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DEVELOPMENT OF MICROCELLULAR PVC FOAM PRODUCTION

Mr. Chrisda Perin

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By	Mr. Chrisda Perin
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tawatchai Charinpanitkul, D.Eng
Thesis Co-Advisor	Surat Areerat, D.Eng

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfilment of the Requirements for the Master's Degree

…………………………………….Dean of the Faculty of Engineering

(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

………………………………………….. Chairman

(Professor Wiwut Tanthapanichakoon, Ph.D.)

………………………………………….. Thesis Advisor

(Associate Professor Tawatchai Charinpanitkul, D.Eng)

…………………………………………… Thesis Co-Advisor

(Surat Areerat, D.Eng)

…………………………………………… Member

(Associate Professor Siriporn Damrongsakkul, Ph.D.)

…………………………………………… Member

(Nattaporn Tonanon, M.Sc.)

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ในงานวิจัยนี้ได้ศึกษาวิธีการเตรียมโฟมพีวีซีแบบไมโครเซลลูลาร์โดยวิธีการทดลองแบบต่อเนื่องเพื่อลดการนำเข้าโฟมพีวีซีจากต่างประเทศโดยใช้สารฟูเชิงเคมีและสารเติมแต่งอื่นๆ ในการผสมกับเรซินพีวีซีโดยการใช้เครื่องมืออัดรีดแบบเกลียวหนอนคู่ เพื่อศึกษาผลของอุณหภูมิของหัวดายที่มีผลต่อความหนาแน่นของโฟมและสัดส่วนต่อร้อยส่วนของเรซินซึ่งใช้สารอโซไดคาร์โบนาไมด์ใช้เป็นสารฟู โดยสารอโซไดคาร์โบนาไมด์จะสลายตัวที่หัวดายในช่วงอุณหภูมิ 160 ถึง 190 องศาเซลเซียส และนอกจากสารอโซไดคาร์โบนาไมด์แล้วยังมีนาโนแคลเซียมคาร์บอเนตที่มีขนาดเฉลี่ย 60 นาโนเมตร โซเดียมไบคาร์บอนเนต และไดไอโซโนนิลพทาเลท เพื่อช่วยในการก่อตัวของฟอง จากการทดลองพบว่าเมื่อเติมอโซไดคาร์โบนาไมด์ ในปริมาณ 0 ถึง 10 สัดส่วนต่อร้อยส่วนของเรซิน จะส่งผลให้ความหนาแน่นลดลงจาก 1.25 กรัมต่อลูกบาศก์เซนติเมตรไปเป็น 0.41 กรัมต่อลูกบาศก์เซนติเมตร แต่โซเดียมไบคาร์บอนเนตใช้ไม่ได้ผลกับการทดลองเนื่องด้วยสมบัติการละลายในพีวีซีไม่ดี และการเติมไดไอโซโนนิลพทาเลทจะทำให้สมบัติเชิงกลของโฟมพีวีซีลดต่ำลง และเมื่อทดสอบสมบัติเชิงกลพบว่าค่าการรับแรงดึงมีค่าค่อนข้างน้อย เนื่องจากการเตรียมโฟมพีวีซีที่มีความหนาแน่นต่ำไม่สามารถควบคุมรูพรุนให้สม่ำเสมอและให้มีลักษณะเป็นเซลล์ปิดได้

ภาควิชา..........วิศวกรรมเคมี......... ลายมือชื่อนิสิต...

สาขาวิชา.........วิศวกรรมเคมี........ ลายมือชื่ออาจารย์ที่ปรึกษา..

ปีการศึกษา..........2547............... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..

##4570209021: MAJOR CHEMICAL ENGINEERING
KEY WORD: MICROCELLULAR/ PVC FOAM/ CONTINUOUS PROCESS

CHRISDA PERIN: DEVELOPMENT OF MICROCELLULAR PVC FOAM PRODUCTION. THESIS ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.ENG. CO-ADVIOR: SURAT AREERAT, D.ENG, 68 pp. ISBN 974-53-1100-6.

This research focuses on investigating methods for preparing microcellular PVC foam with an ultimate aim of reducing its import dependence. The so-called microcellular PVC foam was prepared from PVC resin compounded with azodicarbonamide as a chemical blowing agent and other chemical additives.

In the continuous foaming process using a twin screw extruder, azodicarbonamide is thermally decomposed at die temperature varied in a range of 160 to 190 °C, resulting in generation of microbubbles dispersing in the melting polymer. Chemical additives which are nano-calcium carbonate with nominal diameter of 60 nm and diisononylpthalate (DINP) are added into PVC for enhancing the formation of microcellular pores. The prepared PVC foam density drastically decreased from 1.25 to 0.41 g/cc when azodicarbonamide content was varied from 0 to 10 phr. Meanwhile, it is found that sodium bicarbonate is not effective to help decrease foam density due to its lower solubility in PVC. Addition of DINP into the compounded PVC foam leads to a decrease in its tensile strength. For the prepared PVC with relatively low density, its tensile strength becomes worse because uniform and closed-cell structure is hardly achieved.

Department…..Chemical Engineering..Student’s signature……………………………
Field of study...Chemical Engineering.Advisor’s signature……………………………
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CONTENTS

Page

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF FIGURES

NOMENCLATURES

Alphabetical symbols

A	is area of the micrograph	[cm^2]
c	The concentration of gas in the polymer	[mol/m^3]
D	Diffusion coefficient	[cm^2/s]
d	Average cell size	[cm]
G	The gas-filling (porosity) of the foam	[-]
K_h	Henry's law constant	[mol/(m^{3}Pa)]
M	Magnification factor for micrograph	[-]
m	the ratio of sample weight	[-]
N_0	Cell density	[cells/cm^3]
n	Number of bubbles in the SEM micrograph	[cells]
P_g	Pressure in the bubble	[Pa]
P_{g0}	The inertial pressure in the bubble	[Pa]
P_l	The pressure of polymer melt	[Pa]
R	Radius of bubble	[m]
$\dot{R}$	Rate of expansion	[ms^{-1}]
R_g	Boltzmann constant	[J.mol^{-1}K^{-1}]
t	Time	[s]
V_f	Void fraction	[%]
x	Degree of gas saturation in the polymer melt	[-]

Greek symbols

τ_{rr}	Shear stress	[N/m^2]
η	The viscosity	[Pa.s]
ρ_f	Foamed density	[g/cm^3]
ρ_g	The gas density in the cell	[g/cm^3]
ρ_p	The true density of the polymer phase	[g/cm^3]
ρ	Unfoamed density	[g/cm^3]

CHAPTER I

INTRODUCTION

Polymeric foams industries have been growing because cellular materials offer unique advantages over traditional materials and non-cellular (solid polymers). Polymeric foams have unique insulating properties, impact-resistant characteristics, buoyancy, and outstanding strength-to-weight ratios, among other attributes. Polymeric foams encompass a variety of materials, with densities ranging from 1.6 kg/m^3 to 960 kg/m^3. Foams are directly classified as flexible, semirigid, and rigid. They can be manufactured by the variety of process, depending upon application.

Polyvinylchloride (PVC) foams have been important economical impact on nearly every aspect of life today. PVC foams can be made with or without plasticizers, so they are product between rigid and flexible product. PVC foams provided many advantages over solid PVC product because of their lower density. PVC foams are the following advantages: low volume costs, good insulating properties, good strength properties, chemical stability, and stability at low temperatures, good fire retardant, good sound absorption capability, and weather resistance. Corresponding to all these advantages, it has wide array of applications. Low-density polyvinyl foam is used in insulation, transportation, sport equipment, housing, wind turbine, blade, rigid packaging, and building products. High-density PVC foam is used as plumbing pipes, door panels, cable channels, wall treatment, air-filtration system, sport shoe inserts, and furniture as wood-fiber composite.

Thailand has imported PVC foam for producing in various sport equipments, but there are many companies that can produce PVC foam. However, they do not produce low density PVC foam (lower than 200 kg/m^3) for use in our country. So, if Thailand could produce low density PVC foam by using its current technology, it can reduce the import of low density PVC foam. Therefore, this research has focused on the development of foaming process technology for the ultimate goal of import reduction.

The foaming process could be classified into two schemes, which are batch foaming and continuous foaming. The continuous foaming has processed within extruder and batch process has processed by high pressure reactor. Microcellular polymers were first produced in bath process, because batch process has been taken into account, it is easy to precisely control its operating parameters. Carbon dioxide is used for blowing agent because it has non-toxic, non-flammable and free of ozone depletion. Carbon dioxide is injected in chamber under the condition of “supercritical fluid”, which exists beyond 7.37 MPa and 31.1 °C. In such condition carbon dioxide has much higher dissolubility in the polymer matrix. In batch process, polymer is put in the high pressure chamber (see Figure 1.1). Polymer absorbs by a gas with sufficient time, get to a saturation state. When the pressure is rapidly decreased to the point lower than the critical point, dissolved carbon dioxide will change to the normal state of which solubility is suddenly dropped, and resulting in the formation of fine bubbles in the molten polymer matrix. This initial state involves with the thermodynamic instability, which activate the nucleation of billion of micro cells. Supercritical technique enhances to produce foam having uniform bubbles size, micro bubbles size and high bubbles density.

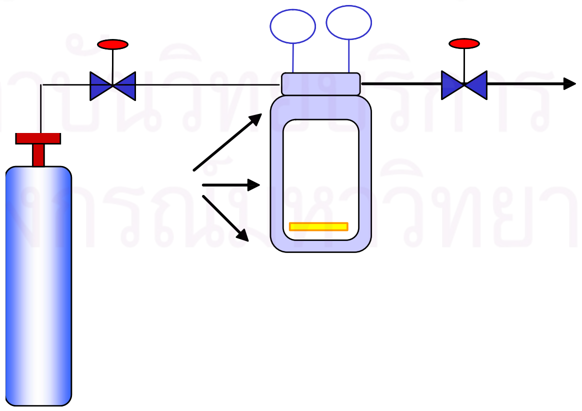


Figure 1.1 Schematic of batch foaming process using high pressure chamber as reactor

In addition, chemical blowing agents have been longer used in the manufacturing process, and they have their history based in bakery products. Chemical blowing agents have lower pressure process than physical blowing agents, and the machineries using in the manufacturing process have the cost is lower than the physical foaming process. Endothermic chemical blowing agents were originally used for polystyrene foam product. Chemical blowing agents also are liquid or solid substance within thermal decomposition; they generate vapors which behave like physical blowing agents. Chemical blowing agents could generate several gases as carbon dioxide and nitrogen. Carbon dioxide give more soluble in plastic, lower vapor pressure than nitrogen, carbon dioxide give finer cells, lower density, better surface apparent, and shorter cycle time than chemical blowing agents that generate nitrogen (2). Thus, chemical blowing agents is once of the choice for this study.

Furthermore, the continuous process (see Figure 1.2) also gives shorter cycle time, shorter saturation time, and lower cost-effective than batch foaming process, and the continuous process was developed based on the same concept of thermodynamic instability (physical blowing agent) as in the batch process. The extruder has been used for both thermal activate foaming (chemical blowing agents) and gas dissolution foaming (physical blowing agents), the extruder has been known not only as, essentially effective in mechanical power, but also as converting thermal energy into processing heat for polymer phase change (2).

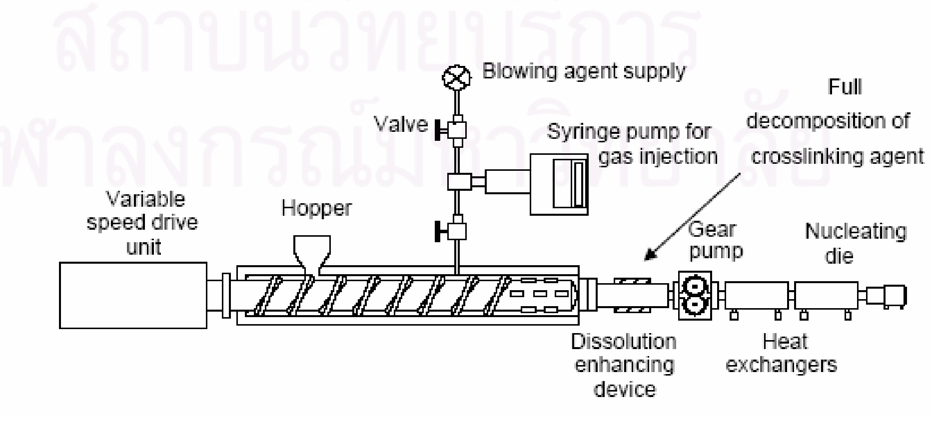


Figure 1.2 Schematic of continuous foaming process using extruder

Finally, the injection mould, (see Figure 1.3) that can be used to produce rigid or plasticized foamed PVC products. Addition of chemical blowing agents such as azodicarbonamide is used for injection molded PVC for increasing impact resistant. If the products are rigid, the type of PVC most often uses a molecular weight of 50,000 to 52,000. Generally, the convey zone of screw has lower the temperature than the decomposition temperature of blowing agents because gas can escape to hopper. The controlling bubble size depends upon pressure in the mould, when higher pressure could be effectively activated fine bubbles size. The basic step of bubble formation and bubble growth is similar to the batch foaming.

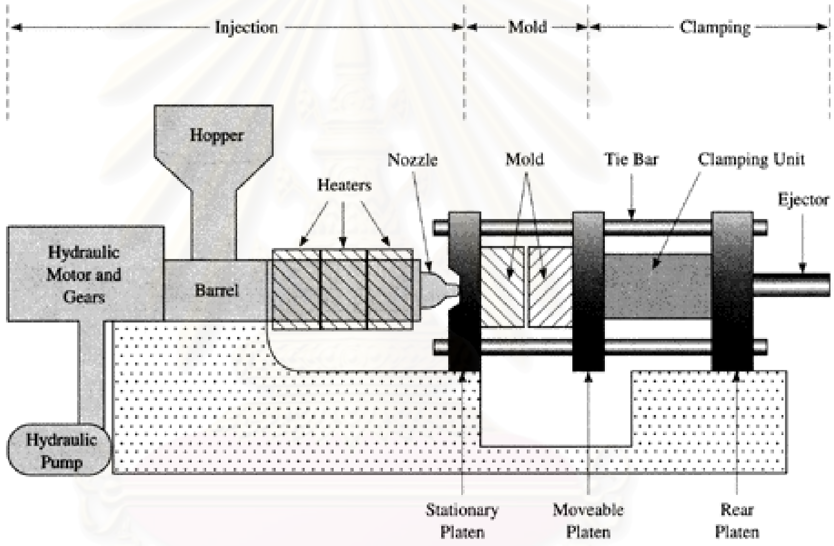


Figure 1.3 Schematic of injection foaming process

Based on the above concept, microcellular foaming process generally consists of three steps. Firstly, bubbles nucleation or the bubbles formation, secondly, bubbles growth, and finally, stabilization of the cellular structure. Characteristic cell morphologies are on the order in the range from 0.1 to 10 micron and bubble density having in the range from 10^9 to 10^{15} cells/cm^3. Characteristics of foams are monitored with scanning electron microscope (SEM) micrographs to estimate an average bubble size and distributed bubbles.

Objectives

To investigate effect of azodicarbonamide, sodium bicarbonate, DINP, screw speed and exit die temperature on the density of PVC foam, cell morphology and mechanical properties.

Scopes

1. Azodicarbonamide in the range from 1 to 10 phr
2. Sodium bicarbonate in the range from 12 to 18 phr
3. DINP in the range from 10 to 30 phr
4. Screw speed in the range from 96 to 192 rpm
5. Exit die temperature in the range from 160 to 190 °C

CHAPTER II

LITERLATURE REVIEW

There are researchable reviews concerning with physical and chemical foaming processes, which have the difference of pressure conditions. A number of the articles of PVC foams have very few. Thus, we will select suitable and useful articles as show:

F. Liu, G. Liu, and Park (14), they have studied controlling melt strength of PP foams using a rotational foam mould. The chemical blowing agent uses an activator such as zinc oxide and/or reducing the decomposition temperature. There are many parameters in this study; which consist of temperature, time, and zinc oxide. Zinc oxide is activator, which also helps lowing decomposition temperature of azodicarbonamide (AZ). For experiments, the cell morphologies are a function of the chemical blowing agent amount, 0.625% AZ together with 0.625% ZnO to yield the best results for threefold expansion, as theoretically predicted.

In the research of Park and Suh (11), they have studied a pressure drop on the nozzle having the diameter of 0.46 millimeter. For designing the nozzle, the viscous and shear are measured for calculating effective size and length of nozzles. The extruder in this study has length per diameter: 25/1 by using nitrogen and carbon dioxide gas under supercritical conditions to mix into high impact polystyrene (HIPS) in the barrel. A static mixer having diameter of 6.8 millimeter is used mixing polymer(HIPS)/fluid, and then polymer/fluid have become homogeneous solution, finally, polymer/fluid solution move through the nozzle suddenly decrease the pressure .

The processing pressure is 5.4 MPa, 10.6 MPa, 18.6 MPa, and 28.3 MPa, that they are used in this study, the resulting processing pressure of 283 bars is effective processing pressure for enhancing cells density of $6x10^9$ cells/cm^3. But processing pressure is 5.4 MPa that cells density is $7x10^5$ cells/cm^3, and cell size in the range from 100 to 200 micron. A larger cell density is expected when the processing pressure is higher.

Abu and Zara (12) have studied a neural network for controlling foam density in a single screw extruder having L/D ratio of 16. Azodicarbonamide is used as blowing agents in this study. The parameters that consist of 3rd barrel zone, temperature of clamp, die temperature, and screw speed. The results of simulation are foam density of simulation approach with foam density of experiment, and the important parameters are screw speed, die temperature, and final barrel zone. If vary this parameters, and foam density will be also known.

Guo and Peng (13) have studied the theory of shear nucleation for explanting a cell structure, but the classical nucleation theory based on the thermodynamic equilibrium process having limitation which can not explain cell structure on the surface. Thus, this research studies the effect of shear on bubble nucleation. Single screw extruder having L/D ratio of 22 is used to blend the nano-$CaCO_3$ (mean diameter 70 nm) with LDPE melt. From experiments, it is not only screw speed but also shear stress disperses a nucleating agent, which is very important for heterogeneous microcellular foaming. We can find that shear effects really have important influence upon bubble nucleation and the calculation results show that it is also a main driving force for bubble nucleation other than the conventional super saturation conditions.

Xu have investigated the effect of varying the geometry of the die on the cell nucleation behavior of extruded PS foams blown with CO_2 (5). Three interchangeable groups of carefully calibrated filamentary dies have been used in the experimental study. The dies were deliberately designed to have either different pressure drop rates while having identical die pressures and flow rates, or different die pressures while having identical pressure drop rates and flow rates. The experimental results revealed that the geometry of the die governs the cell density of extruded PS foams, especially because of its significant effect on the pressure drop rate across the die. However, the effect of the die back pressure on the cell density was found to be marginal, whereas its effect on the cell morphology was found to be predominant. In addition, regardless of die geometry, the CO_2 content proved to be a very sensitive parameter with respect to the cell nucleation behavior of extruded PS foams. On the other hand, the cell density was slightly improved by an increase of the talc content, especially at reduced concentrations of CO_2.

CHAPTER III

THEORY

In the present, there are two methods in industry; chemical blowing agent and physical blowing agent, chemical blowing agent use a chemical additive which can release gas by thermally decomposing, while physical blowing agent use inert gas blowing agent, both chemical blowing agent and physical blowing agent are absolutely different method, chemical blowing agent occur at low pressure or atmospheric pressure, physical blowing agent occur at high pressure. The both processes in producing foamed polymers involve dispersion of gas into a liquid polymer phase, bubbles growth, stabilization of the cellular structure.

The bubble formation has essentially the principle as diffusing the molecule of gas into the polymer, the gas pressure having enough overcoming the polymer pressure for bubble growth, and bubble is not visually observed. While, the thermodynamic instability promotes the cluster of gas bubbles occurring in sort time-scale, the method activate nucleation by increasing the temperature or decreasing the pressure. Thermoplastic having lower conduction is decomposed within higher temperature, thus decreasing pressure is favourite method for the manufacturing process.

The bubble formation is phenomena occurring in homogeneous and heterogeneous phase as physical and chemical phenomena. In general basic step for foam mechanism concern with three steps as: 1. bubble nucleation, 2. bubble growth, and 3. stabilization.

3. 1 Fundamental Principles of Foam Formation

3.1.1 Bubble Nucleation

The bubbles formation in liquid system or polymer melt is the first step for creating the cellular structure. In single phase, the bubbles were formed in the homogeneous liquid process is called self-nucleation (1). In two phases, the bubbles usually form more easily at the liquid-solid interface or heterogeneous phase that the bubbles is called nucleation process, and the solid particles are called nucleating agents such as calcium carbonate, talc, etc. If without solid nucleating agents the liquid phase has actually many microbubbles of air with, and they promote as sites for bubble growth, with the formation of new bubbles not being necessary. The solid particle in the interface is nucleating agents which promote many micro-cells.

The bubbles formation in the liquid system require an increasing in the Gibb free energy of the system[1], ΔG (Equation 1)

$$\Delta G = \sigma A \tag{1}$$

where σ is the surface tension of the liquid and A is the total interface area. Therefore, lowering the surface tension is easy to form the bubbles in the liquid. There are many agents having the surface tension lower than many fluids such the agents as emulsifiers, wetting agents, silicone oil for formation the bubbles. Nucleating agents may be effective to reduce the surface tension at the interface between the liquid and the solid particle.

Figure 3.1 shows the nucleation of sulfur solutions to be applied to nucleation of foam system by La Mer. First let’s assume a fluid system containing a suitable gas for foaming, with no micro-bubbles of air or nucleating agents. The key factors are used explaining easily understanding for bubble nucleation and bubble growth. In zone I, the concentration of gas in solution rise until it exceeds the equilibrium saturation line concentration, *S*, (becomes the supersaturation) and, with more generation occurring, reach the concentration where self-nucleation begins (region RSN). The gas concentration is kept in the critical region (Zone II), self-nucleation will occur. When bubbles have been created to the gas concentration in solution below the level where self-nucleation occurs, gas will diffuse into the cells while no more bubbles will be created, causing them to growth in size (Zone III, region GRB). Bubble growth will continue until the gas concentration in solution has been reduced to the saturation level. *S*.

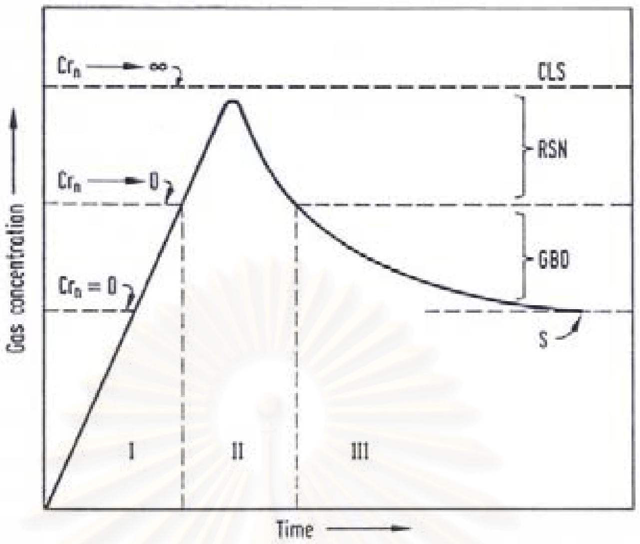


Figure 3.1 Relation between changes in the gas concentration in solution and bubble nucleation and growth (1)

Cr_n = Nucleation rate
CLS = Critical limiting supersaturation
RS = Rapid self-nucleation
Partial relief of supersaturation
GBD = Growth by diffusion
S = Saturation

In the nucleation classical theory for homogeneous nucleation, the nucleation rate is covered by the rate at which invisible gas clusters are energized by effective diffusion. According to Gibbs, a gas cluster containing n molecules can be expressed as following:

$$C(n) = N\exp(-\frac{G(n)}{kT}) \tag{2}$$

where $G(n)$ is the minimum Gibbs free energy to sustain a bubble, N is he number of molecules per unit volume of the metastable state, and k and T are the Boltzmann constant and absolute temperature.

Thus, nucleation rate equal Equation 2, rate of nucleation is Equation 1 to be multiplied by B (Frequency factor)

$$J = BN\exp(-\frac{G(n)}{kT}) \tag{3}$$

In the metastable region, the total Gibbs free energy includes surface area generation, size expansion, and evaporation,

$$G = \sigma A - (P_g - P_l)V_b + n(\mu_g - \mu_l) \tag{4}$$

where the equilibrium, both chemical potential of gas phase and liquid phased are equal, $\mu_g = \mu_l$

$$G = 4\pi r^2\sigma - \frac{4}{3}\pi r^3(P_g - P_l) \tag{5}$$

P_g is the pressure in bubble; P_l is the pressure of polymer melt

Form Equation 5 ΔG (Gibbs free energy), calculating Equation 5 as in Figure 3.2

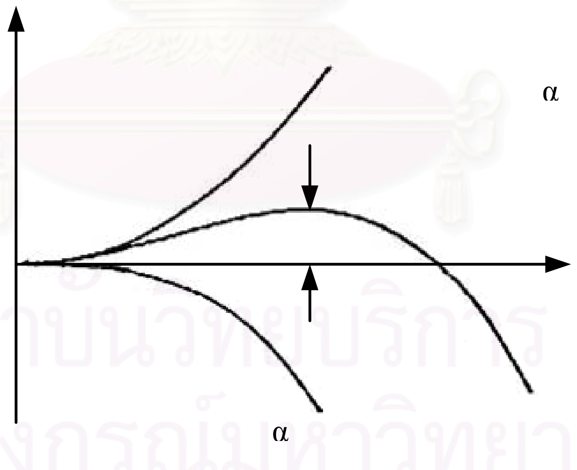


Figure 3.2 Gibbs free energy and cell radius

where the supercritical state $\frac{\partial W}{\partial r} = 0$, thus bubble is formed to be Equation 6

$$R_{bc} = \frac{2\sigma}{(P_g - P_l)} \tag{6}$$

Substitute Equation 6 into Equation 5 interfacial energy, if ΔG (see Figure 3.2) has positive, and then gas will dissolve into the solution, Gibbs free energy have negative system will be stable, while bubble radius have smaller than critical bubble radius will dissolve into the solution.

Minimum Gibbs free energy for overcoming the surface tension or the surface free energy, Equation 6

$$G_{\min} = \frac{16\pi\sigma^3}{3(P_g - P_l)^2} \tag{7}$$

Substitute Equation 7 into Equation 3 as in Equation 8, for nucleation of a dissolved gas on a polymer surface, the steady state nucleation rate can be expressed as

$$J = N\sqrt{\frac{2\sigma}{\pi m}}\exp(-\frac{16\pi\sigma^3}{3kT(P_g - P_l)^2}) \tag{8}$$

where J has units of nucleation per unit area per unit time, N is the number of gas molecules per unit volume, k is Boltmann constant, T is absolute temperature, σ is the surface tension at the bubble interface

3.1.2 Bubble Growth

The bubble growth is formed by diffusion of gas from solution in the liquid phase in to the bubble. Equation 1 leads to the conclusion that, for a given foam volume, the system will be stable with fewer larger bubbles than with smaller bubbles. This factor usually occur the combination or coalescence of bubbles. At the equilibrium gas pressure in a spherical bubble is larger than the pressure in the surrounding fluid, as given by Equation 6,

$$R = \frac{2\sigma}{\Delta P} \tag{6}$$

It also follows that the gas pressure in the small bubble is greater than that in the large bubble, with the difference as in Equation 9,

$$\Delta P_1^2 = 2\sigma(\frac{1}{r_1} - \frac{1}{r_2}) \tag{9}$$

where ΔP_1^2 is the difference in pressure between the two bubbles having radius of r_1 and r_2. Therefore gas will tend to diffuse from the smaller bubble into the larger one.

Simplified model was used in this study, which treats the growth and collapse of a single bubble in an infinite polymer melt (see Figure 3.3).

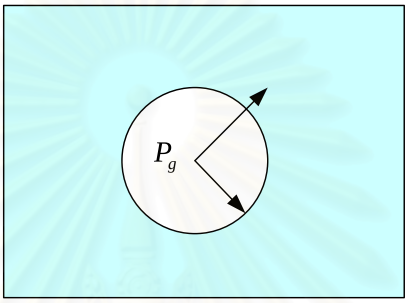


Figure 3.3 Geometry of a single spherical bubble surrounded by an infinite fluid

Bubble growth mechanism is described using the equation of motion, mass balance over the bubble, and gas diffusion in the surrounding polymer phase:

The force balance equation over polymer-gas interface is as following:

$$\tau_{rr} = 4\eta \frac{\dot{R}}{R} = P_g - P_l - \frac{2\sigma}{R} \tag{10}$$

Mass Conservation Equation

Assuming that buildup of absorbed gas on the bubble wall is negligible, the rate of change of the amount of gas within the bubble can be equalized with the rate of diffusion of gas from/into the bubble across its wall towards/from the liquid. Hence, by assuming that the gas inside the bubble is ideal, i.e., $P_g V = nR_g T$, the mass conservation can be obtained:

$$\frac{4\pi}{3}\frac{d}{dt}\left(\frac{P_g}{R_g T}R^3\right) = 4\pi R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R} \tag{11}$$

Rearranging the above equation,

$$P_g^{\cdot} = \frac{3R_g DT\pi}{R}\frac{\partial c}{\partial r}\bigg|_{r=R} - \frac{3P_g}{R}R^{\cdot} \tag{12}$$

Diffusion Equation

To solve Equation 12, the concentration profile is the liquid has to be known. This can be determined by solving the complete diffusion equation for the liquid surrounding the bubble, which for the sphere coordinates reduces to the following relationship:

$$\frac{\partial c}{\partial t} + \frac{\dot{R}R^2}{r^2}\frac{\partial c}{\partial r} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \tag{13}$$

Equation 13 can be solved subject to the boundary and initial conditions below:

$$c(r,0) = c_i, r > R$$

$$c(\infty,t) = c_i, t > 0$$

$$c(R,t) = c_w = K_h P_g$$

The concentration of gas dissolved initially in the polymer melt can be assumed:

$$c_i = x(c_i)_{sat} = xK_h P_l$$

Nomenclatures

c	is the concentration of gas in the polymer	[mol/m^3]
D	is the diffusion coefficient	[cm^2/s]
K_h	is the Henry’s law constant	[mol/(m^{3}Pa)]
P_g	is the pressure in the bubble	[Pa]
P_{g0}	is the inertial pressure in the bubble	[Pa]
P_l	is the pressure of polymer melt	[Pa]
R	is radius of bubble	[m]
$R^{\cdot}$	is rate of expansion	[ms^{-1}]
R_g	is boltzmann constant	[J.mol^{-1}K^{-1}]
t	is time	[s]
x	is degree of gas saturation in the polymer melt	[-]

τ_{rr}	is shear stress	$[N/m^2]$
η	is the viscosity	[Pa.s]

3.1.3 Bubble Stabilization

As the cell wall instability is the main cause for bubble coalescence to happen, the bubble stabilization strategy should be related to the stability of the cell wall and the drainage of the material from the wall that make the separation of the bubbles. To remedy the undesired outcome by suppressing bubble coalescence, it would be desirable to increase the stability of the cell wall. The stability of the cell wall depends upon the polymer melt strength. The polymer melt strength is generally defined as the degree of resistance to the extensional flow of the cell wall during the act of polymer drainage occurring in the cell wall at the time of volume expansion (6). It would be, therefore, desirable to increase the melt strength of the polymer to increase the cell wall degree of resistance to extensional flow, which will increase the cell wall stability. In such a way, the increased cell wall stability will definitely have a suppressive effect on the bubble coalescence. Increasing the viscosity of the molten polymer would increase its melt strength and thereby reduce the drainage effect. The increase of the viscosity may be caused by a temperature reduction, i.e., by keeping the processing temperature as low as possible.

3.1.4 Cell Coalescence

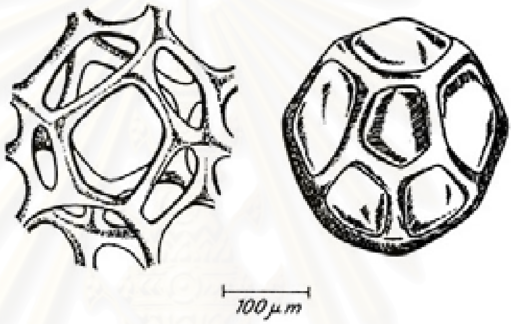
With the continuation of bubble growth, the void fraction increases and thereby the chances for bubbles meeting each other increase as well. Consequently, closely located bubbles come into contact and therefore begin to share a common wall. Because of further bubble growth and the resulting polymer drainage in the bubble wall, the bubble wall thickness decreases, as a result of which it becomes highly stretched and very unstable and therefore prone to rupture. Such cell wall instability causes the common wall between two neighboring cells to rupture and thereby they become transformed into one bigger bubble (6). This transformation is referred to as bubble coalescence. Because of bubble coalescence, the final bubble-population density of the foam decreases. As fine-celled foams are always preferred because of their better mechanical and thermal properties, the deteriorating effect of bubble coalescence on the bubble population density is an undesired outcome of the bubble growth step in polymer foaming and therefore remedial measures have to be undertaken. On the other hand, thermodynamically, the bubble tendency to coalesce can be explained by the tendency of the overall system to lower the total free energy. In polymer foaming, such a tendency is accomplished by reducing the total surface area of two smaller bubbles.

3.1.5 Bubble Coarsening

Undesirably, bubble coalescence is not just bubble density deterioration mechanism occurring in the foaming polymer (6). A distinct bubble density deterioration occurrence takes place when two neighboring bubbles, with different bubble sizes, start to interact driven by the pressure difference between them, which is caused by their size difference. Because of this pressure difference, the gas contained in the smaller bubble diffuses to the larger bubble. This causes a simultaneous tendency for a gradual size change in both bubbles. The smaller bubble manifests such a tendency by a size decrease, i.e., over time it gets smaller and smaller, and eventually collapses, while, in contrast, the larger bubble gets bigger and bigger over the same period. Finally, the former two neighboring differently sized bubbles become a single large bubble. This transformation is referred to as bubble coarsening. Similar to bubble coalescence, bubble coarsening deteriorates the bubble population density. It is, therefore, considered an undesired outcome of the bubble growth stage in polymer foaming, suppression of which requires remedial action. Two principal strategies are commonly used for successful bubble coarsening suppression. The first is based on nucleation of the cells almost simultaneously in order to induce bubble growth uniformity, whilst the second is based on reduction of the processing time as much as possible.

3.2 Open-and Closed-Cell Foamed Polymer

For the morphology and the properties of foamed polymer which is relational to be showed and evaluated qualitatively, the micro structural parameters must be determined. These parameters contain the relative number of open and closed cells, the apparent density, the cell size, the shape, the wall thickness, the distribution of the cells according to size and shape in a given volume, and the specific surface area of the foamed plastic material (1).



(a) **(b)**

Figure 3.4 (a) open gas structure element; (b) closed gas structure element

The shape of cell may be closed-cell (b) or open-cell (a) as in Figure 3.4. Closed-cell is pore and neighbour pore be not interconnecting, its application for thermal insulation, and generally they have more high strength than open-cell. While open-cell must have at least two pores or broken faces, connecting between cell and neighbour cell, and gas or vapour can flow between pore to neighbour pore, when open-cell compares with closed-cell foamed polymer, open-cell have a higher absorptive capacity for water and moisture, a higher puerility to gas and vapour, less effective insulation capabilities for eight heat or electricity, and a better ability to absorb and damp sound (1). The structure of cell depends on the process conditions and nucleating agent for enhancing bubbles density.

3.3 Foam classification

Foamed polymer is classified using the density with a very range of densities, from 3 to 900 kg/m^3 as summarized in Table 3.1. In general, the mechanical properties directly depend on the density with assuming same cellular structure, that most of the physical characteristics of foams are directly related to the density.

Table 3.1 Classification of density of foamed polymer (1)

Type	Density (kg/m^3)
very light	3 - 50
light	50 - 200
medium	200 - 500
heavy	500 - 700
super heavy	≥ 700

Normally, the density is determined by the true densities of the polymer phase and the gas phase. It is related to the gas filling of the foam as in Equation 14

$$\rho = \rho_p (1-G) + \rho_g \tag{14}$$

where ρ_p is the true density of the polymer phase, and is equal to the ratio of the total material mass to the difference between the total volume of the material and the cell volume; ρ_g is the gas density in the cell; and G is the gas-filling (porosity) of the foam, equal to the ratio of cell volume to the total material volume.

In practice, the density of plastic foams is calculated as the ratio of sample weight m to geometrical volume V_0

$$\rho = \frac{m}{V_0} \tag{15}$$

where the density is given in kg/m^3 or g/cm^3.

In addition, foams were classified in terms of their nominal dimension across the cell, BET surface areas, and number of cells per unit volume (4), as summarized in the Table 3.2

Table 3.2 Classification of type of foamed polymer

Foam Type	Cell Size	BET surface area [m^2/g]	cells/cm^3
Commercial foam	100 - 500	0.1 - 1	10^5
Crosslinked polyolefin foam	20 -100	10	10^6
Microcellular foam	1 -10	10 - 20	10^7 - 10^9
Ultramicrocellular foam	0.1	100 - 400	10^9 - 10^{12}

3.4 Cell size and number of cells

Generally, 1 cm^3 of an isotropic plastic foam contains 1,000 to 10,000 cells in the bulk of the material, with sizes distributed so that the deviation of the real size form the mean cell size is within the range of 12% to 25% (rarely up to 50%). Cells sizes and cells size distribution depend not only on the polymer grade but also on the process condition for foaming. The number of cells per unit volume of foam is an important and regularly used parameter, particularly in the estimating the effectiveness of the nucleating agent or the macrostructure homogeneity throughout the bulk of sample.

The cell density, N_0, is defined as the number of cells per cubic centimeter relative to the non-foamed material, and it is calculated by Equation 15 and 16 (7):

For the calculation of cell density with following equations:

$$V_f = 1 - \frac{\rho_F}{\rho_S} \tag{16}$$

$$N_0 = \left(\frac{V_f}{10^{-4} D_{mean}} \right) \tag{17}$$

where the symbols of equations; V_f is the void fraction, ρ_F is the density of foamed sample, ρ_S is the density of unfoamed sample, N_0 is the cell density per unit volume of the original unfoamed polymer, and D_{mean} is the mean cell size in mm.

3.5 Additives for PVC foams

3.5.1 Heat stabilizers

It is know that PVC is thermoplastic unstable at the high temperature. Thus, PVC is added additives for enhancing thermal stability, which is called heat stabilizers. Heat stabilizers of PVC are classified as primary or secondary stabilizers.

A primary stabilizer is a substance that employed as single stabilizer in PVC, three general classes of primary heat stabilizers are lead stabilizers, mixed metal stabilizers, and organatin stabilizers.

A secondary stabilizer is a substance that cannot be employed as the only stabilizer in a commercial PVC application. There are two principle classes of second stabilizers: epoxidized oils and metallic soaps.

For the basic thermal instability of PVC is the direct result of the dehydrohalogenation or unzippering effect of neighboring hydrogen and chlorine atoms in the PVC chain (8). A chemical reaction is essential for primary stabilizer and PVC resin, molecule of the primary stabilizers replace chlorine atom in PVC resin molecule with the a ligand that is thermal less easily thermally displaced. The primary reaction has important basic rules such as thermodynamics, kinetics, and mass transfer.

Figure 3.5 Mechanism of reaction between the primary stabilizer and PVC resin

3.5.2 Plasticisers

Plasticisers have mainly used with PVC and many thermoplastics. Plasticisers are low molecular which is compatible with rigid thermoplastic. It is used for making a compound more flexible, easier to process, and its properties affect flexibility and viscosity. Certain Plasticisers can also perform other functions, assistance in viscosity control, and dispersion of particulate additives such as fillers, pigments, and general lubricant of compound (9). Materials of plasticisers are: esters of phthalates, adipates, mellitates, and di-phthalate ester.

3.5.3 Blowing agents

It is classified as chemical blowing agents and physical blowing agents. Blowing gents are function for creating a cellular structure during processing, usually by formation of inert gas at the process temperature, used for foams and expand materials, and injection moulded structural foam. Most generally, a blowing agent is the substance that in the vapour phase. Physical blowing agents to be used for extrusion are substances that are injected into the process as liquids or gasses. Chemical blowing agents are substances that decompose to generate gasses during the process.

1) Physical blowing agents

In the past, CFCs are used in the manufacturing process, which are popular in spire of their cost. The most important reason is that the CFCs are not flammable, therefore easier to use and handle. In the other hand, CFCs are main cause of the ozone layer to become depleted in the Earth’s atmosphere, and they are banned in order to protect the environment. Furthermore, the inert gasses are alternative to use during the processes, inert gasses are main properties for the process such as non-flammable, easy to use and handle, low cost, non toxic, non-corrosion, and without ozone depletion. Carbon dioxide, nitrogen, and argon are widely used in the manufacturing processes.

Good solubility in the polymer melt is important, which is firstly considered for blowing agents. As the blowing agent dissolves into the melt, it will platicize the melt, lowering its viscosity. The melting temperature is reduced during dissolution of gas into polymer. Physical blowing agents usually occur at high pressure by depending on process condition, and therefore, supercritical state will enhance solubility of gas/polymer. Supercritical fluids have behaviour as gasses and liquids; gasses are good diffusion and liquids are good dissolution. For example, carbon dioxide is widely used as blowing agents for thermoplastic foam, and solvents for extraction, and the critical pressure and critical temperature for supercritical carbon dioxide are 7.5 MPa and 31.1 °C. Above both the critical temperature and critical pressure, carbon dioxide exists as a supercritical fluid (see Figure 3.6).

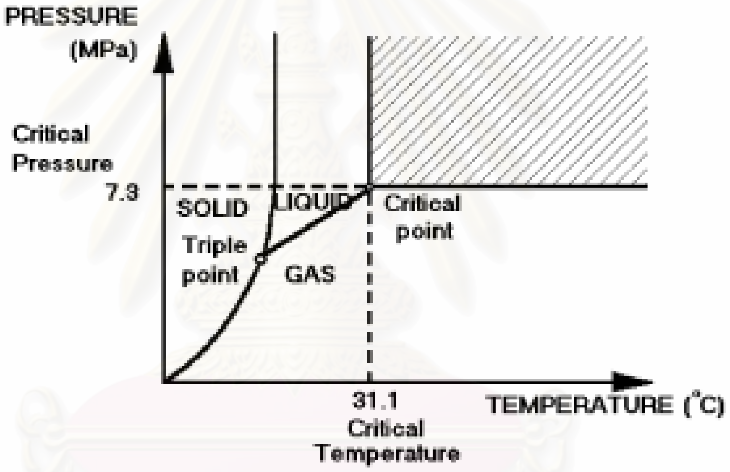
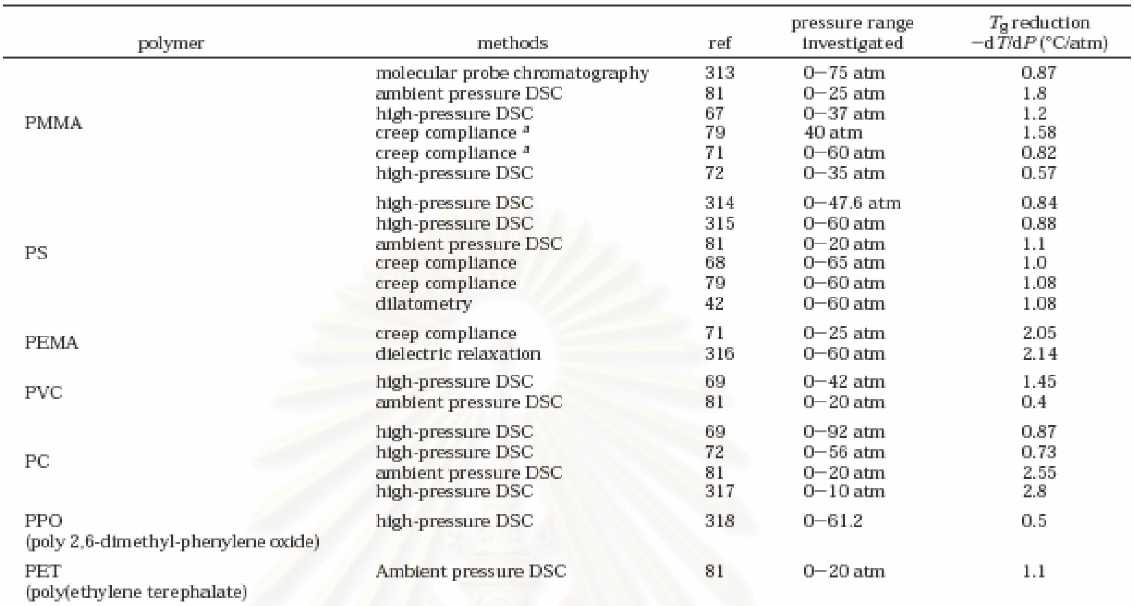


Figure 3.6 Region of the supercritical state in P–T diagram of carbon dioxide.

With under high pressure that have effect on polymer properties. For example, the properties change in continuous polymer processes for amorphous polymers is characterized by the glass transition temperature, T_g. This available experimental methods for measuring T_g depression of polymers under carbon dioxide and relate data are listed in Table 2, in pressure range from 0 to 65 atm (10). Therefore, the reduction of T_g is a thermodynamic effect due to intermolecular interactions between carbon dioxide and the polymer and not just a hydrostatic pressure effect. Reported in Table 3.3 are values of -dT/dP obtained from our analysis of the data in order to make comparisons. Stronger interactions between the polymer and carbon dioxide increase T_g depression.

Table 3.3 Summary of T_g depression of polymers under carbon dioxide



polymer	methods	ref	pressure range investigated	T_g reduction $-dT/dP$ (°C/atm)
PMMA	molecular probe chromatography	313	0–75 atm	0.87
	ambient pressure DSC	81	0–25 atm	1.8
	high-pressure DSC	67	0–37 atm	1.2
	creep compliance [a]	79	40 atm	1.58
	creep compliance [a]	71	0–60 atm	0.82
	high-pressure DSC	72	0–35 atm	0.57
PS	high-pressure DSC	314	0–47.6 atm	0.84
	high-pressure DSC	315	0–60 atm	0.88
	ambient pressure DSC	81	0–20 atm	1.1
	creep compliance	68	0–65 atm	1.0
	creep compliance	79	0–60 atm	1.08
	dilatometry	42	0–60 atm	1.08
PEMA	creep compliance	71	0–25 atm	2.05
	dielectric relaxation	316	0–60 atm	2.14
PVC	high-pressure DSC	69	0–42 atm	1.45
	ambient pressure DSC	81	0–20 atm	0.4
PC	high-pressure DSC	69	0–92 atm	0.87
	high-pressure DSC	72	0–56 atm	0.73
	ambient pressure DSC	81	0–20 atm	2.55
	high-pressure DSC	317	0–10 atm	2.8
PPO (poly 2,6-dimethyl-phenylene oxide)	high-pressure DSC	318	0–61.2	0.5
PET (poly(ethylene terephalate)	Ambient pressure DSC	81	0–20 atm	1.1

2) Chemical blowing agents

Chemical blowing agents have firstly used in explosive and bakery product. Chemical blowing agents are endothermic and exothermic, which are solid or liquid substances that can be decomposed under certain conditions to generate gasses. The gasses are that behave like a physical blowing agent in the foaming process. The most conditions occur on atmospheric pressure or low pressure. The gas yield, a measure of the volume of gas is generated by given mass. The gas yield effect on the process and product. Carbon dioxide is more solute in plastics and has lower vapour pressure than nitrogen, thus, it is normally easier to work with. Chemical blowing agents that generate carbon dioxide usually offer finer cells, lower densities, better surface appearance, and shorter cycle time than chemical blowing agents that generate nitrogen.

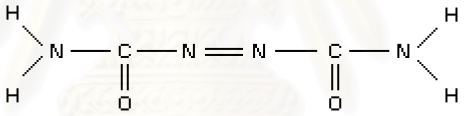
Exothermic chemical blowing agents generate thermal energy during their composition, but endothermic chemical blowing agents consume thermal energy during their composition. The fact is the chemical blowing agents decomposition reaction generate or consume heat normally very little, and effect on the temperature of the polymer melt or the product.

The main chemical blowing agents have a great effect on its foaming and processing behaviour. Contemplating the most regularly used chemical blowing agents, the endothermic chemical blowing agents generate carbon dioxide as the main foaming gas, and endothermic chemical blowing agents generate nitrogen as the main foaming gas. Some of common chemical blowing agents are:

Azodicarbonamide (AZ)

Azodicarbonamide decomposes in a temperature range of about 205 °C to 215 °C. There are many substances as an activator for lowing decomposition temperature range by up to about 40 °C. Common activators include zinc oxide, zinc stearate, urea, and many tin or zinc-containing PVC stabilizers. The reaction of azodicarbonamide can leave residual materials.

Chemical formula:



Gas composition:	65%	Nitrogen
	24%	Carbon monoxide
	5%	Carbon dioxide
	5%	Ammonia

The most importance criteria needed for a successful chemical blowing agents selection include decomposition temperature, rate of gas release, gaseous composition, ease of dispersion, storage stability, toxicity, and cost. Basically, considering well-suited properties of chemical blowing agents depend on foaming process, and the decomposition temperature has essentially higher than the melt temperature (T_m) of polymer. The success of actual selection of the chemical blowing agents will depend on desired and the commercially available chemical blowing agents chemical properties are. Table 3.4 lists commercially used chemical blowing agents.

Table 3.4 Generally used chemical blowing agents (2)

Common name	Chemical name	Endo or Exo	Decomposition temperature, °C	Gas yield cc/gm	Main foaming gas
Citric acid/ Sodium bicarbonate		Endo	160-210	120	CO_2
AZ	Azodicarboamide	Exo	205-212	220	N_2
OBSH	p,p’-Oxybis (benzene) sulfonyl hydrazide	Exo	158-160	125	N_2
TSH	p-Toluee sulfonyl hydrazide	Exo	110-120	115	N_2
TSS	p-Toluee sulfonyl semicarbazide	Exo	228-235	140	N_2
DNPT	Dinitrosopenta methylenetetramine	Exo	190	190	N_2
5PT	5-Phenyltetrazole	Exo	240-250	220	N_2
SBH	Sodium borohydride	Endo	*	2000	H_2

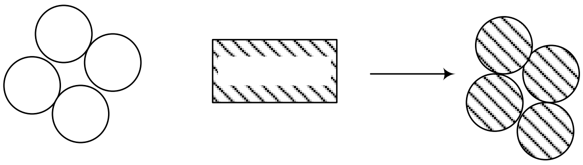
* SHB is chemically activated by exposure to water.

3.5.4 Filler

Nanoscale fillers have been an attractive approach for achieving good properties. Various naoscale fillers, including montmorillonite, silica, aluminium, and especially calcium carbonate, have been reported to enhance mechanical properties and thermal properties of polymers, such as toughness, stiffness and heat resistance. It is well known that surface modification of nanoscale fillers play an important role in the preparation of nanocomposites. Nanoscale fillers are usually organically modified in order to reduce the filler aggregation and enhance the interaction between the filler and polymer matrix, hence acquiring good dispersion of the filler in the polymer matrix. In addition, the properties of nanocomposites are greatly dependent on the filler's aspect ratio, surface area and interactions between the filler and polymer matrix. For example, layered silicates and fibers exhibit good reinforcing effects on many polymeric matrixes due to their large aspect ratio, but this kind of filler with a high aspect ratio does not obviously improve the toughness, and sometimes even decreases it. In contrast, spherical mineral nanoparticles are quite different. Their low aspect ratio but large surface area could result in a strong interfacial interaction between filler and polymer matrix. These particles were reported to be able to greatly increase strength, modulus, as well as toughness. Nano-$CaCO_3$ is one of the most common spherical nanoscale fillers used in preparation of nanocomposites. A study on polypropylene (PP)/nano-$CaCO_3$ composites revealed the dramatic toughening effect of nano-$CaCO_3$ on PP, but the yield strength of PP was slightly decreased, because of the nucleating effect of nano-$CaCO_3$. Adding resin polymer with amount of nano-$CaCO_3$ range from 1 to 4 phr that is called nucleating agents, which can decrease a surface tension of polymer for forming microbubbles.

3.5.5 Lubricants

It is known that lubricants have function as adding to compound to migrant to surface during processing or use, to form a separate layer, preventing sticking to mould surface, or other materials. And they have also properties affected productivity, cycle time; product surface/quality. Lubricants are form as synthetic waxes; polyethylene wax and or hydrocarbon wax. Especially, calcium stearate is widely used with PVC.



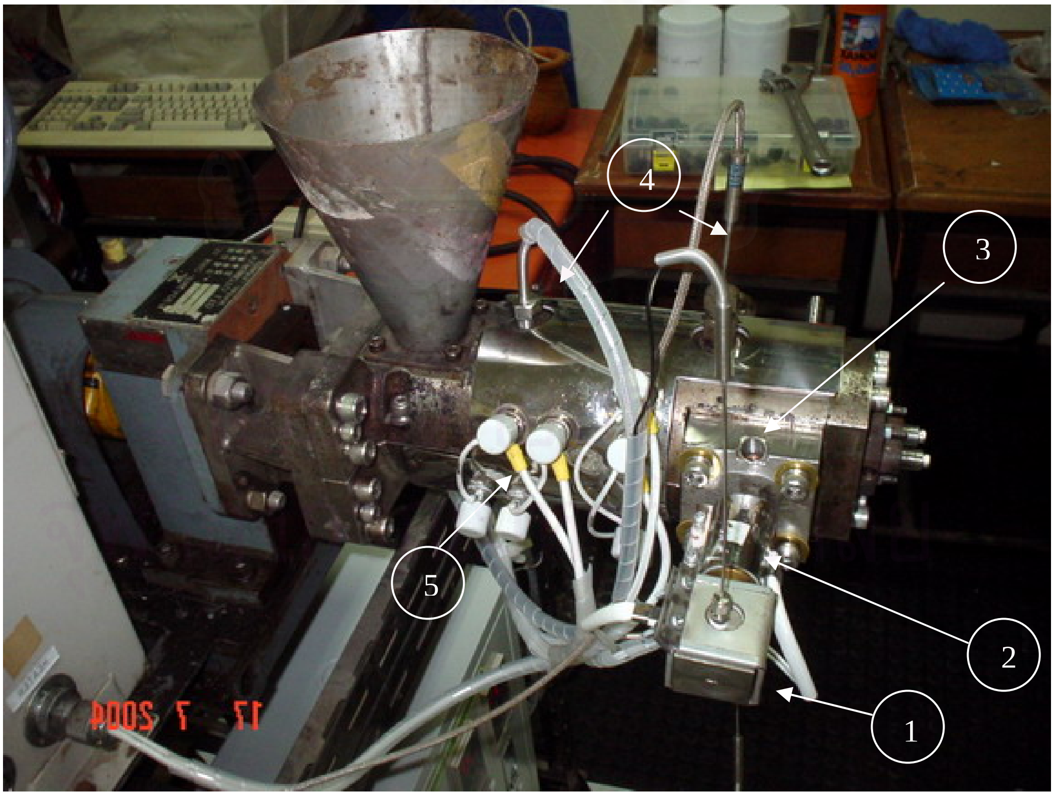
CHAPTER IV

EXPERIMENTAL

4.1 Experimental Setup

Twin Screw Extruder

Figure 4.1 shows a schematic of extrusion system used in this study. It consists of a 0.4 to 0.75 kW twin screw extruder (Kurimoto: KRC S1) driven with a speed control gear box, revolution of paddle in the range 90 to 360 rpm, 25 millimeter diameter of paddle, 255 millimeter length of barrel, band heaters covering around the barrel with two zones of which; feeding zone and mixing zone. It has 10.5 L/D that is short twin screw extruder for extrusion foaming process.



1. Slit die
3. Pressure port
5. Heater band
2. Static mixer
4. Thermocouples

Figure 4.1 Twin screw extruder

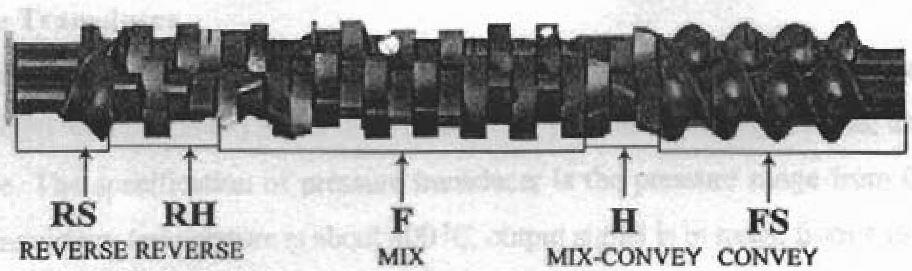
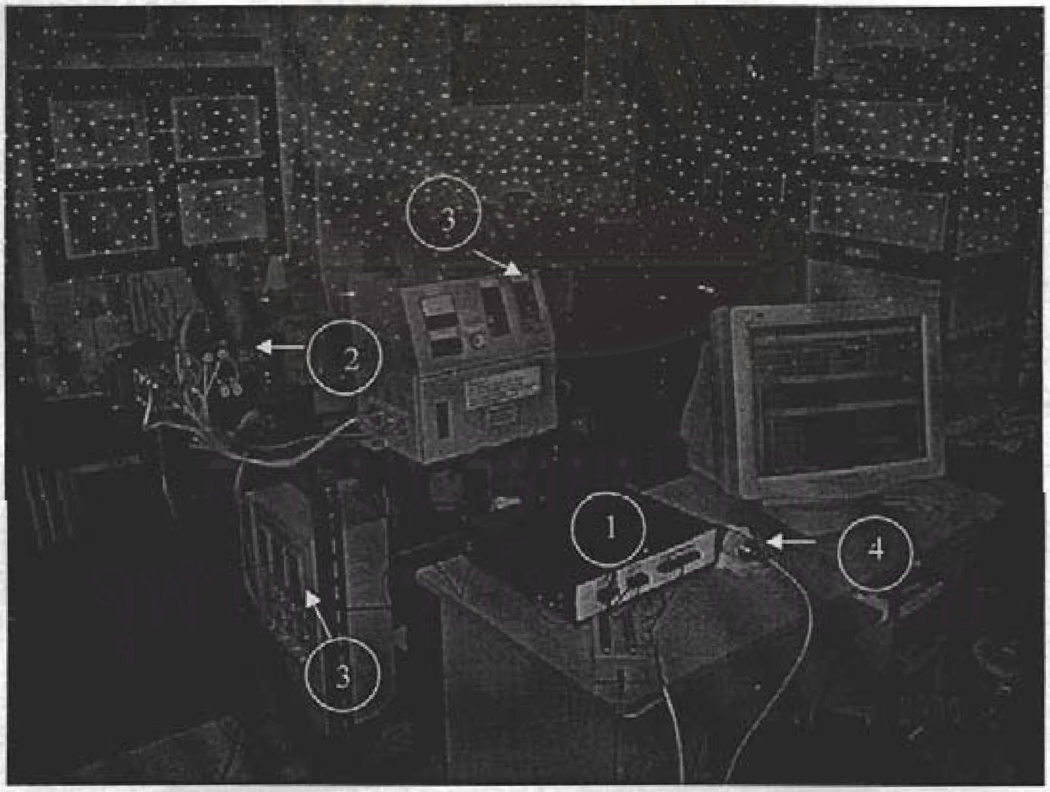


Figure 4.2 Twin screw extruder as a segment type: consist of three paddles

Figure 4.2 shows the paddles and screw; the critical parts of twin screw extruder (KRC Kneader), are mounted on a pair of horizontal parallel shafts which co-rotated at a same speed. Three types of paddles are available consist of Flat paddle for kneading (Type F), Helical paddle for kneading and conveying (Type H), and Reverse helical paddle for kneading and reversing (Type RH).



1. Data logger
2. Twin screw extruder
3. Temperature control
4. Pressure transducer

Figure 4.3 Twin screw extruder and data logger system

Pressure Transducer

Figure 4.4 shows a pressure transducer used in this study. Pressure transducer (Dynisco: PT 4604-5CB-6-T80) is used monitoring pressure foaming process, and strain gage type. The specification of pressure transducer is the pressure range from 0 to 500 bar, the maximum temperature is about 400 °C, output signal is in range from 4 to 20 mA, and ±0.5 % accuracy.

Figure 4.4 Pressure transducer

Data Logger

This data logger (see Figure 4.4) is an instrument to be produced for recording the data of temperature and pressure during the extrusion foaming process. It is connected into the die adaptor with pressure transducer after the mixing zone. There are many ports used in this work: 2 ports of pressure and 4 ports of temperature. It has highest speed of records in 5 points per second and easier to use by excel, which is middle speed of records.

Figure 4.5 Recording system or data logger during connecting with a computer

Temperature Control System

This temperature control system as shown in Figure 4.6 is digital type that can be used PID or on-off control, and suitable to J and K type of thermocouple.

Figure 4.6 The temperature control system

4.2 Raw Materials

PVC Resin

Suspension PVC resins were supplied by Vinythai Public Co, Ltd. (Bangkok, Thailand), in the form of compounded PVC powder. There are two types of PVC compounds used in this work: with K value of 58 (SIAMVIC 258RB) and K value of 66 (SIAMVIC 266RC). PVC resin with K value of 58 is low molecular weight polymer and K value of 66 is medium molecular weight one.

Nano-Calcium Carbonate

$CaCO_3$ was supplied by Sand and Soil Co, Ltd. (Bangkok, Thailand), it has a mean particle size of 60 nanometer as shown in Figure 4.7, and according to manufacturer’s data.

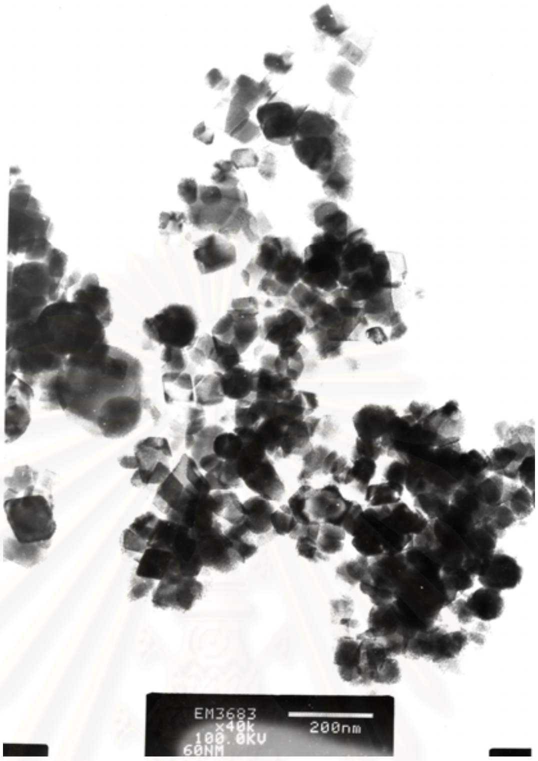


Figure 4.7 TEM micrographs of nano-$CaCO_3$

Activator

Ba- Zn BL 125 from Cosmos chemical Co. Ltd. (Bangkok, Thailand) was chosen as an activator additive for Azodicarbonamide (AZ). Ba- Zn BL 125 was in a powder form, with a purity of 99%, according to manufacturer's data.

Chemical Blowing Agents

Azodicarbonamide (AZ) from Chemin Co. Ltd. (Bangkok, Thailand) was chosen a blowing agent or a foaming agent. AZ was in a form of a yellow powder with an average particle size of 8 micron according to manufacturer's data. The operating temperature range of AZ is reported to be between 160 and 190 °C, which indicates that it is suitable blowing agent for processing polymers at this temperature interval. This is important because of its decomposition temperature range between 204 and 215°C, while its gas-yield is around 220 cm^3/g. The gas product release by the decomposition of AZ comprises 65% N_2, 24% CO, 5% CO_2, and 5% NH_3.

Sodium bicarbonate ($NaHCO_3$) from Gredman Thailand Co. Ltd. was chosen as a blowing agent. $NaHCO_3$ was in a form of white powder (food grade), according to manufacturer's data. The gas product release by the decomposition of $NaHCO_3$ comprises CO_2.

Plasticiser

DINP (diisononylpthalate) from Thai MC Co, Ltd. (Bangkok, Thailand) was used as a platiciser in foam extrusion process. DINP was in a form of clear liquid and widely used with PVC for more flexible and easier to process.

Heat Stabilizers

Inorganic compound of Cd/Ba/Zn from Cosmos chemical Co, Ltd. (Bangkok, Thailand) was used as heat stabilizers. Cd/Ba/Zn was in a form of red liquid and widely used.

Lubricant

PE wax from clariant company limited was as used a lubricant. PE wax was a form of white granule. PE wax used for applications such as process ability improver for PVC and various resins.

4.3 Preparation of PVC Compound

1. First, weigh the additives and PVC resin according to the desirable formulation.
2. Mix various additives contents into the V-Shape mixer as shown in Figure 4.8, and then, rotate it well in order to obtain the homogeneous particles for 10 minutes, and mix liquid stabilizer and DINP with PVC resin in a plastic bottle for 5 minutes.
3. Pre-mix the additives with stabilizer/DINP/PVC resin that are stirred for 5 minutes.
4. Finally, heat the barrel to 80 °C and the additives/PVC resin are fed into the barrel through the hopper and are completely mixed by the screw motion.

Figure 4.8 V-shape mixer

4.4 Experimental Procedure of continuous process

1. Heat the barrel to 145-150 °C of feeding zone and 160-190 °C of mixing zone until steady state.
2. The PVC compound is fed into the barrel through the hopper and is completely melted by the screw motion.
3. The solidified foam samples are randomly chosen at each processing condition, which are measured using electronic densimeter (see Figure 4.9, MD-200S) adopts Archimedes' principle, and are characterized using a scanning electro microscope (SEM, JEOL JSM-5400).
4. The foam samples are dipped in liquid nitrogen and then fractured to expose the cellular structure.

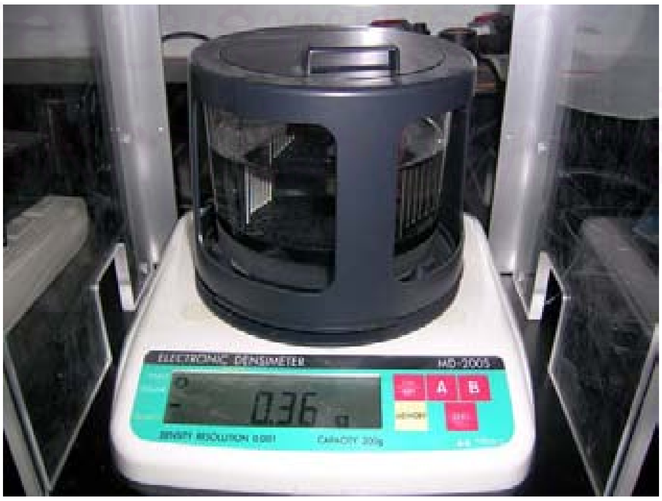


Figure 4.9 Electronic densimeter MS-200S

4.5 Experimental Procedure of batch process

1. The sheets were put in the high pressure chamber as shown in Figure 4.10.
2. It was flushed with carbon dioxide for 3 times to expel the air out. Then it was filled with carbon dioxide to 16.5 MPa at the required temperature.
3. This condition is held for 3 hours, after that it is depressed quickly to atmospheric pressure.
4. Finally, the sheets are cooled down and taken out for characterization.

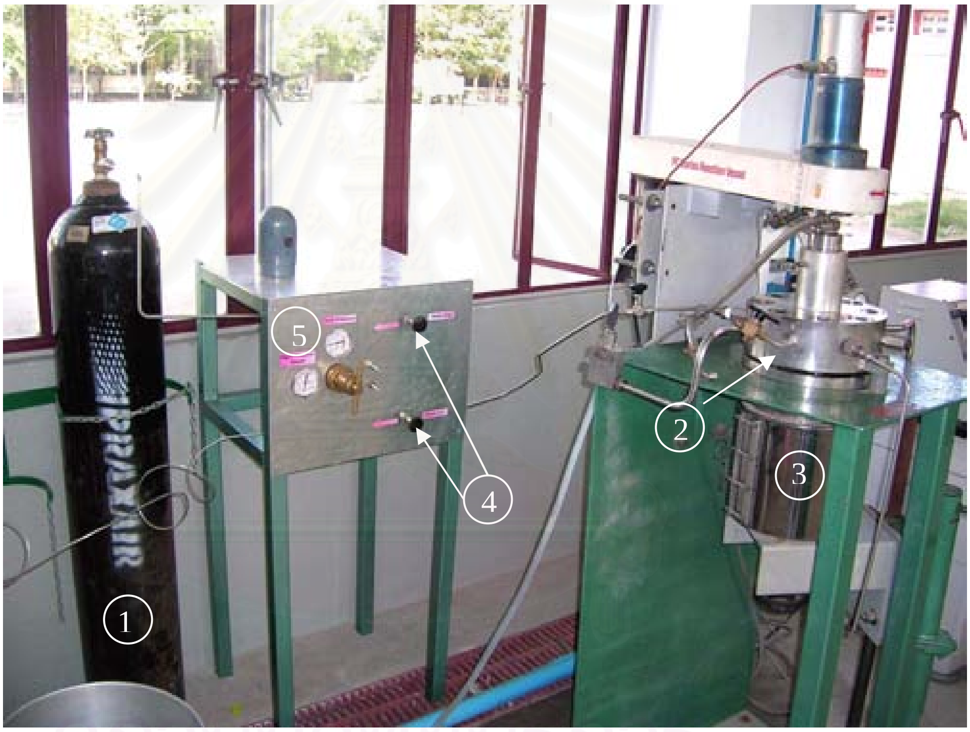


Figure 4.10 Experimental set up of batch process

1. Carbon dioxide tank
2. High pressure chamber
3. Heater
4. Metering valve
5. Pressure gauge

4.6 Tensile and bending test

Tensile test is carried out according to ASTM D636 on Universal Testing Machine LLOYDLR 100 K. Bending test is carried out according to ASTM D0747.10. It shown in Figure 4.11 and 4.12, samples are machined from shape of mould. The tensile testing machine pulls the sample from both ends and measures the force required to pull the specimen apart and how much the sample stretches before breaking**.**

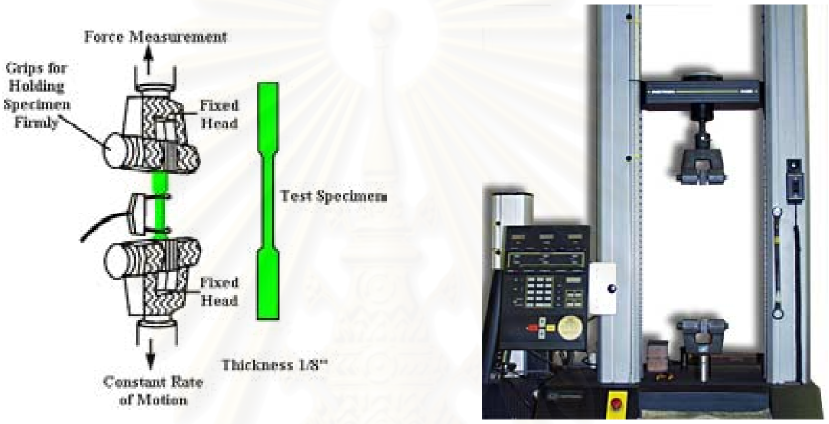


Figure 4.11 Tensile test (LLOYDLR 100 K) for specimen apart

Figure 4.12 Universal testing machine (LLOYD 500D) for bending test

CHAPTER V

RESULTS AND DISCUSSION

First, possibility to prepare PVC microcellular foam is investigated by using a batch process of which experimental procedures are explained in Chapter 4. Supercritical carbon dioxide is used as a blowing agent while $CaCO_3$ with nanosize is employed as a nucleating agent. Then, in preparation of PVC foam by using a continuous process the influences of PVC foam properties, which are chemical blowing agents content, plasticizer and die temperature on foam density and cell morphology, are investigated. The important chemical additives utilized in this work are shown in Table 5.1. It is known that the chemical blowing agent will affect cell morphology and foam density. Thus, amount of azodicarbonamide (AZ) and sodium bicarbonate ($NaHCO_3$) content are varied. It is well known that $NaHCO_3$ can generate carbon dioxide gas with yield lower than that of AZ, and $NaHCO_3$.

Meanwhile, DINP is used as a plasticizer because it can help reduce processing temperature. Nano-$CaCO_3$ is also utilized as nucleating agent are investigated. It should be noted that investigation on effects of nano-scaled $CaCO_3$ on foaming process using twin screw extruder is initiated in this work. The twin screw extruder is employed in this work because it can provide good mixing and continuous. Based on experimental results, effective the process conditions including operability processing the exit die temperature and the screw speed are determined.

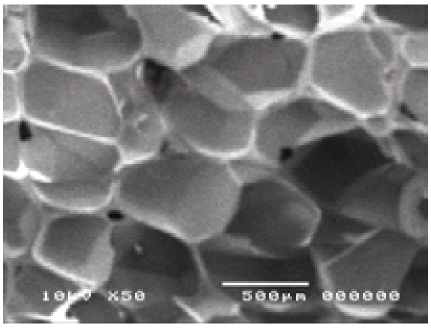


Figure 5.1 Cell morphology of PVC foam from DIAB Company (Italy)

Figure 5.1 presents cell morphology as closed-cell and 544 micron of mean cell size. The PVC foam is big cell size that is classified conventional foam. The PVC foam from DIAM Company is used for foam core materials in the marine industry. The PVC foam from DIAM Company is compared with obtained PVC foam from this experiment, for improving process conditions and formulations.

Table 5.1 Main formulation of PVC compound in this study

Chemical Type	**Function**	**Content** (phr)
Suspension PVC resin (solid), K of 58	Polymer	100
PE wax (solid)	Lubricant	2
Cd/Ba/Zn (liquid)	Heat stabilizer	3
Ba-Zn BL 125 (solid)	Activator	4
DINP (liquid)	Plasticizer	10-30
Nano-$CaCO_3$ (solid)	Cell nucleating agent	2-10
Azodicarbonamide (solid)	Organic blowing agent	1-10
or Sodium bicarbonate (solid)	Inorganic blowing agent	12-18

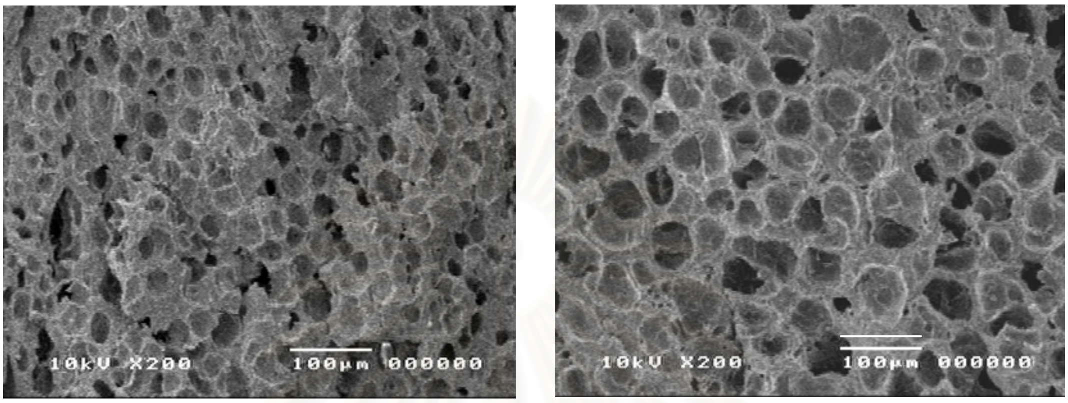
Regarding to suggestion of reference (7), and other additives; the composition of PE wax, Cd/Ba/Zn, solution and Ba-Zn 125 is fixed.

5.1 Batch process

In order to look into the possibility of employing nano-scaled $CaCO_3$ as a nucleating agent, a batch process for preparation of PVC foam is conducted. The nano- scaled $CaCO_3$ exhibits a normal size of 60 nm with cubic morphology as shown in Figure 4.7. Content of the $CaCO_3$ added is 2 and 4 phr. Supercritical carbondioxide is used as a blowing agent which is fed into foaming chamber at the pressure of 16.5 MPa and the temperature of 110 °C.

From Figure 5.2, it could be clearly seen that the increasing content of nano-scaled $CaCO_3$ could provide microcellular structure with higher uniformity. The obtained PVC foam is also taken to characterize its density as shown in Table 5.2.

The density of the obtained PVC foam with nano-scaled $CaCO_3$ of 4 phr is about 0.84 g/cc. However, it is still too high for the application of windsurf. The next step is to investigate foam preparation by using a twin screw extruder.



(a) 2 phr of nano-$CaCO_3$ **(b)** 4 phr of nano-$CaCO_3$

Figure 5.2 The SEM micrographs of PVC foam obtained from batch process with pressure of 16.5 MPa

Table 5.2 Relationship of foam density pressure and expansion ratio

Nano-$CaCO_3$ (phr)	Solid density ρ_s (g/cc)	Foam density ρ_f (g/cc)	Expansion ratio $\beta = \frac{\rho_S}{\rho_f}$	Cell density (Cells/cm^3)
2	1.32	1.16	1.14	2.7×10^4
4	1.21	0.84	1.44	4.3×10^5

Note: Cell density is calculated from Equations 16 and 17.

5.2 Continuous process

It is found that a batch process could provide the microcellular foam with the lowest density of 0.84 g/cc at the highest pressure of 16.5 MPa. But it is still too heavy to be used as surfboard. Therefore, a continuous process using a twin screw kneader is taken to investigate instead.

It is known that the kneading speeds of twin screw extruder affect on residence time, resulting in cell growth control. Thus, effective screw speed is initially investigated. The variable range of the screw speed of this twin screw extruder is 96 to 192 rpm. Based on the experimental results, dependence of foam density or expansion ratio on the screw speed is shown in Table 5.3.

Table 5.3 Dependence of foam density on the varied

Screw speed (rpm)	**Mass flow rate (kg/min)**	**Residence time (sec)**	**Volume expansion ratio** $\beta = \frac{\rho_S}{\rho_f}$
96	16.4	29	1.74
120	26.5	18	1.36
144	32.7	15	1.30
168	39.9	12	1.29
192	56.9	8	1.18

Note: free volume of barrel is 100 ml.

The increase in the foam density with the increasing screw speed is attributable to an increase in mass flow rate of the foaming polymer. The mass flow rate as a function of the screw speed is plotted in Figure 5.3.

Meanwhile, the increasing screw speed also leads to shortening residence time of polymer in the kneader. Therefore, the screw speed of 96 rpm which provides the lowest mass flow rate but the longest residence time could provide the compounded foam with lower density. Based on this result, the following experimental will be conducted to determine most suitable screw speed.

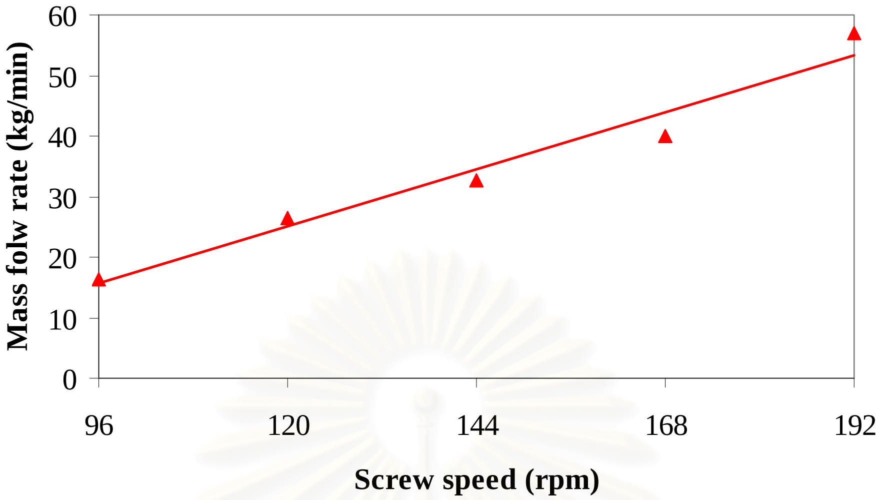


Figure 5.3 Relationship between the screw speed and the mass flow rate

5.2.1 Chemical blowing agent calculation

The concentration of the chemical blowing agent (CBA) in the polymer-CBA mixture has to be commensurated to the desired (or required) magnitude of volumetric expansion of the material. This parameter is referred to as the volume expansion ratio. This indicates that an appropriate relationship between the CBA amount and the require volume expansion ratio has to be developed.

Equation 18 which is used to calculate the percentage (by weight) of the selected CBA that should be used to obtain a given volume expansion ratio is presented.

$$\%CBA = 100\left(\frac{\beta - 1}{\rho_S \varphi}\right) \tag{18}$$

$$\varphi = \varphi_{STP}\left(\frac{T_C}{T_{room}}\right) \tag{19}$$

Equation 18 involves the volume expansion ratio, the density of the polymer and the gas yield of the selected CBA. But the data describing the gas yield of CBAs (φ) provided by the suppliers are referred to room temperature conditions, while the composition of CBAs and thereby the expansion of polymeric foams occurs at elevated temperatures, which are beyond the polymer melting temperature.

The decreasing temperature will gradually reduce the maximum possible gas volume. Since the polymer freezing will be initiated at the onset crystallization temperature, and since the polymer will be ultimately frozen at crystallization peak temperature, the structure of the foam will be fixed at this temperature. This indicates that the occupied gas volume at the crystallization temperature determines the void fraction of the foam. The crystallization temperature of polymers occurs at temperatures much higher than the room temperature, the volume of the generated gas by the decomposition of the CBA at this high temperature will be significantly larger than the volume of the same gas at room temperature. Therefore, prior to introducing the gas yield data in Equation 18 the data for the gas provided by the manufacturer (at the room temperature) should be corrected to their corresponding values at crystallization temperature by using he relationship provided in Equation 19.

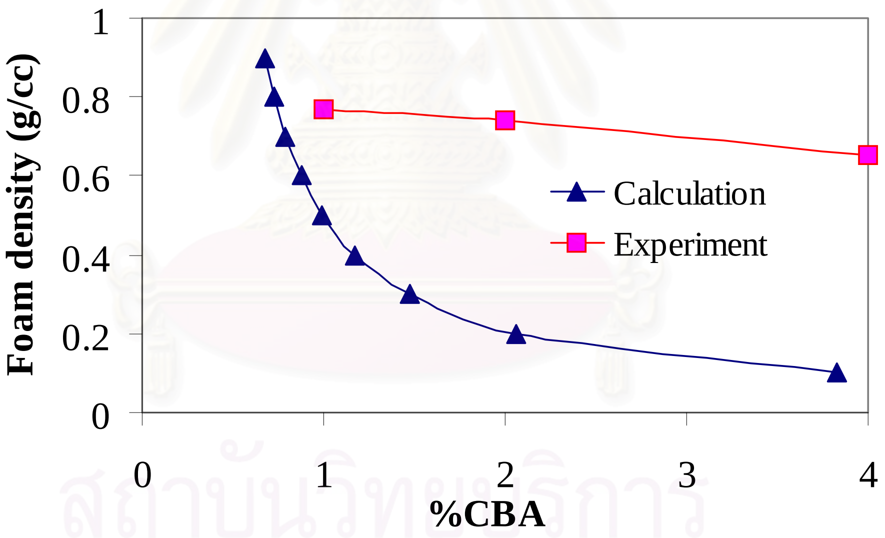


Figure 5.4 The relationship between foam density and CBA content by calculation

Figure 5.4 presents CBA content and foam density which are obtained from experiments and calculation by using of Equations 18 and 19. CBA contents from calculation differ in experiment due to occurring cell coalescence. Thus, Equation 18 can not use to predict for this experiment.

5.2.2 Effect of die temperature on foam density

The processing temperature is another important parameter that affects the final foam structure. The temperature of polymer melt affects the foam density and cell size, thus affecting the melt viscosity, the degree of fusion, and gas generation from the blowing agent. For a successful foaming process, the temperature of the melt lie in an interval between values that are giving a sufficiently low viscosity of the melt to allow cell formation and expansion and a sufficiently high viscosity of the melt to prevent cell collapsing. Therefore, the effect of temperature on the cell morphology of PVC foam is also studied. Four different temperatures (160, 170, 180, and 190 °C) are used in the experiments. A little amount of AZ (1 phr) is charged into the twin screw extruder for each experiment.

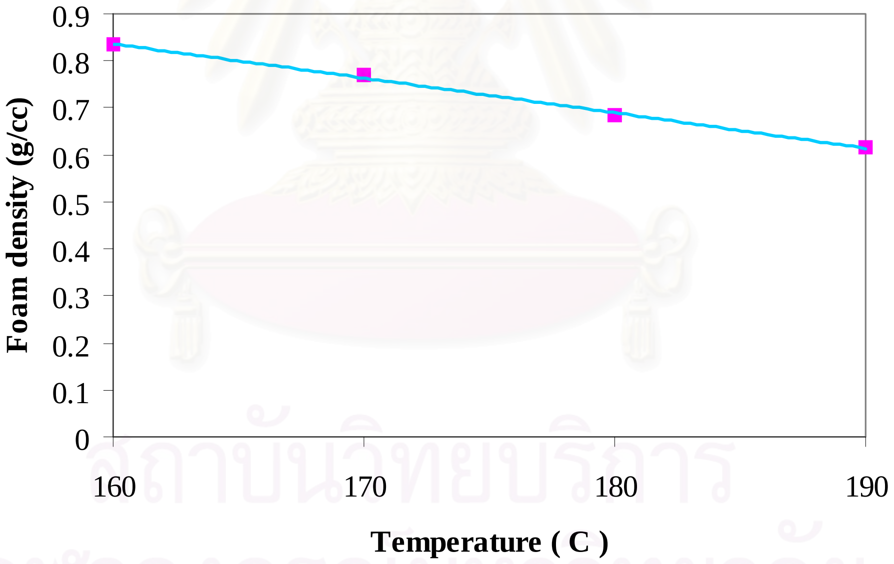
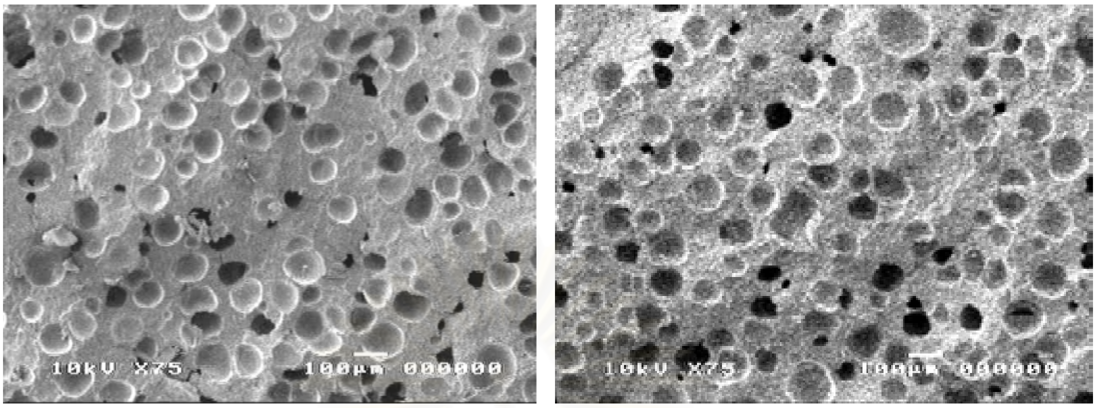


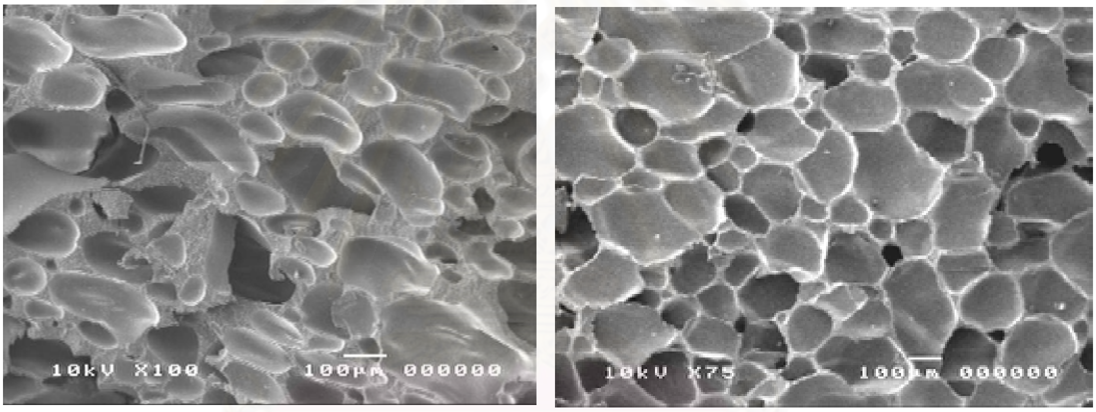
Figure 5.5 Effect of die temperature on the densities of PVC foam

Figure 5.5 shows foam density as a function of temperature. The temperature does significantly affect the density of PVC foam. The density of PVC foam decreases with an increase in temperature due to the decrease viscosity. The bubbles usually form more easily at the lower viscosity.

5.2.3 Effect of die temperature on cell morphology of PVC foam



(a) T_{die} = 160 °C **(b)** T_{die} = 170 °C



(c) T_{die} = 180 °C **(d)** T_{die} = 190 °C

Figure 5.6 Effect of die temperatures on cell morphology

Figure 5.6 shows the effect of temperature on cell morphologies of PVC foam. At 160 °C, AZ begins to decompose and liberate gases. At 160 and 170 °C, the bubbles are uniform small cell size and when the temperatures increase from 180 to 190 °C. At higher temperatures, the viscosity of polymer is lower. In Figure 5.6, as temperature increases further, the nucleated cells grow, and the melt is expands. It is found that the cells become big cells due to the reduction of the surface free energy.

As a result, during the experiments with high temperature, the melt strength of PVC is lowered at the interface of the polymer melt and the growing gas bubble. This promotes severe cell coalescence and reduces the cell population density. However, a low temperature is not practical for production because of prolonged cycle times.

5.2.4 Effect of azodicarbonamide (AZ)

The nucleation of microbubbles and their volume expansion of PVC foam were investigated with changing AZ contents while keeping other additives constant. The effects of changing AZ content on the expansion ratio, foam density, and cell morphology are discussed in this subchapter. The formulations of compounding PVC foam prepared in this work are summarized in Table 5.4.

Table 5.4 Formulation of PVC foam

Chemical Type	Function	Content				
		1	**2**	**3**	**4**	**5**
Suspension PVC resin (solid), K value of 58	polymer	100	100	100	100	100
PE wax (solid)	Lubricant	2	2	2	2	2
DINP (liquid)	Plasticizer	10	10	10	10	10
Cd/Ba/Zn (liquid)	Heat stabilizer	3	3	3	3	3
$CaCO_3$ (solid)	Cell nucleating agent	4	4	4	4	4
Ba-Zn BL 125 (solid)	Activator	4	4	4	4	4
Azodicarbonamide (solid)	Blowing agent	**2**	**4**	**6**	**8**	**10**

Note: Cd/Ba/Zn as heat stabilizer is more suitable than Ba/Zn due to Cd as unique metal to replace chloride atoms. Previously, Ba/Zn was mixed with PVC resin but this PVC compound decomposes thermally at higher temperature than 150 °C.

1) Effect of the AZ contents on foam density

Foam densities were measured using electronic densimeter (MS-200S). Though not mentioned in detail, other separate investigation reveals that temperature of the die should be kept constant at 190 °C. Therefore, the exit die (cylindrical shape) temperature of 190 °C, and the screw speed of 96 rpm was employed while the AZ content was varied in a range of 0 to 10 phr. The PVC foam obtained at AZ content of 10 phr exhibits the lowest density of 0.46 g/cc.

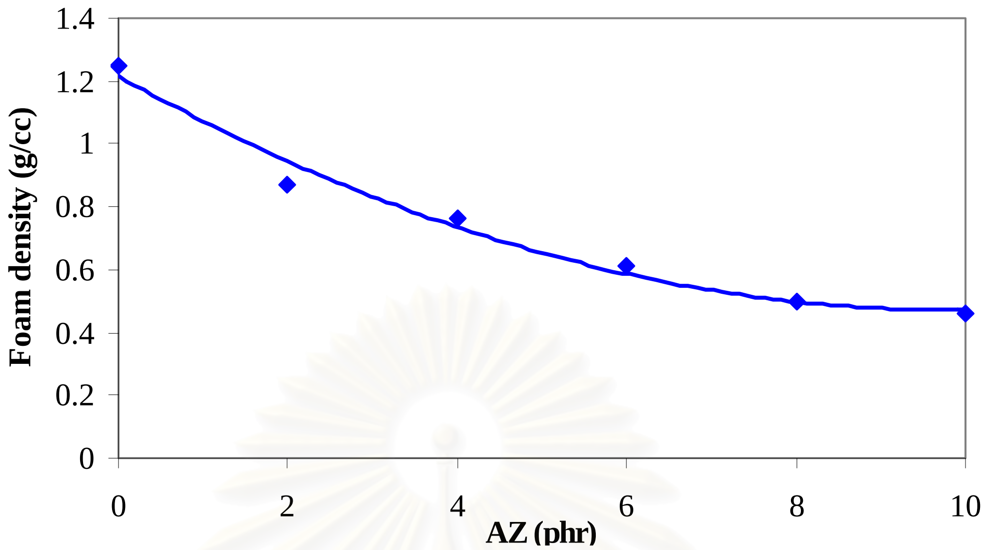


Figure 5.7 Effect of AZ on the foam densities of PVC at exit die (cylindrical shape) temperature of 190 °C

Figure 5.7 shows the effect of the AZ content on the density of PVC foam product in this work. The exit die used in these experiments has cylindrical shape. It is found from other previous experiments that slit die could not provide the desired PVC foam because it gave rise to very high pressure cause by fiction between the die and the flowing polymer. A small amount of AZ could significantly decrease the density of the PVC foam. Higher AZ content could promote much more generation microbubbles within the polymer matrix. However, with the excess amount of AZ range from 8 to 10 phr, there was only small change in the foam density because cell coalescence became more enhanced and excess high pressure arose gas microbubbles could also destroy cell wall.

It could be clearly seen that without addition of AZ, the obtained foam density is 1.25 g/cc while its appearance is solid plastic containing no cellular structure. However, with addition of AZ, the PVC foam could be extruded with stable shape as shown in Figure 5.8.

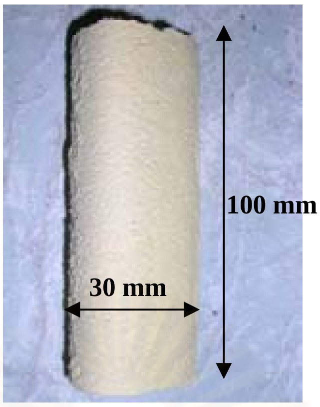
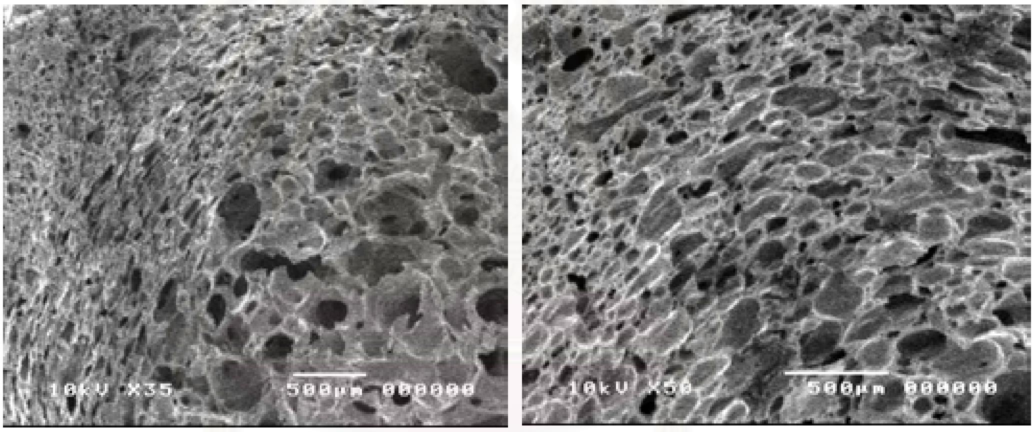
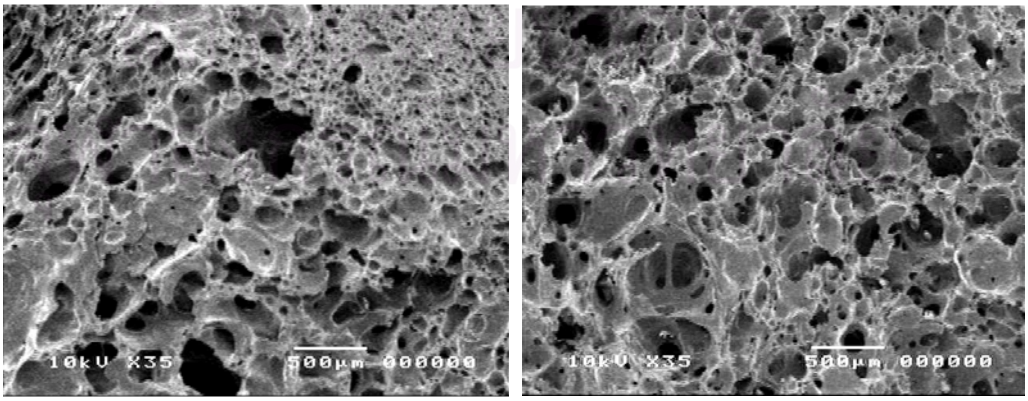


Figure 5.8 PVC foam product as dimension with length of 100 mm, width of 30 mm, and thickness of 8 mm

2) Effect of AZ contents on cell morphology



(a) 2 phr of AZ **(b)** 4 phr of AZ



(c) 6 phr of AZ **(d)** 8 phr of AZ

Figure 5.9 Effect of AZ on cell morphology of PVC foam at 190 °C

Besides qualitative analyses of effect of AZ content on the PVC foam density, its effect on the morphology of microcellular structure is also investigated. Figure 5.9 illustrates the experiment results that obviously describe the effect of AZ content on cell morphologies in the obtained PVC foams. It is observed that the cell structure is poor. Thus, too much AZ composition also results in a poor cell structure because of too high pressure gas.

Although, addition of AZ could help generate microbubbles, but it also inevitably reduce the so-called melt strength because of coalescence of the microbubbles within the polymer matrix. Excess AZ content could result in poor cell structure because it gave rise to excess gas pressure which in turn led to the bubble coalescence. In order to avoid this problem the melting process of the compound foam should be conducted at as low temperature as possible.

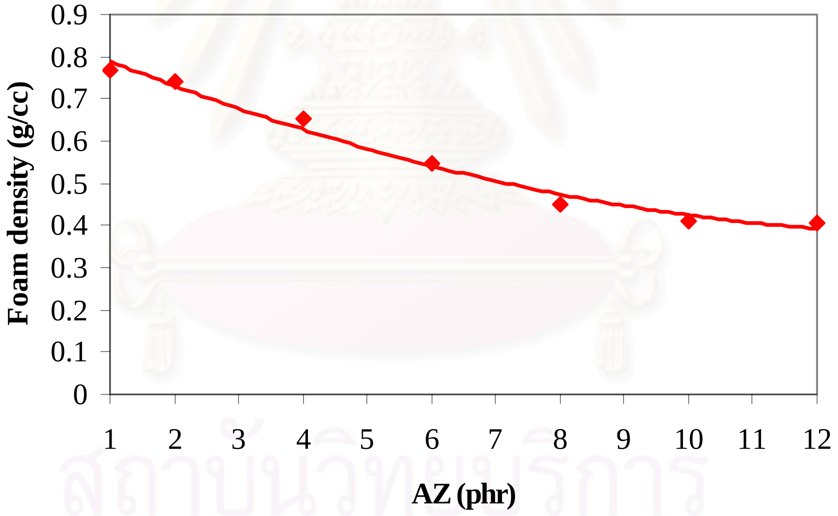
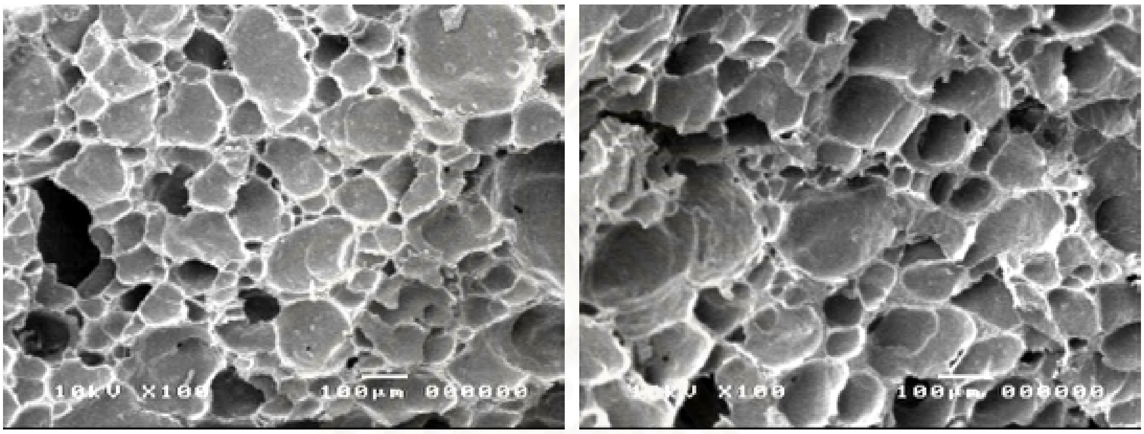
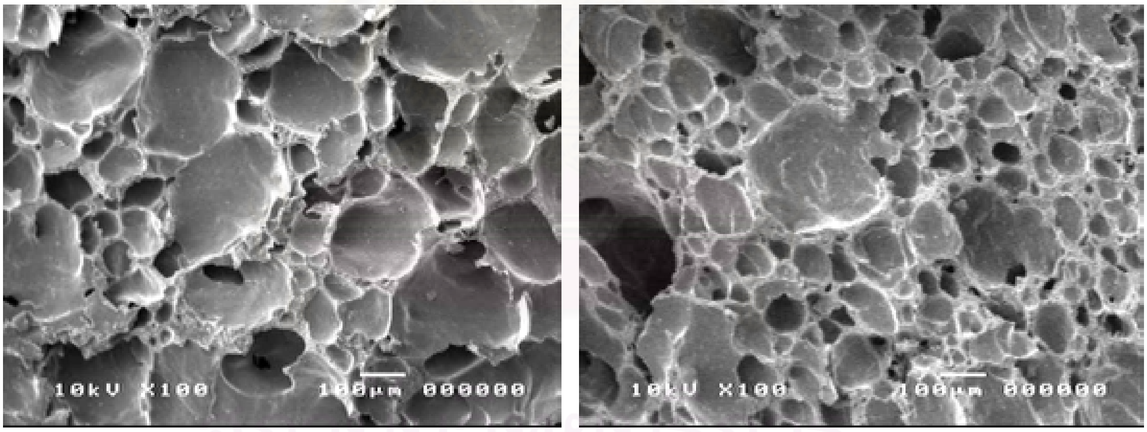


Figure 5.10 Effect of AZ on the densities of PVC foam at exit die (rectangular shape) temperature of 170 °C

Figure 5.10 also presents the effect of the AZ content on the density of obtained PVC foam. However, the shape of the die employed here was rectangle. It is employed to prepare samples of PVC foam which could be taken to analyze tensile and bending strength. As mentioned previously, the compounding temperature is kept as low as possible at 170 °C in order to maintain its melt strength. Addition of AZ with very few amount of 1 phr could significantly reduce the PVC foam density. However further increasing the AZ content could help decrease the foam density with less significantly because of the promoted cell coalescence. Under this condition, the obtained foam density went down further to 0.41 g/cc.



(a) 2 phr of AZ **(b)** 4 phr of AZ



(c) 6 phr of AZ **(d)** 8 phr of AZ

Figure 5.11 Cell structure at various contents of AZ at 170 °C

Similarly, the effect of AZ content on the cell morphology was also investigated with the operating temperature of 170 °C. Figure 5.11 presents the cell structure of the obtained PVC foam at 170 °C. It should be noted that most of microcellular pores are closed-cell. Collapsing of cell wall led to under cell boundary and wider cell size distribution, resulting in a less significant decrease in the foam density.

5.2.5 Effect of sodium bicarbonate ($NaHCO_3$) contents on foam density

In stead of using AZ, $NaHCO_3$ was employed as a nucleating agent which could provide microbubbles of carbon dioxide. The gas yield effect on the process and product. Carbon dioxide is more solute in plastics and has lower vapour pressure than nitrogen, thus, it is normally easier to work with. However $NaHCO_3$ with the same mass as AZ could provide few yields of gas bubbles (120 cc/gm). $NaHCO_3$ have lower gas yield than AZ (220 cc/gm) and AZ generate mainly nitrogen. $NaHCO_3$ also generate carbon dioxide gas which is accessible to smaller pores than nitrogen, because of the larger kinetic energy of the molecules at high temperature (13). Thus, in this work $NaHCO_3$ is used in the range of 12 to 18 phr. The formulations of PVC foam at various $NaHCO_3$ content is summarized in Table 5.5.

Table 5.5 Formulation of PVC foam

Chemical Type	**Function**	**Content**			
		1	**2**	**3**	**4**
Suspension PVC resin (solid), K of 58	polymer	100	100	100	100
PE Wax (solid)	Lubricant	2	2	2	2
DINP (liquid)	Plasticizer	10	10	10	10
Cd/Ba/Zn (liquid)	Heat stabilizer	3	3	3	3
$CaCO_3$(solid)	Nucleating agent	4	4	4	4
Ti_2O(solid)	Pigment	4	4	4	4
Ba-Zn BL 125(solid)	Foaming activator	4	4	4	4
$NaHCO_3$(solid)	Blowing agent	**12**	**14**	**16**	**18**

Ti_2O is added in this formulation because Ti_2O as white colorant widely used in vinyl formulations. When Ti_2O is used in formula and is observed in refracted light. Ti_2O exist commercially in two crystal forms, anatase and rutile. Rutile pigments have the highest refractive indices of white pigments and are much more resistant to chalking than anatase. Anatase pigments have generally a slightly bluer shade; they are slightly lower in refractive index and are slightly easier to disperse. (7)

Similarly, the obtained foam densities were measured using electronic densimeter (MS-200S). From some trial error investigations, it was found that when $NaHCO_3$ was employed, the die temperature should be kept constant at 160 °C, and the screw speed was fixed at 96 rpm. The foam densities decreased as the content of $NaHCO_3$ was increased as shown in Table 5.7.

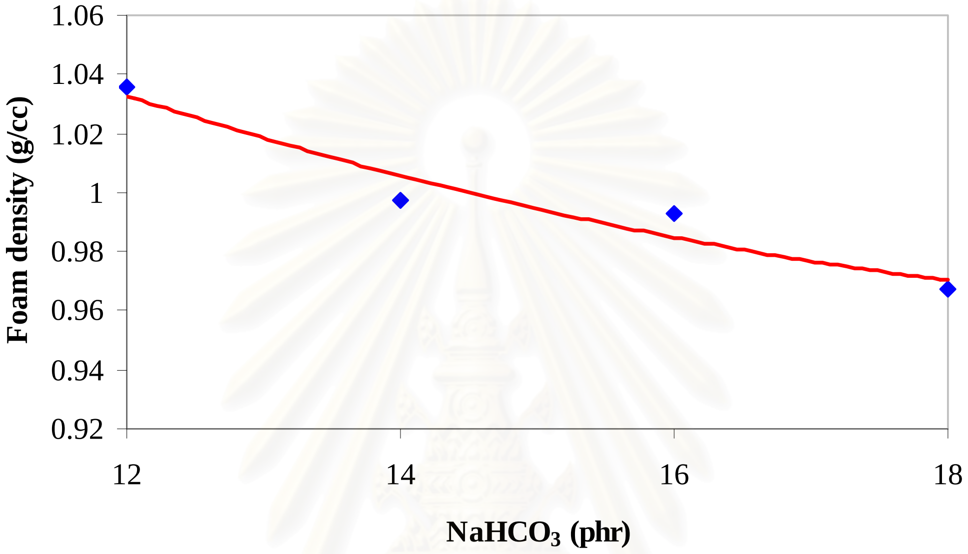


Figure 5.12 Effect of $NaHCO_3$ on the foam densities

Figure 5.12 graphically shows the effect of the $NaHCO_3$ content on the density of the prepared PVC foam. Considering the effect of blowing agent, the density of the PVC foam slightly decreased when the amount of $NaHCO_3$ was increased from 12 to 18 phr. This could be implied that solubility of $NaHCO_3$ in the PVC matrix is very low because of $NaHCO_3$ as inorganic and PVC as organic. Then, bubble formation hardly took place under the condition of high viscosity at 160 °C. Compared with AZ, $NaHCO_3$ is considered as a chemical additive which could provide small amount of microbubbles, resulting is higher foam density.

5.2.6 Comparison of foam densities obtained from employing AZ and $NaHCO_3$

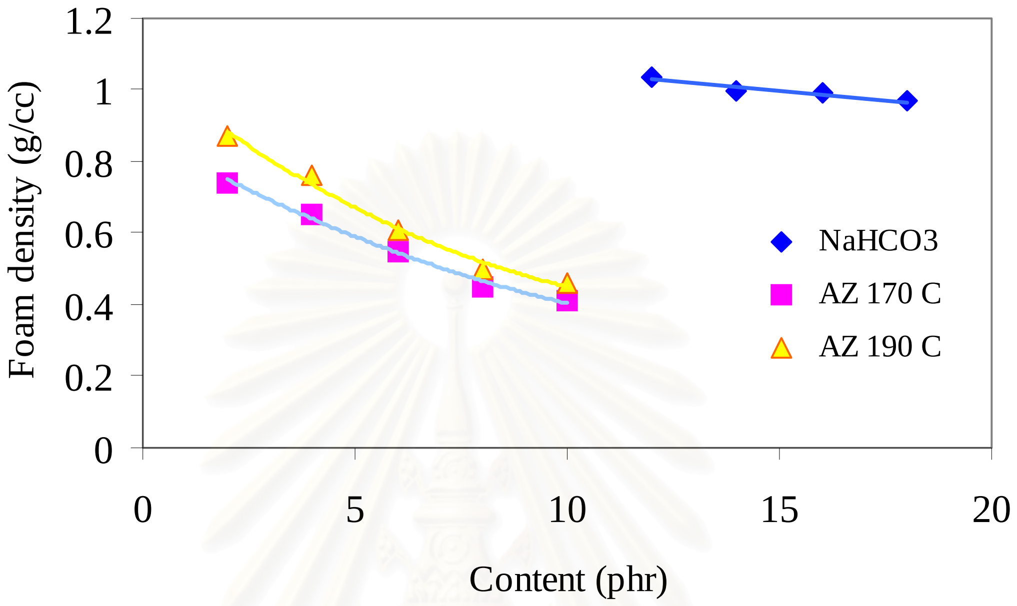


Figure 5.13 Effect of AZ and $NaHCO_3$ on the densities of PVC foam

Figure 5.13 shows the comparison of the density of the PVC foam obtained when employing azodicarbonamide and sodium bicarbonate. As described previously, although, sodium bicarbonate content is highly added in the range from 12 to 18 phr, its effect on the foam densities was less significant. Therefore, this could lead us to a conclusion that AZ is more suitable than $NaHCO_3$ to provide microcellular pore in the PVC foam matrix.

5.3 Mechanical properties

The determination of mechanical properties of PVC foams is necessary for both academic study and industrial practice. The mechanical properties of rigid PVC foams are controlled by compound formulations and processing conditions. In this study, the mechanical properties focusing on tensile and bending strength of PVC foam are studied. Since the results obtained from these analyses are very beneficial for design and/or selection of the most suitable foams for the desired applications, improving the accuracy of these analyses is still an active challenge for this study.

5.3.1 Tensile test

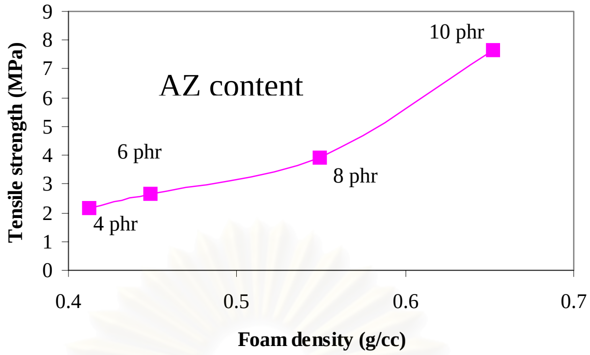


Figure 5.14 Relationship between foam density and tensile strength

Figure 5.14 shows relationship between foam density (AZ contents) and tensile strength. It should be noted that tensile strength is increased with the increase in the density of PVC foam. For the prepared PVC with relatively low density, its tensile strength becomes worse because uniform and close-cell structure is hardly achieved. In generally, tensile strength depends on cell morphology or cell structure. A smaller cell size the PVC foams have more tensile strength than. Moreover, tensile strength depends on also distribution of the cells according to size and shape and closed-cell have more high strength than open-cell (1). A higher AZ content cell size becomes big cell due to cell coalescence and its tensile strength becomes worse. With 0.1 g/cc density of PVC foam from DIAB Company has more tensile strength than obtained PVC foam in experiment due to a higher uniform cell size. The tensile strength of PVC foam from DIAB Company is shown in Table B-6.

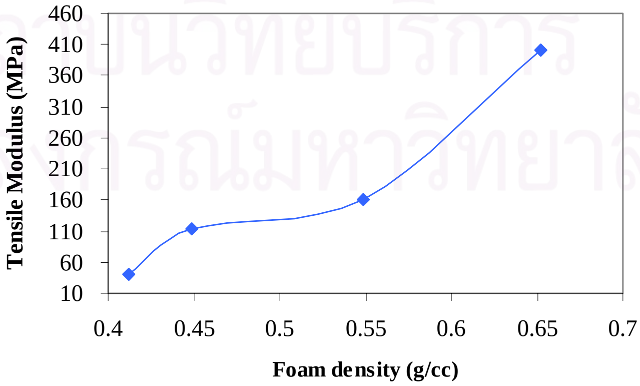


Figure 5.15 Relationship between foam density and tensile modulus

In Figure 5.15, tensile modulus of the PVC foam is shown to increase with foam density. These results confirm that tensile strength depends on the cell morphology.

5.3.2 Effect of tensile DINP contents on tensile strength and tensile modulus

In flexible and semirigid formulations of PVC foam, plasticizers are key ingredients, although other compounding ingredients are also extremely important. Plasticizers impart flexibility and play an important role in heat processing by reducing the viscosity of the molten material to insure good flow properties. In general, at a higher concentration plasticizer (more than 15-20%) the materials become softer and tougher, with a lower tensile strength, a lower modulus, and a higher elongation at break and a higher impact strength (14). However, it was also discovered that lightly plasticizer compounds are more rigid and brittle at a low temperature than unplasticizers ones because of the phenomenon termed antiplasticizers (14). The effect of the plasticizer concentration on the tensile strength at yield for obtained PVC foam is shown in Figure 5.16.

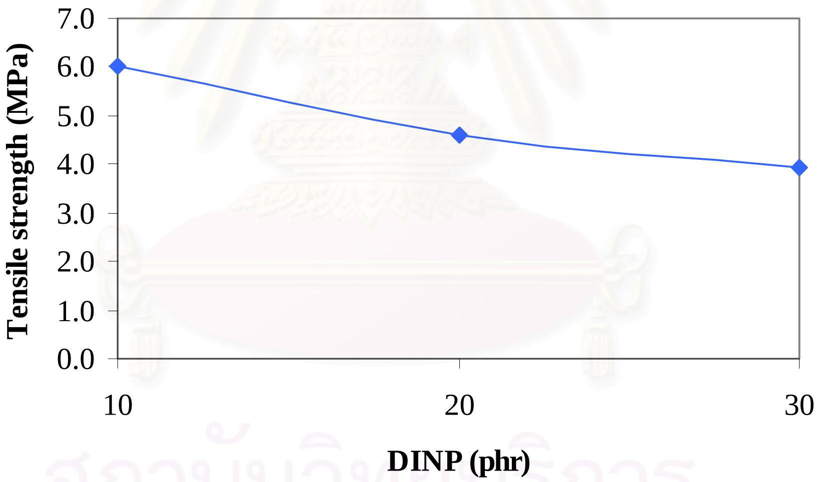


Figure 5.16 Relationship between DINP and tensile strength

Figure 5.16 shows relationship between DINP contents and tensile strength. It is found that DINP contents increased with a decrease in strength since DINP acts as a plasticizer to soften PVC foam. Although, DINP could help lowered process temperature but it also promote a reduced strength. Thus, addition of DNIP content of 10 phr is suitable to provide with rigid foam extrusion process.

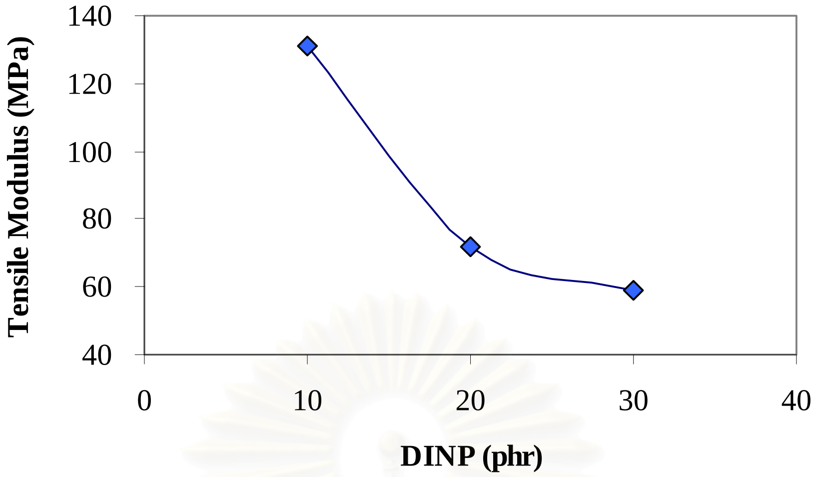


Figure 5.17 Relationship between DINP and tensile modulus

Figure 5.17 shows the tensile modulus for PVC foam with various concentration of DINP. As in the case yield strength, a small amount of DINP in PVC compound lead to an increase in tensile modulus because of antiplasticization. At higher plasticizer contents, the tensile modulus decrease significantly as a result of the plasticization effect.

5.3.3 Bending test

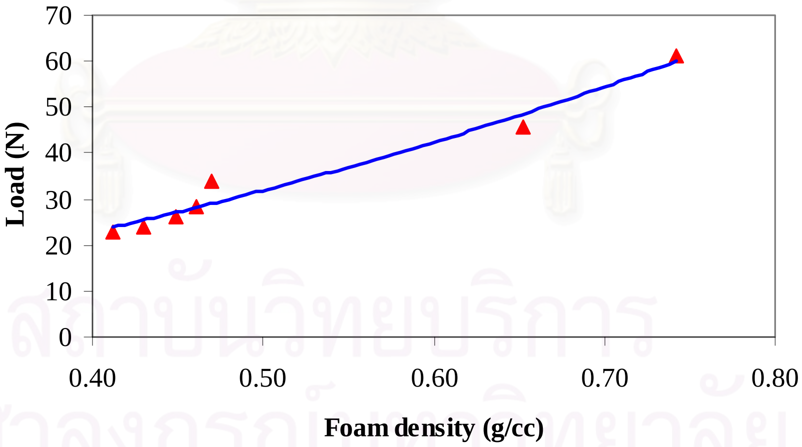


Figure 5.18 Relationship between foam density and maximum load

Figure 5.18 shows relationship between foam density and maximum load used for bending test. It should be noted that maximum load increased with an increase in the density of PVC foam. The relative thickness of cell walls increases with rising foam density. A lower foam density cell sizes are big cells and its maximum load becomes worse.

CHAPTER VI

SUMMARIES AND RECOMMENDATIONS

In this study, the effects of chemical blowing agents, nucleating agent on the density of extruded PVC foam using the twin screw extruder were investigated. The density of PVC foam was controlled by varying the AZ and $NaHCO_3$ content and the exit die temperatures. This experiment conducted in this study lead to the following conclusion:

1. The screw speed of 96 rpm which provide the lowest mass flow rate but the longest residence time could provide the compounded foam with the lowest density.
2. A high temperature promotes severe cell coalescence and reduces the cell population density.
3. Higher AZ content could promote much more generation of microbubbles within the polymer matrix. However, with the excess amount of AZ, high pressure arose gas microbubbles could destroy cell wall.
4. The AZ content could help decrease the foam density with less significantly because of the promoted cell coalescence.
5. Cell coalescence is the strongest cell morphology-deteriorating factor in the processing PVC foam.
6. Compared with AZ, $NaHCO_3$ is considered as a chemical additive which could provide few yield of microbubbles, resulting is higher foam density.
7. AZ is more suitable than $NaHCO_3$ to provide microcellular pore in the PVC foam matrix.
8. Addition of DNIP content of 10 phr is suitable to provide with rigid foam extrusion process.
9. For the prepared PVC with relatively low density, its tensile strength becomes worse because uniform and close-cell structure is hardly achieved.

Recommendations for future studies

1. Blending PVC resin with other polymer, such as polyurea, for improving cross-linking should be studied.
2. Cross-linking agents for improving bonding between PVC and other materials should be further investigated. For example, silane, which is known to be an abundant cross-linking agent for PVC, might be worth to use in future investigation.
3. After dry blending, polymer mixture should be compounded by twin screw extruder or two roll mill for improving solubility between PVC and additives.
4. It is interesting to study the effect of the longer residence time by increasing viscosity of the blended polymer and changing extruder with longer L/D to improve mixing conditions of compounded polymer.
5. Other additives for improving melt strength at high temperature should be found out.

REFERENCES

1. Klempner, D., and Frisch, K.C. Handbook of Polymeric Foams ad Foam Technology. Munich Vienna, New York : Hanser, (1991).
2. Lee, S. T. Foam Extrusion Principles and Practice. Lancaster Basel : Technomic Publishing, (2000) : 47-148.
3. Oshima, M. Control and Design Problems in Material Processing How can Process Systems Engineers Contribute to Material Processing IFAC Dynamics and Control of Process System. Elsevier, (2001).
4. Throne J.L. Thermoplastic Foams. Hinckley OH, Sherwood Publishers, (1996) : 11
5. Xu, X., Park, C. B., Xu, D., and Pop-Iliev, R. Effects of Die Geometry on Cell Nucleation of PS Foams Blown With CO_2. Polymer Engineering and Science. 43 (July 2003) : 1378-1390.
6. Liu, F., Liu, G., and Park, C.B. Rotational Foam Molding of Polypropylene with Control of Melt Strength. Advances in Polymer Technology. 22 (2003) : 280–296.
7. Nass, L.I. Encyclopedia of PVC. 2 nd ed. (n.p.): Dekker (1986): 49.
8. Murphy, J.. Additives for Plastic Hand Book. Elsevier Advanced Technology, (1996) : 204.
9. Tomasko, D.L., Li, H., Liu, D., Han, X., Wingert, M.J., Lee, L. J., and Koelling, K.W. A Review of CO_2 Applications in the Processing of Polymers. Ind. Eng. Chem. Res. 42 (2003) : 6431-6456.
10. Park, C.B., and Suh, N.P. Filamentary Extrusion of Microcellular Polymers Using a Rapid Decompressive Element. Polymer Engineering and Science. 36 (1996) : 34-46.
11. Abu-Zahra, N.H. Neural Network Approach to Density Control of Rigid PVC Foam in Extrusion Process. Polymer processing XVIII. (2003) : 122-126.
12. Guo, M.C., and Peng, Y.C. Study of Shear Nucleation Theory in Continuous Microcellular Foam Extrusion. Polymer Testing. (2003) : 705-709.
13. Hironori, O., Takahiro, U., Keisuke, M., and Taro, E. Dynamics of CO_2 molecules confined in the micropore Applied surface science. (2005).
14. Matuana, L.M., Park, C.B., and Balatinecz, The effect of Low Levels of Plasticizer on the Rheological and Mechanical Properties of Polyvinyl Chloride/Newsprint-Fiber Composites. Journal of Vinyl and additive Technology. 3 (1997) : 265-273

APPENDICES

APPENDIX A

INTERNATIONAL CONFERENCE

Regional symposium on Chemical Engineering (RSCE) 2004 on 1-3 December 2004 in Bangkok, Thailand

Batch process for preparing microcellular PVC foam using supercritical carbon dioxide

Chrisda Perin[*,1], Surat Areerat[2], Wiwut Tanthapanichakoon[1] and
Tawatchai Charinpanitkul[1]
[1]Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Bangkok THAILAND
[2]Department of Chemical Engineering, Faculty of Engineering,
King Mongkut Institute of Technology Ladkrabang, Bangkok THAILAND
[*]Corresponding E-mail: periny75@yahoo.com

Abstract

This research focuses on investigating methods of preparing microcellular PVC foam, with the ultimate aim of reducing import dependence. The so-called microcellular PVC foam will be prepared from compounded PVC with the assistance of a physical blowing agent - supercritical carbon dioxide.

In the batch foaming process carbon dioxide is fed into a chamber under high pressure conditions to maintain its supercritical stage; whilst keeping the temperature higher than T_g of compounded PVC. After leaving for a sufficient time period, carbon dioxide will dissolve into the polymer matrix, as much as its solubility in the compounded PVC. Then the high pressure chamber will be depressurized quickly leading to nucleation of small bubbles of carbon dioxide in the polymer matrix. Effects of influential factors including foaming temperature and pressure as well as saturation time will be investigated. Furthermore, influence of nano-calcium carbonate as a nucleating agent, on bubble density and bubble size, will also be investigated in term of suitable amount for PVC compounding. It is expected that the

microcellular PVC foam obtained will exhibit the microcellular pore with an average size about 10 micron and high porosity.

Keywords; Microcellular, PVC foam, Supercritical carbon dioxide, Batch process

Introduction

Thailand has imported PVC foam for producing various sport equipments, especially a surf board. Many companies in Thailand produced PVC foam on variously applications but which can not produce PVC foam to be used with surf board. PVC foam with in the part of surf board will be low density and high strength because which be used for floating on the ocean, and impacted by winds and waves. PVC foam of the surf board is produced in the range of density: 0.8-1.1 g/cm^3, while solid PVC is the density of 1.4 g/cm^3. PVC foam is extensively used for such application because of its outstanding properties such as low density but high strength, good weather resistance, good electrical insulation performance, high elastic modulus and excellent chemical resistance1). Therefore, this research has focused on the development of foaming process technology for the ultimate goal of import reduction.

The foaming process could be classified into two schemes, which are batch foaming and continuous foaming. The continuous foaming has processed within extruder and batch process has processed by high pressure reactor. In this experimental study, first batch process has been taken into account because it is easy to precisely control its operating parameters. Carbon dioxide is used for blowing agent because it has non-toxic, non-flammable and free of ozone depletion. Carbon dioxide is injected in chamber under the condition of “supercritical fluid”, which exists beyond 7.37 MPa and 31.1 °C2). In such condition carbon dioxide has much higher dissolubility in the polymer matrix. But when the temperature and/or pressure are intentional decreased to the point lower than the critical point, dissolved carbon dioxide will change to the normal state of which solubility is very low, and resulting in the formation of fine bubbles in the molten polymer matrix.

Based on the above concept, microcellular foaming process generally consists with three steps. First polymer/saturation process, bubble nucleation and bubble growth. Characteristic cell morphologies are on the order in the range 0.1-10 micron and bubble density having in the range 10^9-10^{15} cells/cm^3. Supercritical technique enhances to produce foam having uniform bubbles size, micro bubbles size and high bubbles density. Characteristics of foams are monitored with scanning electron microscope (SEM) micrographs to estimate an average bubble size and distributed bubbles. For concept of fundamental of the batch process which will be applied to be the continuous process with twin screw extruder.

Experimental

Materials

The polymer used in this experiment is Suspension PVC with K value of 58 supplied by Vinythai Public Company Limited. Diisononyl phthalate (DINP) is used as a plasticizer while Nano-calcium carbonate is used as a nucleating. Pure carbon dioxide is used as a blowing agent.

Sample preparation

1. PVC was compounded with plasticizer and nucleating agent in a high turbo speed mixer. The initial mixing was set at the temperature of 55 °C and then, mixed PVC resin and additives for 10 minutes. The concentration of DINP was fixed at 10 phr. After this, the compound mixtures were mixed again in twin screw extruder. And then, PVC compound have been cutted, which is thickness of 2 mm.

2. The samples were put in the high pressure vessel. It was flushed with carbon dioxide for 3 times to expel the air out. Then it was filled with carbon dioxide to 100 bars and the required temperature. This condition is held for 3 hours, after that it is depressed quickly to atmospheric pressure. Finally, the sheets are cooled down and taken out for characterization.

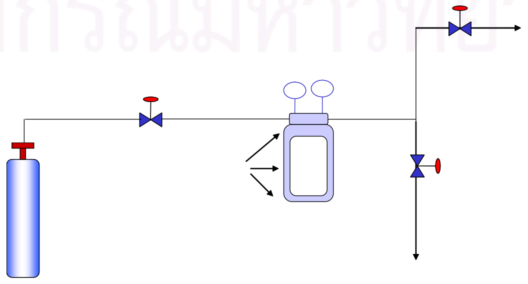


Figure Schematic of a batch microcellular foaming process

Formulations

The research uses a regular rigid foam formulation in table. Calcium carbonate is nucleating agent to enhance the bubble density into the polymer.

Table the ingredients of PVC foam

Function	Chemical type	phr
Suspension PVC resin	K value of 58	100
Plasticizer	DINP	10
Wax	PE wax	2
Stabilizer	Cd/Ba/Zn	3
Nucleating agent	$CaCO_3$	varied

Characterization of Foam Structure

A scanning electro microscope (SEM) analysis was performed to characterize the PVC foam sample. The PVC foam sheets were froze in liquid nitrogen and split to notice the surface, and then gold-coated for improved conductivity.

For the calculation of cell density with following equations:

$$V_f = 1 - \frac{\rho_F}{\rho} \tag{1}$$

$$N_o = \left(\frac{nM^2}{A}\right)^{3/2} \left(\frac{1}{1 - V_f}\right) \tag{2}$$

where the symbols of equations:

V_f is the void fraction, ρ_F is the density of foamed sample, ρ is the density of unfoamed sample, N_o is the cell density per unit volume of the original unfoamed polymer, n is the number of bubble in micrograph, M is magnification factor of the micrograph, A is area of the micrograph. The densities were determined according to ASTM standard D792 by an Archimedes water displacement technique by:

$$\text{Density} = 0.9975 \left(\frac{M_a}{M_w}\right) \tag{3}$$

Where M_a and M_w are the weight of sample in the air and measured whilst immersed in the distilled water.

Experimental preliminary results and discussion

The effect of foaming temperature in batch foaming process was first investigated. It was not found that the cellular pore was formed at 150 °C while pressure was fixed at 10 MPa, and saturation time of 3 hours. The cellular pore is checked by measuring changed-density and a scanning electro microscope (SEM) analysis. This could be implied that at lower saturation time of 3 hours, carbon dioxide could not dissolve into the molten polymer to the saturation. So, the saturation time of gas could be increased for enhancing the bubble into the polymer.

Acknowledgment

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References

1. Baldwin, D.F., Tate, D.E., Park, C.B., Cha, S.W., and Suh, N.P. (1994) Microcellular plastic processing technology (1), Seikei-kakon, **6**(3): 190.
2. Park, C. B., Behravesh, A. H., and Venter, R. D. (1998) Low density microcellular foam processing in extrusion using CO_2, Polymer engineering and science, **38**(11): 1813.
3. Matuana, L.M., Park, C. B., and Balatinecz, J.J. (1998) Structures and mechanical properties of microcellular foamed polyvinyl chloride, Cellular polymer, **17**(1): 1-16.

APPENDIX B

EXPERIMENTAL DATA

Table B-1 Chemical blowing agent calculation

T_{room}	Room temperature (K)	303
T_C	Crystalline temperature (K)	383
φ_{STP}	gas yield (ml/g)	220
φ	gas yield (ml/g)	322
ρ_S	solid density (g/cc)	1.25
ρ_F	foamed density (g/cc)	As shown in table B-2
β	volume expansion ratio (-)	1.79
$\%CBA$	Chemical blowing agent	As shown in table B-2

Table B-2 The relationship between foam density and CBA content

ρ_F	$\%CBA$ (By weight)
0.9	0.68
0.8	0.73
0.7	0.79
0.6	0.88
0.5	0.99
0.4	1.17
0.3	1.47
0.2	2.06
0.1	3.83

Table B-3 AZ contents and foam density

The exit die (cylindrical shape) temperature of 190 °C, and the screw speed of 96 rpm

AZ (phr)	Density (g/cc)
0	1.25
2	0.87
4	0.76
6	0.61
8	0.50
10	0.46

Table B-4 $NaHCO_3$ contents and foam density

The exit die (rectangular shape) temperature of 160 °C, and the screw speed of 96 rpm

$NaHCO_3$	Density (g/cc)
0	1.250
12	1.036
14	0.998
16	0.993
18	0.968

Effect of K value on foam density

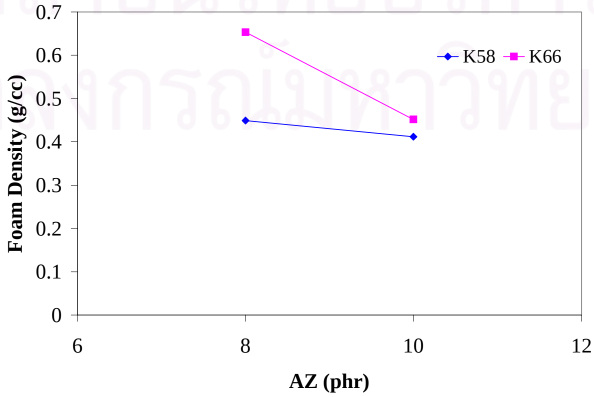

Figure B-1 Effect of K value on the densities of PVC foam at exit die (rectangular shape) temperature of 180 °C

Figure B-1 presents K value of 58 and 66 at 8 and 10 phr of AZ. The density of PVC foam increases with an increase K value because K value of 66 is molecular weight higher than K value of 58. The molecular weight or K value indicates a viscosity of PVC. A lower viscosity, the bubbles are easy to growth and form. This study is indicated K of 58 which promotes obtained low density of PVC foam. Thus, K value of 66 is not suitable to be used in low density of PVC foam process.

Table B-5 Formulation of PVC foam

Chemical Type	**Function**	**Content (phr)**				
		1	**2**	**3**	**4**	**5**
Suspension PVC resin (solid), K of 58	Polymer	100	100	100	100	100
PE wax(solid)	Lubricant	2	2	2	2	2
DINP (liquid)	Plasticizer	10	10	10	10	10
Cd/Ba/Zn (liquid)	Heat stabilizer	3	3	3	3	3
Tacl (solid)	Cell nucleating agent	4	4	4	4	4
Ba-Zn BL 125 (solid)	Activator	**12**	**14**	**16**	**18**	**20**
ZnO (solid)	Activator	**12**	**14**	**16**	**18**	**20**
Azodicarbonamide (solid)	Blowing agent	**12**	**14**	**16**	**18**	**20**

Adding amount of ZnO, range from 10 to 20 phr, which affects mechanical properties due to too much ZnO. Too much AZ content destroys the cell structure and is direct result of too high pressure gas. Although, ZnO help activate AZ to decompose at a low temperature but ZnO promotes poor mechanical properties. Thus, ZnO should add amount of ZnO in the range from 1 to 4 phr.

Table B-6 Mechanical properties of PVC foam from DIAB Company

Properties	**Unit**	**H100**	**H130**	**H200**
Density, nominal	kg/m^3	100	130	200
Tensile strength ASTM 1623	MPa	3.1	4.2	7.0
Compressive strength ASTM D1621	MPa	1.7	2.6	4.5

Effect of nano-$CaCO_3$ content on foam density

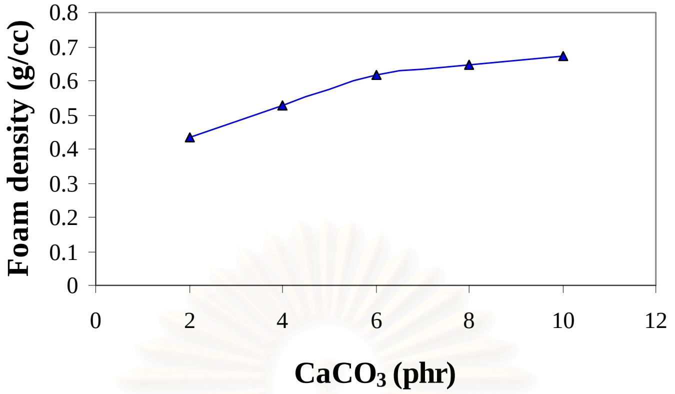

Figure B-2 Effect of $CaCO_3$ content on the densities of PVC foam at exit die (rectangular shape) temperature of 185 °C, K value of 66, and 4 phr of AZ content.

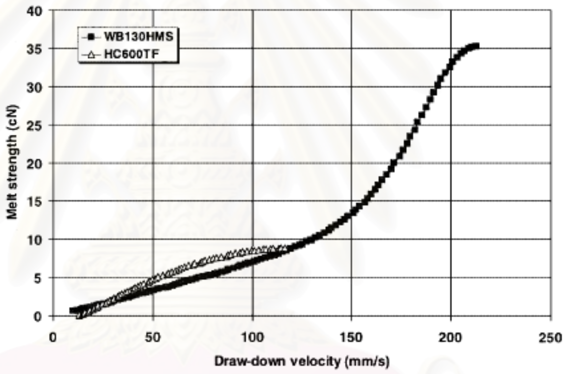

Figure B-3 Melt strength and melt extensibility of polypropylene melts

The melt strength and melt extensibility of these materials can be seen from Figure B-3, both measured by using the so-called Rheotens method (Goettfert Rheotens; 230 °C; L/D = 30/2 mm; 120 mm/s2 acceleration): Here, a melt strand is extruded through a capillary die and pulled down with an increasing velocity (at constant acceleration) by using a pair of wheels, and the force is measured till rupture occurs. ***The maximum force is called the melt strength*** and the draw-down velocity at break is a measure of melt extensibility. Obviously, the linear polypropylene (HC600TF) has a low level of melt strength and melt drawability. On the contrary, the long-chain branched propylene polymer (WB130HMS) shows a very high melt strength in combination with an almost doubled melt extensibility. The nonlinear increase in force indicates strain hardening, which is well known from long-chain branched materials, such as low-density polyethylene.

VITA

Mr. Chrisda Perin was born on July 2, 1975, in Chiangmai, Thailand. He gradated from high school at Chonradsadornumrung School in 1993. He entered Suranaree University of Technology, Northern East Thailand in May 1994, and received his Bachelor Degree of Chemical Engineering from School of Engineering in 1998. And then, he has worked as a active officer of military in Chachengsao for one year. He went back to join the Polymer Engineering, as a research assistance, Suranaree University for six months. In April 2002, he has worked as auditor of Cleaner Technology, Thailand Environment Institute, Bangkok, Thailand.