EXPERIMENTAL ANALYSIS OF POLYMER NANOCOMPOSITE FOAMING USING CARBON DIOXIDE

DISSERTATION

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ABSTRACT

Currently, the polymer foam industry is testing carbon dioxide (CO2) for its applicability as a physical blowing agent (PBA) due to the phase-out of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) according to the Montreal Protocol[1]. CO2 is one of most promising alternatives because it is environmentally safe, non-toxic, non-flammable and inexpensive. However, CO2 has its drawbacks, such as low solubility and high diffusivity in comparison with other blowing agents. Therefore CO2 sometimes leads to foams with higher density and/or poor surface quality, and almost always requires higher operating pressures than other agents. Currently, the concept of adding nanoparticles to a polymer is being investigated around the world as one possible way to overcome these problems. Polymer blends can be another approach.

In general, generating foams using a PBA includes saturating the polymer with the PBA at a certain pressure and temperature via thorough mixing. Then the mixture is subjected to a sudden thermodynamic change (temperature increase or pressure drop), resulting in the escape of the PBA and formation of the cellular structure. The typical foaming process includes cell nucleation, cell growth, and cell stabilization, the first two being the focus of this study. In the foaming process, several operating variables, e.g.
temperature, pressure, pressure drop rate, and material related properties, e.g. solubility, diffusivity, and viscosity are crucial. In this study, primary attention was given to the effects of the material related properties on cell nucleation and cell growth. The reduction of gas solubility (or supersaturation) is the driving force of the foaming process. Diffusivity as well as viscosity affect both cell nucleation and growth.

Two equations of state (EOS), Sanchez-Lacombe (S-L) EOS and perturbed chain statistical associating fluid theory (PC-SAFT), were used to model the solubility and also phase boundaries (binodal and spinodal curves). Nucleation is a very complex phenomenon in physical foam processing and its experimental and theoretical studies cannot provide sufficient information to have a clear picture of the nucleation phenomenon. Proposed scaling functions provide a possible way to calculate the energy barrier in the nucleus formation, $W$. Cell nucleation rate data were extracted from the paper by Guo [2] et al. and also by our experiments. From the phase boundaries predicted, several parameters in the nucleation theory, e.g. $\gamma$, $\Delta P$, and $W$ were calculated based on the experimental data. Several sets of $W/W^{cl}$ and $\Delta \mu/\Delta \mu_s$ were calculated. The initial slope of the possible scaling function was calculated by the diffuse interface theory. A possible scaling function (exponential decay type equation) was correlated to describe the relationship between $W/W^{cl}$ and $\Delta \mu/\Delta \mu_s$ based on the calculation from experimental data. It provided insight for the connection between the phase boundary and the complex nucleation behavior.
Shear viscosity of polymers and nanocomposites were measured by parallel plate rheometry under a nitrogen blanket. Shear viscosity of polymers and nanocomposites under high pressure CO\textsubscript{2} were studied via unique modified high pressure Couette rheometry. The effects of nanoparticles on shear viscosity of polymer w/ and w/o CO\textsubscript{2} were compared.

The permeability coefficient, defined as the product of the solubility coefficient and diffusivity, of CO\textsubscript{2} and water vapor in polymer nanocomposites and foams were measured near ambient temperature and pressure. The effects of nanoparticle and foam morphology on permeation were studied. The results provided valuable feedback on the design of polymer nanocomposites and foams, as well as an approximation for relative values of diffusivities in polymers under foaming conditions (higher temperatures and pressures).

To gain more insight on the early stages of the foaming process, \textit{in-situ} observation of batch foaming and a quenching method were used to study foams with different cell growth times. In addition, the quantitative cell nucleation rate was measured by our novel experimental setup.

Based on these experimental studies (rheology and permeation, \textit{in-situ} observation and quantitative measurement) and modeling (phase boundary prediction and scaling function correlated), a deeper and more comprehensive understanding of polymer and nanocomposite foaming was achieved.
Carbon nanofibers (CNFs) and activated carbon (AC) were used as additive/nucleation agents in polystyrene extrusion foaming. Both fillers showed promising application in insulation foams based on foam density, thermal conductivity, IR transmission, thermal stability, and compressive modulus. In addition, water acted as a co-blowing agent in the PS/wet AC foaming process.
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CHAPTER 1

INTRODUCTION

1.1 Plastic foams

Plastic foams are widely used in applications such as insulation, cushions, shock- and sound-absorbents, and scaffolds for cell attachment and growth [3-5]. In general, plastic foams consist of a minimum of two phases, a polymer solid phase and a gas phase derived from a blowing agent. There may be more than one solid phase present, such as polymer blend and fillers [5]. A foaming system typically includes the polymer, foaming agent, nucleating agents and other additives. These components are described in the following in more detail.

A wide variety of polymers are used for foaming applications, such as polyurethane (PU), polyisocyanurate (PIR), polystyrene (PS), polyolefin, poly (vinyl chloride) (PVC), epoxy, and so on. According to the 2001 U.S. polymer foam market report, PS foam possesses about 26% of the market, only second to PU (53%) [6]. PS foams are used in a variety of applications, such as cushioning, thermal insulation, packaging, structural components, and marine applications [5]. As one of the most...
versatile thermoplastic resins available for the production of low-cost plastic foams, PS is the major polymer in this study.

Generally, there are two types of foaming agents: chemical blowing agents (CBAs) and physical blowing agents (PBAs). CBAs are individual compounds or mixtures that release gases (such as N₂, CO₂) as a result of chemical reactions and most CBAs are solids. CBAs are mostly used in foaming of PU. PBAs are compounds that release gases as a result of physical processes, e.g. evaporation, desorption, at elevated temperature or reduced pressure. Most PBAs are volatile chemicals such as chlorofluorocarbons (CFCs), hydrocarbons (HCs)/alcohols, and inert gases (CO₂, N₂, argon, water). Among them, CFCs were most widely used in the foam industry. For example, CFC-12 (CCl₂F₂) was used in PS foaming and CFC-11 (CCl₃F) was used in PU foaming. However, due to the depletion of the ozone layer, the use of CFCs or their derivatives such as hydrochlorofluorocarbons (HCFCs), will be illegal in the US starting in 2010.

To obtain cells with controlled structure and uniform distribution, nucleating agents are necessary additions to the foaming formulation [5]. Talc, graphite, silicon oxide, and titanium oxide are common nucleating agents used in the foam industry. Nucleating agents can serve as “hot spots” and substantially reduce the energy required for the formation of nucleation centers for a gaseous phase. Additives are usually added to either reinforce the foams or in other cases achieve special functions, such as flame retardancy.
The gas phase in a plastic foam is usually distributed in voids called cells or bubbles. In this context “cell” and “bubble” are interchangeable. The plastic foam can be classified according to different standards. For example, if the bubbles are interconnected, it is termed open-cell. If the bubbles are discrete and the gas phase of each is independent of the other bubbles, it is a closed-cell foam. In our study, all the foams have closed-cell structure unless otherwise stated.

According to the size of the cells, polymer foams can be classified as macrocellular (>100μm), microcellular (1-100 μm), ultramicrocellular (0.1-1 μm), and nanocellular (0.1-100 nm) [7]. Only the first two types will be studied here.

1.2 Carbon dioxide in thermoplastic foams

Currently, three types of material have the potential to replace CFCs and HCFCs. The first are hydrofluorocarbons (HFCs). They have no known effects on the ozone layer. However, HFCs are expensive and still greenhouse gases and some HFCs are flammable. The second are hydrocarbons/alcohols. They are considered fire hazards due to their high inflammability and volatile nature. The third type are inert gases, e.g. H₂O, CO₂, and N₂. CO₂ has higher solubility in polymers than the other two and the supercritical state of CO₂ (31°C, 7.38 MPa) is easy to reach. A particularly attractive and useful feature of supercritical CO₂ (ScCO₂) is that it has a more liquid-like density, and subsequent solvation strength, while possessing transport properties, i.e., viscosities and diffusivities, that are more like gases. These properties can be “tunable” because the density of CO₂
can be easily tuned by adjusting temperature and pressure [8]. It can be obtained from existing industrial processes without further contribution to the greenhouse effect.

In addition, ScCO₂ is well known to swell and plasticize many amorphous polymers. It can significantly reduce the glass transition temperature (\( T_g \)) and viscosity of the polymer matrix [9]. This feature can be utilized in the polymer foaming process. For example, in continuous extrusion foaming, high temperature is usually applied from the hopper to the gas injection point to ensure a complete melting of the polymer. Once the gas is injected, the barrel temperature can be decreased due to the reduction of the viscosity. This decreasing temperature profile will benefit both the processing cost and the final foam structures. In summary, of all these potential alternatives, CO₂ is the most preferable.

Extensive research [10-15] has been carried out in polymer foaming with CO₂ during the past several decades. CO₂ foaming has been used in industry for low-value foam products (e.g. packaging) while its applications in producing high-value or high-strength foams are still in progress. CO₂ is being explored for products ranging from low-density insulation (<0.04 g/cm³) to high-density structural foams (~0.7 g/cm³). Typical microcellular foams exhibit higher mechanical strength-to-weight ratio than common structural foams. The challenges of CO₂ as a foaming agent are dimensional instability during the foam-shaping process and poor control of cell size and density. Some of these result from the high diffusivity of CO₂, compared to CFCs, out of the foam.
1.3 Polymer nanocomposite foams

Polymer nanocomposites were developed to overcome some drawbacks of CO$_2$. Polymer nanocomposites refer to a class of reinforced polymer with a low percentage of well-dispersed nanoparticles. A small amount of well-dispersed nanoparticles in the polymer may serve as nucleation sites to facilitate the cell nucleation process. The presence of nanoparticles may enhance mechanical and physical properties, the heat distortion temperature, and fire resistance of polymer foams [7]. In addition, Plate-like nanoparticles can also reduce gas diffusivity in the polymer matrix.

Nanocomposites usually refer to composites in which at least one dimension of the filler is on the order of a few nanometers. They include the use of three different types of nanoparticles [7]. The first type is platelet-like with a thickness in the nanometer range and lateral dimensions in the range from several hundred nanometers to a few micrometers. Clays are a good example in this category. Two types of organically modified nanoclays, a commercially available Cloisite 20A (20A for short) and custom modified MHABS (2-methacryloyloxyethylhexadecyldimethylammonium bromide) [16] were used to fabricate nanocomposites in this work. The second type has an elongated structure (fiber or tube shaped) with two dimensions at the nanometer scale, such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs). The third type has all three dimensions in the range of nanometer, such as spherical silica particles. In addition, activated carbon (AC) is a highly porous particle with a very high internal surface area (1000–3000 m$^2$/g). Although AC is not a nanoparticle, its pores are in the nanometer
range (1–10 nm). It has excellent adsorptive property for organic molecules and very good IR absorption characteristics. It was also used as an additive in polymeric foams. In this study, PS nanocomposites were the focus and four additives (e.g. 20A, MHABS, CNFs, and AC) were used.

Typically, three approaches have been adopted to synthesize polymer nanocomposites: solution blending, melt blending, and *in-situ* polymerization [7]. In solution blending, a solvent or solvent mixture is used to disperse the nanoparticles and dissolve the polymer matrix. Ultrasonication is commonly used to improve dispersion. The nanoparticles can be disaggregated in a good solvent due to stronger interaction between the solvent and nanoparticles than the van der Waals force that stacks the layers together. But an appropriate solvent is not always easy to select. Instead of using the solvent as the medium, nanoparticles can be directly mixed with a molten polymer by an extruder. However, strong shear force tends to break single fibers (e.g. CNFs) into many shorter pieces, which deteriorates the properties where the high aspect ratio of the particle is important. In these two methods, limited interaction between polymer chains and nanoparticles leads to limited polymer chain penetration, resulting in an intercalated structure. Third, nanoparticles can be mixed with the monomer before polymerization takes place in *in-situ* polymerization. In general, nanoparticles then have a better dispersion in the polymer matrix, resulting in an exfoliated structure. In our study, PS+20A and PS+CNFs nanocomposite and PS+AC composite were prepared by melt blending. Exfoliated PS+MHABS nanocomposite was synthesized by *in-situ* polymerization.
1.4 Polymer blend foams

A polymer blend is defined as a mixture of two or more polymers. However, it is a frequent industrial practice to add a small quantity of a second polymer to modify the processability of the base material [17]. Polymer blend foams have been used to accomplish a wide range of objectives. For example, one objective was to use a second polymer phase to form open cell foams. Lee et al. used either PP [18] or PS [19] to generate open cell PE foams. Park et al. [20] studied the open-celled foaming extrusion process with low-density polyethylene (LDPE) and LDPE/PS blends. They pointed out that the basic strategy for achieving a high open-cell content is to induce a hard/soft melt structure with crosslinking and to foam this non-homogeneous melt structure. The hard sections formed by crosslinking assist in maintaining the shape of each cell and the overall foam structure, while the soft sections easily open up the cell walls during cell growth. Since too hard a polymer matrix would adversely affect cell opening, an optimum amount of crosslinking and processing temperature are two key parameters to achieve a high open-cell content.

Taki et al. [21] studied the foaming of polyethylene glycol (PEG)/PS blends. In their study, the foam of PEG/PS blends showed a unique bimodal (large and small) cellular structure, in which the large-size cells embraced a PEG particle. They concluded that the differences in the transport properties, morphology of the blend, and CO2-induced viscosity depression are the control factors for creating this unique bimodal cellular structure in PEG/PS blends.
Han et al. [22] studied CO₂ foaming based on PS/PMMA (poly(methyl methacrylate)) blend and nanoclay. PMMA and nanoclay composite was blended as a dispersed phase with PS in a twin-screw extruder. The mixture was then batch foamed with supercritical CO₂. It was found that the cell density of foams based on the blend was higher than that based on the weighted average of the two pure polymer components at the same foaming conditions, demonstrating the enhancement of foaming by polymer blends. An interesting result was that the cell size decreased and the cell density increased with the increase of the PMMA domain size. The authors posed a hypothesis that large PMMA domains serve as a CO₂ reservoir and the nucleation in the PS phase was enhanced by the diffusion of CO₂ from the PMMA phase to the PS phase; on the other hand, very small PMMA domains could not function as CO₂ reservoir, so they were not able to facilitate nucleation. They also observed a much higher cell density and smaller cell size when nanoclay was located at the interface of the PMMA and PS domains due to the heterogeneous nucleation.

In general, the use of polymer blends in the foaming process can improve foaming processability by increasing strain hardening and other rheological properties [23]. For immiscible polymer blends, interfaces or dispersed domains may serve as nucleation sites. Through the adjustment of blend composition, the rheological properties, the absorption of the foaming agent, the open/closed cell content, and the mechanical strength of foams can be manipulated [22].
In this study, we focused on the foaming of an immiscible polymer blend PS/PMMA (PMMA was the dispersed phase and PS was the continuous phase) to explore heterogeneous nucleation.

1.5 Cell nucleation and growth

The mostly widely used method of producing foams involves dispersing a gas throughout a fluid polymer phase and stabilizing the resultant foam. The foam is, in most cases, expanded by increasing the bubble size before stabilizing the system. Thermoplastics are formed first as solids, then melted to provide the fluid phase, foamed, and then cooled to solidify and thus stabilize the foam. On the other hand, thermosetting plastic foam systems are foamed while only partially reacted and still fluid, followed by curing to the thermoset state to stabilize the foam. Only thermoplastic foaming will be discussed in this study.

In general, the foaming process comprises three fundamental steps [24]. These are cell nucleation, cell growth, and cell stabilization.

In the context of foaming, cell nucleation is the formation of a new gas phase from a metastable melt phase, requiring an activation energy barrier to be surmounted to induce the phase separation. Cell nucleation can be classified into homogenous nucleation and heterogeneous nucleation. Heterogeneous nucleation is typically thought to occur at the interface of the polymer and additive or at microvoids in the polymer. The activation energy barrier is smaller for heterogeneous nucleation than homogeneous
nucleation. That is one reason nanoparticles can enhance nucleation. Nucleation can only occur when a polymer melt is supersaturated with a blowing agent. Such a supersaturated state can be achieved either by a quick pressure drop or temperature increase. Cell nucleation is a complex process and is challenging for both experimental and theoretical studies.

After nucleation, the cell will grow by diffusion of gas into the cell until it eventually stabilizes or ruptures. Cell growth is also an extremely complex process involving coupled heat, mass, and momentum transport. Some important parameters are solubility and diffusivity of the blowing agent in the polymer matrix, shear and extensional viscosities of the polymer-blowing agent system and thermal conductivity of the components. Cell growth in polymer blends and polymer composites is even more complex. In addition, cell coalescence and cell coarsening can occur during the growth stage. The void fraction increases with cell growth, therefore, cells close to one another come into contact with each other to share a common wall. Further cell growth will make the wall thinner until it ruptures and the two cells become a bigger cell. This is cell coalescence. When two adjacent cells with different cell sizes coalesce, the pressure difference in the two cells caused by the size difference will force the gas to diffuse from the small cell to the big cell. Eventually, the small cell diminishes and the big cell becomes bigger. This phenomenon is referred to as cell coarsening [24]. Both cell coalescence and coarsening are undesired in most cases and deteriorate cell density and properties of the final foam product.
A common way to stop cell growth (i.e. cell structure stabilization) is to decrease the temperature to increase the viscosity of the polymer matrix. There are ways to increase the stability of cell wall to alleviate cell coalescence and coarsening, such as increasing the melt strength of the polymer matrix and adding nanoparticles. Cell stabilization is not a topic of this study.

Visualization of the foaming process is a common method to study the foaming process, including cell growth [2,25,26] and cell coalescence [27]. Usually a high speed camera is used to record the process of the cell growth. With the assumption that each nucleation site only produces one bubble, no cell coalescence happens, and all bubbles grow to a certain detectable size (usually in the magnitude of a micron), quantitative bubble nucleation and growth rate can be approximated by counting the number of bubbles and measuring the size of bubbles on the time-sequenced micrographs.

1.6 Foam processing

The foaming process can be carried out in a batch or continuous system. In batch foaming [28-30], pre-shaped samples are placed in a pressurized autoclave to achieve equilibrium, then cell nucleation and growth are induced by pressure release or temperature increase. Compared with batch foaming, a continuous extrusion process [11,12,14,15,31-33] is more attractive due to its higher productivity, easier control, and more flexible product shaping. For a typical extrusion foaming process, CO\textsubscript{2} is injected into the extruder barrel after melting the polymer resin, then the two components are
mixed together to get a single phase by screw rotation and sometimes an in-line mixer. Usually, nucleation is initiated by the large pressure drop in the die [34].

Fig. 1.1 shows the interrelation among parameters affecting final foam morphology for a continuous extrusion foaming process. For batch foaming, one of the main operating variables is the pressure release rate. In this study, we mainly focused on three material related properties, solubility and diffusivity of CO₂ in polymers and nanocomposites, and shear viscosity of polymers and nanocomposites under high pressure CO₂.

There is a sufficient amount of research on gas solubility in a variety of polymers, though the quantitative connection between the solubility and the fundamentals of the foaming process, such as cell nucleation rate, is still unclear. Obtaining diffusivity measurements of high pressure blowing agents in the polymer matrix is not an easy experiment, therefore comparably less data are reported in the literature. Similarly, due to difficulties of experimental techniques, very few data on rheology (e.g. shear and extensional viscosities) are reported for polymers with high pressure blowing agents, especially at low shear rates.

Solubility is one of the most important factors for foaming. The reduction of gas solubility is the driving force for foaming. Although the solubility depression is the driving force of foaming, solubility itself plays a very important role in foaming process. High gas solubility means a large amount of gas can be desorbed during the foaming process, favoring cell nucleation and efficient cell growth. Thus, a certain level of solubility is necessary to get low density foams. Experiments [35,36] show that cell
density, which is connected with nucleation rate, increases exponentially with increasing gas solubility. Therefore, high solubility is also essential to produce microcellular foams. However, all these comments or conclusions are only based on experimental results. The fundamentals that underline the quantitative relationship between solubility (or solubility reduction) and nucleation rate are still unclear. In this study, we explored the possible relationship between phase boundaries (including the solubility curve) and nucleation rate. Understanding nucleation rate is essential for relating process variables to foam morphology.

Diffusivity also affects both cell nucleation and growth. A higher diffusivity favors fast nucleation and therefore fine-cell structure, due to a large amount of blowing agent desorbed in a short period of time. Blowing agents with higher diffusivity escape from the polymer matrix faster, usually resulting in smaller cells and sometime cell rupture. In general, smaller molecules (e.g. CO$_2$) have higher diffusivity than bigger molecules (e.g. CFCs). Therefore, from the point view of diffusivity, CO$_2$ is suitable to produce foams with high cell density and foam density and CFCs are suitable for production of foams with lower cell density and foam density.

Rheological behavior of polymers in the presence of blowing agent mainly affects the cell growth. It is another important parameter for modeling and prediction of cell growth rate. In particular, the extrusion foaming process is largely controlled by the complex rheological behavior of the polymer-blowing agent mixture in the die and during shaping. Although the importance of rheology (shear rheology and extensional rheology) on the foaming process is widely recognized, the scientific literature in this filed is
relatively scarce, mainly due to technical difficulties. In this study, shear viscosity of polymers and nanocomposites under high pressure CO₂ was investigated.
Figure 1.1: Main parameters affecting final foam morphology for a typical continuous extrusion foaming process.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

Although there exists a vast literature on all aspects of polymer foaming, this chapter focuses on the following four topics most relevant to this dissertation: bubble nucleation and bubble growth, including theoretical and experimental studies; solubility of CO₂ in polymers, including experimental techniques and modeling by Equations of State (EOS); permeation of CO₂ in polymers and foams; and rheological behavior of polymers under high pressure CO₂.

2.1 Bubble nucleation and bubble growth

2.1.1 Bubble nucleation theories

In the area of polymer of foaming, cell nucleation is defined as the formation of a new gas phase from a metastable melt phase, requiring an activation energy barrier to be surmounted to induce phase separation.
In general, three methods may lead to phase separation: changes in pressure, temperature, and composition. The essential features of the pressure-induced phase separation (PIPS) can be depicted in Fig. 2.1 [37]. The binodal curve is the phase equilibrium curve, where the first composition derivative of the free energy vanishes (or the chemical potentials of both phases are equal). The spinodal curve defines the limit of metastability of a homogeneous phase [38]. For a binary mixture, it is a locus of points where the second composition derivative of the free energy vanishes. If the system is subjected to a shallow pressure quench and brought into the metastable region (path AB), the phases separate through the nucleation and growth mechanism; however, if the system is subjected to a deeper quench and brought into the unstable region (path AC), the phases separate via the spinodal decomposition mechanism. The nucleation and growth mechanism is almost always encountered in the polymer foaming process for reasons explained later.

Although a variety of theoretical models [39] have been proposed during the past decades, the Classical Nucleation Theory (CNT) is still among the most successful models for quantitative prediction of nucleation phenomena [40]. It was also widely used [35,41-48] to describe bubble nucleation in the polymer foaming process, though it seriously underpredicts the bubble nucleation events in polymer processing [44, Han, 1990 #243].

A brief description of classical nucleation theory is as follows [49,50]. The steady state nucleation rate $J_{ss}$ is given by

$$J_{ss} = J_0 e^{-\frac{W}{k_B T}},$$  \hspace{1cm} \text{(Eq. 2.1)}

where $J_n$ is the number of critical nuclei formed per unit time in a unit volume of the parent phase; $W$ is the reversible work of critical nucleus formation; $k_b$ is the Boltzmann factor and $T$ is the absolute temperature. By considering the dynamic process of the formation of a bubble, Blander and Katz [51] derived the expression of $J_o$ for bubble nucleation in liquids:

$$J_o = N \left( \frac{2\gamma}{\pi m B} \right)^{1/2},$$  

(Eq. 2.2)

where the prefactor $N$ is the number density of the liquid. In the polymer foaming process, it is the number density [44,46] of the blowing agent molecule in polymer-blowing agent solutions. $m$ is the mass of the gas molecule, $\gamma$ is the interfacial tension between the metastable parent phase and the new nucleating phase, and $B$ is a dimensionless constant.

In the nucleation process [52], $\alpha$ represents the metastable phase and $\beta$ represents the nucleating phase that has the same temperature and chemical potential as the metastable phase. Since $W$ appears in the exponent (Eq. 2.1), its accurate calculation is essential. The $W$ below is the exact expression derived by Gibbs:

$$W = \frac{16\pi\gamma^3}{3(\Delta P)^2},$$  

(Eq. 2.3)

Where $\Delta P = P^\beta - P^\alpha$, within $P^\beta$ is the pressure phase $\beta$ and $P^\alpha$ is the pressure of the phase $\alpha$.

Direct application of Eq. (2.3) is very difficult because $\gamma$ is unknown. The value of $\gamma$ depends strongly on the size of the critical nucleus, or the curvature of the critical
nucleus. Accordingly, the classical nucleation theory introduces an approximation through replacing $\gamma$ by the surface tension of the flat interface $\gamma_\infty$ (i.e. macroscopic interfacial tension), which is accessible experimentally, although still difficult for polymer-gas systems. With this approximation, the classical reversible work, $W^{cl}$, is expressed as [52]:

$$W^{cl} = \frac{16\pi\gamma_\infty^3}{3(\Delta P)^2}$$  \hspace{1cm} (Eq. 2.4)

The calculation of the reversible work of nucleation using this expression will bring significant error because of the approximation $\gamma \approx \gamma_\infty$. In addition, the measurement of macroscopic interfacial tension $\gamma_\infty$ is still difficult for polymer-gas systems because of the high viscosity and rheological characteristics of polymers [53]. Moreover, from thermodynamic considerations, the nucleation barrier is expected to go to zero at the spinodal [54]. $W$ vanishes at the spinodal because $\gamma = 0$ at this condition, while $W^{cl}$ does not because $\gamma_\infty > 0$. Nevertheless, scaling theorems discussed below may provide a connection between $W$ and $W^{cl}$ that will lead to better understanding of $W$ through calculation of $W^{cl}$.

Because of the several orders of error between the prediction of classical theory and experimental results, many researchers have made effort to understand nucleation at a molecular level by using computer simulation [55] and statistical mechanical density functional theory (DFT) [56]. However, until now, their ability to make quantitative predictions is still limited. Accordingly, many researchers pursued phenomenological approaches. For example, Gránásy [57] proposed the diffuse interface theory (DIT) for
vapor condensation and crystal nucleation. Recently, it was extended to bubble nucleation [58].

McGraw and Laaksonen [59] made an important progress by proposing the scaling theorem. They proposed that the displacement between $W^{cl}$ and $W$ is only a function of temperature. It constrains the departure from classical nucleation theory and can guide the construction of phenomenological nucleation theories. Talanquer [54], Kashchiev [60] and Kusaka [58] proposed scaling functions that are independent of the material and ensure thermodynamic consistency, i.e. the vanishing of the energy barrier $W$ at the spinodal. The scaling function proposed by Kashchiev [60] is:

$$\frac{W}{W^{cl}} = (1 - \xi)(1 + \frac{1}{2} \xi^2)^2 \quad (\xi = \Delta P / \Delta P_s),$$  \hspace{1cm} (Eq. 2.5)

where $\Delta P$ has the same meaning as in Eq. (2.3) and $\Delta P_s$ is the value of $\Delta P$ evaluated at the spinodal. $\xi$ can be considered as the degree of normalized supersaturation.

Another kind of phenomenological model may be found through the possible connection between the nucleation behavior and the phase diagrams. Ten Wolde and Frenkel [61] showed that the presence of a metastable fluid-fluid critical point could dramatically change the pathway for the formation of a crystal nucleus. And when close to this critical point, the free energy barrier for the crystal nucleation is strongly reduced, therefore the nucleation rate increases by several orders of magnitude. This research showed the connection between the phase diagram and nucleation behavior. Recently, Obeidat [62] studied nucleation rates of water and heavy water by equations of state. Two accurate equations of state were used to calculate the pressure difference between the new and old phases. Then the reversible work of critical nucleus formation was
evaluated. The temperature dependence of the nucleation rate predicted by this method was close to experimental results. Since the phase diagrams of polymer-gas systems can be predicted well by some equations of state, we propose to explore a possible connection (such as a scaling function) between the phase diagrams and nucleation with available experimental nucleation data.

Classical nucleation theory was empirically extended to describe the heterogeneous nucleation, such as polymer foaming with additives. It still has a similar expression as homogeneous nucleation:

\[ J_{het} = J_1 e^{-W_{het}/k_BT} \]  
\[ W_{het} = \frac{W}{4}(2 + \cos \theta)(1 - \cos \theta)^2 \]

where \( W_{het} \) is the reversible work of critical nucleus formation in heterogeneous nucleation, \( J_1 \) is the pre-exponential factor for heterogeneous nucleation and \( \theta \) is the contact angle of the polymer-additive-gas interface [42,43].

There are many restrictions to the application of the homogeneous nucleation equation. For example, in homogeneous nucleation, no pre-existing gas cavities can exist in the bulk or on the container walls. Furthermore, even the highly idealized cases of nucleation in boiling and nucleation in isothermal gas desorption are still not completely understood [63], not to say accurate description of heterogeneous nucleation.
2.1.2 Experimental techniques for bubble nucleation

The accurate measurement of nucleation is still a big challenge. A variety of devices and methods have been developed to investigate homogeneous gas-liquid nucleation and a number of chemical compounds have been studied. Fig. 2.2 gives an overview of different methods and their measurement ranges.

The nucleation pulse method is one of the most successful experimental setups and is described in detail by Strey et al. [40]. The vapor-carrier gas mixture is adiabatically expanded to a lower pressure $P_{\text{exp}}$ and consequently to a lower temperature, which is inside the metastable regime. Nuclei form in the supersaturated vapor phase. After a short period of time $\Delta t$, slight recompression of the mixture is exerted to abruptly stop nucleation and still keep a supersaturated vapor phase. Thus, the already formed nuclei can still grow. By this way, nucleation and growth are decoupled. The number density $N$ of droplets is determined by constant-angle-Mie-scattering (CAMS). Fig. 2.3 shows a typical pressure pulse and the corresponding light scattering signal. CAMS is widely used to characterize particle number and size because of the following advantages [64]: no significant influence on the kinetics of the observed processes; short response time compared to typical particle formation times; simultaneous and independent quantitative measurement of particle size and number concentration; and an absolute method independent of external standards or empirical calibrations.
Since nucleation and growth are decoupled, the nucleation time is the length $\Delta t$ of the plateau of the pressure pulse, which can be determined geometrically. The nucleation rate can be calculated as

$$J = \frac{N}{\Delta t}.$$  \hspace{1cm} (Eq. 2.8)

Comparing with the measurement of droplet nucleation from vapor, the literature about the measurement of bubble nucleation is rare. In one of the few experimental measurements of homogeneous bubble nucleation rate, Strey and coworkers \[65\] have extended the nucleation-pulse method to measure the nucleation rate as a function of supersaturation in gas-saturated liquids at constant temperature.

By counting the number of bubbles formed, a large number of publications present intriguing conclusions about foaming behavior. They usually assume each nucleation site produces a bubble, no bubble coalescence occurs, and all bubbles nucleate and grow to a certain detectable size. Colton and Suh \[41\] were among the earliest to study nucleation by this method. The authors measured nucleation by counting the number of cells using scanning electron microscopy (SEM) of the foamed PS but no information on the experimental bubble sizes was given. In most cases, the sample is quenched at cold temperatures in an effort to prevent cell coalescence. For physical blowing agent-assisted polymeric foaming with the use of nucleation agents, several authors presented foaming data using heterogeneous nucleation \[16,66-68\].

Han and Han \[45,46\] studied bubble nucleation in concentrated polymeric solutions (40, 50, and 60 wt. % PS in toluene with two initial pressures, 400 and 600 psi) using laser light scattering (i.e. CAMS). To be able to use the Mie’s scattering theory, the
growth of bubbles was assumed to be monodispersed, thereby neglecting multiple scattering effects. A lot of information for bubble nucleation and growth was obtained in their study, including the critical bubble size and the total number of bubbles nucleated.

2.1.3 Bubble growth theory

Bubble growth is a complex process, involving mass transfer, momentum transfer, and heat transfer. Street et al. [69] established the initial framework for analyzing bubble growth. A finite envelope of fluid was placed around the bubble, later referred to as the single bubble model. A theoretical model was presented for the heat, mass, and momentum transfer processes governing the growth of a vapor bubble in a solution consisting of a viscous liquid and a dissolved blowing agent. The vapor bubble is formed by nucleation of the blowing agent dissolved in the liquid and grows by expansion of the gas against the viscous liquid accompanied by diffusion of the blowing agent from the liquid to the bubble. The viscous liquid was assumed to be non-Newtonian (power law). The resulting system of nonlinear differential and partial differential equations was solved by finite difference methods. Their results for growth at short times in an infinite medium indicated that the combined momentum and mass-transfer processes were significant in the determination of the bubble size as a function of time. Most importantly, they also showed the viscosity of the melt and the diffusivity of the blowing agent determined the initial growth rate.

Since then, many improved models [39,70-72] have been published. For example, the effect of the viscoelastic property of the polymer melt was included in some models.
Venerus et al. [73] carried out a viscoelastic simulation of bubble growth with the Phan-Thien Tanner (PTT) model. This model can be used to describe bubble growth or collapse in a nonlinear viscoelastic fluid, and takes into account convective and diffusive mass transport as well as surface tension and inertial effects. Predictions by this model showed the importance of fluid elasticity for bubble growth. These predictions indicated that for diffusion-induced bubble growth in viscoelastic liquids, the lower bound for growth rate was given by growth in a Newtonian fluid and the upper bound by diffusion-controlled growth. The influence of the viscoelastic property of the polymer on bubble growth dynamics was shown to be relatively minor in comparison to fluid elasticity. However, this simulation has been done by using the thin-boundary layer approximation around the bubble. Furthermore, they treated the liquid as infinite, therefore, the final bubble size can not be expressed. More practically, diffusion-induced bubble growth models concerning the finite liquid surrounding the bubble have been developed [74-76].

Recently, Otsuki [77] developed a multi-mode Phan-Thien Tanner (PTT) model to analyze the dynamic growth behavior of spherically symmetric bubbles with the diffusion of a foaming agent (CO$_2$). Changes in the dissolved foaming agent concentration in the polymer and in the strain of the polymer melt surrounding the bubbles were simulated with the Lagrangian finite element method (FEM). The simulation technique was validated by comparison with the bubble growth data, which were experimentally obtained from visual observations of the PP/CO$_2$ batch foaming system [25]. The simulation results demonstrated that the strain-hardening characteristic of polymer did not strongly affect the bubble growth rate; the linear viscoelastic characteristic was more
influential; and the bubble nucleus population, surrounding pressure, initial dissolved foaming agent concentration, and diffusivity were more important factors than the viscoelastic characteristics. However, this model can be further improved due to some assumptions used, e.g., the volume of gas in a bubble follows the ideal gas law and the effect of dissolved gas on the viscoelastic characteristic is ignored.

2.1.4 Experimental techniques for bubble growth

In general, the same method used for bubble nucleation is used for bubble growth for polymer foaming. Actually, tiny bubbles are measured and/or counted to obtain the bubble density and bubble nucleation data, with the assumption that one nucleation site grows to one bubble. Therefore, most authors obtain the bubble nucleation and growth data by the same experimental technique or setup.

The widely used method is recording the foaming process by a high-speed camera. The bubble growth data can be obtained by analyzing the micrographs. Several researchers obtained bubble growth rate data in the polymer foaming process by using this method. Taki [25,26] conducted in-situ visual observations for batch foaming processes of PP and PP-clay nanocomposites with CO₂ to understand bubble nucleation and growth in the early stage. They developed a high-pressure autoclave, which has two sapphire windows on the walls. A high-speed digital camera with a microscope could observe the bubble nucleation and bubble growth behavior of the early stage of foaming in situ. The series of micrographs were analyzed in order to investigate the effect of clay
content on bubble nucleation and growth. Their results showed that the clay enhanced bubble nucleation as a nucleation agent and retarded the growth of bubbles at the early stage of foaming. In addition, some interesting phenomena, such as bubble coalescence [27], were also observed and studied. Guo et al. [2] used a similar experimental setup but a much higher speed camera to study the microcellular foaming with higher pressure drop. A PS-CO₂ system was used and the maximum pressure-drop rate achievable was 2.5 GPa/s from the designed system. Bubble growth curves were shown and the effects of pressure drop rate and CO₂ content on foaming were discussed.

Han and Han [45,46] studied bubble nucleation in concentrated PS-toluene solutions using laser light scattering (i.e. CAMS). Both bubble nucleation and growth information were obtained by taking advantage of simultaneous and independent quantitative measurement of particle size and number concentration of the CAMS. But this technique has not been used for polymer-diluent systems.

2.2 Solubility of CO₂ in polymers

2.2.1 Experimental technique and data

The solubility of CO₂ in a variety of polymers has been studied due to the wide application of CO₂ in polymer processing, e.g. impregnation, particle formation, foaming, and blending [34]. For all these processes, solubility of CO₂ in the polymer matrix is always essential. PS, PS nanocomposites, and PMMA were used in this study and
therefore literature on the solubility in these systems will be reviewed. The affinity of 
CO₂ for a polymer, or solubility of CO₂ in a polymer, is associated with the interaction 
between CO₂ and the polymer. CO₂ molecule is a symmetric and linear molecule and has 
no electrical dipole. Therefore, solubility of CO₂ in most polymers is only around several 
weight percent due to the non-polarity of the CO₂ molecule. However, CO₂ exhibits a 
large quadrupole moment. As a result, the solubility of CO₂ increases with increasing 
content of polar functional groups on the polymer. In our system, PMMA has a stronger 
affinity than PS because it possesses carbonyl groups [78].

In general, there are four types of experimental techniques for solubility 
measurement: barometric (pressure decay) method, frequency modulation, gravimetric 
method, and chromatographic method.

The pressure decay method is popular because the experimental setup is simple 
and inexpensive. The mass of gas absorbed by a polymer is obtained by subtracting the 
amount remaining in the gas phase after equilibrium from the amount of gas initially 
contacted with the polymer. However, it is difficult to apply at high temperatures for 
polymer melts because of the lack of suitable pressure sensors [79] and concern of 
degradation. The degradation results from the long time to reach equilibrium due to a 
large amount (several grams) of polymer sample used for enough accuracy. Further, a 
very accurate equation of state for the gas phase is needed and the volume of the system 
needs to be very accurately calibrated.

Gravimetric methods are also commonly used. One early and simple gravimetric 
method is described as follows. The desorption curve can be obtained by measuring the
weight change of a polymer after being removed from a high pressure cell to a microbalance at ambient conditions. From the analytical solution to diffusion from a flat plate, the curve of weight vs. time can be extrapolated to time zero to obtain an estimate of the solubility. This method is not appropriate when the release of CO₂ changes the shape of the sample, e.g. highly plasticized polymer. Recently, Several researchers [80] have used an electronic microbalance inside a pressure vessel for in situ measurement. It has the advantages of requiring a small sample size (hence short measurement time) and high sensitivity (on the order of micrograms). In our study, another commonly used microbalance, MSB (magnetic suspension balance) was used. This has many advantages similar to the electronic microbalances with the added advantage that the sample and balance are mechanically isolated. The sample is magnetically levitated inside a high-pressure vessel while the balance electronics remain at ambient conditions. This makes it suitable for the measurement of gas solubility and diffusivity in polymers at high temperatures and pressures. A distinct merit of MSB is that the microbalance can be tared and calibrated during measurements. However, the buoyancy correction, which depends on the swelling factor, is especially important for this type of balance. The swelling factor can be estimated either by experimental measurement or by equations of state [81].

The method of frequency modulation, using a quartz crystal microbalance (QCM) [82,83] is accurate but the sample preparation is challenging. Therefore, it was seldom used unless a real-time monitoring of a process is required. The gravimetric method is most widely used. Another rarely used method is chromatographic method. Edwards et al. [84] used a mass spectrometric tracer pulse chromatography, MSTPC, to measure the
solubility of CO₂ in PMMA over a wide range of temperatures. This method has many advantages over some traditional methods described above. For example, the experiments are very fast because the polymer is distributed as a thin film with nanometer to micrometer thickness, so the systems can achieve thermodynamic equilibrium rapidly.

There are plenty of literature data on solubility of CO₂ in PS, especially above its glass transition temperature \( (T_g, \text{ around } 100^\circ \text{C for PS}) \). For example, Sato \textit{et al.} [85] measured the solubility of CO₂ in PS by a pressure decay method at temperatures from 100°C to 180°C and pressures up to 20 MPa. Sato \textit{et al.} [79] also used a magnetic suspension balance (MSB) to measure the solubility of CO₂ in PS. These cover the common temperature and pressure ranges of foaming experiments. In addition, the PS used has similar molecular weight and distribution to ours.

There are also solubility data of CO₂ in PMMA. The review by Tomasko \textit{et al.} [34] lists available literature data of CO₂ in a variety of polymers, including PS and PMMA until 2003. However, for PMMA, most literature data on solubility of CO₂ are focused on low temperatures \(<100^\circ \text{C}\) and low pressures \(<2 \text{ MPa}\) [80], i.e. not typical foaming conditions (around 100°C and >5 MPa). Edwards \textit{et al.} [84] used a chromatographic method to measure the solubility of CO₂ in PMMA over a wide range of temperatures (–10 to 180°C) and pressures (up to 9 MPa). However, they did not specify the PMMA in the paper, e.g. molecular weight, although they claimed their data agree remarkably well with other source considering the variation in experimental procedures and polymer molecular weights.
2.2.2 Modeling by equations of state (EOS)

Solubility modeling by equations of state (EOS) is a very important method because of the experimental difficulty. Appropriate modeling by EOS can decrease experimental effort tremendously. In our research, two equations of state were used: Sanchez-Lacombe (S-L) EOS and perturbed chain statistical associating fluid theory (PC-SAFT).

The Sanchez-Lacombe equation of state was presented in 1976. It is based on a well-defined statistical mechanical mode and has another name: the lattice fluid theory [86-89]. Its ability to describe the mixtures with large size differences makes it especially powerful in the modeling of polymer-solvent systems [90]. For its application, the polymer should be above its $T_g$, so it can be modeled as a liquid [91]. The equation of state is:

$$
\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] = 0
$$

(Eq. 2.9)

where $\tilde{T}$, $\tilde{P}$, and $\tilde{\rho}$ are reduced temperature, pressure, and density respectively. $r$ is the number of lattice sites occupied by a molecule. The definition of the reduced parameters, $r$, and mixing rule can be found anywhere [88] or Appendix A. As we can see, the form of the equation is simple. Pure fluids are completely characterized by three parameters ($T^*, P^*, \rho^*$) and only one additional parameter, the binary interaction parameter, $k_{ij}$, is needed to describe binary systems. In this model lattice site vacancies are introduced to take account for the compressibility and density changes that are important for systems
under high pressure or undergoing phase transition [90]. There are numerous publications of the applicability of this theory to different systems. For example, it has been used to model solubility and diffusivity of gases in polymers under high pressure [85,92], high-pressure phase behavior of binary and ternary polymer-solvent systems [90,93].

By applying Wertheim’s first-order theory and extending it to mixtures, Chapman et al. [94] derived the Statistical Associating Fluid Theory (SAFT) equation of state for chain mixtures. The agreement with molecular simulation and experimental data was shown to be excellent. Then many modifications of the SAFT model were proposed over the years, such as modified SAFT by Huang and Radosz [95,96], LJ (Lennard-Jones)-SAFT versions [97,98], Simplified SAFT by Fu and Sandler [99], and VR (Variable Range) -SAFT [100]. Despite many theoretical improvements, the SAFT model suggested by Huang and Radosz is one of the most successful modifications and has been applied widely in the industry.

By applying the second-order perturbation theory of Barker and Henderson [101,102] to a hard-chain reference fluid, Gross and Sadowski [103] developed an equation of state for square-well chains. This theory was compared to simulation data of homonuclear chain molecules and mixtures and was found to give good results. Then they derived a dispersion expression for chain molecules by applying the perturbation theory and adjusting the appropriate model constants to the pure-component properties of \( n \)-alkanes. The new equation of state uses the same chain term and association term as the earlier SAFT equations. Because a hard-chain fluid, rather than spherical molecules, serves as a reference for the perturbation theory, this model is referred to as Perturbed-
Chain SAFT (PC-SAFT) [104]. In terms of the compressibility factor $Z$, the equation of state is given as an ideal gas contribution ($Z^{id}=1$), a hard-chain contribution (hc), a dispersive term (disp), and an association contribution (assoc) according to:

$$Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc}$$  \hspace{1cm} (Eq. 2.10)

Each term ($Z^{hc}, Z^{disp}, Z^{assoc}$) has a complicated expression, listed in Appendix B. The effect of multipole interactions (such as dipole-dipole forces) is not separately taken into account in this equation yet [105]. But for common polymer-gas systems, such as PMMA-CO$_2$, PE-CO$_2$, PS-CO$_2$, this will not affect greatly the modeling results.

Similar to S-L EOS, there are three characterization parameters (segment diameter $\sigma$ in ml/mol; segment-segment interaction energy $\varepsilon/k$ in Kelvin; and segment number $m$) for each pure component for non-associating systems. An interaction parameter $k_{ij}$, is needed for modeling binary systems. But the $k_{ij}$ for PC-SAFT has less temperature dependence than in the S-L EOS, making it less reliant on experimental data. As one of the most advanced equations of state, the PC-SAFT was applied with excellent performance in modeling liquid-liquid, vapor-liquid, and solid-liquid equilibria of non-associating and associating components from low molecular mass up to polymers and copolymers [104-107]. In general, it gives better performance than the widely used SAFT modified by Huang and Radosz in most systems [104]. Gross and Sadowski [106] obtained the pure-component polymer parameters by simultaneous fitting four parameters - three pure-component parameters and $k_{ij}$ - to pure polymer liquid density and binary phase equilibrium data for a single polymer-solvent system. The polymer parameters determined by this way can be used to predict phase behavior in other mixtures.
Kouskoumvekaki et al. [108] developed a method for estimating pure-component parameters for polymers for the PC-SAFT. Their method was based on pure-polymer PVT data and extrapolating equations that relate the polymer parameters to those of the corresponding monomer. The obtained parameters were therefore unique for each polymer and independent of any mixture data.

Not only can these two equations of state be used for prediction of the solubility curve (part of the binodal curve) of gas in polymers, they can also be used to predict the binodal and spinodal curves in the whole range. For example, Xiong and Kiran used the S-L EOS and SAFT to predict binodal and spinodal curves (or phase boundaries) of PE-\textit{n}-pentane [90] and PE-\textit{n}-butane [109] solutions. Koak \textit{et al.} [110] also used S-L EOS to model the binodal and spinodal curves of HDPE-\textit{n}-hexane. To the author’s best knowledge, modeling of phase boundaries by PC-SAFT is rare.

2.3 Gas permeation in polymers and foams

2.3.1 Permeation theory

Diffusivity studies of CO$_2$ in PS and PMMA are quite limited [34,111] due to experimental difficulty. The theory and common experimental techniques can be found in the review written by Tomasko \textit{et al.} In this study, however, we mainly focus on another indirect way, measuring permeability coefficient near ambient temperature and pressure,
to get comparative approximation for different polymers and nanocomposites.

The transmission of gas or vapor over a plastic film can be described as the following four steps: [112]

1. Absorption of gas or vapor molecules onto the surface of the film (high pressure side);
2. Dissolution of the gas or vapor into the polymer matrix;
3. Diffusion through the film under certain concentration gradient;
4. Desorption from the other surface of the film (low pressure side).

After a build-up period, the steady state will be reached. Fig. 2.4 shows a schematic of permeation through a film in the steady state. $C_1$ and $C_2$ are the concentrations of gas or vapor at two surfaces, $p_1$ and $p_2$ are pressures of gas or vapor at equilibrium with the film, $l$ is the thickness of the film.

Under steady state conditions, the transmission (flux) is given by Fick’s first law, i.e.

$$q = \frac{D \cdot (C_1 - C_2)}{l}$$

(Eq. 2.11)

If it is assumed that Henry’s law applies at both interfaces, i.e. solubility coefficient,

$$S = \frac{C_1}{p_1} = \frac{C_2}{p_2}$$

(Eq. 2.12)

Eq. 2.11 can be expressed as

$$q = \frac{D \cdot S \cdot (p_1 - p_2)}{l}$$

(Eq. 2.13)
The product of $D$ and $S$ is defined as permeability coefficient (or permeability constant) $P$. i.e.

$$P = D \cdot S = \frac{l \cdot q}{(p_1 - p_2)}$$

(Eq. 2. 14)

Permeability coefficient $P$ is found to be independent of thickness in most cases [113], so it is used to characterize the permeability of material.

2.3.2 Temperature dependence

The temperature dependences of $S$, $D$, and $P$ over a moderate temperature range can be represented by the Arrhenius-type [113,114] relationships:

$$S = S_0 \cdot \exp(-\Delta H_S / RT)$$

(Eq. 2. 15)

$$D = D_0 \cdot \exp(-E_d / RT)$$

(Eq. 2. 16)

$$P = P_0 \cdot \exp(-E_p / RT)$$

(Eq. 2. 17)

Where $\Delta H_S$ is the heat of solution, $E_d$ is the activation energy for diffusion, $E_p$ is the activation energy for permeation, $T$ is the absolute temperature, and $S_0$, $D_0$, and $P_0$ are pre-exponential factors respectively. From the above equations, the following expression can be obtained:

$$E_p = \Delta H_S + E_d$$

(Eq. 2. 18)

The sign of $E_p$ is determined by signs of $\Delta H_S$ and $E_d$. $E_d$ is always positive since $E_d$ increases when the temperature increases. The sign of $\Delta H_S$ is not obvious. Sorption of a gas or vapor in a polymer can be considered as two processes, condensation and mixing.
Therefore $\Delta H_S$ can be expressed as the sum of the heat of condensation, $\Delta H_c$, and the heat of mixing, $\Delta H_m$.

$$\Delta H_S = \Delta H_c + \Delta H_m$$  \hspace{1cm} (Eq. 2.19)

For permanent gases, such as O$_2$, or CO$_2$ around room temperature, $\Delta H_c$ can be neglected and $\Delta H_m$ is a small positive number, therefore, $\Delta H_S$ is a small positive number, i.e. $S$ increases slightly with increasing temperature. For condensable vapors, such as water, $\Delta H_S$ is negative due to the large value of $\Delta H_c$, therefore $S$ decreases with increasing temperature. Thus, based on the above discussion, $E_p$ is positive for permanent gases, and can be positive, negative, or nearly zero for condensable vapors.

**2.3.3 Concentration dependence**

Temperature and concentration (and its temporal and spatial distribution) of absorbed penetrant within the polymer are two major factors that affect polymer chain segmental motion. In general, increasing temperature provides energy for increasing segmental motion. In other words, an increase of temperature leads to an increase of free volume directly related to the bulk expansion of the polymer. The presence of absorbed penetrant also generally increases the free volume of the polymer. However, the concentration dependence can be different from temperature dependence due to the possibility of specific component interactions (modes of sorption). If the sorption is ideal, without specific interaction between the penetrant and polymer, the change in the system free volume with increasing concentration will be proportional to the change by
temperature increase. This is called ‘temperature-concentration equivalence’ (‘superposition’), similar to the temperature-time equivalence for viscoelastic behavior [113].

To better understand the concentration dependence, different modes of sorption should be revisited. Sorption [113] is a term used to describe the penetration and dispersion of penetrant molecules in a polymer matrix to form a mixture. The common four types of modes are shown in Fig. 2.5. The simplest mode of sorption obeys Henry’s law, i.e. the solubility coefficient is a constant and independent of sorbed concentration. This is an ideal solution behavior that the sorbed molecules are randomly dispersed in the polymer matrix. This behavior is observed when the solubility of permanent gases in polymer is very small (< ~ 0.2%) due to the lack of strong polymer-permeant interactions. The second type follows the Langmuir equation. Namely, at very low pressure, there is a linear relationship between sorbed concentration and pressure; at relatively high pressure, the concentration increases slowly toward the maximum sorption. This behavior happens in the sorption process of some dyes in ionic polymers or polymers containing polar groups. It also occurs when certain gases or vapors are sorbed in composite or heterogeneous media where the polymer is the continuous phase with dispersion of high-area fillers. The third type follows the Flory-Huggins equation, where the permeant-permeant interaction is stronger than the permeant-polymer interaction such that the solubility coefficient increases continuously with pressure. This behavior is observed when the permeant is a strong solvent or swelling agent for the polymer. It is also observed in the system of water in relatively hydrophobic polymers (e.g.
polyalkylmethacrylates) [115]. The fourth type can be regarded as a combination of the second type at low pressure and the third type at higher pressure. It frequently happens when water is sorbed in more hydrophilic polymers, such as wool, silk, and cellulosic materials [115].

When the sorption does not follow Henry’s law, it is dependent on the sorbed concentration. For example, if the sorption meets Flory-Huggins type of isotherm equation, it can be shown as Eq. 2.20,

\[ S = S(0) \exp(\sigma \cdot c) \]  
\text{(Eq. 2. 20)}

where \( c \) is permeant concentration, \( \sigma \) is a constant characterizing the concentration dependence of \( S \), and \( S(0) \) is the value when \( c \) is 0. The concentration dependence of \( D \) can be represented in terms of vapor activity \( a_1 \),

\[ D = D(0) \exp(\alpha \cdot a_1) \]  
\text{(Eq. 2. 21)}

where \( \alpha \) is a constant characterizing the concentration dependence of \( D \) and \( D(0) \) is the value when \( a_1 \) is 0.

Since \( P \) is product of \( S \) and \( D \), we can get the following expression by combining Eq. 2.20 and Eq. 2.21.

\[ P = P(0) \exp(\sigma \cdot c + \alpha \cdot a_1) \]  
\text{(Eq. 2. 22)}

where \( P(0) = S(0) \cdot D(0) \). When Henry’s law is obeyed, i.e. \( S \) is a constant and independent of permeant concentration, Eq. 2.22 can be simplified to just an exponential dependence on the vapor activity (pressure). The permeability coefficient shows linear dependence of the vapor activity (pressure) at low pressure [116].
2.3.4 Physicochemical characteristics of polymers

Among physicochemical characteristics of polymers, crystallinity, crosslinking, and orientation have significant effects on permeation behavior. It is accepted that at temperature well below the melting point, crystalline domains in polymer can be regarded as inaccessible to most permeants, i.e. they act as impermeable barriers [117]. Crosslinking in both crystalline and non-crystalline polymers decreases the diffusion coefficient although solubility coefficient does not change much except at high degrees of crosslinking or when the permeant significantly swells the polymer [118]. Orientation of polymer materials introduces an asymmetric structure such that the diffusion rate differs relative to the axis of orientation [119]. The general conclusion is that the rate is slowest when parallel to the axis and fastest when perpendicular to the axis. The rate is in between in a randomly oriented sample. In addition, homogeneity of the polymer can also affect the permeation. For example, inert fillers are widely used in polymers for characteristic modification. They can either increase or decrease the barrier properties of polymers, dependent on the degree of compatibility and adhesion between the polymer and filler. It is suggested [113] that for a polymer to possess good barrier properties for most permeants, it should have the following properties:

- Some degree of polarity, e.g. in nitrile, chloride, fluoride, acrylic or ester groups;
- High chain stiffness;
- Inertness to permeants;
- Some bonding or attraction between chains;
• High glass transition temperature $T_g$;
• Close chain-to-chain packing ability by molecular symmetry, order, crystallinity, or orientation.

2.4 Rheological behavior of polymers under high pressure CO$_2$

2.4.1 Introduction and scaling theories

Let us review the rheological properties of pure polymers or polymer nanocomposite before considering the effect of diluents. We only focus on the shear viscosity of all the rheological properties. The terms of shear viscosity, dynamic viscosity, and complex viscosity are commonly shown in the rheology community. Shear viscosity $\eta$ is related to the shear stress $\sigma$ and the velocity gradient, or shear rate $\dot{\gamma}$, through the equation

$$\eta = \frac{\sigma}{\dot{\gamma}}$$  \hspace{1cm} (Eq. 2.23)

In cases where the shear rate is not constant but varies in a sinusoidal manner, both shear rate and shear stress are sinusoidal. In these dynamic mechanical experiments, the stress is out of phase with the rate of strain unless the fluid is Newtonian. In this situation, a complex viscosity $\eta^*$, defined as the following, can be measured.

$$\eta^* = \eta' - i \eta''$$  \hspace{1cm} (Eq. 2.24)
The dynamic viscosity $\eta'$ is the part of the complex viscosity that measures the rate of energy dissipation. Similarly, the imaginary viscosity $\eta''$ measures the elasticity, or stored energy. These two viscosities are computed from the real and imaginary parts of the shear modulus using the following expressions:

$$\eta' = \frac{G'}{\omega} \quad \text{(Eq. 2.25)}$$

$$\eta'' = \frac{G''}{\omega} \quad \text{(Eq. 2.26)}$$

Where $\omega$ is the frequency of the oscillations in radians per second. The storage modulus, $G'$, is defined as the component of the stress in phase with the strain divided by the strain amplitude; the loss modulus, $G''$, is defined as the component of the stress out of phase with strain divided by the strain amplitude. The Cox-Merz relationship [120] allows frequencies and complex viscosities to equal shear rates and shear viscosity values.

The zero-shear viscosity, $\eta_0$, of a shear-thinning polymer is commonly used as the single viscosity value to describe the viscosity curve. The zero-shear viscosity is the limiting shear viscosity at low shear rates. It can be computed by dynamic mechanical data:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \quad \text{(Eq. 2.27)}$$

Where $G''$ is the loss modulus defined by Eq. (26). The variables that influence the zero-shear viscosity include polymer molecular weight, molecular weight distribution, chain branching, temperature, and pressure. These topics are covered in most textbooks [121] of polymer rheology. For polymer solutions, the concentration of the polymer also affects
the zero-shear viscosity. Different scaling theories were developed to describe the effects of temperature, pressure, and concentration.

Various Research groups [122] have shown that the viscosity reduction of polymer melts in the presence of dissolved CO$_2$ could be described in terms of the classical viscosity scaling theory. Gerhardt [123] et al. have shown that classical viscoelastic scaling factors can be employed to superpose the viscosity curves for CO$_2$-swollen melts onto the viscosity curve for pure PDMS at the same temperature and pressure. They combined a free-volume expression for the viscosity of a diluted polymer melt with equation-of-state theories for the volumetric properties of PDMS-CO$_2$ mixtures to develop models for the CO$_2$ concentration-dependent viscoelastic scaling factors. The predicted viscoelastic scaling factors were found to be in very good agreement with experimental data. The model predictions showed that mixing of gaseous CO$_2$ into the swollen PDMS phase was highly non-ideal, and that significant free volume was added to the melt upon CO$_2$ dissolution, which was believed to be the principal mechanism for viscosity reduction. The free volume theory of Gerhardt [123] et al. was used by Kwag [124] et al. to predict viscoelastic scaling factors describing the effect of CO$_2$ concentration on the viscosity curves of polystyrene melts. Lee [125] et al. proposed a model using the generalized Cross-Carreau equation and Doolittle’s free theory to describe the viscosity of PS-CO$_2$. Recently, Royer [126] et al. developed a free volume model based on Williams-Landel-Ferry (WLF) equation, which is obtained directly from Doolittle’s free volume theory, and Chow’s model. All these theoretical studies suggest
that the free volume plays an important role in reduction of polymer melt viscosity by dissolved gas.

Scaling of isothermal shear viscosity data as a function of shear rate to a reference temperature is a general practice in polymer rheology. The curve generated from such scaling is termed as a master curve. Similarly, this concept has been extended to generate a master curve using pressure and CO₂ concentration. The master curve allows rescaling of viscosity data from a reference situation to different processing conditions [124,126,127].

One of the most widely used equations among scaling theories is the Williams-Landel-Ferry (WLF) equation [128]. Above \( T_g \), the shear viscosity depends on the availability of free volume, which is the part of the sample volume not actually occupied by the polymer molecules. The WLF equation assumes that a linear temperature dependence on fractional free volume from \( T_g \) until 100 \(^{°}C \) \( + T_g \) is nearly universal for many amorphous polymers and their solutions. The WLF equation describes the ratio of zero-shear viscosity at \( T_2 \) to that at \( T_1 \):

\[
\log(a_r) = \log\left(\frac{\eta_0(T_2)}{\eta_0(T_1)}\right) = \frac{c_1(T_2 - T_1)}{c_2 + T_2 - T_1}
\]  \hspace{1cm} (Eq. 2.28)

\( c_1 \) and \( c_2 \) have a fundamental basis and have also been experimentally determined for most common polymer systems. The glass transition temperature \( T_g \) is usually chosen as the reference temperature \( T_1 \).

WLF-Chow equation developed by Royer et al. [126] is widely used to calculate the pressure shift factor \( a_p \), concentration shift factor \( a_c \), and their combination \( a_p \cdot a_c \).
\[
\log(a_p) = \frac{\log[\eta(T, P, c)]}{\log[\eta(T, P_0, c_0)]} = \frac{c_1(T - T_{g, \text{mix}, P_0})}{c_2 + T - T_{g, \text{mix}, P_0}} - \frac{c_1(T - T_{g, \text{mix}, P})}{c_2 + T - T_{g, \text{mix}, P}} \quad \text{(Eq. 2.29)}
\]

\[
\log(a_c) = \frac{\log[\eta(T, P_0, c)]}{\log[\eta(T, P_{00}, c_0)]} = \frac{c_1(T - T_{g, P_0})}{c_2 + T - T_{g, P_0}} - \frac{c_1(T - T_{g, \text{mix}, P_0})}{c_2 + T - T_{g, \text{mix}, P_0}} \quad \text{(Eq. 2.30)}
\]

The first shift factor accounts for hydrostatic pressure with a known concentration of diluent, while the second equation removes the concentration to allow direct comparison with diluent-free atmospheric-pressure viscosity. The structure of the equations is similar to the Penwell et al. [129]. It does not rely upon any \(P-V-T\) data other than specifying the \(T_g\) change with pressure and concentration. The latter is governed by the Chow model [130].

2.4.2 High pressure polymer/diluent viscosity experiments

A high pressure diluent creates a complicated, but important situation. Many viscosity studies have been performed on these systems for industrial applications ranging from dying to foaming. Because the solvent is also a compressed fluid, both pressure and concentration must be considered.

Most experimental studies in the literature employed slit and capillary dies, which provide data at high shear rates. However, their limitation is that the large pressure drop across a capillary or slit die limits the concentration of diluent that can be dissolved in the polymer melt, as to ensure no phase separation occurs. A backpressure regulator or nozzle can be used to keep the diluent in the solution and to control the die flow.
resistance. The meaning of individual viscosity measurements from these methods is complicated by the fact that they correspond to a range of pressures rather than representing viscosity at a particular pressure. Unlike other rheometers, correction factors are typically required in capillary rheometry.

Han and Ma [131-133] measured the viscosity of three grades of polystyrene and low density polyethylene, each, using three CFC blowing agents. They were among the first to calculate the $a_p \cdot a_c$ shift factor, which they termed the viscosity reduction factor, and they reported it to be independent of temperature. Gendron and coworkers used an extrusion slit rheometer to measure the viscosity of many polymer/diluent combinations, including: PP/CO$_2$ [134]; PS/HCFC-142b and PS/HFC-134a [135]; and PP/HCFC-142b, PP/n-pentane, HDPE/HCFC-142b, linear low density PE/HFC-142b, and PS/n-pentane [136].

Several studies have investigated the viscosity of PS/CO$_2$. Royer et al. [126] used a slit die to investigate three grades of polystyrene from 200 to 250°C. Kwag et al. [137] studied PS/CO$_2$ viscosity on a capillary rheometer. Lee et al. [138] and Areerat et al. [139] also employed capillary rheometers, while Xue and Tzoganakis [140] used contraction slit dies, all to measure PS/CO$_2$ viscosity.

There are two relevant studies in the literature of high-pressure diluent-plasticized viscosities measured by a rotational rheometer, by Flichy et al. [141] and by Oh et al. [142,143] Flichy et al. measured viscosities of polymer-inorganic suspensions under CO$_2$, but they approximated the average shear rate. Oh et al. constructed a high pressure Couette rheometer and measured Newtonian viscosities of PS-CO$_2$, but did not calculate
any shift factors or magnitudes of depression. In their second publication [142], they correlated their results at 100°C to a WLF-type fit, but unfortunately they did not provide any explanation of the equation or the values of its parameters.

Wingert et al. [144,145] systematically studied the shear viscosity of PS / CO₂ by a modified Couette rheometer. Shear viscosity of PS / CO₂ was measured from 140 to 180°C and from 3 to 6 wt.% CO₂. The pressure effect was studied by measuring the shear viscosity of PS under an insoluble gas (Helium). Several shift factors, \(a_p\cdot a_c\), \(a_p\), and \(a_c\), were compared with the model predications by WLF-Chow model. A satisfactory agreement was achieved.
Figure 2.1: Schematic representation of the PIPS and pressure-quench path to different depths of penetration
Figure 2.2: Different techniques for homogeneous nucleation experiments and their respective ranges in nucleation rate [146]
Figure 2.3: Typical nucleation pulse and corresponding light scattering signal [40]
Figure 2.4: Permeation of gas or vapor through a film in the steady state
Figure 2.5: Schematic of common isotherm plots of sorbed concentration versus pressure. (A: Henry’s law; B: Langmuir equation; C: Flory-Huggins equation; D: BET equation)
3.1 Introduction

CO$_2$ is the most preferable one among all potential alternatives to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) because it is nonflammable, inexpensive, essentially nontoxic and environmentally friendly [8]. However, CO$_2$ has its drawbacks. Low solubility and high diffusivity in polymers compared to CFCs/HCFCs/HFCs often lead to foams with higher density and/or poor surface quality, and almost always requires higher operating pressures than other blowing agents. These drawbacks impede the development of CO$_2$ as a foaming agent at an industrial scale. Adding nanoparticles to the polymer foaming process is one possible way to overcome these problems [7].

Polymer nanocomposites refer to a class of reinforced polymers with a low percentage of dispersed nanoparticles. Nanoparticles can offer several benefits to the foaming process. First, they may serve as nucleating sites. Relatively low solubility of CO$_2$ in PS leads to inefficient homogeneous nucleation power, resulting in foams with
higher density (i.e. cell number density is not high enough). However, heterogeneous nucleation is the dominating mechanism when the nanoparticles are added. Heterogeneous nucleation is faster due to much lower nucleation energy required. Large surface area and number density of nanoparticles enhance the heterogeneous nucleation, resulting in high cell number density, therefore lowering the foam bulk density. Because of the dramatic nucleation effect of nanoparticles, the operation pressure can be decreased to reduce the cost. In other words, lower solubility of CO₂ due to lower pressure is enough for efficient nucleation because of the great enhancement of nanoparticles. Second, nanoparticles can align along cell walls and struts to provide mechanical reinforcement, thermal stability and, in some cases, fire retardancy. Furthermore, some nanoparticles such as organoclays can greatly reduce gas permeability in the polymer matrix [147,148], which is advantageous for retaining CO₂ in the foaming process and providing barrier properties in applications. Therefore, the problem of the rough foam surface because of high diffusivity of CO₂ in polymer matrix can be possibly solved with the introduction of nanoparticles. In summary, polymer nanocomposites have the potential to overcome the major disadvantages, i.e. low solubility, high diffusivity, and high operation pressure, of using CO₂ as the physical blowing agent. In addition, nanoparticles can also bring other potential benefits, such as reinforcement.

A variety of nanoparticles were used for polymer nanocomposite foam fabrication. Two types of organically modified clays, a commercially available Cloisite 20A (20A for short) and custom modified MHABS [16] (nanoclay treated with 2-methacyloyloxyethylhexadecyldimethylammonium bromide), were used to fabricate
nanocomposites. The exfoliated clay structure of MHABS showed much stronger nucleation effect in comparison with the intercalated clay 20A, resulting in much smaller cell size and higher cell number density. Batch foaming of PS/CNFs (carbon nanofibers) nanocomposites has been studied in our laboratory [66]. With the addition of CNFs, high-density microcellular foams with very small cells and uniform cell size distribution were obtained. A similar trend was observed for PS/CNFs nanocomposite foams produced by extrusion process. For instance, PS/5% CNFs foam with an average cell size of 4.1 μm was prepared using a single screw extruder [149]. Without CNFs, the cell size of PS foam was around 8.7 micron at the same extrusion conditions.

Activated carbon (AC) is a highly porous particle with a very high internal surface area (1000~3000 m²/g). Although AC is not a nanoparticle, its pores are in the nanometer range (1~10 nm). It has excellent adsorptive property for organic molecules and very good IR absorption characteristics. AC is widely used for water decolorization, odor removal, purification, and automobile fuel emission control. However, only one open literature is on the application of AC as an additive in polymeric foams [150].

Extruded PS foams with either CNFs or AC as an additive for thermal insulation applications were the focus of this study. The heat transfer characteristics of plastic foams are well known and documented [151]. In general, the thermal conductivity of a cellular foam is composed of the following components: solid phase conduction $k_s$, gas phase conduction $k_g$, radiative energy transfer $k_r$, and convective heat transfer $k_c$. For insulation foams, such as extruded PS foams, the cell size is relatively small (less than 4 mm), so the convection component is negligible [152]. For low-density foams, the conduction
accounts for 70-80% and the radiation for 20-30% of the total heat transfer. Desirable foams in the application of thermal insulation have low bulk density, appropriate cell size (100~250 μm), and good IR absorption. Bimodal foam structure can further reduce the thermal conductivity [153]. The motivation of using CNFs and AC is that both have good IR absorption, resulting in lower radiative heat transfer $k_c$ [151]. In addition, water (moisture), air, and other gases or liquid adsorbed on CNFs, and especially AC, can serve as co-blowing agents and facilitate the formation of lower foam density.

3.2 Experimental

PS (Nova 1600 from NOVA Chemicals, Inc.) was used as received. The foaming agent CO$_2$ (>99.9%) was provided by Praxair. Vapor grown CNFs (PR-24-PS, supplied by Applied Science Inc.) were pyrolytically stripped to remove the surface organic contamination. The average diameter of these CNFs was 100 nm and the original length ranged from 30 to 100 μm. AC with an average diameter of 38 μm, which was designed specially for application to foaming, was provided by MeadWestvaco Corp. To obtain the AC with different moisture content (wet AC), an amount of water was sprayed on the particles to exceed the maximum adsorption capacity (about 4 g water / g AC) and mixed well with the AC. These samples were put in the oven for different time periods to desorb water to obtain desired moisture contents. PS foams with the addition of talc (manufactured by Luzenac) were used as a reference because talc is a widely used additive in the current extrusion foaming industry.
Foam extrusion of these materials were carried out by pumping the blowing agent CO₂ into a twin screw extruder (Leistritz ZSE-27; L/D = 40; D = 27 mm) through a syringe pump (ISCO 1000D) using an injection port located at L/D = 16. Fig. 3.1 shows the screw design of the twin screw extruder. PS pellets and 1 wt.% of additive (talc, CNFs or AC) were hand-mixed and poured in the hopper. The extruder was outfitted with a slit die, a shaping die, and rollers (HAAKE FP1 Film Postex) for foam uptake. To compare foam samples with different additives on an equal basis, different foaming conditions (screw speed: 50 rpm; feed speed: 50 rpm; CO₂ pressure: 6.41-10.45 MPa; die temperature: 120-130 °C; die pressure: 6.97-11.59 MPa; roller speed: 100-300 rpm) were used to produce a series of foam samples with a range of density for each additive. Only samples with very similar density (0.05 g/cm³) were used for property comparison. The extrusion conditions are listed in Table 3.1. Samples were cut and removed before entering the rollers to keep foam cell undamaged.

We also studied the effect of moisture content in the AC on the foam, i.e. comparison between addition of dry and wet AC. Similar extrusion conditions were used for dry AC and wet AC. The screw speeds of the feeder and extruder were kept at 50 rpm. The pressure of CO₂ was kept at 6.24~6.38 MPa (905~925 psi). Die temperature was kept at 130°C and the die pressure was in the range of 9.31~10.0 MPa (1350~1450 psi). The openings of the slit die and shaping die were kept constant.

The specimens for characterization were prepared by cutting segments (about 7cm×7cm) out of extruded foams and then sanding them to achieve a thickness of 7±0.05
mm. This sample thickness was used for most property measurements unless otherwise stated. It should be noted that the skin of the foam was removed during sanding.

The foam density was measured according to ASTM D792. A scanning electron microscope (SEM, HITACHI S-4300) was used to observe the cell morphology of foam samples. Samples were freeze-fractured in liquid nitrogen, and the fracture surface was sputter-coated with gold. Details about the image analysis can be found elsewhere [66].

The heat conductivity of foams was measured using a heat flow meter (FOX 200, LaserComp). The temperature difference of the upper and lower plates was set at 40°C. For each test, the apparatus provided two values of thermal conductivity, calculated using signals of the upper and lower heat flow meters. The average value of the two results was the final value of thermal conductivity corresponding to the average temperature of the upper and lower plates. Infrared (IR) transmission was measured using an in-house IR transmission tester. IR transmission is the ratio of transmitted power to incident power. The incident power, provided by an 810 nm laser, was 0.5 watts for all samples measured. The distance between the optical fiber output of the laser diode and the power meter was kept at 5 cm. The thermal expansion coefficient (TEC) was determined using a thermomechanical analyzer (TMA 2940, TA Instruments) operated at a heating rate of 5°C/min with a 0.02 N preloaded force. The samples for the TEC tests were cubes with each dimension of 5 mm.

The compressive properties were measured by using an INSTRON (Instron 1322) testing machine. The crosshead speed of compression was set at 0.45 mm/min.
3.3 Results and discussion

Foams for insulation have the following requirements. First of all, the bulk density is usually in the range of 0.025-0.035 g/cm³ and the cell size is usually in the range of 100–250 μm. This combination of bulk density and cell size usually gives low thermal conductivity values. In addition, a high IR absorption lowers thermal conductivity. Foams with a bimodal foam morphology are shown to have even lower thermal conductivity than uniformly distributed foams. Furthermore, good mechanic properties are preferable due to the application. In the following, properties such as the density, cell size, IR absorption, and mechanic modulus are discussed.

3.3.1 Comparison between CNFs and AC as additives in PS foaming

Foam samples with the bulk density around 0.05 g/cm³ were chosen for comparison unless otherwise stated. Representative SEM images and bulk densities of these foam samples are shown in Fig. 3.2. From the images, PS and PS/1% AC foams have a uniform foam structure, while PS/1% CNFs foam shows a bimodal like cell structure. Fig. 3.3 shows the number distribution in cell size of these four foam samples. The PS/1% CNFs foam shows a very different cell distribution from the other three. It has a high percentage of small cells together with a low percentage of large cells. For example, the number of cells from 30 to 90 μm represents about 70% of the total cells. This distribution is connected with its physical properties and is discussed later.
Mechanical properties, especially compressive properties, are important for foam applications. The reduced compressive moduli of the four foams are shown in Fig. 3.4. Compressive modulus is the slope of the initial linear region of the stress-strain curve in a compressive test. The reduced compressive modulus, defined as the ratio of compressive modulus to bulk density, is to normalize the effect of bulk density on properties. With addition of AC or CNFs, the foams showed better compressive properties than either PS or PS/1% talc foams.

Thermal stability is quantified as the thermal expansion coefficient in this study. Fig. 3.5 shows a typical measurement curve from the thermomechanical analyzer (TMA). For PS foams (with or without fillers), the dimensional change showed a linear relationship below 80 °C. This linear portion of the curve was used to calculate the thermal expansion coefficient. Fig. 3.6 shows the thermal expansion coefficients of these four foams. As expected, the thermal expansion coefficient decreases with the addition of fillers. Among the samples tested, the addition of CNFs provided the best improvement of thermal stability.

As shown in the introduction section, the thermal conductivity of insulation foams includes two components: conduction and radiation. The radiation part accounts for about 20-30% of the total heat transfer through insulation foams. Decreasing the radiative energy transfer is one important strategy to improve thermal insulation properties. The measurement of IR transmission can be a relevant estimation of radiative energy transfer. Fig. 3.7 shows IR transmission after 5 seconds for these four foams. Both PS/1% CNFs and PS/1% AC foams show lower IR transmission than either PS or PS/1% talc foams. In
other words, PS/1% CNFs and PS/1% AC foams provided better IR absorption because of the presence of carbon particles. After 10 seconds of laser radiation, there were only small dents on the surfaces of PS and PS/1% talc foams. However, there were large dents on PS/1% CNFs and PS/1% AC foams. For the PS/1% CNFs foam, there were actually holes through the sample caused by laser radiation. This result implies that CNFs may provide stronger radiation absorption than AC.

Thermal conductivity is the most important property for thermal insulation foams. Fig. 3.8 shows thermal conductivity values of solid PS and PS with 1% fillers at 20°C. The samples (diameter: 6.5 cm) were made by compression molding at 180°C. With the addition of fillers, the PS composites were expected to have higher thermal conductivity than pure PS because fillers are more conductive than pure PS [154,155]. That is the case for PS/1% talc and PS/1% CNFs. However, PS/1% AC shows a lower thermal conductivity value than PS. This is possibly due to the air trapped in the AC particles when preparing the PS/1% AC composite. Some tiny bubbles were observed at the fracture surface by breaking the PS/1% AC plate. This was also confirmed by the lower density of PS/1% AC plate (0.995 g/cm³) than PS plate (1.041 g/cm³). The existence of bubbles in the PS/1% AC plate resulted in a lower thermal conductivity value than PS. Fig. 3.9 shows thermal conductivity values at 20 °C for the four different foams. More than one sample (with different density) is shown for PS/1% CNFs and PS/1% AC foams. The following trends can be observed from the figure: the PS/1% talc foam has the highest thermal conductivity; PS/1% AC foams have the same thermal conductivity as PS foams; PS/1% CNFs foams have the lowest thermal conductivity. Within the
narrow range of bulk density, the measured thermal conductivity values did not vary much for the same type of foam samples. Fig. 3.10 shows thermal conductivity values of the four foams measured at different temperatures. The trend is the same at all temperatures. When comparing Fig. 3.8 and Fig. 3.9, thermal conductivity values of foams are about 1/3 that of solids. However, the trend for solids and foams is not the same. For example, PS/1% CNFs has a higher thermal conductivity than PS in Fig. 3.8. But, PS/1% CNFs foams have a lower thermal conductivity than the PS foam in Fig. 3.9. Therefore, foam morphology plays an important role in thermal conductivity. Since all foam samples have a similar bulk density, we postulate that the lowest thermal conductivity values of the PS/1% CNFs foams are from their cell size and perhaps the cell size distribution. As shown in Fig. 3.3, the PS/1% CNFs foam has a high percentage of small cells and some large cells. Fig. 3.11 shows the cell area distribution (based on the SEM images) of the four foams. For the PS/1% CNFs foam, there are two peaks, one around the cell size of 90 μm and the other from 150-250 μm. This “pseudo-bimodal” foam structure, not shown in the other three foams, may be responsible for the improved thermal insulation, i.e. small cells for low heat conduction [151] and large cells for low bulk density. That may be the reason for better thermal insulation properties shown in bimodal foam structure than unimodal foam structure. Fig. 3.12 shows the number and area distribution of four PS/1% CNFs foams with different density, foamed under different extrusion conditions. The “pseudo-bimodal” foam structure is shown in all four PS/1% CNFs foams, resulting in a lower thermal conductivity (Fig. 3.9).
3.3.2 Effects of water content on PS/AC foams

Bimodal foam structure has been shown to possess great toughness and better insulation than conventional unimodal structure.[156] Two methods are commonly used to achieve bimodal foam structure: two stage extrusion foaming and using co-blowing agent. In the latter method, water is commonly used. As described above, AC shows exceptional adsorption of water. This feature can be possibly used to achieve bimodal foam structure. In this study, PS/1% AC with different water content (water/AC = 0.07, 0.54, and 0.97) was prepared and foamed at the same condition. Fig. 3.13 shows representative SEM images of the foams. PS and PS/1% talc foams prepared under the same condition are also shown for comparison. However, there are only small differences in the SEM images between PS/1% dry AC and PS/1% wet AC foams in Fig. 3.13. Although the number of bigger bubbles increases with addition of water, the bimodal foam structure was not achieved. From Fig. 3.14, the PS +wet AC foam (density: 0.0566 g/cm$^3$) has more large bubbles (in the range of 210-510 $\mu$m) than PS +dry AC foam (density: 0.0687 g/cm$^3$). The increasing number of larger bubbles accounts for the lower density in the PS +wet AC foam.

Fig. 3.15 shows thermal conductivity and IR transmission data for the six foams in Fig. 3.13. Comparing with the PS/1% dry AC foam, PS/1% wet AC foams have lower bulk densities and thermal conductivities. The IR transmission values are about constant. Decreasing density and thermal conductivity benefit thermal insulation properties of foams. However, a different water content in AC does not cause a notable change in
thermal conductivity and IR transmission data in Fig. 3.15. The possible reason is that most water was lost during the extrusion foam process. During extrusion, we observed most water evaporated and stream came out from the feeder. In addition, we have to point out that the ratios of water/AC given above are for preparation of wet AC. After the PS/wet AC was fed into the extruder, water was lost due to high processing temperatures. Samples taken out at CO2 injection port showed from TGA that most of the water initially present was lost. Loss of water during extrusion explains well why different ratios of water/AC did not result in considerably different foam properties. Therefore, the water cannot be maintained well during extrusion for the physical mixture of PS and wet AC. There are many possible ways for keeping water even at elevated temperatures. For example, when some surfactant was added during preparation of wet AC, more water was kept (35% more than without surfactant) during extrusion. In addition, superabsorbent polymers (SAP) can be added as well. The currently ongoing effort is keeping water by in-situ polymerization. In other words, styrene, mixed with wet AC, was used to synthesize PS. By that way, the water may be better maintained during the extrusion process.

3.4 Conclusion

CNFs and AC were used as additive/nucleation agents in PS extrusion foaming. Both fillers showed promising application in insulation foams based on foam density, thermal conductivity, IR transmission, thermal stability, and compressive modulus.
Overall, CNFs are better than AC due to the unique foam structure ("pseudo-bimodal") observed in this study. Water worked as a co-blowing agent in the PS/ wet AC foaming process. Bulk density was reduced but bimodal structure was not observed. The reason is that water has not been well controlled in the extrusion process and most water evaporated due to high extrusion temperatures. Water used as a co-blowing agent is still the appropriate direction to achieve bimodal foam structure. Currently, other methods are being tested to maintain water in the extrusion process.
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| Other         | The openings of the slit die and shaping die are adjusted accordingly |

Table 3.1: Extrusion conditions for preparing foam samples with density close to 0.05 g/cm³
Figure 3.1: Screw configuration of the ZSE-27 Leistritz twin screw extruder
Figure 3.2: Representative SEM images of (a) pure PS foam (bulk density: 0.048±0.001 g/cm³), (b) PS/1% talc foam (bulk density: 0.051±0.001 g/cm³), (c) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³), and (d) PS/1% AC foam (bulk density: 0.057±0.001 g/cm³)
Figure 3.3: Number distribution in cell size of (a) pure PS foam (bulk density: 0.048±0.001 g/cm³) and PS/1% talc foam (bulk density: 0.051±0.001 g/cm³); (b) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³) and PS/1% AC foam (bulk density: 0.057±0.001 g/cm³)
Figure 3.4: Reduced compressive moduli of (a) pure PS foam (bulk density: 0.048±0.001 g/cm³), (b) PS /1% talc foam (bulk density: 0.051±0.001 g/cm³), (c) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³), and (d) PS/1% AC foam (bulk density: 0.057±0.001 g/cm³). The average was taken from 4 samples for each type of foam.
Figure 3.5: A typical graph from measurement of TMA (the linear part from 40-80°C, shown as thicker line on the figure, was used to calculate the thermal expansion coefficient)
Figure 3.6: Thermal expansion coefficients of (a) pure PS foam (bulk density: 0.048±0.001 g/cm³), (b) PS/1% talc foam (bulk density: 0.051±0.001 g/cm³), (c) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³), and (d) PS/1% AC foam (bulk density: 0.057±0.001 g/cm³). The average was taken from 3 samples for each type of foam.
Figure 3.7: IR transmission after 5 seconds of (a) pure PS foam (bulk density: 0.048±0.001 g/cm³), (b) PS/1% talc foam (bulk density: 0.051±0.001 g/cm³), (c) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³), and (d) PS/1% AC foam (bulk density: 0.057±0.001 g/cm³). The average was taken from 5 samples for each type of foam.
Figure 3.8: Thermal conductivity values of solid PS and PS composites at 20 °C: (a) pure PS, (b) PS/1% talc, (c) PS/1% CNFs, and (d) PS/1% AC. The average was taken from 3 samples for each type of solid.
Figure 3.9: Thermal conductivity values of polymer and polymer composite foams at 20 °C: (a) pure PS foam, (b) PS/1% talc foam, (c) PS/1% CNFs foam, and (d) PS/1% AC foam. The average was taken from 3 samples for each type of foam.
Figure 3.10: Thermal conductivity values at four temperatures of (from left to right): (a) pure PS foam (bulk density: 0.048±0.001 g/cm³), (b) PS/1% talc foam (bulk density: 0.051±0.001 g/cm³), (c) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³), and (d) PS/1% AC foam (bulk density: 0.057±0.001 g/cm³). The average was taken from 3 samples for each type of foam.
Figure 3.11: Area distribution for (a) pure PS foam (bulk density: 0.048±0.001 g/cm³) and PS/1% talc foam (bulk density: 0.051±0.001 g/cm³); (b) PS/1% CNFs foam (bulk density: 0.051±0.001 g/cm³) and PS/1% AC foam (bulk density: 0.057±0.001 g/cm³)
Figure 3.12: Number (a) and area (b) distribution for four PS/1% CNFs foam with different density
Figure 3.13: Representative SEMs of the foams under the similar extrusion condition: screw speeds of the feeder and extruder were 50 rpm; pressure of CO$_2$ was 6.24-6.38 MPa (905-925 psi); die temperature was 130$^\circ$C and the die pressure was 9.31-10.0 MPa (1350-1450 psi); the opening of the slit die and shaping die were kept constant.
Figure 3.14: Number (a) and area (b) distribution for PS+ dry AC and PS+ wet AC (water/AC=0.07) foams under the same extrusion condition.
Figure 3.15: Density, thermal conductivity (a), and IR transmission (b) data for the six foams in Fig. 3.13 (bars represent density and the curve represents thermal conductivity in (a) and IR transmission in (b))
CHAPTER 4

FOAMING DYNAMICS

4.1 Introduction

To have a better and deeper understanding of the foaming process, two types of information are needed. The first one is a description of what happens after we release the pressure to trigger cell nucleation and growth. To achieve this qualitative information, an \textit{in-situ} observation is necessary. Second, quantitative information about cell nucleation and cell growth are important. According to the literature, optical methods can be used to achieve both. By recording the foaming process, qualitative information of how foaming happens is easy to obtain. Assuming that one nucleation site grows to one bubble, the number of cells can be counted and cell nucleation rate can be calculated. By tracking the size of cells, the cell growth rate can also be obtained. Several researchers obtained cell nucleation and growth rate data in the polymer foaming process by using this method. Taki [25,26] conducted \textit{in-situ} visual observations for batch foaming processes of PP and PP-clay nanocomposites with CO$_2$ to understand bubble nucleation and growth in the early stages. They developed a high-pressure autoclave that has two sapphire windows on
the walls. A high-speed digital camera with a microscope was used to observe the bubble nucleation and bubble growth behavior of the early stages of foaming in situ. Guo et al. [2] used a similar experimental setup but a much higher speed camera to study microcellular foaming with a higher pressure drop. A PS-CO₂ system was used and the maximum pressure-drop rate achievable was 2.5 GPa/s from the designed system. However, in their studies, the sample touched the sapphire windows and heterogeneous nucleation might occur in their experimental setup. Nevertheless, these data are the only available data on bubble nucleation rates in polymers and have been used below for analysis. Our new system was designed to minimize heterogeneous nucleation.

PS and PMMA were used as the polymers for foaming in our experiments. As mentioned above, polymer nanocomposites and blend (PS/PMMA) were used for foaming. Therefore, the effects of nanoparticles and the interface of the polymer blend were also studied. In this study, the PS/PMMA bilayer was used as a simplified model for PS/PMMA blends and was used to study foaming dynamics and gain insight into phase interface effects on bubble nucleation.

4.2 Experimental

4.2.1 Material

PS (CX5197; \(M_w=187,000, M_n=86,000\)) was from Total Petrochemicals (formerly Atofina) and PMMA (PL-150; \(M_w=80,200; M_n=41,700\)) was from Plaskolite. The
foaming agent CO₂ (>99.9%) was provided by Praxair and used without further purification.

4.2.2 Sample preparation

PS, PMMA, PS nanocomposites, and PS/PMMA bilayers were made by compression molding. For bilayer samples, PS and PMMA plate samples with thickness of 1 mm were made by the procedure above, then the two plates were put in another square mold of thickness 2 mm. Thirty minutes of melting was allowed to bond the two plates together. Plates from compression molding were cut into preferred dimensions and smoothed by fine sand paper. We used two types of samples. The first type was a small strip (for pure PS, PMMA, or PS nanocomposites, 2.5 mm × 2 mm × 15 mm; for PS/PMMA bilayer, 2 mm × 2 mm × 15 mm.). In other words, for these strips, PS/PMMA bilayer was little bit narrower, but the thickness of all these strips was 2 mm. A sample thinner than 2 mm deformed too easily and fell at the experimental temperature and pressure. Another type of sample was a plate with dimensions of 7 mm × 20 mm × 0.6 mm cut from the plate made by compression molding. This type of sample was used to achieve quantitative cell nucleation and growth data. If the sample was too thick (> 1 mm), it was too difficult to count the number of cells by analyzing the images because there were some bubbles behind the bubbles being counted in the viewing direction. On the other hand, if the sample was too thin (<0.4 mm), the sample warped under the
experimental conditions, resulting in the sample moving out of the focal plane of the camera.

4.2.3 Experimental setup and procedure

The experimental setup based on a custom high-pressure (up to 34 MPa), high temperature (up to 250 °C) variable-volume view cell (Thar Technologies, Inc.) used in interfacial tension measurements [157] was modified for observation of the foaming process. Fig. 4.1 shows the view cell and experimental setup. In this study, the volume of the cell was fixed to allow for a controlled pressure release rate. The pressure inside the cell was controlled by a syringe pump (ISCO 500D), which operated in a constant pressure mode. The temperature inside the cell was controlled by cartridge heaters and a temperature controller to an accuracy of ±0.5 °C. A CCD camera with an adjustable lens was used to capture the video. A Fiber-Lite model 181-1 gooseneck illumination system (Fisher scientific) provides uniform back-lighting.

For the strip-shaped sample (polymer or bilayer sample), it was placed on an aluminum sample holder in the vessel. Fig. 4.2 shows the images of the sample holder. The distance between contact points on the sample holder was about 5 mm, so the length of the sample above the holder was about 10 mm. For the sheet-shaped sample, it was placed vertically. The sample was about 7 mm × 20 mm and the thickness was about 0.6 mm. The vessel was closed, and then pressurized with CO₂ at a desired pressure (e.g., 5.44 MPa (800 psi)) and temperature (e.g., 100°C). The sample was allowed to
equilibrate for 24 hours. For complete foaming studies, the pressure was released quickly (about 9 seconds) to atmospheric pressure and the sample was taken out and put in ice water to stop bubble growth. For intermediate time quenching experiments, cool high pressure N₂ (about 5°C) was quickly injected into the vessel after some amount of time of pressure release to stop the bubble growth. The sample was taken out for optical observation or SEM analysis. The entire process was monitored by the CCD camera. Only the middle part of the sample was focused on for two reasons: first, a high-magnification movie was preferred for quantitative analysis so only one part of the sample could be monitored; second, foaming of the bottom part was affected by the aluminum sample holder and the top was affected by the interface of polymer and CO₂. The video showed that quenching by cool N₂ was very efficient because there was no observable bubble growth after the cool N₂ was injected.

4.3 Results and discussion

4.3.1 Qualitative results for batch foaming

From the movies of PS, PMMA, and bilayer, we found that PS and PMMA started to foam at around the same time after the initiation of pressure release (69 seconds for PS and 67 seconds for PMMA), and the bilayer started to foam at the interface at about 34 seconds after the pressure release. Fig. 4.3 shows some snapshots of PS, PMMA, and PS/PMMA bilayer at several different time periods. It clearly shows that
bubbles nucleate and grow earlier at the interface than in the pure polymer phases, likely due to a heterogeneous nucleation mechanism present in the bilayer sample. In general, the heterogeneous nucleation rate is much higher than the homogeneous nucleation rate due to lower activation energy. This is the theoretical basis for increasing foaming efficiency by adding nucleation agents or blending two polymers (the dispersive phase can serve as a nucleation agent). The time the sample starts to foam we describe here is based on when the first bubble appears in the video and does not mean the bubble nucleation begins at that time. The literature shows very short bubble nucleation time (in the order of millisecond) [40] for most systems. Since in our results bubbles are detectable earlier in the interface than in the pure polymer phase, we believe nucleation (heterogeneous) occurs earlier than in pure polymer phases (homogeneous).

In addition, we observed that some bubbles collapsed along the interface. And this phenomenon was repeatable. Fig. 4.4 shows chronological snapshots of bubble growth then collapse at the interface. Considering the bubble indicated by an arrow in the figure, its size increased from 65 seconds to 78 seconds, then decreased after 78 seconds. The possible reason is that the interface of PS and PMMA is weaker compared to bulk phases. Bubbles at the interface grow to a certain size causing separation of the two layers and gas escapes along the interface resulting in partial collapse. We observed this rapid collapse in our videos and did not observe it for pure polymer samples. Fig. 4.5 shows SEMs of the PS/PMMA interface for samples with foaming time of 120 seconds (from start of pressure release). This figure is a collage of several micrographs in order to show the whole sample.
Furthermore, from analysis of the final foam samples, bubbles in the PMMA phase were greater in number and smaller in size than in the PS phase. In our hypothesis, bubbles start growing from the interface, then in PS and PMMA bulk phases. The viscosity plays an important role when bubbles grow. As will be shown in Chapter 7, at our experimental conditions (100°C, CO₂ pressure 5.44 MPa), the viscosity of the PMMA phase was higher than in the PS phase [158]. Therefore, the PMMA phase initially gave more resistance to bubble growth. Analysis of the distribution of bubble density and size with position (from PS/PMMA interface to polymer/CO₂ interface) and time helped us understand this issue. Fig. 4.6 shows bubble number distributions of the bilayer samples at 63 seconds and 120 seconds. It provides clear evidence that bubbles nucleate and grow earlier at the interface. For a better understanding, results of additional foaming time periods are needed and bubble size distribution information is also important.

Although the bilayer representation is a over-simplified model for describing polymer blends since the domain size of the dispersive phase is only in the range of microns, it gives us some invaluable information about bubble nucleation and growth in the early stage of blend foaming process.

4.3.2 Quantitative results for batch foaming

In the quantitative study of cell nucleation and growth, a thin sheet (length: 20mm; width: 7mm; thickness: about 0.6 mm) was placed vertically. The “free-standing”
sample did not touch any solid surface and heterogeneous nucleation could be possibly avoided. Since obtaining homogeneous cell nucleation and growth was our goal, PS+ CO₂ system was chosen. Three effects in the foaming process, initial CO₂ pressure, temperature, and final CO₂ pressure, were investigated. All three factors are related to the driving force of foaming. The final CO₂ pressure was zero (ambient) unless otherwise stated.

Ten cases, shown in Table 4.1, were studied to investigate the effects of the initial pressure, temperature, and the final pressure. The second column shows the initial pressure and temperature used. The final pressure was 389 psi for case (4) and 0 for all other cases. The third column shows the initial CO₂ solubilities and the fourth column shows some comments. Case (1)-(7) provided useful information. Case (1), (2), and (6) were used to study the temperature effect; case (1), (3), and (5) were used to study pressure effect; case (3) and (4) were used for investigating the effect of the final pressure. Case (8)-(10) were not used for the quantitative nucleation rate extraction. In case (8), the condition (800 psi and 100°C) was used for the qualitative study above. However, the bubbles were not uniform and the recorded images could not be used for calculation. The reason may be the low solubility (3.41 wt.%) under this condition. When new bubbles nucleated at some spots, CO₂ from the surrounding polymer diffused to these spots to supply gas for bubble growth, leading to less nucleation adjacent to those spots due to the reduction of supersaturation. To increase the driving force for nucleation, a higher initial pressure (1200 psi) in case (9) was used. The bubbles nucleated more uniformly, but the sample was severely warped because of the stronger Tₙ reduction by a
higher CO₂ pressure. In case (10), a low temperature combined with a low pressure did not trigger any foaming. To summarize, for the sample to remain straight after 24 hours at the experimental conditions, comparatively lower temperatures are preferable. In our study, temperatures in the range of 60-80°C were used. For the sample to have enough nucleation, high initial pressures (i.e. higher solubility) were preferred. In our study, pressures in the range of 1000-1500 psi were used. In case (4), the final pressure 389 psi rather than 0 was used. Although there were only a limited number of bubbles foamed and the bubbles were distributed unevenly, the result was still used for the quantitative calculation.

Fig. 4.7 shows the pressure profiles for the cases (1)-(7). The time “0” is when the pressure starts to drop. Table 4.2 summarizes the average and maximum pressure drop rates for each case. For the calculation of the average pressure drops, 98% of total pressure drop was used. For example, in case (3), it took about 7.1 seconds for the pressure drop from 1000 psi to 20 psi and about 10 seconds for 20 psi to 0. For the calculation of the average pressure drop rate, pressure difference was 1000-20=980 psi and the elapsed time was 7.1 seconds. This choice (98%) accurately characterized the average pressure drop rate. In addition, the maximum pressure drop rate in the seven cases was less than 6 MPa/s, much less than in Guo’s paper, in which the minimum pressure drop rate 20 MPa/s was used. This may explain why we observed the bubbles much longer after the pressure drop (longer than 50 seconds in our cases and less than 1 second in their cases). The reason we used smaller pressure drop rate was that a higher
pressure drop rate led to a much higher nucleation rate and the cells coalesced more readily, resulting in difficulties to count the number of cells and track the bubble growth.

The whole foaming process was recorded and the movie was analyzed to obtain the cell number density growth curve (cell number density vs. time) and cell size growth curve (cell diameter vs. time). After each foaming experiment was finished, pictures of the sample were taken by a microscope. Based on the analysis of these images, final cell number density and average cell diameter were obtained. Table 4.3 summarizes what type of information we had, marked by “Y”, for each case that we obtained data.

The following shows some representative results. In case (1), foam cells were observed at about 62s. Fig. 4.8 shows some representative snapshots. On the snapshot at 62s, there were some dark dots. These dots were on the camera and were not foam bubbles. When the foam started, there were hundreds of bubbles on the screen. The bubbles grew or coalesced with time.

As shown in Table 4.3, case (1) and case (3) gave more information than other cases. Here case (3) is used to show the representative snapshots, the microscopic images, the bubble number and size growth curves. Foaming started about 95s after the start of the pressure drop. Fig. 4.9 shows some representative snapshots from the movie. These snapshots are not as clear as the ones in Fig. 4.8, however, the snapshots at every second were compared to count the bubble numbers and measure bubble sizes, therefore obtaining the curves of bubble number and size growth. Fig. 4.10 shows a plot of cell number density vs. time; Fig. 4.11 shows a plot of cell diameter vs. time of five randomly chosen cells. Fig. 4.12 shows the curves of cell cross section area vs. time for the five
cells in Fig. 4.11. From the $R^2$ values ($R^2$ is 0.93, 0.99, 0.98, 0.97, and 0.95 for bubbles 1-5 respectively), we can conclude that there is a rough linear relationship between the cell cross section area with time; this indicates the bubble growth is a diffusion-controlled process. This is consistent with the observation by other researchers [25,26]. Since it is a linear relationship, we can extrapolate the curves to find the time when the nucleation started. We found nucleation starts around 88 seconds in this case. The pressure drop finished within about 20 seconds. Therefore, the pressure drop (driving force) and nucleation were decoupled. However, in Guo’s paper, the nucleation began before the pressure drop was finished. The possible reason is the difference of pressure drop rate. As will be shown in Chapter 5, the decoupling of pressure drop and nucleation brings convenience for nucleation rate calculation. When microscopic images of the final foam sample were taken, we found there was more than one layer of bubbles. As mentioned above, in the experiments, a thin sample (with thickness about 0.4-0.7mm) was used because if the sample was too thick, it was hard to count the number of bubbles because there might be bubbles behind the bubbles being counted in the viewing direction. However, the sample was still not thin enough to guarantee a single layer of bubbles because the cell diameter was still much smaller than the thickness of the sample. When taking the images by a microscope, different depth in the sample was focused to obtain a series of images. These images were carefully compared to count the total cell number. Fig. 4.13 shows four representative images, each of which was by different focusing depth. Therefore, in case (3), there were four layers of bubbles in the sample. The final cell density was calculated based on the total cell number and sample dimension. Based
on calculations of these four microscopic images, the cell number density of the final foam sample is 7.98E+04 cells/cm³. It is different from the maximum cell number density 1.55E+05 cells/cm³ on Fig. 4.10. The cell number density based on the microscopic images was used for nucleation rate calculation since the microscopic images were much clearer.

In case (4), the final pressure 389 psi was used. The smaller driving force led to much lower nucleation efficiency. There were only a few cells on the sample and these cells were well separated. Although the result could not provide good data for bubble number density information because it was not well distributed, it could provide useful information for bubble growth for a longer time because the cells were still separated in the final foam sample. Fig. 4.14 shows the cell diameter vs. time (a) and cell cross section area vs. time (b) for case (4). R² is 0.98, 0.98, and 0.97 for bubbles 1-3 respectively in (b), indicating again the bubble growth is a diffusion-controlled process. Again, extrapolation of these curves demonstrates the decoupling of pressure drop and nucleation.

Table 4.4 summarizes the results based on the microscopic images and movies. In case (7), there were many layers of bubbles and these bubbles were close to each other, therefore it was impossible to count the total number of bubbles. The cell number density 5.80E6 cells/cm³ was calculated assuming the bubbles were uniformly distributed in all dimensions. The major goal of these results is to provide quantitative nucleation data, which was shown in Chapter 5. By comparing the results of the seven cases, some
qualitative conclusions for the effects of initial pressure, temperature, and final pressure on foaming can be obtained.

1. Cell number density. By comparing cases (1), (3), and (5), higher initial pressure led to higher cell number density at the same initial temperature; this was also true by comparing cases (2) and (7). By comparing cases (1), (2), and (6), lower initial temperature led to higher cell number density at the same initial pressure; this was also true by comparing cases (5) and (7). By comparing cases (3) and (4), lower final pressure led to higher cell number density at the same initial pressure and temperature.

2. Average cell diameter in the final foam samples. By comparing cases (1), (3), and (5), higher initial pressure led to smaller cell size at the same initial temperature; this was also true by comparing cases (2) and (7). By comparing cases (1), (2), and (6), higher initial temperature led to larger cell size at the same initial pressure; this was also true by comparing cases (5) and (7).

3. Foaming start time. By comparing cases (1), (3), and (5), higher initial pressure started foaming earlier at the same initial temperature; this was also true by comparing cases (2) and (7). By comparing cases (1), (2), and (6), higher initial temperature started foaming earlier; this was also true by comparing cases (5) and (7).

We have to be aware that these observations are qualitative. To explore how these factors affect foaming, some models are needed. As will be shown in Chapter 5, the
possible relationship between solubility (and phase boundaries), which is a function of pressure and temperature, and nucleation rate was explored.

4.4 Conclusion

To better understand the underlying mechanisms of foaming, an in-situ observation system was built to study foaming of pure PS and PS/PMMA blending. Two different designs were used. A simple PS/PMMA bilayer representation was examined for better understanding of PS/PMMA blend foaming process. Visual observation of batch foaming of this system was conducted and a quenching method was used to study foams with different bubble growth time. The PS/PMMA interface demonstrated strong heterogeneous nucleation comparing to homogeneous nucleation in bulk phases.

A novel “free-standing” sample setup avoided the possible heterogeneous nucleation occurred in other experimental setups. The recorded movies were analyzed to obtain quantitative homogenous nucleation rate and also bubble growth rate. Three effects in foaming process, all related to the driving force of foaming, initial CO$_2$ pressure, temperature, and final CO$_2$ pressure, were investigated.
<table>
<thead>
<tr>
<th>Cases</th>
<th>Initial conditions</th>
<th>Solubility (wt.% CO₂)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1200 psi, 80°C</td>
<td>7.25</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>1200 psi, 60°C</td>
<td>8.20</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>1000 psi, 80°C</td>
<td>6.09</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>1000 psi, 80°C, (389 psi)</td>
<td>6.09</td>
<td>Not uniform</td>
</tr>
<tr>
<td>(5)</td>
<td>1500 psi, 80°C</td>
<td>8.89</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>1200 psi, 70°C</td>
<td>6.66</td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>1500 psi, 60°C</td>
<td>9.84</td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>800 psi, 100°C</td>
<td>3.41</td>
<td>Not uniform</td>
</tr>
<tr>
<td>(9)</td>
<td>1200 psi, 100°C</td>
<td>5.17</td>
<td>Warped severely</td>
</tr>
<tr>
<td>(10)</td>
<td>1000 psi, 60°C</td>
<td>6.68</td>
<td>No foam</td>
</tr>
</tbody>
</table>

Table 4.1: Ten cases studied (in case (4), 389 psi was the final pressure, for all other cases, the final pressure (CO₂) was zero) to investigate the effects of initial pressure, temperature, and final pressure.
<table>
<thead>
<tr>
<th>Cases</th>
<th>Conditions</th>
<th>Average dp/dt (MPa/s)</th>
<th>Maximum dp/dt (MPa/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1200 psi, 80°C</td>
<td>1.00</td>
<td>4.66</td>
</tr>
<tr>
<td>(2)</td>
<td>1200 psi, 60°C</td>
<td>0.92</td>
<td>4.32</td>
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<tr>
<td>(3)</td>
<td>1000 psi, 80°C</td>
<td>0.94</td>
<td>4.46</td>
</tr>
<tr>
<td>(4)</td>
<td>1000 psi, 80°C, (389 psi)</td>
<td>0.66</td>
<td>1.45</td>
</tr>
<tr>
<td>(5)</td>
<td>1500 psi, 80°C</td>
<td>1.17</td>
<td>5.53</td>
</tr>
<tr>
<td>(6)</td>
<td>1200 psi, 70°C</td>
<td>0.91</td>
<td>4.06</td>
</tr>
<tr>
<td>(7)</td>
<td>1500 psi, 60°C</td>
<td>1.00</td>
<td>5.85</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of the pressure profiles (see Fig. 4.7) in cases (1)-(7)
Table 4.3: Summary of the information we obtained (marked by “Y”) for each case

<table>
<thead>
<tr>
<th>Cases</th>
<th>Conditions</th>
<th>From microscopic images</th>
<th>From recorded movies</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cell number density</td>
<td>Average cell diameter</td>
<td>Cell number growth curve</td>
</tr>
<tr>
<td>(1)</td>
<td>1200 psi, 80°C</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>(2)</td>
<td>1200 psi, 60°C</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>1000 psi, 80°C</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>(4)</td>
<td>1000 psi, 80°C, (389 psi)</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>1500 psi, 80°C</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>1200 psi, 70°C</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>1500 psi, 60°C</td>
<td>Y</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Cases</td>
<td>Conditions</td>
<td>Cell number density (cm(^{-3}))</td>
<td>Comments</td>
<td>Foaming starts (s)</td>
</tr>
<tr>
<td>-------</td>
<td>------------------</td>
<td>-----------------------------------</td>
<td>-----------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>(1)</td>
<td>1200 psi, 80°C</td>
<td>1.05 E5</td>
<td></td>
<td>62</td>
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<tr>
<td>(2)</td>
<td>1200 psi, 60°C</td>
<td>2.29 E5</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>(3)</td>
<td>1000 psi, 80°C</td>
<td>7.98 E4</td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>(4)</td>
<td>1000 psi, 80°C, 389 psi</td>
<td>725</td>
<td>A few bubbles, a lot unfoamed space</td>
<td>89</td>
</tr>
<tr>
<td>(5)</td>
<td>1500 psi, 80°C</td>
<td>3.81 E5</td>
<td>Bubble size not uniform</td>
<td>56</td>
</tr>
<tr>
<td>(6)</td>
<td>1200 psi, 70°C</td>
<td>1.52 E5</td>
<td>Some bubbles are overlapped</td>
<td>97</td>
</tr>
<tr>
<td>(7)</td>
<td>1500 psi, 60°C</td>
<td>5.80 E6</td>
<td>Too many bubbles, severely overlapped</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 4.4: Summary of the cell number density, average cell diameter (both from analysis from microscopic images), and foaming start time (based on movies)
Figure 4.1: (Left): apparatus for visualization of a batch foaming process; (right): high pressure view cell
Figure 4.2: Photos of the sample holder used in the *in-situ* observation of foaming: (A) Top view without the sample; (B) Side view without the sample; (C) With the strip-shaped sample; (D) With the plate-shaped sample
Figure 4.3: Snapshots of foaming movies of PMMA, bilayer, and PS at 0, 60, 90, 120 seconds after start of pressure release. The thick dark lines represent the edges (polymer-gas interface) of a transparent sample as viewed with the camera. Refractions from the edges and bubbles are easily observed.
Considering the bubble indicated by an arrow in the figure, its size increases from 65 seconds to 78 seconds, then decreases after 78 seconds.

Figure 4.4: Chronological snapshots of bubble growth then collapse at the interface of the bilayer sample (time is after the start of pressure release, same as in Fig. 4.3).
Figure 4.5: SEMs for PS/PMMA interface (left: PS side; right: PMMA side)
Figure 4.6: The distribution of bubbles in a PS/PMMA bilayer (the interface is at distance = 1mm). The bubbles inside the sample were binned into three locations. Zero bubbles were observed for the farthest PS bin at 63s. Most bubbles were observed at the interface, requiring the semi-log plot. Lines are provided only to guide the eye.
Figure 4.7: Pressure profiles during the foaming process for the cases (1)-(7) (foaming conditions are shown in Table 4.1)
Figure 4.8: Representative snapshots at 62s, 76s, 80s, and 88s after the start of pressure drop for PS foaming process with initial pressure 1200 psi and temperature 80°C (case (1))
Figure 4.9: Representative snapshots at 95s, 103s, 111s, and 119s after the start of pressure drop for PS foaming process with initial pressure 1000 psi and temperature 80°C (case (3))
Figure 4.10: The cell number density vs. time for the PS foaming process with initial pressure 1000 psi and temperature 80°C (i.e., case (3); the first detectable bubble was shown at about 95s after the start of pressure drop and the bubbles overlap after 119s)
Figure 4.11: The cell diameter vs. time for the PS foaming process with initial pressure 1000 psi and temperature 80°C (i.e., case (3))
Figure 4.12: The cross section area of cells vs. time for the five bubbles in Fig. 4.11 (R^2 is 0.93, 0.99, 0.98, 0.97, and 0.95 for bubbles 1-5 respectively)
Figure 4.13: Representative images (30% of the original size) of the foamed sample (with initial pressure 1000 psi and temperature 80°C, i.e., case (3)) by a microscope (there were four layers of bubbles)
Figure 4.14: The cell diameter vs. time (a) and cell cross section area vs. time (b) for the PS foaming process in case (4); \( R^2 \) is 0.98, 0.98, and 0.97 for bubbles 1-3 respectively in (b)
CHAPTER 5

SOLUBILITY MODELING

5.1 Introduction

Modeling solubility by an equation of state (EOS) is important because it is often difficult to obtain data experimentally. Appropriate modeling by EOS can decrease experimental effort tremendously. In addition, the experimental data for phase boundaries (binodal and spinodal) for polymer-diluent systems are very scarce. Kiran[37]’s research group used the time- and angle-resolved light scattering techniques to map out the binodal and spinodal envelopes of some systems, such as PDMS-CO$_2$. However, for those systems in which the gas has a low affinity with the polymer, such as PS-CO$_2$, the data are extremely limited due to experimental difficulties (extremely high pressure is necessary). Therefore, equations of state must be used to predict the phase boundaries in the region where the weight fraction of the gas is higher than the polymer.
5.2 Algorithm for two equations of state

5.2.1 Algorithm for Sanchez-Lacombe EOS

For using the Sanchez-Lacombe EOS (S-L EOS) to predict the phase boundaries, the following assumptions have to be made: The temperature must be above the $T_g$ of the polymer, i.e. the polymer can be modeled as a liquid, and the polymer is assumed to be mono-dispersed. The program code is shown on the Appendix C. The iteration method is always the key for a fast and accurate phase diagram calculation; a good iteration method accelerates the calculation. On the other hand, an inefficient method does not guarantee convergence of the program, therefore not being able to give any result. Several iteration methods were tried and the successful one is based on the chemical potential difference, also used in the program of Appendix B of *Supercritical fluid extraction* by McHugh et al. [159]. The algorithm is shown in Fig. 5.1 and can be described as follows (for binary systems):

1. In this program, we are interested in evaluation of phase boundaries under a constant temperature, i.e. a series of weight fractions will be obtained under a series of pressures. As shown in Fig. 5.2, we need to calculate the two binodal points at some pressure first, then calculate the two spinodal points. Binodal and spinodal points at different pressures are then calculated to get the binodal and spinodal curves.
2. Get input parameters ready. Pure fluids are completely characterized by three parameters \((T^*, P^*, \rho^*)\) and only one additional parameter, the binary interaction parameter, \(k_{ij}\), is needed to describe binary systems. The binary interaction parameter is usually correlated from experimental data. The input of molecular weights for both components is for the calculation of \(r\). In addition, the temperature and pressure are also needed.

3. Initial values for distribution ratio in two phases were guessed, from which the weight fractions in both phases can be evaluated. By combining with parameters in step 2, \(T^*, P^*, \text{ and } r\) for the mixture can be evaluated. From these parameters, reduced parameters \(\tilde{T}\) and \(\tilde{P}\) can be calculated.

4. Reduced density \(\tilde{\rho}\) values in two phases can be calculated by solving Eq. 2. 9.

5. With the known parameters above, including the calculated \(\tilde{\rho}\), chemical potentials in both phases can be evaluated. At equilibrium, the chemical potential of each component in both phases should be equal, i.e. the chemical potential difference is smaller than a tolerance (a very small number, e.g. \(10^{-5}\)). Otherwise, the iteration is used to get a better guess of distribution ratio in two phases. Then go to step 3 until the chemical potential difference is smaller than the tolerance.

6. Up to here, the weight fractions in both phases under this temperature and pressure are calculated, i.e. two binodal points are calculated, shown in Fig. 5. 2 (a).

7. Calculate the chemical potential curve (chemical potential vs. weight fraction of one component) at the weight fraction range within the two binodal points. Two
peaks with a minimum and a maximum respectively can be obtained. The weight fractions at those two extreme points are the two spinodal points at the temperature and pressure. This is shown in Fig. 5.2 (b).

8. Calculate the binodal and spinodal points at higher pressure \((P + \Delta P)\) until the critical point. This is shown on Fig. 5.2 (c).

A large challenge for modeling phase diagrams for polymer-diluent systems is that the extremely small weight fraction of the polymer in the gas underflows the limit of typical computers. For simple solubility prediction, a common assumption is that the weight fraction of the polymer in the gas phase is zero. The calculation becomes much easier because of this assumption. This assumption is verified by modeling the binodal curve in the whole weight fraction region.

5.2.2 Algorithm for PC-SAFT EOS

PC-SAFT is more complex than S-L EOS, however, the algorithm for phase equilibrium calculation is similar. The strategy is the same as shown in Fig. 5.2. The program code is shown in the Appendix D. The core subroutine \(PC-SAFT_PROP\) is available through the authors’[104] website (http://www.bci.uni-dortmund.de/th/de/textonly/content/Forschung-index/Bereiche/pc-saft-download.html).

However, this program can only be used for small molecule systems. For polymer-diluent systems, divergence always occurs. One of the problems is the iteration method.
Modifications were made to make sure it also works for our polymer-diluent systems.

The algorithm can be described as follows (for binary systems):

1. Get input parameters ready. For non-associating systems, i.e. PS-CO$_2$, pure fluids are completely characterized by three parameters: $m$ (segment number), $\varepsilon^0 / k$ (segment-segment interaction, in Kelvin), and $\sigma$ (segment diameter, in angstrom) and only one additional parameter, the binary interaction parameter, $k_{ij}$, is needed to describe binary systems. The binary interaction parameter is usually correlated from experimental data. In addition, the temperature and pressure are also needed. In this program, we are interested in evaluation of phase boundaries under a constant temperature, i.e. a series of molar fractions will be obtained under a series of pressures.

2. Initial values for molar fractions in two phases are guessed so other parameters can be calculated.

By calling the subroutine \texttt{PC\_SAFT\_PROP}, fugacity coefficients of each component on each phase can be calculated. Under phase equilibrium, fugacities of each component in both phases are equal, i.e.

$$f^L_i(T,P,x_i) = f^V_i(T,P,y_i) \quad \text{(Eq. 5.1)}$$

$$f^L_i(T,P,x_i) = x_i \Phi^L_i P \quad \text{(Eq. 5.2)}$$

$$f^V_i(T,P,y_i) = y_i \Phi^V_i P \quad \text{(Eq. 5.3)}$$

Where $f$ represents the fugacity, $x$ represents the molar fraction in the liquid phase, $y$ represents the molar fraction in the gas phase, superscripts $L$ and $V$ represent the liquid phase and gas phase respectively, subscript $i$ represents
component \( i (i = 1, 2) \). At equilibrium, the fugacity of each component in both phases should be equal, i.e. the fugacity difference is smaller than a tolerance (a very small number, e.g. \( 10^{-5} \)). Otherwise, the iteration is used to get a better guess of molar fractions in two phases. Then go to step 2 until the fugacity difference is smaller than a tolerance.

3. Up to here, the weight fractions in both phases under this temperature and pressure are calculated, i.e. two binodal points are calculated.

4. Calculate the fugacity curve (fugacity vs. molar fraction of one component) at the molar fraction range within the two binodal points. Two peaks with a minimum and a maximum respectively can be obtained. The molar fractions at those two extreme points are the two spinodal points at the temperature and pressure.

5. Calculate the binodal and spinodal points at higher pressure \((P + \Delta P)\) until the critical point. Finally, convert molar fractions into weight fractions.

5.3 Prediction of Solubility and phase boundaries

5.3.1 Prediction of Solubility

Both equations of state were used to model the solubility curve. S-L EOS is the most widely used EOS for modeling polymer solutions. On the other hand, PC-SAFT is the state-of-art EOS that gives more accurate prediction in most cases. In the following,
the prediction by both equations was checked to make sure that the codes were correct, then the two were compared for some systems.

**Code-validation of two EOSs**

Since S-L EOS was used in our research group for solubility modeling for several years, the phase diagram code was developed based on that. Several common systems were chosen to make sure the code was correct. For PC-SAFT, since it was a comparatively new EOS and completely new for our group, several systems were chosen to compare with the literature data. For example, as shown in Fig. 5.3, the same system (PP (\(M_w=50,400\), \(M_w / M_n =2.2\))-pentane, \(k_{ij}=0.0137\)) that was used in Gross’s paper was modeled, and the modeling results matched exactly with their results. This gave strong evidence that the code was correct.

**Solubility prediction results**

In our study, these two equations were compared for our system PS-CO\(_2\). Although the binary interaction parameter, \(k_{ij}\), has some physical meaning, in most cases it is correlated from experimental data. Therefore one fair comparison is to check the performance of these two equations with assumption of \(k_{ij} = 0\). Fig. 5.4 demonstrates the solubility prediction of PS (\(M_w=187,000\))-CO\(_2\) at three temperatures by S-L EOS (the top right three curves) and PC-SAFT (the bottom three curves) with assumption of \(k_{ij} = 0\). All
the experimental data are from Sato [79] et al. As shown from the figure, PC-SAFT overpredicts the solubility of CO₂ in PS and S-L underpredicts the solubility. When the solubility of CO₂ is low (<5%), i.e. the weight fraction of PS is higher than 95%, the prediction of both equations is reasonably close to the experimental data. When solubility of CO₂ is higher (>5%), both equations show a greater departure from the experimental data, although PC-SAFT gives comparatively closer prediction.

Since the experimental data on our system (PS-CO₂) are abundant, another comparison is to check the prediction with the \( k_{ij} \) correlated to the experimental data. Figures 5.5-7 demonstrate the results at three different temperatures. Clearly with the correlated \( k_{ij} \), both equations perform much better in comparison with the results with the assumption of \( k_{ij} = 0 \). The predicted results of both equations match the experimental data very well. Therefore, both equations are used to predict the solubility and phase boundaries later.

5.3.2 Prediction of phase boundaries

In comparison with solubility, phase boundaries are more difficult to calculate and predict. As shown on Fig. 2.1, the phase boundaries (binodal and spinodal curves) cover a wider concentration range. The binodal curve is the phase equilibrium curve, where the first composition derivative of the free energy vanishes (or the chemical potentials of both phases are equal). The spinodal curve defines the limit of metastability of a homogeneous phase.[38] The solubility curve is the part of the binodal curve for a
polymer-diluent system where the weight fraction of the diluent is smaller than the polymer. For the modeling of solubility curve, it is assumed that no polymer is in the gas phase. However, for the modeling of the binodal curve, this assumption is not true when the pressure of the diluent is high. PE (polyethylene)-pentane was chosen for the comparison because there are experimental data in the region where the weight fraction of the polymer is less than 20%. Fig. 5.8 shows the binodal curves of PE ($M_w=108,000$)-pentane at 187°C by S-L EOS and PC-SAFT. The interaction coefficients, $k_{ij}$, are correlated to the experimental data of Kiran [90] et al. With the assumption of $k_{ij} = 0$, PC-SAFT gives closer prediction than S-L. With the correlated $k_{ij}$, both equations perform much better than with the assumption of $k_{ij} = 0$. PC-SAFT gives a slightly better prediction than S-L. We also need to mention that the prediction result is very sensitive to the value of $k_{ij}$. Since the value of $k_{ij}$, in most cases, is correlated from experimental data, it is very important to have enough experimental data to correlate the $k_{ij}$ before we use the EOS to calculate the phase boundaries. It is a dilemma for using EOS for phase diagram prediction. Fortunately, as shown later, we have enough experimental data for the $k_{ij}$ correlation for PS-CO$_2$ because we mainly focus on the region where the weight fraction of CO$_2$ is less than 20%.

Fig. 5.9 shows the binodal (solid curve) and spinodal (broken curve) curves of PS ($M_w=187,000$)-CO$_2$ at 180°C by S-L EOS ($k_{ij} = -0.132$). The black curves are for the parts of binodal and spinodal curves when the pressure is lower than 800bar. When the pressure is lower than 800bar, the assumption no PS in the gas is valid. This also proves that we can safely assume that no PS is in the gas phase for typical foaming process
(pressure lower than 200 bar). Fig. 5.9 and 5.10 show the binodal (solid curve) and spinodal (broken curve) curves of PS ($M_w=187,000$)-CO$_2$ at 180°C and 100°C respectively by S-L EOS. Fig. 5.11 shows the prediction of binodal curves of PS ($M_w=187,000$)-CO$_2$ at three temperatures by PC-SAFT with assumption of $k_{ij}=0$. However, when the $k_{ij}$ correlated from the experimental data was used, we could not obtain the curves at higher pressures (>500 bar) because the program did not converge. Fortunately, usually a much lower pressure than 500 bar is used for typical foaming process. Figures 5.12-14 show the prediction of the binodal (right) and spinodal (left) curves at three temperatures respectively by PC-SAFT with $k_{ij}$ correlated from experimental data. Fig. 5.15 shows the comparison of the prediction for binodal and spinodal curves by S-L EOS ($k_{ij}=-0.088$) and PC-SAFT ($k_{ij}=0.1632$) for PS-CO$_2$ at 100°C. The spinodal curves predicted by both equations are reasonably close for typical foaming pressure (<200 bar).

5.4 Connection between phase boundaries and nucleation behavior

5.4.1 Bubble nucleation rate extracted from literature

Bubble nucleation data in the polymer foaming literature are rare. Guo [2] et al. studied the bubble nucleation and growth in PS foaming by using CO$_2$ as the physical foaming agent. In that paper, they obtained the plots of cell number density vs. time and cell size vs. time based on the images recorded by a high-speed camera. Fig. 5.16 shows some representative recorded images. This paper was used to extract the bubble
nucleation rate data. Fig. 5.17 shows their basic experimental setup. As described in the paper, the polymer sample was sandwiched in two sapphire windows. The sample always touched at least one window. Heterogeneous nucleation was unavoidable because of this. However, measurement of homogeneous nucleation rate was their goal. The measured nucleation rate could be several orders of magnitude higher than the intended homogeneous nucleation rate. In our experimental setup, the sample is “free-standing” and the measurement area does not touch any solid surface.

As will be shown later, the corresponding pressure profile is essential for the calculation of parameters in nucleation theory. However, the pressure profiles in the actual foaming process were not shown in the paper. Fortunately, some pressure profiles were sent to us per our request. Fig. 5.18 and Fig. 5.19 show the plots of cell number density vs. time and the corresponding pressure profiles. The cell nucleation rate, defined as the number of nuclei formed per unit volume unit time, can be obtained by differentiating the curve of cell number density vs. time with the assumption that one nucleus grows to one detectable bubble. Since the cell number density has a rough linear relationship vs. time on the semi-log plots, a non-constant nucleation rate can be obtained. This is expected because when the pressure drops, the supersaturation varies, i.e. the driving force for cell nucleation changes with time, leading to non-constant nucleation rate. A rough approximation is the average cell nucleation rate. Our choice is the slope calculated by the starting point and ending point of the cell number density growth curve, i.e. the cell number density difference between the starting point and ending point divided by the time difference between these two points.
5.4.2 Calculation of parameters in nucleation theory

As shown in Eq. 2.1, the reversible work of critical nucleus formation, \( W \), is essential for nucleation rate calculation. Since \( W \) is in the exponential, its accuracy is important for nucleation rate prediction. According to Eq. 2.3, there are two variables: \( \gamma \) and \( \Delta P \). Experimental measurement of \( \gamma \) is almost impossible [157], however, \( \Delta P \) can be calculated by assuming an equivalent thermodynamic path using an equation of state.

There are still some challenges for calculating \( \Delta P \) by using the equation of state. Some assumptions were made to solve these challenges.

1. The calculation of \( \Delta P \) is based on \( \Delta P_{\text{exp}} \), the experimental pressure drop. As shown on Fig. 5.18 and Fig. 5.19, there is a time period before the first bubble is seen. There are two easy choices: the pressure drop from time zero to the time when the curve ends or the pressure drop in the time period from the starting point of the curve to the ending point of the curve. The first choice makes more sense.

2. In Fig. 5.18, the authors [2] claimed that the initial pressure was 21 MPa. However, the bottom left figure (pressure profile) shows that the initial experimental pressure was about 18 MPa. Due to this confusion, the left (black) curve in Fig. 5.18 (maximum pressure drop is 220 MPa/s) was not be used for cell nucleation rate calculation. Therefore, only three of the four cases were used for the extraction of nucleation rates.
3. The parameters used for S-L EOS were not shown in the paper; instead, a previous paper in the same research group was cited. However, the PS used was different in the two papers. \( k_{ij} \) was not given at 180°C. Therefore, in our calculation, the popular set of parameters and \( k_{ij} [85] \) were chosen.

4. The zero time at the plots of cell number density vs. time does not match with the zero time at the plots of pressure profiles. After analysis, it makes sense that the actual zero time on the plots of pressure profiles starts when the pressure begins to drop.

As an example, the right (red) curve (maximum pressure drop: 20 MPa) in Fig. 5.18 is used to calculate the average cell nucleation rate. The assumed equivalent thermodynamic path is shown on Fig. 5.20. The state “1” is the initial state with 180°C, 210.9 bar and 0.075 wt.% CO₂ in PS. The state “2” is the state with 180°C, 172.1 bar and the solubility of CO₂ in PS is less than 0.075 wt.% because of desorbing of CO₂ in the foaming process. The process from state “1” to “2” is the real process, marked with solid-line arrow. The process of “state 1 → state \( \alpha \) → state \( \beta \) → state 2” is an equivalent thermodynamic path, marked with broken-line arrows. The states \( \alpha \) and \( \beta \) have the same meaning with states \( \alpha \) and \( \beta \) in the nucleation theory, i.e. phase \( \alpha \) is the metastable phase and \( \beta \) is the new nucleating phase. When the state changes from “1” to “\( \alpha \)”, only the pressure drops, other properties of the system, including the solubility, do not change. Phase “\( \beta \)” is a hypothetical phase that has the same temperature and chemical potential as the metastable phase \( \alpha \). When the state changes from “\( \beta \)” to “2”, bubbles nucleate and the CO₂ content drops.
Calculation of $\Delta P$

In the S-L EOS, the expression of chemical potential is given and its application in the calculation of parameters is convenient. $P^\alpha$ is the final pressure, in this case, 172.1 bar. States $\alpha$ and $\beta$ have the same chemical potential, $P^\beta$ can be calculated after we know the chemical potential of state $\beta$. As shown in previous chapters, in scaling theorem, $\Delta P/\Delta P_s$ or $\Delta \mu/\Delta \mu_s$ are often used as the normalized supersaturation. Here the subscript $s$ represents “calculating at spinodal”. When the pressure is released to trigger foaming, the physical properties of the PS-CO$_2$ system can be assumed to be constant. A common initial pressure for foaming is lower than 200bar, or the solubility of CO$_2$ is less than 10%. We can take Fig. 5.10 as an example. The spinodal curve ends where CO$_2$ weight fraction is bigger than 25%. Therefore, even when the CO$_2$ pressure is dropped from about 200bar to atmospheric, the spinodal curve cannot be reached. Thus, calculation of $\Delta P_s$ is not achievable “vertically”. Another choice is to calculate it “horizontally”. Since chemical potential at all states, including the metastable state, can be calculated conveniently by the S-L EOS, $\Delta \mu/\Delta \mu_s$ is chosen as the normalized supersaturation used in the correlation of the scaling function.

Calculation of chemical potentials

 Chemical potentials of all four states, “1”, “2”, “$\alpha$”, and “$\beta$”, either in the stable state or the metastable state, can be calculated based on S-L EOS. As shown on Fig. 5.21,
the pressure drops from initial experimental pressure 210.9 bar (state “1”) to the final pressure 172.1 bar (state “2”). The calculations of $\Delta \mu$ and $\Delta \mu_s$ are based on the final pressure and executed horizontally. The spinodal point (point “3”) and binodal point (point “4”) at pressure 172.1 bar can be calculated. Chemical potentials of point “1”, “2”, and “3” can then be calculated. Finally, the values of $\Delta \mu$ and $\Delta \mu_s$ can be obtained.

**Calculation of $\gamma$ and $W$**

After the $\Delta P$ is calculated, the $W$ is only a function of $\gamma$ from Eq. 2.3. Similarly, from Eq. 2.2, $J_0$ is also only a function of $\gamma$. Thus, $J_{ss}$ is only a function of $\gamma$ according to Eq. 2.1. In our hypothesis, $\gamma$ can be solved for by comparing with the nucleation rate data from the experiments. With the known $\Delta P$ and $\gamma$, $W$ can be obtained. To correlate a possible scaling function the relationship between $W/W^{cl}$ and $\Delta \mu/\Delta \mu_s$ is explored. According to the expression of $W$ and $W^{cl}$, $W/W^{cl} = (\gamma/\gamma_\infty)^3$. Here, $\gamma_\infty$ is the macroscopic interfacial tension between PS and CO$_2$, which is measurable by experiment. The data on PS and CO$_2$ system are still very limited. Especially, experimental data at 180°C and in the pressure range of 5~25 MPa are not available. Even the data at other conditions by different researchers or different techniques do not match well [160]. Our data were extrapolated from data by Li[157] et al. assuming that the interfacial tension between PS and CO$_2$ has a linear relationship with temperature. Li’s data were used because PS (Nova) was used in both Li’s paper and Guo’s paper.
5.4.3 Correlation of a possible scaling function

The calculated results for those parameters, e.g. $\Delta P$, $\gamma$, $\Delta \mu$, $\Delta \mu_s$, and $W$, are summed in Table 5.1. According to Fig. 5.21, $\mu_1$ is the chemical potential at initial pressure, $\mu_2$ is the chemical potential at the chosen pressure or final pressure, $\mu_3$ is the chemical potential at the spinodal curve at the chosen pressure, and $\mu_4$ is the chemical potential at the binodal curve at the chosen pressure. The calculated $W/W_{cl}$ and $\Delta \mu/\Delta \mu_s$ values are plotted on Fig. 5.22. $W/W_{cl}$ values decrease with increasing $\Delta \mu/\Delta \mu_s$ values. This trend was expected. As shown in Fig. 5.23, the relationship between $W/W_{cl}$ and supersaturation $\xi$ ($\xi=\Delta \mu/\Delta \mu_s$ or $\Delta P/\Delta P_s$) is expected to be a monotonically decreasing curve. In addition, on this curve, when $\xi=1$, $W=0$, i.e. $W/W_{cl}=0$ due to the vanishing of energy barrier $W$ at the spinodal; also when $\xi=0$, $W=W_{cl}$, i.e. $W/W_{cl}=1$.

Fig. 5.22 only represents a small part of the $W/W_{cl}$ vs. $\xi$ plot, with $W/W_{cl}<0.07$. The $W/W_{cl}$ values in Fig. 5.22 are much smaller than what is shown in Fig. 5.23 at the same $\xi$ values. Since only three cases were studied and the results only covered a small $W/W_{cl}$ or $\xi$ range, a possible scaling could not be correlated. More cases are needed.

5.4.4 Correlation of a possible scaling function based on our data

The “free-standing” design in our experiments (chapter 4) avoided the heterogeneous nucleation. Seven different cases were studied: (1) 1200 psi, 80°C; (2)
1200 psi, 60°C; (3) 1000 psi, 80°C; (4) 1000 psi, 80°C, final pressure 389 psi; (5) 1500 psi, 80°C; (6) 1200 psi, 70°C; and (7) 1500 psi, 60°C. All pressures listed were the initial pressures and the final pressure was zero except case (4). The seven cases were used to study the three effects: temperature, initial pressure, and final pressure. In all cases, the pressure dropped to the final pressure within 10 seconds and foaming started at least 50 second later, based on the recorded movies. In other words, the pressure drop and bubble nucleation were decoupled in our experiments. The starting times for foaming were much longer, e.g. minute vs. second, than those in the paper by Guo [2] et al. There are two possible reasons. The first is that much higher pressure drop rates were used in their experiments. The second is that heterogeneous nucleation, which is much faster than homogeneous nucleation, occurred in their experiments.

There are some differences between the parameter calculation from our experimental results and from the literature (5.4.1, 5.4.2, and 5.4.3). For example, the time $\Delta t$ in the nucleation rate calculation is the time for the pressure drop from initial pressure to the final pressure, rather than the time taken from the start of the pressure drop to the end of the nucleation curve. For the choice of cell number density, the numbers based on the final foam images by the microscope were chosen (see table 4.4). The $\gamma_{\infty}$ values are extrapolated from data [161] assuming a linear relationship between temperature and $\gamma_{\infty}$. Tables 5.2 and 5.3 summarize the calculation for the seven cases. Fig. 5.24 includes the results in Fig. 5.22 and results based on our calculation. It needs to be mentioned that the data point (“diamond” on the curve) was not good because the foaming was not uniform. Except case (4), all other data points calculated based on our
experiments are in a close region. Considering the three data points based on the literature and six data points based on our experiments, these data points in general follow the trend we mentioned above, i.e. $W/W^*$ values decrease with increasing $\Delta \mu/\Delta \mu_s$ values. Fig. 5.25 shows a curve (broken curve) of a possible scaling function based on the data points in Fig. 5.24 except the data point for case (4). The scaling function shown in Fig. 23 is concave down and our proposed possible curve in Fig. 25 is concave up. Muller[162] et al. showed (in Fig. 6) a concave-up scaling curve for the polymer (hexadecane)-CO$_2$ system. When the molecular size increases from hexadecane to PS ($M_w=187,000$), the shape of the curve shown in Fig. 5.25 is reasonable. However, before we make this claim, a good piece of supporting information would be the initial slope of the curve, i.e., the slope at $\xi = 0$ because that may determine if the curve is concave up or down.

Kusaka[58] claimed that the initial slope can be calculated by the diffuse interface theory and recently extended it to bubble nucleation for binary systems. The final result is shown as follows:

$$\frac{\partial \phi}{\partial (\Delta P)}\bigg|_{\Delta P=0} = \frac{3}{2L_0} \left( 1 - T \frac{\partial \Delta S^L}{\partial (\Delta P)}\bigg|_{\Delta P=0} \right)$$  \hspace{1cm} \text{(Eq. 5.4)}

$$L_0 = -T \Delta S^L_0$$  \hspace{1cm} \text{(Eq. 5.5)}

$$\Delta S^L = \rho \left( \frac{S^L}{N^L} - \frac{S^v}{N^v} \right)$$  \hspace{1cm} \text{(Eq. 5.6)}
Where $\Delta S^L$ is calculated at the supersaturation and $\Delta S^L_0$ is $\Delta S^L$ calculated at the co-existence curve. $\rho^L$ is the molecule number density in the liquid mixture. $S^L/N^L$ and $S^V/N^V$ are the entropy of the liquid mixture and gas phase per molecule respectively. The $\Delta P^\prime$ here has the negative value of the $\Delta P$ defined before. Since here $\xi = \Delta P/\Delta s$, the expression for the initial slope calculation is as follows:

$$\frac{\partial \Delta \phi}{\partial \xi} = \frac{\partial \phi}{\partial (\Delta P^\prime)} \cdot \Delta P^\prime = \frac{3\Delta P^\prime}{2L_0} \left( 1 - T \frac{\partial S^L}{\partial (\Delta P^\prime)} \right)$$  \hfill (Eq. 5.7)

Similarly, the $\Delta P^\prime$, here has the negative value of the $\Delta P$ defined before.

To calculate the initial slope, the key is to calculate the entropies. The entropy of the liquid mixture or gas phase was given by [87] (eq. (C.10)),

$$S/N = -rK \left\{ \frac{1}{\lambda \rho} \ln(1 - \lambda) + \frac{1}{\mu \rho} \ln \lambda + \sum_{i=1}^{\infty} \frac{\phi_i}{r_i} \ln \phi_i \right\}$$  \hfill (Eq. 5.8)

Where $K$ is the Boltzmann constant and other factors are defined in Appendix A. The value of $\frac{\partial \Delta S^L}{\partial (\Delta P^\prime)} \big|_{\Delta P^\prime=0}$ can be obtained by numerical method. Similar to the example shown in Fig. 5.20, assuming the system has a pressure drop from the initial pressure $P_1$ to the final pressure $P_2$ (equal to $P^\prime$), $P^\prime$ can be calculated. By the equation of state, the entropies (per molecule) of the liquid mixture $S^L_1/N^L_1$ and gas phase $S^V_1/N^V_1$ at the co-existence curve (i.e. initial equilibrium state, pressure $P_1$) can be calculated by Eq. 5.8. Similarly, at the supersaturated state, the entropies (per molecule) of the liquid mixture $S^L_2/N^L_2$ (at
pressure $P^\alpha$) and gas phase $\frac{S_1^v}{N_1^v}$ (at pressure $P^\beta$) can be calculated. Therefore, we have

the expression of $\frac{\partial \Delta S_L}{\partial (\Delta P)}\bigg|_{\Delta P=0}$,

$$\frac{\partial \Delta S_L}{\partial (\Delta P)}\bigg|_{\Delta P=0} = \rho^L \left[ \frac{S_1^L}{N_1^L} - \frac{S_1^v}{N_1^v} \right] \left( \frac{S_2^L}{N_2^L} - \frac{S_2^v}{N_2^v} \right) \frac{\Delta P}{\Delta P^s}$$  \hspace{2cm} (Eq. 5.9)

Here $\rho^L$ is assumed to be a constant. It should be a very good assumption for very small $\Delta P$.

The initial condition of case (7), 1500 psi, 60°C, was used to calculate the initial slope. The calculation results are shown in Table 5.4. Here, different final experimental pressures were chosen to have different $\Delta P$ values. As we mentioned above, $\Delta P_s$ cannot be calculated for our system because the spinodal curve is not reachable in the region we are interested. 1 bar was used as the final experimental pressure to calculate the lower limit of $\Delta P_s$. It showed that the $\Delta P_s$ should be larger than 78.2 bar. Since the slopes calculated are negative, the real slopes values are even smaller than the values shown in Fig. 5.4. The results are also plotted in Fig. 5.26. Different $\Delta P$ values were used to calculate the slopes and negative values were obtained. Since $\Delta P_s$ was larger than 78.2 bar, the slopes should have been even more negative. From the trend of the curve, a large negative number is expected for the true initial slope of the scaling function. This figure also showed that when the molecular weight of the polymer decreases, the slope becomes less negative. We postulate that with decreasing molecular weight, the initial slope
becomes less negative. This is consistent with the result shown by Muller[162] et al. (in Fig. 6). These observations verify the possible shape shown in Fig. 5.25. From the trend, the scaling function can be an exponential decay type equation. We had nine data points calculated from the experimental data and we also knew that when $\xi = 1$, $W/W_{cl} = 0$ and when $\xi = 0$, $W/W_{cl} = 1$. We correlated a scaling function (with $R^2=0.9997$) based on these data points:

$$\frac{W}{W_{cl}} = 0.9\exp(-523\xi) + 0.1\exp(2.139\xi)$$  \hspace{1cm} (Eq. 5.10)

The calculations based on the experimental data and prediction by this scaling function are shown on Fig. 5.27. However, more experimental data and systems need to verify the generality of this scaling function for bubble nucleation in polymer foaming process.

5.5 Conclusion

Solubility of the blowing agent in the polymer and solubility reduction during the foaming process are essential. Two equations of state, S-L EOS and PC-SAFT, were used to model the solubility and also phase boundaries (binodal and spinodal curves). Nucleation is a very complex phenomenon in physical foam processing and its experimental and theoretical studies cannot provide all of the information to have a clear picture of the nucleation phenomenon. The scaling function provides a possible way to calculate the energy barrier in the nucleus formation, $W$. Cell nucleation rate data were extracted from the paper by Guo [2] et al. and also from our experimental data. Based on
the phase boundaries predicted, several parameters in the nucleation theory, e.g. $\gamma$, $\Delta P$, and $W$ were calculated based on the experimental data. Several sets of $W/W^{*}$ and $\Delta \mu/\Delta \mu_s$ were calculated. The initial slope of the possible scaling function was calculated by the diffuse interface theory. A possible scaling function (exponential decay type equation) was correlated based on the calculation from experimental data. It provided insight for the connection between the phase boundary and the complex nucleation behavior.
<table>
<thead>
<tr>
<th>Foaming condition</th>
<th>180°C, 21MPa, dp/dt=20Mpa/s</th>
<th>180°C, 10MPa, dp/dt=50Mpa/s</th>
<th>180°C, 15MPa, dp/dt=50Mpa/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell density (cm⁻³)</td>
<td>2.00E+08</td>
<td>7.00E+06</td>
<td>1.80E+08</td>
</tr>
<tr>
<td>Time (s)</td>
<td>0.188</td>
<td>0.5</td>
<td>0.105</td>
</tr>
<tr>
<td>Initial pressure (MPa)</td>
<td>21.07</td>
<td>10.0</td>
<td>14.83</td>
</tr>
<tr>
<td>Ending pressure (MPa)</td>
<td>17.21</td>
<td>5.87</td>
<td>11</td>
</tr>
<tr>
<td>( P_α ) (MPa)</td>
<td>17.21</td>
<td>5.87</td>
<td>11</td>
</tr>
<tr>
<td>( P_β ) (MPa)</td>
<td>19.68</td>
<td>9.28</td>
<td>13.84</td>
</tr>
<tr>
<td>( ΔP ) (MPa)</td>
<td>2.47</td>
<td>3.41</td>
<td>2.84</td>
</tr>
<tr>
<td>( ΔP_{exp} )</td>
<td>3.88</td>
<td>4.13</td>
<td>3.83</td>
</tr>
<tr>
<td>( \mu_4 ) (J.mol⁻¹)</td>
<td>-38049</td>
<td>-41917</td>
<td>-39643</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Binodal point (polymer weight fraction) at chosen pressure</th>
<th>0.9376</th>
<th>0.9781</th>
<th>0.9594</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_3 ) (J.mol⁻¹)</td>
<td>-35837</td>
<td>-36769</td>
<td>-36338</td>
</tr>
<tr>
<td>Spinodal (polymer weight fraction) at chosen pressure</td>
<td>0.727</td>
<td>0.7588</td>
<td>0.7444</td>
</tr>
<tr>
<td>( \mu_2 ) (J.mol⁻¹)</td>
<td>-37567</td>
<td>-40252</td>
<td>-38823</td>
</tr>
<tr>
<td>Binodal (polymer weight fraction) at initial pressure</td>
<td>0.924</td>
<td>0.963</td>
<td>0.946</td>
</tr>
<tr>
<td>( Δ\mu ) (J.mol⁻¹)</td>
<td>482</td>
<td>1665</td>
<td>820</td>
</tr>
<tr>
<td>( Δ\mu_3 ) (J.mol⁻¹)</td>
<td>2212</td>
<td>5148</td>
<td>3305</td>
</tr>
<tr>
<td>Nucleation rate (cells/cm³/s)</td>
<td>1.06E+09</td>
<td>1.40E+07</td>
<td>1.71E+09</td>
</tr>
<tr>
<td>Mixture density at initial pressure (g/cm³)</td>
<td>0.9717</td>
<td>0.9756</td>
<td>0.9737</td>
</tr>
<tr>
<td>( N ) (cm⁻³)</td>
<td>1.01E+21</td>
<td>4.94E+20</td>
<td>7.19E+20</td>
</tr>
<tr>
<td>( γ ) (N/m)</td>
<td>0.0049</td>
<td>0.0063</td>
<td>0.0054</td>
</tr>
<tr>
<td>CO₂ density at chosen pressure (g/cm³)</td>
<td>0.239</td>
<td>0.073</td>
<td>0.145</td>
</tr>
<tr>
<td>( γ_{∞} ) (N/m)</td>
<td>0.012</td>
<td>0.018</td>
<td>0.014</td>
</tr>
<tr>
<td>( W ) (J)</td>
<td>3.23E-19</td>
<td>3.60E-19</td>
<td>3.27E-19</td>
</tr>
<tr>
<td>( W/kT )</td>
<td>51.66</td>
<td>57.61</td>
<td>52.30</td>
</tr>
<tr>
<td>( W/W^{el} )</td>
<td>0.0681</td>
<td>0.0429</td>
<td>0.0574</td>
</tr>
<tr>
<td>( \Delta\mu/\Delta\mu_s )</td>
<td>0.2179</td>
<td>0.3234</td>
<td>0.2481</td>
</tr>
</tbody>
</table>

Note: the definitions of \( \mu_1, \mu_2, \mu_3, \) and \( \mu_4 \) are in Fig. 5.21

Table 5.1: Parameter calculation for the three cases in Guo’s paper (the right curve in the top figure in Fig. 5.18 and two curves in Fig. 5.19)
<table>
<thead>
<tr>
<th>Case</th>
<th>Case (1)</th>
<th>Case (2)</th>
<th>Case (3)</th>
<th>Case (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pressure (psi)</td>
<td>1200</td>
<td>1200</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>80</td>
<td>60</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Kij used in S-L EOS</td>
<td>-0.072</td>
<td>-0.048</td>
<td>-0.072</td>
<td>-0.072</td>
</tr>
<tr>
<td>T* for CO2 in S-L EOS</td>
<td>276.71</td>
<td>277.91</td>
<td>276.71</td>
<td>276.71</td>
</tr>
<tr>
<td>Cell density (cm⁻³)</td>
<td>1.05E+05</td>
<td>2.29E+05</td>
<td>7.98E+04</td>
<td>725</td>
</tr>
<tr>
<td>Time for pressure drop(s)</td>
<td>8.1</td>
<td>8.746</td>
<td>7.136</td>
<td>6.257</td>
</tr>
<tr>
<td>P_initial(MPa)</td>
<td>8.276</td>
<td>8.276</td>
<td>6.897</td>
<td>6.897</td>
</tr>
<tr>
<td>P_final(MPa)</td>
<td>0.166</td>
<td>0.166</td>
<td>0.138</td>
<td>2.766</td>
</tr>
<tr>
<td>Pα (MPa)</td>
<td>0.166</td>
<td>0.166</td>
<td>0.138</td>
<td>2.766</td>
</tr>
<tr>
<td>Pβ (MPa)</td>
<td>6.98</td>
<td>6.86</td>
<td>6.02</td>
<td>6.34</td>
</tr>
<tr>
<td>ΔP (MPa)</td>
<td>6.814</td>
<td>6.694</td>
<td>5.882</td>
<td>3.574</td>
</tr>
<tr>
<td>ΔP_exp</td>
<td>8.11</td>
<td>8.11</td>
<td>6.759</td>
<td>4.131</td>
</tr>
<tr>
<td>μ4 (J.mol⁻¹)</td>
<td>-41566</td>
<td>-38976</td>
<td>-42218</td>
<td>-33550</td>
</tr>
<tr>
<td>Binodal point (polymer weight fraction) at final pressure</td>
<td>0.9985</td>
<td>0.9983</td>
<td>0.9988</td>
<td>0.9754</td>
</tr>
<tr>
<td>μ3 (J.mol⁻¹)</td>
<td>-29519</td>
<td>-28070</td>
<td>-29521</td>
<td>-29365</td>
</tr>
<tr>
<td>Spinodal (polymer weight fraction) at final pressure</td>
<td>0.6922</td>
<td>0.708</td>
<td>0.6923</td>
<td>0.6857</td>
</tr>
<tr>
<td>μ2 (J.mol⁻¹)</td>
<td>-31142</td>
<td>-29287</td>
<td>-31504</td>
<td>-31375</td>
</tr>
<tr>
<td>Binodal (polymer weight fraction) at initial pressure</td>
<td>0.9275</td>
<td>0.918</td>
<td>0.9391</td>
<td>0.9391</td>
</tr>
<tr>
<td>Δμ (J.mol⁻¹)</td>
<td>10424</td>
<td>9689</td>
<td>10714</td>
<td>2175</td>
</tr>
<tr>
<td>Δμ4 (J.mol⁻¹)</td>
<td>12047</td>
<td>10906</td>
<td>12697</td>
<td>4185</td>
</tr>
<tr>
<td>Nucleation rate (cells/cm³/s)</td>
<td>1.30E+04</td>
<td>2.62E+04</td>
<td>1.12E+04</td>
<td>1.16E+02</td>
</tr>
<tr>
<td>Mixture density at initial pressure (g/cm³)</td>
<td>1.0343</td>
<td>1.046</td>
<td>1.0352</td>
<td>1.0352</td>
</tr>
<tr>
<td>N (cm⁻³)</td>
<td>1.03E+21</td>
<td>1.17E+21</td>
<td>8.63E+20</td>
<td>8.63E+20</td>
</tr>
<tr>
<td>γ (N/m)</td>
<td>0.0096</td>
<td>0.0093</td>
<td>0.0087</td>
<td>0.0064</td>
</tr>
<tr>
<td>CO2 density at final pressure (g/cm³)</td>
<td>0.002</td>
<td>0.003</td>
<td>0.002</td>
<td>0.045</td>
</tr>
<tr>
<td>γ∞ (N/m)</td>
<td>0.0364</td>
<td>0.0378</td>
<td>0.0364</td>
<td>0.03</td>
</tr>
<tr>
<td>W (J)</td>
<td>3.19E-19</td>
<td>3.01E-19</td>
<td>3.19E-19</td>
<td>3.44E-19</td>
</tr>
<tr>
<td>W/kT</td>
<td>65.51</td>
<td>65.42</td>
<td>65.43</td>
<td>70.55</td>
</tr>
<tr>
<td>W/Weff</td>
<td>0.0183</td>
<td>0.0149</td>
<td>0.0137</td>
<td>0.0097</td>
</tr>
<tr>
<td>Δμ/Δμ₄</td>
<td>0.8653</td>
<td>0.8884</td>
<td>0.8438</td>
<td>0.5197</td>
</tr>
</tbody>
</table>

Table 5.2: Parameter calculation for our experimental results: case (1) 1200 psi, 80°C; case (2) 1200 psi, 60°C; case (3) 1000 psi, 80°C; case (4) 1000 psi, 80°C, final pressure 389psi.
<table>
<thead>
<tr>
<th>Case</th>
<th>Case (5)</th>
<th>Case (6)</th>
<th>Case (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pressure (psi)</td>
<td>1500</td>
<td>1200</td>
<td>1500</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Kij used in S-L EOS</td>
<td>-0.072</td>
<td>-0.048</td>
<td>-0.048</td>
</tr>
<tr>
<td>T* for CO2 in S-L EOS</td>
<td>276.71</td>
<td>277.39</td>
<td>277.91</td>
</tr>
<tr>
<td>Cell density (cm⁻³)</td>
<td>3.81E+05</td>
<td>1.52E+05</td>
<td>5.80E+06</td>
</tr>
<tr>
<td>Time for pressure drop(s)</td>
<td>8.69</td>
<td>8.865</td>
<td>10.08</td>
</tr>
<tr>
<td>P_initial(MPa)</td>
<td>10.345</td>
<td>8.276</td>
<td>10.345</td>
</tr>
<tr>
<td>P_final(MPa)</td>
<td>0.207</td>
<td>0.166</td>
<td>0.207</td>
</tr>
<tr>
<td>Pα (MPa)</td>
<td>0.207</td>
<td>0.166</td>
<td>0.207</td>
</tr>
<tr>
<td>Pβ (MPa)</td>
<td>8.24</td>
<td>6.92</td>
<td>7.94</td>
</tr>
<tr>
<td>ΔP (MPa)</td>
<td>8.033</td>
<td>6.754</td>
<td>7.733</td>
</tr>
<tr>
<td>ΔP_exp</td>
<td>10.138</td>
<td>8.11</td>
<td>10.138</td>
</tr>
<tr>
<td>μ₄ (J.mol⁻¹)</td>
<td>-41033</td>
<td>-40299</td>
<td>-38394</td>
</tr>
<tr>
<td>Binodal point (polymer weight fraction) at final pressure</td>
<td>0.9982</td>
<td>0.9986</td>
<td>0.9979</td>
</tr>
<tr>
<td>μ₅ (J.mol⁻¹)</td>
<td>-29517</td>
<td>-28641</td>
<td>-28068</td>
</tr>
<tr>
<td>Spinodal (polymer weight fraction) at final pressure</td>
<td>0.6921</td>
<td>0.7246</td>
<td>0.708</td>
</tr>
<tr>
<td>μ₂ (J.mol⁻¹)</td>
<td>-30751</td>
<td>-30198</td>
<td>-28985</td>
</tr>
<tr>
<td>Binodal (polymer weight fraction) at initial pressure</td>
<td>0.9111</td>
<td>0.9334</td>
<td>0.9016</td>
</tr>
<tr>
<td>Δμ (J.mol⁻¹)</td>
<td>10282</td>
<td>10101</td>
<td>9409</td>
</tr>
<tr>
<td>Δμ₄ (J.mol⁻¹)</td>
<td>11516</td>
<td>11658</td>
<td>10326</td>
</tr>
<tr>
<td>Nucleation rate (cells/cm³/s)</td>
<td>4.38E+04</td>
<td>1.71E+04</td>
<td>5.75E+05</td>
</tr>
<tr>
<td>Mixture density at initial pressure (g/cm³)</td>
<td>1.0331</td>
<td>1.0414</td>
<td>1.0456</td>
</tr>
<tr>
<td>N (cm⁻³)</td>
<td>1.26E+21</td>
<td>9.49E+20</td>
<td>1.41E+21</td>
</tr>
<tr>
<td>γ (N/m)</td>
<td>0.0106</td>
<td>0.0094</td>
<td>0.01</td>
</tr>
<tr>
<td>CO₂ density at final pressure (g/cm³)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>γ∞ (N/m)</td>
<td>0.0364</td>
<td>0.0371</td>
<td>0.0378</td>
</tr>
<tr>
<td>W (J)</td>
<td>3.09E-19</td>
<td>3.05E-19</td>
<td>2.8E-19</td>
</tr>
<tr>
<td>W/kT</td>
<td>63.45</td>
<td>64.42</td>
<td>60.94</td>
</tr>
<tr>
<td>W/Wcl</td>
<td>0.0247</td>
<td>0.0163</td>
<td>0.0185</td>
</tr>
<tr>
<td>Δμ/Δμₛ</td>
<td>0.8928</td>
<td>0.8664</td>
<td>0.9112</td>
</tr>
</tbody>
</table>

Table 5.3: Parameter calculation for our experimental results: case (5) 1500 psi, 80°C; case (6) 1200 psi, 70°C; case (3) 1500 psi, 60°C.
<table>
<thead>
<tr>
<th></th>
<th>103.45</th>
<th>103.45</th>
<th>103.45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial P (bar)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial T (°C)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Polymer weight fraction</td>
<td>0.9016</td>
<td>0.9016</td>
<td>0.9016</td>
</tr>
<tr>
<td>PS $M_W$ (kg/mol)</td>
<td>187</td>
<td>187</td>
<td>187</td>
</tr>
<tr>
<td>CO$_2$ $M_W$ (kg/mol)</td>
<td>0.044</td>
<td>0.044</td>
<td>0.044</td>
</tr>
<tr>
<td>Final P ($P_0$) (bar)</td>
<td>102.85</td>
<td>102.75</td>
<td>102.65</td>
</tr>
<tr>
<td>$P_0$ (bar)</td>
<td>102.94</td>
<td>102.91</td>
<td>102.89</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>0.09</td>
<td>0.16</td>
<td>0.24</td>
</tr>
</tbody>
</table>

At initial P,
\[
\frac{S_i^V}{N_i^V} = 1.33E-22, 1.33E-22, 1.33E-22
\]

At initial P,
\[
\frac{S_i^L}{N_i^L} = 1.09E-22, 1.09E-22, 1.09E-22
\]

At initial $P_0$,
\[
\frac{S_i^V}{N_i^V} = 1.33E-22, 1.33E-22, 1.33E-22
\]

At initial $P_\alpha$,
\[
\frac{S_i^L}{N_i^L} = 1.09E-22, 1.09E-22, 1.09E-22
\]

Density of liquid mixture (kg/m³) | 1044.10 | 1044.10 | 1044.10 |

Molar of PS per m³ in liquid (mol/m³) | 5.03 | 5.03 | 5.03 |

Molar of CO₂ per m³ in liquid (mol/m³) | 2334.987273 | 2334.987273 | 2334.987273 |

Total molars (mol/m³) | 2340.02 | 2340.02 | 2340.02 |

$\rho^L$: molecular number density (molecules/m³) | 1.40869E+27 | 1.40869E+27 | 1.40869E+27 |

$\Delta S^L$ (J/K/m³) | -3.3127E+04 | -3.3140E+04 | -3.3146E+04 |

$\Delta S^L_0$ (J/K/m³) | -3.2824E+04 | -3.2824E+04 | -3.2824E+04 |

\[
\frac{\partial \Delta S^L_i}{\partial (\Delta P)} (J/K/m³/Pa) = 0.033638093, 0.019752922, 0.013442464
\]

$L_0 = -T\Delta S^L_0$ (J/m³) | 1.0930E+07 | 1.0930E+07 | 1.0930E+07 |

\[
\frac{T\partial \Delta S^L_i}{\partial (\Delta P)} (J/m³/Pa) = 11.20148484, 6.577722935, 4.476340545
\]

\[
\frac{\partial \phi}{\partial (\Delta P)}_{\Delta \rho=0} = 3 \cdot \left( 1 - T \frac{\partial \Delta S^L_i}{\partial (\Delta P)}_{\Delta \rho=0} \right) (\text{Pa}^{-1}) = -1.4000E-06, -7.6545E-07, -4.7707E-07
\]

$\Delta P_s$ (larger than) (bar) | 78.2 | 78.2 | 78.2 |

$\frac{\partial \Delta \phi}{\partial \xi} \bigg|_{\xi=0}$ (smaller than) | -10.9 | -6.0 | -3.7 |

Table 5.4: Summary of the initial slope calculation
Figure 5.1: Algorithm of implementing Sanchez-Lacombe EOS for prediction of binodal and spinodal curves
Figure 5.2: Schematic showing calculation of the binodal and spinodal curves: (a) get two binodal points (red points) at the initial pressure; (b) get two spinodal points by calculating the chemical potential curve within the two binodal points; (c) get binodal and spinodal points at a higher pressure until the critical point.
Figure 5.3: PP ($M_w=50,400$, $M_w / M_n =2.2$)-pentane solubility modeling by PC-SAFT at three temperatures. (this is the same system modeled in Gross’s paper and the modeling results match exactly with their results; $k_{ij} =0.0137$; the experimental data are from Martin[163] et al. 1999 )
Figure 5.4: Solubility modeling of PS ($M_w=187,000$)-CO$_2$ at three temperatures by S-L EOS (the top right three curves) and PC-SAFT EOS (the bottom three curves) with assumption of $k_{ij} = 0$ (three different colors represent three different temperatures respectively; experimental data are from Sato [79] et al.)
Figure 5.5: Solubility modeling of PS($M_w=187,000$)-CO$_2$ at 180°C by S-L EOS (the red curves with $k_{ij} = 0$, -0.132) and PC-SAFT EOS (the black curves with $k_{ij} = 0$, 0.196) with ($k_{ij} = -0.132$ and 0.196 are correlated from experimental data of Sato [79] et al.)
Figure 5.6: Solubility modeling of PS ($M_w=187,000$)-CO$_2$ at 140°C by S-L EOS (the red curves with $k_{ij} = 0, -0.117$) and PC-SAFT EOS (the black curves with $k_{ij} = 0, 0.1732$) with ($k_{ij} = -0.117$ and $0.1732$ are correlated from experimental data of Sato [79] et al.)
Figure 5.7: Solubility modeling of PS ($M_w=187,000$)-$\text{CO}_2$ at 100°C by S-L EOS (the red curves with $k_{ij} = 0, -0.088$) and PC-SAFT EOS (the black curves with $k_{ij} = 0, 0.1632$) with ($k_{ij} = -0.088$ and $0.1632$ are correlated from experimental data of Sato [79] et al.)
Figure 5.8: Solubility modeling of PE ($M_w=108,000$)-pentane at 187°C by S-L EOS (the red curves with $k_{ij} = 0.016$) and PC-SAFT EOS (the black curves with $k_{ij} = -0.0033$) with ($k_{ij} = 0.016$ and -0.0033 are correlated from experimental data of Kiran [90] et al.)
Figure 5.9: Binodal (solid curve) and spinodal (broken curve) curves of PS ($M_w=187,000$)-CO$_2$ at 180°C by S-L EOS ($k_{ij} = -0.132$) ($k_{ij} = -0.132$ is correlated from experimental data of Sato [79] et al.).
Figure 5.10: Binodal (solid curve) and spinodal (broken curve) curves of PS ($M_w=187,000$)-CO$_2$ at 100°C by S-L EOS ($k_{ij} = -0.088$) ($k_{ij} = -0.088$ is correlated from experimental data of Sato [79] et al.)
Figure 5.11: Prediction of bimodal curves of PS ($M_w=187,000$)-CO$_2$ at three temperatures (red represents 180°C, blue represents 140°C, and black represents 100°C) by PC-SAFT EOS with assumption of $k_{ij}=0$ (three different colors represent three different temperatures respectively; experimental data are from Sato [79] et al.)
Figure 5.12: Prediction of binodal (right) and spinodal (left) curves of PS ($M_w=187,000$)-CO$_2$ at 100°C by PC-SAFT ($K_{ij}=0.1632$)
Figure 5.13: Prediction of binodal (right) and spinodal (left) curves of PS \((M_n=187,000)\)-CO\(_2\) at 140°C by PC-SAFT \((K_{ij} = 0.1732)\)
Figure 5.14: Prediction of binodal (right) and spinodal curves of PS ($M_w=187,000$)-CO$_2$ at 180°C by PC-SAFT ($K_{ij}=0.196$).
Figure 5.15: Comparison of the prediction for binodal and spinodal curves by S-L EOS ($k_{ij} =-0.088$) and PC-SAFT ($k_{ij} =0.1632$) for PS-CO$_2$ at 100°C in the region covering typical foaming pressure.
Figure 5.16: Representative images in PS-CO$_2$ foaming under two different pressure drop (temperature is 180°C) in Guo’s paper[2]
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Figure 5.18: Cell number density vs. time (top plot; left curve: maximum pressure drop $dP/dt=220$ MPa/s; right curve: for maximum pressure drop $dP/dt=20$ MPa/s) and corresponding pressure profiles (bottom left: maximum pressure drop $dP/dt=220$ MPa/s; bottom right: maximum pressure drop $dP/dt=20$ MPa/s) (From Guo[2] et al.’s paper and their courtesy)
Figure 5.19: Cell number density vs. time (top plot; left curve: initial pressure is 15 MPa; right curve: initial pressure is 10 MPa) and corresponding pressure profiles (bottom left: initial pressure is 15 MPa; bottom right: initial pressure is 10 MPa) (From Guo[2] et al.’s paper and their courtesy)
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Figure 5.24: Relationship between $W/W^{cl}$ and $\Delta\mu/\Delta\mu_s$, including results in Fig. 5.22 and calculation based on our experimental results: (case (1) 1200 psi, 80°C; case (2) 1200 psi, 60°C; case (3) 1000 psi, 80°C; case (4) 1000 psi, 80°C, final pressure 389 psi; case (5) 1500 psi, 80°C; case (6) 1200 psi, 70°C; and case (7) 1500 psi, 60°C)
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6.1 Introduction

Diffusivity, as well as solubility, affects both cell nucleation and growth. A higher diffusivity favors fast nucleation and therefore fine-cell structure, due to a large amount of blowing agent desorbed in a short period of time. Blowing agents with higher diffusivity escape from the polymer matrix faster, usually resulting in smaller cells and sometime cell rupture. In general, smaller molecules (e.g. CO₂) have higher diffusivity than bigger molecules (e.g. CFCs). Therefore, from the point view of diffusivity, CO₂ is suitable to produce foams with high cell density and foam density and CFCs are suitable for production of foams with lower cell density and foam density.

One benefit for using nanoparticles is to reduce the diffusivity of CO₂ in the polymer matrix. First of all, nanoparticles, especially nanoclays, can be good barriers for diffusion. Second of all, the viscosity increase by the addition of nanoparticles in the polymer matrix also slows down the diffusion of gas. To study the diffusion of CO₂ through the polymer nanocomposites in the foaming process, two major aspects need to
be explored. The first one is the effect of high pressure, i.e. measurement of diffusivity of CO₂ in polymers or nanocomposites under high pressures. The experimental data are very limited, even for pure polymers, due to technical difficulties. The review by Tomasko[34] et al. lists available diffusivity data of CO₂ in molten polymers, including PS. Handa [111] et al. reported the diffusivity of CO₂ in PMMA at both below and above \( T_g \) of neat PMMA. The second one is the nanoparticle effect, i.e. the influence of nanoparticle size, shape, and dispersion. In our lab, the MSB (Magnetic Suspension Balance) is used to study the pressure effect on diffusivity of CO₂ in polymers. For the effect of nanoparticles, the permeability coefficient at ambient pressures and temperatures was measured for polymers, nanocomposites, polymeric foams, and polymer nanocomposite foams. Using this method, the effect of nanoparticles on diffusion can be quantified. As described below, the permeability coefficient is directly connected to the diffusivity. In addition, there may be a direct connection between diffusion at ambient conditions and under high pressures and temperatures.

The permeability coefficient for a gas penetrant through a solid film is derived from Fick’s law and Henry’s law: [112]

\[
P = D \cdot S = \frac{l \cdot q}{(p_1 - p_2)}
\]  
(Eq. 6.1)

Where \( P \) [cm\(^3\)(STP)-mm/cm\(^2\)-s-cmHg] is the permeability coefficient or permeability constant, \( q \) [cm\(^3\)(STP)/cm\(^2\)-s] is the transmission rate, i.e. the amount of gas diffusing across unit area of the film in unit time, \( D \) [cm\(^2\)/s] is the diffusion coefficient, \( S \) [cm\(^3\)(STP) (gas)/ cm\(^3\) (film)-cmHg] is the solubility coefficient, \( p_1 \) [cmHg] and \( p_2 \)
[cmHg] are the pressures of diffusing gas on both sides, and \( l \) [mm] is the thickness of the film. The permeability coefficient \( P \) is found to be independent of thickness in most cases [113], so it is used to characterize the permeability of a material.

The temperature dependence of \( S, D, \) and \( P \) over a moderate temperature range can be represented by Arrhenius-type relationships:[113,114]

\[
S = S_0 \cdot \exp\left(-\Delta H_S / RT\right) \quad \text{(Eq. 6. 2)}
\]

\[
D = D_0 \cdot \exp\left(-E_d / RT\right) \quad \text{(Eq. 6. 3)}
\]

\[
P = P_0 \cdot \exp\left(-E_p / RT\right) \quad \text{(Eq. 6. 4)}
\]

Where \( \Delta H_S \) is the heat of solution of the gas in the polymer, \( E_d \) is the activation energy for diffusion, \( E_p \) is the activation energy for permeation, \( T \) is the absolute temperature, and \( S_0, D_0, \) and \( P_0 \) are pre-exponential factors respectively. From the above equations, the following expression can be obtained relating the activation energy for permeation to the heat of solution and activation energy for diffusion:

\[
E_p = \Delta H_S + E_d \quad \text{(Eq. 6. 5)}
\]

The permeation of gas or vapor in polymer films has theoretical importance through this connection to solubility and diffusivity. On the other hand, the permeation of plastic films and other packaging materials to gases and vapors is of practical interest. In particular, the permeability constants for water vapor, CO\(_2\) and oxygen are needed for design of packaging. The food packaging industry places particular demands on the barrier requirements of the packaging materials selected [113]. In our research, CO\(_2\) is used as the foaming agent. When the foaming process is complete, CO\(_2\) may leave or stay
in the polymer, depending on its diffusivity (or permeability) at the ambient temperature. Therefore, the permeability of the blowing agent CO\textsubscript{2} needs to be properly addressed and studied. In foam research, permeability is regarded to impact the dimensional stability of foams manufactured from low-modulus resins [17]. The hydrocarbons used as blowing agents in low density polyethylene (LDPE) permeate out of the foam 5 to 60 times faster than the rate of air permeating into the cell, causing the pressure inside the cells to drop below atmospheric. This leads to bubble collapse or shrinkage during short-term aging [164]. In addition, in thermal insulating foams, such as PS foams, the conductivity of the gas trapped inside the cell is important, which contributes to the overall thermal conductivity of foams, along with the conductivity of polymer and radiative (infrared) transmission [165]. Since CO\textsubscript{2} (thermal conductivity $k = 16.65$ mW/(m·K) at 27°C) in the foam will be replaced gradually by air, which has poorer thermal resistance ($k = 26.24$ mW/(m·K) at 25°C) [166], CO\textsubscript{2} should remain within the foam as long as possible for the purpose of thermal insulation. Furthermore, the presence of nanoparticles is regarded to greatly reduce the permeability from that of the pure polymer [148]. Therefore, it is necessary to study the permeability of CO\textsubscript{2} in PS nanocomposites and foams to provide valuable feedback for foam design, such as the bubble size distribution and dispersion of nanoparticles in the polymer matrix. On the other hand, permeation of water vapor [167,168] has been widely studied, it is interesting to study the permeation of water vapor through the foams to provide more supportive information for nanocomposite foam design.
Experimental studies on CO₂ and water vapor permeation in polymers can be traced to as early as several decades ago. A particularly good discussion, including descriptions, analysis, and comments on many techniques has been given by M. Lomax [169,170]. Several methods are based on the so-called “time-lag technique” [171]. The permeation of gas or vapor through a plastic film can be essentially described as the gas or vapor dissolving in one surface of the film, diffusing through the film, and evaporating from the other surface of the film (low pressure side) [112]. After a comparatively short time, steady state can be established meaning that gas diffuses at a constant rate if constant pressure difference is maintained across the film. Generally, there are two types of measurements: [114] measuring the change in pressure under conditions of constant volume and temperature; or measuring the change in volume under constant temperature and pressure. The former was more widely used [112,172-175] because all three parameters (permeability coefficient $P$, diffusion coefficient $D$, and solubility coefficient $S$) could be calculated from the single experiment—$P$ from the steady state flux, $D$ from the time lag, and $S$ as $P/D$. [113] The simple gravimetric method [148,176] was also used in water vapor permeation measurements.

For CO₂ and water vapor, permeability coefficients and activation energy for permeation, $E_p$, have been tabulated [119,177] for many polymers. PS and PMMA (poly(methyl methacrylate)) are usually not used in packaging material, therefore experimental data for these two materials are scarce. However, the barrier properties of polymer nanocomposites have drawn a lot of interest recently and the systems studied are shown in Table 6.1. Modeling of permeation in polymer nanocomposites has also been
carried out [178,179]. To our best knowledge, permeation of CO\textsubscript{2} and water vapor on PS nanocomposites has not been reported nor has data on permeation of polymer nanocomposite foams.

In our study, commercial apparatus PERMATRAN-C Model 4/41 and PERMATRAN-W Model 3/33 from Mocon were used respectively to measure steady state permeation data of CO\textsubscript{2} and water vapor.

6.2 Experimental

6.2.1 Material

PS (CX5197; $M_w = 187,000$, $M_n = 86,000$) from Total Petrochemicals (formerly Atofina) and PMMA (PL-150; $M_w = 80,200$; $M_n = 41,700$) from Plaskolite were used as received. The foaming agent CO\textsubscript{2} (>99.9\%) was provided by Praxair. Two types of organically modified clays, a commercially available Cloisite 20A (20A for short) and custom modified MHABS, were used to fabricate nanocomposites. Vapor grown CNFs (PR-24-PS, Applied Science Inc.) were pyrolytically stripped to remove the surface organic contamination. The average diameter of these CNFs was 100 nm and the original lengths ranged from 30 to 100 µm. The PS+20A nanocomposite and PS+CNFs nanocomposite were mechanically blended at 200°C using a twin-screw extruder (Leistritz ZSE-27; $L/D = 40$; $D = 27\text{mm}$) and pelletized. To study the effect of nanoparticle concentration on permeation, two different loadings (3 wt.% and 5 wt.%) of nanocomposite were fabricated. The exfoliated nanocomposite PS+MHABS (with weight
percent of about 20% MHABS) was synthesized from an *in-situ* polymerization and then diluted using pure PS by the same twin-screw extruder at 200°C and pelletized. The temperatures were chosen for compounding PS+20A, PS+CNFs, and PS+MHABS that were good for processing and minimizing degradation.

6.2.2 Sample preparation

All PS, PMMA, PS+20A, PS+MHABS, and PS+CNFs were in pellet form (from the manufacturers or by pelletizing). The plate samples were compression molded according to the following procedure. Polymer pellets were placed in a square mold in the hydraulic unit (model #3925, Carver) at 180°C (for PS and PMMA, 200°C for PS+20A, PS+MHABS, and PS+CNFs). After 30 minutes of melting, the press (about 10 tons) was applied to compress the pellets into a square shape with thickness of about 0.7 mm. The thickness of the plates (and also foam plates) were measured by a caliper (Mitutoyo Corp.) with an accuracy of 0.01 mm.

For foams, polymer plates that were about 2 mm thick were compression molded then sandwiched between steel plates in a high pressure vessel at 13.8 MPa and 100°C (83°C was also used to get PS foam with a different cell size). The samples were allowed to equilibrate at pressure for 24 hours, then the pressure was released quickly (about 15 seconds) to atmospheric pressure, and the bubble growth was stopped by putting the sample in ice water 60 seconds after pressure release (the amount of time it took to open the high pressure vessel and take out the samples).
6.2.3 Characterization of foam structure

A scanning electron microscope (SEM, HITACHI S-4300) was used to observe the cell morphologies of foam samples. Details about sample preparation and image analysis can be found elsewhere [66]. Three SEM images (at different spots and with over 50 cells on the image) were analyzed to get the average cell diameter. The cell numbers on three SEM images (at different spots and with over 200 cells on the image) were counted to get the average cell number density. Over 100 different spots were chosen (including walls and struts) to get the average cell wall thickness. Because of non-uniform cell morphology, the standard deviations of these evaluations were comparatively large, especially for cell wall thickness.

6.2.4 Permeation measurement

Commercial apparatus (PERMATRAN-C Model 4/41 and PERMATRAN-W Model 3/33 from Mocon) were used to measure steady state permeation data of CO₂ and water vapor respectively. All the samples were big enough to cover the permeation area (a circle of area 50 cm²). Permeant CO₂ (>99.99%) and carrier gas N₂ (>99.998%) were provided by Praxair. Water (HPLC grade) was from Fisher Scientific. For both measurements, the pressure of the carrier gas was 0.310 MPa (gauge pressure, 45 psig) controlled by a regulator. Its flow rate was 100 sccm (standard cubic centimeters per minute). For CO₂ measurement, the pressure of CO₂ was 0.10 MPa (gauge pressure, 14.5 psig) monitored by a pressure gauge (Sensotec, model: AG 300) and the flow rate was
100 sccm. It usually takes one or two days (continuous mode was used) to achieve a steady state permeation data value. The data have been corrected to standard pressure (0.10 MPa).

6.3 Results and discussion

For most literature data on polymer permeation, film thicknesses of about 0.25 mm (10 mil) or less were used. In our study, the thickness was about 0.7 mm for polymer plates and about 3 mm for foam samples; hence we refer to our samples as “plates” rather than “films”. The sample selection in our study is of more practical interest for our applications as PS and PMMA are rarely applied in film form. It is well known that, for most systems, the permeability coefficient is independent of thickness [113], therefore, it is used to compare permeation properties between samples with different thickness.

Permeability measurements were validated by checking for repeatability and comparing with the available literature data. Fig. 6.1 shows the repeatability of PS+5% 20A plate for CO₂ permeation and PS+5% 20A foam samples for water vapor. Sample A and B are foamed at the exact same conditions (i.e. samples in the same batch). The error bars show the standard deviation. Elberaïchi [176] et al. reported that the permeability coefficient of water vapor in PMMA ($M_w=70,000$) is $2 \times 10^{-6}$ cm³(STP)·mm/cm²·s·cmHg at 20°C. Our datum is $1.52 \times 10^{-6}$ cm³(STP)·mm/cm²·s·cmHg at 20°C. Both $P$ and $E_p$ values of CO₂ and water vapor in PS are available. Table 6.2 gives the comparison
between our data and the literature. Our datum agree reasonably well with Paine’s datum, which is the most recent and widely cited.

In the following sections, the experimental data of CO₂ and water vapor in polymer nanocomposites and foams are presented. Then the activation energy for permeation is discussed for both cases of CO₂ and water vapor. Finally, the effect of foam morphology on permeation is studied based on CO₂ experimental permeation data.

6.3.1 CO₂ permeation

_Polymer and polymer nanocomposite plates_

Transmission rate data can be obtained directly from the apparatus. Fig. 6.2 shows CO₂ transmission rates for five different plates at three temperatures. For all systems the transmission rate increases with increasing temperature. According to Eq. 2.11, the permeability coefficient can be calculated from the transmission rate, plate thickness and pressure difference across the sample. The upstream CO₂ pressure was measured by the pressure gauge and kept constant. The partial pressure of CO₂ on the sweep (permeate) side can be reasonably assumed to be 0. Fig. 6.3 shows the relationship between permeability coefficients and the reciprocal of absolute temperature. A log-linear relationship is observed in agreement with Eq. 2.17. The permeability coefficients of PMMA plates are about one order of magnitude lower than PS and the three PS nanocomposites. PMMA has a stronger affinity than PS because it possesses carbonyl
groups [78]. We hypothesize that the strong interaction between PMMA and CO₂ retards the transport of CO₂, therefore decreasing the permeability coefficient.

When comparing the permeability coefficient of PS and three different PS nanocomposites, we found that $\text{PS} > \text{PS+5\% 20A} \approx \text{PS+5\% CNFs} > \text{PS+5\% MHABS}$. The reason for this order may be the dispersion of nanoparticles in the polymer matrix. *In-situ* polymerization was used to synthesize highly exfoliated PS+MHABS nanocomposite and melt blending was used to fabricate intercalated PS+20A and PS+CNFs nanocomposites. For intercalated nanocomposites, polymer chains penetrate into clay layers. However, for exfoliated nanocomposites, the clay is completely delaminated. Exfoliated nanocomposites can achieve much better property improvement per unit weight [16]. Here, PS+MHABS nanocomposite has a better barrier property than PS+CNFs and PS+20A.

The permeation reduction by nanoparticles can be seen more clearly when the data are plotted as relative permeability, defined as the ratio of permeability coefficients of the PS nanocomposite plate to the pure PS plate. Similarly, the relative permeability of PS nanocomposite foam can be defined as the ratio of permeability coefficients of the PS nanocomposite foam to the pure PS foam. Fig. 6.4 shows relative permeability coefficients at 25°C for the three PS nanocomposite plates and foams. To take the concentration of nanoparticle into consideration, the results of PS+3\% CNFs were also shown. Increasing CNFs content significantly decreases the permeability values. Messersmith [148] *et al.* used *in-situ* polymerization to synthesize a nanocomposite with full delamination (exfoliated) and a solvent casting technique to form nanocomposite
films with oriented silicate layers. Their results showed that the permeability of the PCL+OMTS (poly (ε-caprolactone) + organically modified mica-type silicate) nanocomposite was reduced 11% and 39% by 3 wt.% and 6 wt.% of nanoclay respectively. A roughly linear relationship between relative permeability and fraction of nanoclay was observed. In our work, *in-situ* polymerization was also used to synthesize the exfoliated PS + MHABS nanocomposite. Fig. 6.4 shows an approximate 33% reduction of the permeability coefficient with 5 wt.% MHABS, which agrees well with the literature data.

*Polymer and polymer nanocomposite foams*

Fig. 6.5 shows the permeability coefficients of five different foams at three different temperatures. A similar trend as the polymer nanocomposite plates (Fig. 6.3) was observed except that PS+5% CNFs foam has lower permeability coefficient values than both PS+5% 20A and PS+5% MHABS foams. This trend is also shown by the relative permeability of foams in Fig. 6.4 and should be related to the foam morphology (including the cell size distribution, wall thickness, and strut thickness), as well as nanoparticle dispersion. Comparing Fig. 6.3 and Fig. 6.5, we can conclude that permeability coefficients of foams are about one order of magnitude higher than their corresponding plates. The reason is that CO₂ needs to permeate much less polymer in the foam than in the plate for the same thickness of sample. In addition, results for the
PMMA foam are consistent with the results of the PMMA plate, indicating again the strong interaction between PMMA and CO₂.

6.3.2 Water vapor permeation

*Polymer and polymer nanocomposite plates*

The same samples (here PS+3% CNFs represents PS+CNFs nanocomposite) for CO₂ permeation measurement were used for water vapor permeation measurement. The partial pressure of water vapor at different temperatures can be referred to in a steam table. The partial pressure of water can be assumed to be 0 on the other side, as with CO₂ permeation. According to Eq. 2.11, the permeability coefficient can be calculated. Fig. 6.6 shows the relationship between permeability coefficients with reciprocal of absolute temperatures. It clearly demonstrates the linear relationship between logₚ and reciprocal temperature. When comparing the permeability coefficient of PS and three different PS nanocomposites, we found a similar trend to CO₂, i.e. PS > PS+3% CNFs > PS+5% 20Å > PS+5% MHABS with similar explanations. However, here PMMA has close permeability coefficient values with PS and its nanocomposites. PMMA is an exception in CO₂ permeation because of its strong interaction with CO₂. However, water is not regarded to have strong interaction with any polymers or polymer nanocomposites in our studied systems. The uncommon positive slopes of these lines will be explained below.
Fig. 6.7 shows the permeability coefficients of five different foams at three different temperatures. It shows a similar trend as Fig. 6.6, but here PMMA foam has the highest permeability coefficient values. Because of the effect of foam morphology, it does not show the exact trend as the corresponding plates (Fig. 6.6). By combining Fig. 6.6 and Fig. 6.7, we can conclude that the permeability coefficients of foams are about one order of magnitude higher than their corresponding plates, even for PMMA foams and plates. Comparing Fig. 6.3 and Fig. 6.6 as well as Fig. 6.5 and Fig. 6.7, we can conclude that: with the exception of PMMA plates and foams, which have strong interaction with CO₂, permeability coefficients of water vapor are about two orders of magnitudes higher than corresponding values for CO₂. In addition, for both CO₂ and water vapor, nanoparticles can significantly decrease the permeation when comparing polymer nanocomposites with corresponding pure polymers or polymer nanocomposite foam with corresponding pure polymer foams.

6.3.3 Temperature effect

The results in Fig. 6.3 and Fig. 6.6 demonstrate that logP is linear with reciprocal temperature, which is widely accepted.[113] The activation energy for permeation $E_p$ can be calculated from the plot of logP vs. $1/T$ and is provided in Table 6.3 and also Fig. 6.8. According to Eq. 2.18, $E_p$ can be represented as the sum of $\Delta H_S$ and $E_d$. $E_d$ is always

180
positive because the diffusion coefficient always increases with increasing temperature. The sign of $\Delta H_S$ can be positive or negative. [113] For permanent gases, such as O$_2$, N$_2$, or CO$_2$ in our measurement temperatures, $\Delta H_S$ is positive; for condensable vapors such as water $\Delta H_S$ is negative. Therefore, $E_p$ is always positive for permanent gases and can be positive, negative, or close to zero for condensable vapors. This can possibly explain the negative $E_p$ for permeation of water vapor in PMMA, PS and PS nanocomposites and foams. The above comments are also summarized in Table 6.4. Negative $E_p$ is uncommon, however, it exists for some systems. For instance, Mogri [180] et al. shown negative $E_p$ of water vapor in poly(ethyl methacrylate) and poly(propyl methacrylate). Hubbell [171] et al. have also shown negative $E_p$ of water vapor in Kapton H (poly[N, N'-(p,p'-oxydiphenylene) pyromellitimide]). To the authors’ best knowledge, data for $E_p$ of water vapor in PMMA, PS, and its nanocomposites are not available.

When comparing the $E_p$ data for both plates and foams, we observe that PMMA has much higher $E_p$ values than PS and PS nanocomposite. In addition, polymer nanocomposite plates and foams (except PS+5% CNFs plate) have higher $E_p$ values than PS and PS foams respectively. Combining this result with our permeability coefficient data, we can conclude that: in general, for both plates and foams, the permeability coefficient $P$ drops and activation energy for permeation $E_p$ increases with addition of nanoparticles. This means nanoparticles make the permeation through polymer matrix more difficult. PMMA plates and foams have much lower $P$ and higher $E_p$ than PS and PS nanocomposites and foams, due to the stronger interaction of CO$_2$ and PMMA.
6.3.4 Foam morphology

As shown in Fig. 6.3 and 6.5-7, the permeation reduction from PS plate to PS nanocomposite plates is different from the reduction from PS foam to PS nanocomposite foams. It implies that the foam morphology plays an important role and should also be appropriately addressed. To explore the effect of foam morphology on permeation, we studied pure PS foam with different cell size (and therefore cell density, cell wall thickness) foamed under different conditions. Foam samples were also prepared under conditions of 13.8 MPa, 83°C. Fig. 6.9 gives representative SEM images of foams under conditions of 13.8 MPa, 100°C (a) and 13.8 MPa, 83°C (b). The images show that the bubble size increases with increasing temperature. Fig. 6.10 shows the permeability coefficients of CO₂ for the two PS foam samples. We assume that when CO₂ permeates through the foam sample, only the polymer (i.e. cell walls and struts) needs to be considered as the barrier. The inside of each cell, filled with CO₂ or air, contributes negligibly as a barrier. For simplicity, we also assume that CO₂ permeates on a straight route through the foam regardless of the nature of the barriers along that route. Then we expect to see a linear relationship on the plot of $P$ vs. cell diameter / cell wall thickness ratio (in this plot $P$ for the plate was used for cell diameter of zero). Fig. 6.11 shows a linear trend and verifies these assumptions. $R^2 = 0.9893$ is reasonably good considering the cell structure of these foams, with a fairly wide distribution of cell size and cell wall thickness.

Fig. 6.12 shows representative SEM images of five different foams under the same foaming condition (13.8 MPa and 100°C). Table 6.5 gives the SEM analysis results.
of cell diameter, cell wall thickness, and cell density. As shown in Fig. 6.13, all these data points also follow this correlation. This result suggests that foam structure plays a more important role than nanoparticles in determining the permeability coefficient values for nanocomposite foams. This makes sense because volume or weight percentage of the nanoparticles in the foam samples is very low.

6.4 Conclusion

Commercial apparatus were used to measure steady state permeability coefficients \( (P) \) of \( \text{CO}_2 \) and water vapor in PMMA, PS, and PS nanocomposites and their corresponding foams at three different temperatures. Based on the experimental results, the following conclusions can be drawn.

1. Permeability coefficients of water vapor are about two orders of magnitude higher than \( \text{CO}_2 \).
2. Permeability coefficients of foams are about one order of magnitude higher than plates.
3. For both plates and foams, nanoparticles considerably decrease permeation values. In addition, exfoliated nanocomposite PS+MHABS shows better barrier property than intercalated nanocomposites, PS+20A and PS+CNFs.
4. \( E_p \) values for water vapor permeation are negative, which is uncommon, but can be possibly explained by a big absolute value of the heat of solution \( (\Delta H_S) \).
5. In general, the activation energy for permeation, $E_p$, is reduced by addition of nanoparticles in the PS matrix. This shows that nanoparticles make the energy barrier for permeation higher.

6. The PMMA plate and foam have much lower $P$ for CO$_2$ and higher $E_p$ than PS and PS nanocomposites and foams, due to the strong interaction of CO$_2$ and PMMA.

7. Foam structure is shown to play a more important role than nanoparticles in determining the permeability coefficient values for nanocomposite foams.
<table>
<thead>
<tr>
<th>Polymer nanocomposite systems</th>
<th>Permeants</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane (PU) / organo-montmorillonite</td>
<td>O₂</td>
<td>Choi et al. (2004)[181]</td>
</tr>
<tr>
<td>Epoxy (EP) / organo-montmorillonite and PU / organo-montmorillonite</td>
<td>O₂</td>
<td>Osman et al. (2004)[182]</td>
</tr>
<tr>
<td>High density polyethylene (HDPE) nanocomposite</td>
<td>O₂</td>
<td>Osman et al. (2004)[183]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride) (PVDF) / montmorillonite</td>
<td>CO₂, He, H₂</td>
<td>Gain et al. (2004)[184]</td>
</tr>
<tr>
<td>Poly (1-trimethylsilyl-1-propyne) (PTMSP) / fumed silica nanocomposite</td>
<td>N₂</td>
<td>Andrady et al. (2004)[185]</td>
</tr>
<tr>
<td>NBR / organo-montmorillonite</td>
<td>H₂O</td>
<td>Kim et al. (2004)[168]</td>
</tr>
<tr>
<td>Sulphonated poly (ether ether ketone) (SPEEK) / laponite or MCM-41</td>
<td>H₂O, CH₃OH</td>
<td>Karthikeyan et al. (2005)[167]</td>
</tr>
<tr>
<td>Nylon-6 / ultrafine full-vulcanized powdered Rubber / montmorillonite (UFPRM)</td>
<td>N₂</td>
<td>Dong et al. (2005)[186]</td>
</tr>
<tr>
<td>PS / organoclay</td>
<td>O₂</td>
<td>Meneghetti et al. (2006)[187]</td>
</tr>
<tr>
<td>(PP)/ethylene-propylene-diene rubber (EPDM) blend / organo-montmorillonite</td>
<td>CO₂, O₂</td>
<td>Frounchi et al. (2006)[188]</td>
</tr>
</tbody>
</table>

Table 6.1: Permeation studies on polymer nanocomposites after 2004
<table>
<thead>
<tr>
<th></th>
<th>Author and year</th>
<th>$P$ (cm$^3$(STP)·mm/cm$^2$·s·cmHg)</th>
<th>$E_p$ (KJ/mol)</th>
<th>$P$ (cm$^3$(STP)·mm/cm$^2$·s·cmHg)</th>
<th>$E_p$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO$_2$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paine [177] et al. 1962</td>
<td>0.88×10$^{-8}$ at 30°C</td>
<td>1.2×10$^6$ at 25°C, 90% r.h. *</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brubaker [114] et al. 1952</td>
<td>3.7×10$^{-8}$ at 30°C</td>
<td>4.19</td>
<td>8.95×10$^{-7}$ at 25°C, 92% r.h. *</td>
<td>about 0</td>
<td></td>
</tr>
<tr>
<td>Doty [172] et al. 1946</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Korvezee [189] et al. 1947</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Water vapor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>0.65×10$^{-8}$ @ 30°C</td>
<td>2.725</td>
<td>1.57×10$^{-6}$ at 25°C at 100% r.h. *</td>
<td>-3.078</td>
<td></td>
</tr>
</tbody>
</table>

r.h.: relative humidity.

Table 6.2: Comparison with literature data for PS permeability coefficient of CO$_2$ and water vapor
<table>
<thead>
<tr>
<th>System</th>
<th>CO₂</th>
<th>Water vapor</th>
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<tr>
<td></td>
<td>$P_0$</td>
<td>$E_p$</td>
</tr>
<tr>
<td></td>
<td>(mol·m/m²·s·Pa)</td>
<td>(Kj/mol)</td>
</tr>
<tr>
<td>Plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>$2.62\times10^{-14}$</td>
<td>2.725</td>
</tr>
<tr>
<td>PS+5% MHABS</td>
<td>$3.57\times10^{-14}$</td>
<td>3.495</td>
</tr>
<tr>
<td>PS+5% 20A</td>
<td>$2.69\times10^{-14}$</td>
<td>3.100</td>
</tr>
<tr>
<td>PS+3% CNFs</td>
<td>$2.54\times10^{-14}$</td>
<td>2.839</td>
</tr>
<tr>
<td>PMMA</td>
<td>$2.52\times10^{-12}$</td>
<td>11.389</td>
</tr>
<tr>
<td>Foam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>$1.20\times10^{-13}$</td>
<td>1.582</td>
</tr>
<tr>
<td>PS+5% MHABS</td>
<td>$3.22\times10^{-13}$</td>
<td>3.017</td>
</tr>
<tr>
<td>PS+5% 20A</td>
<td>$2.13\times10^{-13}$</td>
<td>2.541</td>
</tr>
<tr>
<td>PS+3% CNFs</td>
<td>$8.05\times10^{-14}$</td>
<td>1.314</td>
</tr>
<tr>
<td>PMMA</td>
<td>$6.49\times10^{-11}$</td>
<td>11.649</td>
</tr>
</tbody>
</table>

Table 6.3: $E_p$ values of permeation of CO₂ and water vapor in polymers, composites, and foams
<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_m$</th>
<th>$\Delta H_C$</th>
<th>$\Delta H_S$</th>
<th>$E_d$</th>
<th>$E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanent gas</td>
<td>+ (small)</td>
<td>$\sim 0$</td>
<td>+ (small)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Condensable vapor</td>
<td>+ (small)</td>
<td>- (big)</td>
<td>- (big)</td>
<td>+</td>
<td>+, -, or $\sim 0$</td>
</tr>
</tbody>
</table>

Table 6.4: Sign of $E_p$ for permanent gases and condensable vapors
<table>
<thead>
<tr>
<th>System</th>
<th>Average cell diameter (μm)</th>
<th>Average cell wall thickness (μm)</th>
<th>Average cell density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>82.6 ± 18.4</td>
<td>7.0 ± 5.6</td>
<td>(1.7 ± 0.2)×10⁶</td>
</tr>
<tr>
<td>PS+5% MHABS</td>
<td>41.4 ± 9.9</td>
<td>4.7 ± 2.5</td>
<td>(1.1 ± 0.2)×10⁷</td>
</tr>
<tr>
<td>PS+5% 20A</td>
<td>46.9 ± 12.8</td>
<td>7.7 ± 7.4</td>
<td>(6.2 ± 1.4)×10⁶</td>
</tr>
<tr>
<td>PS+5% CNFs</td>
<td>25.1 ± 6.4</td>
<td>3.4 ± 2.4</td>
<td>(1.3 ± 0.7)×10⁷</td>
</tr>
<tr>
<td>PMMA</td>
<td>95.8 ± 26.9</td>
<td>5.4 ± 3.9</td>
<td>(8.4 ± 2.6)×10⁵</td>
</tr>
</tbody>
</table>

Table 6.5: SEM analysis results of five different foams under conditions of 13.8 MPa and 100°C
Figure 6.1: Repeatability of CO$_2$ permeability coefficient in PS+5% 20A plate (a) and water vapor permeability coefficient in PS+5% 20A foam (b)
Figure 6.2: CO$_2$ transmission rate data for plates at different temperature ($T$)
Figure 6.3: CO$_2$ permeability coefficient for plates at different temperature (1/T)
Figure 6.4: Relative permeability coefficients at 25°C for the three PS nanocomposite plates and foams
Figure 6.5: CO₂ permeability coefficient for foams at different temperature (1/T)
Figure 6.6: Water vapor permeation coefficient for plates at different temperature ($1/T$)
Figure 6.7: Water vapor permeation coefficient for foams at different temperature ($1/T$)
Figure 6.8: Activation energy for permeation, $E_p$, of CO$_2$ and water vapor in polymer nanocomposites and foams.
Figure 6.9: Representative SEM images of PS foams under conditions of (a) 13.8 MPa, 100°C (Cell diameter: 82.6 ± 18.4 μm; and cell wall thickness: 7.0 ± 5.6 μm) and (b) 13.8 MPa, 83°C (Cell diameter: 41.5 ± 12.4 μm; and Cell wall thickness: 13.0 ± 10.9 μm)
Figure 6.10: Permeability coefficient of CO$_2$ for two PS foams ((a) and (b) prepared at different conditions) at different temperature (1/T)
Figure 6.11: Permeability coefficient with cell diameter / cell wall thickness ratios of PS plates and foams (the PS plate is assumed to be foams with cell diameters of zero; the straight line is the trendline)
Figure 6.12: Representative SEM images of five foams under same foaming condition (13.8 MPa and 100°C): (a) PS, (b) PMMA, (c) PS+5% CNFs, (d) PS+5% 20A, and (e) PS+5% MHABS
Figure 6.13: Permeability coefficient with cell diameter / cell wall thickness ratios of PS and nanocomposite plates and foams (the PS and nanocomposite plates are assumed to be foams with cell diameters of zero)
CHAPTER 7

RHEOLOGY

7.1 Introduction

The rheological behavior of polymers in the presence of blowing agent mainly affects the cell growth rate. In particular, the extrusion foaming process is largely controlled by the complex rheological behavior of the polymer-blowing agent mixture. Although the importance of rheology (shear rheology and extensional rheology) in foaming is widely recognized, the scientific literature in this field is relatively scarce, mainly due to technical difficulties.

Shear rheometers are typically classified in two categories: drag driven and pressure driven. Typical pressure driven rheometers are either capillary or extrusion slit die rheometers. They are more commonly used to measure the viscosity of SCF (supercritical fluid)-polymer solutions than drag driven systems. However, one limitation is that the large pressure drop across a capillary or slit die limits the concentration of SCF that can be dissolved in the polymer melt. Thus, viscosities are usually measured at less than saturation SCF concentrations to prevent phase separation. Another limitation is that the data correspond to a range of pressures rather than a particular pressure. Recently,
many authors have reported the measurement of viscosity with SCFs in this manner [126,133,190-192]. In addition, this technique can only measure the high shear rate (shear-thinning) regime. To measure the Newtonian plateau (zero-shear viscosity), other devices must be used. Rotational rheometers overcome the problem of average pressures by allowing the polymer to come to equilibrium with the diluent. Furthermore, it has the ability to measure low shear rates that often correspond to the Newtonian regime (zero-shear viscosity). Flichy et al. [141] and Oh et al. [142,143] measured high-pressure diluent-plasticized viscosities by a rotational rheometer. Wingert [144] in our lab studied viscosity of PS under high pressure CO₂.

As mentioned in the previous chapters, polymer nanocomposite foams may overcome the two major disadvantages of using CO₂ as a physical blowing agent. We are interested in how the viscosity of polymer nanocomposites changes under high pressure CO₂. We focus on two nanocomposites, PS + 20A and PS + CNFs. Both nanocomposites were fabricated by melt blending using extrusion. 20A is representative for nanoclay and CNFs is a good example of tube-like nanoparticles. The effect of the type and shape of nanoparticles on rheology is a very interesting topic. In addition, polymer blend foam can be another possible way to solve the problems of low solubility and high diffusivity of CO₂. Because CO₂ has higher solubility and lower diffusivity in PMMA than PS (shown in the previous chapters), PMMA was used as a dispersed phase in the PS matrix to achieve an immiscible polymer blend. To have a better understanding of the blend foaming, shear viscosity of PMMA under high pressure CO₂ was also measured to compare with PS.
7.2 Experimental

7.2.1 Materials

PS (CX5197; $M_w = 187,000$, $M_n = 86,000$) was from Total Petrochemicals and PMMA (PL-150; $M_w = 80,200$, $M_n = 41,700$) was from Plaskolite. Both were used as received without further purification. Zinc stearate, a common lubricant/plasticizer found in many commercial PS grades, was not present in CX5197. CO$_2$ (>99.9%) was supplied by Praxair.

Vapor grown carbon nanofibers (PR-24-PS, supplied by Applied Science Inc.) were pyrolytically stripped to remove the surface organic contamination. The average diameter of these CNFs was 100 nm and the original length ranged from 30 to 100 µm. Melt blending was used to fabricate the PS+5% CNFs nanocomposite. In this process, CNF powder and PS pellets were fed into a DACA microcompounder, a small twin-screw extruder in which the compounding time, temperature, and screw speed can be controlled. Samples were compounded for 3 minutes at 180°C and 150 rpm. It was called microcompounded PS+5% CNFs. To check the length of CNFs after the compounding, the sample was dissolved by THF (tetrahydrofuran) and then centrifuged for the SEM test (by a Phillips XL30 SEM). As shown in Fig. 7.1, CNFs were shortened by the shearing of the microcompounder, with an average length of only 2.6 µm. Pure PS was also processed through the microcompounder with the exact same condition for comparison with PS+5% CNFs. It was called “microcompounded PS”.

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The PS+ 20A (Cloisite 20A from Southern clay, referred to as 20A for short) nanocomposite was mechanically blended at 200°C using a twin-screw extruder (Leistritz ZSE-27; \(L/D = 40; D = 27\text{mm}\); screw speed 300 rpm) and pelletized. This will be referred to as “extruded PS+5% 20A”. Pure PS was also processed through the extruder with the exact same condition for comparison with PS+5% 20A. This will be referred to as “extruded PS”.

To compare the rheological behavior between PS, PS+5% CNFs, and PS+5% 20A, it was ideal to use the exact same processes and conditions for them. For example, we could process them all by extrusion or microcompounding. However, the extruder could not be used for PS+ CNFs composite because of the large amount of CNFs required (due to high price of CNFs) and the severe shortening of CNFs length by higher shear rate in the extruder. Moreover, we had a good knowledge of the rheological properties of the PS+ CNFs made by the same procedure (microcompounding) [193]. It should still be appropriate to compare the effects of 20A and CNFs even though we used different processes if we compare the PS composites to the corresponding PS with the same processing history.

7.2.2 Apparatus

The rheometer (model: MCR 500) is manufactured by Anton Paar. Its frequency range is from 0.0001 to 100 Hz. The rheometer is compatible with several geometric
accessories. Our studies involved the Couette high pressure cell and parallel plates, operated in oscillatory mode.

High pressure measurements used a Couette geometry that houses an inset cup and bob inside a high pressure cell; details are presented in Fig. 7.2. The high pressure cell has the capability of holding pressures up to 20 MPa. High pressure carbon dioxide was delivered to the high pressure vessel via an ISCO 500D syringe pump. The pressure was detected by a Honeywell Sensotec AG400. This cell has also been used by Flichy et al. for the rheology of poly(propylene glycol) with CO₂ [141]. It was found that the Couette cell possessed a thermal gradient when used at high temperatures (above 100°C). The gradient occurred because the cell relied on one band heater to heat the entire length of the cup. However, the mass of the metal headspace housing (which includes the magnet, threads, and bearings) above the cup was substantial and reduced the temperature of the bob. This was because the bob was directly connected and thermally influenced by the metal housing temperature. My former colleague solved this problem by hooking up a variable voltage device to provide extra heat for the rheometer. Design of experiments was employed to determine the proper band heater (from the MCR-500) and cord heater settings to allow for thermally stable operation.

7.2.3 Experimental procedure

Full operating procedures and selected equipment schematics are given elsewhere [145]. Here only a brief description is given.
For shear viscosity measurement at room pressure, the parallel-plate geometry was used. Thin (1 mm) circular discs of polymers or polymer nanocomposites were made by compression molding with the protection of nitrogen. For measurement, the rheometer was operated in oscillatory mode. The whole measurement was performed under protection of nitrogen to minimize degradation.

For the high pressure measurement, special tools were used to assist efficient melting. The extremely long diffusion and equilibrium time (several months) was significantly eliminated by introducing a porous cup. The porous cup had a solid outside and a porous inside, which allows the CO₂ to quickly distribute to all the sides and even the bottom of the polymer melt. It was made from sintered 316 stainless steel. This porous cup was able to reduce the diffusion in the measurement region, a 1 mm distance, to a couple of hours from many months. The fact that the porous cup produced statistically equivalent data with the normal cup at room pressure proved that the porous cup did not affect the measurement. Under proper operation, the region below the bob did not influence the viscosity measurement. However, if only two hours of saturation time were used, that region may not be sufficiently plasticized with carbon dioxide, and could affect the results. To ensure that this region was sufficiently plasticized, more than 48 hours of total equilibration time was used. During the equilibration time, the temperature was maintained at 140°C. Then, the temperature was raised to the desired level and pressure was adjusted to maintain the desired CO₂ concentration.

For PS and PS nanocomposites, each sample was tested at three temperatures (180°C, 190°C, 200°C) and four concentrations (0, 3, 4, and 5 wt.% CO₂). In other
words, for each concentration, three temperatures were tested. The pressure was adjusted while the temperature was increased from a lower one to a higher one so that the concentration of CO$_2$ was a constant. The appropriate pressure to achieve the desired carbon dioxide concentration at a given temperature was determined by the Sanchez-Lacombe equation of state. It was correlated to an experimental sorption study by Sato [79] et al. To achieve the same concentration, the same CO$_2$ pressure was used as for pure PS. This made sure that the CO$_2$ concentration in the PS matrix was the same for PS and the two PS nanocomposites. For PMMA, though, the same temperature and CO$_2$ pressure were used as the PS because for polymer blend foaming, the two polymers experience the same temperature and pressure.

7.3 Results and discussion

7.3.1 Comparison between PS and PMMA w/ and w/o high pressure CO$_2$

In polymer blend (PS/PMMA) extrusion foaming by high pressure CO$_2$, the die temperature ranges from 115 to 130°C. In batch foaming, 80~120°C is usually used. However, under those temperatures, the viscosity of either PS or PMMA is so high that it exceeds the limit of our rheometer. In addition, longer times are needed for the polymer sample to relax completely to achieve steady state data. Thus, the lowest temperature we measured for PS was 150°C and for PMMA was 160°C. Fig. 7.3 shows the master curve for PMMA and PS (reference temperature: 160°C). As shown on the figure, over most of
the shear rate range, PMMA has higher shear viscosity than PS. In addition, at lower shear rates, PMMA is clearly entering the Newtonian plateau. For PS, on the other hand, the viscosity will increase significantly if we interpolate the data at low shear rates. In other words, PS in our study has higher zero-shear viscosity, but significantly lower viscosities at most shear rates.

Fig. 7.4 shows shear viscosity of PMMA and PS under high pressure CO₂ at 150°C and 160°C. At both temperatures, the weight fraction of CO₂ in PS is 3%. For comparison, viscosities of PMMA and PS at 160°C without CO₂ are also shown. CO₂ has higher solubility in PMMA than PS under the same pressure, resulting in stronger viscosity depression. For example, based on data on 160°C, the viscosity difference between PMMA and PS is smaller with CO₂ than without CO₂. However, PMMA still has higher viscosity than PS with the presence of CO₂ at the pressures and shear rates we measured. In addition, in the presence of CO₂, the rheological behavior is shifted from the non-Newtonian regime to near the Newtonian regime.

7.3.2 Comparison between PS+ CNFs and PS+ 20A w/ and w/o high pressure CO₂

Fig. 7.5 shows master curves for extruded PS+5% 20A, as received PS, extruded PS, microcompounded PS+5% CNFs, and microcompounded PS (from top to bottom) with a reference temperature of 200°C. Comparing the master curves of extruded PS and extruded PS+5% 20A, the addition of nanoclay causes a significant viscosity increase. Similarly, addition of CNFs increases viscosity when comparing the curves of
microcompounded PS and PS+5% CNFs. Furthermore, when comparing as received PS with either extruded or microcompounded PS, significant degradation occurs in the latter two. Surprisingly, microcompounding results in even more severe degradation than extrusion. In the extrusion process, 200°C and 300 rpm were used; in the microcompounding, 180°C and 150 rpm were used. Due to higher temperature and higher rpm, more degradation was expected in the extrusion process. The possible reason that microcompounding led to more degradation than extrusion was the residence time in the process. In the microcompounding, after 3 minutes of mixing, the motor was stopped and then the sample (3 grams each batch) was extruded out. For extrusion, the residence time was less than 3 minutes due to the high rpm used. In other words, longer residence time in the microcompounder could lead to more severe degradation. This demonstrates the importance of processing history (e.g. heat, shear) for viscosity studies.

Figures 7.6-11 shows the shear viscosity of PS+5% 20A and PS+5% CNFs respectively at 180°C, 190°C, and 200°C under different CO₂ concentration (0, 3, 4, and 5 wt.%). In general, with addition of either CNFs or 20A, the viscosity of the PS is higher than the neat PS w/ or w/o CO₂. To compare the effect of CO₂ on these systems, we calculated the values of \( a_p \cdot a_e \). The \( a_p \cdot a_e \) shift factor can be obtained by forming a master curve of viscosity-shear rate data with and without high-pressure CO₂. Viscosity was shifted an equal amount on both axes to produce a graph of \( \eta/a_p \cdot a_e \) versus \( \gamma \cdot a_p \cdot a_e \) (\( \eta \) is viscosity; \( \gamma \) is shear rate) at a given temperature. Fig. 7.12 shows the shift factor \( a_p \cdot a_e \) of extruded PS+5% 20A, extruded PS, microcompounded PS, and
microcompounded PS+5% CNFs at 180°C. When comparing the shift factors of PS+5% 20A and PS+5% CNFs with the corresponding PS, we can conclude that the addition of both fillers increases the shift factor, i.e. the viscosity is reduced less under high pressure CO2. This makes perfect sense because the addition of solid filler increases the viscosity w/ or w/o CO2. Moreover, addition of CNFs shows larger viscosity reduction than 20A, indicating a higher CO2 affinity of CNFs than 20A. To confirm this, adsorption data for CO2 on CNFs and 20A under high pressure is necessary and this work is ongoing.

7.4 Conclusion

Shear viscosities of PS and PMMA were studied w/ and w/o high pressure. Results show PMMA has higher viscosity than PS in the shear rate range studied. Under the same temperature and pressure, PMMA also has higher viscosity than PS although higher CO2 solubility in PMMA leads to larger viscosity reduction.

Carbon nanofibers (CNFs) and nanoclay (20A) have been used as reinforcement additives and nucleation agents in the PS foaming process with supercritical CO2 as the blowing agent in our laboratory. The extrusion foaming process, as well as the final foam structure, is largely controlled by the complex rheological behavior of the PS-CO2-nanoparticle mixture. In this study, master curves of PS, PS+5% CNFs, and PS+5% 20A without CO2 were formed based on measurement by a parallel plate rheometer. Results showed that addition of nanoparticles significantly increased the viscosity of the neat polymer. In addition, to have a better understanding of the foaming process, steady state
shear viscosity of PS in the presence of the blowing agent CO₂ and nanoparticles was measured by a modified Couette rheometer. The effect of high pressure CO₂ on these systems was characterized by shift factors. It was found that, under the same temperature and CO₂ pressure, CO₂ reduced viscosity less for both PS-nanoclay and PS-CNFs than neat PS. Between the two types of nanoparticles, addition of CNFs showed larger viscosity reduction than 20A, indicating a higher CO₂ affinity of CNFs than 20A.
Figure 7.1: Representative SEM images for CNFs: (a) raw; (b) by microcompounding (the PS+5% CNFs sample was dissolved by THF to remove PS and then centrifugated)
Figure 7.2: Schematic of cup and bob in high pressure Couette rheometer
Figure 7.3: Master curves of PS and PMMA (reference temperature: 160°C)
Figure 7.4: Shear viscosity of PMMA and PS w/ and w/o CO₂ at 150°C and 160°C. In both temperatures, weight fraction of CO₂ in PS is 3%. All PS data are from Wingert [145]
Figure 7.5: Master curves for extruded PS+5% 20A, as received PS, extruded PS, microcompounded PS+5% CNFs, and microcompounded PS (from top to bottom) with reference temperature 200°C.
Figure 7.6: Shear viscosity of microcompounded PS+5% CNFs and microcompounded PS at 180°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.7: Shear viscosity of extruded PS+5% 20A and extruded PS at 180°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.8: Shear viscosity of microcompounded PS+5% CNFs and microcompounded PS at 190°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.9: Shear viscosity of extruded PS+5% 20A and extruded PS at 190°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.10: Shear viscosity of microcompounded PS+5% CNFs and microcompounded PS at 200°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.11: Shear viscosity of extruded PS+5% 20A and extruded PS at 200°C under different CO₂ concentration (0, 3, 4, and 5 wt.%)
Figure 7.12: Shift factor $a_p \cdot a_c$ of extruded PS, extruded PS+5% 20A, microcompounded PS, and microcompounded PS+5% CNFs at 180°C
CHAPTER 8

CONCLUSION

In this research, environmentally benign carbon dioxide (CO$_2$) was used as a physical blowing agent in the foaming of PS, PS+ PMMA blend, and PS nanocomposites. Two types of organically modified nanoclays, a commercially available Cloisite 20A (20A for short) and custom modified MHABS (2-methacryloyloxyethylhexadecyldimethylammonium bromide) and CNFs (carbon nanofibers) were used to fabricate nanocomposites. In addition, activated carbon (AC), which has pores in the nanometer range, was also used as an additive.

CNFs and AC were used as additive/nucleation agents in PS extrusion foaming. Both fillers showed promising application in insulation foams based on foam density, thermal conductivity, IR transmission, thermal stability, and compressive modulus. Overall, CNFs were better than AC due to the unique foam structure (“pseudo-bimodal”) observed in this study. Water worked as a co-blowing agent in the PS/ wet AC foaming process.

The typical foaming process includes cell nucleation, cell growth, and cell stabilization, the first two being the focus of this study. In the foaming process, several
operating variables, e.g. temperature, pressure, pressure drop rate, and material related properties, e.g. solubility, diffusivity, and viscosity are crucial. In this study, primary attention was given to the effects of the material related properties on cell nucleation and cell growth.

Two equations of state (EOS), Sanchez-Lacombe (S-L) EOS and perturbed chain statistical associating fluid theory (PC-SAFT), were used to model the solubility and also phase boundaries (binodal and spinodal curves). Nucleation is a very complex phenomenon in physical foam processing and its experimental and theoretical studies cannot provide sufficient information to have a clear picture of the nucleation phenomenon. Proposed scaling functions provide a possible way to calculate the energy barrier in the nucleus formation, $W$. Cell nucleation rate data were extracted from the paper by Guo [2] et al. and also by our experiments. From the phase boundaries predicted, several parameters in the nucleation theory, e.g. $\gamma$, $\Delta P$, and $W$ were calculated based on the experimental data. Several sets of $W/W^{cl}$ and $\Delta \mu / \Delta \mu_s$ were calculated. The initial slope of the possible scaling function was calculated by the diffuse interface theory. A possible scaling function (exponential decay type equation) was correlated to describe the relationship between $W/W^{cl}$ and $\Delta \mu / \Delta \mu_s$ based on the calculation from experimental data. It provided insight for the connection between the phase boundary and the complex nucleation behavior.

Shear viscosity of polymers and nanocomposites were measured by parallel plate rheometry under a nitrogen blanket. Results showed that addition of nanoparticles significantly increased the viscosity of the neat polymer. In addition, steady state shear
viscosity of PS in the presence of the blowing agent CO₂ and nanoparticles (CNFs and 20A) was measured by a unique modified Couette rheometer. It was found that, under the same temperature and CO₂ pressure, CO₂ reduced viscosity less for both PS-nanoclay and PS-CNFS than neat PS. Between the two types of nanoparticles, addition of CNFs showed larger viscosity reduction than 20A, indicating a higher CO₂ affinity of CNFs than 20A.

The permeability coefficient ($P$), defined as the product of the solubility coefficient and diffusivity, of CO₂ and water vapor in polymer nanocomposites and foams were measured near ambient temperature and pressure. The effects of nanoparticles and foam morphology on permeation were studied. For both plates and foams, nanoparticles considerably decrease permeation values. The PMMA plate and foam have much lower $P$ for CO₂ and higher $E_p$ (permeation activation energy) than PS and PS nanocomposites and foams, due to the strong interaction of CO₂ and PMMA. The results provided valuable feedback on the design of polymer nanocomposites and foams, as well as an approximation for relative values of diffusivities in polymers under foaming conditions (higher temperatures and pressures).

To gain more insight on the early stages of the foaming process, in-situ observation of batch foaming and a quenching method were used to study foams with different cell growth times. In addition, quantitative cell nucleation rates were measured by our novel experimental setup. The heterogeneous nucleation was mostly avoided. Three effects in the foaming process, initial CO₂ pressure, temperature, and final CO₂
pressure, were investigated. These cell nucleation rate data provided valuable information for modeling and theoretical correlation (e.g. scaling function).

Based on these experimental studies (rheology and permeation, \textit{in-situ} observation and quantitative measurement) and modeling (phase boundary prediction and scaling function correlation), a deeper and more comprehensive understanding of polymer and nanocomposite foaming was achieved.
CHAPTER 9

RECOMMENDATIONS FOR FUTURE WORK

9.1 PS nanocomposite extrusion foaming

Two major questions remain in the work of PS nanocomposite extrusion foaming. The first one is, why did the addition of CNFs in PS extrusion foaming result in a bimodal foam structure. It was repeatable under different extrusion conditions. We need to find out if it was because of the dispersion of CNFs in the PS matrix or was there something to do with the characteristics of the CNFs used, e.g. shape, surface feature, etc. It is comparatively easy to study the effect of dispersion. In our experiments, the PS pellets and CNFs particles were placed in a bag and shaken by hand to achieve even mixing. A better mixing can be achieved, for example, by two loss-in-weight feeders (one for the polymer pellets and the other for the CNFs particles). Those experiments can be used to identify or exclude the reason of dispersion of CNFs particles. To study the effects of the characteristics of the CNFs would be more difficult.

The other question is the efficient addition of water in the foaming of PS+ wet AC. Experiments showed that the water did work as a co-blowing agent, however, most
water was evaporated in the extruder. Figuring out a way to maintain the water in the extrusion process remains challenging. Other researchers are intensively investigating retaining water by in-situ polymerization.

9.2 Solubility modeling

Although PC-SAFT was shown to perform better than S-L EOS for solubility or phase boundary calculation, it was not used to explore the possible connection between the phase boundary and nucleation theorem. One reason was that the phase boundary prediction of these two equations was very close for the PS-CO₂ system. Another reason was that S-L EOS was much easier to use. As a future project, PC-SAFT should be used for studying the connection between phase boundary and nucleation phenomena due to its higher accuracy.

9.3 Permeation

In the water vapor permeation data, all the activation energies for permeation (\(E_p\)) are negative, including PS, PMMA, PS nanocomposite plates and corresponding foams. As discussed above, negative \(E_p\) is rare. Further validation by thinner samples for both PS and PMMA is needed. For the water vapor permeation measurement, saturated water vapor at the test temperature was used. When using unsaturated water vapor, the permeability coefficient
was different from that measured at saturated water vapor. One assumption we made was that the absorption curves followed Henry’s law. However, PMMA and PS are shown [119] to not completely follow Henry’s law, i.e. the solubility coefficient is dependent on sorbed concentration (partial pressure or RH (relative humidity). The reason for the discrepancy of the results between saturated water vapor and certain RH, i.e. the dependence of permeability coefficient on RH, needs to be found.

9.4 Rheology

In our research, shear viscosity of polymers (PS and PMMA) and polymer nanocomposites (PS+ 20A, PS+ CNFs) under high pressure was studied by the unique experimental setup. The result indicates that CNFs has more affinity with CO₂ than nanoclay 20A. In addition, the experimental result from another project demonstrates that PS+ CNFs composite has bigger $T_g$ reduction than PS under higher pressure CO₂. The effect is pronounced especially for some loadings of CNFs. Since there exists direct relationship between rheology and $T_g$, The effect of CNFs loading on the rheology under higher pressure CO₂ will be a very interesting topic.

When comparing the effects of two nanoparticles (CNFs and 20A) on the shear viscosity of PS with the presence of high pressure CO₂, two different processes were used to fabricate the two types of nanocomposites. The extrusion was used for 20A and microcompounding was used for CNFs. Although it should still be appropriate to compare the effects of 20A and CNFs since we compared the PS composites to the
corresponding PS with the same processing history, it is ideal to use the same process for both sample preparations. Extrusion is preferred due to better dispersion of nanoparticles in the polymer matrix. Thus we should prepare the sample PS+5% CNFs by extrusion using the same condition as for PS+20A. PS+5% CNFs by this process should also be used for high pressure rheology experiment. The results can be used to compare directly with the results of PS+5%20A. On the other hand, we can study the effect of process by comparing rheological properties of PS+5% CNFs fabricated by extrusion and microcompounding.

In addition, extensional viscosity of polymers and nanocomposites under high pressure is essential to under extrusion foaming process. Experimental data are very limited due to technical difficulties. Any data in this area will be valuable.

9.5 Foaming dynamics

The experimental setup (sample is “free-standing”) is a novel design. It can be widely used to observe foaming process and give quantitative cell nucleation and growth data. However, there are a lot of improvements on this setup. First, our new digital camera, which has the speed of 120 fps, would provide clearer high-speed movie than the current one. However, due to the lack of the corresponding software, we did not use it. We should request the manufacturer of the grabber board to provide the corresponding software that can be used to record movies. Otherwise, we should purchase the “development kit” but we need to write programs. Or a new grabber board compatible
with the new camera can be purchased. Second, a lens with a high resolution and magnification (>100x; current one is about 5x) can be used to catch clearer pictures and smaller cells. Third, a steel table and a 3-D positioner are useful add-ons. The camera and high-pressure view cell can be mounted on the steel table. Then the process can be more stable. A 3-D positioner can help accurately adjust the relative position between the view cell and camera.

In our study, the effects of initial pressure, temperature, and final pressure in PS-CO$_2$ foaming process were studied. We still need to study foaming at higher initial pressures. With a higher pressure, a lower initial temperature can be used, i.e. a wider temperature range can be studied. In addition, the effect of different final pressure needs to be further studied. Only one case relevant to the effect of the final pressure was studied. With the same initial pressure and temperature, different final pressure leads to different driving force, i.e. different $\Delta \mu / \Delta \mu_s$. These results can be used to verify if the scaling theorem can be used in polymer foaming. Other factors, such as pressure drop rate, can be investigated by modification of this setup. The pressure drop rate can be manipulated by changing the inner volume of the view cell and size of the release valve (e.g. from 1/8” to 1/4” or 1/16”) or the opening of the release valve. This experimental setup can be used to investigate the foaming of other polymers and nanocomposites. Fundamental data on cell nucleation and growth rate of these systems are very important.

In addition, the PS we used has a wide molecular weight distribution, however, from the point of view of fundamental research, PS with lower polydispersity and no additives will be more appropriate.


7. L. J. Lee; C. Zeng; X. Cao; X. Han; J. Shen; G. Xu, *Composites Science and Technology,* **65**, 2344 (2005).


145. M. J. Wingert. in Chemical and Biomolecular Engineering Department; The Ohio State University, Columbus: 2007, p 215.


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APPENDICES
APPENDIX A

SANCHEZ-LACOMBE (S-L) EOS
The S-L EOS has the following expression:

\[ \tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho} \right] = 0 \]  
(Eq. A. 1)

Where \( \tilde{T}, \tilde{P}, \tilde{\rho} \) are reduced temperature, pressure, and density respectively. \( r \) is the number of lattice sites occupied by a molecule and is defined as:

\[ r = \frac{MP^*}{RT^* \rho^*} = \frac{M}{\rho^* \nu^*} \]  
(Eq. A. 2)

The reduced parameters for a pure component are

\[ \tilde{T} = T / T^* \text{ where } T^* = \epsilon^*/R \]  
(Eq. A. 3)

\[ \tilde{P} = P / P^* \text{ where } P^* = \epsilon^*/\nu^* \]  
(Eq. A. 4)

\[ \tilde{\nu} = 1 / \tilde{\rho} = V / V^* \text{ where } V^* = n(r \nu^*) \]  
(Eq. A. 5)

\[ \tilde{\rho} = \rho / \rho^* \text{ where } \rho^* = M / r \nu^* \]  
(Eq. A. 6)

Where \( T \) is absolute temperature, \( \epsilon^* \) is the interaction energy per mer, \( R \) is the gas constant, \( P \) is the system pressure, \( \nu^* \) is the close-packed molar volume of a mer, \( V^* \) is the close-packed volume of the mixture, \( \rho \) is the solution density, and \( M \) is the molecular weight. Pure fluids are completely characterized by three characteristic parameters \( (T^*, P^*, \rho^*) \) or, equivalently, \( \epsilon^*, \nu^*, \) and \( r \).

For binary or multicomponent systems, the following mixture rules[92] can be used.

\[ \phi_i = \frac{w_i / \rho^*_i}{\sum_j (w_j / \rho^*_j)} \]  
(Eq. A. 7)
\[
\phi_i^0 = \frac{\phi_i P_i^*/T_i^*}{\sum_j (\phi_j P_j^*/T_j^*)} \\
\]
(Eq. A. 8)

\[
1/r = \sum_i (\phi_i^0/r_i^0) \\
\]
(Eq. A. 9)

\[
P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \\
\]
(Eq. A. 10)

\[
P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{0.5} \\
\]
(Eq. A. 11)

\[
T^* = P^* \sum_i (\phi_i^0 T_i^* / P_i^*) \\
\]
(Eq. A. 12)

Where \(k_{ij}\), a parameter that accounts for the interaction between component \(i\) and \(j\), is usually correlated from experimental data.

The chemical potential is:

\[
\frac{\mu_i}{RT} = \ln \phi_i + \left(1 - \frac{r_i}{r_j}\right) + r_i \rho \left(\sum_{j=1}^k \phi_i \chi_{ij} - \sum_{j=1}^k \sum_{\nu=1}^k \phi_i \phi_j \chi_{ij}\right) + r_i \left\{ -\frac{\tilde{\rho}}{T_i} + \frac{\tilde{P}_i}{T_i} + (\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r_i} \ln \tilde{\rho}\right\} \\
\]
(Eq. A. 13)

When simplified to binary systems,

\[
\frac{\mu_i}{RT} = \ln \phi_i + \left(1 - \frac{r_i}{r_j}\right) + r_i \rho \left(\frac{(P^*_i + P^*_j - 2P_{ij}^*)v_i \phi_j}{RT}\right) + r_i \left\{ -\frac{\tilde{\rho}}{T_i} + \frac{\tilde{P}_i}{T_i} + \tilde{v} \left( (1 - \tilde{\rho})\ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_i} \ln \tilde{\rho}\right)\right\} \\
\]
(Eq. A. 14)
APPENDIX B

PC-SAFT
PC-SAFT (Perturbed Chain Statistical Associating Fluid Theory) can be expressed as the sum of compressibility factor $Z$ or Helmholtz free energy. Here the first case is given.

$$Z = 1 + Z^{hc} + Z^{disp} + Z^{assoc} \quad \text{(Eq. B. 1)}$$

In the systems we studied, the last term can be neglected.

The hard-chain contribution:

$$Z^{hc} = \bar{m} Z^{hs} - \sum_{i} x_{i} (m_{i} - 1) \rho \frac{\partial \ln g_{ii}^{hs}}{\partial \rho} \quad \text{(Eq. B. 2)}$$

$$\bar{m} = \sum_{i} x_{i} m_{i} \quad \text{(Eq. B. 3)}$$

Where $x_{i}$ is the mole fraction of chains of component $i$, $m_{i}$ is the number of segments in a chain of component $i$, $\rho$ is the total number density of molecules, $g_{ii}^{hs}$ is the radial pair distribution function for segments of component $i$ in the hard sphere system, and the superscript $hs$ indicates quantities of the hard-sphere system.

$$Z^{hs} = \frac{\xi_3}{(1-\xi_3)} + \frac{3 \xi_2^2}{\xi_0 (1-\xi_3)^3} + \frac{3 \xi_0^2}{\xi_3 (1-\xi_3)^3} \quad \text{(Eq. B. 4)}$$

$$g_{ij}^{hs} = \frac{1}{(1-\xi_3)} \left[ \frac{d_i d_j}{d_i + d_j} \right] \xi_3 + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2 \xi_2^2}{(1-\xi_3)^3} \quad \text{(Eq. B. 5)}$$

Where

$$\xi_n = \frac{\pi}{6 \rho} \sum_{i} x_{i} m_{i} d_{i}^{n} \quad n \in \{0, 1, 2, 3\} \quad \text{(Eq. B. 6)}$$
The perturbation contribution:

\[ Z^{\text{disp}} = -2\pi\rho \frac{\partial (\eta l_1)}{\partial \eta} - m^2 e \sigma^3 - \pi \rho \bar{m} \left[ C_1 \frac{\partial (\eta l_1)}{\partial \eta} + C_2 \eta l_2 \right] m^2 e^2 \sigma^3 \]  
(Eq. B.7)

\[ \frac{\partial (\eta l_1)}{\partial \eta} = \sum_{j=0}^{6} a_j (\bar{m}) (j + 1) \eta^j \]  
(Eq. B.8)

\[ \frac{\partial (\eta l_2)}{\partial \eta} = \sum_{j=0}^{6} b_j (\bar{m}) (j + 1) \eta^j \]  
(Eq. B.9)

\[ C_1 = \left( 1 + \frac{8\eta - 2\eta^2}{(1 - \eta)^4} + \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^3} \right) \]  
(Eq. B.10)

\[ C_2 = \frac{\partial C_1}{\partial \eta} = -C_1 \left( \frac{m - 4\eta^2 + 20\eta + 8}{(1 - \eta)^5} + \frac{2\eta^3 + 12\eta^2 - 48\eta + 40}{[(1 - \eta)(2 - \eta)]^3} \right) \]  
(Eq. B.11)
! This program is right for the calculation of binodal and spinodal of polymer solution.

! This program is similar to sl2a

! This difference between this program and SL2 is here we use the mixing rules(by Kiran 1993).

Parameter (N=2) !# of components
Implicit DOUBLE PRECISION (A-H,O-Z)
Integer POLYFLAG
Dimension H(N,990000),Q(N,990000),POTV(N),POTL(N),TEST(N),SL(N,N)
Dimension AMW(N),TS(N),PS(N),RHOS(N),U(N),V(N),SP(N),POT(10000)
double precision X(N),Y(N)
Common/SANCHEZ/AMW,RHOS,TS,PS,SL
Character*12 Name
Open(Unit=15,File='SL2_aa2a.DAT',Status='OLD')
Open(Unit=16,File='SL2_aa_out2a.dat',Status='NEW')
Open(Unit=17,File='SL2_aa_binodal2a.dat',Status='NEW')
Open(Unit=18,File='SL2 aa_spindal2a.dat',Status='NEW')
Open(Unit=19,File='SL2 aa_potentia2 curve1a.dat',Status='NEW')
GASR=8.314

Do 10 I=1,N ! Input T(C),P(bar),T*(C),P*(BAR),RHO*(KG/M3)
    ! Mw(KG/MOL),SL(interaction term)
    Read(15,*) AMW(I)
10  Read(15,*) TS(I),PS(I),RHOS(I)

Do 50 I=1,N-1
Do 60 J=1,N-1
    Read(15,*) SL(I,J+1)
    SL(J+1,I)=SL(I,J+1)
60  Continue
50  Continue

Write(16,*)'Kij=',SL(1,2)
Read(15,*) T
T=T+273.15
Write(*,')'T=',T-273.15
Write(*,12)
Write(*,13)
Write(16,12)
Read(15,*)PLOW,PHIGH,PINC
Read(15,*) H(1,1),H(2,1)
12  Format(/,1X,'X-Heavy',8X,'Y-Heavy',12X,'Pressure',6X,'Den-liquid',
     $5X,'Den-Vapor',2X,'# Iterations') !!!!X,Y ARE WEIGHT FRACTIONS
Write(16,13)
Format(35X,'(Bar)',8X,'(Kg/M3)',10X,'(Kg/M3)')

H(1,1)=4D1 ! for polymer, h(1,1) should be high enough. 20 will get
H(2,1)=0.5D-21 ! unreasonable results.

P=PLOW
DP=PINC

Do 20 ICOUNT=1,3000
   Do 30 JFLAG=1,98999
      Y(1)=1.d0
      Y(2)=0.
      X(1)=Y(1)/H(1,JFLAG)
      X(2)=1.d0-X(1)
      If ((X(1).LT.0.0).OR.(X(1).GT.1.0)) Goto 115
         CALL SLCHEMPOT(T,P,Y,POTV,DENV,0,N)
         CALL SLCHEMPOT(T,P,X,POTL,DENL,1,N)
         Q(1,JFLAG)=(POTL(1)-POTV(1))/(AMW(1)*PS(1)*1.E5*T/TS(1)/RHOS(1))
         Q(1,JFLAG)=DEXP(Q(1,JFLAG))  !!!!! THE STANDARD FROM HONGBO
         TEST(1)=ABS(Q(1,JFLAG)-1.0)
         If(TEST(1).GE.0.00001) Then
            H(1,JFLAG+1)=H(1,JFLAG)*Q(1,JFLAG)
         Else
            Goto 35
         Endif
      30 Continue
   Goto 115

35 If(P.LE.50.0) THEN
   DP=PINC
   Write(*,*),'THE TIE LINE DID NOT CONVERGE!'
   Goto 115
Else
   If(H(2,JFLAG).GT.0.10) DP=1
   If(H(2,JFLAG).GT.0.70) DP=0.5
   If(H(2,JFLAG).GT.0.80) DP=0.1
   If(H(2,JFLAG).GT.0.99) Goto 75
Endif

PNEW=P+DP
SS2=X(2)+(PNEW-P)*((X(2)-U(2))/(P-POLD))
If (ICOUNT.EQ.1) SS2=X(2)
SS1=1.-SS2
TT2=Y(2)+(PNEW-P)*((Y(2)-V(2))/(P-POLD))
If (ICOUNT.EQ.1) TT2=Y(2)
TT1=1.-TT2
H(1,1)=TT1/SS1
H(2,1)=TT2/SS2
U(1)=X(1)
U(2)=X(2)
V(1)=Y(1)
V(2)=Y(2)
IF (Y(2).LT.1.D-100) Y(2)=0.D0
Write(*,85) X(2),Y(2),P,DENL,DENV,JFLAG
Write(16,85) X(2),Y(2),P,DENL,DENV,JFLAG
Write(17,85) Y(2),X(2),P
85 Format(1X,D18.9,2X,D18.9,4X,F8.2,4X,F9.3,5X,F9.3,9X,I6,2X,F7.4)

!!!!!!!!!!! calculate the spinodal points --STARTS

I_lower=int(Y(2)*10000)+1
I_upper=int(X(2)*10000)
I_critical=int(0.0304*10000)  !get it from the binodal results.
Do 90 I=I_lower,I_upper
   SP(2)=I*1./10000
   SP(1)=1.-SP(2)
   CALL SLCHEMPOT(T,P,SP,POTV,DENV,1,N)
   POT(I)=POTV(2)
   !If (P.GT.104.00) POT(I)=int(POTV(2)/100)*100 !when pressure is big
   !we should reduce the soundness of the data
IF (P.EQ.1501.) WRITE(19,*) SP(2), POT(I)

90 CONTINUE

IMAX=I_LOWER
IMIN=I_UPPER
POTMAX=POT(IMAX)
POTMIN=POT(IMIN)

Do 92 I=I_LOWER+1, I_CRITICAL
   IF (POT(I).GT.POTMAX) THEN
      POTMAX=POT(I)
      IMAX=I
   ENDIF
92 CONTINUE

IMAX=I_LOWER
IMIN=I_UPPER
POTMAX=POT(IMAX)

Do 93 I=I_LOWER+1, I_CRITICAL,-1
   IF (POT(I).LT.POTMIN) THEN
      POTMIN=POT(I)
      IMIN=I
   ENDIF
93 CONTINUE

! Do 91 I=I_lower+1, I_upper-5 ! if in the whole region, can't get spinodals.
! I don't know why.
! IF (POT(I).GT.
! IF ((POT(I).GT.POT(I-1)).AND.(POT(I).GT.POT(I-2)))
! .AND.(POT(I).GT.POT(I-3)).AND.(POT(I).GT.POT(I-4))
! .AND.(POT(I).GT.POT(I-5)).AND.(POT(I).GT.POT(I+1))
! .AND.(POT(I).GT.POT(I+2)).AND.(POT(I).GT.POT(I+3))
! .AND.(POT(I).GT.POT(I+4)).AND.(POT(I).GT.POT(I+5))) THEN
! IMAX=I
! ENDIF
!
! IF ((POT(I).LT.POT(I-1)).AND.(POT(I).LT.POT(I-2)))
! .AND.(POT(I).LT.POT(I-3)).AND.(POT(I).LT.POT(I-4))
! .AND.(POT(I).LT.POT(I-5)).AND.(POT(I).LT.POT(I+1))
! .AND.(POT(I).LT.POT(I+2)).AND.(POT(I).LT.POT(I+3))
! .AND.(POT(I).LT.POT(I+4)).AND.(POT(I).LT.POT(I+5))) THEN
! IMIN=I
! ENDIF
!
91 CONTINUE
WRITE(16,*)
"I_LOWER,I_UPPER,IMAX,IMIN" ,I_LOWER,I_UPPER,IMAX,IMIN
WRITE(16,*)

!IF(P.LE.107) THEN ! CLOSE TO CRITICAL POINTS, SPINODAL ISN'T ACCURATE.
    WRITE(16,* )"SPINODAL POINT",IMAX*1./10000,IMIN*1./10000
    WRITE(18,85 ) IMAX*1./10000,IMIN*1./10000,P
!ENDIF
!Else
! Write(16,* ) "can not find the spinoal point at this pressure"
!ENDIF

!!!!!!!!!!!!!!calculate the spinodal points --ENDS

If(P.GE.PHIGH) Then
    Write(* ,*)'UPPER PRESSURE BOUNDF REACHED'
    Goto 115
Endif
P=P+DP
POLD=P-DP
20 Continue
75 Write(* ,*) 'NEAR THE MIXTURE CRITICAL POINT'
115 Write(16,116)
    Write(* ,116)
116 Format(/// ,8X,'THE PROGRAM IS COMPLETED')
END

Subroutine SLCHEMPOT(T,P,Y,CHEMP,DEN,NNN,N)
Implicit REAL*8(A-H,O-Z)
DOUBLE PRECISION Y
Dimension TS(2),PS(2),AMW(2),RHOS(2),CHEMP(2),SL(2,2)
Dimension Y(2),PHI(2),PHIO(2),RO(2),PPC(2,2) !RO IS "r0"
Dimension XX(2)
Common/SANCHEZ/AMW,RHOS,TS,PS,SL
GASR=8.314
!!!!!!GET THE RHOSMIX AND RO
  Do 10 I=1,N
10   RO(i)=AMW(i)*PS(i)*1.E5/(GASR*TS(i)*RHOS(i))

RHOSMIX=0
  Do 15 I=1,N
15   RHOSMIX=Y(i)/RHOS(i)+RHOSMIX
    RHOSMIX=1.0/RHOSMIX

!!!!!!get the FAI0
  SUMPHI=0.0
  Do 20 I=1,N
20   SUMPHI=SUMPHI+Y(I)/RHOS(i)
  Do 25 I=1,N
25   PHI(i)=Y(I)/RHOS(i)/SUMPHI

!!!!!!get the FAI0
  SUMPHIO=0.0
  Do 30 I=1,N
30   SUMPHIO=SUMPHIO+PHI(I)*PS(I)/TS(I)
  Do 35 I=1,N
35   PHIO(I)=PHI(I)*PS(I)/TS(I)/SUMPHIO

!!!!!!get the RMIX
  RMIX=0.0
  Do 40 I=1,N
40   RMIX=RMIX+PHIO(I)/RO(I)
    RMIX=1./RMIX

!!!!!!get the mixing parameter PSMIX
  PPC(1,2)=(1-SL(1,2))*SQRT(PS(1)*PS(2))
  PPC(2,1)=PPC(1,2)
  PPC(1,1)=PS(1)
  PPC(2,2)=PS(2)

  PSMIX=0.0;
Do 45 I=1,N  
    Do 50 J=1,N  
        PSMIX=PSMIX+PHI(I)*PHI(J)*PPC(I,J)  
    50 CONTINUE
45 CONTINUE

!!!! THE FOLLOWING IS FOR VSMIX  
VSMIX=PHIO(1)*GASR*TS(1)/PS(1)+PHIO(2)*GASR*TS(2)/PS(2)

!!!!!! the following is used to get TSMIX (the mixing rule for tsmix is different from Sato's)
TSMIX=PHI(1)/(T/TS(1))  
TSMIX=PSMIX+TS(1)/PS(1)/PS(2)))*PHI(2)/(T/TS(2))  
TSMIX=TS(1)/PS(1)+TS(2)/PS(2)))*PHI(2))  
TSMIX=TSMIX-PHI(1)*PHI(2)*(PS(1)+PS(2)-2*PPC(1,2))*VSMIX/(GASR*T)  
TSMIX=TSMIX*T

!!!!!!!!!!!!!!!!!!!!!!!!!!!! MIXING RULES END

TR=T/TSMIX  
PR=P/PSMIX

Call GETRHO(TR,PR,RMIX,RHOR,NNN) !GETRHO calculates density

DEN=RHOR*RHOSMIX

!!!!!!! CALCULATE THE POTENTIALS
DPR=PS(1)+PS(2)-2*PPC(1,2)

Do 80 I=1,N
80 XX(I)=DPR*TS(I)/(PS(I)*T)

GAMA1=TS(1)/PS(1)/TS(2)/PS(2))  
GAMA2=1./GAMA1  
A1=LOG(PHI(1))+(1-RO(1)/RO(2)*GAMA1)*PHI(2)
A1 = A1 + RO(1) * RHOR * XX(1) * PHI(2)**2
A1 = A1 * GASR * T
A2 = 1./RHOR*((1-RHOR)*LOG(1-RHOR)+RHOR*LOG(RHOR)/RO(1))
A2 = A2 - RHOR/(T/TS(1)) + P/PS(1)/RHOR/(T/TS(1))
A2 = A2 * GASR * T * RO(1)
CHEMP(1) = A1 + A2

if (Y(2).eq.0.) then
  CHEMP(2) = 8888
  goto 1000
end if
B1 = LOG(PHI(2)) + (1 - RO(2)/RO(1)*GAMA2)*PHI(1)
B1 = B1 + RO(2)*RHOR*XX(2)*PHI(1)**2
B1 = B1 * GASR * T
B2 = 1./RHOR*((1-RHOR)*LOG(1-RHOR)+RHOR*LOG(RHOR)/RO(2))
B2 = B2 - RHOR/(T/TS(2)) + P/PS(2)/RHOR/(T/TS(2))
B2 = B2 * GASR * T * RO(2)
CHEMP(2) = B1 + B2

1000 Return
END

Subroutine GETRHO(T,P,R,RHO,NNN)
Implicit REAL*8(A-H,O-Z)
Dimension ROOT(3)
RHO=0.001
STEP=0.001
TOL=0.00001

Do 20 IJ=1,3
  ROOT(IJ)=0.0
  Do 10 I=1,10001
    If(RHO.LT.1.0) Then
      F=RHO**2+P+T*(LOG(1.0-RHO)+(1.0-1.0/R)*RHO)
      If(ABS(F).GE.TOL) Then
        If(((IJ.EQ.1).or.(IJ.EQ.3)).And.(F.LT.0.0)).or.((IJ.EQ.2).And.(F.GT.0.0))) Then
          RHO=RHO-STEP
        End If
      End If
    End If
  End Do
20 Continue
END
STEP = STEP * 0.1
RHO = RHO + STEP
Else
RHO = RHO + STEP
Endif

Else
ROOT(IJ) = RHO
STEP = 0.001
RHO = RHO + STEP
Goto 5
Endif

Else
ROOT(I) = RHO
STEP = 0.001
RHO = RHO + STEP
Goto 5
Endif

10 Continue
5 Continue
20 Continue

!write(16,*), root(1), root(2), root(3)
If(NNN.EQ.1) Then
  Do 30 I = 1, 3

30     If(ROOT(I).GT.1.0) ROOT(I) = -1.0
      RHO = DMAX1(ROOT(1), ROOT(2), ROOT(3))
  Else
      RHO = DMIN1(ROOT(1), ROOT(2), ROOT(3))
      If(RHO.GT.1.0) RHO = -1.0
  Endif
Return
END
APPENDIX D

PROGRAM CODE FOR PC-SAFT
PROGRAM STAND_ALONE

IMPLICIT NONE

INTEGER nc, nph,I_lower,I_upper,I_critical,IMAX,IMIN

PARAMETER (nc=20,nph=2)
INTEGER ncomp, nphas
DOUBLE PRECISION lnphi(nph,nc),AMW(nc),SP_X(2),SP_M(2),f(nph,nc)
DOUBLE PRECISION t,p,densys(nph,nc),x_sys(nph,nc),m_sys(nph,nc)
DOUBLE PRECISION parame(nc,5),kij(nc,nc),x_temp(nph,nc)
DOUBLE PRECISION d_sta(nph),logphix(10000),phi(nph,nc)
     DOUBLE PRECISION w_low,w_high,f_max
INTEGER i,j, iso, number
DOUBLE PRECISION resid1,resid2, x_new(nph,nc),fvek1,fvek2,x_save,
&     df1dx,df2dx,df1dy,df2dy,betrag,dens(nph),end_pt,
&     delta,logphix_max,logphix_min
CCC

DOUBLE PRECISION H(2,100000),Q(2,100000),TEST(2)
INTEGER ICOUNT, JFLAG,I_max
CCC

COMMON /condit/ t,p,densys,x_sys,ncomp,nphas
COMMON /system/ parame,kij
COMMON /staval/ d_sta

ncomp = 2
nphas = 2
number =41

OPEN (45,FILE='output.txt')
   OPEN (48,FILE='output_mole.txt')
   OPEN (49,FILE='spinodal_X.txt')
   OPEN (50,FILE='spinodal_M.txt')
   OPEN (51,FILE='output_fugacity1.txt')
   OPEN (52,FILE='output_fugacity2.txt')
   OPEN (53,FILE='output_fugacity3.txt')
   OPEN (54,FILE='output_fugacity4.txt')
   c  write (45,*)' x(1), t °C, p / bar'
   c  write (45,*)'
CCC

OPEN (46,FILE='output_density.txt')
   OPEN (47,FILE='output_concentration.txt')
CCC

OPEN (85,FILE='parame.inp')

268
READ (85,*) t
READ (85,*) p
  READ (85,*) AMW(1)
  READ (85,*) AMW(2)
DO i=1,ncomp
  DO j=1,3
    READ (85,*) parame(i,j)
  END DO
END DO
READ (85,*) kij(1,2)
  kij(2,1)=kij(1,2)
cccc READ (85,*) x_new(1,1),x_new(2,1)
READ (85,*) d_sta(1),d_sta(2)
  READ (85,*) H(1,1),H(2,1)
CLOSE (85)

t = t + 273.15d0
p = p*1.d5

write (*,*) ''
write (*,*) ' press 1 : for calculation of isotherms'
write (*,*) ' press 2 : for calculation of isobars'
read (*,*) iso
write (*,*) ' enter the end point for the calculation'
IF (iso.EQ.1) THEN
  write (*,*) ' end pressure in [bar]'
  read (*,*) end_pt
  delta = (end_pt*1d5 - p)/DBLE(number-1)
  p = p - delta
ELSE
  write (*,*) ' end temperature in [°C]'
  read (*,*) end_pt
  delta = (end_pt+273.15d0 - t)/DBLE(number-1)
  t = t - delta
ENDIF
write (*,*) ''

DO j = 1, number
  IF (iso.EQ.1) p = p + delta
  IF (iso.EQ.2) t = t + delta
w_low=0.0
If (P.LE.100.0) THEN
w_high=0.4
Else
w_high=0.8
Endif

x_sys(2,1) = 1.d0
x_sys(2,2) = 1.d0 - x_sys(2,1)

m_sys(1,1) = (w_high+w_low)/2.0
m_sys(1,2) = 1.d0 - m_sys(1,1)

x_sys(1,1)=m_sys(1,1)/AMW(1)/(m_sys(1,1)/AMW(1)+m_sys(1,2)/AMW(2))
x_sys(1,2)=1-x_sys(1,1)

WRITE(45,*) "-------------------------"
phi(1,1)=exp(lnphi(1,1))
phi(2,1)=exp(lnphi(2,1))
If (ABS((f(2,1)-f(1,1))/f(2,1)).LE.0.0001) Then

WRITE(45,*) x_sys(2,2),m_sys(1,2), P/1.E5
Else
If ((f(2,1)-f(1,1)).LE.0.0) then
w_high=m_sys(1,1)
Else
w_low=m_sys(1,1)
Endif
GOTO 11
Endif
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!! calculate the spinodal points --STARTS

f_max=0.0
I_max=0
Do 90 I=1,10000
m_sys(1,1)=I*1./1d4
m_sys(1,2)=1d0-m_sys(1,1)
x_sys(1,1)=m_sys(1,1)/AMW(1)/(m_sys(1,1)/AMW(1)+m_sys(1,2)/AMW(2))
x_sys(1,2)=1-x_sys(1,1)

90 WRITE(45,*) m_sys(1,1)
WRITE(45,*) "x_sys(1,1), x_sys(1,2)",x_sys(1,1), x_sys(1,2)
CALL PC_SAFT_PROP (lnphi)
phi(1,1)=exp(lnphi(1,1))
f(1,1)=phi(1,1)*x_sys(1,1)
phi(2,1)=exp(lnphi(2,1))
f(2,1)=phi(2,1)*x_sys(2,1)
If (ABS((f(2,1)-f(1,1))/f(2,1)).LE.0.0001) Then

WRITE(45,*) x_sys(2,2),m_sys(1,2), P/1.E5
Else
If ((f(2,1)-f(1,1)).LE.0.0) then
w_high=m_sys(1,1)
Else
w_low=m_sys(1,1)
Endif
GOTO 11
Endif

270
CALL PC_SAFT_PROP (lnphi)
phi(1,1)=exp(lnphi(1,1))
f(1,1)=phi(1,1)*x_sys(1,1)
if (f_max.le.f(1,1)) then
    f_max=f(1,1)
    I_max=I
Else
    goto 91
endif
90    CONTINUE
91    continue

!    WRITE(49,*)
"I_LOWER,I_UPPER,IMAX,IMIN",I_LOWER,I_UPPER,IMAX,IMIN
!    WRITE(49,*) "SPINODAL POINT",SP_X(1),SP_X(2),P/1.D5
WRITE(50,*) 1-I_max/1.d4,P/1.D5

!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!! calculate the spinodal points --ENDS

2    CONTINUE

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

222    END

SUBROUTINE ZIELFKT (x,phi,resid1,resid2)

INTEGER nc, nph
PARAMETER (nc=20,nph=2)
DOUBLE PRECISION phi(nph,nc),x(nph,nc)
DOUBLE PRECISION resid1,resid2
SUBROUTINE PC_SAFT_PROP (lnphi)

IMPLICIT NONE

resid1 = x(1,1)*phi(1,1) - x(2,1)*phi(2,1)
resid2 = x(1,2)*phi(1,2) - x(2,2)*phi(2,2)

RETURN
END
densys : iteration result for the density in all phases

It may for example be defined:

```c
INTEGER nc, nph
PARAMETER (nc=20,nph=2)
INTEGER ncomp, nphas
DOUBLE PRECISION t,p,densys(nph),x_sys(nph,nc)
DOUBLE PRECISION parame(nc,5),kij(nc,nc)
DOUBLE PRECISION d_sta(nph)

COMMON /condit/ t,p,densys,x_sys,ncomp,nphas
COMMON /system/ parame,kij
COMMON /staval/ d_sta
```

If in your program, 'x_mole' is used for mole fractions instead of 'x_sys' as in the example given above, then all 'x_sys' have to be replaced by 'x_mole' in this SUBROUTINE.

```c
----local variables--------------------------------
INTEGER i,ph
DOUBLE PRECISION lnphi(nph,nc)
DOUBLE PRECISION xtrans(nc),dstart,parsys(nc,25),lnfugcoe(nc),den
```

```c
DO 1 ph = 1,nphas
 _write(46,*) 'ph=',ph
ccc
  dstart = d_sta(ph)
  DO 11 i = 1,ncomp
    xtrans(i) = x_sys(ph,i)
    parsys(i,1) = parame(i,1)
    parsys(i,2) = parame(i,2)
    parsys(i,3) = parame(i,3)
  11 CONTINUE
ccc
```
CALL PHIEOS (lnfugcoe,xtrans,t,p,parsys,kij,ncomp,dstart,den)

densys(ph) = den
DO 12 i = 1,ncomp
  lnphi(ph,i) = lnfugcoe(i)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
!   write(46,*) 'lnphi(',ph,',',i,')', lnphi(ph,i)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
12 CONTINUE
1 CONTINUE

RETURN
END

c***************************************************************************
c***************************************************************************
c***************************************************************************
SUBROUTINE PHIEOS (lnphi,x,t,p,parame,kij,ncomp,densta,dense)

IMPLICIT NONE

c-----variables used in the parameter list of subroutine-------------------
  INTEGER nc
  PARAMETER (nc=20)
  INTEGER ncomp

  DOUBLE PRECISION phi(nc)
  DOUBLE PRECISION kij(nc,nc)
  DOUBLE PRECISION pges,pgesdz,gij(nc, nc)
  DOUBLE PRECISION fres
c------------------------
  DOUBLE PRECISION x(nc),t,p,parame(nc,25),mseg(nc)
  DOUBLE PRECISION densta,dense,dap_dx(nc,7),dbp_dx(nc,7)
  DOUBLE PRECISION order1,order2,apar(7),bpar(7)
  DOUBLE PRECISION A,B,C,D,AA,BB(nc),CC(nc),DD(nc),EFF(nc),
  & QQ(nc,nc),PIJK(nc,nc,nc)
  DOUBLE PRECISION PI, RGAS, NA, KBOL, TAU
  DOUBLE PRECISION uij(nc,nc),d00ij(nc,nc),d0(nc)
c-----------------------------------------------

c-----local variables-----------------------------------------------
  INTEGER i, k, m
  DOUBLE PRECISION zms, rho, m_mean, term1, term2
  DOUBLE PRECISION mhs(nc), mdisp(nc), mcha(nc), mpart(nc),
  & myres(nc), myresq, lnphi(nc)
  DOUBLE PRECISION dgijdx(nc, nc, nc),ddendx(nc)
  DOUBLE PRECISION zres, zges
DOUBLE PRECISION I1, I2, I1_dx, I2_dx,
&     ord1dx, ord2dx, ddrdx,
&     drdpkt, te1, te2, te3, dte1dx, dte2dx, dte3dx

c--------obtain parameters and density independent expressions-------
CALL PERTPAR (kij,
1     ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
2     order1,order2,apar,bpar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK,
3     PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

C-----run density iteration-------------------------------
CALL DENSITR (pges,pgesdz,gi,
1     ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
2     order1,order2,apar,bpar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK,
3     PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

C-----residual Helmholtz free energy-----------------------------
CALL F_EOS (fres,gi,
1     ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
2     order1,order2,apar,bpar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK,
3     PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

zms         = 1.d0 - dense
rho          = 6.d0 * dense / (PI*D)
m_mean       = A

C-----compressibility factor z = p/(kT*rho)-------------------------
zges = (p * 1.d-30)/(KBOL*t*rho)

zres = zges - 1.d0

C-----calculation the derivatives of f to mole fraction x (d(f)/d(x))---
DO 1 k = 1,ncomp

C-------d(f)/d(x) : hard sphere contribution--------------------------
term1 = DLOG(zms)*(-1.d0+3.d0*CC(k)**2.d0-2.d0*CC(k)**3.d0)
&     + (3.d0*CC(k)**2.d0 - 3.d0*CC(k)**3.d0)
&     * dense / zms**2.d0
term2 = (3.d0*CC(k)+3.d0*EFF(k)-CC(k)**3.d0 + AA*DD(k))/zms
&     + dense*3.d0 * BB(k) / zms**2.d0

275
& + 2.d0 * CC(k)**3.d0 / zms**3.d0
mhs(k) = mseg(k) * (term1 + term2 * dense)

\[ ddendx(k) = \text{dense/}D\text{mseg(k)d0(k)**3.d0} \]

\[ \text{DO 10 i = 1, ncomp} \]
\[ \text{mcha(k) = mcha(k)+(1.d0-mseg(k))*DLOG(gij(k,k))} \]

\[ \text{I2} = \text{I2} + \text{bpar(m+1)*dense**DBLE(m)} \]
\[ \text{I2} = \text{I2} + \text{dbp}\_dx(k,m+1)*dense**DBLE(m) \]

\[ \text{ord1dx} = 0.d0 \]
\[ \text{ord2dx} = 0.d0 \]
\[ \text{ord1dx} = \text{ord1dx} + 2.d0*mseg(k)*x(i)*mseg(i)*d00ij(i,k)**3.d0 *uij(i,k)/t \]

\[ \text{ord2dx} = \text{ord2dx} + 2.d0*mseg(k)*x(i)*mseg(i)*d00ij(i,k)**3.d0*(uij(i,k)/t)**2.d0 \]

\[ \text{te1} = zms**4.d0 * (2.d0-dense)**2.d0 \]
\[ te_2 = \text{zms}^2 \cdot (\text{zms}^2 \cdot (2 - \text{dense})^2 \cdot \text{dense} + 20) \]
\[ \text{te}_3 = \text{dense} \cdot (8 - 2 \cdot \text{dense}^2) \cdot \text{dense} \cdot (2 - \text{dense})^2 \cdot (8 - 2 \cdot \text{dense}) \]
\[ \text{drdpkt} = \text{te}_1 / (\text{te}_2 + \text{m}_\text{mean} \cdot \text{te}_3) \]
\[ \text{dte}_1 \text{dx} = (-4 \cdot \text{zms}^3 \cdot (2 - \text{dense})^2 \cdot \text{dense} \cdot (8 - 2 \cdot \text{dense}) \cdot \text{ddendx}(k) \]
\[ \text{dte}_2 \text{dx} = \text{dte}_1 \text{dx} + (3 \cdot \text{ddendx}(k) \cdot (2 - \text{dense})^2 \cdot (8 - 2 \cdot \text{dense}) \cdot \text{dense} \cdot (2 - \text{dense})^2 \cdot (8 - 2 \cdot \text{dense}) \cdot \text{ddendx}(k) \]
\[ \text{dte}_3 \text{dx} = \text{ddendx}(k) \cdot (\text{te}_3 / \text{dense}) \]
\[ \text{ddrdx} = (\text{dte}_1 \text{dx} + (\text{m}_\text{mean} \cdot \text{ddte}_3 \text{dx} + \text{mseg}(k) \cdot \text{te}_3) / (\text{te}_2 + \text{m}_\text{mean} \cdot \text{te}_3)^2) \]
\[ \text{mdisp}(k) = -2 \cdot \text{order}_1 \cdot \text{I}_1 \cdot \text{dx} + \text{order}_1 \cdot \text{dx} \cdot \text{I}_1 \]
\[ \text{c} \quad \text{d}(f) / \text{d}(x) : \text{summation of all contributions} \]
\[ \text{mpart}(k) = \text{mhs}(k) + \text{mcha}(k) + \text{mdisp}(k) \]
\[ \text{w} \quad \text{write}(46, \text{'mpart}(k), \text{mhs}(k), \text{mcha}(k), \text{mdisp}(k) =', \text{mpart}(k)) \]
\[ \text{c} \quad \text{mpart}(k), \text{mhs}(k), \text{mcha}(k), \text{mdisp}(k) \]
\[ \text{DO} \quad \text{i} = 1, \text{ncomp} \]
\[ \text{myresq} = \text{myresq} - x(i) \cdot \text{mpart}(i) \]
\[ \text{END DO} \]
myresq = myresq + fres + zres

DO k = 1, ncomp
   myres(k) = myresq + mpart(k)
   lnphi(k) = myres(k) - DLOG(zges)
END DO

RETURN
END

SUBROUTINE P_EOS (pges,pgesdz,gij,
                   ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
                   order1,order2,apar,bpar,A,B,C,AA,BB,CC,DD,EFF,QQ,PIJK,
                   PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)
IMPLICIT NONE

c-----variables used in the parameter list of subroutine----------
INTEGER nc
PARAMETER (nc=20)
INTEGER ncomp

DOUBLE PRECISION pges,pgesdz,gij(nc, nc)
DOUBLE PRECISION x(nc),t,p,parame(nc,25),mseg(nc)
DOUBLE PRECISION densta,dense,dap_dx(nc,7),dbp_dx(nc,7)
DOUBLE PRECISION order1,order2,apar(7),bpar(7)
DOUBLE PRECISION A,B,C,AA,BB(nc),CC(nc),DD(nc),EFF(nc),
                QQ(nc,nc),PIJK(nc,nc,nc)
DOUBLE PRECISION PI, RGAS, NA, KBOL, TAU
DOUBLE PRECISION uij(nc,nc),d00ij(nc,nc),d0(nc)
INTEGER  i, j, m
DOUBLE PRECISION rho,zms,m_mean,ddendv
DOUBLE PRECISION term1,term2,term3
DOUBLE PRECISION phs,pdisp,pcha,pideal

DOUBLE PRECISION dgijdz(nc,nc),dgijd2(nc,nc),zmsdz,
&    dvzdz,te1dz,te2dz,
&    te3dz,pdspd,zfdspd,fchdz,fchd2, pchadz,
&    piddz,phsdz
DOUBLE PRECISION I2, edI1dz, edI2dz, edI1d2, edI2d2,
&    z00, z00_dz, z00_d2, z00_d3,
&    drdpkt, drdpdz, drdpd2

DOUBLE PRECISION rho    = 6.d0 * dense / (PI*D)
DOUBLE PRECISION zms    = 1.d0 - dense
DOUBLE PRECISION m_mean = A

C-----gij , the derivative dgijdz=d(gij)/d(dense) ------------------
C-----and dgijd2 = dd(gij)/d(dense)**2 -----------------------------
DO 2 i = 1, ncomp
   j=i
   gij(i,j) = 1.d0/zms  + 3.d0*QQ(i,j)*dense/zms**2.d0
   dgijdz(i,j) = (1.d0+3.d0*QQ(i,j)) /zms**2.d0
   dgijd2(i,j) = 2.d0*qq(i,j)**2.d0/zms**3.d0
   &      dense*(6.d0**2/dense)*zms**2.d0
   &      dense**2.d0/zms**3.d0 + dense**2.d0/zms**4.d0
   &      +dense**2.d0/zms**5.d0
   &      +2.d0*(QQ(i,j)**2)/zms**2.d0
   &      +2.d0*(QQ(i,j)**2/zms**3.d0
   &      +dense**2.d0/zms**3.d0 + (9.d0*dense
   &      + 12.d0*qq(i,j)*dense)/zms**4.d0 + (12.d0*qq(i,j)
   &      + 6.d0+2.d0*qq(i,j))/zms**3.d0
2   CONTINUE

C-----derivations of dense to volume (ddendv = -d(dense)/d(volume)---
ddendv = dense**2.d0   *6.d0/ PI /D

C-----p : ideal gas contribution-------------------------------
pideal = rho

C-----p : hard sphere contribution---------------------------
term1  = (A-C**3.d0/D**2.d0) / zms
term2  = (3.d0*B*C/D-C**3.d0/D**2.d0)/zms**2.d0
term3 = (2.d0*C**3.d0/D**2.d0)/zms**3.d0
phs = ddendv*(term1 + term2 + term3)

c-----p : chain term-----------------------------------------------
fchdz = 0.d0
DO 4 i= 1, ncomp
   fchdz = fchdz + (x(i)*(1.d0-mseg(i)))
&                  *(1.d0/gij(i,i)) * dgijdz(i,i)
4 CONTINUE
pcha = ddendv * fchdz

c-----p : dispersion contribution---------------------------------
c-----edI1dz is equal to d(dense*I1)/d(dense)-------------------
edI1dz = 0.d0
edI2dz = 0.d0
DO 6 m=0,6
   I2 = I2 + bpar(m+1)*dense**DBLE(m)
edI1dz = edI1dz + apar(m+1)*DBLE(m+1)*dense**DBLE(m)
edI2dz = edI2dz + bpar(m+1)*DBLE(m+1)*dense**DBLE(m)
6 CONTINUE

z00 = 1.d0 + m_mean*(4.d0*dense-2.d0*dense**2.d0)/ZMS**3.d0
& + (1.d0 - m_mean)*(5.d0*dense-2.d0*dense**2.d0)
& /(ZMS*(2.d0-dense))
z00_dz = m_mean*(-2.d0*dense**2.d0+4.d0*dense+4.d0)/ZMS**4.d0
& + (1.d0 - m_mean)*(dense**2.d0-8.d0*dense+10.d0)
& /(ZMS*(2.d0-dense))**2.d0
drdpkt = 1.d0/(Z00 + dense*Z00_dz)

c---
z00_d2 = m_mean*(-4.d0*dense**2.d0+8.d0*dense+20.d0)/ZMS**5.d0
& + (1.d0 - m_mean)
& *(-2.d0*dense**3.d0+24.d0*dense**2.d0-60.d0*dense+44.d0)
& /(ZMS*(2.d0-dense))**3.d0
drdpdz = (-2.d0*z00_dz -z00_d2*dense)*drdpkt**2.d0

c be aware: rho=6.d0*dense/(PI*D)
fdspdz = -2.d0*PI *6.d0/(PI*D) * edI1dz * order1
& -( PI *6.d0*dense/(PI*D) * drdpdz* m_mean *I2 *order2
& +PI *6.d0/(PI*D) * drdpkt* m_mean *edI2dz *order2 )
pdisp = ddendv* fdspdz

c-----p summation, p is obtained in unit [Pa] -----------------------

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\[ p_{\text{ges}} = p_{\text{ideal}} + p_{\text{hs}} + p_{\text{disp}} + p_{\text{cha}} \]
\[ p_{\text{ges}} = p_{\text{ges}} \times (KBOL \times t) / 1.\text{d}-30 \]

---

**Calculating the derivatives of \( P \) to dense**

---

The derivatives are useful for the density-iteration using a gradient (Newton) algorithm.

---

**Abbreviations**

- \( z_{ms dz} = -1.\text{d}0 \)
- \( dv_{zd} = 2.\text{d}0 \times \text{dense} \times 6.\text{d}0 / \pi / D \)

---

**\( d(p) / d(\text{dense}) \): Ideal gas contribution**

- \( p_{id dz} = 6.\text{d}0 / (\pi \times d) \)

---

**\( d(p) / d(\text{dense}) \): Hard sphere contribution**

- \( t_{e1 dz} = (a - c \times 3.\text{d}0 / d \times 2.\text{d}0) / (-zms \times 2.\text{d}0) \times zms dz \)
- \( t_{e2 dz} = (3.\text{d}0 \times b \times c / d - c \times 3.\text{d}0 / d \times 2.\text{d}0) \times 2.00 / (-zms \times 3.\text{d}0) \times zms dz \)
- \( t_{e3 dz} = (2.\text{d}0 \times c \times 3.\text{d}0 / d \times 2.\text{d}0) \times (-3.\text{d}0) / zms \times 4.\text{d}0 \times zms dz \)
- \( p_{hs dz} = dv_{zd} \times (\text{term1} + \text{term2} + \text{term3}) + \text{ddendv} \times (t_{e1 dz} + t_{e2 dz} + t_{e3 dz}) \)

---

**\( d(p) / d(\text{dense}) \): Chain term**

- \( f_{chd2} = 0.\text{d}0 \)
- \( DO \ 8 \ i = 1, n\text{comp} \)
- \( f_{chd2} = f_{chd2} + (x(i) \times (1.\text{d}0 - \text{msseg}(i))) \)
- \( *(dgijd2(i,i)/gij(i,i)-dgijdz(i,i)**2.\text{d}0) \times gij(i,i)**2.\text{d}0) \)
- \( 8 \ \text{CONTINUE} \)
- \( p_{chadz} = \text{ddendv} \times f_{chd2} + dv_{zd} \times f_{chd2} \)

---

**\( d(p) / d(\text{dense}) \): Dispersion contribution**

- \( ed_{l1 d2} = 0.\text{d}0 \)
- \( ed_{l2 d2} = 0.\text{d}0 \)
- \( DO \ 10 \ m = 0, 6 \)
- \( ed_{l1 d2} = ed_{l1 d2} + apar(m+1) \times \text{DBLE}(m+1) \times \text{DBLE}(m) \times \text{dense} \times \text{DBLE}(m-1) \)
- \( ed_{l2 d2} = ed_{l2 d2} + bpar(m+1) \times \text{DBLE}(m+1) \times \text{DBLE}(m) \times \text{dense} \times \text{DBLE}(m-1) \)
- \( 10 \ \text{CONTINUE} \)

\[ z_{00 \ d3} = m_{\text{mean}} \times 12.\text{d}0 \times (-\text{dense} \times 2.\text{d}0 + 2.\text{d}0 \times \text{dense} + 9.\text{d}0) / ZMS \times 6.\text{d}0 \]

---

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& / (ZMS*(2.d0-dense))**4.d0
& d r d p d 2 = (-3.d0*z00_d2 -z00_d3*dense)*d r d p k t**2.d0
& + 2.d0/d r d p k t*(d r d p d z)**2.d0
&

f d s p d 2 = - 2.d0.PI *6.d0/(PI*D) * e d l 1 d 2 * order1
& - PI*6.d0/(PI*D)*order2*m_mean* ( d r d p d 2 *12*dense
& +2.d0 *d r d p d z *e d l 2 d z
& + drdpkt *edl2d2 )
p d s p d z = dvzd*d f s p d z + ddendv*f d s p d 2

---

SUBROUTINE DENSITR (pges,pgesdz,gij,
  n comp, x, t, p, parame, mseg, densta, dense, dap_dx, dbp_dx,
  order1, order2, apar, bpar, A, B, C, D, AA, BB, CC, DD, EFF, QQ, PIJK,
  PI, RGAS, NA, KBOL, TAU, d0, uij, d00ij)

IMPLICIT NONE

n c m p

INTEGER nc
PARAMETER (nc=20)
INTEGER ncomp
DOUBLE PRECISION pges,pgesdz,gij(nc, nc)
DOUBLE PRECISION x(nc),t,p,parame(nc,25),mseg(nc)
DOUBLE PRECISION densta,dense,dap_dx(nc,7),dbp_dx(nc,7)
DOUBLE PRECISION order1,order2,apar(7),bpar(7)
DOUBLE PRECISION A,B,C,D,AA,BB(nc),CC(nc),DD(nc),EFF(nc),
  & QQ(nc,nc),PIJK(nc,nc,nc)
DOUBLE PRECISION PI, RGAS, NA, KBOL, TAU
DOUBLE PRECISION uij(nc,nc),d00ij(nc,nc),d0(nc)

---

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c-----local variables-----------------------------------------------
INTEGER i,start,max_i
DOUBLE PRECISION x1,y1,dydx,acc_i
c---------------------------------------------------------------

acc_i = 1.d-10
max_i = 500

i = 0
x1 = densta

1 CONTINUE

i=i+1
dense = x1

y1 = (pges / p) - 1.d0

dydx = pgesdz/p
x1 = x1 - y1/ dydx

CALL P_EOS (pges,pgesdz,gij,
1 ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
2 order1,order2,apar,bpar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK,
3 PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

! write(46,*) 'y1=',y1
! write(46,*) 'x1=',x1
!

IF (x1.GT.0.9d0) x1 = 0

IF (DABS(y1).LT.acc_i) start = 0
IF (i.GT.max_i) THEN
   start = 0
   write (*,*),'density iteration failed'
   ! start = 1
ENDIF

start = 1
C  stop
ENDIF

IF (start.EQ.1) GOTO 1
dense = x1

RETURN
END

C***********************************************************************
***
C***********************************************************************
***
C***********************************************************************
***

SUBROUTINE F_EOS (fres,gij,
1  ncomp,x,t,p,parame,mseg,densta,dense,dap_dx,dbp_dx,
2  order1,order2,apar,bpar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK,
3  PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

IMPLICIT NONE

C-----variables used in the parameter list of subroutine-----------------
INTEGER nc
PARAMETER (nc=20)
INTEGER ncomp
DOUBLE PRECISION fres,gij(nc,nc)
DOUBLE PRECISION x(nc),t,p,parame(nc,25),mseg(nc)
DOUBLE PRECISION densta,dense,dap_dx(nc,7),dbp_dx(nc,7)
DOUBLE PRECISION order1,order2,apar(7),bpar(7)
DOUBLE PRECISION A,B,C,D,AA,BB(nc),CC(nc),DD(nc),EFF(nc),
&                 QQ(nc,nc),PIJK(nc,nc,nc)
DOUBLE PRECISION PI,RGAS,NA,KBOL,TAU
DOUBLE PRECISION uij(nc,nc),d00ij(nc,nc),d0(nc)

C-----------------------------------------
C-----local variables-----------------------------------------------
INTEGER i,m
DOUBLE PRECISION zms,rho,m_mean,term1,term2
DOUBLE PRECISION I1,I2,z00,z00_dz,drdpkt
DOUBLE PRECISION fhs,fdisp,fcha

C--------------------------------------------------------------------------------
c-----abbreviations-------------------------------------------------------------
zms = 1.d0 -dense
rho = 6.d0*dense/(PI*D)
m_mean = A

c-----Helmh. free energy : hard sphere contribution-----------------------------
term1 = -(A-C**3.d0/D**2.d0)*DLOG(zms)
term2 = (C**3.d0/D**2.d0)/(zms**2.d0)+(3.d0*B*C/D*dense
& -(C**3.d0/D**2.d0))/zms
fhs = term1 + term2

c-----Helmh. free energy : chain term------------------------------------------
fcha = 0.d0
DO i = 1,ncomp
     fcha = fcha + x(i) *(1.d0- mseg(i)) *DLOG(gij(i,i))
END DO

c-----Helmh. free energy : dispersion contribution-----------------------------
I1 = 0.d0
I2 = 0.d0
DO m=0,6
     I1 = I1 + apar(m+1)*dense**DBLE(m)
     I2 = I2 + bpar(m+1)*dense**DBLE(m)
END DO

Z00 = 1.d0 + m_mean*(4.d0*dense-2.d0*dense**2.d0)/(zms**3.d0)
& + (1.d0 - m_mean)*(5.d0*dense-2.d0*dense**2.d0)
& /(zms*(2.d0-dense))
z00_dz = m_mean*(-2.d0*dense**2.d0+4.d0*dense+4.d0)/zms**4.d0
& + (1.d0 - m_mean)*(dense**2.d0-8.d0*dense+10.d0)
& /(zms*(2.d0-dense))**2.d0
drdpkt = 1.d0/(Z00 + dense*z00_dz)

fdisp = -2.d0*PI*rho*I1*order1 - PI*rho*drdpkt*m_mean*I2*order2

c-----resid. Helmholtz free energy---------------------------------------------
fres = fhs + fcha + fdisp

RETURN
END

c******************************************************************************
SUBROUTINE PERTPAR (kij, 
1 ncomp,x,t,p,parame,mseg,denssta,dense,dap_dx,dbp_dx, 
2 order1,order2,apar,A,B,C,D,AA,BB,CC,DD,EFF,QQ,PIJK, 
3 PI,RGAS,NA,KBOL,TAU,d0,uij,d00ij)

IMPLICIT NONE

c-----variables used in the parameter list of subroutine-----------------
INTEGER nc
PARAMETER (nc=20)
INTEGER ncomp
DOUBLE PRECISION kij(nc,nc)
DOUBLE PRECISION x(nc),t,p,parame(nc,25),mseg(nc)
DOUBLE PRECISION denssta,dense,dap_dx(nc,7),dbp_dx(nc,7)
DOUBLE PRECISION order1,order2,apar(7),bpar(7)
DOUBLE PRECISION A,B,C,D,AA,BB(nc),CC(nc),DD(nc),EFF(nc),
 & QQ(nc,nc),PIJK(nc,nc,nc)
DOUBLE PRECISION PI, RGAS, NA, KBOL, TAU
DOUBLE PRECISION uij(nc,nc),d00ij(nc,nc),d0(nc)
c--------------------------------------------------------------
c-----local variables-------------------------------------------
INTEGER i,j,k,m
DOUBLE PRECISION m_mean
DOUBLE PRECISION ap(7,3),bp(7,3)
DOUBLE PRECISION d00(nc),u0k(nc)
c--------------------------------------------------------------
c-----constants-----------------------------------------------
PI = 3.14159265359d0
RGAS = 8.31441d0
NA = 6.022045d23
KBOL = RGAS/NA
TAU = PI/3.d0/DSQRT(2.d0)
c-----dispersion term constants---------------------------------
ap(1,1) = 0.91056314451539d0
ap(1,2) = -0.30840169182720d0
ap(1,3) = -0.09061483509767d0
ap(2,1) = 0.63612814494991d0
ap(2,2) = 0.18605311591713d0
ap(2,3) = 0.45278428063920d0
\begin{verbatim}
ap(1,1) = -26.5473624914884d0
ap(1,2) = 8291311787d0
ap(1,3) = 7592087835073d0
ap(1,4) = 7.46922927323d0
ap(1,5) = 6.67284703679646d0
ap(2,1) = 5.4980753450d0
ap(2,2) = 68831158356d0
ap(2,3) = 959304690d0  *2.d0
ap(2,4) = 77607218d0  *2.d0
ap(3,1) = 2.5089420371162d0  *4.d0
ap(3,2) = 30386791194303d0  *4.d0
bp(1,1) = 0.72409469413165d0
bp(1,2) = 0.57554980753450d0
bp(1,3) = 0.09768831158356d0
bp(2,1) = 1.11913959304690d0  *2.d0
bp(2,2) = 0.34975477607218d0  *2.d0
bp(2,3) = -0.12787874908050d0  *2.d0
bp(3,1) = -1.33419498282114d0  *3.d0
bp(3,2) = 1.29752244631769d0  *3.d0
bp(3,3) = -3.05195205099107d0  *3.d0
bp(4,1) = -5.25089420371162d0  *4.d0
bp(4,2) = -4.30386791194303d0  *4.d0
bp(4,3) = 5.16051899359931d0  *4.d0
bp(5,1) = 5.37112827253230d0  *5.d0
bp(5,2) = 38.53445289304990d0  *5.d0
bp(5,3) = -7.76088601041257d0  *5.d0
bp(6,1) = 34.4252230677698d0  *6.d0
bp(6,2) = -26.9710769414608d0  *6.d0
bp(6,3) = 15.6044623461691d0  *6.d0
bp(7,1) = -50.8003365888685d0  *7.d0
bp(7,2) = -23.6010990650801d0  *7.d0
bp(7,3) = -8.67284703679646d0  *7.d0

C-----pure component parameters------------------------------------------
DO 1 i = 1,ncomp
    msegi = parame(i,1)
    do0i = parame(i,2)
    u0ki = parame(i,3)
    parame(i,5) = 0.12d0

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\end{verbatim}
\[ d_0(i) = d_00(i) \times (1.0 - \text{parame}(i,5) \times \text{DEXP}(-3.0 \times \text{parame}(i,3)/t)) \]

1 CONTINUE

c-----combination rules-----------------------------------------------
DO 2 i = 1, ncomp
  DO 21 j = 1, ncomp
    d00ij(i,j) = 0.5d0 \times (d00(i) + d00(j))
    uij(i,j) = (1.0 - kij(i,j)) \times (u0k(i) \times u0k(j))**0.5d0
  21 CONTINUE
  2 CONTINUE

c-----abbreviations---------------------------------------------------
  A = 0.d0
  B = 0.d0
  C = 0.d0
  D = 0.d0
DO i = 1, ncomp
  A = A + x(i) \times mseg(i)
  B = B + x(i) \times mseg(i) \times d0(i)
  C = C + x(i) \times mseg(i) \times d0(i)**2.d0
  D = D + x(i) \times mseg(i) \times d0(i)**3.d0
END DO

AA = A
DO 4 k = 1, ncomp
  BB(k) = B*C / D**2.d0 \times d0(k)**3.d0
  CC(k) = C/D \times d0(k)
  DD(k) = d0(k)**3.d0 / D
  EFF(k) = B/D \times d0(k)**2.d0
DO 41 i = 1, ncomp
  QQ(k,i) = C/D \times (d0(k) \times d0(i)) / (d0(k) + d0(i))
DO 411 j = 1, ncomp
  PIJK(i,j,k) = (d0(i) \times d0(j)) / (d0(i) + d0(j)) / d0(k)
  411 CONTINUE
  41 CONTINUE
  4 CONTINUE

c-----dispersion term parameters for chain molecules------------------
  m_mean = A
DO m=1,7
  apar(m) = ap(m,1) + (1.0 - 1.0/m_mean) \times ap(m,2)
  & + (1.0 - 1.0/m_mean) \times (1.0 - 2.0/m_mean) \times ap(m,3)
bpar(m) = bp(m,1) + (1.d0-1.d0/m_mean)*bp(m,2)
& + (1.d0-1.d0/m_mean)*(1.d0-2.d0/m_mean)*bp(m,3)
END DO

c-----derivatives of apar, bpar to mole fraction ( d(apar)/d(x) )-----
DO k=1,ncomp
  DO m=1,7
    dap_dx(k,m) = mseg(k)/m_mean**2.d0*ap(m,2)
    & + (3.d0*mseg(k)/m_mean**2.d0
    & - 4.d0*mseg(k)/m_mean**3.d0)*ap(m,3)
    dbp_dx(k,m) = mseg(k)/m_mean**2.d0*bp(m,2)
    & + (3.d0*mseg(k)/m_mean**2.d0
    & - 4.d0*mseg(k)/m_mean**3.d0)*bp(m,3)
  END DO
END DO

END

order1 = 0.d0
order2 = 0.d0
DO i = 1,ncomp
  DO j = 1,ncomp
    order1 = order1 + x(i)*x(j)*mseg(i)*mseg(j)
    & *d00ij(i,j)**3.d0 * uij(i,j)/t
    order2 = order2 + x(i)*x(j)*mseg(i)*mseg(j)
    & *d00ij(i,j)**3.d0 * (uij(i,j)/t)**2.d0
  END DO
END DO
RETURN
END