, that is similar in structure to a polymeric molecule, will be very large, will have a very small molar volume, and will dramatically affect the thermodynamics of solubility. From Equation 2.11, the enthalpy of mixing can be increased as a function of the size of the solvent. This condition is unfavorable for polymeric solubility. However, the unfavorable condition can be negated through the interaction parameter of Equation 2.11, if the solubility parameter of the solvent is closed enough to the value of the polymer. This relationship between molecular sizes, molar volume, solubility parameter, similarity of structure, solubility is important as the way to select a solvent. In conclusion, polymer solubility is strongly influenced by temperature, chemical structure, molar volume, and the value for the solubility parameter. It can be seen that the conditions for solubility can be increased by not only increasing the temperature, but by matching the solubility parameters of the solvent and the solute [32].

It is known that the solubility of PP is differential due to the semicrystalline nature of the polymer. It has been found that when the semicrystalline PP is dissolved in general polymeric solvent, the amorphous phase dissolved much faster than the crystalline phase. This can be attributed to the large difference in the effective densities of these two phases, which has been established as an important parameter for polymeric solubility. The crystals are harder to be penetrated by the solvent due to the closed packing found in this phase. Although, there is a concentration potential across the crystal/solvent layer, once the first fraction of solvent penetrates the crystal layer, the solvent starts to act a barrier to keep more solvent from penetrating. It would be undesirable for only the amorphous phase of the matrix material to be dissolved, while the crystalline phase still remains with the target material. But more importantly is the fact that temperature plays a pivotal role in designing a process to effectively dissolve a polymer. The beneficial factor for solubility and crystallinity is that both (solubility and crystallinity) are directly effected in the same way. Therefore, when the temperature of the system is increased, the solubility goes up, the crystallinity goes away, and the mobility of the polymer chains goes up. The preferential state for the best solubility should occur when the polymer is totally melted and the crystalline phase is gone. For PP, the normal melting point is around 165 °C. Therefore, the best window for effective solubility will be at a system temperature that is above 165 °C. Because, most organic solvent are in the gas phase and unsuitable for a dissolution system at this temperature, some stringent criteria must be met by the solvent chosen for this type of selective dissolution process. The dissolution solvent needs to be similar in structure to the PP, have a similar or an equivalent solubility parameter to the PP's parameter, be large enough to accommodate the large size of the polymeric chain, and also needs to have a boiling point that near or above the melting point of the PP. Fortunately, the chemical structure, the melting point, and the size of PP is readily obtainable. Therefore, in order to select the best solvent for dissolution the solubility parameter for PP is needed [34]. The value for the solubility parameter of PP is 18.8 J/cm^3 or MPa$^{1/2}$ [35]. As Equation 2.12, the smaller the difference between the solubility parameters, the higher the degree of solubility in the polymer/solvent system is obtained. At the temperature that is lower than the melting point of PP, instead of dissolving of the polymer the solvent can only swells the polymer. It can be said that the best solubility should occur when the polymer has no crystalline morphology present, when the chains are shorter than the typical polymeric length and when the temperature is favorable for dissolution. It is obvious that two of these conditions can be met by performing the dissolution at a temperature above the melting point of the polymer. The last criteria seem to demand that the polymer chain be somehow reduced in overall size and molecular weight. The reduction in molecular weight of the polymer will result in shorter chains, which will be more suitable for dissolution into a smaller size of solvent. The reduction of molecular weight of a polymer can be accomplished by the degradation techniques such as thermal and chemical degradations [32]. During the degradation, the polymer may disintegrate because of solvent action on the polymer itself or on plasticizers or other additives in the polymer. Generally, the greater the degradation caused by a solvent, the more readily the solvent will penetrate the polymer. Swelling usually takes place prior to degradation [36].

As the system of crosslinked polymer, when a solvent enters in the network, it does not dissolve it but instead swells [37]. Thus the total volume increases to that of the matrix and the solvent. The degree to which the volume increases depends on a) the degree of crosslinking and b) the degree to which the polymer like the solvent described as the previous part. In an amorphous polymer that has been crosslinked into a network; the chains are in entangled and relaxed conformation between two network junctions. However, when the solvent enters the polymer, the solvent molecules move the network junctions away from each other (as the polymer swells in the solvent). As the network junctions move away, the chains attached to these junctions experience a stress that is counteracted by the tendency of the polymer chain to return back to the relaxed state (where the entropy is higher). At some stage, equilibrium is reached wherein the polymer refuses to accept anymore of the solvent. Clearly, this equilibrium depends on how long the chains between network junctions are and the degree to which the polymer chains like to have solvent molecules around them.

The degree of swelling is thus used as a common measure of the degree of crosslinking. The degree of swelling is measured as follows;

1) Measure the dry weight and/or volume of the polymer before swelling,
2) Swell the polymer in a solvent until equilibrium swelling,
3) Measure the weight of the swollen polymer and/or volume of the polymer after equilibrium swelling, and
4) The degree of swelling is measured using the following two swell ratios [37];

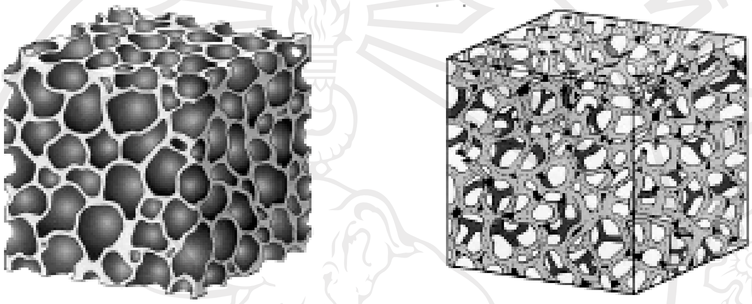
$$\text{Mass swell ratio} = \frac{Mass\ of\ swollen\ polymer}{Mass\ of\ dry\ polymer} \tag{2.13}$$

$$\text{Volume swell ratio} = \frac{Volume\ of\ swollen\ polymer}{Volume\ of\ dry\ polymer} \tag{2.14}$$

2.2 Background on plastic foams

2.2.1 Introduction of plastic foams

Foams are relatively novel forms of polymer-based materials. They are light in weight and versatile, and are employed increasingly in a variety of applications that include thermal and acoustic insulation, core materials for sandwich panels, fabrication of furniture and flotation materials. This material consists of a gas phase dispersed in a solid plastic phase and derives its functions from both. The solid plastic component forms the matrix. The dispersed gas is contained in voids or cells and is often referred to as the blowing or foaming agent. However, the blowing agent used in the production of foams is not always gaseous and chemically identical with the gas component. Some foaming agent are solids, some are liquids. Foams are classified as open-cell or closed-cell. In closed-cell foams each cell is completely enclosed by a thin wall or membrane of plastic, whereas in open-cell foams the individual cells are interconnected as shown in Figure 2.10 (a) and (b), respectively [38].



(a) Closed-cell foam (b) Open-cell foam

Figure 2.10 Models of slabs of typical closed-cell foams and open-cell foams [38].

The terms plastic foam, foamed plastic and cellular plastic are used interchangeably; they refer to foamed plastics regardless of cell structure (open or closed). Plastic foams may be flexible, semi-flexible (or semi-rigid) and rigid, depending on chemical composition and the rigidity of the resin used as a matrix. Flexible foams have a glass transition (T_g) below room temperature, whereas rigid foams have one above room temperature [38]. Plastic foams can be produced in a great variety of densities range from about 1.6 kg/m^3 (0.1 lb/ft^3) to over 960 kg/m^3 (60 lb/ft^3). Since the mechanical properties are generally proportional to the foam densities, the applications of foams usually determine which range of foam densities should be produced. Thus rigid foams used for load-bearing applications require high density, while low densities are used for thermal insulation. Low density flexible foams (~30 kg/m^3) are usually used in furniture and automotive seating, while somewhat higher densities are used for carpet backing and energy-absorbing applications [1].

2.2.2 Composition of plastic foams

2.2.2.1 Plastic matrix

The matrix is made up of the base resin and other compounding ingredients that may include plasticizers, stabilizers, surfactants, dyes, and pigments, fire retardants and fillers. The chemical and physical nature of the matrix is the principal factor in determining most foam properties such as chemical resistance, thermal stability, flammability, specific heat, transition temperature and rigidity. Plastic foams may be either thermoplastic or thermosetting. Typical thermoplastic foams are polystyrene (PS), poly(vinyl chloride) (PVC), the polyolefins; PE and PP, ABS foams. In contrast, common thermosetting foams include polyurethane (also called urethane), phenol-formaldehyde (phenolic), urea-formaldehyde and epoxy foams [2].

2.2.2.2 Gas phase and blowing agents

The composition of the gaseous phase has an important effect on selected properties such as thermal resistance. The blowing agents are used to produce cellular structure during the foaming operation. They are divided into two classes; physical blowing agents and chemical blowing agents. Physical blowing agents undergo only physical change [2]. Physical blowing agents are nearly always the primary sources of blowing gases for low-density foams [21]. The most common are low-boiling organic liquid such as hydrocarbons and halogenated hydrocarbons, which develop cells within the plastic material by changing from liquid to gas during foaming under the influence of heat. When physical blowing agents are used in the process therefore the gas phase of the foam is chemically identical with the blowing agent. Physical blowing agents are classified as either atmospheric or permanent gases or as volatile liquid that evaporate at appropriate conditions to produce blowing gases [2]. Blowing gases must be first dissolved in the polymer to produce fine cells. As with chemical blowing gases, the foam density depends on the amount of gas that is dissolved in the polymer. The ability for a polymer to dissolve a gas or liquid is solubility. Nitrogen, carbon dioxide and argon have limited solubility in most thermoplastics. Atmospheric gases are desired over volatile liquid for several reasons including cost and absence of negative issues such as ozone damage and flammability [21]. The physical blowing gases in liquid state that evaporate at appropriate conditions are called volatile liquids. There are several classes of volatile liquids. Hydrocarbons now dominate the physical blowing agent category, with butane and pentane being preferred for commercial low-density styrenics and olefinic foams. Propane and heptanes are also used, but usually in conjunction with butane and pentane. Hydrocarbons are relatively inexpensive and are easily transported and pumped into extrusion equipment. Hydrocarbons are also flammable. Flammability in finished goods can lead to handling and shipping problems. There are some chlorinated hydrocarbons such as methyl chloride and methylene chloride, and the primary physical blowing gases like chlorofluorocarbons or CFCs; which were used as the refrigerants. These blowing gases were sought because of their very low thermal conductivities, non-flammability, and very high solubility. The low-density foams produced that way were desired in construction for retaining their insulation values for decades. Unfortunately, these gases were found to react with upper atmospheric ozone, thus depleting the earth's ultraviolet protection layer. As a result, these blowing gases based on chlorine are no longer used and restriction.

It is well known that the three fluid states of a substance are liquid, gas and vapor above the critical temperature and pressure. Substances above their critical temperatures (T_c) and pressures (P_c) are sometimes called supercritical fluids. Carbon dioxide and nearly all volatile liquids used in thermoplastic foam extrusion are above their critical temperature and pressure when mixed with polymer melt in a conventional foam extruder. There is evidence that supercritical fluids dissolve more readily in polymers than either liquids or gases [21]. For carbon dioxide the critical point occurs at 73.8 bar and a temperature of 31.1 °C as shown in Figure 2.11 [39-40]. Supercritical fluids have physical properties intermediate to those of gases and liquids. A major advantage of supercritical fluids for organic synthesis is the ability of these physical properties to be tuned simply by a change in pressure and/or temperature [39]. The volatile liquid dosage for low-density foams depends on the melt pressure and temperature and solubility of the foaming agent in the polymer. Typical dosages range from 2 wt% for nitrogen to 3 wt% to 4 wt% for carbon dioxide, to up to 15 wt% for volatile hydrocarbon liquids [21].

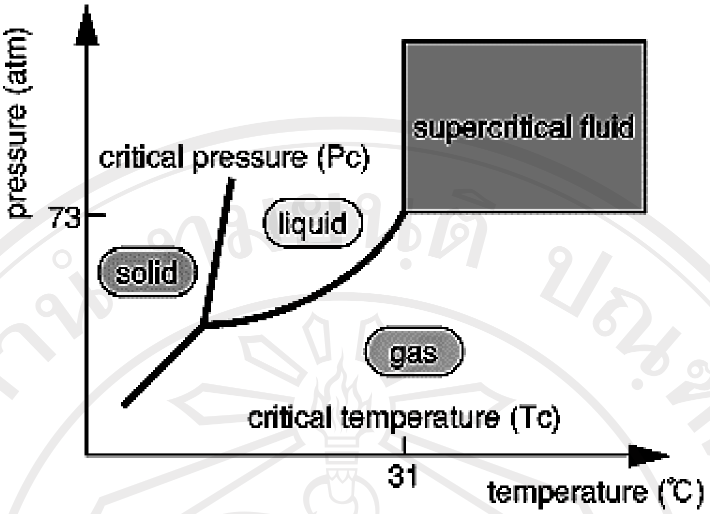


Figure 2.11 Phase diagram of supercritical carbon dioxide [40].

On the other hand, chemical blowing agents are materials that are stable at normal storage temperature and under specific processing conditions, but undergo decomposition with controllable gas evolution at reaction conditions. Popular blowing agents of this class are organic nitrogen compounds (e.g., azodicarbonamide), which mainly produce nitrogen gas [2]. Unlike the function of physical blowing agent in the foaming process, chemical blowing agents are usually the primary sources of blowing gases for higher density foams and sometimes used in combination with physical foaming agents for low-density foams. Nearly all chemical blowing agents are used to produce thermoplastic foams are very pure manufactured chemicals. There are two general classes of chemical blowing agents. If the chemical blowing agent generates heat while reacting to produce the blowing gas, it is exothermic. If it requires heat to react, it is endothermic. Typically, the chemical blowing agent decomposes in a first-order time-dependent fashion. Usually, as the polymer melt temperature increases by 10 °C, the chemical blowing agent decomposition reaction rate doubles [21]. Chemical blowing agents are known to be more expensive than physical blowing gas and they are most effective in reducing in initial density of the plastic; therefore, the low amount of chemical agents up to about 2 wt% is used. Nearly all chemical blowing agents begin as 1 to 20 micron size powders and must either be carefully dosed to minimized air-borne particles or master batch in a carrier polymer [21].

2.2.2.3 Nucleating agents (nucleants)

All foams employ nucleating agents or nucleants in one form or another. The primary role for a nucleants is to provide surface on which bubbles can organize and grow [21]. Nucleating agents are chemical substances which used incorporate in polymers to form nuclei or forming of many small bubbles [2]. There are two general types of nucleants. Passive nucleants simply provide nucleating micro-voids around which micro-bubbles can form. Passive nucleants are either inorganic or organic. Talc and glass fibers are examples of inorganic passive nucleants. Inorganic nucleants are usually micron-sized particles. Smaller particles tend to agglomerate. Coarse particles do not yield fine cells. The interfaces between two polymers or between an organic additive and a polymer can act as sites for bubble nucleation. On the other hand, active nucleants not only provide sites for bubble nucleation but also provide blowing gas to promote micro-bubble formation. As an example, small amounts of chemical foaming agent are often added to a polymer to be foamed with a physical foaming agent [21]. The action of nucleating agents in forming small bubbles in foam formation may be some finely dispersed particles or gases that may serve as nucleating agents [2]. The classification of nucleating agents has been adopted is based on their mode of action [1-2].

1) Gaseous and liquid compounds that produce a supersaturated solution of gas in the formulation, and can form the finest bubbles prior to the action of a blowing agent. Among them are carbon dioxide, nitrogen, sodium bicarbonate, citric acid, and sodium citrate.
2) Finely dispersed organic, inorganic, and metal powders that act by the principle of “hot spots” due to their exothermic reactions which are therefore termed “dynamic nucleators”.
3) Finely dispersed compounds (the classical nucleators) whose mode of action consists of the formation of nucleation centers for a gaseous phase: talc, silicon dioxide, titanium dioxide, diatomaceous earth, kaolin, etc [1-2].

2.2.2.4 Stabilizers

In foaming process, additives are used to produce the stability of the foams. During the growth of cell, the diffusion rates of certain blowing gases in certain polymers are so high. This makes the gas is lost very quickly from the foam. The result is cell collapse and excessive bulk foam shrinkage. This is particularly true for hydrocarbon blowing gases in polyolefins. Small amounts of cell stabilizers, typically fatty acids or titanates, are added to the polymer to inhibit diffusion [21]. Stabilizers are agents used in compounding of some plastics to assist in maintaining the physical and chemical properties of the compounded materials at satisfactory amount throughout the processing, service life of the material, and the parts made from the material [2]. The stabilizers are usually soluble in the polymer at melt temperature but phase separation is occurred when the polymer is cools and the cell membranes are form. Then this phenomenon provides monolayer coating on the membranes. Some additives can act as stabilizers include the following; emulsion stabilizers, viscosity stabilizers, antioxidants, UV stabilizers, light stabilizers, Biocides, Fungicides, Heat stabilizers, and Surfactants, etc. The term "stabilizer" is obviously a general term covering a wide range of additives intended to maintain certain properties at desired levels [2]. Most cell stabilizer dosage levels are less than 1 wt% [21].

2.2.2.5 Cell structure

The interior structure of the foams certainly influence on the type of application of the foamed plastic. Open-cell foams offer the passage of liquids and gas through them. A general principle is that flexible foams have open-cell structure inside the polymer matrix but closed cells are promoted in the rigid foams. The cell structure depends on the process used for the production of the foamed plastic. In general no foam has entirely one type of cell structure. For example, some cases both flexible and rigid foams may be produced with either open or closed cells (e.g., PVC). Open-cell foams have sound absorbing properties and cushioning characteristics. This makes them appropriate for use as acoustic material and in cushioning application. In closed-cell foam, the polymer forms the cell walls, which acts as a barrier to gases and liquids, although gases may pass through the thin wall by the slow process of diffusion. Therefore, closed-cell foam has lower water absorption and lower water vapor permeability than open-cell foams. Moreover, if the gas phase has low thermal conductivity and is captive, closed-cell foam can usually provide higher thermal resistance than open-cell foam [38].

2.2.3 Classification of foams

All commercial foam products (refers only to thermoplastic foam) fall into two major market segments; high-density foams that find primary applications as permanent structures and low-density foams that find primary applications as single-use or disposable products. There are few applications for foams having densities in the ranges of 30% to 60% of those of the un-foamed polymers. Medium-density foams are generally too mechanically weak to serve as permanent structures or too expensive to be used as disposable products [21].

2.2.3.1 High-density foams

Most commercial high-density foams have densities of 75% to 90% of those of the un-foamed polymers. High-density foams normally are used as permanent structures. They are sought for rigidity with weight reduction. Early applications were as wood replacements in mirror frames and furniture components. Typical markets for high-density foams are given in Table 2.2. High-density foams may have near un-foamed density skins and lower-density foam cores [21].

2.2.3.2 Low-density foams

Most commercial low-density foams have densities of 10% to 20% of those of the un-foamed polymers. Low-density foams are usually categorized as flexible or rigid. Typically, if the base polymer is flexible, the foam will be flexible. If the base polymer is rigid, the foam will be rigid. Low-density foams are used as heat and sound barriers, as shock mitigations, and in floatation applications. Rigid low-density foams are thermoformed into rigid food containers. Flexible low-density foams are used in energy absorbing applications. Typical applications for low-density foams are given in Table 2.3. Low-density foams have uniform cell structures and rarely have substantial skins [21].

Table 2.2 Typical market for high-density thermoplastic foams [21].

Market	**Application**
Furniture	Panels, frames, tables, seating, bed structures, drawers and drawer fronts
Cabinetry	TF, stereo component cabinets, equipment housings
Material handling	Pallets, milk and soda cases, containers, chicken coops
Industrial	Battery cases, underground conduits, handholds, transformer housing, trash containers, equipment covers and doors
Consumer	Recreational, musical, toys, coolers, totes, mirror and picture frames, miscellaneous
Construction	Shutters, shingles, windows, doors
Appliances	Washer tops and doors, dishwasher tops and bases, air-conditioner housing and bases
Automotive	Decorative paneling, glove box door, instrument panels, seat frames, fan shrouds, fender liners, vehicle crash barriers
Marine	Fascia, seating, fish boxes, cabin structure

Table 2.3 Typical markets for low-density foams [21].

Market	Application
Comfort cushioning	Automotive, transportation, and furniture seating, mattresses, bedding and carpet underlay
Flotation	Marine pier buffers, in-place flotation for small vessels, marine life vests, pool accessories, child toys
Shock mitigation	Package protection for light bulbs, eggs fruit, electronics, furniture, and machinery, surface protection for furniture and movers as overwrap. Wrestling mats, construction and transportation crash barriers
Thermal barrier	Sidewall and roofing insulation, industrial insulation for coolers, tanks, and reservoirs, appliance and hot water insulation, and insulative packaging containers for beer, burgers, pizza

Regarding to the thermal response of polymer, thermoplastic materials become quite favorable in making common goods through various plastic processes [41] also include the foaming process. Thermoplastic foams possess high strength-to-weight ratios with integral solid skins. Sometimes, the term of cellular thermoplastic or thermoplastic foam is referred to structural foam. Structural-foam construction, when compared to an equivalent amount of conventional foam plastics, results in a 3- to 4- fold increase in rigidity, since rigidity is a function of wall thickness. The original properties of heat and chemical resistance, as well as most electric properties, remain the same as for the solid resins. In the cases with polyolefin materials such as PE or PP, cellular polyolefins contribute many unusual functions to the cellular plastics industry. These foams are tough, flexible, and chemical and abrasion resistance. They are also known to have superior electrical and thermal insulation properties. Their mechanical properties are intermediate between rigid and highly flexible foams. The density of these foams is ranged from 2 lb/ft^3 and higher, approaching that of the solid polymers. Low-density polyolefin foams are being widely used in package cushioning. Energy absorption under continued impact provides protection for delicate electronic parts as well as heavy metal assemblies. Comparatively with other thermoplastic foams, the use of PP foams is increasing rapidly because of the extremely range of grades and properties available include a favorable price advantage. The applications of PP foams are dependent on their characteristics. For example, low-density PP foams (0.7 lb/ft^3) with small closed-cells can be form as the film sheeting for outstanding toughness and strength over a wide range of temperature and humidity, while high-density PP foams can be used in wires and cables [1] and for structural purposes as a protection of surface from abrasion like the typical packages for optical lenses, electrical and electronic equipment, glassware, and ceramics, etc [2].

2.2.4 Foaming methods and the production

The cellular structure in plastics may be produced by physical, chemical or mechanical means. The material can be foamed in a molten or solid state during part of the production. Physical methods include expansion of gas dissolved in a molten plastic by reducing the pressure, and volatilization of low-boiling point nucleating agent within the polymer melted either by application of external heat or under the influence of the heat of reaction. In chemical foaming, the cellular structure is resulted from chemical decomposition of a blowing agent. Furthermore, the plastics can be foamed by the common techniques include foaming-in-place, spraying, extrusion, injection molding, and continuous slab stock production by pouring [38]. It should be noted that foaming technique, the type of polymer, the type of blowing agent, the expansion method, and the post-foaming curing dictate foam formation and its morphology, and thereof the properties. Even with a fixed polymer/gas system and the same foaming method, the amount of voids (blowing agent content), their dispersion and distribution, and void interconnection have profound impact upon its properties and thereby application. For foaming, the independent variables are gas type, gas content, processing conditions, and foaming dynamics, while the dependent parameters are foam structure, morphology, and properties [41]. Many of processes of un-foamed thermoplastics are modified to process thermoplastic foams. Injection molding, blow molding, rotational molding, and extrusion are the primary conversion methods. Injection molding is a cyclic process where polymer pellets are melted in a barrel and then pushed from the barrel into a cold metal mold. The mold has at least two sections. The inside or cavity of the mold has the shape of the product being manufactured. The polymer fills the cavity and is cooled and rigidified. The mold opens, the part is removed, and the process repeats. Blow molding is also a cyclic process where polymer pellets are melted in a barrel, then pushed from the barrel through a die to form a tube of molten polymer. A cold mold, having at least two sections and having a cavity of the shape of the desired part, surrounds the tube and air pressure forces the polymer against the cold mold, rigidifying the polymer. The mold opens, the part is removed, and the process repeats. Rotational molding is a cyclic process where polymer powder is poured into a clamshell mold. The mold assembly is then rotated and heated until the polymer melts and attains the shape of the mold cavity. The mold assembly is then cooled until the polymer rigidifies. The mold is then opens, the part is removed, and the process repeats. Extrusion begins with polymer powder of pellets that are melted in a barrel. The molten polymer is forced continuously through a shaping die to produce the desired profile. Thermoforming is a secondary conversion method that uses extruded sheet as its beginning material. The sheet is heated in an oven until softened and formed with pressure and vacuum against a single-surfaced cold mold. The formed parts are trimmed from the sheet. The sheet that does not become a part is reground and returned to the extruder for reprocessing [21].

2.2.4.1 Production of high-density foams

Injection molding dominates the manufacturing methods for producing high-density foam structures. Extrusion has many applications, ranging from millwork to sanitary piping and conduit, to foam-insulated wire and cable. There are few blow-molded high-density foam applications. High-density foam rotational molding is a growing industry with many marine applications such as canoes. High-density foam competes well with wood, cast white metal, sheet metal, sheet molding compound, and assembled metal parts [21].

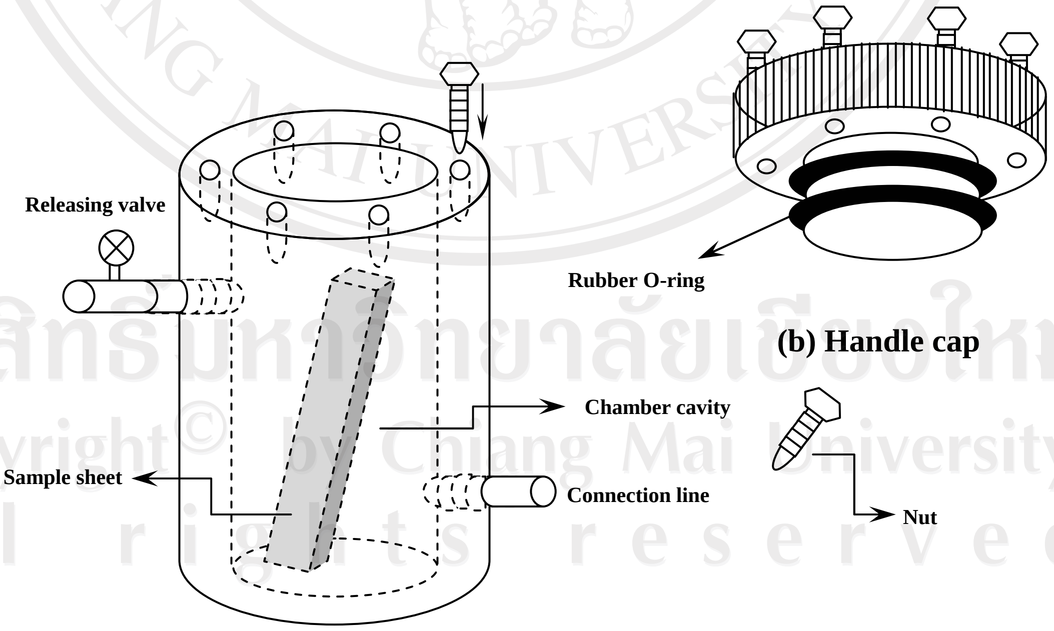
2.2.4.2 Production of low-density foams

Extrusion is the primary method for producing low-density foam sheet, plank, and profile. There are few applications for low-density blow molded parts. Injection molding and rotational molding are not normally used to produce low-density parts. Low-density foams are made by thermally expanding foaming agent-impregnated polymer beads in aluminum molds. Expanded bead foam technology yields insulative cups, coolers, and construction panels. Extruded low-density foam competes with traditional insulation products such as fiberglass and mineral wool as well as with thermoset rigid polyurethane. It competes well with traditional shock mitigation products such as foam rubber and straw as well as with thermoset flexible polyurethane. Extruded low-density plank is used to protect large and heavy shipments. Discrete extruded low-density segments called loose-fill are used in commercial shipping [21].

2.2.5 Conceptual design and detail of batch foaming process equipment

Based on the procedure of the solid-state batch foaming process, the produced foams are performed through two basic steps [42]. First, the preformed polymer samples (polymer sheets that are prepared by the compression molding machine) are saturated with an inert gas at a high pressure in a pressure chamber for a required saturation time range at room temperature. During the gas saturation of the polymer sheets, the sheets will have absorbed several percent by weight of the gas depending on the sheet thickness. After that the saturated polymer sheets are removed from the chamber and they will be allowed to expand in the heating bath for the specific time range dependent on the final cellular structure. This time range is depended on the expected final foam characteristics and it can play an important factor on the cellular morphology of the final foams. Within seconds the polymer sheets is soft enough so that the gas trapped inside the polymer can expand as it pushes the polymer outward. The temperature of the heating media in the bath is set up to soft the polymer, normally closed to the melting point of the polymer [42]. One limitation of this process is that very thick sections (greater than 0.25″) may take too long for the gas to reach the center of the plastic. The gas will have simply migrated between the atoms of the plastics. Using this process with different gasses and foaming temperatures, the cellular structure, cell size, and cell density can be controlled. The cells created are usually extremely small, on the order of 10 microns (half a thousandth of an inch). Note that the plastic part being foamed is limited in size by the size of the pressure vessel. Traditional foaming methods use a gas to create bubbles in a liquid. The bubbles thus formed are much larger (usually obvious to the casual observer. The larger bubbles reduce the strength of the foam more than micron sized cells. Also the minimum thickness of plastic that can be foamed is limited by the cell size. So the advantages of foam are available for much thinner plastic sections using this new process than with traditional foaming processes [42].

In this research, the foams were produced using a home-made pressure chamber. Because a high pressure is used for saturating the polymer sheet, therefore the pressure chamber should be resistance to the pressure range and rust of the solvent used in the experiment. The steel tube was selected as a material for building the chamber. The chamber was built with an inner cavity for containing the polymer sheets as shown in Figure 2.12. The wall of the chamber is connected with a copper pipe line that is from a CO_2 gas tank and another part of the wall is composed of a valve for gas releasing after the process done. At the top of the chamber is a handle cap that used for closing the bottom part (cavity). The handle cap was sculptured to have two grooves for adjoining with two O-rings in order to protect the gas leakage. During the gas saturation steps, both parts (Handle cap and cavity) are assembled with six nuts. Moreover, when CO_2 is flowed through the pipe line it is an intermediate cool liquid and gas, therefore the copper pipe line is coated with an insulating sponge tube in order to protect the distillation of vapor during the saturation. While in the expansion step, the heating bath was designed to have the suitable space for allowance the polymer sheets to be enlarged. The heating bath contains with glycerin oil which used as a heating media. In the process, the heating bath would be exposed to the temperature change from room temperature to the temperature that closed to the melting point of the polymer therefore the Pyrex glass beaker was selected to use as a heating oil container. In this step, the polymer sheets were heated by heat convection from heating plate through the oil bath. The foaming temperatures were ranged from the room temperature to the melting point of the polymer matrix in order to soft and ease the solubility of gas into the matrix. However, the foaming time (or expansion time) will be adjusted upon on what we would like to see from the experiment. For example, if the thickness of polymer sheet is very high the sheet will be allowed to foam in the oil bath for a longer period of time than processing with a thinner sheet. The experimental setup is shown in Figure 2.13.



(b) Handle cap

(a) Bottom part

Figure 2.12 A gas pressure chamber of the gas saturation step.

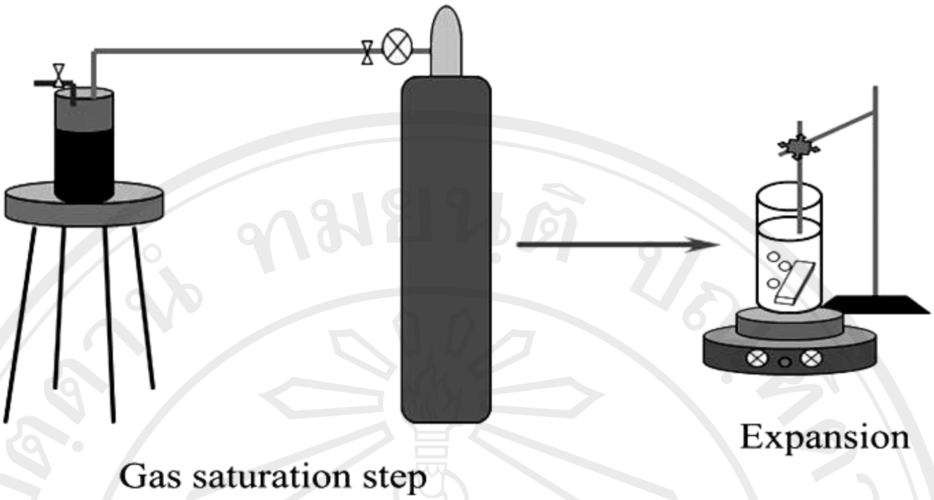


Figure 2.13 Experimental setup of solid-state foaming process.

2.2.6 Conceptual design and detail of tandem extrusion system (Continuous foaming process)

For the design of tandem extrusion system, Naguib [43] used an axiomatic design method which developed by Suh at the Massachusetts Institute of Technology to create an experimental design and construction of the tandem extrusion system. He explained the relationship between the functional requirements (*FRs*); the design problem that concerned to the perceived needs and the possible physical entities were called Design Parameters (*DPs*) which corresponding to each *FRs*. The relationship between the *FRs* and the *DPs* can be expressed by a matrix equation:

$$\{FR_s\} = [A]\{DP_s\} \tag{2.15}$$

or

$$\begin{Bmatrix} FR_1 \\ FR_2 \\ \vdots \\ FR_n \end{Bmatrix} = \begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{bmatrix} \begin{Bmatrix} DP_1 \\ DP_2 \\ \vdots \\ DP_n \end{Bmatrix} \tag{2.16}$$

The *FRs-DPs* relationship for decision the experimental setup for a tandem extrusion system can be described in the following matrix;

$$\begin{Bmatrix} FR_1 \\ FR_2 \\ FR_3 \\ FR_4 \end{Bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{23} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{bmatrix} \begin{Bmatrix} DP_1 \\ DP_2 \\ DP_3 \\ DP_4 \end{Bmatrix} \qquad (2.17)$$

Naguib [43] identified the four functional requirements (FR_s) for producing low-density and fine-celled PP foam as following;

FR_1 = plastication of polymer;

FR_2 = formation of a polymer/gas solution;

FR_3 = nucleation; and

FR_4 = expansion

Moreover, to satisfy the above FRs, the following design parameters (DP_s) are proposed;

DP_1 = heat provided by the plastication screw motion in an Extruder and externally mounted band heaters;

DP_2 = gas injection, diffusion system and gear pump;

DP_3 = thermodynamic instability created by a nucleation die; and

DP_4 = a cooling system that can cool the polymer melt without decreasing its pressure

From the above considerations, Equation (2.16) can be written as;

$$\begin{Bmatrix} FR_1 \\ FR_2 \\ FR_3 \\ FR_4 \end{Bmatrix} = \begin{bmatrix} X & 0 & 0 & 0 \\ X & X & 0 & 0 \\ X & X & X & 0 \\ X & X & X & X \end{bmatrix} \begin{Bmatrix} DP_1 \\ DP_2 \\ DP_3 \\ DP_4 \end{Bmatrix} \qquad (2.18)$$

The elements in the A matrix can be either "X", which denoted a strong relationship between the corresponding FR and DP, or "0", which denoted a weak or absent relationship. The A matrix presents the complete relationship between the FR_s and the DP_s; it can help the designer better understand and improve the design.

In response to FR_1, a single-screw extruder is chosen to plasticate the polymer. There are two heat sources in the system. The primary source is the frictional heat generated by the motion of plasticating screw. The secondary source is the externally mounted band heaters. The band heaters are important in the start-up period but they are not suitable as the only heat source for this process due to the low thermal conductivity of the polymer. Since gas is injected in the polymer after the polymer is completely plasticated, it has no effect on the plastication process. As a result, element A_{12} should be zero. Elements A_{13} and A_{14} should also be zero because nucleation, expansion and shaping take place further down stream and therefore, will have no effect on the plastication stage [43].

FR_2 is satisfied by using a gas injection system with a metering device, and a diffusion enhancing device to produce a homogenous polymer/gas solution. The amount of gas is metered by a gas injection pump which supplied the gas under high pressure into the polymer melt in the extruder. The result is a two-phase polymer/gas mixture. The shear field generated by the motion of plasticating screw stretches the gas bubbles and increases he interfacial surface area when the polymer is conveyed in the extruder barrel. As a result, the gas can diffuse into the polymer matrix more quickly. To further assist the diffusion process and homogenize the polymer/gas solution, a diffusion enhancing device consisting of static mixers is employed. The shear field generated by the plasticating screw motion affects the polymer/gas mixing.

Therefore, element A_{21} should be non-zero. Element A_{23} should be zero because nucleation takes place after formation of the polymer/gas solution. The amount of gas in the polymer melt is dependent on DP_4. In addition, element A_{24} should be zero because the addition of a gear pump decouples *FRs*, which ensures a constant polymer flow rate as long as the gear speed and the extruder speed are not varied. This feature implies that the amount of gas injected into the polymer melt, once set, will become independent of the temperature variations and the die exit settings [43].

In response to FR_3, a rapid pressure drop is chosen to generate thermodynamic instability and thereby promote high nucleation density. The thermodynamic instability is created by a sudden drop in gas solubility in the polymer/gas solution. This is because the gas solubility in polymer is proportional to the pressure of the polymer melt. A rapid drop in the pressure results in a rapid decrease in the solubility of gas in polymer melt. Therefore, a high-nuclei density can be created by dropping the pressure of the polymer/gas solution rapidly. In according to the spindle speed of the plasticating screw affects the system pressure and therefore affects the nucleation rate. As a result, element A_{31} should be non-zero. Element A_{32} should be non-zero as well, because the amount of gas in the polymer/gas solution affects the nucleation density. Elements A_{34} should be zero because the cooling system of a second extruder can cool the polymer melt without sacrificing its pressure [43].

A cooling system is employed to satisfy FR_4. The most dominant parameter that affects the growth of the nucleated cells is the melt temperature. As the gas from the polymer melt diffuses into the nucleated cells, the concentration of the dissolved gas decreases in the region near the cells. This results in a concentration gradient in the melt, which drives the dissolved gas towards the cell. The diffusion of gas into the cells causes the cells to grow. The gas diffusion rate increases with temperature, and therefore, if the melt temperature is too high, the gas can easily escape from the polymer to the environment instead of contributing to cell growth. A high temperature can also promote cell coalescence since the melt strength decreases when the temperature increases. As the cells grow, the walls between them will be stretched and could easily be broken due to the weak melt strength. Thus, adjacent cells will join together, and the cell structure and the cell-population density will deteriorate. Since gas diffusion and cell coalescence can be controlled by lowering the temperature, a cooling system is chosen for satisfying FR_4. A cooling system consisting of a second extruder is introduced. As previously described, the temperature of the polymer/gas solution affects the volume expansion ratio. Thus, A_{41} should be non-zero because the shear heat generated from the plasticating stage affects the temperature of the polymer flow. Element A_{42} should be non-zero since the amount of gas injected affects the expansion ratio. Elements A_{43} should be non-zero because gas loss to the environment is localized if the cell-population density is high [43].

2.2.6.1 Detail Design of the Tandem Extrusion Line

Based on the conceptual design of the overall system for low-density, fine-celled foam extrusion in the previous section, the design of the detail components is carried out in this section. The tandem extrusion system consists of two single-screw extruders, gas injection equipment, a gear pump, a diffusion enhancing device, a heat exchanger, and a filament die. The first extruder is used for plasticating the polymer resin; the gas injection equipment is used for injecting gas into the polymer melt, while the second extruder provides mixing and initial cooling for the polymer melt. The gear pump controls the polymer melt flow rate, independent of temperature and pressure changes, the diffusion enhancing device ensures the homogeneity of the polymer/blowing agent solution and the heat exchanger provides further cooling for the polymer melt to suppress cell coalescence. Shaping and cell nucleation are accomplished in the die. Figure 2.14 shows a schematic of the tandem extrusion system. The detail design of each component is presented in the following sections [43].

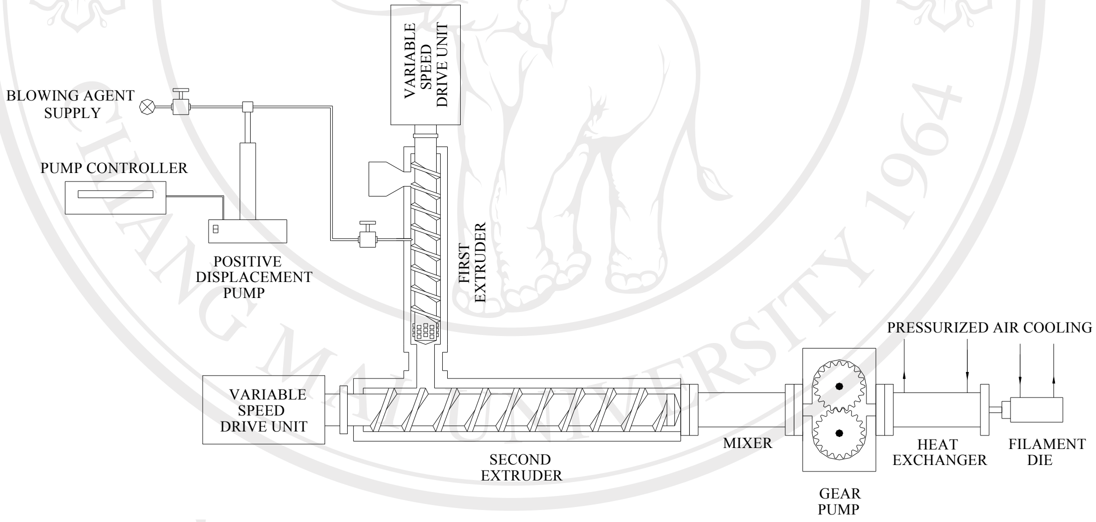


Figure 2.14 Schematic of the tandem extrusion system [43].

1) The First Extruder in the Tandem Line

The extruder used in the single screw extrusion system consists of a 3/4 laboratory extruder (Brabender: 05-25-000) with a 5 hp variable speed drive unit (Brabender: Prep Centre, Model D52T). The screw is a single stage mixing screw (Brabender: 05-00-144) with a 30:1 L/D ratio. The purpose of the mixing stage is to enhance the mixing of the blowing agent and the polymer melted. A schematic of the mixing section is shown in Figure 2.15 [43].

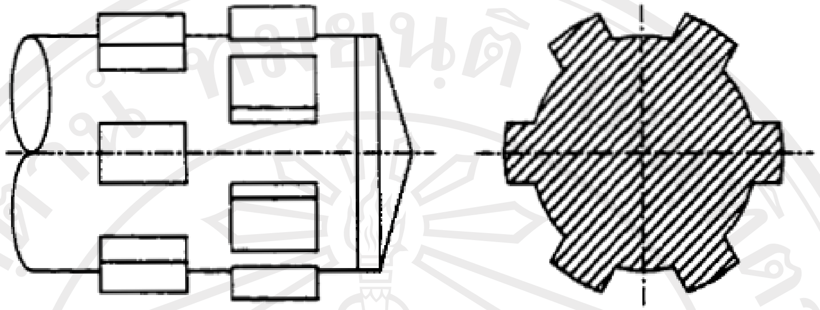


Figure 2.15 Schematic of the extruder mixing section [43].

2) Gas Injection Equipment

The two main components of the gas injection equipment are a positive displacement syringe pump and an in-house design gas injection port. The pump is capable of injecting the blowing agent into the polymer melt at a maximum pressure of 51.7 MPa (7500 psi) with a wide range of flow rate (from 0.01 ml/min to 107 ml/min, depending on the pressure condition). The heart of the gas injection port is a flow restrictor. Therefore, the pumping of gas into the barrel is readily affected by the pressure fluctuation in the barrel. Variation in the injection rate could affect the consistency of foaming significantly. One solution is to maintain a high pressure difference between the gas injection pump and the barrel. The choice of restrictor depends on the required pressure difference and the desired gas flow rate [43].

3) The Second Extruder in the Tandem Line

The second extruder in the tandem extrusion system consists of a 1½ extruder (Killion: KN-150) with a built-in 15 hp variable speed drive unit. The screw motion can generate shear heat in the polymer melt; however, since the second extruder is intended for cooling, it is necessary to keep the generated shear heat to a minimum. In this context, a small length/diameter (L/D) ratio of the screw (18:1) was chosen in the screw design. Moreover, a compression ratio of 1:1 was chosen since the second extruder is intended for maintaining the pressure of the molten polymer.

Polymer melt is fed into the barrel of this extruder from the first extruder through an injection port. Typically, the injection pressure of the melt is around 27.58 MPa (4000 psi). Because of the high pressure, it is necessary to have a dynamic sealing in the second extruder to prevent the melt leaking backward into the motor assembly through the clearance between the screw and the barrel. The proposed solution was to make extra flights on the screw located before the injection port. As the screw rotates, the thrust force generated by the screw motion of these extra flights would push the polymer melt forward preventing the leakage to the back [43].

4) Gear Pump

A gear pump (Zenith: PEP-11), with a 1/2 hp motor drive (Pacific Scientific: Model SR), a speed control unit (Zenith: ZeDrive) and a temperature controller (Eurothem Controls: Model 94), is used in the extrusion system to control the polymer solution flow rate. The gear pump consists of two closely intermeshing gears that rotate in a counter-rotating manner to convey the polymer melt from one end to the other. A schematic of the gear pump is shown in Figure 2.16 [43].

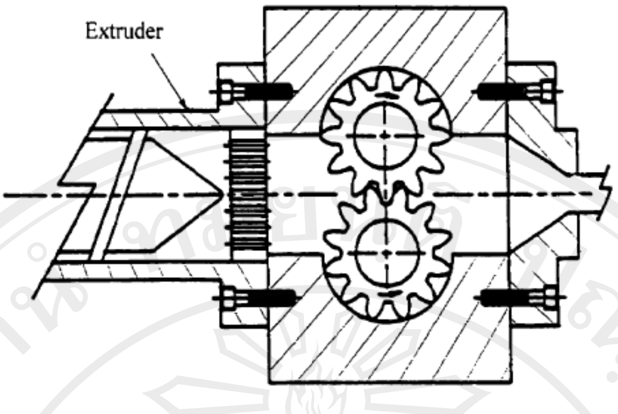


Figure 2.16 Schematic of the gear pump [43].

5) Diffusion Enhancing Device

A diffusion enhancing device is used to ensure the homogeneously mixing of polymer melt and the blowing agent. It consists of an in-house design, mild steel body, a static mixer (Omega: FMX844LS) enclosed in a mild steel case, and two band heaters (Omega: MB1G1J1A1&MBIG2A1A1). The rationale behind this design is to use the static mixer to promote shear mixing, and to maintain a high melt temperature to promote a high diffusion rate of the blowing agent into the polymer melt [43].

6) Heat Exchanger

It is important to cool the polymer melt homogeneously because non-uniform temperature distribution could induce the inhomogeneous cell growth, resulting in an irregular cell structure. Therefore, cooling the polymer melt will increase the melt strength and suppress cell coalescence. The heat exchanger consists of a static mixer (Labcore: H-04669-12) encased in a mild steel body with embedded cooling channels as shown in Figure 2.17. This static mixer is structurally different from the one used in the diffusion enhancing device. This static mixer used in the heat exchanger promoted polymer transport in the radial direction such that the core material is constantly exchanging with the boundary material, whereas the mixer of the diffusion enhancing device does not.

Since the temperature can directly affect the foaming behavior of the polymer, it is important to control the temperature of the heat exchanger precisely. Using band heaters alone with temperature controllers do not provide adequate control because of lack of a cooling source. Consequently, a high pressure gas is introduced to provide cooling for the heat exchanger. The temperature controller controls the air flow through the cooling channel in the heat exchanger using a solenoid value based on the polymer melt temperature. When the temperature is above the set point, the solenoid value opens to let the high pressure air expand and flow through the channel in the heat exchanger. Because of the cooling induced during isentropic expansion, the temperature of air is significantly reduced and the cold air removes the heat from the heat exchanger. When the temperature is below the set point, the band heaters are switched on to provide the necessary heating. Using this band heater/high pressure air arrangement, temperature control of ±1°C was easily maintained [43].

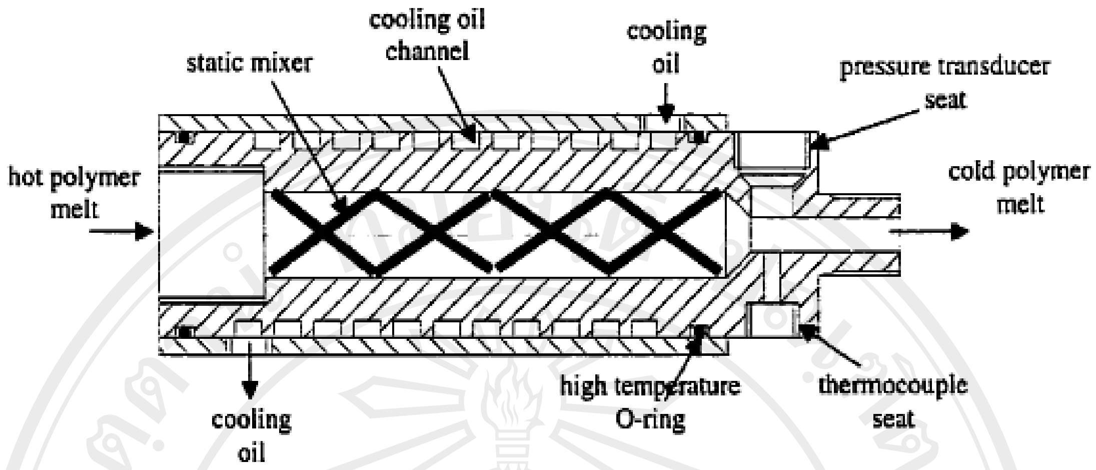


Figure 2.17 Schematic of the heat exchanger (courtesy of Behravesh) [44].

7) Filament Die

The principle function of the filament die is to induce a thermodynamic instability, which promotes nucleation of a large number of cells. The section of the die, which induces a rapid pressure drop, is characterized by a small diameter and is referred to as the nucleation section or capillary section. The effects of die diameter and length on the pressure drop and the pressure drop rate have been clearly explained that a change in length affects the pressure drop rate, while a change in diameter does not influence the pressure drop rate. However, both the die diameter and length affect the pressure drop in the die. For instance, by decreasing the die length without changing the die diameter, the pressure drop decreases while the pressure drop rate remains the same. Thus, a shorter die may be used when a high-pressure drop is experienced during processing. Figure 2.18 shows a schematic of the filament dies used [43].

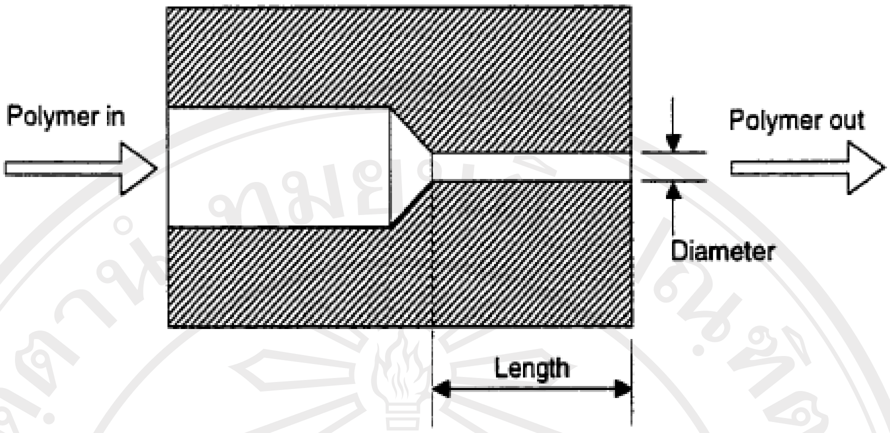


Figure 2.18 A schematic of the filament die [43].

8) Cooling Sleeve

The preventing strategy of the gas escape through the extruded surface can be achieved by cooling of the die using high pressure air while the extrudate flows into the nucleation section of the filament die. In order to cool the entire nucleation section of the die, there is a need to provide a seal channel around the die to circulate the pressurized air. It would be insufficient to make a channel for each die, especially when a large number of dies are to be examined. An alternative design is to make a sleeve with a large circumferential groove, as shown in Figure 2.19. When the sleeve is mounted on the die and sealed at each end using two O-rings, the cooling air can be circulated through the channel [43].

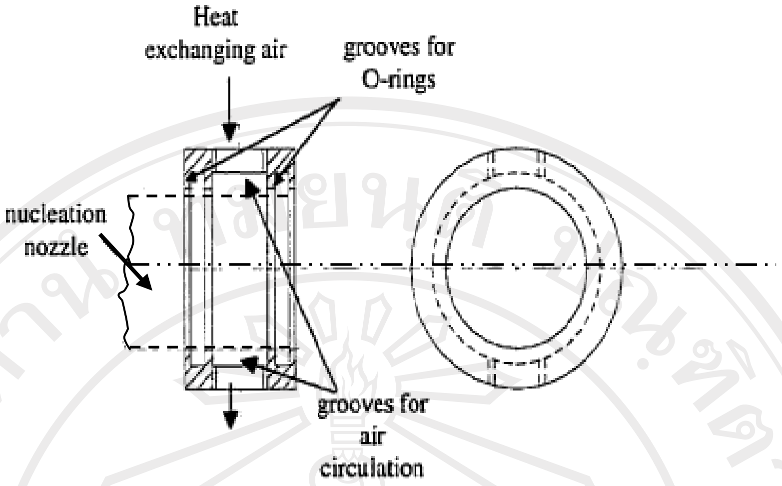


Figure 2.19 A schematic of the cooling sleeve to be mounted on the nucleation nozzle [43].

2.3 Theoretical background

2.3.1 Foam formation

In general, the foaming process comprises of three major steps: formation of polymer and gas, nucleation, and cell growth. The foam formation can be illustrated as following;

1) Mixing of formation of polymer/gas system (the saturation of polymer matrix with an inert gas under high pressure)
2) Cell nucleation (a rapidly thermodynamic instability either the pressure decreased or the temperature increased induces in the bubble nucleation in the polymer matrix)
3) Cell growth (nucleated micro-voids are developed under controlled temperature)

After the foaming, the desired cellular structure with decreased bulk density is promoted [45]. Among different theories or models have been used to describe the formation of cellular structure, the understanding of cell nucleation and cell growth models is a useful to the operating conditions and also the physical properties of the foams. A lot of physical properties such as viscosity, solubility, surface tension, diffusivity, and glass transition temperature, are found to play important roles. The operating system becomes more complex when one considers that these parameters are all functions of temperature, pressure, and CO_2 content [46].

2.3.1.1 Polymer/gas formation

Formation of a single-phase polymer/gas solution requires injection of a soluble amount of blowing agent into a polymer matrix with the assistance of a convective diffusion device in extrusion [47] or injection of gas under a high pressure in a chamber for a batch process. In extrusion foaming process, the amount of gas is metered by a positive displacement pump, which supplies the gas at a fixed rate into the plasticated polymer stream in the extruder. The shear fields generated by the plasticating screw and irregular mixing blades stretch the gas bubbles under high pressure, break them into smaller stretched bubbles, and eventually cause dissolution of the gas into the polymer matrix.

2.3.1.2 Cell nucleation

Cellular structure can be generated in the polymer by homogeneous and heterogeneous nucleation. Nucleation exists in several phase separation processes, such as bubble formation from a polymer/gas solution, water droplets formation from its vapor, and crystal formation from its amorphous phase. During nucleation, molecules conquer an activation energy barrier to accumulate together to create new phase. This is achieved by spontaneous fluctuations in density to form the embryo of the new phase. When a nucleated cell is less than some critical size, it will collapse back into the old phase. Otherwise, the nucleated bubble that exceeds the critical size can spontaneously grow to macroscopic size [46]. Since nucleation occurs as a result of gas dissolved in homogeneous polymer phase, it can be called as self-nucleation whereas if the gas phase is produced by the decomposition of the chemical nucleating agents or the present of the contaminated particles, this cell formation phenomenon can be called heterogeneous nucleation [48].

1) Homogeneous nucleation theory

When the dissolved gas molecules come together for a long enough period of time to produce a stable bubble nucleus the homogeneous nucleation is dominant. The rate at which the bubbles nucleate homogeneously (N_0), which can be expressed as Equation 2.19 [49-51];

$$N_0 = C_0 f_0 \exp\left(-\frac{\Delta G_{\hom o}}{kT}\right) \tag{2.19}$$

Where

C_0 = the concentration of homogeneous nucleation sites

f_0 = the frequency factor of gas molecules joining the nucleus

$= \left(\frac{2\sigma}{\pi m}\right)^{1/2}$

in which σ is the surface tension and m is the mass of the gas molecule

ΔG_{homo} = the critical free energy to form a nucleus of critical size

k = the Boltzmann's constant

T = temperature in Kelvin

Therefore, the critical free energy for homogeneous nucleation can be expressed as Equation 2.20 [48-51].

$$\Delta G_{\mathrm{hom}\,o} = \frac{16\pi\sigma^3}{3(P_i - P_s)^2} \qquad (2.20)$$

Where P_i is the pressure inside the critical bubble and P_s is the pressure of the surrounding the bubble [48-51].

The classical nucleation theory for a homogeneous system predicts that the higher the saturation pressure ΔP, the greater the number of cells nucleated because of the lower activation energy for cell nucleation [52]. In the batch foaming process, the saturation pressure corresponds to the gas concentration in the polymer thus the effect of pressure can be interpreted as its influence on the amount of gas absorbed into the polymer. When the amount of gas is increased, the chance of nucleation is higher and a large number of nucleated cells are achieved [53-55].

In addition, the number of nucleated cells is influenced by the pressure drop rate. This effect can be indicated by the experiment of using various nucleation dies to induce the various pressure drop rates and examined the final foam structures. It was found that the higher pressure drop rate, the greater number of nucleated cells, which can be explained by the mechanism of cell growth/nucleation competition [52]. Therefore, generating a large number of bubbles by dissolving a large amount of gas in the polymer is a critical step to obtain a fine cell structure for PP foams. However, monitoring the amount of gas dissolved in the polymer below the solubility limit according the processing conditions is equally important. Nevertheless, a sufficiently high pressure is required, as stated in Henry's law to maintain a large amount of dissolved gas in the polymer [56].

2) Heterogeneous nucleation theory

Bubble nucleation is heterogeneous when it initiated at some preferred sited by mixing the polymer with an additive or the existence of impurities (i.e., nucleating agents, additives, initiators residue, etc.). Usually, bubbles prefer to nucleate on the interface of the polymer matrix and the contaminated particles due to lower activation energy need to be surmounted [16-18]. By controlling the amount of additive, one can generate the desired number of bubbles. However, it is difficult to generate a large number of microcells using additives due to poor dispersion [57] and agglomeration [58] of the additive particles. Utilizing an appropriate nucleating agent that consists of very small particles well dispersed in the polymer matrix without agglomeration, one could produce a large number of cells for fine-celled foam application [57]. Moreover, the shear force is also affecting the heterogeneous nucleation rate in a dynamic system such as extrusion as the shear force increase, the number of nucleated bubbles increases. When the gas phase in the cavity grows and matured by diffusion of the dissolved blowing agent into the cavity or by a pressure drop, the applied shear force enhances the chance of detaching it from the cavity to generate a bubble [59]. The rate of heterogeneous nucleation (N_1) is given as Equation 2.21 [49-51].

$$N_1 = C_1 f_1 \exp\left(-\frac{\Delta G_{het}}{kT}\right) \tag{2.21}$$

Where

C_1 = the concentration of heterogeneous nucleation sites

f_1 = the frequency factor similar to f_0

ΔG_{het} = the critical free energy to form a nucleus of critical size

It is a complex function of the vibration frequency of atoms, the activation energy for diffusion in the polymer, and the surface area of the critical nucleus. The critical free energy for heterogeneous nucleation is given as Equation 2.22 [49-51].

$$\Delta G_{het} = \frac{16\pi\sigma^3}{3(P_i - P_s)^2} S(\theta) \qquad (2.22)$$

$S(\theta)$ is a function depending only on the wetting angle θ of the particle-gas interface, and it is less than or equal to 1, which expressed as following equation [49-51];

$$S(\theta) = (1/4)(2 + \cos\theta)(1 - \cos\theta)^2 \qquad (2.23)$$

In mixed mode nucleation processes, where both nucleation phenomena are presented. The heterogeneously activated bubbles still grow larger in diameter; because they appear first and gas diffusion starts in the bubbles before the self-nucleated one [49-51].

2.3.1.3 Cell growth

After the nucleation, the external pressure of saturated polymer is decreased the nucleated cells start to grow rapidly. Cell growth is governed by many parameters such as the final foam density, cell size, and distribution, and can be controlled by the temperature which influences the diffusivity and melt viscosity. Temperature control should be performed before cell nucleation since the rate of cell growth is much higher in the initial stages where the cells are small [1]. In the foaming process, it is important to consider the gas loss from the extrudate although the effect of gas loss is generally not dramatic [60]. However, at a high melt temperature, where the diffusivity is high and the viscosity is low, gas escape could be vigorous. This could result in a dramatic drop in foam expansion, resulting in an undesirably high foam density. Moreover, when smaller cells are present, the wall thickness separating the two cells becomes weaker, and thereby the rate of growth is faster, which may cause rupture in the cell wall and cell coalescence [61]. Effectiveness of the diffusion is strongly temperature dependent and it can be described with Arrhenius' equation [62-63].

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{2.24}$$

Where

D = the diffusion coefficient

D_0 = the material dependent diffusion coefficient

E_D = the activation energy in diffusion

R = ideal gas constant

In this expression, the effect of the concentration dependence on the diffusivity is neglected. Since the diffusivity increases as temperature increases, the rate of gas diffusion is enhanced by processing the mixture at a high temperature. Therefore, compared to room temperature, the gas diffusion rate for the polymer mixture is increased at the elevated temperature. According to the classical theory, the growth of the cells increased as the saturation pressure is increased because the pressure inside the cell seeks equilibrium with the outer gas pressure [2, 64].

$$\Delta P = \frac{2\sigma}{r} \tag{2.25}$$

Where r is the critical radius and ΔP is the difference from the pressure inside the bubble and surrounding pressure in the system, respectively. For the batch foaming, the size of small cells can be decreased by increasing the saturation pressure that favors the homogeneous nucleation. While small cells in the molten state of polymer can be achieved by the heterogeneous nucleation and the increase in saturation pressure induce to increase bubble growth [65]. In the case of two bubbles of radius r_1 and r_2, the difference in pressure (ΔP^2) is given by this equation [2].

$$\Delta P^2 = 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{2.26}$$

Therefore, in the system, a diffusion of gas takes place from the small bubbles into the large bubbles, resulting in the disappearance of the small bubbles, while the large bubbles grow in size with time. Moreover, the surface tension is reduced by the addition of the surface-tension depressant. The decrease in the pressure difference between bubbles is resulted and it hence leads to better bubble stability and small average cell size [2].

2.3.1.4 Foam stability

During the growth of cells, the wall of the cell is stretched thin and may promote cell rupture for the molten state of polymer even that of the solid state of polymer in the batch foaming process that the matrix is soften by the increasing of temperature. This is because the surface tension is concerned to the common foaming phenomena in which the viscoelastic behavior plays the hindrance in the foaming.

Therefore, the interior cellular structure should be frozen by lowering the temperature. In addition, the effect of surface active additives that based on their movement from lower surface energy areas to higher ones during bubble growth. They form a thin interface between foam bubble and polymer. The movement of the surface active additives is flowing (Marangoni effect) or diffusive (Gibbs effect). The growing of the cells lowers the surface active additive concentration on the surface leading to increased surface tension, which stabilizes the foam structure. According to the free energy of the system the energy barrier of the cell nucleation can be lowered by reducing the surface tension of the interface between the particle of nucleating agent and the polymer matrix. In three phase polymer foaming the nucleating particles should not be wetted by the polymer. If the polymer wets the particle, gas will not create a bubble on the surface. But if the particle is treated with a surface active additive which lowers the interface of particle and polymer, the gas will form a bubble so that the surface active layer spreads along the surface of the growing cell. When the growth cell contacts with a cooled surface, the collapse of cell membrane is level off. This is an approach to stabilize the cellular structure in the foaming process [2].

2.3.2 Solubility and diffusivity

2.3.2.1 Solubility

Solubility is the measure of the ability of a polymer to accept and retain these small molecules. The solubility is conventionally determined in a batch process over a limited temperature range. In the batch process, a sheet of polymer sample is saturated with the blowing agent by placing it in a high pressure chamber connected to the blowing agent supplier (or gas tank). At this high pressure, the gas will continuously diffuse into the polymer matrix until the solubility limit is reached as shown in Figure 2.20.

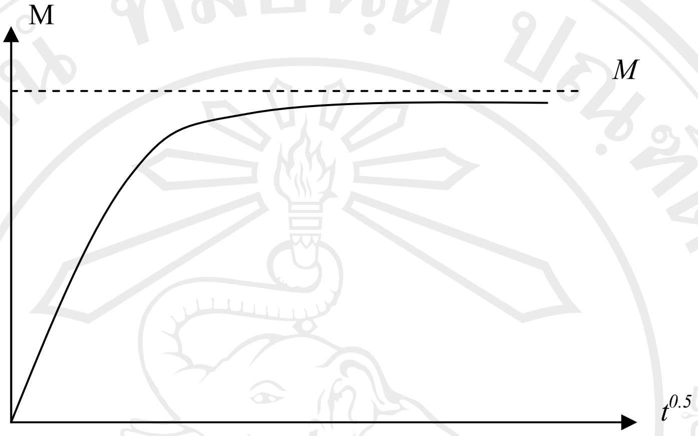


Figure 2.20 Sorption isotherm for typical polymer/gas system.

Although the solubility limit theoretically occurs at time infinity, the instantaneous concentration of the gas in the polymer still can be obtained using the following equation [66].

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{a=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[- \frac{D(2a+1)^2 \pi^2 t_s}{l^2} \right] \qquad (2.27)$$

Where

D = diffusivity (cm^2/s)

M_t = mass uptake at time t (g)

l = sheet thickness (cm)

M_∞ = equilibrium mass uptake after an infinite time (g)

t_s = elapsed time (s)

a = consistency parameter in power law (Pa·s^n)

The amount of mass uptake eventually tends to level off at M_∞ in the absorption process, and the solubility limit can be calculated by dividing the mass uptake (M_∞) by the mass of the polymer sample [66]. Solubility is usually measured in standard gas volumetric uptake per unit weight of liquid or mass uptake per unit weight of solid polymer sheet. The solubility limit is the maximum amount of gas or liquid that can be dissolved in a polymer at a given temperature and pressure. If more liquid or gas is added at a given temperature and pressure, it can only reside in un-dissolved micro-droplets or micro-bubbles. Micro-drops and micro-bubbles grow nearly explosively when the melt pressure is released. Foams with coarse cells and large voids are the results. [21]. As the citation of Guangming Li [67], the solubilities of CO_2 and nitrogen (N_2) in PP at the various temperature and pressure are shown in Figure 2.21 and Table 2.4 [67-68].

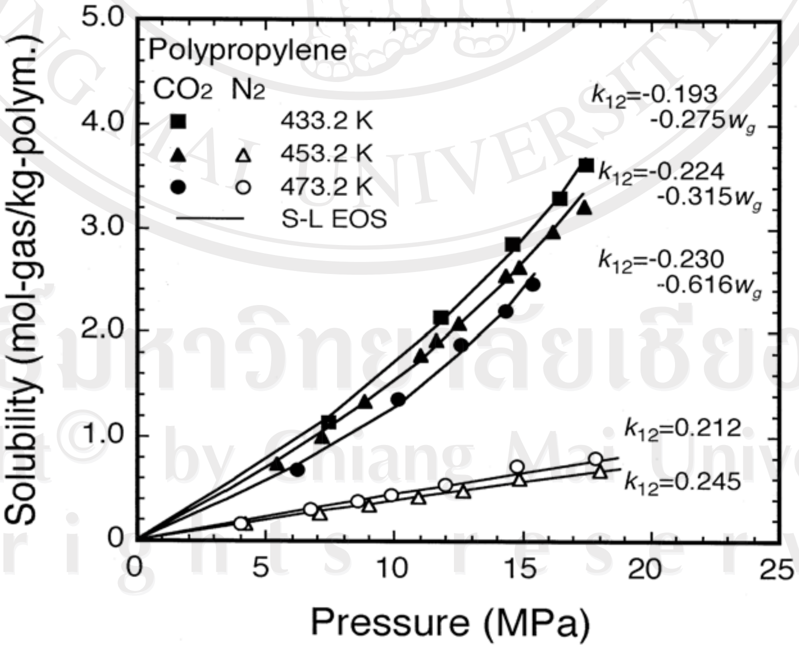


Figure 2.21 Solubility of carbon dioxide and nitrogen in PP [68].

Table 2.4 Solubility of carbon dioxide and nitrogen in PP at 433.2 K and 473.2 K [68].

Carbon dioxide		**Nitrogen**	
Pressure (MPa)	Solubility × 10^2 (g-gas/g-polymer)	Pressure (MPa)	Solubility × 10^2 (g-gas/g-polymer)
433.2 K		***433.2 K***	
7.400	5.03	-	-
11.803	9.48	-	-
14.558	12.53	-	-
16.355	14.51	-	-
17.529	15.87	-	-
473.2 K		***473.2 K***	
6.204	3.02	4.013	4.52
10.113	6.01	6.726	8.55
12.637	8.30	8.545	10.59
14.296	9.68	9.878	12.21
15.397	10.86	11.998	15.14
		14.819	19.99

Moreover, the solubility limit of gas dissolved into the polymer depends on the system pressure and the temperature can be estimated by Henry's law [56].

$$C_s \approx HP_s \tag{2.28}$$

Where

C_s = solubility of gas in the polymer ($\mathrm{cm^3/g}$) or ($g_{gas}/g_{polymer}$)

H = Henry's law constant ($\mathrm{cm^3}$ [STP]/g-Pa)

P_s = saturation pressure (Pa)

The constant H is a function of temperature described by;

$$H = H_0 \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{2.29}$$

Where

R = gas constant (J/K)

T = temperature (K)

H_0 = solubility coefficient constant (cm^3 [STP]/g-Pa)

ΔH_s = molar heat of sorption (J)

The molar heat of sorption, ΔH_s can be a negative or a positive value depending on the polymer-gas system. Equation 2.26 and 2.27 are used for determining the solubility of a blowing agent in the polymer at the processing pressure and temperature, and estimation of the solubility of CO_2 in some polymers [47, 52]. In the actual extrusion foaming process, the ratio of gas to polymer weight is maintained below the solubility limit, by controlling the flow rate of the polymer and gas with injection amount.

2.3.2.2 Diffusivity

Small particles move or migrate through polymers in the free spaces between the molecules. The driving forces are chemical potential, gas concentration gradient, differential partial pressure, or temperature gradient. Small molecule movement is called diffusion. Diffusion coefficients are always associated with a given small molecule moving through a given polymer matrix at a given temperature. The units are area per unit time, such as cm^2/s. Bulky molecules diffuse through the polymers at slower rates than smaller molecules. Diffusion rate is strongly dependent on temperature. Instance, the relative diffusion rates of gases through polyethylene and PP are given in Table 2.5 [21].

Table 2.5 Relative diffusion rates of blowing gases through PE and PP at 188 °C (relative to nitrogen in PE, 6.04×10^{-5} cm^2/s) [21].

Gas	**Polyethylene**	**Polypropylene**
Nitrogen	1	0.58
Carbon dioxide	0.94	0.70

As Figure 2.20, the initial slope of the curve corresponds to the diffusivity of the blowing agent into the polymer matrix, and can be used to calculate the diffusivity using the following equation [66].

$$D \cong \frac{0.04919}{\left(t/l^2 \right)_{1/2}} \qquad (2.30)$$

Where $(t/l^2)_{1/2}$ is the value of (t/l^2) at $M_t/M_\infty = 1/2$. By ranging Equation 2.30, the time required for the completion of absorption can be approximated from Equation 2.31 as following;

$$t_D \cong \frac{\pi}{16} \cdot \frac{l^2}{D} \qquad (2.31)$$

Equation 2.31 indicates that the time of absorption is inversely proportional to the diffusivity (D) and proportional to the square of the diffusion distance (l^2). The diffusivity is mainly a function of temperature, and its influence can be explained by Equation 2.24 [56, 62-63, 66];

2.3.3 Selection of blowing agent

The type of blowing agent used in plastic foam processing is critically important in determination the cell morphology of produced foams. Typically, a physical blowing agent is used for the low-density foam processing unless crosslinking is included in the processing. A chemical blowing agent may also be used for low-density foam processing that involves crosslinking [69]. Low-density foams with a volume expansion ratio higher that 40 times used to be produced using environmentally hazardous blowing agents such as CFCs, HCFCs, etc in extrusion foam process. But because of Montreal protocol, these blowing agents have been or will be eliminated from use [70] Although, some efforts have been made to use an inert gas for low-density foam processing [71] the long chain blowing agents such as isopentane or butane are commonly used in the low-density foam processing [44]. However, an environmentally benign CO_2 gas has been selected to use in this research for producing the low-density PP foams with maximum volume expansion ratios in the extrusion foaming process. In order to determine the type of blowing agent to be used in the low-density PP foam processing, the maximum achievable theoretical volume expansion ratios of the extruded foam can be calculated as the following [72];

$$V_t = \frac{Polymer\,volume + Gas\,volume}{Polymer\,volume} \qquad (2.32)$$

$$\text{or} \qquad V_t = 1 + \frac{m_{gas}}{m_P} \times \frac{v_{gas}}{v_P} \qquad (2.33)$$

Where v_{gas} is the specific volume of blowing agent at the crystallization temperature of PP materials (131 °C, Honam SMS-514), and v_p is the specific volume of PP materials at room temperature [72]. The m_{gas} and m_p are the mass flow rate of gas (g/min) and PP (g/min), respectively. The calculation of theoretical volume expansion ratio is described in chapter 4.

2.4 Microcellular foams and the production strategies

Microcellular foams (MCFs) or microcellular plastics (MCPs) was first invented at the Massachusetts Institute of Technology in early 1980s by the requirement of Eastman Kodak to overcome the heavy competition within United States home market and to improve manufacturing efficiency for its photographic film. Therefore, Eastman Kodak approached Dr. Nam Suh, Mechanical Engineering Department Head of Massachusetts Institute of Technology (MIT) in Cambridge, Massachusetts, to develop a new manufacturing technology that Eastman Kodak could implement. The critical requirements given to Dr. Nam Suh by Eastman Kodak included;

1) Reduce plastic usage
2) Maintain physical properties and
3) Maintain or improve manufacturing efficiency

Applying Dr. Nam Suh technique discovered that the first two criteria could be met by placing very small bubbles into the polymers. Furthermore, the tiny bubbles could be imparted into the plastics by rapidly decreasing the pressure or by rapidly increasing the temperature during processing. The pursuit of this innovative idea led to the invention of microcellular foam technology for the lab scale and commercial manufacturing in response to a challenge by food and film packaging companies to reduce the amount of polymer used in their industries. Today, Trexel is a company funded by private investment and venture capital to develop the microcellular process for plastics extrusion, blow molding, and injection molding applications. Moreover, this new technology is called the MuCell® microcellular process; MuCell and Trexel are registered trademarks of Trexel, Inc [65].

Microcellular foams are referred to any polymeric materials that have closed cells of very small diameters, typically smaller than 50 microns. The cell density can be made to vary a great deal depending on the final application of a given microcellular plastic. MCFs can have as high as 10^{15} cells/cm^3 when the bubble diameter is 0.1 microns, 10^{12} cells/cm^3 for 1 micron, and 10^9 cells/cm^3 for 10 micron diameter cells. In according to the impetus of the original idea for the creation of micro-voids results in a material consuming less material and cost lowering without the compromising the mechanical properties (especially toughness) of the product since failure will tend to initiate at the pre-existing flaw rather than the nucleated micro-voids [45]. These innovative materials have superior thermal and electrical properties when compared to the neat polymer (i.e., prior to microcellular processing), and are often found to have improved performance relative to conventional structural foams. Typically, microcellular plastics exhibit high impact strength (i.e., up to a five-fold increase over neat plastic), high toughness (i.e., up to five-fold increase over neat plastic), high stiffness-to-weight ratio (i.e., three to five times larger than neat plastic), high fatigue life (i.e., up to fourteen-fold increase over neat plastic), high thermal stability, low dielectric constant, and low thermal conductivity [72]. Because of these unique properties, a large number of innovative applications of microcellular plastics can be imaged. These include food packaging with reduced material costs, airplane and automotive parts with high strength-to-weight ratio and acoustic dampening, sporting equipment with reduced weight and high energy absorption, insulative fibers/filaments for fabric, etc [42]. These materials can be applied to most polymers including amorphous thermoplastics, semi-crystalline thermoplastics, liquid crystal polymers, thermosetting plastics and elastomers [72]. Moreover, microcellular plastic process technology has advantages over many conventional polymer foam process because it uses environmentally-friendly gases as blowing agents rather than hydrocarbons, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), or toxic chemical blowing agents [72]. The basic approach to the production of microcellular structures is to continuously form a polymer/gas solution, to nucleate a large number of bubbles using thermodynamic instability via a rapid pressure drop, to suppress cell coalescence by increasing the melt strength, and to induce a volume expansion to a desired expansion ratio. This technique uses a nucleating agent or a chemical/physical blowing agent to nucleate gas bubbles as the conventional foaming process but the distribution of small bubbles is much better than that of conventional foams. While a non-uniform distribution of the agents results in a conventional foam that has a high concentration of gas bubbles or cells in agent rich areas and a low concentration in agent poor areas. It is know that the number and the size of the bubbles are determined by the concentration of the foaming agent. The uniformity of the cell structure and the cell density are limited by the method used to mix the agents and the polymer. In fact, it is rather difficult to obtain a uniform cell structure with a high cell density in the conventional foam processing with a chemical or physical blowing agent. For conventional foams, a typical cell density is in the range of 10^2 to 10^6 cells/cm^3, the cell size is larger than 100 microns, and the cell size distribution is very non-uniform [42]. Over the past decade, substantial research and development have been conducted to gain knowledge about the physical phenomena governing microcellular processing of microcellular polymers. This knowledge has successfully led to the implementation of microcellular batch processes, and semi-continuous processes. In order to overcome the high processing cost of microcellular batch and semi-continuous processing due to their long cycle times, continuous extrusion processes have also been developed.

2.4.1 Batch microcellular processing

The basic concept of microcellular plastic technology was first discovered by Martini and Suh in a form of batch foaming process. The approach of the foaming was saturation of a plastic sheet with an inert gas in a high-pressure chamber and to induce thermodynamic instability by rapidly drop of the gas solubility in the polymer [45]. The process parameters and the product characteristics were determined cooperated with the process design for lightweight plastic products by the previous researchers, such as Waldman, Young, Colton, etc [1]. As the results of their studies, much finer cellular structures were able to obtain from various thermoplastics including PVC, PETG, PMMA, ABS, PC, LDPE, and HDPE, etc. Microcellular foam structures from various semi-crystalline polymers were also developed with the special processing strategies of Colton and Suh [49-50], Baldwin *et al.* [52-53], and Doroudiani *et al.* [9]. Moreover, the study of microcellular plastic in the form of blend was also reported by Rachtanapun *et al*. [10].

In the batch foaming process, microcellular plastics have been produced using thermodynamic instability of a polymer/gas system to promote a large bubble density in the polymer matrix. Microcellular plastics processing involves the following four basic steps to utilize such thermodynamic instability of polymer/gas solution formation, micro-cell nucleation, suppression of cell coalescence, and cell growth. These steps are basic to microcellular processing and are applied to both batch and continuous manufacturing processes [1].

Typically, formation of a polymer/gas solution is accomplished by dissolving an inert gas, such as carbon dioxide or nitrogen into a polymer matrix under a high pressure. This procedure a solution having a high gas concentration (i.e., 5 to 20 wt%) in the polymer matrix. Solution formation is governed by the gas diffusion in the polymer. Diffusion processes are generally slow, resulting in long cycle times.

The next step of microcellular processing involves subjecting the polymer/gas solution to thermodynamic instability to nucleate micro-cells. This is achieved by lowering the solubility of gas in the solution by controlling the temperature and/or pressure. The system is now to have a lowering of free energy in which results in the clustering of gas molecules in the form of cell nuclei. Formation of cell nuclei provides a relatively small mean free distance for the gas molecules in the solution to diffuse through before reaching a cell nucleus (i.e., the gas phase). As the diffusion of gas into the cells, the free energy of the system is lowered. The cell nucleation process can occur homogeneously throughout the material or heterogeneously at high energy regions such as phase boundaries. In the ideal case, nucleation occurs instantaneously. The cell nucleation process is very important in microcellular plastics production in that it governs the cell morphology of material, and to a large extent, the properties of the material [1].

Although a large number of nuclei have been achieved in the nucleation stage, the final cell density of produced foams might not be the same as the initial nuclei density if cell coalescence occurs. Cell coalescence is thermodynamically favored because the total surface area of cells is reduced by coalescence. When the cell density is deteriorated by cell coalescence, the mechanical and thermal properties are deteriorated as well. In order to prevent the deterioration of the properties and to fully utilize the unique properties of microcellular plastics, cell coalescence should be suppressed. When the cells are nucleated, they continue to grow as available gas diffuses into cells, provides little resistance is encountered. The cells grow and the total polymer density decreases as the gas molecules diffuse into the nucleated cells. The rate of cell growth is limited by the diffusion rate and the stiffness of the viscoelastic polymer/gas solution. If the stiffness of the matrix is too high, cell growth is extremely slow [1]. In this case, the solution temperature can be increased to lower the matrix stiffness. In general, the cell growth process is controlled primarily by the time allowed for the cells to grow, the temperature of the system, the state of supersaturation, the hydrostatic pressure or stress applied to the polymer matrix, and the viscoelastic properties of the polymer gas solution [1].

Microcellular plastics were firstly produced in a batch process. Figure 2.22 shows a typical example of a batch process for producing microcellular plastics [73].

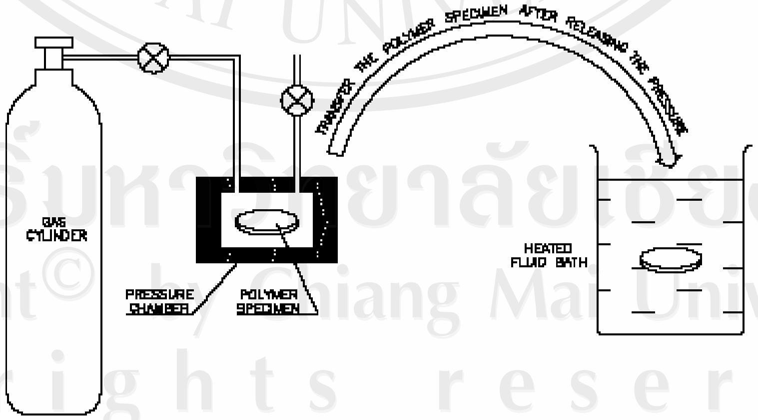


Figure 2.22 Batch microcellular foaming process [73].

In this process, a polymer sample is placed in a high pressure chamber where the sample is saturated with CO_2 or N_2 under high pressure at ambient temperature. Then, a thermodynamic instability is induced by rapidly dropping the solubility of gas in the polymer. This is accomplished by releasing the pressure and heating the sample. This drives nucleation of a myriad of micro-cells and the nucleated cells continue to grow, leading to the foam expansion. One of the disadvantages of the batch process is a very long cycle time required for gas saturation in the polymer because the diffusion rate is very low at the ambient temperature [73].

2.4.2 Semi-continuous microcellular processing

As the efforts to improve the semi-continuous microcellular processing to realizing the microcellular foaming concept to industrial production, there were some research groups have been tried to apply a solid-state microcellular batch process into the semi-continuous microcellular process in which the strategy can be approached by saturating a roll of sheet with a gas channeling material (or an aid of gas permeable material) interleaved between the layers of polymers is prepared. The gas channeling material should consist of a layer of flexible gas material, such as porous paper sheet, particulate material, and fabrics. Next, the roll of polymer sheet and gas channeling material is exposed to the high-pressurized foaming agent (i.e., CO_2) for a period of time sufficient to achieve the desired gas concentration, usually at room temperature. Finally, the pressure is released and the saturated polymer roll is gradually unwound, separated from the gas permeable material, and heated by drawing under tension through a heating station, a water or oil batch which the temperature is higher than T_g

as in the batch foaming process. The semi-continuous microcellular process procedure is shown in as Figure 2.23 [74].

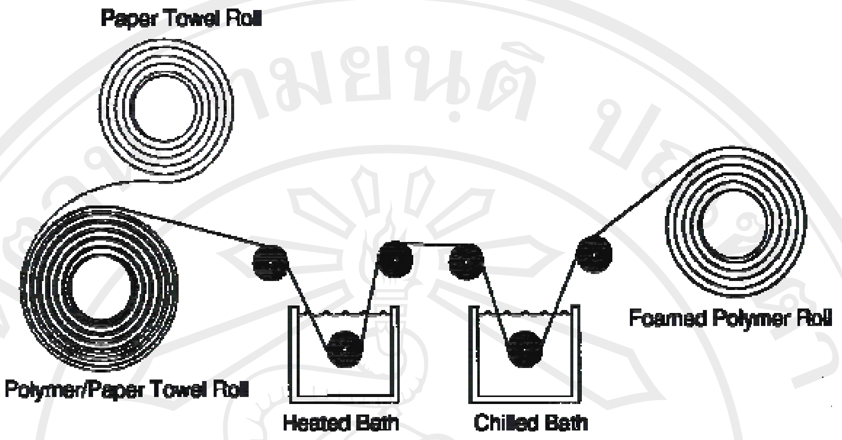


Figure 2.23 Semi-continuous microcellular foaming process [74].

2.4.3 Continuous microcellular processing

Consequently, the extrusion-based continuous microcellular process has been developed to reduce the gas saturation time and the continuous microcellular foaming process is described in detail in the following sections. An extrusion process based on the functional requirements and the chosen design parameters. First, the plastication of the polymer takes place in the extrusion barrel as shown in Figure 2.24 [44]. Then, a metered amount of gas is delivered to the polymer melt stream. Typically, the polymer/gas solution formation is accomplished by saturating a polymer under a high pressure gas. The solution formation is governed by gas diffusion in the polymer matrix. Diffusion processes are normally slow, resulting in long cycle times. The diffusion rate is increased as an increased gas pressure due to the increment of local gas. When increasing the temperature, the diffusivity is also increased. For continuous foaming, mixing the polymer/gas system decreases the gas diffusion distance. Thus the solution formation time and cycle time are decreased [75]. The next phase of microcellular processing involves subjecting the polymer/gas solution to a thermodynamic instability to nucleate microcells. This achieve by lowering the solubility of the solution by controlling the temperature and/or pressure. The system now seeks a state of lower free energy, which results in the clustering of gas molecules in the form of cell nuclei. The formation of cell nuclei provides a relatively small mean free distance for the gas molecules in solution to diffuse through before reaching a cell nucleus (i.e., the gas phase). As the gas diffuse into the cells, the free energy of the system is lowered. The cell nucleation process can occur homogeneously throughout the material or heterogeneously [50]. Once the cells are nucleated, they continue to grow as available gas diffuse into cells and reduce the total polymer density as the gas molecules diffuse into the nucleated cells from the polymer matrix. The rate at which the cells grow is limited by the diffusion rate and the stiffness of the viscoelastic polymer/gas solution. If the stiffness of the matrix is too high, cell growth is extremely slow. In this case, the solution temperature can be increased to lower the matrix stiffness. In generally, the cell growth process is controlled primarily by the time allowed for the cells to grow, the temperature of the system, the state of supersaturation, the hydrostatic pressure or stress applied to the polymer matrix, and the viscoelastic properties of the polymer/gas solution [76]. Finally, a microcellular structure with a large cell density is produced when the polymer/gas solution experience a thermodynamic instability in a rapid-heating nucleation device [75].

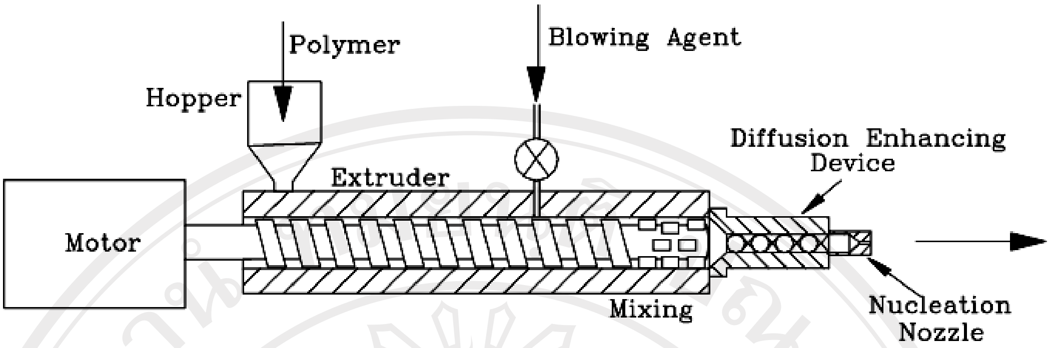


Figure 2.24 Schematic of continuous microcellular foaming process [44].

2.5 Low-density, fine-celled foams and the production strategies

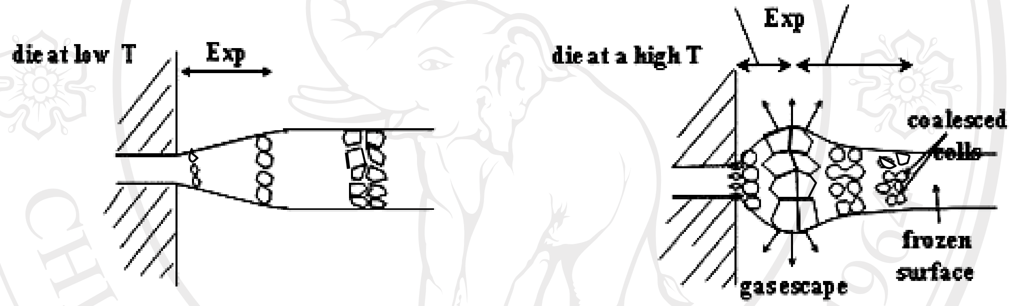
During the production of fine-celled PP foams is limited by available processing technologies. Foams produced in a state-of-art conventional extrusion process have cells larger than 100 μm, a cell density lower than 10^6 cells/cm^3, and a broad cell size distribution. However, in their favor the expansion ratio of conventional foams can be very high up to 50 times. In contrast, microcellular polymers have been produced with expansion ratios of 1 to 10 times the initial volume. Moreover, in the continuous foaming process the blowing agent that promotes foam expansion may escape through the exterior skin of the foam resulting in contraction of the foam [60, 71, 77-78]. Because the expansion of foam relies on the presence of blowing agent within the foam, it is desirable to devise a means for preventing gas loss in order to achieve a large volume expansion ratio.

Although, PP is one of the most widely used commodity materials but this material possess weak melt strength, which increases the difficulties in the continuous foaming process when compared to other plastics. When the melt strength is too weak, the cell walls separating the bubbles may not have enough strength to bear the extensional force and may rupture very easily during the foaming. As a result, the foamed PP products usually have high open-cell content and thus are unsatisfactory for many applications.

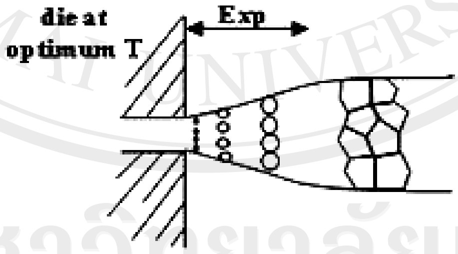
In order to improve the foamability and thermo-formability, material modification or new resin developments have been conducted for PP materials. Earlier efforts included crosslinking of PP resins and significantly improved volume expansion ratio, cell uniformity, and thermo-formability of their foams were observed [13, 79-81]. Moreover, the surface quality and melt fracture of extruded PP have been studied by many researchers [82-84]. Baik and Tzoganakis [83] observed from their study on controlled rhelogy PP that the extrudate distortion decreased with increasing the shear rate for a given material and processing conditions. And the severity of extrudate distortion decreased as the die aspect ratio was increased. Sammler *et al.* [84] studied melt fracture for high-melt-strength (HMS) PP. The presence of this melt fracture is expected from the strong elastic component observed in the extensional rheology, and the long chain branching is the most probable molecular origin of spurt melt fracture in the branched PP materials. The foaming behaviors of various PP resins have been investigated. The cell nucleating behavior and the final cell density of extruded PP foams with various nucleating and blowing agents were extensively studied for fine-celled PP foam applications [6, 85-87]. The explanations of foaming behavior and the foaming approach can be concluded and described as the following.

2.5.1 Fundamental mechanisms governing volume expansion of PP foams

The final volume expansion ratio of the extruded PP foams blown with a blowing agent is governed either by gas loss through the foam skin or by crystallization of the polymer matrix. In general, depending on the exiting the die the foaming extrudate exhibits one of the shapes depicted in Figure 2.25 [12], upon on the temperature of the extrudate. At higher temperature, the cross section of the extrudate expands suddenly as a result in it has a higher initial angle and this angle decrease as the processing temperature decreases. Below an optimum processing temperature, the foaming of extrudate is inhibited and the initial angle is substantially reduced. The mechanisms governing the volume expansion of PP foams are explained in the following sections [88].



(a) At low temperature **(b) At high temperature**



(c) At optimum temperature

Figure 2.25 Shapes of extrudate PP foams at various temperatures at the die [12].

1) <u>Gas loss</u>

The gas loss phenomena which occur during foam processing can be correlated with the melt temperature. The diffusivity of blowing agents at elevated temperature is very high; therefore, if the processing temperature is too high, the gas can easily escape from the extruded foam because of its higher diffusivity at elevated temperatures. In addition, as the cell expansion increases the cell wall thickness decreases and the resulting rate of gas diffusion between cells increases. Consequently, the rate of gas escape from the foam to the environment increases. Gas escape through the thin cell walls decreases the amount of gas available for the growth of cells resulting in lowered expansion. Moreover, if the cells do not freeze quickly enough, they tend to shrink due to loss gas through foam skin causing overall foam contraction [88]. The mechanism is schematically shown in Figure 2.26 [12].

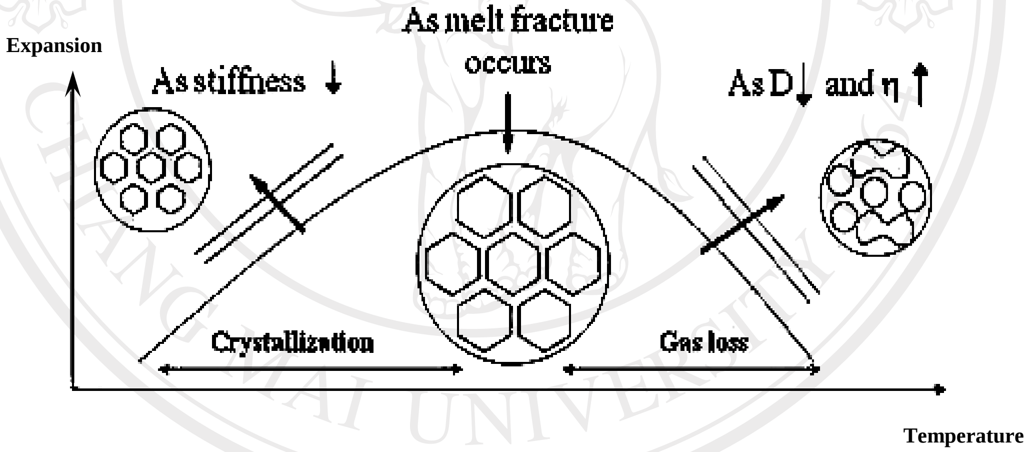


Figure 2.26 Schematic of volume expansion mechanism [12].

This phenomenon of gas escape at high temperature and the resultant foam contraction during the cell growth stage at elevated temperatures were observed during experimentation. It was observed that the extruded foam initially expanded as the nucleated cells grew very fast and then eventually contracted. The maximum expansion occurred very close to the die exit with the diameter of the initially expanded foam being larger than that of the final foam. This indicates that the volume expansion ratio of the initially expanded state was considerably high and therefore the shapes of expanded cells at this state were not spherical but polyhedral with thin cell walls (see Figure 2.26) [12].

2) Crystallization

The crystallization behavior of semicrystalline materials is another critical factor that affects the maximum expansion ratio in plastic foam processing. For semicrystalline polymers, the polymer melt solidifies at the moment of crystallization during cooling. Therefore, in the foam processing of PP the foam structure freezes at the crystallization temperature during the foaming process. If the crystallization occurs in the primitive stage of foaming before the dissolved blowing agent fully diffused out of the plastic matrix and in the nucleated cells, then the foam cannot be fully expanded. Therefore, in order to achieve the maximum volume expansion ratio from the PP foam the crystallization (for solidification) should not occur before all the dissolved gas diffuses out into the nucleated cells. Upon exiting the die, the temperature of melt decreases due to external cooling outside the die and the cooling effect due to isotropic expansion of the blowing gases. Thus the processing temperature at the die determines the time after which the polymer melt solidifies. Therefore, in order to give enough time for the gas to diffuse into the polymer matrix, the processing temperature should be high enough. It should be noted that if the processing temperature is too close to the crystallization temperature, the polymer melt would be solidified too quickly before the foam is expanded fully as shown in the initial section of Figure 2.26 [88].

On the other hand, if the temperature is too high then the solidification time might be too long and the gas that has diffused out of the plastic melt to the nucleated cells might escape out of the foam as discussed above. This indicates that there is an optimum processing temperature for achieving maximum expansion as shown in the middle section of Figure 2.26. If the melt temperature is too high then the maximum volume expansion ratio is governed by gas loss and the volume expansion ratio will increase as the processing temperature decreases. If the processing temperature is too low then the volume expansion ratio is governed by the solidification (the crystallization) of PP, and the volume expansion ratio will increase as the temperature increase [88].

2.5.2 Strategies for promoting high volume expansion

The basic approach to promotion of a large volume expansion ratio with PP materials is four folds;

1) To use a branched material for preventing cell coalescence;
2) To use a long-chain blowing agent with low diffusivity;
3) To lower the melt temperature for decreasing gas loss during expansion; and
4) To optimize the processing conditions in the die for avoiding too quick crystallization.

One of the most important strategies for promoting large expansion of PP foams is use of branched PP materials. Because of the weak melt strength, cell coalescence will be observed in the extruded foams with linear PP materials [6]. When cells are coalesced, the cell density and cell size uniformity are not only deteriorated, but the volume expansion ratio is also greatly sacrificed because of accelerated gas loss through opened cell walls. Therefore, use of branched PP materials is essential for low density as well as fine-celled foam processing.

Another strategy that is required to obtain low-density PP foams is to use a long chain blowing agent [56]. Since the inert gas have higher volatility and therefore higher diffusivity than the long-chain blowing agents, the blowing gases can escape easily during expansion [60, 71, 77-78]. Therefore, it is very difficult to obtain a low-density foam with a large expansion ratio of over forty-fold with an inert gas. On the other hand, the long-chain blowing agents have low diffusivity offers a tremendous advantage in controlling cell growth to achieve a very high expansion ratio over forty-fold. With a lower diffusivity, the cell growth rate is slower, and thereby gas escape can be more easily blocked. As a consequence, a high volume expansion ratio can be easily achieved.

As the thickness of the cell walls decreases in low-density foam production, the cell-to-cell diffusion rate is increased, and therefore the diffusion rate of gas escaping out of the foam to the environment increases. Gas escape through the thin walls will decrease the amount of gas available for the growth of cells. As a result, if the cells do not freeze, they tend to collapse and cause the foam contraction. In order to produce low-density foams, gas diffusion through the skin of the extrudate foams must therefore be prevented. One way of preventing gas escape from the foam is to freeze the skin of the extrudate [60, 71, 77-78]. Since the diffusivity drops dramatically as the temperature decreases [56], the rate of gas escape can be substantially reduced by freezing the skin of the foams. The surface of the extrudate can be quenched by lowering the die temperature. Therefore, the basic strategy for promoting large volume expansion in the extrudate foam is to freeze the foam skin by controlling the die temperature [77].

The melting temperature also needs to be lowered to obtain a high volume expansion ratio. The temperature of the polymer melt flowing into the die significantly affects the amount of blowing agent that escape to the environment because the diffusion rate of the blowing agent in the cell walls can be retarded by lowering the temperature of polymer melt [77]. The PP melt with dissolved blowing agent should be cooled uniformly down to a very low temperature using a cooling device before the melt gets to the die. The cooling device can be a heat exchanger consisting of a homogenizing static mixer on the inside and a cooling medium such as high-pressure gas or cold water running outside the heat exchanger.

On the other hand, if the melt temperature is too low, the expansion of foam may not be fostered. The high stiffness of melt at a low melt temperature will retard the cell growth rate in the beginning and too quick crystallization of melt will stop cell growth during foam processing. As a result, the final expansion ratio may not be enough. Therefore, in order to maximize the volume expansion ratio of PP foams, the stiffness of the polymer melt and the timing of crystallization should be properly controlled by choosing an appropriate temperature of the polymer melt flowing in the die. In the other words, proper selection of the melt temperature is extremely important in controlling the volume expansion of extruded foams [89].

2.6 Characterization of final foams

In order to investigate the effect of processing conditions such as gas saturation time and foaming temperature in the solid-state batch foaming process or the influences of die geometry, pressure drop rate, die/pressure at the exiting die on the foam characteristics, the final foam will be performed as the measurement of density and the evaluation of cellular morphology using the photographs. The last investigation can elucidate the cellular structure such as void fraction, average cell size, and cell density, etc. The information of the investigations is described as the following;

1) Relative density determination

The relative density of the final foams is determined according to water displacement method (ASTM D-792) [90]. The mass of the sample in air (m_{air}) and distilled water (m_{water}) are measured with an analytical balance with an accuracy of 0.1 mg. The density of the samples (ρ_f) is calculated as [91];

$$\rho_f = \frac{m_{air}}{m_{water}} \times \rho_{water} \tag{2.34}$$

The ratio of the bulk density of foamed sample (ρ_f) and un-foamed sample and un-foamed sample (ρ) can depict the void fraction (V_f) as this equation [90].

$$V_f = 1 - \frac{\rho_f}{\rho} \tag{2.35}$$

2) Cellar morphology investigation

The samples, foamed or not, are fractured in liquid nitrogen, coated with an approximately 10 nm thick layer of gold on the fractured surface and observed with scanning electron microscopy (SEM; JEOL JSM-5910 LV) micrographs. The cell structure parameters, such as cell diameters and cell density are characterization using the method suggested by Matuana et al [90]. The cell density (N_0) of final foams is calculated through the counted cell number (*n*; number of bubbles) in the defined area of the SEM image (A_i) at the studied magnification factor of the image (*M*). Therefore, the cell density can be determined by using this equation [90].

$$N_0 = \left[\frac{nM^2}{A_i}\right]^{3/2} \times \left[\frac{1}{1-V_f}\right] \tag{2.36}$$

Moreover, cell density can be calculated as the method of Naguib *et al.* [15] described as following;

$$N_0 = \left[\frac{n}{L^2}\right]^{3/2} \times 10^{12} \times v_a \tag{2.37}$$

Where L^2 (or $L \times L$) is a defined area and v_a is the expansion ratio of each sample which calculated as the ratio of bulk density of un-foamed sample to bulk density of foamed sample as shown in Equation 2.38 [15]. This equation is used for determined the cell density in the case of low-density PP foams as described in chapter 4.

$$v_a = \frac{\rho}{\rho_f} \tag{2.38}$$

As the calculated values from Equation 2.35 and 2.36, the average cell size can be determined as Equation 2.39 [90].

$$d = \sqrt[3]{\frac{6V_f}{\pi N_o (1-V_f)}} \tag{2.39}$$