A Systematic Study of Solubility of Physical Blowing Agents and Their Blends in Polymers and Their Nanocomposites

by

Mohammad Monirul Hasan

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy, Graduate Department of Mechanical & Industrial Engineering, University of Toronto

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ABSTRACT

The solubility of a blowing agent (BA) in polymer melts is a critically important parameter affecting the plastic foams fabrication. Theoretically, cell nucleation occurs when the pressure of the polymer/gas mixture drops below the solubility pressure. For effective process design, accurate solubility data for blowing agents in polymers is necessary. However, getting more accurate solubility data is a big scarce. Through this research, it was possible to generate more accurate solubility and pressure-volume-temperature (PVT) data and to verify various equations of states (EOS).

During the last two decades, due to ozone-depleting-potential (ODP) and global warming issues of BAs, the plastic foam industry has experienced serious regulatory, environmental, and economical pressures. In response to this, researchers and industry have been exploring the uses of blowing agent blends. Nevertheless, very limited fundamental research on the foaming mechanism using blowing agent mixtures has been conducted. The end results of this research is expected to provide guidance to choose the optimal composition of environmental-friendly blowing agent blends and offer insights to develop sustainable foaming technology.

This thesis also highlights a comprehensive research for the PVT and solubility behavior of polymer nanocomposites (PNCs). By using the magnetic suspension balance
(MSB) and $PVT$ apparatus, it was possible to determine the solubility behavior of PNC more accurately. Fully experimental results indicated that infusion of nanoparticles decreases the volume swelling as well as solubility and diffusivity. It was hypothesized that infusion of organoclay nanoparticles generates a significant amount of solidified (solid-like) polymer near its surface and consequently reduces total absorption capacity of the system. However, it is believed that the solubility behavior of polymeric composites fully depends on the interaction or affinity between fillers (micro or nano) and gas. In other words, if the nanoparticles (such as CaCO$_3$, aluminum oxide, tin oxide) or fillers (such as carbon black, zeolites, silica gel) are highly polar and/or porous, overall sorption (absorption + adsorption) might increase due to adsorption phenomenon. Through the solubility, $PVT$ and modeling of nanocomposites, this research has advanced the understanding of the effect of nanoparticles on solubility that governs different physical phenomena (such as cell nucleation and, cell growth) during plastic foaming.
To my lovely & beautiful wife, Rowzatul Zannat,  
For your deeply love, strong  
support, and inspiring  
encouragement  

To my most adorable daughter and son,  
Zerin Jasmin Hasan & Zayan Jaseen Hasan,  
for the big hug and Sweet smile everyday  

To my parents and family members  
For endless love, support  
and encouragement  

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advice and relentless support
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<thead>
<tr>
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<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>= Helmholtz energy [J]</td>
</tr>
<tr>
<td>CS</td>
<td>= Costas and Sanctuary</td>
</tr>
<tr>
<td>$c_i$</td>
<td>= Chain (molecule) flexibility; 3$c$ is total external degrees of freedom attributed to a chain (molecule)</td>
</tr>
<tr>
<td>$d$</td>
<td>= Bond length in PCM EOS</td>
</tr>
<tr>
<td>EOS</td>
<td>= Equation of state</td>
</tr>
<tr>
<td>$G_m$</td>
<td>= Molar Gibbs free energy for polymer/gas mixture [J/mol]</td>
</tr>
<tr>
<td>$H$</td>
<td>= Enthalpy [J]</td>
</tr>
<tr>
<td>$i$</td>
<td>= Planck’s constant $6.6260755 \times 10^{-34}$ [J.s]</td>
</tr>
<tr>
<td>$k, k_B$</td>
<td>= Boltzmann’s constant $1.380658 \times 10^{-23}$ [J/K]</td>
</tr>
<tr>
<td>$m_i$</td>
<td>= Molar mass of segment (mer) of “i” component [g/mol]</td>
</tr>
<tr>
<td>$M$</td>
<td>= Molecular weight of per molecule [g/mol], $M = m_is_i$</td>
</tr>
<tr>
<td>$N_a$</td>
<td>= Avogadro’s number $6.0221367 \times 10^{23}$</td>
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<td>$P$</td>
<td>= Pressure [Pa]</td>
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<td>= Characteristic pressure of component “i” [Pa], $P_i^* = \frac{qz\epsilon_i^*}{sv_i}$</td>
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<td>$\bar{P}, P_r$</td>
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<td>PCM</td>
<td>= Prigogine cell model</td>
</tr>
<tr>
<td>PC-SAFT</td>
<td>= Perturbed Chain Statistical Associating Fluid Theory</td>
</tr>
<tr>
<td>$qz$</td>
<td>= The number of nearest neighbor sites per chain-like molecule (s-mer), $s_i(z - 2) + 2$.</td>
</tr>
<tr>
<td>$Q$</td>
<td>= $(\sqrt{V})^{-1}$ Dimensionless identity for SS-EOS</td>
</tr>
<tr>
<td>$Q_{comb}$</td>
<td>= The combinatorial factor for PCM</td>
</tr>
<tr>
<td>$r$</td>
<td>= Number of mer per molecule, $r = \frac{MP^<em>}{RT^</em> \rho^*}$</td>
</tr>
<tr>
<td>$R$</td>
<td>= Gas constant $8.3143$ [J/(mol·K)]</td>
</tr>
<tr>
<td>$S$</td>
<td>= Entropy [J/K]</td>
</tr>
<tr>
<td>SAFT</td>
<td>= Statistical Associating Fluid Theory</td>
</tr>
<tr>
<td>$s_i$</td>
<td>= Number of mers per molecule of component “i”</td>
</tr>
</tbody>
</table>
SL = Sanchez–Lacombe
SS = Simha–Somcynsky
$S_w$ = Volume swelling ratio
$T$ = Temperature [K]
$T_i^*$ = Characteristic temperature of component “i” [K], $T_i^* = \frac{q_z e_i^*}{ck_b}$

$T, T_r$ = Reduced temperature $T/T^*$
$\nu_i^*$ = Characteristic volume per mer of component “i” [m$^3$/mer]
$V_i^*$ = Characteristic volume of component “i” (m$^3$/mol)
$\bar{V}, V_r, \bar{V}$ = Reduced volume, $V_r = V/V^*$ or $\bar{V} = v/v^*$
$\chi_i$ = Mole fraction of “i” component in mixture system
$x$ = Solubility (g-gas/g-polymer)
$y$ = Occupied lattice site fraction
$Z$ = 12, the lattice coordination number
$\varepsilon_i^*$ = Characteristic energy per mer of component “i” (J/mer)
$\eta$ = $2^{-1/6} y Q^{1/3}$ dimensionless number for SS-EOS
$\phi_1$ = Volume fraction of gas in mixture system
$\phi_2$ = Volume fraction of polymer in mixture system
$\mu_i^g$ = Chemical potential of gas in vapor phase [J/mol]
$\mu_i^p$ = Chemical potential gas in the polymer melt [J/mol]
$\rho^*$ = Characteristic density of bulk material [g/cm$^3$]
$\Lambda$ = de Broglie wavelength
$\delta$ = Flexibility parameter
$\omega$ = Lattice-site volume
$\Gamma$ = PCM geometrical constant
$\tilde{\rho}$ = Reduced density $1/\bar{V}$
**Subscripts**

0 = Indicates ideal condition  
1 = Indicates gas  
2 = Indicates polymer  
i = Indicates component number or component in x-direction  
j = Indicates component number in y-direction  
F = Indicates foam  
G, g = Indicates gas

**Superscripts**

G, g = Indicates gas or vapor  
P, p = Indicates polymer
CHAPTER 1. INTRODUCTION

1.1 Polymeric Foam

Nowadays, we cannot imagine our life without foamed plastic. We use quite number of foamed plastic every day. Polymeric foams are widely used as heat and sound insulators, food trays, decorative items, toys, automotive parts, sporting goods, footwear, cushions, support materials, packaging so and so forth. [1-4]. Polymeric foams are widely used in aforementioned applications because of their excellent strength-to-weight ratio, flexibility, good impact properties, good thermal and sound insulation properties, buoyancy, comfort, and material cost saving [1-4].

Polymeric foams are mainly two classes: thermoplastic and thermoset foams. Thermoset foams (such as polyurethane (PU)) are generally heavily cross-linked so cannot be reprocessed whereas thermoplastic foams (such as polystyrene (PS), polyvinylchloride (PVC), and polyolefin) can be reprocessed and recycled easily. Furthermore, the polymeric foams can be classified as closed cell (rigid, semi-rigid), open cell (semi-flexible, or flexible), depending upon their compositions, and other physical and thermal characteristics [5-7]. The cell geometry (open vs close, size and shape) greatly affect the foam properties. Thus, open cell foams are most suitable for acoustical insulation whereas closed cell foams are most suitable for thermal insulation [1-7].

The foaming methodology basically requires three steps [5, 7](Figure 1.1). First, single phase formation of polymer/gas solution is done by introducing a gaseous phase into melt. Then cell nucleation followed by cell growth occurs by thermodynamic instability (either by decreasing the pressure or increasing the temperature). Finally, bubble stabilization and shaping take place by solidifying the melt.
The gaseous phase in any polymeric foam material derives from the use of blowing agents (BAs) in the foam manufacturing process. There are two types of blowing agents used to produce foams: chemical blowing agents and physical blowing agents. The chemical blowing agents are the chemical compounds which give-off gases under the foam processing conditions, either due to chemical reactions or due to thermal decomposition. On the other hand, the physical blowing agents are simply inert gases (like nitrogen, carbon dioxide, argon), volatile hydrocarbons (like propane, butane, pentane) and low boiling chlorofluorocarbons (CFC's), hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's) [1-7]. However, the selection of resins, blowing agents and manufacturing processes depends on mostly cost, process feasibility and end users requirements [1-7].

![Diagram of foam manufacturing process](image)

**Gas Solubility Effect**

Figure 1.1 Schematic of foam manufacturing process [8]

When gas dissolves in polymer, the volume-based property, such as density, shows dramatic change. Polymeric foam density is defined as[5]:

$$\rho_F = \frac{W_p + W_g}{V_p + V_g}$$

1-1

where \(\rho\), \(W\), and \(V\) denote density, weight, and volume, and subscripts \(F\), \(p\), and \(g\) represent foam, polymer, and gas, respectively. Since under normal circumstances gases possess a large volume
to weight ratio, the more gas dissolves in, the lower the density of the polymer/gas mixture. However, solubility determines how much gas can be dissolved into a polymer, whereas diffusivity dictates how soon the dissolution is complete [5].

1.2 Solubility

Solubility is defined as the amount of physical blowing agent (PBA) that can be dissolved into a unit mass of polymer at a particular temperature and a pressure (where the unit is g-PBA/g-Polymer). Physical blowing agents (PBAs) are low-boiling, volatile liquids and gases, including aliphatic and halogenated hydrocarbons (HFC and CFC), low boiling alcohols (methanol, ethanol), ethers, ketones, aromatic hydrocarbons, carbon dioxide (CO$_2$), and nitrogen (N$_2$). The solubility is not only a critically important parameter for fabricating plastic foams, but also an important property developing blowing agents (BAs) and evaluating their performances.

![Figure 1.2 Bubble nucleation inside a die](image)

For effective process design, the system pressure should be at least high enough to dissolve all of the injected gas into the polymer melt. When the polymer/gas solution exits the extrusion die, the pressure will drop dramatically, which will initiate the bubble nucleation. The bubbles’ nucleation stage is crucial in plastic foaming process due to the formation of a microcellular structure. Theoretically, cell nucleation occurs when the pressure of the
polymer/gas mixture drops below the solubility pressure (or threshold pressure [9] to be exact), as shown in Figure 1.2. The cell nucleation mechanism has been described in detail by lot of researchers [10-14] where the nucleation rate was governed by the degree of supersaturation, i.e., a metastable state determined by the saturation or solubility information.

Blander and Katz [10-12] have reviewed the classical nucleation theory to estimate the rates of bubble nucleation in pure liquids. The work of formation, \( W \), for a spherical bubble of radius \( R \) is shown in equation 1-2.

\[
W = 4\pi R^2 \sigma - \frac{4\pi}{3} R^3 (P_{go} - P_i) + n(\mu_{new} - \mu_{old})
\]

where \( \sigma \) is the surface tension; \( P_{go} \) is the pressure of the bubble at the moment it is formed, which is typically determined as a saturation pressure in a pure component system or solubility pressure corresponding to the amount of dissolved gas in the mixture system; \( P_i \) is the pressure of the system; \( n \) is the number of bubbles; \( \mu_{new} \) and \( \mu_{old} \) are the chemical potentials of the new phase and old phase, respectively. Hence, the solubility pressure information is required for the calculation of the nucleation point and nucleation rate. Also to study surface tension of polymer/gas mixture, solubility information is a prerequisite. Therefore, the solubility of gases in a polymer melt during the plastic foam processing condition has been of great interest to foaming manufacturers and researchers.

Solubility information also plays a very important role in foaming with injection molding machine. In our group, Lee et al. [15] found the cavity pressure of a foaming mold has a significant influence on cell nucleation (Figure 1.3). He claimed that if the cavity pressure is lower than the solubility pressure (or the threshold pressure [9]) of the injected gas and if the pressure before the gate is high enough, cell nucleation occurs at the gate with a high pressure drop rate. In such cases, the cell density will be high. However, if the cavity pressure is higher
than the solubility pressure (or the threshold pressure), cell nucleation occurs along the mold cavity with a low pressure drop rate, resulting in a low cell density.

Figure 1.3 Bubble nucleation inside a mold in injection molding machine (a) nucleation starts at gate (generates high cell density) (b) nucleation starts in the mold cavity (generates low cell density) [15]

1.3 Environmental Concerns of Physical Blowing Agents (PBAs)

Polymeric foams are extensively used as heat insulators, food trays, electronic packaging, supporting materials, and so on because of their many advantageous characteristics such as low thermal conductivity, light weight, and high impact strength. However, since the plastic foam industry is facing the challenge to develop next generation PBAs that have a zero ozone-depletion potential and low global warming potential [16-19], it is urgent to find environmentally nonhazardous substances which can be used as a long-term replacement for CFCs and HCFCs in foam manufacturing. Currently, there has been active research devoted to the development of new blowing agents for foam manufacturing. The potential replacement candidates for blowing
agents are hydrofluorocarbons (HFCs) (i.e., 134a, 152a, or experimental HFCs) [20-23], hydrocarbons (HCs) (include aliphatic hydrocarbons from 1-7 carbon atoms in the molecule) [24, 25], inert gases such as carbon dioxide (CO$_2$) [26-32] or nitrogen (N$_2$) [32-35], and mixtures of the PBAs. Honeywell is trying to develop their 4$^{th}$ generation refrigerant and blowing agents for PS foaming for insulation (Figure 1.4). At the same time DuPont is also trying to develop low GWP BAs for foaming. These indicate that due to GWP replacement of HFCs is big challenge for foam industries.

### Low GWP HFO = 4$^{th}$ Generation technology

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<td>CFC-11</td>
<td>HCFC-22</td>
<td>HFC-134a</td>
<td>HFO-1234ze</td>
</tr>
</tbody>
</table>

**Continuous Reducing Environmental Impact**

Figure 1.4 Innovation of new blowing agents by Honeywell [36]

Inert gases are effectively being used for manufacturing fine-celled or microcellular foams [26-35]. However, compared to large molecular weight blowing agents, the inert gas blowing agents have lower solubility and higher volatility, and therefore, higher diffusivity. As a result, gaseous blowing agents can escape easily during expansion. Therefore, it is very difficult to obtain low-density foam with a large expansion ratio. Nevertheless, information on the
solubility and diffusivity of these gases and their blends in polymers necessary for the optimal design of the foaming process is still lacking.

1.4 Verification of Equation of States (EOS)

Figure 1.5 Solubility of CO$_2$ in Linear PP at 180°C using SL-EOS and SS-EOS [37]

Equation of State (EOS) is a mathematical relation between volume, pressure, temperature, and composition of a closed system. Therefore, the EOS is a good representative of the applied thermodynamic model. Among the various EOS, the Simha-Somcynsky (SS) [38-40], Sanchez-Lacombe (SL) [41, 42], Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [43, 44], Flory–Orwoll–Vrij (FOV) [45-47] so and so forth EOS are well known and extensively used. Among these EOS, SL and SS are the mostly used EOS specially to predict volume swollen and solubility of polymer due to gas absorption.

During last fifty years, the solubility of gases in polymers determined by using either gravimetric or volumetric method had to depend on EOS to determine the swelling of polymer
due to gas dissolution. In our group, Li et al. [37] found that solubility determined by various EOS are not same (Figure 1.5). In Figure 1.5, the corrected solubility was defined as the swollen volume was predicted using EOS and incorporated with MSB data to measure the total solubility. At the same time, solubility was theoretically predicted using SS and SL-EOS which was named as calculated solubility. Due to lack of fully experimental accurate data, the solubility of gases determined by various EOS was not verified.

1.5 Scarcity of Solubility Data for Blowing Agent Blends

In order to circumvent the aforementioned drawbacks, blending the primary blowing agent with a secondary co-blowing agent has been suggested [48, 49]. In this process, the main PBA is chosen for its expansion performance while the co-blowing agent is selected to provide an insulation or cell nucleation property [48, 49]. Although it is a common industrial practice to use a mixture of gases in polymeric foaming processes, the information on the role played by each PBA component during the foaming process is scarce in the current literature. Furthermore, the optimal process design requires solubility data for the gas mixtures in polymers.

1.6 PVT and Solubility Behaviors of Nanocomposites

In microcellular foaming, the nanoparticle, especially organoclay, has drawn a great deal of interest as a nucleating agent due to its low price and high aspect ratio [50-52]. It has been claimed that the cell density increases significantly (102-103 times) with adding even a small amount of the nanoparticles. This is a result of the heterogeneous nucleation effect in the presence of nanoparticles. Recently, Utracki and his coworkers [53, 54] tried to investigate the PVT behavior of the polymeric nanocomposites. They have found that determining the actual PVT behavior of nanocomposites is far more complex than simply assuming that the composite is a random mixture of polymers and nanoparticles. Since solubility plays a key role in
microcellular foaming, and nanoparticles, like organoclay, are incredibly effective as a nucleating agent, the effect of the particles and its dispersion on solubility is of immense interest.

1.7 Research Scope

Since the solubility of blowing agents and their blends in polymer melts play a key role in the plastic foaming processing, this research was focus on the following aspects:

i. To propose technically sound, experimental approaches and thermodynamic models for the $PVT$ and solubility behaviors of polymer/gas mixture (binary) and polymer/gas-blends (ternary) systems.

ii. To obtain reliable (more accurate) $PVT$ and solubility data, and thermodynamic properties of various polymer/blowing agent and polymer/blends mixtures by systematic investigation. In the case of polymer/blends mixtures, the overall solubility of the blowing agent blends, as well as the solubility of each individual component in the polymer can be obtained. The solubility data and thermodynamic properties will be very helpful for evaluating new blowing agent blends in the plastic foaming process.

iii. To verify the accuracy of solubility data determined by using the various EOS and correct them with the help of a visualization system.

iv. To determine the effect of nanoparticles on the solubility of the blowing agents in polymer melts.

1.8 Thesis Format and Outline

This section provides a brief overview of the present thesis.

Chapter 2 includes the literature survey on the thermodynamic study of the phase equilibrium in polymer system and gas solubility in polymer melts. The important developments
on recent researches on PVT and solubility studies with both theoretical approaches and experimental approaches are reviewed in details.

Chapter 3 introduces the general research methodologies for the study of PVT and solubility behavior of polymers and their nanocomposites. It was found that there are some deviations existing among the thermodynamic models in terms of theoretical solubility and swollen volume prediction. As a result, further investigation was done to verify the equation of states (EOS).

Chapter 4 is concerned with the verification of EOS by using the PVT and solubility data of various semi-crystalline, amorphous and copolymers. It was found that for any polymers/gas mixtures the solubility and swollen volume predicted by SS-EOS are closer to experimental data compared to SL-EOS prediction. Consequently, it was concluded that SS-EOS prediction is reliable for predicting the swollen volume and the solubility of polymer/gas mixtures, and it was used for the rest of the research.

Chapter 5 introduces the study of PVT and solubility behavior of polymers/gas blends (ternary system). The overall solubility of gas blends (CO₂/N₂) in polymer as well as the amount of each gas component in polymer was determined by using experimental data, SS-EOS and the interaction parameters between the gas and polymer. It was found that for CO₂/N₂ blend, CO₂ helps to absorb more N₂ in polymer.

Chapter 6 and Chapter 7 investigate the effect of nucleating agents such as nanoparticles (like Organoclay) on the PVT and solubility behaviors of polymers, for the fully exfoliated and intercalated cases, respectively. A model developed by Utracki and Simha was adopted to describe the PVT and solubility behavior of polymer nanocomposites (PNCs). However, in presence of gas the PVT behavior of PNC/gas mixture is much more complicated than that of
PNC, and all the possible approaches to determine the swollen volume and the solubility are discussed in these chapters. Finally, all approaches were compared with fully experimental data.

Chapter 8 provides a summary and conclusions of the research. Recommendations for future work are also presented in Chapter 8.
CHAPTER 2. THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Statistical Thermodynamics and Phase Equilibrium

The study of physical chemistry can be divided into two broad classes of phenomena: macroscopic and microscopic[55-57]. In the macroscopic world we deal with quantities such as internal energy ($U$), enthalpy ($H$), entropy ($S$), heat capacities ($C_p$), and so forth. Whereas in the microscopic world we deal with wave functions, particle momenta, kinetic and potential energies, energy levels, and so forth. In the macroscopic world we study the bulk properties of matter which contains on the order of $10^{23}$ molecules or particles. The main theoretical framework for the study of bulk properties in chemistry is thermodynamics (or kinetics), and the fundamental equations are the first, second, and third laws of thermodynamics. On the other hand, the microscopic world, deals with the properties of individual molecules or particles. The usual theoretical framework of the microscopic world is quantum mechanics (or classical mechanics), and the fundamental equations are Schrödinger's equations (or Newton's laws) [56, 57].

However, the properties of bulk matter obviously depend on the properties of the particles of which it is composed [55, 56]. It is a big question, how are the microscopic properties of individual molecules related to the properties of a sample which contains $10^{23}$ molecules? In other words, how can we find the properties of a bulk sample from the properties of the molecules? The statistical thermodynamics attempts to address this kind of question. We can think of statistical thermodynamics as a process of model building. We construct a (theoretical) model of the particles, atoms, molecules, etc., which makes up the sample, and statistical thermodynamics will tell us what the bulk properties will be. For instance, if our model
is a collection of molecules which do not interact with each other, we will get the bulk properties of an ideal gas. If we want to get the properties of a nonideal gas (which is the most cases in extrusion or injection), we have to go back to the model and put in the properties of the molecules which will make the gas nonideal. In this case a potential energy of interaction between the molecules should be included.

In Boltzmann's definition, entropy is a measure of the number of possible microscopic states (or microstates) of a system in thermodynamic equilibrium, consistent with its macroscopic thermodynamic properties (or macrostate) [55-58]. The microstate of the system is a description of the positions and momenta of all the atoms. In principle, all the physical properties of the system are determined by its microstate. However, because the number of atoms is so large, the motion of individual atoms is mostly irrelevant to the behavior of the system as a whole. Provided the system is in thermodynamic equilibrium, the system can be adequately described by a handful of macroscopic quantities, called "thermodynamic variables": the total energy \( E \), volume \( V \), pressure \( P \), temperature \( T \), and so forth. The macrostate of the system is a description of its thermodynamic variables. Boltzmann's entropy is the expression of entropy \( S \) at thermodynamic equilibrium in the micro-canonical ensemble and it is defined as equation (2-1) [55-58].

\[
S = k_B \ln \Omega
\]  

2-1

where \( k_B \) is Boltzmann's constant and \( \Omega \) is the number of microstates consistent with the given macrostate.

According to the classical thermodynamic theory [55, 59], when the whole multiphase system is in equilibrium at constant \( T \) and \( P \), for any component \( i \) in the system, the chemical potential \( \mu_i \) must be the same throughout the whole multiphase (like \( \alpha, \beta, \gamma \) etc.) system (Equation 2-2).
\[ \mu_i^g = \mu_i^B = \mu_i^\gamma \quad \text{....} \]

Figure 2.1 shows the thermodynamic equilibrium of a polymer and gas system (closed system). In this case, in order to be in equilibrium state, the chemical potential of blowing agent (BA) in gaseous phase \( \mu_{BA}^g \) should be equal to the chemical potential of blowing agents (BA) in polymer/gas mixture liquid phase \( \mu_{BA}^l \).

\[ \mu_{BA}^g = \mu_{BA}^l \]

In order to thermodynamically study a closed system, a statistical thermodynamic model for the system should be proposed first. After the successful setup of the statistical thermodynamic model, it can be used to calculate all state properties (like enthalpy, entropy, Gibb’s free energy etc.) of the system. Equation of state (EOS) is a mathematical relation between volume, pressure, temperature, and composition \([55, 56]\) of a closed system. Therefore, the EOS is a good representative of the applied thermodynamic model.

![Thermodynamic constitution for solubility study](image)

Figure 2.1 Thermodynamic constitution for solubility study

The physical properties of every substance depend directly on the nature of the molecules of the substance. Therefore, the ultimate generalization of physical properties of fluids will require a complete understanding of molecular behavior, which we do not yet have. Though its origins are ancient, the molecular theory was not generally accepted until about the beginning of
the nineteenth century, and even then there were setbacks until experimental evidence vindicated the theory early in the twentieth century. Many pieces of the puzzle of molecular behavior have now fallen into place and computer simulation can now describe more and more complex systems, but as yet it has not been possible to develop a complete generalization.

Deviations from the ideal gas law \((PV = NRT)\), though often small, were finally tied to the fundamental nature of the molecules. The equation of van der Waals [55, 57, 60, 61], the virial equation [62, 63], and other equations of state express these quantitatively [55, 59]. Such extensions of the ideal-gas law have not only facilitated progress in the development of a molecular theory but, more important for our purposes here, have provided a framework for correlating physical properties of fluids.

2.2 Van der Waals Theory [55, 57, 60, 61]

In the situation where no experimental value of the needed property is at hand, the value must be estimated or predicted. ‘‘Estimation’’ and ‘‘prediction’’ are often used as if they were synonymous, although the former properly carries the frank implication that the result may be only approximate. Estimates may be based on theory, on correlations of experimental values, or on a combination of both. A theoretical relation, although not strictly valid, may nevertheless serve adequately in specific cases. Completely empirical correlations are often useful, but one must avoid the temptation to use them outside the narrow range of conditions on which they are based.

In general, the stronger the theoretical basis, the more reliable the correlation. Most of the better estimation methods use equations based on the form of an incomplete theory with empirical correlations of the parameters that are not provided by that theory. Introduction of empiricism into parts of a theoretical relation provides a powerful method for developing a
reliable correlation. For instance, the van der Waals equation [55, 57, 60, 61] of state is a modification of the simple $PV = NRT$; setting $N=1$,

$$ \left( P + \frac{a}{V^2} \right) (V - b) = RT $$ \hspace{1cm} 2-4

Equation (2-4) is based on the idea that the pressure on a container wall, exerted by the impinging molecules, is decreased because of the attraction by the mass of molecules in the bulk gas; that attraction rises with density. Further, the available space in which the molecules move is less than the total volume by the excluded volume $b$ due to the size of the molecules themselves. Therefore, the "constants" (or parameters) $a$ and $b$ have some theoretical basis though the best descriptions require them to vary with conditions, that is, temperature and density. The correlation of $a$ and $b$ in terms of other properties of a substance is an example of the use of an empirically modified theoretical form.

Although a variety of molecular theories may be useful for data correlation, there is one theory which is particularly helpful. This theory, called the law of corresponding states or the corresponding-states principle, was originally based on macroscopic arguments, but its modern form has a molecular basis.

### 2.3 Law of Corresponding States

As the properties of substances are determined by the behavior of the molecules in these substances, the behavior of the molecules must be understood to know the properties of substances. Many molecular theories have been proposed to describe the properties of substances. One of these, the Corresponding States theory, is especially useful. For more than one hundred years, the corresponding-states principle has been used as the most useful, most reliable and most universal theory.
Proposed by van der Waals in 1873 [55, 57, 60, 61], the law of Corresponding States claims that the equilibrium properties depend on certain intermolecular forces and that the equilibrium properties are related to the critical properties in a universal manner. The law of Corresponding States provides the single most important basis for the development of correlations and estimation methods. In 1873, van der Waals showed it to be theoretically valid for all pure substances whose \( PVT \) properties could be expressed by a two-constant equation of state such as Equation (2-4).

Pitzer [64, 65] and Guggenheim [60] have stated a set of assumptions sufficient to lead to the principle of corresponding states and has shown that argon, krypton, and xenon have several properties in accordance with the principle. The law of Corresponding States holds well for fluids containing simple molecules and, upon semi-empirical extension with a single additional parameter, it also holds for “normal” fluids where molecular orientation is not important, i.e., for molecules that are not strongly polar or hydrogen-bonded. The relation of pressure to volume at constant temperature is different for different substances; however, two-parameter corresponding states theory asserts that if pressure \((P)\), volume \((V)\), and temperature \((T)\) are divided by the corresponding critical properties \((P_c, V_c,\) and \(T_c)\), the function relating reduced pressure \((P_r)\) to reduced volume\((V_r)\) and reduced temperature \((T_r)\) becomes the same for all substances. The reduced property is commonly expressed as a fraction of the critical property: \(P_r = P/P_c ; V_r = V/V_c ;\) and \(T_r = T/T_c\).

To illustrate the law of Corresponding States, Figure 2.2 shows reduced \(PVT\) data for Argon, Methane, Nitrogen, Ethylene, Carbon dioxide, 1,1,1,2-Tetrafluorohexane and water [66]. In effect, the critical point is taken as the origin. The data for saturated liquid and saturated vapor coincide well for the two substances. The isotherms (constant \(T_r\), of which only one is shown, agree equally well.
Figure 2.2 The law of corresponding states

applied to the PVT properties of (o)Argon; (+) Methane; (Δ) Nitrogen; (x) Ethylene; (*)Carbon dioxide; (◊)1,1,1,2-Tetrafluorochlorohydrocarbons; (□)water[66]

Successful application of the law of corresponding states for correlation of PVT data has encouraged similar correlations of other properties that depend primarily on intermolecular forces. Many of these have proved valuable to the practicing engineer. Modifications of the law are commonly made to improve accuracy or ease of use. The two-parameter law of corresponding states can be derived from statistical mechanics when severe simplifications are introduced into the partition function. Sometimes other useful results can be obtained by introducing less severe simplifications into statistical mechanics to provide a more general framework for the development of estimation methods. The fundamental equations describing various properties (including transport properties) can sometimes be derived, provided that an expression is available for the potential-energy function for molecular interactions. This function may be, at least in part, empirical; but the fundamental equations for properties are often
insensitive to details in the potential function from which they stem, and two-constant potential functions frequently serve remarkably well.

Small, spherically-symmetric molecules (for example, CH₄) are well fitted by a two-constant law of Corresponding States. However, nonspherical and weakly polar molecules do not fit as well; deviations are often great enough to encourage development of correlations using a third parameter, e.g., the acentric factor w. The acentric factor is obtained from the deviation of the experimental vapor pressure-temperature function from that which might be expected for a similar substance consisting of small spherically-symmetric molecules. Typical corresponding-states correlations express a desired dimensionless property as a function of \( P_r, T_r \), and the chosen third parameter.

Unfortunately, the properties of strongly polar molecules are often not satisfactorily represented by the two- or three-constant correlations which do so well for nonpolar molecules. An additional parameter based on the dipole moment has often been suggested but with limited success, since polar molecules are not easily characterized by using only the dipole moment and critical constants. As a result, although good correlations exist for properties of nonpolar fluids, similar correlations for polar fluids are often not available or else show restricted reliability.

Instead of using pure statistical mechanics, it is much more convenient to, first, give a visual picture of the liquid state and then to translate this model into a partition function, and ultimately into the thermodynamic and mechanical properties of the liquid. In this way the mechanical tool used is far less cumbersome than using a formal approach. Equations of state (EOS) provide with useful descriptions of gas or polymer liquid systems. All of these methods are based on a corresponding-states principle that enables the properties of the multi-component mixture to be calculated in terms of the properties of a suitably defined single reference component.
2.4 Equation of State for Polymers

The pressure-volume-temperature (PVT) relationship for polymeric materials is a subject of importance to polymer scientists and engineers, particularly from a process design standpoint. Equally important is the need for equations of state that adequately described this behavior over a wide range of temperature and pressure. Equations of state provide us with useful descriptions of polymer liquid systems. As a minimum requirement they provide us with accurate fitting functions with which the PVT data can be analyzed. They also provide us with valuable thermodynamic information and can be used to predict the properties of polymer blends and solutions.

Considering the fact that a liquid has properties intermediate between a gas and a solid, the first theories developed at the beginning of this century were inspired by features of imperfect gases or of the crystalline state. A brilliant start was given by the fundamental work of van der Waals [61] for pure components as well as for mixtures.

Comparison with a crystal suggested the rigid lattice model, where the changes upon mixing of all relevant thermodynamic properties may be expressed in terms of a lattice partition function. One of the major successes of this model was the evaluation of the combinatorial factor for polymer solution by Flory and Huggins [67, 68]. Interesting results were obtained by an extension of the powerful techniques used in the theory of imperfect gases.

In 1937-38, an important step was made by Lennard-Jones and Devonshire [69-71] using a free volume theory (or cell model) to express the thermodynamic properties in terms of intermolecular forces. This model was extended around 1950 by Prigogine [72] and Garikian to multi-component systems. They introduced in this way an equation of state which is successful in predicting the relations between intermolecular forces and excess functions. The change in the
average motion of a molecule due to the change in environment is one of the important factors introduced by this model.

The Prigogine-Flory [67, 68, 73-75] theory has the advantages of intuitive appeal and mathematical simplicity. Furthermore it is versatile and is the only simple approach which can account for phenomena like the phase separation which occurs in polymer solutions on increasing the temperature (LCST).

For nearly half a century, the renowned Flory-Huggins theory [67] has played a central role in our understanding of the thermodynamics of polymer-solvent and polymer-polymer mixing. However, by its disregard of changes in volume and local disorder with composition, the Flory-Huggins theory fails to reflect changes in the liquid structure, the accounting of which is necessary for determining accurate solution properties. The SS EOS model [38, 76-78] considers a lattice of sites, each of which capable of accommodating either a small molecule or a chain segment. Also, as with the lattice fluid theory, the hole theory adopted an improvement of the cell model for the liquid state by the introduction of vacancies in the lattice, which describes the major part of the thermal expansion; however, changes in the cell volume, which have a non-negligible influence on the thermodynamic properties, are also allowed.

Equations of state for fluids can be broadly classified into two categories: empirical and theoretical, although some equations, with at least a modest claim to a theoretical basis, are sometimes called semi-empirical. Empirical equations are useful primarily for presenting experimental data in analytical form, thereby facilitating integration and differentiation of the data to obtain desired thermodynamic properties. The theoretical or semi-empirical EOS can be divided into mainly four categories: i) cell model, ii) lattice fluid model iii) hole model, and iv) tangent-sphere model. All of these are explained in brief in the next following sections.
2.4.1 Cell Models

In the cell model, one models the polymer molecules as having two distinct sets of modes. Internal modes are those associated with internal motions of the molecules which do not contribute to the equation of state properties of the liquid. The external modes are those associated with the intermolecular interactions which will affect the $PVT$ properties of the system. In reality there can be no clear distinction made between internal and external modes. This concept, however, which was proposed by Prigogine [74, 79, 80] allows us to adapt the cell model formalism to describe polymer liquids. Among cell models Prigogine’s Cell Model (PCM) [74, 79, 80], Flory-Orwoll-Vrij (FOV) [81, 82] and Perturbed-Hard-Chain (PHC)[83] are well known.

2.4.1.1 Prigogine’s Cell Model (PCM)

The physical picture of Prigogine's cell model [74, 79, 80] for pure chain-like molecules is essentially the same as that of the incompressible lattice model: the system contains $N$ molecules each composed of $r$ segments (or "mers") arranged on a lattice (with coordination number $z$) having a total of $rN$ sites. One molecule occupies $r$ neighboring lattice sites. While the physical view of the cell theory is similar to that of the lattice theory, the cell model differs through its description of inter- and intra-molecular forces.

At finite temperatures, each mer is displaced from its central position in the lattice site due to thermal fluctuations. However, its displacement is restricted by spring-like forces exerted on it by mers in neighboring lattice sites to which it is connected and dispersion forces exerted on it by all other mers in the system. As a result, each mer is effectively confined to a "cell" whose volume is characterized by $d$, the bond-length between successive mers in a chain; $R$, the (average) distance between nearest-neighbor mers of different chains; and $R^*$, the separation distance at the minimum of the (as yet unspecified) pair potential between unbonded mers. At
zero temperature, \( R = d \) because the mers then all lie at equidistant central positions on the lattice. If we ignore interactions between mers which are not nearest neighbors, \( R^* = R = d \) because the system must be in the state of lowest energy. While \( d \) and \( R^* \) are molecular constants, \( R \) (and hence the cell volume) increases with increasing temperature. Further, since the definition of a segment is somewhat arbitrary, it is convenient to define \( d = R^* \). Hence the cell volume is \( v \sim R^3 \) and the characteristic volume of a mer is \( v^* \sim (R^*)^3 \). The total volume of the system is \( V = Nrv \). Since \( v \leq v^* \), free volume is introduced into the lattice model.

The equation of state for this system is found from differentiation of the configurational partition function \( Q \)

\[
P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} \tag{2-5}
\]

where \( Q \) can be written as

\[
Q = Q_{\text{comb}} \left[ \frac{V_f}{\Lambda^3} \right]^N \left[ q_{\text{rot,vib}} \right]^N \exp \left( -\frac{E_0}{k_B T} \right) \tag{2-6}
\]

where \( V_f \) is the "free volume" available to the center of mass of a molecule as it moves in volume \( V \), \( \Lambda \) is the de Broglie wavelength, \( q_{\text{rot,vib}} \) is the rotational and vibrational partition function of the \( r \)-mer molecule in the "mean-field" of all other chains in the system, \( Q_{\text{comb}} \) is the combinatorial factor (the number of ways of arranging \( N \) \( r \)-mers on a lattice with \( Nr \) lattice sites), \( E_0 \) is the potential energy of the system with every mer located at the central position of its lattice site and \( k_B \) is the Boltzmann constant.

The temperature and density dependence of \( q_{\text{rot,vib}} \) is difficult to determine, especially for large polyatomic molecules. The extent to which a large asymmetric molecule can rotate or vibrate depends on the mean-field exerted on it by the surrounding fluid as well as on internal
modes unaffected by the surrounding fluid. Consequently, $q_{\text{rot,vib}}$ can be factored into an internal part which depends only on temperature and an external part which depends on volume:

$$q_{\text{rot,vib}} = q_{\text{int}}(T) q_{\text{ext}}(V)$$ \hspace{1cm} 2-7

Since the internal part depends only on temperature, it does not appear in the equation of state.

To obtain an expression for $q_{\text{ext}}$ consideration must be given to the degrees of freedom of large asymmetric molecules.

First, consider a rigid $r$-mer molecule; all bond lengths, bond angles and torsional angles are fixed. This rigid molecule has three degrees of freedom, the same as that for a spherical molecule (one for each translational coordinate). Second, consider an $r$-mer molecule which is completely flexible (i.e., the molecule does not have any restriction on bond length, bond angle or torsional angle), this molecule has a maximum of $3r$ degrees of freedom. The number of degrees of freedom for a real large asymmetric molecule lies somewhere in-between. To approximate the number of external degrees of freedom while leaving them unspecified, a parameter $c$ is introduced such that the total number of effective external degrees of freedom per $r$-mer molecule is $3c$, such that $1 < c < r$. When coupled with Prigogine's approximation that enteral rotational and vibrational degrees of freedom can be considered equivalent translational degrees of freedom, we write

$$\frac{V_f}{\Lambda^3} q_{\text{rot,vib}} = \frac{V_f}{\Lambda^3} q_{\text{int}} q_{\text{ext}} = q_{\text{int}}(T) \left(\frac{V_f}{\Lambda^3}\right)^c$$ \hspace{1cm} 2-8

where $3(c-1)$ reflects the number of external rotational and vibrational motions, i.e., those rotational and vibrational motions that are affected by the presence of neighboring molecules.

Equations (2-6) and (2-8) summarize the fundamental aspects of the cell model. To proceed further, we need to specify the dependence of free volume $V_f$ and potential energy $E_0$ on cell volume $v$. Subsequent variations of Prigogine's cell model differ primarily in their choice of
expressions for these quantities. Prigogine's approximation [74] for \( V_f \) as a function of reduced cell volume, defined as \( V = \frac{v}{v^*} \), is based on a face-centered cubic arrangement of segments around a central segment:

\[
V_f = N r v^* \gamma (\tilde{v}^{1/3} - 2^{-1/6})^3 \tag{2-9}
\]

where \( \gamma \) is a geometrical constant.

The dependence of \( E_0 \) on \( V \) is derived from assuming various potentials (including harmonic, Lennard-Jones, and square-well potentials) [74, 80] between segments of the chain with segments in nearest-neighbor cells. The commonly-used form of Prigogine's cell model is that from the Lennard-Jones potential:

\[
E_0 = \frac{1}{2} N e q z [\frac{A}{\tilde{v}^4} - \frac{B}{\tilde{v}^2}] \tag{2-10}
\]

where \( \varepsilon \) is the well depth at the minimum of the potential. The product \( qz \) is given by \( qz = r(z-2) + 2 \) where \( z \) is the lattice coordination number; \( q \) represents the external surface area of the \( r \)-mer. Thus \( qz \) is the number of unbonded nearest-neighbor segments surrounding a single chain. Constants \( A \) and \( B \) are from the Lennard-Jones potential, given a specific geometry (\( A = 1.2045 \) and \( B = 1.011 \) for a face-centered cubic lattice). Equation (2-10) gives the summation of the potential energy felt by each segment of a chain from surrounding nonbonded nearest-neighbor segments multiplied by the total number of chains. Substituting Equations (2-9) (2-10) into Equation (2-6) and differentiating according to Equation (2-5) gives the equation of state for Prigogine's cell model (PCM):

\[
\frac{\tilde{P}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 2^{-1/6} + \frac{2}{\tilde{v}^4} [\frac{A}{\tilde{v}^4} - \frac{B}{\tilde{v}^2}]} \tag{2-11}
\]

where \( \tilde{P} \), \( \tilde{v} \) and \( \tilde{v} \) are reduced pressure, volume and temperature respectively and defined as:

\[
\tilde{P} = \frac{P}{P^*} = \frac{pr v^*}{qz \varepsilon}, \quad \tilde{v} = \frac{v}{v^*}, \quad \text{and} \quad \tilde{T} = \frac{T}{T^*} = \frac{c_k b T}{qz \varepsilon} \tag{2-12}
\]

and \( P^*, v^* \) and \( T^* \) are the characteristic parameters.
2.4.1.2 Flory-Orwoll-Vrij (FOV) Equation of State

Since 1960 there have been two especially important developments in polymer solution thermodynamics: one experimental and one theoretical. Freeman and Rowlinson [84] observed experimentally that many hydrocarbon polymers dissolved in hydrocarbon solvents phase separated at high temperatures. These nonpolar polymer solutions exhibited what are known as lower critical solution temperature (LCST), a critical point phenomena that is relatively rare among low molecular weight solutions. The Flory-Huggins theory [67], which ignores the equation of state properties of the pure components, completely fails to describe the experimentally observed LCST behavior. It was recognized that the common appearance of LCST behavior in polymer solutions must be related to the large size difference between polymer and solvent molecules. Soon after the discovery of the universality of LCST behavior in polymer solutions, Flory and co-workers [45, 81] developed a new theory of solutions that considers the “equation of state” properties of the pure components. According to the FOV theory [45, 81, 82], the polymer solution can be constructed as following lattice model where all the cells are occupied by either the polymer chain segments or the small solvent molecule segments (mers), the volumes of which are dissimilar (illustrated in Figure 2.3). This new theory of solutions, hereafter referred to as the Flory theory, demonstrates that mixture thermodynamic properties strongly depend on the thermodynamic properties (volume, compressibility etc.) of each component.
The Flory-Orwoll-Vrij (FOV) equation of state [45, 81, 82] for pure chain-like fluids is a simplified version of the Prigogine cell model. Instead of using a face-centered cubic geometry, Flory assumes a simple cubic geometry which gives

\[ V_f = N r v^* \gamma (\bar{v}^{1/3} - 1)^3 \]  \hspace{1cm} 2-13

where \( \gamma \) is a geometrical constant pertaining to a simple-cubic lattice. For the potential energy \( E_0 \), Flory proposed the simpler expression.

\[ E_0 = - \frac{r N s \eta}{2 \bar{v}} \]  \hspace{1cm} 2-14

where \( s \) is the mean number of external contact sites per segment of molecule and reflects the mean interaction between a pair of nonbonded segments in the \( r \)-mer-chain liquid. Substitution of Equations (2-13) and (2-14) into the partition function yields the equation of state:

\[ \frac{\bar{P} \bar{v}}{\bar{T}} \equiv \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 1} \frac{1}{\bar{v} \bar{T}} \]  \hspace{1cm} 2-15

where the reduced pressure (\( \bar{P} \)), volume (\( \bar{v} \)) and temperature(\( \bar{T} \)) are defined as:
\[ \bar{P} = \frac{P}{P^*} = \frac{2(\nu^*)^2 P}{s\eta} \quad \bar{\nu} = \frac{\nu}{\nu^*} = \frac{V/rN}{V^*} \quad \text{and} \quad \bar{T} = \frac{T}{T^*} = \frac{2\nu^* c k_B T}{s\eta} \]

2-16

and \( P^*, \nu^* \) and \( T^* \) are the characteristic parameters.

Flory et al. [45, 81, 82] define the total number of external degrees of freedom per molecule as \( 3r_c \); hence in the FOV equation, \( c \) is defined per segment, whereas in the PCM and PHC equations, \( c \) is defined per molecule. This difference in notation affects primarily the definitions of characteristic quantities for each equation of state.

### 2.4.2 Lattice-Fluid (LF) Models

In the lattice fluid model the lattice size is fixed, which implies that the volume increases in this model by an increase in the number of vacant lattice sites. The increase in entropy of the system is modeled by the behavior of the density of vacant lattice sites. Among LF models Sanchez-Lacombe (SL) [42, 85], Costas and Sanctuary (CS)[86-88], Panayiotou-Vera (PV) [89-92] so and so forth are well known.

#### 2.4.2.1 Sanchez-Lacombe (SL) Equation of State

Like the cell models, the Sanchez-Lacombe (SL) equation of state for chain-like fluids is also based on the incompressible-lattice model but compressibility is introduced in a different manner. The lattice is occupied by both \( r \)-mers and vacant lattice sites. The total number of lattice sites in the system, \( N_r \), is

\[ N_r = N_0 + rN \]

2-17

where \( N_0 \) is the number of vacancies. The close-packed volume of a molecule, assumed to be independent of temperature and pressure, is \( rv^* \) where \( v^* \) is the volume of a single mer and is equal to the volume of one lattice site. The total volume of the system is

\[ V = (N_0 + rN)v^* \]

2-18

A reduced density is defined as the fraction of occupied lattice sites.
\[ \tilde{\rho} = \frac{1}{\bar{\nu}} = \rho \nu^* = \frac{\nu^*}{\bar{\nu}} = \frac{rN}{N_0 + rN} \]  \hspace{1cm} (2-19)

where \( \rho = N_r/V \) is the density of segments, \( \nu = V/N_r \) is the volume per segment and \( \bar{\nu} \) is reduced volume.

The energy of the lattice depends only on nearest-neighbor interactions. For a pure component, the only non-zero interaction energy is the mer-mer pair interaction energy \( \varepsilon \). Vacancy-mer and vacancy-vacancy interaction energies are zero. The SL model assumes random mixing of vacancies and mers; therefore, the number of mer-mer nearest-neighbors is proportional to the probability of finding two mers in the system. The lattice energy is

\[ E = -\frac{Z}{2} N_r \varepsilon \left( \frac{rN}{N_0 + rN} \right)^2 = -N_0 \epsilon^* \tilde{\rho}^2 \]  \hspace{1cm} (2-20)

where \( \epsilon^* = \frac{Z \varepsilon}{2} \).

The configurational partition function for this system is written

\[ Q = Q_{comb} \exp\left(-\frac{E}{k_B T}\right) \]  \hspace{1cm} (2-21)

The combinatorial factor \( Q_{comb} \) is identical to that of the Flory-Huggins incompressible-lattice partition function \([67]\) where the solvent is replaced by a vacancy

\[ Q_{comb} = \left(\frac{\delta}{\sigma}\right)^N \frac{(N_0 + rN)!}{N_0! N!} \frac{1}{(N_0 + rN)^N (\sigma-1)} \]  \hspace{1cm} (2-22)

where \( \delta \) is the flexibility parameter of the \( r \)-mer and \( \sigma \) is a symmetry number; both of these are assumed to be constants and therefore do not appear in the equation of state. Substitution of Equations (2-20) and (2-22) into Equation (2-21) and differentiation according to Equation (2-5) yields the SL lattice-fluid equation of state

\[ \frac{\tilde{P} \tilde{\nu}}{T} - \frac{1}{r} \left[ 1 + \tilde{\nu} \ln \left( 1 - \frac{1}{\bar{\nu}} \right) \right] - \frac{1}{\tilde{\nu} T} \]  \hspace{1cm} (2-23)

where the reduced (~) and characteristic (*) pressure and temperature are defined by
\[ \tilde{P} = \frac{P}{p^*} = \frac{P_0}{p^*_0} \quad \text{and} \quad \tilde{T} = \frac{T}{T^*} = \frac{k_B T}{\varepsilon^*} \quad \text{(2-24)} \]

Equation (2-23) shows that PVT data for polymer liquids are relatively insensitive to polymer molar mass. As polymer molecular weight increases, the \(1/r\) term becomes insignificant. In the limit of infinite polymer molecular weight, Equation (2-23) suggests a corresponding-state behavior for polymer liquids.

**2.4.2.2 Panayiotou and Vera (PV) [89-92]**

Panayiotou and Vera [89-92] use the quasi-chemical approximation to account for nonrandom mixing of holes and mers. In a random mixture, the number of nearest-neighbor vacancy (0)-mer (1) contacts is proportional to the product of their respective number of surface contacts. Hence, in a random mixture:

\[ N_{01}^0 = \frac{Z}{2} N_q \left( \frac{N_0}{N_0 + qN} \right) \frac{qN}{N_0 + qN} = \frac{Z}{2} N_q (1 - \theta) \theta \quad \text{(2-25)} \]

where the superscript \(^0\) denotes a random mixture and \(\theta = qN/(N_0 + qN)\) is the surface fraction of r-mers; \(\theta\) is related to the reduced density by

\[ \theta = \frac{\left( \frac{2}{T} \right) \tilde{\rho}}{1 + \left( \frac{2}{T} \right) \tilde{\rho}} \quad \text{(2-26)} \]

Due to attractive forces, the number of vacancy-mer contacts decreases as temperature decreases and the number of vacancy-vacancy and mer-mer contacts increases. The quasichemical approximation estimates the effect of temperature and attractive forces on \(N\) for a real mixture according to

\[ N_{01} = N_{01}^0 \Gamma_{01}; \quad \Gamma_{01} = \frac{2}{1 + \sqrt{1 - 4(1 - \theta) \exp\left( \frac{\varepsilon}{k_B T} \right) - 1}} \quad \text{(2-27)} \]

where \(\Gamma_{01} \leq 1\) is called the vacancy-mer non-random factor and \(\varepsilon\) is the mer-mer free energy of interaction

\[ \varepsilon = \varepsilon_h + T \varepsilon_s \quad \text{(2-28)} \]
which is composed of an enthalpic contribution, $\varepsilon_h$, and an entropic contribution, $\varepsilon_s$. The vacancy-vacancy and mer-mer non-random factors $\Gamma_{00}$ and $\Gamma_{11}$, are related to $\Gamma_{01}$ by

$$\theta \Gamma_{01} + (1 - \theta) \Gamma_{00} = 1 \quad \text{and} \quad (1 - \theta) \Gamma_{01} + \theta \Gamma_{11} = 1$$

2-29

The inclusion of non-random mixing causes two modifications of the lattice-fluid partition function. First, the lattice energy is now a function of temperature as well as the number of vacancies:

$$E = -N_{11} \varepsilon = -N_{11}^* \Gamma_{11} \varepsilon$$

2-30

Second, because the number of nearest-neighbor contacts is different from that in a random mixture, the combinatorial factor must also indicate that the number of allowed configurations in the non-random mixture is different from that in the random mixture. The lattice-fluid partition function becomes:

$$Q = Q_{\text{comb}} Q_{\text{NR}} \exp\left(-\frac{E}{k_B T}\right)$$

2-31

where $Q_{\text{comb}}$ is Guggenheim's approximation for the combinatorial factor for a random mixture and $Q_{\text{NR}}$ is the contribution to the combinatorial factor due to non-random mixing of vacancies and mers. According to the quasi-chemical approximation, $Q_{\text{NR}}$ takes the form

$$Q_{\text{NR}} = \frac{N_{11}! N_{00}! [\left(\frac{N_{11}}{2}\right)]^2}{N_{11}! N_{00}! [\left(\frac{N_{00}}{2}\right)]^2}$$

2-32

The resulting Panayiotou and Vera (PV) EOS is

$$\frac{p\varphi}{T} = \varphi \ln\left(\frac{\varphi}{\varphi - 1}\right) + \frac{Z}{2} \ln\left(\frac{\varphi + \varphi - 1}{\varphi}\right) - \frac{Z}{2} \ln \Gamma_{00}$$

2-33

The reduced and characteristic parameters are defined by

$$\bar{p} = \frac{p}{p^*} = \frac{p v_0^*}{\left(\frac{Z}{2}\right)\varepsilon} \quad \bar{\varphi} = \frac{\varphi}{N_{11} v_0^*} \quad \bar{T} = \frac{T}{T^*} = \frac{\varphi}{\left(\frac{Z}{2}\right)\varepsilon}$$

2-34

where $v_0^*$ is the characteristic volume of a lattice vacancy which is assumed constant for all fluids; hence, $v_0^*$ is not an adjustable parameter but there are two adjustable parameters.
associated with the interaction energy, $\varepsilon_h$ and $\varepsilon_s$, in Equation (2-28). Since $\varepsilon$ is assumed to be temperature dependent, $p^*$ and $T^*$ are also temperature dependent. Equation (2-33) reduces to the CS EOS if non-randomness in mixing is neglected, i.e., $\Gamma_{00} = \Gamma_{01} = \Gamma_{11} = 1$.

### 2.4.3 Holes Models

Hole models of polymer liquids combine two methods for incorporating compressibility into the lattice model. The first method is to include lattice vacancies and the second is to vary the cell volume. The addition of vacancies to the cell-model partition function, Equation (2-6), yields the partition function for the hole model:

$$Q(N, V, T) = Q_{\text{comb}}(N, y)[V_t(V; y, \omega)]^N \exp\left[-\frac{E_0(V; y, \omega)}{k_BT}\right]$$  \hspace{1cm} 2-35

where $y$ and $\omega$ are variables related to the total volume; $y$ is the fraction of occupied lattice sites

$$y = \frac{N_r}{N_0 + N_r}$$  \hspace{1cm} 2-36

and $\omega$ is the "cell" volume or volume per lattice site

$$\omega = \frac{V}{N_0 + N_r}$$  \hspace{1cm} 2-37

Through $y$, the combinatorial factor is given a dependence on volume. Mixing r-mers with vacancies provides an additional source of entropy. The density is altered through changes in the cell volume and through addition or removal of vacancies. The original cell model is recovered when $y = 1$. Flory's approximation for $Q_{\text{comb}}$ [Equation (2-22)] is most commonly used. Combining Equations (2-35) and (2-36) gives

$$V = \frac{N_r \omega}{y}$$  \hspace{1cm} 2-38

which indicates the dependence of volume on the independent variables $y$ and $\omega$. In order to determine an additional relation between $V$, $\omega$ and $y$, one of the independent variables is treated as an order parameter. The additional relation is obtained by minimizing the Helmholtz energy.
with respect to the order parameter. The choice of \( y \) or \( \omega \) as the order parameter is a key assumption in the development of hole models. In Equation (2-34), the free volume and lattice energy are functions of the lattice-site volume \( \omega \) (which is analogous to \( \nu \) in the original cell models), and the fraction of occupied sites \( y \). The free volume is affected by the presence of vacant lattice sites because segments neighboring vacant lattice sites gain some additional space to translate, rotate or vibrate. The lattice energy is affected because mers can not only interact with other mers, but also interact with vacancies. As a result, the dependence of the free-volume and lattice energy on \( y \) and \( \omega \) requires specification.

### 2.4.3.1 Simha-Somcynsky (SS) Equation of State

Simha and Somcynsky [38, 78, 93, 94] choose the volume per lattice site, \( \omega \), as the order parameter. Minimization of the Helmholtz energy with respect to \( \omega \) is used to derive an additional equation relating \( V \), \( \omega \) and \( y \):

\[
-\frac{1}{k_B T} \left( \frac{\partial A}{\partial \omega} \right)_{N,Y,T} = \left( \frac{\partial \ln Q}{\partial \omega} \right)_{N,Y,T} = 0
\]

At constant \( V \), \( \omega \) and \( y \) are linearly related by Equation (2-38); therefore, Equation (2-39) can also be written as

\[
\left( \frac{\partial \ln Q}{\partial y} \right)_{N,Y,T} = 0
\]

Although Equations (2-39) and (2-40) are equivalent, Equation (2-40) is more convenient because the derivative with respect to \( y \) is easier to obtain algebraically. The equation of state is computed from:

\[
p = k_B T \left( \frac{\partial \ln Q}{\partial y} \right)_{N,T,\omega} = k_B T \left( \frac{dy}{dV} \right) \left( \frac{\partial \ln Q}{\partial y} \right)_{N,T,\omega} = \frac{1}{k_B T} \left( \frac{\partial \ln Q}{\partial y} \right)_{N,T,\omega}
\]

To determine bulk thermodynamic properties, the order parameter \( \omega \) is held constant in the differentiation of Equation (2-41).
To use Equation (2-41), we need an expression for \( V_i \); two expressions have been proposed. The first one averages linearly over single modes of motion or free-lengths with respect to the fraction of occupied sites, \( y \):

\[
\tilde{v}_f^{1/3} = \left( \frac{V_f}{v^*} \right)^{1/3} = y(\tilde{\omega}^{1/3} - 2^{1/6}) + (1 - y)\tilde{\omega}^{1/3}
\]

(2-42)

Where \( \tilde{\omega} = \omega/v^* \) is the reduced cell volume, and \( \tilde{v}_f \) is the reduced free volume. The second averages linearly over the free volumes:

\[
\tilde{v}_f = \frac{V_f}{v^*} = y(\tilde{\omega}^{1/3} - 2^{1/6})^3 + (1 - y)\tilde{\omega}
\]

(2-43)

The first term in both expressions represents a solid-like contribution that is analogous to the free-volume expression in Prigogine’s original cell model, Equation (2-9). The second term in both expressions represents a gas-like contribution that is reminiscent of the free volume of an ideal gas. Both expressions assume a face-centered cubic lattice. Equation (2-42) is the more commonly used, but both yield similar results.

For the lattice energy, the expression derived using the Lennard-Jones potential[69-71, 95] with a face-centered cubic lattice is used but weighted by the fraction of occupied sites

\[
E_f = \frac{1}{2} yNqz\varepsilon \left[ \frac{A}{\tilde{\omega}} - \frac{R}{\tilde{\omega}} \right]
\]

(2-44)

where, as before, \( qz = r(\epsilon - 2) + 2 \). Reduced quantities are defined by

\[
\tilde{P} = \frac{Prv^*}{qz\varepsilon} \quad \tilde{v} = \frac{V}{Nrv^*} = \frac{v}{v^*} \quad \tilde{T} = \frac{T}{T^*} = \frac{ckBT}{qz\varepsilon}
\]

(2-45)

The volume per segment, \( v = V/Nr \), is different from the volume per cell, \( \omega \). The reduced lattice site volume \( \tilde{\omega} \) is related to the reduced volume, \( \tilde{v} \) by \( \tilde{\omega} = y\tilde{v} \).

Adopting Equation (2-41) for the free volume, the resulting equation of state is

\[
\frac{\tilde{P}v}{\tilde{T}} = \left[ 1 - 2\tilde{v}y(y\tilde{v})^{-\frac{1}{3}} \right]^{-1} + \left( \frac{2y}{T} \right)(y\tilde{v})^{-2}[1.011(y\tilde{v})^{-2} - 1.2045]
\]

(2-46)

Applying the condition given by Equation (2-40) gives
\[
\left(\frac{s}{3c}\right)\left[\frac{s-1}{s} + \frac{y^{-1}}{3} \ln(1 - y)\right] = (1 - \eta)^{-1} (\eta - \frac{1}{3}) + \left(\frac{y}{6\eta}\right)(y\tilde{\nu})^{-2}[2.409 - 3.033(y\tilde{\nu})^{-2}]
\]

where \(\eta = 2^{-1/6} y(y\tilde{\nu})^{-1/3}\). Here \(3c/s\) is the flexibility parameter, which is the number of effectively external degrees of freedom per segment of the \(s\)-mer \((r = s)\). Hence, given reduced temperature and pressure, Equations (2-46) and (2-47) are solved simultaneously for \(y\) and \(\tilde{\nu}\).

The ratio \(c/s\) which appears explicitly in Equation (2-47) can be calculated from the characteristic quantities by

\[
\frac{s}{c} = \frac{p^*v^*}{k_B T^*}
\]

The SS EOS, given by Equations (2-46) and (2-47), also produces a three-parameter corresponding-states behavior.

### 2.4.4 Tangent-Sphere Models

Within the last twenty years, there has been increased interest in developing equations of state for polymers and polymer mixtures that no longer rely on a lattice description of molecular configurations. Although a rigorous statistical-mechanical treatment for polymers in continuous space is difficult because of their asymmetric structure, large number of internal degrees of freedom, and strong coupling between intra- and inter-molecular interactions, a relatively simple model has emerged which portrays chain-like fluids as freely-jointed tangent hard spheres [96-99]. A hard-sphere chain (HSC) equation of state can be used as the reference system in place of the hard-sphere reference used in most existing equations of state for simple fluids. Despite their simplicity, hard-sphere-chain models take into account some significant features of real chain-like fluids such as excluded-volume effects and chain connectivity.

A common feature of HSC equations of state is that they express the properties of the chain fluid in terms of the properties of simpler fluids, usually unbonded hard spheres or dimers.
A fortunate feature of some hard-sphere-chain-based theories is that the reference equations of state can be extended to hard-sphere chain mixtures without using mixing rules. Only attractive terms require mixing rules.

To describe the properties of a real polymer, it is necessary to introduce attractive forces by adding a perturbation to an HSC equation of state. Because the influence of attractive forces on fluid structure is weak, a van der Waals type or other mean-field term (e.g., square-well fluids) is usually used to add attractive forces to the reference hard-sphere-chain equation of state. Although numerous details are different, most hard-sphere-chain-based equations of state follow from statistical-mechanical perturbation theory; as a result, the equation of state can be written as

\[
\frac{P}{\rho kT} = \left(\frac{P}{\rho kT}\right)_{\text{ref}} + \left(\frac{P}{\rho kT}\right)_{\text{pert}}
\]

where \( P \) is the pressure, \( \rho = \frac{N}{V} \) is the number density, \( N \) is the number of molecules, \( V \) is the volume of the system, and \( T \) is the absolute temperature. In Equation (2-48), the first term represents the reference equation of state, here taken as a fluid of hard-sphere chains \( \left(\frac{P}{\rho kT}\right)_{\text{ref}} = \left(\frac{P}{\rho kT}\right)_{\text{HSC}} \), and the second term is the perturbation to account for attractive forces. The next section presents the forms of the reference and perturbation terms for three different HSC based equations of state for pure chain-like fluids. Among HSC models Statistical Associated-Fluid Theory (SAFT) [96, 100], Perturbed Hard-Sphere-Chain (PHSC) [101-103], Perturbed-Chain Statistical Associated-Fluid Theory (PC-SAFT) so and so forth are well known.

**2.4.4.1 Statistical Associated-Fluid Theory (SAFT)**

The Statistical Associated-Fluid Theory (SAFT) [96, 100] is based on the first-order theory of Wertheim's thermodynamic perturbation theory of polymerization (TPT) [104] for hard-sphere chains as the reference system. Wertheim's theory was developed by expanding the
Helmholtz energy in a series of integrals of molecular-distribution functions and the association potential. Using some physical arguments, Wertheim showed that many integrals in this series are zero which results in a simplified expression for the Helmholtz energy. Wertheim applied his theory to hard-chain fluids and developed first-order and second-order thermodynamic perturbation theories (TPT1 and TPT2). The first-order theory is applicable only to flexible chain molecules. In the second-order theory, effects of chain conformation and branch structure are taken into account, but a detailed knowledge of the triplet distribution function is required [105].

According to the first-order theory the hard-sphere-chain equation of state is

\[
\left(\frac{p}{\rho k_B T}\right)_{HSC} = 1 + r^2 b \rho g(d^+) - (r - 1)\left[\rho \frac{\delta \log(d^+)}{\delta}\right]
\]

where \(g(d^+)\) is the radial distribution function of hard spheres at contact, as calculated from the Carnahan-Starling equation, \(r\) is the number of tangent hard-spheres per molecule, and \(b\) is the second virial coefficient of hard spheres prior to bonding to form chains:

\[
b = \frac{2\pi}{3} d^3
\]

In Equation (2-48), the first two terms are the non-bonding contributions and the last term reflects chain connectivity. Equation (2-48) obeys the ideal-gas law in the limit \(\rho \to 0\).

To model a real fluid, a perturbation term is needed in addition to Equation (2-49) to include attractive forces. Chapman et al. [100] adopted the dispersion term derived by Cotterman et al. [106] from molecular-simulation data for Lennard-Jones fluids [69-71, 95].

For the dispersion term, Huang and Radosz [107, 108] used a series initially fitted by Alder et al. [109] to molecular-dynamics data for a square-well fluid

\[
\left(\frac{p}{\rho k_B T}\right)_{pert} = r \Sigma_{\alpha} \Sigma_{\beta} D_{\alpha \beta} \left[\frac{u}{k_B T}\right]^\alpha \left[\frac{\eta}{\eta_{cp}}\right]^\beta
\]

where \(\eta_{cp} = 0.7405\), is the packing fraction of hard spheres at the closest packing, and
\[ u = \varepsilon \left( 1 + \frac{e}{k_B T} \right), \quad \frac{e}{k_B} = 10K \]  

where \( \varepsilon \) is the well depth of the potential. In Equation (2-53), \( D_{\alpha\beta} \) are universal constants which have been refitted to accurate \( PVT \), internal energy, and second virial coefficient data for argon \[106\]. The effective hard-sphere diameter \( d \) depends on temperature as suggested by the Barker-Henderson perturbation theory \[110\]

\[ d = \sigma \left[ 1 - C \exp \left( \frac{-3\varepsilon}{k_B T} \right) \right], \quad C = 0.12 \]

where \( \sigma \) is the effective hard-sphere diameter at zero temperature; it is also called the distance of separation at minimum potential energy.

The SAFT equation of state has been applied to describe thermodynamic properties of polymers as well as solvents \[107, 111\]. In general, it was found to correlate experimental data with good accuracy, except at low pressures and high temperatures, or at high pressures and low temperatures. For polymers, experimental SAFT EOS parameters are independent of molar mass, as required by theory.

2.4.4.2 Perturbed-Chain Statistical Associated-Fluid Theory (PC-SAFT)

Advances in statistical mechanics and an increase in computer power have allowed the development of equations of state based on molecular principles that are accurate for real fluids and mixtures. The development of the Perturbed-Chain (PC) SAFT equation-of-state is described in detail by Gross and Sadowski \[43, 44, 112, 113\]. In the framework of PC-SAFT, molecules are assumed to be chains of freely jointed, spherical segments. Perturbed-Chain SAFT is suitable for the calculation of phase equilibrium and the thermophysical properties of pure components and mixtures. It has been tested against experimental data for numerous systems and found to give excellent results. When compared to other equations of state, Perturbed-Chain SAFT is found to be more precise for the correlation of experimental data and more predictive especially
when applied to mixtures [43, 44, 112, 113]. It has been very reliable for extrapolations over the regions where parameters were fitted. However, use of PC-SAFT EOS in the solubility measurement of gas/polymer mixture is a scarce because of inadequate data.

2.5 Review on Solubility of Gases in Polymers

The solubility of gas in polymer melts is defined as the maximum amount of gas that can be desolved into the polymer at a particular temperature and a particular pressure. As discussed in chapter 1, it is obvious that solubility information play a significant role in foam industry. The knowledge of gas solubility and the effects of dissolved gases on the physical properties of the polymer melts, such as swollen volume, glass transition temperature, melting temperature, isothermal compressibility, surface tension, viscosity, crystallization and thermal expansion coefficients are very important factors for polymer processing [114-119].

Last fifty years, numerous efforts have been made to investigate solubility of gases in polymer melts through a variety of approaches including the experimental measurements [120-125] and theoretically thermodynamic calculation [126-137]. All the previous studies found in the literature that considered solubility of gases in polymer can be categorized into three classes: (1) fully experimental, (2) experimental measurements with theoretical compensation, and (3) theoretically thermodynamic calculations.

2.5.1 Experimental Approaches

Fully experimental approaches are very rare in deed. However, many researchers tried to measure the solubility of gases experimentally.

2.5.1.1 Modified Magnetic Suspension Balance (MSB)[122]

Ohshima and his coworkers [122] tried to measure the solubility of gas in polymer by modifying a magnetic suspension balance (MSB). The densities of poly(ethylene glycol)
(PEG)/CO₂ and polyethylene (PE)/CO₂, were measured above melting temperatures of the polymers under CO₂ pressures in the range 0–15 MPa. They found that the dissolution of CO₂ in polymer reduced density of both PEG/CO₂ and PE/CO₂ systems but the degree of CO₂ induced-density reduction was different between two polymer/CO₂ systems.

A magnetic suspension balance (MSB) was modified to measure the density of the polymer/gas systems. A thin disc-shaped platinum plate was submerged in the considered polymer/CO₂ single-phase solution in the MSB high-pressure cell. The weight of the plate was measured while keeping CO₂ pressure and temperature in the sorption cell at a specified level. Since the buoyancy force exerted on the plate by the polymer/CO₂ solution reduced the apparent weight of the plate, the density of the polymer/CO₂ solution could be calculated by subtracting the true weight of the plate from its measured weight.

Figure 2.4 Details of MSB for density measurement by Ohshima at el. [122]

When the platinum plate is submerged in polymer/CO₂ solution, the measured weight of the plate becomes smaller than the true weight of the plate due to a buoyancy force exerted on the plate by the polymer/CO₂ solution. The buoyancy force is equal to the weight of polymer/CO₂ solution displaced by the plate and it is calculated by multiplying the plate volume
by the density of polymer/CO₂ solution. Therefore, knowing the volume and mass of the plate a priori, the density of polymer/CO₂ solution can be calculated from the buoyancy force or the apparent weight of the platinum plate.

The force balance equation around the plate and the wire is expressed by

$$w_{\text{readout}}(P, T) = w_{\text{ref}} - (V + \alpha V_w) \rho_{\text{sol}} - ((1 - \alpha)V_w + V_B) \rho_{\text{CO}_2} + \frac{\pi d \rho_{\text{sol}} \cos \theta}{g}$$

2-55

where $\rho_{\text{sol}}$ and $\rho_{\text{CO}_2}$ are the density of polymer/CO₂ solution and CO₂, respectively. $w_{\text{readout}}(P, T)$ is the readout value of the apparent total weight of the plate, wire and measuring load hook at the experimental temperature, T, and CO₂ pressure, P, condition. $w_{\text{ref}}$ is the apparent total weight of the plate, wire and measuring load hook at a reference temperature and pressure condition. $V$ and $V_w$ are the volume of the platinum plate and that of the wire, respectively. $V_B$ is the volume of measuring load hook; $\alpha$ is the volume fraction of the wire submerged in the solution; $d$ is diameter of the wire connecting the platinum plate to the measuring load hook; $c$ is surface tension of polymer/CO₂; $\theta$ is contact angle between the wire and the polymer/CO₂ solution as shown in Figure 2.4(b); $g$ is the gravitational constant. The subscript i, for example $d_i$ and $V_{w,i}$ in Figure 2.4(b), indicates that it is the value in the case of using the i-th wire.

Considering that the plate and wire were both made of platinum, the temperature and pressure corrections of the volumes, $V$ and $V_w$, were made using Equation (2-56).

$$\frac{V}{V_{\text{ref}}} = \frac{V_w}{V_{w,\text{ref}}} = \left(1 - 3 \frac{1-2\nu}{E} (P - P_{\text{ref}}) \times \exp(\xi(T - T_{\text{ref}}))\right)$$

2-56

where $V_{\text{ref}}$ and $V_{w,\text{ref}}$ are reference volumes of platinum plate and wire; $m$ and $E$ are Poisson’s ratio and Young’s modulus of the platinum, respectively (given by 0.38 and 1.68 MPa, respectively). $\xi$ is the coefficient of thermal expansion, which is $9.1 \times 10^{-6} \text{ K}^{-1}$.
The surface tension of polymer/CO$_2$, $\gamma$, and contact angle, $\theta$, were unknown and no literature value was available. To eliminate $\gamma$ and $\theta$ from the balance equation, Equation (2-55), two wires in different diameter, $d_1$ and $d_2$, were used. The density measurements were conducted using each wire individually at the same temperature and pressure. Assuming that the two wires have the same surface tension, $\gamma$, and contact angle, $\theta$, against the polymer, Equation (2-55) can be transformed into

$$\frac{\pi \gamma \cos \theta}{g} = \frac{1}{d_1} (w_{\text{readout,1}} - w_{\text{ref,1}} + (V + \alpha_1 V_{w,1}) \rho_{\text{sol}} + ((1 - \alpha_1)V_{w,1} + V_B) \rho_{\text{CO}_2})$$

$$= \frac{1}{d_2} (w_{\text{readout,2}} - w_{\text{ref,2}} + (V + \alpha_2 V_{w,2}) \rho_{\text{sol}} + ((1 - \alpha_2)V_{w,1} + V_B) \rho_{\text{CO}_2})$$

Equation (2-57)

Finally, they calculated the density of polymer/CO$_2$, $\rho_{\text{sol}}$ using the Equation (2-58)

$$\rho_{\text{sol}} = \frac{d_2 (w_{\text{readout,1}} - w_{\text{ref,1}} + ((1 - \alpha_2)V_{w,1} + V_B) \rho_{\text{CO}_2}) - d_1 (w_{\text{readout,2}} - w_{\text{ref,2}} + ((1 - \alpha_2)V_{w,2} + V_B) \rho_{\text{CO}_2})}{d_1 (V + \alpha_2 V_{w,2}) - d_2 (V + \alpha_1 V_{w,1})}$$

Equation (2-58)

This method has some limitations. It is only suitable for low viscosity polymers. This one also has accuracy issue due to position changeover of the balance causing by dragging force on the plate while moving up and down into the viscous polymer. Despite of this limitation, the method provides a new scheme of measuring the density of polymer/gas solution and can be applied to variety of low molecule and CO$_2$ systems.

**2.5.1.2 In-line Method [120, 138]**

Xathanthos and his co-workers developed an inline method to measure the solubility of gases in polymers. They measured the solubility of three different inert gases (CO$_2$, N$_2$ and Ar) in two polymer systems (PS and PET) using in-line method. Overall, the in-line data compare favorably with off-line data where Henry’s law constants were obtained from the slope of solubility/equilibrium gas pressure plots. They found that due to enhanced homogenization/dissolution, data obtained with the twin-screw extruder show better consistency and a higher degree of sensitivity in detecting differences in the solubility of different gases when compared
with those obtained from experiments using a single screw extruder. Solubility of CO$_2$ in PS was also found to decrease with increasing throughput in the foaming process while it is not affected by differences in screw speed.

A schematic of the experimental setup is shown in Figure 2.5. An optical flow cell and manually controlled valve were installed at the end of the extruder. The specially designed optical cell consists of a rectangular housing with two sapphire windows screwed on both sides of the cell. A pressure transducer and a retractable thermocouple were also installed on the cell to measure the melt pressure and temperature at the window respectively. The restricting valve was also specially designed to offer accurate and fine control of the melt pressure at the window in a wide pressure range.

![Figure 2.5 Schematic of experimental setup by Xanthos et al. [120]](image)

The important parameters such as the melt pressure and temperature at the die and the window, the gas pressure and flow rate were digitized using Keithley Metrabyte’s modules. The
modules were connected to a serial port of a computer. A program was developed to achieve real
time data acquisition. Solubility data are generated by observing/recording the onset of bubble
formation/dissolution in the gas-laden melt through the window using a microscope-CCD
camera-monitor/recorder system. Depending on the combination of lenses and monitor sizes, this
system can offer a wide range of overall magnification ranging from 40 to about 200.

2.5.1.3 Pressure Decay Method [123, 125, 139-143]

The pressure decay method was first proposed by Newitt and Weale in 1948 for the
experimental measurement of gases solubility in polystyrene melt [123]. The principle used in
the gases solubility determinations was measurement of the pressure drop, due to gas sorption by
the polymer, in a closed sorption chamber of known volume at a constant temperature. A high
pressure gas pump was used to generate the compressed gases. The compressed gases were
admitted into the sorption chamber which was kept at constant temperature [139, 140].

Using the pressure decay experimental approach, Lundberg at el. measured the solubility
of nitrogen and methane in polyethylene [142], solubility of methane in polystyrene [141], and
solubilities of methane in polyisobutylene [143]; Newitt at el. investigated the solubility of
hydrogen and nitrogen in polystyrene [123]; Durrill and his coworkers systematically determined
the solubility of nitrogen, helium, carbon dioxide, and argon in polyethylene, polyisobutylene,
polypropylene, polystyrene and polymethylmethacrylate [140].

Since the setup is very simple pressure decay method is relatively very popular. However, there are a few deficiencies associated with the pressure decay method for the
solubility study. First, the temperature control to achieve a uniform temperature profile inside the
sorption chamber is a big challenge and it is also difficult to conduct the experiment at high
temperatures/pressures due to lack of accurate pressure sensors with a small inner volume.
Second, a large polymer sample quantities is typically required and therefore a long saturation
time is observed. Third and most critical, all the previous works based on experimental approaches did not consider the swollen volume of polymer due to the dissolution of gas in polymer melt at higher pressure. As a results, this ignorance generated a significant error on the determination of solubility data.

2.5.1.4 Piezoelectric Sorption Method

Bonner at el. [125, 144, 145] developed a novel experimental technique for determination of gas sorption by polymers at elevated temperatures and pressures. The method consists of measurement of frequency changes due to gas sorption by a polymer layer coated on a piezoelectric quartz crystal. First, they determined the frequency of a clean (uncoated) crystal at ambient condition. Then, they coated the crystal with polymer prior to the commencement of gas sorption. Finally, the relevant frequency change of the crystal coated with polymer was determined which was used to determine the absorption. During the experiments, temperature effect, pressure effect, and the neat polymer coating effect were taken care of.

The apparatus used for our gas-sorption experiments is shown schematically in Figure 2.6. Gas from a cylinder source is fed directly (or continuously compressed if higher pressures are desired) through a saturation column past a quartz crystal coated with the polymer of interest. The saturation column provides sufficient heat transfer area to bring the gas to the temperature of the thermostatically controlled oven in which the quartz crystal, housed in a metal cell, and the saturator are contained. Pressure is read with a precision pressure gauge. The apparatus can be operated as a continuous-flow experiment or as a static experiment in which the same sample of gas is held in the crystal cell for the duration of the experiment.
Sauerbrey at el. [125, 145] showed that there is a linear relationship between the frequency decrease and the mass of material deposited on a piezoelectric crystal surface. Using Sauerbrey’s relationship, the weight fraction of solvent absorbed by polymer was calculated using Equation 2-59.

\[ w_1 = \frac{\Delta m'}{\Delta m' + \Delta m_0} = \frac{\Delta F'}{\Delta F' + \Delta F_0} \]

2-59

where \( \Delta F' \) is the frequency decrease due to the solvent mass (\( \Delta m' \)) sorbed by polymer on the crystal, and \( \Delta F_0 \) is the frequency decrease due to the initially applied polymer coating of mass \( \Delta m_0 \). This method has some limitations. It requires lots materials and data might not be very accurate.

2.5.1.5 Gas-liquid Chromatography

The gas-liquid chromatography was first applied by Prausnitz at el [119, 146-148] to obtain the gas solubility in polymer at high temperature. The chromatography column was first prepared with coated with polymer. Afterward, the column was placed in a constant temperature bath, and the temperature was controlled precisely. Here helium was used as a carrier gas. The solute (gas) was then injected into an injection block. A thermal conductivity detector was used.
to detect and to record solute concentrations in the carrier gas. The solute retention time in column was accurately measured. The schematic of a gas-liquid chromatography for gas sorption measurement is shown in Figure 2.7.

![Schematic of a gas-liquid chromatography for gas sorption](image)

Figure 2.7 Gas-liquid Chromatography apparatus for gas sorption [119, 147]

Using this gas-liquid chromatography apparatus, the solubility of ethylene, n-butane, benzene, toluene, in low density polyethylene were measured successfully [148]. The solubility of ketone, acetone, vinyl acetate, methyl chloride, ethane, ethylene and carbon dioxide in polyethylene and in ethylene-vinyl acetate copolymer were investigated [119, 147]. This method is very simple and rapid to measure the solubility of gases/liquids in polymers. However, it is not suitable for higher pressure.

2.5.1.6 Gravimetric Method

The gravimetric method was applied to study the sorption of gas in polymer melt. Based on the gravimetric method, Bonner etc. studied the sorption of benzene in polyisoprene and
polyisobutylene at 80°C; the sorption of cyclohexane in polyisobutylene at 100°C; and the sorption of cyclohexane in ethylenevinyl acetate copolymer (EVA), isooctane in EVA, isoctane in poly(vinyl acetate) at 110°C [149]. Baird investigated the kinetics sorption of n-pentane in polystyrene at 30°C [150]. The solubility of vinyl chloride monomer (VCM) in PVC powders has been studied by Berens etc. at temperatures from 30 to 110°C [151]. Berens etc. also investigated the solubility of nitrogen, carbon dioxide, vinyl chloride, methanol, acetone, n-butane, and benzene in PVC at temperatures below Tg [151-154]. Kamiya et al. precisely determined the solubility of gases in polymers at high pressure. The solubilities of N₂ and CO₂ in LDPE, CO₂ in polycarbonate (PC); and N₂, CH₄, C₂H₆, and CO₂ in polysulfone and PS were measured as a function of pressure up to 50 atm [155-159]. They carefully measured the polymer swelling and exactly determined the solubility of N₂, Ar, CO₂ in poly(vinyl benzoate) at 25-65 °C and up to 5 MPa [155, 157].

Typically a quartz spring or a microbalance with precision was employed and measured the in situ weight gain of a polymer sample as gas dissolved into polymer sample. The schematic of a sorption apparatus based on the gravimetric method is illustrated as below.
Gravimetric method is a very accurate measurement approach for the sorption of gas in polymer at low pressure range and at low temperature. One of the major defects of this method is that it cannot be applied to high temperature above the polymer melting temperature. Even it may be applied at high pressure. A correction for buoyancy is necessary at high gas density [157]. However, the buoyancy effect generated from the swollen volume of polymer sample due to the dissolution of gas in polymer was often ignored, which brought a significant error especially at high pressure range. The difficulty/ignorance on getting the swollen volume is another significant drawback for this gravimetric method.

**2.5.1.7 Magnetic Suspension Balance (MSB) Combined with PVT Apparatus**

In our group, we measured the solubility of CO₂ in linear and branched PP using a magnetic suspension balance (MSB) combined with a PVT apparatus [124]. The MSB is a unique contactless weight measurement instrument, which consists of two parts: the high pressure and high temperature absorption chamber, where the sample is located, and the microbalance, which is isolated from the sample in ambient conditions. In comparison to
traditional balances, the test polymer is located in a titanium sample holder and not directly connected with the balance; the titanium sample holder and the test polymer sample hang on a so-called suspension magnet (permanent magnet) during the measurement. The suspension magnet is kept in a freely suspension/ floating state inside the sorption chamber because of the magnetic attraction force transmitted from an electromagnet, which is connected to an external electro balance. The weight to measure is therefore precisely transmitted by the magnetic force from the closed and pressure-proof metal sorption chamber to the microbalance, which is isolated outside of the sorption chamber in ambient conditions.

When gas goes into the polymer, polymer swells and it has a significant effect on solubility measurement. Since MSB cannot measure the swelling phenomenon, a PVT apparatus was used to determine the swollen volume ($V_s$). Finally the solubility was calculated by using the Equation 2-60.

$$X_{\text{solubility}} = \frac{m_{\text{gas}}}{m_{\text{sample}}} = \frac{m_{\text{sample}}(P,T)-m_{\text{sample}}(0,T)+\rho_{\text{gas}}(V_B+V_P+V_S)}{m_{\text{sample}}}$$  \hspace{1cm} 2-60

where $\rho_{\text{gas}}$ is the density of the gas inside the chamber at temperature $T$ and pressure $P$, which can be measured \textit{in situ} by the magnetic suspension balance; $V_B$, $V_P$, and $V_S$ are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices), the volume of pure polymer at temperature $T$ and pressure $P$, and the swollen volume of the polymer due to gas dissolution, respectively. $V_B$ is usually determined in advance with a blank experiment. $V_P$ typically can be determined using the Tait equation of state [160, 161] from Gnomix or PVT apparatus data for each polymer. The details could be found in the next chapter. This method is more accurate and suitable to compare with the EOS data and test the validity of EOS.
2.5.2 Experimental Measurements Combined with Theoretical Compensation Approaches

This is a very common approach. In this approach, first the solubility (apparent solubility) of gas in polymer is determined using any apparatus/equipment without the swollen volume effect. Afterward, the swollen volume is predicted by using any equation of state (EOS, like FOV, SAFT, SL, and SS so and so forth) and incorporated it to calculate the total solubility. This approach could be named as semi-empirical approach. Since the swollen volume has significant effect on solubility especially at high pressure, precise swollen volume data is required to determine the solubility accurately.

As we have discussed in the precious section, neither experimental approach nor pure theoretical approach can provide a very reliable gas solubility data in polymer melt, especially at high temperature and pressure condition. Recently, many experimental results have verified that a high gas solubility in polymer produced substantial volume swelling in polymer sample with dissolved gas [155-159, 162-164]. This gas induced dilation of polymer became a significant factor on the solubility determination when the experimental approaches were employed for the solubility measurement. The previous proposed experimental approaches work well at low pressure range where the dilation does not affect the measurement data much. However, those experimental approaches which ignored the dilation of polymer totally failed on the determination of accurate gas solubility data in polymer melt at high pressure where the density of gas and the dilation of polymer both increased and became a significant factor on the solubility measurement.

Several methods have been proposed to consider the dilation effect during the solubility determination. At lower temperature (below melting temperature), usually the gas sorption and dilation of polymer are investigated at the same time. Afterwards, the sorption data was corrected with the measurement of dilation of polymer [164-166]. This approach is applicable to the
sorption study of gas in polymer at low temperature (below melting temperature), where the measurement on dilation of polymer can be achieved. More recently, Handa etc. proposed that the dilation of polymer due to the gas sorption could be mathematically predicted based on the total amount of gas dissolved in polymer and the molar volume of the gas in the polymer [167]. This approach is lack of theoretical support when the high pressure gas is applied, because it assumed the dissolved gas was the only factor to the dilation of polymer.

Very recently, a theoretical approach was proposed to predict the dilation of polymer which is required for the correction on the experimentally measurement sorption data. The theoretical correction/compensation was based SL EOS. It is the first time that a thermodynamic model is applied in the swollen polymer system. Based on this newly proposed method, Sato et al. [127-130, 133, 168-171] investigated the solubilities of HFC-134a, HCFC-142b, and HFC-152a in polystyrene and the solubilities of CO$_2$ in PS, PPO and PPO/PS blends, biodegradable polymer (PBS), PP and HDPE. Ohshima et al. also used an MSB to determine the solubility of CO$_2$ in low density polyethylene (LDPE), HDPE, PP, PS, ethylene(ethylacrylate) copolymer (EEA), LDPE + titanium dioxide (TiO$_2$) composite, and polypropylene + clay nanocomposites [134, 172-174]. They also used the SL-EOS to calculate the swollen volume of the polymer + gas solution for various concentrations of gas.

In our group, Li et al. also worked extensively on measuring the solubilities of various blowing agents in polymer melts [175-183]. They measured the solubility of CO$_2$ and N$_2$ in PS, PP, HDPE, and polylactic acid (PLA) by using the MSB. They also could not accurately determine blowing agent solubility due to a lack of polymer melt volume swollen experimental data by gas dissolution. Consequently, they too had to rely on equations of state (EOS), such as the Simha-Somcynsky (SS) or Sanchez-Lacombe (SL) EOS with no verified validity, to estimate the swollen volume. They found that the effect of swelling on solubility was more conspicuous at
a higher pressure. This was due to increased buoyancy with a higher gas density and the higher swollen volume. They also measured the solubility of HFC134a, HFC152a, and HFC134a + HFC152a blends in PS. They proposed a ternary model for the gas blends + polymer system and determined the solubility pressure to maintain a specific amount and composition of the blends in the PS melt [176]. To study phase equilibria and to determine gas solubility, they applied the following three equations of state to a linear-PP + CO₂ system: SL, SS, and the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) [136]. It was found that the interaction parameter in the SL strongly depends on temperature, whereas with the SS and the PC-SAFT, interaction parameters are weak temperature functions. In addition, they noted that the swelling ratios determined by using various equations of state differed from each other and that consequently their solubilities also differed. Since the validity of using these equations of state for predicting the swollen volume was not verified for any polymer + gas mixtures, it was not clear which of them accurately predicted swelling and/or solubility. Li et al. indicated that most published solubility data at elevated pressures might not be accurate and that, therefore, there was a need to first measure the swollen volume to find out which EOS can accurately predict the swollen volume.

2.5.3 Thermodynamic Approaches (Theoretical Approaches)

The solubility of gases in polymers also could be measured theoretically using various EOS. There are so many EOS used to determine the solubility of gases in polymer; SL-EOS and SS-EOS are very widely used among them. Since there are so many EOS, only SL-EOS and SS-EOS will be discussed in more details for this research.

Besides the experimental approaches discussed in the previous sections, many researchers had applied the thermodynamic models to correlate the experimentally measured solubility data [122, 124, 184] or to predict the solubility data using Equation 2-3 [130, 132, 133,
171, 185, 186]. As illustrated in section, the Equation 2-3 is the primary criterion for equilibrium and the thermodynamic fundamental basis for formulating problems in phase-equilibrium system.

Therefore, in the solubility study of a polymer/gas system, Equation 2-3 is simplified as Equation 2-61.

\[ \mu^g_{BA} = \mu^1_{BA} \]  

2-61

where \( \mu^g_{BA} \) is the chemical potential of gas component in vapor phase at system temperature and pressure; \( \mu^1_{BA} \) is the chemical potential of gas component dissolved in polymer melt. The schematic for the thermodynamic constitution for the solubility study in the above described system is illustrated as below, Figure 2.1.

**2.5.3.1 Flory-Huggins Based Thermodynamic Approaches**

The first thermodynamic model applied to theoretically investigate the solubility of gas in polymer is the Flory-Huggins theory [46, 187]. According to Flory-Huggins theory, the activity \( \alpha_i \) of the gas (solute) dissolved in polymer melt can be determined using Equation 2-62.

\[ \ln \alpha_1 = \ln \phi_1 + \phi_2 + \chi \phi_2^2 \]  

2-62

where \( \phi_1 \) and \( \phi_2 \) are the volume fractions of solute and solvent respectively, and \( \chi \) is the Flory-Huggins coefficient.

In addition, the activity of gas (solute) dissolved in polymer melt is determined by the ratio between the fugacity of gas in vapor phase (at system temperature and pressure), \( f_1 \), and the gas standard state fugacity (pure solute liquid at system temperature), \( f_1^0 \).

\[ \ln \alpha_1 = \ln \left( \frac{f_1}{f_1^0} \right) \]  

2-63

The Flory-Huggins theory represents data reasonably well over limited concentration ranges. However, the Flory-Huggins theory failed to accurately reproduce isothermal data over
wide concentration ranges due to the fact that Flory-Huggins theory ignores volumetric changes caused by pressure, temperature and mixing [188]. Another challenge associated with the use of Flory-Huggins theory is that it is difficult to define the standard state for supercritical fluids when system temperature and pressure go beyond the critical condition.

2.5.3.2 SL-EOS

Motivated to improve the Flory-Huggins theory on the solubility study, Panayiotou et al. [89-92] proposed formalism based on fluid-lattice theory for multicomponent fluid mixtures system. Then, the solubility of gas in polymer can be theoretically calculated based on the proposed SL EOS [42, 85] approach. Since SL EOS is a quantitative theory applicable to gaseous as well as to the liquid state, the chemical potential of gaseous phase can be calculated in a same as that in liquid phase (polymer/gas mixture phase) avoiding the definition of the standard state for gas which is required in Flory-Huggins theory. In order to solve the equilibrium equation Equation 2-61, the following equations were derived for the calculation of chemical potential of pure gas (at temperature T and pressure P) \( \mu_{BA}^g \), and chemical potential of gas dissolved in polymer \( \mu_{BA}^1 \) (at temperature T and pressure P),

\[
\mu_{BA}^g = r_1^0 RT \left[ -\frac{\rho_1}{\bar{\rho}_1} + \frac{P_1}{\bar{\rho}_1 T_1} + \left( \frac{1}{\rho_1} - 1 \right) \ln (1 - \bar{\rho}_1) + \frac{1}{r_1^0} \ln \bar{\rho}_1 \right]
\]

\[
\mu_{BA}^1 = RT \left[ \ln \phi_1 + \left( 1 - \frac{\rho_1}{\phi_1} \right) \phi_2 + r_1^0 \bar{\rho} \left( \frac{P_1 + P_2 - 2P_1^*}{P_1^* T_1^*} \right) \phi_2^2 \right] + r_1^0 RT \left[ -\frac{\rho_1}{\phi_1} + \frac{P_1}{\bar{\rho}_1 T_1} + \left( \frac{1}{\rho_1} - 1 \right) \ln (1 - \bar{\rho}_1) + \frac{1}{r_1^0} \ln \bar{\rho}_1 \right]
\]

Where subscript 1 is for gas and 2 is for polymer; \( \bar{P}, \bar{\rho}, \) and \( \bar{T} \) are reduced pressure, density and temperature; \( \phi_1 \) and \( \phi_2 \) are the volume fractions; \( P^*, \nu^* \) and \( T^* \) are the characteristic parameters. It was found that the theoretical calculation result was much dependent on the value of \( k_{12} \), binary interaction parameter required in SL EOS for the constitution of binary components mixture system. However, \( k_{12} \) cannot be determined from the theory alone.
Typically, $k_{ij}$ is obtained from the best fit of experimental solubility data [128-131]. Sato et al. concentrated on measuring the solubilities and diffusivities of CO$_2$, N$_2$, hydrofluorocarbons (HFC-134a, HFC-152a), hydrochlorofluorocarbon (HCFC-142b), n-butane, and isobutane in polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), polyvinyl acetate (PVAc), biodegradable polymer, polyphenylene oxide (PPO), and PPO + PS blends at various melt temperatures and pressures by using the pressure-decay method or the gravimetric method with a magnetic suspension balance (MSB) [126-133, 168-171, 189, 190]. However, to estimate the swollen volume due to the dissolved gas, they had to rely on the Sanchez-Lacombe equation of state (SL-EOS), which is used to determine solubility with the pressure-decay or gravimetric methods. Ohshima et al. also used an MSB to determine the solubility of CO$_2$ in low-density polyethylene (LDPE), HDPE, PP, PS, ethylene + ethylacrylate copolymer (EEA), LDPE + titanium dioxide (TiO$_2$) composite, and polypropylene + clay nanocomposites [134, 172, 174]. They also used SL EOS to determine the solubility theoretically.

2.5.3.3 SS-EOS

After developing the EOS in 1969, Simha et al. applied the lattice-hole theory (SS-EOS) to study the gas solubility in polymer melt. As usual, the chemical potential of pure gas (at temperature T and pressure P) $\mu_{BA}^p$ and chemical potential of gas dissolved in polymer (at temperature T and pressure P) $\mu_{BA}$ are first derived based on SS EOS [38, 40, 191]. Particularly, Equation. 2-66 was used to calculate the $\mu_{BA}^p$. [38, 40, 191].

$$\mu_{BA}^p = \Delta \mu + \mu_0 = \int_v^{\infty} \left( P - \frac{RT}{V} \right) dV + (PV - RT) + RT \ln \left( \frac{P}{k_B T} \left( \frac{N_A h^2}{2 \pi m_v RT} \right)^{\frac{3}{2}} \right)$$ 2-66

where $\Delta \mu$ is the chemical potential difference between the real gas and the ideal gas. An accurate real gas equation of state is typically required to solve integral part of Equation 2-66 and to get $\mu_{BA}^p$ for pure gas in vapor phase.
In the meantime, according to classical thermodynamic theory for mixtures, Equation 2-67 was used to calculate the $\mu_{BA}^1$, which is the chemical potential of gas dissolved in polymer melt [38, 40, 191].

$$\mu_{BA}^1 = G_m + x_2 \frac{\partial G_m}{\partial x_1}$$  \hspace{1cm} 2-67

Where $G_m$ is the molar free energy of the polymer/gas mixture determined in Equation 2-68 [38, 40, 191].

$$\frac{G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \ln \left( \frac{Y}{S} \right) + S \frac{1-y}{y} \ln (1-y) + (s-1) \ln \frac{e}{z-1}$$  \hspace{1cm} 2-68

$$c \left[ \ln \left( \frac{\nu^{*}(1-\eta)^3}{Q} \right) - \frac{3}{2} c_1 x_1 \ln \frac{2 \pi m_1 RT}{(N_a h)^2} - \frac{3}{2} c_2 x_2 \ln \frac{2 \pi m_2 RT}{(N_a h)^2} + \frac{cyQ^2(1.011Q^2-2.409)}{2T} + c[(1-\eta)^{-1} + \frac{2yQ^2(1.011Q^2-1.2045)}{2T}] \right]$$

Many researchers used SS-EOS to measure the solubility of gases in polymers theoretically. Simha at el. measured the solubility of argon, methane and carbon dioxide in two polymers, polyethylene and cis-polybutadiene [40]. In our group, Li et al. also used SS-EOS to measure the theoretical solubility of CO$_2$ and N$_2$ in both linear and branched Polypropylene (PP) [181]. They also used SS-EOS to predict the solubility of CO$_2$ and N$_2$ in PS and polylactic acid (PLA) by using the MSB [8, 135, 175].

### 2.6 Review of Solubility of Gases in Polymeric Nanocomposites (PNC)

Use of nanoparticles (especially organoclay) as a nucleating agent to increase the cell density ($10^2$-$10^3$) in microcellular foaming is a common practice [192, 193]. However, very few studies on solubility have been conducted in this area [134, 194]. Moreover, the $PVT$ behaviors of the PNC/gas mixture that would govern the solubility of PNC are still unknown. Recently, Utracki and Simha [53, 54] have investigated the $PVT$ behavior of PP-based and PA-based PNC
systems. They eventually developed a model to describe the $PVT$ behaviors of those nanocomposites in consideration of the soft section (neat polymer) and the hard section (the nanoparticles wrapped with solidified polymer). However, the $PVT$ behaviors of nanocomposites with dissolved gas would be even more complex and have not been investigated. Since the amount of swelling with dissolved gas is required to determine the solubility [195], the interaction of the polymer and the gas molecules in the presence of nanoparticles should be studied. In this study, our efforts are focused on the effects of the nanoparticles on the $PVT$ and solubility behaviors.

### 2.7 Summary and Critical Analysis

Solubility is one of the most important parameters in the design and optimization of a foam extrusion process, since it plays a significant role in almost all stages of the foaming process including gas dissolution, bubble nucleation/growth and cell structure stabilization. The continuing theoretical development of the thermodynamics of the liquid state is widely known. It seems worthwhile to briefly review the earlier theoretical approaches that have led to the modern theories used in the present work. The purpose of most theories of the liquid state is to devise methods for interpreting the macroscopic behavior of liquid systems in terms of their microscopic properties.

Numerous theoretical equations of state for polymer liquids have been developed. These, at the minimum, provide accurate fitting functions with which to analyze $PVT$ data. The equations also provide valuable thermodynamic information and can be used to predict the properties of polymer blends and solutions. It seems that nearly all equations of state for polymer liquids provide a reasonably good fit to $PVT$ data, especially at low pressures. However, there is a major difference between the various equations in their abilities to fit $PVT$ data over a wide range of pressure and to predict thermodynamic properties of polymer blends and solutions,
particularly phase separation behavior. Most equations require an empirical interaction parameter, determined from at least one experimental data point, in order to describe accurately the phase behavior. This review is concerned only with the equations' \( PVT \) fitting capabilities for polymer liquids and gas mixture.

There are numerous equations of state in the literature which propose to describe polymer liquids. Among these, SL, SS and SAFT have been widely used [38, 93, 191, 196]. We examined the assumptions on which these various equations are based and compared them using \( PVT \) data for a wide range of polymer data. We demonstrated that those theories based on the hole model (SS-EOS) best describe the polymer liquid state.
3.1 Introduction

It is obvious from the earlier chapter 1 and 2, the information about the solubility of blowing agents (gases) in polymers are very important for polymer processing or foam industries. For effective optimization of thermoplastic foams processing, accurate solubility data is necessary. Last fifty years, several researchers measured the solubility of various gases in polymers based on a variety of experimental approaches. Thermodynamic models based equations of state (EOS) had also been developed to predict solubility theoretically at the phase equilibrium condition. Among the EOS, SL-EOS [126-133, 168-171, 189, 190], SS-EOS [37, 39, 189] and SAFT EOS [43, 44] are mostly used EOS to predict solubility of gases in polymers. Since when gas goes into the polymer, polymers swell a lot especially at high pressure, several researchers also measured the solubility using experimental approach combined with theoretical swelling correction to determine the solubility more accurately. In this chapter, we have applied all these three approaches to determine the solubility of gases in semi-crystalline polymers and have tried to verify EOS.

3.2 Methodology

3.2.1 Determination of Solubility of Gases in Polymers

There are basically three ways to determine the solubility of gases in polymers: (i) a fully experimental approach, (ii) a semi-empirical approach, and (iii) a theoretical approach based on EOS. All these approaches are applied in this works and compared both the semi-empirical and theoretical approaches with experimental approach to determine which EOS predicts better solubility.
3.2.1.1 Experimental Approach (Magnetic Suspension Balance (MSB) Combined with a PVT Apparatus)

3.2.1.1.1 Magnetic Suspension Balance (MSB)

A gravimetric method, the magnetic suspension balance from Rubotherm GmbH, Germany, was used to measure the sorption of gas in polymer melts. A schematic of the magnetic suspension balance system is shown in Figure 3.1. A detailed description of the experimental apparatus and procedures is available in previous publications [124, 186, 195, 197], and a brief procedure is described below.

Figure 3.1 Schematic of overall magnetic suspension balance system [8]

1-Electromagnet; 2-Permanent magnet; 3-Position sensor; 4-Coupling device; 5-Sample holder

Before beginning the sorption experiment, a precisely weighed polymer sample of mass, $m_{\text{sample}}$, was placed in the sealed absorption chamber, degassed in the vacuum, and preheated to a designated temperature. The balance readout at vacuum ($P \approx 0$) and temperature ($T$) for the polymer sample without any dissolved gas was recorded as $m_{\text{sample}}(0,T)$; this value reflected the weight of the sample at vacuum. High-pressure gas was subsequently charged into the chamber,
and sorption occurred. When the saturation stage was reached, sorption stopped and the weight readout from the balance was recorded as $m_{\text{sample}}(P, T)$ at pressure ($P$) and temperature ($T$). Hence, weight gain from the dissolved gas in the polymer, $m_{\text{gas}}$, was calculated as follows in Equation 3-1:

$$m_{\text{gas}} = m_{\text{sample}}(P, T) - m_{\text{sample}}(0, T) + \rho_{\text{gas}}(V_B + V_P + V_S)$$  \hspace{1cm} 3-1

where $\rho_{\text{gas}}$ is the density of the gas inside the chamber at temperature $T$ and pressure $P$, which can be measured in situ by the magnetic suspension balance; $V_B$, $V_P$, and $V_S$ are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices), the volume of pure polymer at temperature $T$ and pressure $P$, and the swollen volume of the polymer due to gas dissolution, respectively. $V_B$ is usually determined in advance with a blank experiment. $V_P$ typically can be determined using the Tait equation of state [160, 161] from Gnomix or PVT apparatus data for each polymer.

By ignoring the polymer’s swollen volume ($V_S$) in Equation 3-1, the measured weight gain of a polymer with mass, $m_{\text{sample}}$ at room temperature and pressure, can be transformed to the apparent solubility of Equation 3-2, $X_{\text{apparent}}$, which is less than the actual solubility:

$$X_{\text{apparent}} = \frac{m_{\text{sample}}(P, T) - m_{\text{sample}}(0, T) + \rho_{\text{gas}}(V_B + V_P)}{m_{\text{sample}}}$$  \hspace{1cm} 3-2

The $X_{\text{apparent}}$ was calculated using the magnetic suspension balance. As shown in Eqs. 3-1 and 3-2, it is impossible to accurately measure gas solubility in the polymer melt without considering the swollen volume ($V_S$). To accurately determine solubility, correction of the buoyancy effect on the apparent solubility data is essential, especially in a high-pressure condition where gas density (i.e., $\rho_{\text{gas}}$) is high and the swollen volume (i.e., $V_S$) is large. The working principle of the MSB is illustrated in Figure 3.2 with more details. The real setup of the MSB is shown in Figure 3.3.
3.2.1.1.2 Determination of Swollen Volume Using PVT Apparatus

Gas solubility can also be fully determined by empirical measurements. Instead of predicting the $V_s$ in Equation 3-1 using an EOS, it can be directly measured using a high-pressure, high-temperature cell [183, 198, 199]. The schematic of the experimental set-up of the PVT apparatus is illustrated in Figure 3.4. Details of the apparatus and procedure can be found in our previous work [183, 198, 199]. It is assumed that the polymer pendant or sessile drop is axisymmetric to
start with, which means the droplet profile is symmetrical with its vertical centerline. At the beginning of each experiment, the camera parameters, such as the working distance relative to the drop sample and the image contrast through the optical lens, were adjusted for maximum zoom. At the same time, care was taken to ensure the best image quality at the boundary. A calibration was then made to determine the pixel size in x and y orientation, with regard to the XY stage movement. Since the unit step length of the stage was known, calibration determined the size of the pixel’s metric length based on the stage’s movement. This part of the procedure was crucial because it provided the conversion factor between the image pixel size and the real drop’s metric dimension during image reconstruction. It also helped to correct any potential optical distortion.

When the image reconstruction is complete, the precise edge detection algorithm is used to detect the drop boundary and to generate the edge pixel coordinates. The Canny edge detector [200], which is based on the first derivative and defines the detection and localization criteria of a class of edges, is the most successful subpixel edge detector. It is used to identify boundary profile coordinates. To improve the accuracy of drop profile coordinates, repeated points (i.e., a pixel with the same grey-levels at one location) are averaged into distinctive data
Figure 3.4 Working principle of the *in situ* visualization system [53]

Figure 3.5 PVT Apparatus [53]

1-XY Stage, 2-CCD Camera, 3-Vibration free Table, 4- Visualization Chamber, 5-Rotational Device, 6-Water Cooling, 7-Syringe Gas Pump 8-Light Source, 9-Blue filter, 10-Polarization filter, 11-Pressure Transducer
points \((x_i, x_j)\) using a smoothing technique. The drop profile could be represented using an \(f(x)\) notation after a spline fits through all the points.

The composite Simpson’s 1/3 method, which has superior and finer segments than the Trapezoidal rule, was selected from other numerical integration methods [201]. The trapezoidal rule for integration finds the area under the line connecting the endpoints of a panel; whereas Simpson’s rule finds the area under the parabola which passes through three points on a curve. In other words, the rule approximates the curve by a series of parabolic arcs and the area under the parabolas is approximately the area under the curve. However, in most of cases, the function which needs to be integrated may not be smooth over the entire interval. This may be caused from the oscillatory function or the lack of derivatives at certain points. In such cases, Simpson's rule may give very poor results. One of the best ways to resolve this problem is by breaking up the interval into a number of small subintervals. Simpson's rule is then applied to each subinterval, with the results being summed to produce an approximation for the integral over the entire interval. This approach is termed as composite Simpson's rule. Therefore, composite Simpson’s 1/3 rule was applied for integration to compute the final volume of the polymer + gas solution drop, and it takes the following form in Equations 3-3 and 3-4:

\[
I = \int_a^b f(x) \, dx = \frac{1}{3} h \left[ f(x_0) + 4 \sum_{i=1,3,5} f(x_i) + 2 \sum_{j=2,4,6} f(x_j) + f(x_n) \right]
\]

where \(h\) is the "step length" between the interval \([a, b]\), which is split up in subintervals \(n\) and given by:

\[
h = \frac{(b-a)}{n} = \frac{(x_n-x_1)}{n}
\]

For volume integration, Simpson’s 1/3 rule is expressed and approximated in Equations 3-5 to 3-8 in drop profile points as follows:
\[ V_{\text{total}} = \int_a^b \pi \times f(x)^2 \, dx \approx \frac{1}{3} \pi \times h \times \sum_{i,j}^N \left( R_{i,j}^2 + R_{i,j} \times r_{i,j+1} + r_{i,j+1}^2 \right) \]

where

\[ R_{i,j} = \frac{(x_{2N+1,i,j} - x_{i,j})}{2} \]

\[ r_{i,j+1} = \frac{(x_{2N+1,i,j+1} - x_{i,j+1})}{2} \]

\[ h = \frac{(x_j - x_i)}{N} \]

where \( V_{\text{total}} \) is the total volume of the drop; \( R_{i,j} \) is the radius of drop at \( j^{\text{th}} \) layer, \( r_{i,j+1} \) is radius of the drop at \( j+1^{\text{th}} \) layer; and \( f(x) \) represents the drop profile function. Also \( i = 1, 2, \ldots 2N \) (in \( x \)-direction) and \( j = 1, 2, \ldots N \) (in \( y \)-direction) and \( 2N \) is the total number of pixel points.

![Flowchart](image)

Figure 3.6 Flow chart of overall methodology for \( PVT \) measurement system[202]

The flowchart of overall methodology for \( PVT \) measurement system is shown in Figure 3.6. The volume swelling ratio, \( S_w \) (Equation 3-9), in this study was defined by comparing the
final equilibrium volume with the initial volume, which was calculated using the Tait equation as follows:

\[
S_w = \frac{V(T, P, t_{eq})}{V(T, P, t_{ini})} = \frac{V(T, P, t_{eq})}{m_{sample}v(T, P)}
\]

where \(V(T, P, t_{eq})\) is the measured equilibrium polymer + gas solution volume at temperature \(T\), pressure \(P\), and equilibrium time \(t_{eq}\); \(V(T, P, t_{ini})\) is the volume of the neat polymer sample calculated at temperature \(T\) and pressure \(P\) using the Tait equation which was derived from Gnomix apparatus data. Once \(V_S\) was determined, the experimental solubility of blowing agent (BA) was determined by using the \(V_S\) value in Equation 3-11 where \(X_{\text{apparent}}\) was determined by using the magnetic suspension balance (MSB).

After calculating the swelling ratio \(S_w\), the swollen volume \(V_s\) and solubility \((X_{\text{corrected}})\) was determined using the Eqs. 3-10 and 3-11 where \(V_p\) and \(v_p\) is the total and sp. Volume of polymer respectively.

\[
V_s = V_{mix} - V_p = (S_w - 1)V_p
\]

\[
X_{\text{corrected}} = X_{\text{apparent}} + \frac{\rho_{\text{gas}}V_S}{m_{sample}} = X_{\text{apparent}} + \rho_{\text{gas}}(S_w - 1)v_p
\]

### 3.2.1.1.3 Experimental Verification

The proposed reconstruction methodology was already verified in our previous publication by measuring the volume of a precision stainless steel sphere with a known volume and by comparing the specific volume data measured from this methodology and from the Gnomix method [185, 202]. Details can be referred to References [185, 202]. It was shown that the error involved in this \(PVT\) measurement is less than 2%. 

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3.2.1.4 Uncertainty Analysis

A magnetic suspension balance from Rubotherm GmbH, Germany was used to measure the solubility. The resolution of the balance is 10 µg with a relative error of less than 0.002 % of the measured value. The reproducibility (standard deviations) of the machine is ± 20 µg. Each experiment was conducted at least three times to obtain repeatability of the proposed data. Since the solubility is not a directly measured quantity, various factors contribute towards the precision of the solubility results. Uncertainty in the pressure measurement is ± 0.5 % of reading, and temperature was ± 0.1 K. There was some uncertainty of the solubility resulting from each experiment, and the maximum uncertainty was found to be less than ± 4 % with 95% level of confidence. This statistical analysis is suitable for small number of observation [203].

3.2.1.2 Semi-Empirical Approach

Gas solubility can also be determined by empirically measuring gas uptake and theoretically predicting swelling data. A gravimetric method, the magnetic suspension balance from Rubotherm GmbH, Germany, can be used to measure the sorption (\( X_{\text{apparent}} \)) of CO\(_2\) in polymer melts. Meanwhile, SS or SL EOS could be used to predict the swollen volume (\( V_s \)). Afterward, semi-empirical solubility could be determined by using the Equations 3-10 and 3-11. The more details of theoretical swelling are shown in the next section.

3.2.1.3 Theoretical Approach Based on EOS

In order to obtain reliable solubility data, the accurate swollen volume data is mandatory. However, due to lacking of experimental PVT apparatus of polymer/gas mixture, solubility of BA in polymers are determined theoretically using various EOS like SL, SS, so and so forth. With the proper construction of the thermodynamic models, the phases in equilibrium, which are the vapor phase and the polymer melt phase with dissolved gas, can be described accurately. Therefore, in order to determine the phase equilibrium, the thermodynamic model adopted in the
study should be applied to both vapor (single or pure component phase) and the polymer/gas solution phase (mixture phase). However, in order to apply the statistical thermodynamic models for multi-components system (polymer/gas mixture), a proper mixing rule should also be considered. The thermodynamic models based on SL EOS, SS EOS, and revised SS EOS are developed to study the phase equilibrium and PVT of polymer with dissolved gas in equilibrium. The details are described in the next following sections.

3.2.1.3.1 Theoretical Approach Based on SL-EOS

As described in chapter 2, the SL EOS scaling parameters of all the components (including polymer and gases) can be optimized from the thermodynamic properties for each of the components. The SL-EOS characteristic parameters for each component are characteristic pressure $p^*$ (MPa), characteristic bulk specific volume $V^*$ (cm$^3$/g), and characteristic temperature $T^*$ (K). In details, for volatile component, i.e. gases, the gas-liquid saturation curves up to the critical point are usually applied to extract the scaling parameters. The scaling parameters for various BAs are taken from literature. For polymer, the experimental PVT data from Gnomix machine could be used to extract the optimal SL EOS scaling parameters, with which the SL EOS yields the best PVT fitting to the experimental data. The scaling parameters for various polymers could also be found in literatures.

After extraction of the characteristic parameters, the pure component system can be described as usual. The molecular weight of the pure component is $M$, g/mol. It is considered that each molecule comprises $r$ mers (i.e., $r$ is the number of mer per molecule); $\varepsilon^*$ the total interaction energy per mole mers, J/mol; $v^*$ is the characteristic volume (close packed volume) of segment/mer, m$^3$/mol mer). Therefore, according to the SL-EOS all the characteristic parameters are rewritten as below,
\[ T^* = \frac{\varepsilon^*}{R} \quad P^* = \frac{\varepsilon^*}{T^*} \quad \rho^* = \frac{1}{v^*} = \frac{M}{r v^*} \quad \text{and} \quad r = \frac{M P^*}{R T^* \rho^*} \]

(3-12)

where \( \rho^* \) is characteristic density of bulk material (g/cm\(^3\)) and R is the ideal gas constant, 8.314 (J/K·mol). Therefore, the reduced properties are written as below,

\[ \tilde{P} = \frac{P}{P^*} = \frac{\rho v^*}{\varepsilon^*} \quad \text{and} \quad \tilde{T} = \frac{T}{T^*} = \frac{k_B T}{\varepsilon^*} \]

(3-13)

And the equation of state of the pure component system is written as usual

\[ \frac{\tilde{P} \tilde{v}}{\tilde{T}} = \frac{1}{r} \left[ 1 + \tilde{v} \ln \left( 1 - \frac{1}{\tilde{v}} \right) \right] - \frac{1}{\tilde{v} T} \]

(3-14)

The SL EOS was also extended to the multi component system. In our research, we are focusing on the binary system, which is the mixture of blowing agent (gas) and polymer melt in equilibrium. However, the proper mixing rule should be adopted to the binary system to generate the generalized SL EOS for the mixture system [42, 85, 204]. For the mixed SL EOS model, one reason that combining rules become necessary is that each pure component has its own unique mer volume \( v^* \), whereas in the mixture all mers are required to have the same average close-packed volume \( v^* \). There are two mixing rules during the development of the SL EOS for the mixture. (1) the mer volume \( v^* \) for each component (\( v_1^*, v_2^*, v_3^* \ldots v_i^* \)) modified so that in the mixture all mers have the same average mer volume \( v^* \) (2) the total number of mers in the mixture, i.e. \( r \), are kept constant during the adjustment of the mer volume for each component.

\( W_1 \) and \( W_2 \) are the mass fraction for each component in the binary mixture and \( W_1 + W_2 = 1 \). Therefore the concentration of mer for each individual component before mixing (\( \phi_1^0, \phi_2^0 \)) are defined as below,

\[ \phi_1^0 = \frac{r_1^0 N_1}{r_1^0 N_1 + r_2^0 N_2} = \frac{r_1^0 N_1}{r N} \quad \phi_2^0 = 1 - \phi_1^0 \]

(3-15)
where $N_1$ is the molecule number of component 1 in the mixture, which has the $r_1^0$ mers per each molecule before the mer volume adjustment (mixing) and $N_2$ is the molecule number of component 2 in the mixture, which has the $r_2^0$ mers per each molecule before the mer volume adjustment (mixing). The total number of mers in the binary mixture, therefore is defined by

$$r = x_1 r_1 + x_2 r_2 = x_1 r_1^0 + x_2 r_2^0 = \frac{1}{\left(\frac{\phi_1}{r_1^0} + \frac{\phi_2}{r_2^0}\right)}$$  \hspace{1cm} 3-16

According to the mixing rules, the close-packed volume fraction for each component ($\phi_1, \phi_2$) is defined by

$$\phi_1 = \frac{w_1}{\rho_1 + \rho_2} \quad \text{and} \quad \phi_2 = \frac{w_2}{\rho_1 + \rho_2} = 1 - \phi_1$$  \hspace{1cm} 3-17

Then the average close-packed mer volume is

$$v^* = \phi_1 v_1^* + \phi_2 v_2^*$$  \hspace{1cm} 3-18

The characteristic pressure for the binary mixture is

$$P^* = \phi_1^2 P_1^* + \phi_2^2 P_2^* + \phi_1 \phi_2 P_{12}^*$$  \hspace{1cm} 3-19

$$P_{12}^* = (P_1^* P_2^*)^{0.5}(1 - k_{12})$$  \hspace{1cm} 3-20

Where $k_{12}$ is the interaction parameter between component 1 and 2.

And after obtaining the characteristic parameters for the mixture, the chemical potential for the gas component (component 1) in both phases (using Equation 2-3) were obtained by Equations 3-21 and 3-22.

$$\mu_1^\theta = r_1^0 RT \left[ -\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{\rho}_1}{\tilde{T}_1} \frac{1}{\tilde{\rho}_1 - 1} \right] \ln(1 - \tilde{\rho}_1) + \frac{1}{r_1^0} \ln \tilde{\rho}_1$$  \hspace{1cm} 3-21
\[ \mu_i = RT \left[ \ln \Phi_1 + \left(1 - \frac{r_1}{r_2} \right) \Phi_2 + \Phi_2 r_1^0 \rho \frac{P_{1^*} + P_2^* - 2 P_{1^2}}{P_{1^*} T_{1^*}} \right] + r_1^0 RT \left[ - \frac{\tilde{\rho}_1}{T_{1^*}} + \frac{\tilde{\rho}_1}{\tilde{\rho}_{1^*} T_{1^*}} \right] + \left( \frac{1}{\tilde{\rho}_1} - 1 \right) \ln(1 - \tilde{\rho}_1) + \frac{1}{r_1^0} \ln \tilde{\rho} \right] \]

3.2.1.3.2 Theoretical Approach Based on SS-EOS

Lattice-hole theory in the formulation of Simha and Somcynsky (SS) was also employed to compute the free energy of mixing and the chemical potential of the dissolved gas. As discussed in chapter 2, according to the SS theory, the polymer segment sizes should be adjusted in such a way that the close-packed molar volumes of the polymer segments (mers) match those of the gas molecules [40]. Therefore, in accordance with the polymer/gas system we were studying, the new SS scaling parameters for polymers were obtained according to the BAs.

In a similar way to the SL EOS approach, the saturation curve for BAs and the PVT property for polymers are used for the extraction of the optimal characteristic parameters for them. According to the classical thermodynamic, the accurate PVT EOS for pure component (gas molecules in the vapor phase) is required to calculate the chemical potential or the fugacity. In this study the most accurate analytical EOS for gases, i.e., Wagner EOS [205, 206], is applied for the determination of chemical potential in vapor phase. After the extraction of the characteristic parameters for each component, the SS EOS can be applied to the multicomponent system, i.e. binary mixture system (polymer/gas) in this study. For understand each component, all the parameters are listed in nomenclature.

The molar fractions \(x_i\) of each component in the binary mixture, site fractions \(X_i\), average total number of mers \(s_i\) per molecule, the average external degrees per molecule \(c\), average q per molecule, average mer molecular weight \(m\) for the binary mixture of each component in the binary mixture, the average characteristic volume of mer \(v^*\), and the average characteristic interaction energy of mer \(\varepsilon^*\) are given by the following equations:
After obtaining the characteristic parameters for the mixture, the equation of state of the binary mixture system are written as two coupled equations as below

\[
x_1 = \frac{N_1}{N_1 + N_2} = 1 - x_2
\]

\[
X_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} = 1 - X_2
\]

\[
s = x_1 s_1 + x_2 s_2
\]

\[
c = x_1 c_1 + x_2 c_2
\]

\[
q = x_1 q_1 + x_2 q_2
\]

\[
m = \frac{x_1 s_1 m_1 + x_2 s_2 m_2}{x_1 s_1 + x_2 s_2}
\]

\[
v^* = \left( \frac{X_1^2 \varepsilon_{12}^4 v_1^{4} + 2X_1 (1-X_1) \varepsilon_{12}^4 v_{12}^{4} + (1-X_1)^2 \varepsilon_{12}^4 v_{22}^{4}}{X_1^2 \varepsilon_{1}^* v_{12}^{4} + 2X_1 (1-X_1) \varepsilon_{12}^* v_{12}^{4} + (1-X_1)^2 \varepsilon_{22}^* v_{22}^{4}} \right)^\frac{1}{2}
\]

\[
\varepsilon^* = \left( \frac{X_1^2 \varepsilon_{12}^4 v_1^{2} + 2X_1 (1-X_1) \varepsilon_{12}^4 v_{12}^{2} + (1-X_1)^2 \varepsilon_{12}^4 v_{22}^{2}}{X_1^2 \varepsilon_{1}^* v_{12}^{2} + 2X_1 (1-X_1) \varepsilon_{12}^* v_{12}^{2} + (1-X_1)^2 \varepsilon_{22}^* v_{22}^{2}} \right)^\frac{2}{2}
\]

where \( \varepsilon_{12} = \delta_{\varepsilon} (\varepsilon_{1}^* \varepsilon_{2}^*)^{1/2} \) and \( v_{12}^* = \delta_{v} \left( v_{1}^{*1/3} + v_{2}^{*1/3} \right)^3 \)

Finally chemical potential of gas (component 1) in gas and gas in polymer are calculated using the following equations:

\[
\frac{\bar{p} \bar{v}}{\bar{T}} = (1-\eta)^{-1} + \frac{2y Q^2(1.011Q^2 - 1.2045)}{\bar{T}}
\]

\[
\left( \frac{s}{3c} \right) \left[ \frac{s - 1}{s} + \frac{\ln(1-y)}{y} \right] = \frac{\eta - \frac{1}{3}}{1 - \eta} + \frac{y}{6T} Q^2(2.409 - 3.033Q^2)
\]

where y is the occupied site fraction; Q = \((y \bar{V})^{-1}\); \( \eta = 2^{-1/6} y Q^{1/3} \)
\[
\mu_1^g = \Delta \mu + \mu_0 = \int_{V}^{\infty} \left( P - \frac{RT}{V} \right) dV + (PV - RT) + RT \ln \left( \frac{P}{k_B T} \left( \frac{N_a h^2}{2 \pi m_1 RT} \right)^{3/2} \right) \quad 3-34
\]

\[
\mu_1^l = G_m + x_2 \frac{\partial G_m}{\partial x_1} \quad 3-35
\]

where \( G_m \) is the molar free energy of the polymer/gas mixture determined in Equation \( 2-68 \) \([38, 40, 191]\).

\[
\frac{G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \ln \left( \frac{Y}{S} \right) + S \frac{1-y}{y} \ln(1-y) + (s-1) \ln \left( \frac{e}{z-1} \right) - 3-36
\]

\[
c \left[ \ln \left( \frac{v^*(1-\eta)^3}{Q} \right) \right] - \frac{3}{2} c_1 x_1 \ln \left( \frac{2 \pi m_1 RT}{(N_a h)^2} \right) - \frac{3}{2} c_2 x_2 \ln \left( \frac{2 \pi m_2 RT}{(N_a h)^2} \right) + \\
\frac{c y Q^2 (1.011 Q^2 - 2.449)}{2T} + c [(1-\eta)^{-1} + \frac{2y Q^2 (1.011 Q^2 - 1.2045)}{2T}]
\]

### 3.3 Modeling

We propose a general approach that combines the experimental solubility measurement and the thermodynamic models. Firstly, a gravimetric method is carried out to experimentally measure the gas sorption in a polymer melt (apparent solubility, \( X_{\text{apparent}} \)). Secondly, the SS and SL-EOS are applied to calculate the phase equilibrium (theoretical solubility, \( X_{\text{theory}} \)) and the swollen volume of polymer, \( V_s \). Thirdly, the theoretically predicted swollen volume, \( V_s \) can be used to complete the correction on the apparent solubility, \( X_{\text{apparent}} \), and then to obtain the actual solubility or corrected solubility, \( X_{\text{corrected}} \).

It is presumed that with the proper constitution of thermodynamic models which are applicable to pure polymer or polymer/gas mixture system, it should be possible to theoretically predict both the gas solubility in polymer melt (phase equilibrium) and the swollen volume of polymer with dissolved gas accurately. Therefore, the optimum interaction parameters for the
thermodynamic model are obtained in such way that the deviation between $X_{\text{corrected}}$ and $X_{\text{theory}}$ is minimized. It was observed that the interaction parameter for SL-EOS is temperature dependant where as for SS-EOS is independent of temperature[124, 195].

![Flow chart of the proposed approach for solubility study](image)

**Figure 3.7 Flow chart of the proposed approach for solubility study**

### 3.4 Comparison Between SL and SS EOS

Flory-Huggins theory [67] has played a central role in our understanding of the thermodynamics of polymer-solvent and polymer-polymer mixing. However, this theory disregards of changes in volume and local disorder with composition and fails to reflect changes in the liquid structure, the accounting of which is necessary for determining accurate solution
properties. The SS EOS model [38, 76-78] considers a lattice of sites, each of which capable of accommodating either a small molecule or a chain segment. Also, as with the lattice fluid theory, the hole theory adopted an improvement of the cell model for the liquid state by the introduction of vacancies in the lattice (hole \( h=1-y; y \) is the occupied site fraction), which describes the major part of the thermal expansion; however, changes in the cell volume, which have a non-negligible influence on the thermodynamic properties, are also allowed.

The Simha-Somcynsky lattice-hole theory describes an amorphous assembly of chain molecules on a lattice with sites occupied by chain segments. In addition, to simulate molecular disorder, there is a fraction \( h \) of vacancies, which is a type of free volume quantity. The configurational thermodynamic properties, such as the \( PVTC \) (EOS) relations or the cohesive energy density, are then characterized by three quantities, i.e., the maximum attraction, \( \varepsilon^* \), between a pair of chain segments, the corresponding segmental repulsion volume, \( v^* \), and the number \( 3c \) of volume-dependent, external degrees of freedom. In terms of these quantities and the number \( s \) of segments per chain, the three characteristic pressure temperature, and volume parameters can be defined as

\[
P^* = \frac{zq\varepsilon^*}{sv^*} \quad T^* = \frac{zq\varepsilon^*}{Rc} \quad \text{and} \quad V^* = \frac{v^*}{M_s}
\]

3-37

with \( M_s \) the molar segmental mass, \( zq = s(z - 2) + 2 \), the number of interchain contacts in a lattice of coordination number \( z = 12 \), and \( R \) the gas constant. The variables of state, \( P, T, V \), are then scaled by \( P^*, T^*, V^* \), to define a universal, reduced \( \tilde{P} - \tilde{V} - \tilde{T} \) surface, common to all liquids. Provided the theory is quantitatively successful, a superposition of experimental and theoretical lines yields the scaling parameters and thus the characteristic quantities defined in Equation 3-37.

The S-S theory yields a reduced free energy function, \( \tilde{F} \), as

\[
\tilde{F} = \tilde{F}[\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T})]
\]

3-38
According to Equation 3-38, $\bar{F}$ depends on reduced volume, $\bar{V}$, reduced temperature, $\bar{T}$, and the hole fraction $h$, which in turn varies with $\bar{V}$ and $\bar{T}$. The latter dependence is obtained by minimizing the free energy at a specified volume and temperature. For the binary mixture system (polymer/gas) interaction parameters $\delta_e$ and $\delta_v$ are used to minimize the theoretical and corrected solubility, and they are most of time insensitive to temperature.

In SL-EOS total cell volume is kept constant. In the lattice fluid model the lattice size is fixed, which implies that the volume increases in this model by an increase in the number of vacant lattice sites. The increase in entropy of the system is modeled by the behavior of the density of vacant lattice sites. For the binary mixture system (polymer/gas) interaction parameters $k_{12}$ is used to minimize the theoretical and corrected solubility, and they are most of time sensitive to temperature.

In the lattice fluid model the lattice size is fixed, which implies that the volume increases in this model by an increase in the number of vacant lattice sites. Hole models (SS-EOS) of polymer liquids combine two methods for incorporating compressibility into the lattice model (SL-EOS). The first method is to include lattice vacancies (hole) and the second is to vary the cell volume (where SL assume fixed). It is believed that since SS-EOS uses more molecular information of both gas and polymers than SL-EOS and incorporates compressibility into SL, it might be able to predict better than SL-EOS.

3.5 Summary

The three approaches have been discussed elaborately in this chapter: (i) a fully experimental approach, (ii) a semi-empirical approach, and (iii) a theoretical approach based on EOS. All these approaches were applied in this works and compared both the semi-empirical and theoretical approaches with experimental approach to determine which EOS predicts better
solubility. It is obvious that fully experimental approach to determine the solubility of BAs in polymer is the most accurate one. The solubilities of BAs in polymers were determined fully experimentally by using a MSB and the swellings were determined using in-house \textit{PVT} apparatus. Afterward, the rest two approaches were compared to verify the capability of EOS to predict the solubility as well as swollen volume accurately. It was observed that SS-EOS has better prediction capability compared to SL-EOS. In the rest of the chapters, the solubilities of BAs in polymers were determined according to these three approaches.
CHAPTER 4. COMPARISON OF EQUATION OF STATES (EOS)

4.1 Introduction

Plastics are the most commonly used materials in the world. In recent years, extensive research on advanced polymer composites has allowed the automotive industry to produce cost-saving and lightweight automotive parts. However, there has been a substantial increase in the price of crude oil, which is the main component of most plastics. Consequently, manufacturers who produce plastic products have made extensive efforts to reduce their material costs, which typically account for about 70% of their production costs. In this context, plastic foaming presents a solution to the continuous rise in the cost of plastic resins because it requires less material. Furthermore, with customized cellular morphology, the following areas of plastic foaming will be improved either individually or in combination with each other: mechanical properties[207], thermal insulation capacities [195], acoustical insulation capacities [208], optical properties[84].

In a polymer + gas system, solubility is the maximum amount of gas that can be dissolved in the polymer at a specific temperature and pressure without phase separation. Solubility data help to determine processing conditions that are required for such applications as polymer modification, viscosity measurement, blending, and microcellular foaming, where a single-phase solution is mandatory to avoid phase separation [209, 210]. In microcellular foaming, cell nucleation is accomplished by a rapid pressure drop that drastically reduces the solubility of the gas in the polymer. This pressure drop governs the final cell morphology and the foam’s properties[8]. Consequently, solubility data over a wide range of pressures and temperatures play an important role in processing microcellular foams [114]. Each of the
following physical properties of a polymer melt is important in processing and is affected by the amount of dissolved gases contained in the melt: the swollen volume, isothermal compressibility, thermal expansion coefficient [115], viscosity [116-118], and surface tension [209, 211, 212]. Since the 1950s, much effort has gone into the investigation of gas solubility in polymer melts. Research methods have included experimental measurements and theoretical thermodynamic calculations. Volumetric and gravimetric methods have been widely used to measure the solubility of different blowing agents (BAs) in polymers; however, neither method could solely determine solubility because of the polymer + gas mixture’s swelling phenomena, especially at high temperatures and pressures. To accurately measure solubility the swollen volume or density of the polymer + gas solution must be determined. Swelling due to gas dissolution in the polymer can be obtained by either an EOS prediction or by measurement [213].

Sato et al. have contributed greatly to the measurement of the solubility of various blowing agents, including supercritical fluids, in a number of foamable resins, and the foaming industry has effectively applied their data [126-133, 168, 171]. Sato et al. concentrated on measuring the solubilities and diffusivities of CO2, N2, hydrofluorocarbons (HFC-I34a, HFC-152a), hydrochlorofluorocarbon (HCFC-142b), n-butane, and isobutane in polystyrene (PS), in polypropylene (PP), high-density polyethylene (HDPE), polyvinyl acetate (PVAc), biodegradable polymer, polyphenylene oxide (PPO), and in PPO + PS blends at various melt temperatures and pressures by using the pressure-decay method or the gravimetric method with a magnetic suspension balance (MSB). However, to estimate the swollen volume due to the dissolved gas, they had to rely on the Sanchez–Lacombe equation of state (SL-EOS), which is used to determine solubility with the pressure-decay or gravimetric methods. Ohshima et al. also used a magnetic suspension balance (MSB) to determine the solubility of CO2 in low-density polyethylene (LDPE), HDPE, PP, PS, ethylene + ethylacrylate copolymer (EEA), LDPE +
titanium dioxide (TiO₂) composite, and PP + clay nanocomposites [134]. They also used the Sanchez–Lacombe equation of state (SL–EOS) to calculate the swollen volume of the polymer + gas solution for various concentrations of gas. Handa et al. also investigated the solubility of blowing agents in polymer and liquids [167, 214]. They measured the solubility and diffusivity of CO₂ in PS, filled polyvinylchloride (FPVC), unplasticized polyvinylchloride (UPVC), and syndiotactic polystyrene (sPS) by using the in situ gravimetric method (i.e., a Cahn D110 electronic microbalance). However, they did not consider the swollen volume caused by gas dissolution in the polymer. Due to a lack swelling data, most researchers used an equation of state, such as the SL–EOS, to predict the swelling that determines solubility. Since the validity of the SL–EOS has not been verified yet for the polymer + gas systems, solubility accuracy would be governed by the accuracy of the swollen volume, especially at elevated pressures.

Li et al. also worked extensively on measuring the solubilities of various blowing agents in polymer melts [8, 135, 136, 195, 197]. They measured the solubility of CO₂ and N₂ in PS, PP, HDPE, and polylactic acid (PLA) by using the MSB. They also could not accurately determine blowing agent solubility due to a lack of polymer melt volume swollen experimental data by gas dissolution. Consequently, they too had to rely on equations of state (EOS), such as the Simha–Somcynsky (SS) or Sanchez–Lacombe (SL) EOS with no verified validity, to estimate the swollen volume. They found that the effect of swelling on solubility was more conspicuous at a higher pressure. This was due to increased buoyancy with a higher gas density and the higher swollen volume. They also measured the solubility of HFC134a, HFC152a, and HFC134a + HFC152a blends in PS. They proposed a ternary model for the gas blends + polymer system, and determined the solubility pressure to maintain a specific amount and composition of the blends in the PS melt [195]. To study phase equilibria and to determine gas solubility, they applied the following three equations of state to a linear-PP + CO₂ system: Sanchez–Lacombe (SL), Simha–
Somcynsky (SS), and the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) [136]. It was found that the interaction parameter in the SL strongly depends on temperature, whereas with the SS and the PC-SAFT, interaction parameters are weak temperature functions. In addition, they noted that the swelling ratios determined by using various equations of state differed from each other, and that consequently their solubilities also differed. Since the validity of using these equations of state for predicting the swollen volume was not verified for any polymer + gas mixtures, it was not clear which of them accurately predicted swelling and/or solubility. Li et al. indicated that most published solubility data at elevated pressures might not be accurate, and, that therefore, there was a need to first measure the swollen volume to find out which EOS can accurately predict the swollen volume.

Recently, Funami et al. developed a new technique to measure the density of the polymer + gas mixture [122]. They modified the existing magnetic suspension balance (MSB) system and determined the density of the polymer + gas mixture directly by measuring the buoyancy force exerted on a platinum plate that was submerged in the polymer melt. They measured the densities of polyethylene glycol (PEG) + CO₂ and the polyethylene (PE) + CO₂ solutions above the melting temperature and at 0 to 15 MPa pressure, and the results were promising. However, their modified MSB is only suitable for low viscous polymers with very low molecular weight. Also, while changing the plate position, the dragging force generates unavoidable measurement errors, especially when the viscosity is high. Gendron et al. also tried to measure the solubility of a CO₂ + ethanol blend in PS at various pressures and temperatures using an ultrasonic instrument developed in their laboratory for both off-line and on-line measurement during the extrusion process [215]. They measured the degassing pressures (i.e., the pressure at which phase separation occurs) as a function of temperature by using an ultrasonic signal, and found parabolic shape curves. By comparing degassing pressures with MSB data from Sato et al. they concluded
that at high temperatures, the degassing pressures corresponded reasonably to the solubility data related to the CO\textsubscript{2} content. But since this solubility reflects the dynamic nature of the flow, the dynamic solubility (i.e., the gas solubility) in the oriented molecules, may be different from the static solubility. Xanthos and his co-workers measured the dynamic solubility of CO\textsubscript{2}, N\textsubscript{2}, and Ar in PS and poly(ethylene terephthalate) (PET) using their self-designed in-line optical window system[120, 121, 138]. They found that the solubility of CO\textsubscript{2} in PS decreases with increased throughput in the foaming process, and that solubility is independent of screw speed. They also found that data points deviated greatly from the published data in the low pressure range, and they speculated that this might have been caused by inhomogeneities in the temperature and gas concentration. But since cell nucleation may not occur easily at a low gas concentration (i.e., at a low pressure) the moment the cell nucleation was observed may not have corresponded to the pressure below the solubility pressure.

Many researchers have also tried to predict swelling phenomena either by measuring the sample’s change in lengths [120, 121, 138, 156, 165, 174, 216-220] or by \textit{in situ} visual observation of the interface position between the gas phase and the polymer melt system [118, 119, 199, 219, 221-225]. However, sample preparation to release internal stresses and to ensure isotropic behavior is somewhat complicated when measuring sample lengths. Moreover, since the sample shape changes above the glass transition temperature, it is not possible to determine length changes above this temperature. Tomasko and co-workers [226] also tried to measure the solubility of poly(methyl methacrylate) (PMMA) at (303 to 333) K by predicting swelling using an \textit{in situ} visualization system. They also determined solubility by measuring the mass loss of a polymer sample with regular geometry after removing it from the pressure cell and extrapolating it to zero time. However, this method is limited to a temperature below the glass transition temperature, and experimental solubility data at a high temperature and pressure are rare.
To our knowledge, no literature verifies that the equation of state approach determines the solubility of blowing agents in polymers, especially at high temperatures and pressures. A need, therefore, exists to completely experimentally measure swelling and solubility at higher temperatures and pressures, and to compare the results with various EOS approaches to predict the best EOS thermodynamic model. In this study, the solubilities of CO$_2$ and N$_2$ in semi-crystalline and amorphous polymers like linear and branched PP, LDPE, and PS were measured at a high temperature of up to 493 K and a high pressure of up to 31 MPa. Finally, experimental data were compared with semi-empirical and theoretical solubility data determined by using the SS and the SL equations of state for accuracy.

4.2 Experimental

4.2.1 Materials

In this study, Linear PP (DM 55) and branched PP (Daploy WB130HMS) were procured from Borealis, and LDPE (NOVAPOL 0522, with a density of 0.920 g/cm$^3$ and a melt flow index (MFI) of 4.5 g/10min (ASTM D 1238)) was procured from NOVA Chemicals, Calgary, Canada. PS (DOW Styron® 685D, $T_g$=381.4 K, $M_w$=3.39x10$^5$, $M_n$=1.96x10$^5$, MFI=1.5 g/10 min, density of 1.040 g/cm$^3$) was procured from the Dow Chemical Company. CO$_2$ (Coleman grade, 99.99% purity) and N$_2$ (99.99% purity) were received from Linde Gas Canada. All of these materials were used as received.

4.2.2 Experimental Procedure

The solubility measurement is performed in the following procedures:

STEP 1. A 3 mm thick disk of polymer sample (approximately 0.5 gram) was precisely weighed first and placed in the sample container.
STEP 2. The absorption chamber was sealed and preheated to a designated temperature by a Julabo TD-6 Heating Circulator, which was also used to precisely control the temperature of the chamber throughout the measuring process.

STEP 3. The sample was degassed in vacuum until the mass becomes stable. The reading of the balance at vacuum ($P = 0$) and temperature ($T$) was recorded as $m(0, T)$.

STEP 4. High pressure gas is then introduced into the sorption chamber and maintained at the desired pressure by a syringe pump (260D, ISCO). Hence the high pressure gas starts to permeate into the polymer sample.

STEP 5. Once the sample is saturated with gas (i.e., the mass of the polymer sample becomes stable, no weight change any more), the reading of the balance is recorded as $m(P, T)$, where $P$ is the saturation pressure and $T$ is the system temperature.

STEP 6. Finally, the amount of gas dissolved in the polymer, $m_{gas}$, can be calculated by using the following equation:

$$m_{gas} = m_{sample}(P,T) - m_{sample}(0,T) + \rho_{gas}(V_B + V_p + V_s) \quad 4-1$$

By ignoring the polymer’s swollen volume ($V_s$) in Equation 3-1, the measured weight gain of a polymer with mass, $m_{sample}$ at room temperature and pressure, can be transformed to the apparent solubility of Equation 3-2, $X_{apparent}$, which is less than the actual solubility:

$$X_{apparent} = \frac{m_{sample}(P,T) - m_{sample}(0,T) + \rho_{gas}(V_B + V_p)}{m_{sample}} \quad 4-2$$

Afterward, the swelling ratio ($S_w$) was measured by using a $PVT$ apparatus. Finally, the gas solubility ($X_{corrected}$) was determined by using the Eqs 3-10 and 3-11.

$$V_s = V_{mix} - V_p = (S_w - 1)V_p \quad 4-3$$

$$X_{corrected} = X_{apparent} + \frac{\rho_{gas}V_s}{m_{sample}} = X_{apparent} + \rho_{gas}(S_w - 1)V_p \quad 4-4$$
4.3 Swelling and Solubility Behaviors of PP in the Presence of CO₂

4.3.1 PVT Data for PP

The PVT data for pure linear and branched PP were obtained from Datapointlabs (Ithaca, NY) using Gnomix PVT Apparatus. Moldflow PVT equations were then derived based on the measurement data. The moldflow PVT equations are listed below for linear PP (Equation 4-5) and branched PP (Equation 4-6), respectively.

\[
v_{p, \text{pure}} = \left( \frac{7.46 \times 10^6}{6.45 \times 10^9 + P} + \frac{1.06 \times 10^2 \times T}{9.86 \times 10^7 + P} \right) \times 1000
\]

\[
v_{p, \text{pure}} = \left( \frac{6.485 \times 10^6}{5.773 \times 10^9 + P} + \frac{1.221 \times 10^2 \times T}{1.146 \times 10^8 + P} \right) \times 1000
\]

where the specific volume \( v_{p, \text{pure}} \) is in cc/g, the temperature \( T \) is in (°C) and pressure \( P \) is in (Pa).

Table 4-1 Scaling parameters of PP for SS-EOS and SL-EOS [181]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( P^*/\text{MPa} )</th>
<th>( V^*/(\text{cm}^3/\text{g}) )</th>
<th>( T^*/\text{K} )</th>
<th>( M_n/(\text{g/mole}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-EOS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear PP</td>
<td>536.0</td>
<td>1.2470</td>
<td>19,352</td>
<td>105,473</td>
</tr>
<tr>
<td>Branched PP</td>
<td>596.0</td>
<td>1.1975</td>
<td>15,907</td>
<td>122,395</td>
</tr>
<tr>
<td>CO₂</td>
<td>954.2</td>
<td>0.5860</td>
<td>2,960</td>
<td>44.01</td>
</tr>
<tr>
<td>SL-EOS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear PP</td>
<td>312.2</td>
<td>1.1563</td>
<td>679.5</td>
<td></td>
</tr>
<tr>
<td>Branched PP</td>
<td>384.6</td>
<td>1.1044</td>
<td>649.1</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>720.3</td>
<td>0.6329</td>
<td>208.9 + 0.459T</td>
<td></td>
</tr>
</tbody>
</table>
Furthermore, the PVT data of these pure materials (linear PP and branched PP) were used to derive the corresponding characteristic parameters: $P^*, V^*, T^*$ for both the SS-EOS and the SL-EOS. All the characteristic parameters are listed in Table 4-1.

**4.3.2 Swelling Behavior of PP in Presence of CO$_2$**

The PVT data of both linear and branched PP/CO$_2$ solutions was measured at (453 to 493) K temperature and at a pressure of up 31 MPa using a new PVT measurement apparatus. The effects of branching structures on PVT behaviors were examined by comparing the volume swelling results for linear and branched PP/CO$_2$ mixtures. In general, the volume swelling was found to increase as the pressure was increased, and the volume swelling decreased as the temperature was increased (Figure 4.1). It was surmised that, due to its branched structure, branched PP exhibited less swelling in comparison to linear PP. In addition to branching, polymer chain entanglement also contributed to a curbing of the volume expansion once the CO$_2$ gas filled the initial free volume for both mixtures at higher pressures.

![Figure 4.1 Comparison of swelling ratio, $S_w$][202]
4.3.3 Solubility of CO₂ in PP

The solubility of CO₂ in both linear and branched PP was completely experimentally measured at (453 to 493) K temperature and at a pressure of up 31 MPa. The maximum pressure and temperature that can be attained in the magnetic suspension balance chamber is 34.5 MPa and 523 K, respectively. All the experimental data are given in Tables 1 to 6 in the appendix section. Once the swelling ratio was measured by the PVT apparatus [124, 202], the empirical solubility was determined by using the magnetic suspension balance to measure the apparent solubility and by putting the value of the swollen volume into Equation 4-4. Figure 4.2 shows the solubility of CO₂ in linear and branched PP, respectively. It was observed that solubility increases as pressure increases, but that it decreases as temperature increases for both polymers. Other researchers have observed a similar trend [8, 127-133, 168, 173, 195, 197, 213].

When a polymer melt is subjected to a high-pressure gas, two competing mechanisms affect the specific volume of the polymer + gas mixture: (i) the hydrostatic pressure effect, and (ii) swelling due to gas absorption [198, 199]. Hydrostatic pressure acts to decrease the specific volume, as well as the free volume; whereas swelling helps to increase both of them. Usually swelling is more dominant when gas goes into the polymer. Dissolved CO₂ causes a plasticization effect that reduces viscosity. This increases chain mobility by increasing the free volume and reducing surface tension, both of which are critical microcellular foaming parameters. It was also noted that solubility is concave to the pressure axis. In other words, after a certain pressure, solubility didn’t increase linearly with increasing pressure. Rather, the solubility of CO₂ in both PP melts shows a leveling off trend above 31 MPa. Wissingner et al. [165, 166] and Rajendrain et al. [223] also observed a similar trend. Rajendrain at al. used the magnetic suspension balance to measure the solubility of CO₂ in PMMA at temperatures ranging from (323 to 353) K and at pressures of up to 25 MPa. They also measured the swollen volume.
Figure 4.2 Experimental solubility, $X$ (g-gas/g-polymer) of CO$_2$ in PP
by using *in situ* visualization. They found both swelling and solubility curves began to level off above 15 MPa. Knez and his co-workers [227] applied the Sanchez–Lacombe (SL) and the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) EOS to predict the solubility of supercritical CO\(_2\) in poly(L-lactide) and poly(D,L-lactide) + glycolide at three different temperatures between (308 and 323) K and up to a 30 MPa pressure. They found that the solubility curve is concave to the pressure axis and starts to level off at high pressures (above 15 MPa). They also claimed that both the Sanchez–Lacombe (SL) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) were reliable models to describe the phase equilibrium of PLLA + CO\(_2\) and PLGA + CO\(_2\) systems under the proposed working conditions.

It was further found that linear PP absorbs more CO\(_2\) than branched PP for a particular temperature and pressure, especially at a higher pressure. This is due to the swelling effect discussed in an earlier paper [202]. It is believed that the branched molecular chain structure causes greater entanglement, which can generate a higher resistance to volume expansion. Therefore, a branched chain structure generates less accommodation for small gas molecules dissolving into the polymer melt, and exhibits a less swollen volume than a linear chain structure (Fig. 4.1). According to Hiemenz [228], branched polymer chains result from the presence of monomer with a functionality of greater than two. This branching might produce a three-dimensional network of polymer. The solubility and mechanical behavior of branched polymers largely depends on whether the extent of polymerization is above or below the threshold (gel point) for the formation of such a network. Hiemenz has also shown several reaction possibilities in the presence of multifunctional reactants. Though branched PP helps to increase the melt strength of the PP blend, it is obvious that the addition of branched PP to linear PP will decrease the overall solubility. However, interesting is the question of how much short-chain or long-chain branching affects solubility, which is beyond the research scope of this paper to answer.
4.3.4 Comparison of Solubility of CO$_2$ in PP- Theoretical, Semi-empirical, and Experimental Values

As is well known, solubility data that were determined completely experimentally would have much greater accuracy and reliability. After we determined solubility experimentally, we compared the results with our previous data, which had been calculated using the Simha–Somcynsky (SS) and the Sanchez–Lacombe (SL) equations of state (EOS) [181]. All the characteristic parameters for the polymers and gas are given in Table 4-1. The solubility of CO$_2$ determined from the SS and the SL EOS for both linear and branched PP are shown in Figures 4.3 and 4.4, respectively. It was observed that for both types of PP, the solubilities predicted by the SS and the SL were quite close to the experimental value at a low temperature and pressure (i.e., less than 13.8 MPa), but the SS-EOS showed a better agreement at higher temperatures and pressures compared with the SL-EOS. This is due to the swollen volumes determined by the SL and SS EOS, which are shown in Figures 4.5 and 4.6. The interaction parameters are given in Tables 4-2 and 4-3.

Table 4-2 Interaction parameters of SS-EOS and SL-EOS for linear PP and CO$_2$

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>SL-EOS</th>
<th>SS-EOS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k12</td>
<td>$\delta_e$</td>
</tr>
<tr>
<td>453</td>
<td>-0.2343</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>-0.2718</td>
<td>1.1582</td>
</tr>
<tr>
<td>493</td>
<td>-0.3091</td>
<td></td>
</tr>
</tbody>
</table>
Table 4-3 Interaction parameters of SS-EOS and SL-EOS for branched PP and CO$_2$

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>SL-EOS</th>
<th>SS-EOS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k12</td>
<td>$\delta_e$</td>
</tr>
<tr>
<td>453</td>
<td>-0.1663</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>-0.1968</td>
<td></td>
</tr>
<tr>
<td>493</td>
<td>-0.2333</td>
<td></td>
</tr>
</tbody>
</table>

Since the swollen volume predicted by the SL is higher than that predicted by the SS, the semi-empirical and theoretical solubilities determined by the SL are also higher than the SS-EOS. These results indicate that SS is able to predict solubility more accurately than the SL equation of state (EOS). The SS and SL, along with four other theoretical equations of state, have been comprehensively tested for $PVT$ data in 56 polymers by Rodgers [229]. SS-EOS shows excellent capabilities for describing polymer melt $PVT$ data over a wide range of temperatures and pressures. Moreover, the application of the SS–EOS in the multicomponent fluid system used to predict the mixture's $PVT$ behavior has been previously studied [39, 40]. The SS-EOS might be a good candidate to predict the $PVT$ behavior of a polymer + gas mixture.
Figure 4.3 Comparison of experimental, semi-empirical and EOS-based solubility, $X$ (g-gas/g-polymer) of CO$_2$ in linear PP
Figure 4.4 Comparison of experimental, semi-empirical and EOS-based solubility, $X$ (g-gas/g-polymer) of CO$_2$ in branched PP
The SL EOS has been extensively used to predict the solubility of blowing agents in polymer melts because of its simplicity. Recently, however, several researchers have tried to modify the SL EOS to better correlate it with experimental data [230-232]. To this end, Machida et al. tried to modify the interaction energy parameter ($\varepsilon^*$) of the SL–EOS [230]. Since hydrogen bonding and ionic interaction depend on temperature, they modified the interaction energy term as a function of temperature in the form of the Langmuir equation to manage the temperature...
Figure 4.6 Comparison of experimental and EOS swelling ratio, $S_w$ for branched PP [202]
effect. Then they compared the modified SL with the original one by computing the volumetric
data for the group of non-polar fluids, polar fluids, and ionic liquids and claimed that the
modified SL provides better $PVT$ representation and could be used for mixtures. Krenz et al. also
tried to modify the original SL–EOS adopting Neau’s modified SL and included a Peneloux-type
volume translation [232]. They proposed that the modified SL equation can perform vapor-liquid
equilibrium (VLE), liquid-liquid equilibrium (LLE), and vapor-liquid-liquid equilibrium (VLLE)
calculations for polyethylene + ethylene + hexane mixtures across a wide range of temperatures,
pressures, and compositions.
On the other hand, the swollen volumes predicted by the SS–EOS for both PPs are still much higher than the experimental data at a higher temperature and at any pressure (see Figures 4.5 and 4.6). This indicates that the SS should be modified for predicting the PVT behavior of the polymer + gas mixture more accurately, especially at high temperatures. Recently, a few researchers tried to modify the SS-EOS to better correlate it with the experimental data [233-236]. Based on the statistical theory for the thermal defects of an imperfect crystal, Zhong et al. proposed an exponential relation between occupied-site fraction ($y$) and reduced temperature ($\tilde{T}$), and developed a simplified SS-EOS version [233, 234]. They then applied the modified SS to determine the PVT behavior of 11 polymers, and found it very promising. Wang et al. [236] realized that although the SS-EOS can predict the PVT behavior of polymer much better than other EOS, it does not predict as well for gases at low pressures. They proposed to modify the free volume contribution of the SS by incorporating the perturbed hard-chain theory of Beret and Prausnitz with two universal constants to the free volume term. They also determined the characteristic parameters for the modified SS EOS for 44 low-molecular weight substances and 64 polymers. They then calculated the absolute average deviations (AADs) for critical temperature, critical pressure, and vapor pressures, which they found to be very reasonable, while AAD for critical density and saturated liquid density at the normal boiling point were a bit larger. It was also found that though swelling predicted by the SS EOS at high temperature (Figures 4.5 and 4.6) is way off from the empirical data, only the swelling at high pressure has a significant effect on solubility determination (Figures 4.3 and 4.4). This suggests that modification of the SS EOS is necessary for better prediction of swelling and solubility especially for high temperatures and pressures.

Since all of the above modifications for both the SS and the SL EOS are based on experimental data, the validity of these modifications strongly depends on the empirical value.
To predict the $PVT$ behavior of the polymer + gas solution, further modification of the SS-EOS is required. To accomplish this modification, more accurate solubility data with a wide range of temperatures and pressures are essential.

4.4 Swelling and Solubility Behaviors of LDPE in the Presence of CO$_2$

4.4.1 $PVT$ Data for LDPE

The $PVT$ data of Gnomix $PVT$ Apparatus for pure LDPE were obtained from McGill University Lab (Figure 4.7). The $PVT$ equations were then derived based on the measurement data. The $PVT$ equations are listed below for LDPE (Equation 4-7).

$$v_{p, \text{pure}} = (1.1753 + 8.058 \times 10^{-4} T) \times (1 - 0.089 \ln(1 + P \exp(1.7175 \times 10^{-3} T)))$$  

where, the specific volume $v_{p, \text{pure}}$ is in cc/g, the temperature $T$ is in ($^\circ$C) and pressure $P$ is in (MPa). Furthermore, the $PVT$ data of this pure material was used to derive the corresponding characteristic parameters: $P^*$, $V^*$, $T^*$ for both the SS-EOS and the SL-EOS. All the characteristic parameters are listed in Table 4-4.
Table 4-4 Scaling parameters for SS-EOS and SL-EOS for LDPE and CO₂[183]

<table>
<thead>
<tr>
<th>Substance</th>
<th>$P^*/$MPa</th>
<th>$V^*/$(cm$^3$/g)</th>
<th>$T^*/$K</th>
<th>$M_\nu$/(g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SS-EOS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td>727.8</td>
<td>1.1677</td>
<td>10,550</td>
<td>122,388</td>
</tr>
<tr>
<td>CO₂</td>
<td>954.2</td>
<td>0.5860</td>
<td>2,960</td>
<td>44.01</td>
</tr>
<tr>
<td><strong>SL-EOS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td>349.4</td>
<td>1.1285</td>
<td>679</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>720.3</td>
<td>0.6329</td>
<td>208.9 + 0.459T</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$-7.56\times10^{-4}T^2$</td>
</tr>
</tbody>
</table>

Figure 4.7 Gnomix Data of LDPE
4.4.2 Swelling Behavior of LDPE in Presence of CO₂

The PVT data of LDPE/CO₂ solutions was measured at (383 to 463) K temperature and at a pressure of up to 21 MPa using a PVT measurement apparatus. In general, the volume swelling was found to increase as the pressure was increased, and the volume swelling decreased as the temperature was increased (Fig. 4.8). It was observed that as pressure increases, more gas goes into the polymer and the polymer swells more. However, as temperature increases gas diffuses out more than it getting in to the polymer and as a result swelling decreases. It was also noted that as pressure increases above 17 MPa swelling ratio becomes closer for all three temperatures. This might be due to leveling off the solubility at lower temperature (383K) and above 17MPa. In other words, at 383K and above 17MPa gas diffuses into the polymer is no longer linearly related to the pressure and as a result, polymer doesn’t swells linearly with pressure.

![Swelling Ratio Comparison](image.png)

Figure 4.8 Comparison of swelling ratio, $S_w$ of LDPE.
4.4.3 Solubility of CO$_2$ in LDPE

The solubilities of CO$_2$ in LDPE was measured at temperatures from (383 to 463) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. All the experimental data are given in Tables 7 to 9 in the appendix section.

Once the swelling ratio was measured by the PVT apparatus [124, 202], the empirical solubility was determined by using the magnetic suspension balance to measure the apparent solubility and by putting the value of the swollen volume into Equation 4-4. Figure 4.9 shows the solubility of CO$_2$ in LDPE. It was observed that solubility increases as pressure increases, but that it decreases as temperature increases for both polymers. Other researchers have also observed a similar trend [8, 127-133, 168, 173, 195, 197, 213].

![Figure 4.9 Experimental solubility, X (g-gas/g-polymer) of CO$_2$ in LDPE](image-url)
4.4.4 Comparison of Solubility of CO$_2$ in LDPE- Theoretical, Semi-empirical, and Experimental Values

The solubility data that were determined completely experimentally would have much greater accuracy and reliability. After determining the solubility experimentally, the results were compared with EOS which had been calculated using the SS and the SL EOS [181].

![Figure 4.10 Comparison of experimental, semi-empirical and EOS-based solubility, X (g-gas/g-polymer) of CO$_2$ in LDPE](image-url)

Figure 4.10 Comparison of experimental, semi-empirical and EOS-based solubility, $X$ (g-gas/g-polymer) of CO$_2$ in LDPE
All the characteristic parameters for the polymers and gas are given in Table 4-2. The solubilities of CO₂ determined from the SS and SL EOS for LDPE are shown in Figures 4.10. The interaction parameters are given in Tables 4-5.

Table 4-5 Interaction parameters of SS-EOS and SL-EOS for LDPE and CO₂

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>SL-EOS</th>
<th>SS-EOS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k12</td>
<td>δₑ</td>
</tr>
<tr>
<td>383</td>
<td>-0.082</td>
<td>0.9831</td>
</tr>
<tr>
<td>423</td>
<td>-0.1337</td>
<td>1.0033</td>
</tr>
<tr>
<td>463</td>
<td>-0.1982</td>
<td>1.0207</td>
</tr>
</tbody>
</table>

The solubility of CO₂ in LDPE was also determined by Ohsimha et al. [134, 237]. The data are very close. However, they used SL-EOS to predict the swollen volume and thus to determine the total solubility. Since solubilities determined by using various EOS are not same, these solubilities should be verified by comparing with the fully experimental data which is very rare. In this research, it was a given a try to verify the EOS or at least to get an EOS which could be depend on to determine the solubilities of gases in polymers. Like linear and branched PP, the experimental solubility of CO₂ in LDPE was used to verify SS and SL EOS. It was observed that the solubility determined by both SL and SS EOS were very close to the experimental data. However, SS-EOS predicts little better than SL EOS for LDPE case. It is believed that since SS-EOS uses more molecular information of both gas and polymers than SL-EOS, it might be able to predict better than SL-EOS.
4.5 Swelling and Solubility Behaviors of PS in the Presence of CO₂ or N₂

4.5.1 PVT Data for PS

The pressure-volume-temperature (PVT) data for pure PS was obtained by using a Gnomix PVT apparatus and provided by Datapoint Labs (Ithaca, NY). The moldflow PVT equation (Tait equation) was then derived based on the measurement data. The moldflow PVT equation is listed below for PS (Equation 4-8).

\[
v_{p,\text{pure}} = (0.9724 + 5.996 \times 10^{-4}(T - 376.37)) \times (1 - 0.089 \ln(1 + \frac{10^P}{1797.84 \exp(-4.761 \times 10^{-5}(T - 376.37)})\text{ )})
\]

where \( v_{p,\text{pure}} \) is the specific volume and in cc/g, the temperature \( T \) is in K and pressure \( P \) is in MPa.

Table 4-6 Scaling parameters for SS-EOS and SL-EOS for PS, CO₂ and N₂ [175, 181].

<table>
<thead>
<tr>
<th>Substance</th>
<th>( P^*/\text{MPa} )</th>
<th>( V^*/(\text{cm}^3/\text{g}) )</th>
<th>( T^*/\text{K} )</th>
<th>( M_w/(\text{g/mole}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SS-EOS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>807.8</td>
<td>0.9621</td>
<td>16042</td>
<td>1.96x10⁵</td>
</tr>
<tr>
<td>CO₂</td>
<td>954.2</td>
<td>0.5860</td>
<td>2,960</td>
<td>44.01</td>
</tr>
<tr>
<td>N₂</td>
<td>384.3</td>
<td>0.9475</td>
<td>1226.9</td>
<td>28.01</td>
</tr>
<tr>
<td><strong>SL-EOS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>407.4</td>
<td>0.9023</td>
<td>739.1</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>720.3</td>
<td>0.6329</td>
<td>208.9 + 0.459T</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( - 7.56 \times 10^{-4}T^2 )</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>103.6</td>
<td>1.2447</td>
<td>159.0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.11 Comparison of Tait equation and experimental data for pure PS

Figure 4.12 Comparison of SL-EOS and experimental data for pure PS
Figure 4.13 Comparison of SS-EOS and experimental data for pure PS

The measured PVT data and Tait equation are compared in Fig. 4.11. It can be observed that Tait equation and the measured data have pretty close values. Furthermore, the PVT data of these pure materials (PS) were used to derive the corresponding characteristic parameters: $P^*$, $V^*$, $T^*$ for both the SS- and SL-EOS. All of the characteristic parameters are listed in Table 4-6. The measured PVT data, SL- and SS EOS are compared in Figures 4.12 and 4.13. It can be observed that the SS-EOS prediction for the specific volume of pure PS is better than that by the SL-EOS when compared to the measured data.

4.5.1.1 Swelling Behavior of PS in the Presence of CO$_2$

The PVT data of PS/CO$_2$ solutions was measured at temperatures from 403 to 463 K and pressures up to 21 MPa by using a new PVT measurement apparatus. At each temperature, the
pressure started from 6.9 MPa (1000 psi) up to 20.69 MPa (3000 psi), at increments of 3.45 MPa (500 psi). At each pressure level, the PS/CO₂ solution was maintained for 1.5 hours to ensure that system equilibrium was reached. Equilibrium was considered to be achieved when the total volume of the polymer/gas solution no longer changed. In general, it was found that the volume swelling increases as the pressure is increased, and the volume swelling decreases as the temperature is increased (Figure 4.14).

When a polymer melt is exposed to high pressure gas, two competing mechanisms will affect the specific volume. On the one hand, the hydraulic pressure will decrease the specific volume of the compressible polymer/gas solution. On the other hand, the dissolved gas under high pressure would cause the polymer to swell and increase the specific volume. The latter is typically higher than the hydraulic pressure effect. This means that the presence of gas evidently enhances the overall activity of the polymer/gas system [238], and thus creates more free volume for the penetration of CO₂ molecules after the gas fills the existing free volume. The increased specific volume (i.e., increased free volume) causes an increase in the solubility and diffusivity [239]. The dissolved CO₂ causes a plasticization effect that reduces the viscosity of the polymer/gas mixtures and increases the chain mobility [240, 241]. Also, this increased specific volume decreases the surface tension of the polymer [242]. In summary, despite the hydraulic compression effect, high-pressure gas increases the specific volume and thereby affects the
Figure 4.14 Swelling ratio $S_w$ of PS in the presence of CO$_2$

solubility, diffusivity, viscosity and surface tension. All of these fundamental parameters are critical in determining the foaming behaviours, and it should be emphasized that the swelling caused by gas dissolution governs all of these parameters. When the pressure is increased at a constant temperature, the volume of the polymer/gas mixture also increases, which also holds true for the volume swelling ratio. Since the solubility of CO$_2$ increases with an increase in the pressure as mentioned above [181], more CO$_2$ dissolves into the PS matrix, which would induce more volume swelling.

When the pressure is constant, higher temperatures result in less volume swelling in the PS/CO$_2$ solution. As the temperature increases, the polymer chains become softer and more relaxed. As a result, both the free and specific volumes increase. On the other hand, the solubility of CO$_2$ in PS is known to decrease as the temperature increases (Figure 4.15). This means that there is an increase in CO$_2$ diffusion from the polymer matrix at a higher temperature in
comparison to the situation where the polymer has more free volume. Therefore, despite the increased free volume in the PS matrix, the PS/CO₂ solution will lose CO₂ at a higher temperature. As the pressure climbs higher, the volume swelling is governed by the gas content, and its temperature sensitivity decreases.

4.5.1.2 Solubility of CO₂ in PS

The solubility behavior of PS/CO₂ solutions was measured at temperatures from 403 to 463 K and pressures up to 21 MPa by using an MSB and a PVT apparatus. At each temperature, the pressure started from 6.9 MPa (1000 psi) up to 20.69 MPa (3000 psi), at increments of 3.45 MPa (500 psi). At each pressure level, the PS/CO₂ solution was maintained for 4 to 5 hours to ensure that system equilibrium was reached. Equilibrium was considered to be achieved when the total mass of the polymer/gas solution no longer changed. The solubility of CO₂ in PS is shown in Figure 4.15. In general, it was found that the solubility of CO₂ in PS increases as the pressure is increased, and decreases as the temperature is decreased (Figure 4.15). However, it was noticed that the solubility of CO₂ in PS is much less than that in PP [124, 181].

When the pressure is constant, higher temperatures result in lower solubility in the PS/CO₂ solution. As the temperature increases, the polymer chains become softer and more relaxed. As a result, both the free and specific volumes increase. On the other hand, the heat of solution (change in enthalpy, ΔH) is negative for CO₂ + polymer case. It can be seen from the Arrhenius equation (\( S = S_0 e^{-\frac{\Delta H}{RT}} \)) that if heat of solution is negative solubility decreases with temperature. As a result, as the temperature increases, the solubility of CO₂ decreases.
4.5.1.3 Swelling Behavior of PS in the Presence of N₂

The PVT data of PS/N₂ solutions was measured at temperatures of 403 to 463 K and pressures up to 21 MPa by using a new PVT measurement apparatus. At each temperature, the pressure started from 6.9 MPa (1000 psi) up to 20.69 MPa (3000 psi), at increments of 3.45 MPa (500 psi). At each pressure level, the PS/N₂ solution was maintained for 1.5 hours to ensure that system equilibrium was reached. Equilibrium was considered to be achieved when the total volume of the polymer/gas solution no longer changed. In general, it was found that the volume swelling increases as the pressure is increased, and the volume swelling increases as the temperature is increased (Figure 4.16).
For $N_2$, gas solubility increases as the temperature is increased (Figure 4.17). This indicates that the free volume increases at a higher temperature, and chain mobility dominates the gas diffusing out of the polymer. As a result, swelling increases with temperature for the PS/$N_2$ system.

### 4.5.1.4 Solubility of $N_2$ in PS

The solubility behavior of the PS/$N_2$ solutions was measured at temperatures from 403 to 463 K and pressures up to 21 MPa by using an MSB and a $PVT$ apparatus. At each temperature, the pressure started from 6.9 MPa (1000 psi) up to 20.69 MPa (3000 psi), at increments of 3.45 MPa (500 psi). At each pressure level, the PS/$N_2$ solution was maintained for 4 to 5 hours to ensure that system equilibrium was reached. Equilibrium was considered to be achieved when the total mass of the polymer/gas solution no longer changed. The solubility of $N_2$ in PS is shown in Figure 4.17.
In general, it was found that the solubility of N₂ in PS increases as the pressure is increased, and decreases as the temperature is decreased. However, it was observed that the solubility of N₂ in PS is much less than that of CO₂ in PS and PP. It was also noticed that unlike CO₂, solubility of N₂ increases as temperature is increased. This is due to heat of solution (change in enthalpy) is positive in the N₂ case whereas it is negative for CO₂ case. It can be seen from the Arrhenius equation \( S = S_0 e^{-\Delta H/RT} \) that if heat of solution is positive solubility increases with temperature.

### 4.5.2 Solubility of CO₂ and N₂ in PS and Henry’s Law

The temperature dependence of the Henry’s Law constant was examined using the measured solubility data. Henry’s Law constant, \( K_p \) (kg MPa/cm³ (STP)), is defined by the following equation:
\[ K_p = \frac{P}{S} \]  

where \( P \) is the partial pressure in MPa and \( S \) is the solubility of gas in polymer in cm\(^3\)(STP)/kg.

Stiel et al. [32] proposed a linear relationship between \( \ln(1/K_p) \) and \( (T_c/T)^2 \) for non-polar solutes in molten LDPE. The Henry’s Law constant and \( (T_c/T)^2 \) are related by the following equation:

\[ \ln \left( \frac{1}{K_p} \right) = A + B \left( \frac{T_c}{T} \right)^2 \]

where \( A, B \) are the constants and \( T_c \) is the critical temperature of the gas in K.

Table 4-7 Henry’s Law constant for CO\(_2\) +PS system

<table>
<thead>
<tr>
<th>( T, ) K</th>
<th>( T_c, ) K</th>
<th>( (T_c/T)^2 )</th>
<th>Henry’s Constant, ( K_p ) (MPa kg/cm(^3)(STP))</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>303.25</td>
<td>0.5662</td>
<td>0.000371</td>
<td></td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>303.25</td>
<td>0.5140</td>
<td>0.000413</td>
<td>1.7765</td>
<td>6.8877</td>
</tr>
<tr>
<td>463</td>
<td>303.25</td>
<td>0.4290</td>
<td>0.000474</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-8 Henry’s Law constant for N\(_2\) +PS system

<table>
<thead>
<tr>
<th>( T, ) K</th>
<th>( T_c, ) K</th>
<th>( (T_c/T)^2 )</th>
<th>Henry’s Constant, ( K_p ) (MPa kg/cm(^3)(STP))</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>126.3</td>
<td>0.0982</td>
<td>0.003067</td>
<td></td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>126.3</td>
<td>0.0892</td>
<td>0.002585</td>
<td>6.9064</td>
<td>-11.125</td>
</tr>
<tr>
<td>463</td>
<td>126.3</td>
<td>0.0744</td>
<td>0.002330</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.18 Henry’s Law constant for CO$_2$ in PS

Figure 4.19 Henry’s Law constant for N$_2$ in PS
After calculating the solubility of CO$_2$ and N$_2$ at 403, 423, and 463 K, the Henry’s Law constant ($K_P$) and $T_c/T$ were determined and they are listed in Tables 4-7 and 4-8. Afterwards, a graph that depicts $\ln(1/K_p) \times (T_c/T)^2$ was plotted (Figures 4.18 and 4.19) and constant values A and B were determined by using the least square method. Thus, after obtaining the values of A and B and plugging these values into Equation 4-10, we get:

For CO$_2$,

$$\ln\left(\frac{1}{K_p}\right) = 1.7765 + 6.8877\left(\frac{T_c}{T}\right)^2$$  \hspace{1cm} 4-11

For N$_2$

$$\ln\left(\frac{1}{K_p}\right) = 6.9064 - 11.125\left(\frac{T_c}{T}\right)^2$$  \hspace{1cm} 4-12

By using Equations 4-11 and 4-12, the solubility of CO$_2$ and N$_2$ in PS can be calculated at any temperature and pressure.

**4.5.3 Comparison of Swelling of PS in the Presence of CO$_2$ or N$_2$ – Theoretical and Experimental Values**

After experimentally determining swelling, I compared the results with my previous data, which had been calculated by using the SS- and SL-EOS [181]. All of the characteristic parameters for the polymers and gas are given in Table 4-3. The volume swelling ratio of CO$_2$ and N$_2$ as determined from the SS- and the SL-EOS for PS are shown in Figures 4.20 and 4.21, respectively. It can be observed that for both types of gas, the swelling ratios
Figure 4.20 Comparison of experimental and EOS-based Swelling, $S_w$ of PS in presence of CO$_2$ predicted by the Simha–Somcynsky (SS) and the Sanchez–Lacombe (SL) was quite close to the experimental value at a low pressure (i.e., less than 10 MPa), but the Simha–Somcynsky (SS) showed a better agreement at any temperature and higher pressures compared with the Sanchez–Lacombe (SL). It was also noticed that though SL-EOS predicts better swollen volume for N$_2$ case (small amount of swollen volume), SS-EOS predicts more accurately for CO$_2$ case (significant amount of swollen volume). This indicates better prediction capability of Simha–Somcynsky (SS) equations of state (EOS) to predict significant amount of swelling of polymer/gas mixture. The interaction parameters are given in Tables 4-9 and 4-10.
4.5.4 Comparison of Solubility of CO$_2$ and N$_2$ in PS- Theoretical, Semi-empirical, and Experimental Values

Since completely experimentally determined solubility would have much greater accuracy and reliability, after experimentally determining solubility, I compared the results with my previous data, which had been calculated by using the SS- and the SL-EOS [181]. All of the characteristic parameters for the polymers and gas are given in Table 5-1. The solubilities of CO$_2$ and N$_2$ that are determined from the SS- and the SL-EOS for both CO$_2$ and N$_2$ in PS are shown in Figures 5.12 and 5.13, respectively. It can be observed that for both types of gases, the solubilities predicted by the SS and the SL are quite close to the experimental values at low
temperatures and pressures (i.e., less than 15 MPa), but the SS-EOS shows a better agreement at higher temperatures and pressures compared with the SL. This is due to the swollen volumes determined by the SL- and SS-EOS, which are shown in Figures 5.10 and 5.11.

Table 4-9 Interaction parameters of SS-EOS for PS/N₂ and PS/CO₂

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>PS/CO₂</th>
<th>PS/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>δₑ</td>
<td>1.1065</td>
<td>1.3512</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>1.1365</td>
<td>0.8850</td>
</tr>
<tr>
<td>423</td>
<td>δₑ</td>
<td>1.1050</td>
<td>1.3589</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>1.1260</td>
<td>0.9114</td>
</tr>
<tr>
<td>463</td>
<td>δₑ</td>
<td>1.1130</td>
<td>1.3800</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>1.1142</td>
<td>0.9187</td>
</tr>
</tbody>
</table>

Since the swollen volume predicted by the SL-EOS is less than that predicted by the SS-EOS for the CO₂ case, the semi-empirical and theoretical solubilities determined by the former are also less than that by the latter. These results indicate that the SS-EOS is able to more accurately predict solubility than the SL-EOS for higher solubility cases.

Table 4-10 Interaction parameters of SL-EOS for PS/N₂ and PS/CO₂

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>PS/CO₂</th>
<th>PS/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>k₁₂</td>
<td>-0.0920</td>
<td>0.2156</td>
</tr>
<tr>
<td>423</td>
<td>k₁₂</td>
<td>-0.1125</td>
<td>0.2148</td>
</tr>
<tr>
<td>463</td>
<td>k₁₂</td>
<td>-0.1674</td>
<td>0.2216</td>
</tr>
</tbody>
</table>
Figure 4.22 Comparison of experimental, semi-empirical and EOS-based solubility, $X$ (g-gas/g-polymer) of CO$_2$ in PS
Summary

Whether a gravimetric or volumetric method is used to measure the solubility of blowing agents (BAs) in polymer, an EOS has been used to compensate for the buoyancy effect of swelling that occurs due to gas dissolution. As a result of this limitation, the obtained solubility data are inadequate, especially at a high pressure where swelling is dominant. A magnetic suspension balance combined with a PVT apparatus was successfully applied to study the swelling behavior of linear and branched PP + CO$_2$ and LDPE+CO$_2$ solutions, and to determine...
the solubility of CO$_2$ in those polymers at high temperatures and pressures. It was noted that branched PP swells less than linear PP due to the entanglement effect of branched PP. Thus, branched PP can only accommodate a smaller amount of gas, resulting in a decreasing solubility trend. For both linear and branched PP, the hydrostatic effect of pressure is clearly shown at a high pressure (i.e., above 21 MPa) and the volume swelling ratio eventually approaches a plateau region.

The solubility behavior of amorphous material – PS, was studied. It was noticed that the solubility of CO$_2$ in molten polymer linearly increases with pressure and decreases with temperature. However, the solubility of N$_2$ increases with both pressure and temperature. This is because the heat of solution (change in enthalpy) is positive in the N$_2$ case. As a result, as temperature increases, the solubility of N$_2$ increases, whereas in the CO$_2$ case, the heat of solution is negative and thus as temperature increases, the solubility decreases. It was also observed that at a specific temperature and pressure, the solubility of CO$_2$ in PS is significantly higher than that in N$_2$. Henry’s Law constants for the solubilities of CO$_2$ and N$_2$ gases were also determined. By using Henry’s Law constants, two equations of solubilities as a function of temperature were also derived for both CO$_2$ and N$_2$. It was found that the gases exhibit less solubility in PS compared with semi-crystalline material (PP) [181]. In comparison to PP, it was observed that the solubilities of both N$_2$ and CO$_2$ in amorphous PS significantly low. This information indicates that both N$_2$ and CO$_2$ may not be adequate to achieve low density PS foam due to low solubility, unless an extremely high processing pressure can be applied.

Since the Sanchez–Lacombe (SL) and the Simha–Somcynsky (SS) EOS are widely used to determine the swollen volume of a polymer + gas solution or to determine the solubility of blowing agents in polymers that have different values, the EOS should be verified. From these results some inferences can be made regarding EOS accuracy. Since various equations of state
are used to determine the solubility of blowing agents, the Simha–Somcynsky equation of state (SS–EOS) might be one of the best candidates to accurately predict the solubility of gases in semi-crystalline polymers. In the future, the Simha–Somcynsky equation of state (SS–EOS) should be modified to better correlate with the empirical data, especially at high temperatures and pressures.
CHAPTER 5.  PVT AND SOLUBILITY BEHAVIORS OF POLYMER IN PRESENCE OF GAS BLENDS

5.1 Introduction

During the last two decades, the plastic foam industry has experienced serious regulatory, environmental, and economic pressure. Before they were banned from international use by the 1987 Montreal Protocol [243], high ozone-depleting-potential (ODP) chlorofluorocarbons (CFCs) were widely used in the foam industry [2] to produce polymer foams. During the subsequent move away from CFCs, low-ODP hydrochlorofluorocarbon-based (HCFC-based) BAs, such as HCFC-22, HCFC-141b, and HCFC-142b, were used. However, because HCFCs also deplete the ozone layer, although less so than CFCs, HCFC-based foams were phased out of North America in January 2010 [244].

There is, therefore, an urgent need for new alternative zero-ODP BAs in the plastic foam industry. The list of potential candidates for zero-ODP BAs [132, 186, 245-247] includes the following: hydrofluorocarbons (HFCs), hydrocarbons (HCs), water, ethanol, CO\textsubscript{2}, and N\textsubscript{2}. Nevertheless, the relatively low solubility and high diffusivity of these possible surrogate polymer gases have made the foaming process challenging [248-250]. Plastic foams produced by using only one of these BAs do not have the same properties as those of CFC-blown plastic foams. Consequently, BA mixtures that optimize foam performance have been explored to create foams that meet client and industry demands. Several successful examples of BA mixtures have been reported by researchers or patented by the industry [2, 116, 251-253]. Such BA mixtures are needed to improve foam performance as well as increase the productivity and flexibility of various foam applications. However, to date, little fundamental research on the solubility determination of BA blends has been reported.
To the best of my knowledge, there is very little or no literature on any EOS or experimental approaches that can determine the solubility of BA blends in a polymeric system other than Ref 137. There is especially a lack of literature found for the solubility of CO\textsubscript{2} and N\textsubscript{2} BA blends in PS, at high temperatures and pressures. The BA blends of CO\textsubscript{2} and N\textsubscript{2} are particularly interesting because PS foam boards are manufactured in Europe and North America by using CO\textsubscript{2} as one of the BAs now [254], and N\textsubscript{2} has such a high nucleating effect [255].

In this study, the solubilities of CO\textsubscript{2}, N\textsubscript{2}, and CO\textsubscript{2}+N\textsubscript{2} blends (25:75, 50:50 and 75:25) in PS were measured at high temperatures up to 190°C and high pressures up to 21 MPa. Cost-effective foam processing typically requires solubility at high temperatures and pressures. The validity of EOS has not been verified for polymer/gas mixtures although SS-EOS has been observed to work well for PP and CO\textsubscript{2} [124, 185]. However, the previous solubility studies (chapter 4) are restricted to a single-gas/single-polymer system. The investigating of the solubility of BA blends in polymer and the phase equilibrium of a multi-component mixture system is a challenge for the following two reasons: (1) the composition ratio of BAs in the vapor phase is not the same as that of BAs dissolved in polymer melt, and (2) the effect of one BA on the solubility of another BA is not understood. Since SS-EOS is capable to predict PVT and solubility of gas in polymers (chapters 4), it was also used for the blend gas systems. Swelling and solubility, therefore, were fully experimentally measured at high pressures and temperatures. Afterward, the solubility of each gas in the polymer was determined by using the SS-EOS. The solubility of gas blends in a polymer melt was investigated by using our previously developed method for gas blends [137]. The theoretical framework for the blend system has been developed by Li [137] and is shown in next following sections. He measured the solubility of HFC 134a and 152a blends in PS using MSB and SS-EOS. Since the PVT apparatus was not developed at that time, he had to use SS-EOS to predict the swollen volume theoretically. As a
result, his data were semi-empirical. However, in this study, the solubility of CO₂ and N₂ gas blends in PS were fully experimentally measured by using the MSB and PVT apparatus and thus more accurate data for gas blends were obtained. However, SS-EOS was used to predict the amount of each gas component in polymer melts. Since the prediction capability of SS-EOS for the gas blend systems was not verified, it was also one of the interests. Therefore the predicted swelling and solubilities were compared with experimental values to verify. Moreover, the temperature effects on solubility of CO₂ and N₂ in polymers in opposite manner and the solubility of N₂ is much less than CO₂ in polymers. The effect of less soluble gas on more soluble gas (vice versa) was also one of the interests.

5.2 Theoretical Framework

As discussed in Chapter 2, in a system containing several phases, equilibrium among these phases means that certain thermodynamic requirements must be met. It is obvious that under equilibrium all phases attain the same temperature \( T \) and pressure \( P \). Furthermore, according to classical thermodynamics [54, 58], when the system is under phase equilibrium at constant \( T \) and \( P \), the chemical potential \( (\mu_g^g, \mu_l^l) \) of component \( i \) in all phases (e.g., \( g, l \), etc.) must be equal:

\[
\mu_g^g = \mu_l^l
\]

5.2.1 Binary System: Single Gas and Single Polymer

The solubility study of a pure gas (i.e., a gas with a single component) in a polymer melt was described in Chapters 3 and 4. When a pure gas was investigated, equilibrium existed between the vapor phase (phase with a single gas component) and the polymer-gas phase (phase with two components). The mass fraction of the gas dissolved in the polymer melt, i.e. the theoretical solubility \( X_{\text{theory}} \), can be calculated using the phase equilibrium theory Equation 5-1:
Here, \( \mu_1^V (P,T) \) is the chemical potential of the gas in the vapor phase and \( \mu_1^P(P,T,X_{theory}) \) is the chemical potential of the gas in the polymer-gas solution phase. The solubility of pure CO\(_2\) and N\(_2\) in PS were separately investigated and the results are illustrated in Figure 5.1. CO\(_2\), N\(_2\), and PS are denoted as Components 1, 2, and 3, respectively.

Figure 5.1 Phase equilibrium between the pure vapor phase and polymer/gas mixture (a) CO\(_2\) and PS, (b) N\(_2\) and PS

With the equations that follow, the interaction parameters for each gas component (CO\(_2\) or N\(_2\)) with the PS molecules in the polymer phase can be separately obtained. The SS-EOS in Equation 5-2 was used to calculate \( \mu_1^V(P,T) \) in the single component vapor phase [27, 29, 120, 121, 142]:

\[
\mu_1^V(P,T) = \mu_1^P(P,T,X_{theory})
\]

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\[
\mu^V(P, T) = RT \left[ \ln y + s \frac{1 - y}{y} \ln(1 - y) - \frac{1.011(yV)^{-4} - 2.409(yV)^{-2}}{2T} \right]
\]

Similarly, Equation 5-3 was used to calculate \( \mu^P(P, T, X_{theory}) \) in the two-component (polymer and gas) mixture phase [27,29]:

\[
\mu^P(P, T) = G_m + x_2 \frac{\partial G_m}{\partial x_1}
\]

Here, \( G_m \) is the molar free energy of the polymer-gas mixture (two-component mixture phase) and represented in Equation 5-4 [27, 29, 121, 142]. The procedures for handling the binary mixture system were discussed in detail in Chapter 2. It is worth noting that the key to setting up a proper thermodynamic model for the binary mixture system is by determining the parameters \( \partial \) and \( \partial \) that govern the interaction between each individual pure gas component and the polymer.

\[
G_m \frac{RT}{\mu^P(P, T)} = \left[ x_1 \ln x_1 + x_2 \ln x_2 + (s - 1) \ln \left( \frac{e}{z - 1} \right) + \ln(y / s) + s \frac{1 - y}{y} \ln(1 - y) + \frac{2yQ^2(1.011Q^2 - 1.2045)}{T} \right] - \frac{3c_1x_1}{2} \ln \frac{2\pi m_1RT}{(N_a h)^2} - \frac{3c_2x_2}{2} \ln \frac{2\pi m_2RT}{(N_a h)^2} + \frac{cyQ^2(1.011Q^2 - 2.409)}{2T}
\]
The next section shows that the study of the binary mixture system is a prerequisite for the study of the ternary mixture system of the two-gas blend and the polymer.

5.2.2 Ternary System: Gas Blend (Two-Gas Mixture) and Polymer

The establishment of a proper thermodynamic model for a polymer-gas blend system (a ternary mixture system) is a difficult task. In this study, CO$_2$/N$_2$ blends (i.e., 25:75, 50:50, 75:25), was used to study the gas mixture in a polymer. In this study, CO$_2$, N$_2$, and PS are denoted as Components 1, 2, and 3, respectively. The phase equilibrium was theoretically determined by using the previously established general thermodynamic model for the ternary mixture system [137]. With the application of a proper thermodynamic model to this ternary mixture system, it is possible to not only predict the total amount of gas mixture dissolved in the polymer, but also the actual amount of each individual gas component dissolved in the polymer under phase equilibrium conditions.

The criteria for the existence of phase equilibrium in a polymer-gas mixture system (ternary mixture system), expressed in Equation 5-5, can be rewritten as follows since the chemical potential for each gas component (1 or 2) is identical under equilibrium conditions in all phases (i.e., the vapor and the polymer-gas mixture phases):

$$
\mu_{\text{gas},1}^V(P,T,m_i) = \mu_{\text{gas},1}^p(P,T,n_1,n_2)
$$

$$
\mu_{\text{gas},2}^V(P,T,m_2) = \mu_{\text{gas},2}^p(P,T,n_1,n_2)
$$

In the above equations, the composition of the vapor phase is represented by $m_i$ and the composition of the polymer phase is represented by $n_i$.

By using Equations 5-5 and 5-6, the total amount of dissolved gas mixture in the polymer, that is, $(n_1+n_2)$, and the actual amount of each individual gas dissolved in the polymer ($n_i$), were theoretically determined. Since a vapor (gas mixture) reservoir with a known and fixed
composition $m_i$ was used in this study, these two coupled equations were solved for the two unknowns, $n_1$ and $n_2$, at constant $T$ and $P$. $X_{theory}$ hereafter was determined, i.e., 

$$\frac{n_1 + n_2}{1 - (n_1 + n_2)}.$$ 

In order to solve the system of equations given by Equations 5-5 and 5-6, a thermodynamic model must be established to calculate $\mu_i^V$ and $\mu_i^P$, the chemical potentials for the gas component in the vapor phase (binary gas mixture) and polymer phase (ternary mixture phase), respectively. $\mu_i^V$ is determined in the usual way, similar to the method used to determine the chemical potential in a binary mixture, via Equations 5-3 and 5-4. The calculation applies an EOS [54, 58] to derive $\mu_i^P$ in a ternary mixture system. The proposed method for calculating $\mu_i^P$ is shown in the following steps.

First, in a ternary mixture system, the molar fraction of component 1, $x_1$, and the molar fraction of component 2, $x_2$, are the two independent composition variables of the mixture, which is represented as

$$x_1 + x_2 + x_3 = 1$$

Second, the molar Gibbs free energy of the ternary mixture can be written as

$$G_m = x_1 \mu_1 + x_2 \mu_2 + x_3 \mu_3 = x_1 \mu_1 + x_2 \mu_2 + (1-x_1-x_2) \mu_3$$

$$= x_1 (\mu_1 - \mu_3) + x_2 (\mu_2 - \mu_3) + \mu_3$$

The Gibbs-Duhem equation [112] for the system under equilibrium at constant temperature $T$ and pressure $P$ states that

$$\sum x_i D \mu_i = 0$$

$$x_1 (D \mu_1 - D \mu_3) + x_2 (D \mu_2 - D \mu_3) + D \mu_3 = 0$$

The Equation 5-9 can be written as
\[
\begin{align*}
    &x_1 \left( \frac{\partial \mu_1}{\partial x_1} - \frac{\partial \mu_3}{\partial x_1} \right) + x_2 \left( \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_3}{\partial x_2} \right) + \frac{\partial \mu_3}{\partial x_2} = 0 \quad (5-10) \\
    &x_1 \left( \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_3}{\partial x_2} \right) + x_2 \left( \frac{\partial \mu_1}{\partial x_2} - \frac{\partial \mu_3}{\partial x_2} \right) + \frac{\partial \mu_3}{\partial x_2} = 0
\end{align*}
\]

The two above equations provide the fundamental relations between the chemical potentials of all the components. In order to derive the chemical potential for each component in the ternary mixture system, the following equations must also be adopted:

\[
\begin{align*}
    &\frac{\partial G_m}{\partial x_1} = \mu_1 - \mu_3 \quad (5-11) \\
    &\frac{\partial G_m}{\partial x_2} = \mu_2 - \mu_3
\end{align*}
\]

Based on Eqs. 5-8, and 5-11, the chemical potential for each component in the ternary mixture system are therefore determined as below:

\[
\begin{align*}
    \mu_3 &= G_m - x_1 \frac{\partial G_m}{\partial x_1} - x_2 \frac{\partial G_m}{\partial x_2} \quad (5-12) \\
    \mu_1 &= G_m + (1 - x_1) \frac{\partial G_m}{\partial x_1} - x_2 \frac{\partial G_m}{\partial x_2} \\
    \mu_2 &= G_m - x_1 \frac{\partial G_m}{\partial x_1} + (1 - x_2) \frac{\partial G_m}{\partial x_2} \quad (5-14)
\end{align*}
\]

In brief, a general approach to setting up a thermodynamic model for the study of phase equilibrium in a polymer-gas mixture system was successfully established by using an EOS, and the SS-EOS was used as an example in this study. The molar Gibbs free energy of the ternary mixture, that is, \(G_m\), is determined per usual means [121, 142]:
\[
\frac{G_m}{RT} = \left[ x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + (s-1) \ln \left( \frac{e^y}{z-1} \right) + \ln(y/s) + s \frac{1-y}{y} \ln(1-y) \right]
\]

\[
- c [ \ln \nu^* (1-\eta)^3 / Q ] + c [(1-\eta)^{-1} + \frac{2yQ^2(1.011Q^2 - 1.2045)}{T}]
\]

\[
- \frac{3}{2} c_1 x_1 \ln \left( \frac{2\pi m_1 RT}{(N_a h)^2} \right) - \frac{3}{2} c_2 x_2 \ln \left( \frac{2\pi m_2 RT}{(N_a h)^2} \right) - \frac{3}{2} c_3 x_3 \ln \left( \frac{2\pi m_3 RT}{(N_a h)^2} \right)
\]

\[
+ \frac{cyQ^2(1.011Q^2 - 2.409)}{2T}
\]

In addition, by applying the SS-EOS to the ternary mixture system, the PVT properties of the mixture can be theoretically calculated [81, 84, 92]. With these calculated properties, the swollen volume of polymer melt due to the dissolution of gas mixture \(V_s\) can then be resolved under equilibrium [81, 84, 92].

Similar to those for the binary mixture system, the following mixing rules must be developed when applying the SS-EOS to the ternary mixture system.

\[
x_1 = \frac{N_1}{N_1 + N_2 + N_3}
\]

\[
X_1 = \frac{x_1 q_1 z}{q z} = \frac{x_1 q_1 z}{x_1 q_1 + x_2 q_2 + x_3 q_3}
\]

\[
q = x_1 q_1 + x_2 q_2 + x_3 q_3, \quad c = x_1 c_1 + x_2 c_2 + x_3 c_3
\]

\[
s = x_1 s_1 + x_2 s_2 + x_3 s_3, \quad m = \frac{x_1 s_1 m_1 + x_2 s_2 m_2 + x_3 s_3 m_3}{s}
\]

\[
\varepsilon_{12}^* = \delta_{e,12} (\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2} \quad \varepsilon_{13}^* = \delta_{e,13} (\varepsilon_{11}^* \varepsilon_{33}^*)^{1/2} \quad \varepsilon_{23}^* = \delta_{e,23} (\varepsilon_{22}^* \varepsilon_{33}^*)^{1/2}
\]

\[
v_{12}^* = \delta_{v,12} \left( \frac{\nu_{11}^{1/3} + \nu_{22}^{1/3}}{8} \right)^3 \quad v_{13}^* = \delta_{v,13} \left( \frac{\nu_{11}^{1/3} + \nu_{33}^{1/3}}{8} \right)^3 \quad v_{23}^* = \delta_{v,23} \left( \frac{\nu_{22}^{1/3} + \nu_{33}^{1/3}}{8} \right)^3
\]

\[
v^* = \left( \frac{X_1^2 \varepsilon_{11}^* \nu_{11}^* + X_2^2 \varepsilon_{22}^* \nu_{22}^* + X_3^2 \varepsilon_{33}^* \nu_{33}^* + 2X_1 X_2 \varepsilon_{12}^* \nu_{12}^* + 2X_1 X_3 \varepsilon_{13}^* \nu_{13}^* + 2X_2 X_3 \varepsilon_{23}^* \nu_{23}^*}{X_1^2 \varepsilon_{11}^* \nu_{11}^* + X_2^2 \varepsilon_{22}^* \nu_{22}^* + X_3^2 \varepsilon_{33}^* \nu_{33}^* + 2X_1 X_2 \varepsilon_{12}^* \nu_{12}^* + 2X_1 X_3 \varepsilon_{13}^* \nu_{13}^* + 2X_2 X_3 \varepsilon_{23}^* \nu_{23}^*} \right)^{1/2}
\]

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Therefore, in order to apply the SS-EOS to the ternary mixture system, the molecular interaction parameters $\delta_e$ and $\delta_v$, illustrated in Figure 5.2, must be determined in advance. Since there are three components in the polymer phase (ternary mixture), the molecular interactions in the ternary mixture are between 1 and 2, 1 and 3, 2 and 3. It is assumed that the interaction of each gas component with the polymer molecules is not affected by the presence of the other gas components. Therefore, among the three sets of molecular interaction parameters, 1-2, 1-3 and 2-3, the values of $(\delta_{e,13}, \delta_{v,13})$ and $(\delta_{e,23}, \delta_{v,23})$ previously obtained from the binary system (Chapter 5) can be applied to the ternary mixture system as is.

\[
\varepsilon = \frac{(X_1^2 \varepsilon_{11}^* \gamma_{11}^2 + X_2^2 \varepsilon_{22}^* \gamma_{22}^2 + X_3^2 \varepsilon_{33}^* \gamma_{33}^2 + 2X_1X_2 \varepsilon_{12}^* \gamma_{12}^2 + 2X_1X_3 \varepsilon_{13}^* \gamma_{13}^2 + 2X_2X_3 \varepsilon_{23}^* \gamma_{23}^2)^2}{X_1^2 \varepsilon_{11}^* \gamma_{11}^4 + X_2^2 \varepsilon_{22}^* \gamma_{22}^4 + X_3^2 \varepsilon_{33}^* \gamma_{33}^4 + 2X_1X_2 \varepsilon_{12}^* \gamma_{12}^4 + 2X_1X_3 \varepsilon_{13}^* \gamma_{13}^4 + 2X_2X_3 \varepsilon_{23}^* \gamma_{23}^4}
\]

Figure 5.2 Phase equilibrium between the vapor phase blends and polymer/gas ternary mixture

Thus, in this research, only one set of molecular interaction parameters $(\delta_{e,12}, \delta_{v,12})$ must be determined through the proposed approach. The approach (flow chart), which is used to determine the interaction parameters, is illustrated in Figure 5.3 [137]. All these theoretical frame works to predict the each gas component in polymer melts were developed by Li [137]. After measuring the overall $PVT$ and solubility behaviors of CO$_2$ and N$_2$ blends in PS, the amount of each gas component was theoretically predicted using SS-EOS.
Figure 5.3 Flow chart for determining the optimal interaction parameters

T, P, gas density, P*, V*, T*, X_{apparent},
(\delta_{e,12}, \delta_{v,12}), (\delta_{e,13}, \delta_{v,13}), (\delta_{e,23}, \delta_{v,23}), \delta_{e}, \delta_{v}

Change interaction parameters \delta_{e}, \delta_{v}

Determine X_{theory}, V_s, and X_{corrected}

\sum(X_{theory} - X_{corrected})^2 is Minimum

No

Yes

END
5.3 Experimental

5.3.1 Materials

The PS used in this study was provided by the Dow Chemical Company (PS, Styron PS685D), and has a melt flow index of 1.5 g/10 min., specific gravity of 1.04 g/cm$^3$, and glass transition temperature of 108°C. The BAs used in this study were CO$_2$ (99.99 % purity), N$_2$ (99.998 % purity) and CO$_2$+N$_2$ blends with various weight ratios (25/75, 50/50, and 75/25). These were all provided by Linde Gas/BOC, Canada.

5.3.2 Apparatus and Experimental Procedure

Gas solubility was determined by empirically measuring gas uptake through the use of an MSB. Swelling was analyzed by using a laboratory developed PVT apparatus for high temperatures and pressures.

As mentioned in the previous chapters, a gravimetric method that uses an MSB from Rubotherm GmbH, Germany, was used to measure the sorption of CO$_2$ in polymer melts. A detailed description of the experimental apparatus and procedures is available in prior publications [124, 137], and a brief summary is provided below.

Before beginning the sorption experiment, a precisely weighed polymer sample was placed in a sealed absorption chamber, degassed in a vacuum chamber, and preheated to a designated temperature. The balance readout at vacuum P~0 and temperature T for the polymer sample without any dissolved gas was recorded as $m(0,T)$. This value reflects the weight of the vacuum.

High-pressure gas was subsequently charged into the chamber, and sorption took place. When the saturation stage was reached, the sorption ceased, and the weight readout from the balance was recorded as $m(P,T)$ at pressure $P$, and temperature $T$. Hence, the mass gained ($m_g$) from the dissolved gas in the polymer was calculated as follows in Equation 6-17:
\[ m_g = m(P, T) - m(0, T) + \rho_{\text{gas}}(V_B + V_P + V_S) \]  

where \( \rho_{\text{gas}} \) is the density of the gas inside the chamber at temperature \( T \) and pressure \( P \), which can be measured in situ by the MSB, and \( V_B, V_P, \) and \( V_S \) are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices) and pure polymer at temperature \( T \) and pressure \( P \) and the swollen volume of the polymer due to gas dissolution, respectively. \( V_B \) is usually determined in advance with a blank experiment. \( V_P(P, T) \) can typically be determined by using Tait’s equation [160, 161] for each polymer.

By ignoring the polymer’s swollen volume \( (V_S) \) in Equation 1, the measured weight gain of \( m_g \) of a polymer with a mass \( m \) at STP, can be transformed as follows to the apparent solubility of Equation 6-18, \( X_{\text{apparent}} \), which is less than the actual solubility:

\[ X_{\text{apparent}} = \frac{m(P, T) - m(0, T) + \rho_{\text{gas}}(V_B + V_P)}{m} \]  

\( X_{\text{apparent}} \) was calculated by using an MSB. As shown in Equations 5.17 and 5.18, it is impossible to accurately measure gas solubility in the polymer melt without considering the swollen volume \( (V_S) \). To accurately determine solubility, correction of the buoyancy effect on the apparent solubility data is essential, especially in a high-pressure condition where gas density (i.e., \( \rho_{\text{gas}} \)) is high and the swollen volume (i.e., \( V_S \)) is large.

The swollen volume was then measured by using an in-situ visualization system [185, 202] and coupled in the following equation to determine the exact solubility:

\[ X_{\text{corrected}} = X_{\text{apparent}} + \frac{\rho_{\text{gas}} \times V_S}{m} \]  

5.3.3 Determination of Scaling Parameters for SS-EOS

As usual, the SS-EOS scaling parameters for all components (CO\(_2\), N\(_2\) and PS) were optimized using the thermodynamic properties for each component. Data from the gas-liquid
saturation curves up to the critical point usually applied to extract the scaling parameters for gases. The PVT data for PS685 were obtained from Moldflow lab.

For PS, the SS-EOS scaling parameters were adjusted to yield the best fit to the experimental PVT data, as demonstrated in Fig. 5.4. It should be mentioned that the SS-EOS theory requires that the polymer segment sizes be adjusted in such a way that the molar repulsion volumes of the polymer segments match those of the gas molecules [29]. Therefore, in accordance with the polymer-gas system being studied, the new SS scaling parameters for PS were obtained. The SS scaling parameters for all components are listed in Table 5-1.

Table 5-1 Scaling parameters for SS-EOS [175, 181]

<table>
<thead>
<tr>
<th>SS Parameters</th>
<th>CO₂</th>
<th>N₂</th>
<th>PS 685D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P^*$ (MPa)</td>
<td>954.2</td>
<td>384.3</td>
<td>807.8</td>
</tr>
<tr>
<td>$V^*$ (cc/g)</td>
<td>0.586</td>
<td>0.9475</td>
<td>0.9621</td>
</tr>
<tr>
<td>$T^*$ (K)</td>
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<td>1227</td>
<td>16044</td>
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<tr>
<td>$S$</td>
<td>1</td>
<td>1</td>
<td>7309</td>
</tr>
<tr>
<td>$C$</td>
<td>1</td>
<td>1</td>
<td>1142</td>
</tr>
<tr>
<td>$M_n$ (g/mole)</td>
<td>44.01</td>
<td>28.01</td>
<td>$1.96 \times 10^5$</td>
</tr>
</tbody>
</table>
5.4 Results and Discussion

5.4.1 Determination of Pure Gas Solubility

5.4.1.1 Solubility of $CO_2$ and $N_2$ in PS

As previously discussed in Chapter 5 (Section 5.2.1), the solubilities of pure $CO_2$ and $N_2$ in PS at 403, 423 and 463 K ($130^\circ$C, $150^\circ$C and $190^\circ$C) were first investigated by using an MSB to measure the apparent solubility. The interaction parameters ($\delta_e$ and $\delta_v$) for each individual gas component and polymer were individually determined at 403, 423 and 463 K and listed in Table 5-2.
Table 5-2 Interaction parameters for PS/CO$_2$ and PS/N$_2$

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>PS/CO$_2$</th>
<th>PS/N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>$\delta_e$</td>
<td>1.1065</td>
<td>1.3512</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>1.1365</td>
<td>0.8850</td>
</tr>
<tr>
<td>423</td>
<td>$\delta_e$</td>
<td>1.1050</td>
<td>1.3589</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>1.1260</td>
<td>0.9114</td>
</tr>
<tr>
<td>463</td>
<td>$\delta_e$</td>
<td>1.1130</td>
<td>1.3800</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>1.1142</td>
<td>0.9187</td>
</tr>
</tbody>
</table>

After determining the apparent solubility by using an MSB, the theoretical and compensated solubilities of CO$_2$ and N$_2$ were determined by using SS-EOS and shown in Figures 5.5 and 5.6, respectively.
Figure 5.5 Solubility of CO₂ in PS

Figure 5.6 Solubility of N₂ in PS
5.4.2 Determination of Gas Blend Solubility

5.4.2.1 Interaction Parameters for CO\textsubscript{2}/N\textsubscript{2} in the Polymer Phase

In this study, gas blends of CO\textsubscript{2} and N\textsubscript{2} in three different compositions (25:75, 50:50, 75:25; mass ratios CO\textsubscript{2}:N\textsubscript{2}) were used. The compositions of the gas blends were chosen to cover a large range so that these experimental combinations might provide more accurate information for the ternary mixture system.

Table 5-3 Interaction parameters for CO\textsubscript{2}/ N\textsubscript{2} blends

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>CO\textsubscript{2}/N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>$\delta_e$</td>
<td>1.6866</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>0.8743</td>
</tr>
<tr>
<td>423</td>
<td>$\delta_e$</td>
<td>1.8036</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>0.8766</td>
</tr>
<tr>
<td>463</td>
<td>$\delta_e$</td>
<td>1.9635</td>
</tr>
<tr>
<td></td>
<td>$\delta_v$</td>
<td>0.8813</td>
</tr>
</tbody>
</table>

The interaction parameters for each individual gas component (CO\textsubscript{2}, N\textsubscript{2}) and polymer were individually determined at 403, 423 and 463 K and listed in Table 5-2; therefore, the interaction parameters for CO\textsubscript{2} or N\textsubscript{2} in the polymer phase were optimized according to the research methodology illustrated in Fig. 3.7 for the binary system. It was assumed that the interaction parameters for CO\textsubscript{2}/N\textsubscript{2} in the polymer phase strongly depend on temperature, but will not be affected by the composition of the polymer phase. Thereby, the interaction parameters for CO\textsubscript{2}/N\textsubscript{2} in the polymer phase were determined in such a way that the measurements for all gas
blends (25:75; 50:50; 75:25) were taken into account at one temperature during the calculation. The optimal interaction parameters for CO₂/N₂ determined in this way are listed in Table-5-3. The measured density of the blend gases and estimated by the SS-EOS are compared in Fig. 5.7. The density of the gas blends were measured by using the sinker of the MSB. The resolution of the MSB is 10 μg with a relative error of less than 0.002 % of the measured value. The reproducibility (standard deviations) of the machine is ± 20 μg. It is obvious that SS-EOS estimation is very close to the measured density for all gas blends at all temperatures and pressures.

Figure 5.7 Comparison of gas blend density between measured and estimated by SS-ES
5.4.2.2 Swelling Behavior of PS in Presence of CO$_2$/N$_2$ Blend

Volume measurements for the PS/CO$_2$, PS/N$_2$, and PS/CO$_2$+N$_2$ solutions were conducted at 403, 423 and 463 K by using a high-pressure gas and gas mixture. At each temperature, the pressure ranged from 7 MPa up to 21 MPa, at increments of 3.5 MPa. At each pressure level, the polymer/gas solution was maintained for 1.5 hours to ensure that system equilibrium was reached. Equilibrium was considered to be achieved when the total volume of the polymer/gas solution no longer changed. The volume of the polymer was also determined by using Tait’s equation [160, 161]. Following this, the volume swelling ratio was calculated by using Equation 3-9 for each polymer/gas system.

\[
S_w = \frac{V(T,P,t_{eq})}{V(T,P,t_{ini})} = \frac{V(T,P,t_{eq})}{m_{sample}v(T,P)}
\]

Figure 5.8 shows the volume swelling ratios of the CO$_2$+N$_2$ blends at 25:75, 50:50 and 75:25 in PS due to the dissolution of the gas mixture. It can be observed that the swelling ratio of the PS/CO$_2$+N$_2$ solution increases as the pressure is increased and decreases as the temperature is increased. When the pressure is increased at a constant temperature, the volume of the polymer/gas mixture and the volume swelling ratio both also increase. Since the solubility of CO$_2$+N$_2$ increases with an increase in pressure, as mentioned above, more CO$_2$+N$_2$ is dissolved into the PS matrix, which induces an increase in the volume swelling.
When a polymer melt is exposed to a high-pressure gas, two competing mechanisms will affect the specific volume. In the first case, the hydraulic pressure will decrease the specific volume of the compressible polymer/gas solution. In the second case, the dissolved gas under high pressure will cause the polymer to swell and increase the specific volume. The volume in the latter case is typically higher than that in the former case. This means that the presence of gas evidently enhances the overall activity of a polymer/gas system [238], and thus creates more free volume for the penetration of the gas molecules after the gas fills the existing free volume. The increased specific volume (i.e., increased free volume) causes an increase in the solubility and diffusivity of the polymer/gas mixture(s) [238]. The dissolved gas causes a plasticization effect.

Figure 5.8 Swelling, $S_w$ of PS in presence of CO$_2$+N$_2$ blends (a), 25:75; (b), 50:50; (c), 75:25.
that reduces the viscosity of the polymer/gas mixtures and increases their chain mobility [240, 241]. This increased specific volume also decreases the surface tension of the polymer [242]. In summary, despite the hydraulic compression effect, high-pressure gas increases specific volume and thereby affects the solubility, diffusivity, viscosity and surface tension of polymer/gas mixture(s).

![Diagram](image)

Figure 5.9 Comparison of swelling, $S_w$ of PS in the presence of CO$_2$, N$_2$ and CO$_2$/N$_2$ blend (a), 403K; (b), 423K; (c), 463K

Figure 5.9 shows a comparison of PS swelling at specific temperatures and various pressures due to gas dissolution. When the pressure is constant, higher temperatures result in less volume swelling in the PS/CO$_2$ solution. As the temperature increases, the polymer chains
become softer and more relaxed. As a result, both the free and specific volumes increase. On the other hand, the solubility of CO$_2$ in PS is known to decrease as temperature increases (Figure 5.4). This means that there is an increase in CO$_2$ coming out from the polymer matrix at a higher temperature in comparison to the circumstance where the polymer has more free volume. Therefore, despite the increased free volume in the PS matrix, the PS/CO$_2$ solution will lose CO$_2$ at a higher temperature. As the pressure climbs higher, the volume swelling is governed by the gas content, and its sensitivity to temperature decreases. For N$_2$, gas solubility increases as the temperature is increased (Figure 5.6). This indicates that for N$_2$, the free volume increases at a higher temperature, and chain mobility increases and at the same time more gas goes in to polymer due to positive heat of solution. As a result, swelling increases with temperature for the PS/N$_2$ system. However, in the polymer/gas-blend system, the two gases will behave in the opposite manner, depending on the temperature. They will reach equilibrium at a certain point, and will act on each other, and also with the polymer in a triangular relationship. It is obvious that the swelling is mainly governed by the CO$_2$ content for the blend systems. However, the sensitivity of the swelling ratio to the CO$_2$ content decreases as the temperature is increased (Figure 5.9c).

**5.4.2.3 Overall Solubility of CO$_2$+N$_2$ in PS**

Once the swelling ratio was calculated, the solubility was determined by using an MSB, and the swollen volume was calculated by using Equation 5-19. The solubilities of the CO$_2$+N$_2$ blends are shown in Figure 5.10. The solubility behavior of the blended (CO$_2$+N$_2$) gas in PS also linearly increases with pressure and decreases as the temperature increases. However, it was also noticed that for the 25:75 (CO$_2$:N$_2$) blend (Figure 6.9a), the solubilities at both 423 K (150°C) and 463 K (190°C) become closer due to the opposite solubility behavior of both gases with temperature where N$_2$ is dominant (as it comprises 75% of the blend).
Subsequently, the solubilities of the blended gases were compared with the individual solubilities (Figure 5.10). It was observed that at a higher temperature (463 K), the solubilities for both the 50:50 and 75:25 blends are very close. This could be due to the increase in the solubility of N\textsubscript{2} and decrease in the solubility of CO\textsubscript{2} as the temperature is increased, which may govern its overall solubility. This could be verified by determining the amount of each gas component in polymer.
Figure 5.11 Comparison of solubility behavior of PS in presence of CO₂, N₂ and CO₂/N₂ blend

(a), 403K; (b), 423K; (c), 463K

Figure 5.11 shows the solubilities of CO₂, N₂, and CO₂+N₂ in PS. It can be observed that the solubility of CO₂ increases as the pressure is increased and decreases as the temperature is increased, whereas for N₂, the solubility increases as both temperature and pressure are increased. It is clear that the solubility of CO₂ is much higher than that of N₂ in PS at any temperature and pressure. It is also obvious that the swelling effect is the dominating factor for accurately measuring solubility at high temperatures and pressures. It should be noted that solubility is mainly governed by the CO₂ content for the blend systems. However, the sensitivity of the solubility to CO₂ content decreases at high temperatures and low pressures (Figure 5.11c,)
7 and 10.4 MPa). This might be due to the small amount of CO₂ that is dissolved into the PS (less than 2%) at a high temperature (463 K) and a low pressure (up to 10.4 MPa).

5.4.3 Comparison of Swelling of CO₂+ N₂ Blends in PS- Theoretical and Experimental Values

After experimentally determining swelling, the swelling ratio was also theoretically determined by using the SS-EOS [181]. All of the characteristic parameters for the polymers and gas blends are given in Tables 5-1, 5-2 and 5-3.

Figure 5.12 Comparison of experimental and EOS-based swelling, \( S_w \) of PS in presence of CO₂ +N₂ blends
The volume swelling ratios of the PS in the presence of the CO$_2$+N$_2$ blends as determined from the SS-EOS are shown in Figure 5.12. It can be observed that for all types of gas blends, the swelling ratios predicted by the SS-EOS are quite close to the experimental values. This indicates the better prediction capability of SS-EOS to predict significant amounts of swelling in both polymer/gas and polymer/gas mixtures. However, at higher temperatures, the prediction accuracy is reduced. It can also be noticed that even though the SS-EOS predicts better swollen volumes for binary system (gas + polymer), it overestimates for the blend cases. It was also observed that SS-EOS predicts swollen volume more accurately for higher ratios of CO$_2$+N$_2$ (above 50:50) and lower temperatures. For lower ratio (25:75), SS-EOS predicts swollen volume accurately for higher temperature (463K). However, it underestimates for lower temperatures and higher pressures.

5.4.4 Comparison of Solubility of CO$_2$+N$_2$ Blends in PS- Theoretical, Semi-empirical, and Experimental Values

Since solubility that is completely experimentally determined would have much greater accuracy and reliability, after experimentally determining the solubility, the results were compared with my previous data, which had been calculated by using the SS-EOS [181]. All of the characteristic parameters for the polymers and gas blends are given in Tables 5-1, 5-2 and 5-3. The solubilities of the CO$_2$+N$_2$ blends in PS as determined from the SS-EOS are shown in Figure 5.13. It can also be noticed that although SS-EOS predicts better swollen volumes (greater swollen volume) in the cases with a higher CO$_2$+N$_2$ ratio (above 50:50), the SS-EOS predicts less accurately in cases where the CO$_2$+N$_2$ blend has a lower ratio (25:75) (less solubility) for all three temperatures. This is due to the swollen volumes that were determined by the SS-EOS, which are shown in Figure 5.12. These results indicate that the SS is able to more accurately predict solubility for a higher solubility case in both individual gas and gas blends in polymers.
Determination of Each Dissolved Gas Component of CO$_2$/N$_2$ in PS

In addition to determining the overall solubility of the BA blend, it is important to know the solubility of each individual component in the total dissolved gas blends. The theoretical calculation of the solubility of each individual component (N$_2$ or CO$_2$) in the total amount of dissolved gas blends was successfully predicted with the proposed thermodynamic model.
Table 5-4 Solubility of each component in polymer for CO$_2$+N$_2$ blends 25:75

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Pressure, MPa</th>
<th>Solubility (g-BA/g-Polymer)</th>
<th>CO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>CO$_2$+N$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>403</td>
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Table 5-5 Solubility of each component in polymer for CO$_2$+N$_2$ blends 50:50

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<tr>
<th>Temperature, K</th>
<th>Pressure, MPa</th>
<th>Solubility (g-BA/g-Polymer)</th>
<th>CO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td>CO$_2$+N$_2$</td>
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<td></td>
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### Table 5-6 Solubility of each component in polymer for CO$_2$+N$_2$ blends 75:25

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</table>

(Section 5.2.2). Solubility determined by the SS-EOS for overall and each gas component are shown in Tables 5-4, 5-5 and 5-6 for 25:75, 50:50, and 75:25 blends of CO$_2$+N$_2$ respectively.

It is clear that CO$_2$ governs the overall solubility due to more solubility than N$_2$. However, for lower ratio of CO$_2$:N$_2$ (25:75, Table 5-5) and at higher temperature (463 K) N$_2$ has significant effect and dominates on over all solubility. This is because as the temperature increases, the solubility of N$_2$ also increases whereas the solubility decreases in the case of CO$_2$. Another interesting finding is that because CO$_2$ is more soluble than N$_2$, the ratio of N$_2$ to CO$_2$ in the polymer melt phase is much lower than that in the vapor phase. This finding indicates that if a gas blend is applied during the foaming process, the less soluble component (here, it is N$_2$) tends to diffuse more rapidly and easily during the phase separation or nucleation process than the more soluble component. Therefore, when a gas blend is applied, the less soluble gas
component will contribute more to nucleation than the more soluble gas component. It is assumed that the relatively higher chemical potential associated with the less soluble gas in the polymer melt phase causes the less soluble gas to stay in the vapor phase when nucleation/phase separation is initiated. It is also obvious that CO$_2$ helps to dissolve more N$_2$ in PS melts.

5.4.6 Composition Ratio of Blowing Agents: In the Reservoir vs In the Polymer

The theoretical calculations that use the SS-EOS showed that the composition of the dissolved N$_2$/CO$_2$ blend in the polymer phase is different from that in the vapor phase in contact with the polymer phase. The relationship between the amount of N$_2$ (in wt%) in the vapor reservoir and that in the polymer melt phase was calculated and is shown in Figure 5-13 for 403, 423, and 463 K, respectively. It is to be noted that here the ratio in vapor-phase (reservoir) is N$_2$:CO$_2$ not CO$_2$:N$_2$ as mentioned in the earlier sections. The theoretical calculations demonstrate that, because more CO$_2$ than N$_2$ dissolved in the PS melt, the composition of N$_2$ in the polymer phase is much lower than that in the reservoir. In other words, in order to maintain a certain ratio of N$_2$/CO$_2$ in the polymer sample, a higher than desired ratio of N$_2$/CO$_2$ should be applied in the reservoir. It was also noticed that as the temperature increases, the composition of N$_2$ (in wt%) in polymer also increases, due to increased solubility of N$_2$ in polymer with increasing temperature.

By using the thermodynamic model obtained from this research, it is now possible to understand how the presence of one component in a gas blend affects the solubility and phase equilibrium of another component. The presence of a more soluble gas component in a gas mixture will result in a higher concentration of the more soluble gas in the polymer melt phase. According to the predicted results shown in Figure 5-14, pressure does not affect the relationship between the ratios in the vapor reservoir and the polymer melt phase. However, the relationship between the ratios in the vapor reservoir and polymer melt phase is affected by temperature. As
the temperature increases, the ratios in the polymer melt phase and the vapor reservoir increase, and this should be verified by experimental work. However, due to the limitations of the experimental data, this theoretical data could not be verified.

Figure 5.14 Composition of N₂ (wt%) in polymer phase vs. composition of N₂ (wt%) in vapor phase
5.5 Ternary System and In Situ Foaming [256]

Foaming behavior of PS in presence of CO₂/N₂ blends was also studied by using the batch foaming visualization system and the foaming processes were observed and captured with high speed camera[256]. A circular disc 6.5 mm in diameter was punched from the PS films and placed inside a high pressure and high temperature chamber with clear sapphire windows. There was a PET film with a center hole between the sapphire and the PS samples to avoid heterogeneous nucleation. In this study, the main goal was to study the foaming behavior of PS when different compositions of CO₂-N₂ gas blends were used. Therefore, the Psat and –dP/dt|max were kept constant at 10.34 MPa (1500 psi) and 15 MPa/s (2176 psi/s), respectively. To study the effect of temperature on the performance of BAs, three Tsys were used: 100°C, 140°C and 180°C [256].

Figure 5-15 shows snapshots of the video of all samples at 100°C, 140°C and 180°C. It was observed that the cell nucleation rate and cell density were significantly higher in the region where PS was in contact with the PET; in addition, there was an earlier onset of cell nucleation. This demonstrated that heterogeneous nucleating effect was substantial. Similar phenomena were observed for the other experimental cases, except for the cases foamed with 100% N₂ and the 25% CO₂-75% N₂ gas blend at 100 °C (refer to Figure 5-15), where no cells were formed in either region due to the limited plasticization effect of these gas blends at 10.34 MPa (gas solubility ≈ 0.0043 and 0.022 g-BA/g-polymer, respectively). In some other cases (i.e., 100% N₂ at 140°C, and 100% CO₂ at 140°C and 180°C), cells only nucleated in the region where PS and PET were in contact.

For the 100% CO₂ cases, the cells only nucleate at 100°C. This could be attributed to the increased diffusivity of CO₂ as temperature increases[132]. Since the thickness of the sample film was only 200 μm (which was chosen to ensure clear visibility of the individual bubbles) and
gas could have escaped through both the top and bottom surfaces in the suspended region, the increased diffusivity could have caused significant gas loss at the higher temperatures. As a result, the level of supersaturation decreased. Therefore, cell nucleation was less likely to occur spontaneously.

![In situ foaming images](image)

Figure 5.15 In situ foaming images[256]

The gas loss effect seemed to be less pronounced for the CO$_2$-N$_2$ blends and 100% N$_2$ cases in this study. This could be due to the lower diffusivity of N$_2$ in molten plastics as compared to CO$_2$ [171]. Nevertheless, at a low temperature (100°C) where the gas loss effect is believed to be less significant, the cell density of the 75% CO$_2$-25% N$_2$ case was still slightly higher than the 100% CO$_2$ case, thus showing the synergistic or complementary effect of CO$_2$-N$_2$ gas blends. In particular, this suggest that the addition of N$_2$ to CO$_2$ could help lessen the gas loss
effect during foaming processes, which could lead to foams with higher cell density and volume expansion ratio.

The cell density with respect to the unfoamed volume ($N_{\text{unfoamed}}$) versus time in the suspended regions of the plastic samples for all five BA cases are plotted in Figures 5-16. In each figure, the average cell density of the three experiments is shown, the characterization is based on the observable bubbles, and the error bars signify the standard deviations. It was noticed that as the temperature increases, the onset of cell nucleation occurs earlier, and takes less time to complete. This is due to the decreased surface tension and the increased mobility of gas molecules at higher temperatures.

The 75% CO$_2$-25% N$_2$ cases yielded the widest processing window as foams with high cell density were obtain at all three temperatures (100 °C, 140 °C and 180 °C). The average cell densities were also the highest (3.71 x 10$^6$ to 4.35 x 10$^6$ cells/cm$^3$) when compared to the other gas blends at each temperature. The nucleation rates for this gas blend were also among the highest when compared to the other four BAs (i.e., highest at 100°C and 180°C and second highest at 140°C). It was hypothesized that this foaming behavior was a result of an increased plasticization effect of CO$_2$ when compared to the cases with lower CO$_2$ content, which helped to dissolve extra N$_2$ that was required to induce cell nucleation. This hypothesis was confirmed from the each gas compositional data, which was derived from the overall gas solubility.
Nevertheless, this study provided directions for identifying such an optimal composition: a high percentage of CO$_2$ and a low percentage of N$_2$. This study also demonstrated that supercritical N$_2$ is a feasible alternative to alcohols as a co-blowing agent to supercritical CO$_2$ in PS foaming processes. It is expected that this knowledge could be applied to the other polymers that are currently foamed with blowing agent blends of CO$_2$ and an alcohol.
5.6 Summary

In the last two decades, physical BA blends have attracted significant attention in both the scientific and industrial communities. However, fully experimental data are still scarce. In this chapter, the solubilities of CO\(_2\) and N\(_2\) blends in PS are measured by using an MSB. The swollen volumes due to gas dissolution were determined by using a PVT apparatus for high temperatures and pressures. The solubility of CO\(_2\) in PS linearly increases with pressure and decreases with temperature. However, the solubility of N\(_2\) increases with both temperature and pressure. It is also noticed that at any temperature and pressure, the PS absorbs more CO\(_2\) than N\(_2\). For a CO\(_2\)+N\(_2\) blend system, only the overall solubility of the blend in polymer is measured which also linearly increases with pressure and decreases with temperature. Afterward, the actual amount of each gas in the polymer is determined by using a thermodynamic model for a ternary system based on the SS-EOS. It is confirmed that SS-EOS can predict the PVT and solubility behaviors not only for the binary system (polymer + gas) but also for the ternary system (polymer + gas blend). An effort has been made to understand the solubility of the complicated mixture system (multi-component mixture system) in polymer at phase equilibrium. Due to the solubility differences between the two BA components, the mass distributions in the reservoir and polymer are different. Moreover, the theoretical data of each gas component dissolved in polymer indicate that CO\(_2\) might help to dissolve more N\(_2\) in polymer. However, due to the lack of experimental data, this theoretical data cannot be verified but should be done so in the future.
CHAPTER 6. EFFECTS OF FULLY EXFOLIATED NANOPARTICLES ON THE PVT AND SOLUBILITY BEHAVIORS OF POLYMER

6.1 Introduction

In microcellular foaming, the nanoparticle, especially organoclay, has drawn a great deal of interest as a nucleating agent due to its low price and high aspect ratio. It has been observed that the cell density significantly increases ($10^2$-$10^3$ times) by adding even a small amount of nanoparticles. This is the result of the heterogeneous nucleation effect in the presence of nanoparticles. It has been claimed that the nanoparticles act as nucleus sites for bubble nucleation [154, 192, 213]. As a result, more bubble nuclei are developed for the same amount of gas, which results in a smaller cell size and a higher cell density. Since nanoparticles can be used as a nucleating agent for microcellular foaming, there is great deal of interest in further determining the details on their solubility to gain a better understanding of the foaming behavior of the nanocomposites.

6.2 Theoretical Background

Nanoparticles have been used for foaming in the last couple of decades [52, 257] and solubility plays very important role in cellular or microcellular foaming. However, there have been only a few studies conducted with regards to solubility in this area [134, 258]. Arrerat et al. [134] measured the solubility of CO$_2$ in a LDPE/TiO$_2$ nanocomposite by using an MSB and the SL-EOS. They showed that even though a nanocomposite polymer shows less apparent solubility compared to the neat system, the actual gas absorption by the polymer remains the same. On the other hand, Lee and his colleagues [194] measured the solubility of CO$_2$ in a PS nanocomposite
at 50°C by measuring the weight gain of the polymer in a high pressure chamber. They showed that with the infusion of nanoparticles, the solubility increases. They also observed that exfoliated PS nanocomposites absorb more gas than the neat and intercalate structures and thus have the highest cell densities during foaming. However, the mechanisms that determine the solubility of gas in PNC have not yet been identified. Moreover, the PVT behaviors of a PNC/gas mixture that would govern the solubility of PNC [124, 137, 175, 239] are unknown. Since the gas absorption phenomenon in a polymeric melt strongly depends on the swelling behavior of the molten material, the understanding of accurate PVT behavior is extremely important for a solubility study.

Recently, Utracki and Simha [259, 260] investigated the PVT behavior of PP-based PNC systems. They found that determining the actual PVT behavior of nanocomposites is far more complex than that for a simple mixture of polymer and nanoparticles. They first determined the overall PVT behaviors of the nanocomposites with and without a compatibilizer (binary and ternary systems, respectively), by using a Gnomix machine and then determined the average interaction parameters of the SS-EOS from the PVT behaviors. They also determined the interaction parameters for neat and solid nanoparticles from the average value by adopting an arbitrary exponential function. They eventually developed a model to describe the PVT behaviors of those nanocomposites in consideration of the soft section (neat polymer) and the hard section (nanoparticles wrapped with solidified polymer). However, the PVT behaviors of nanocomposites with dissolved gas would be even more complex and have not been investigated. Since the amount of swelling with dissolved gas is required to determine solubility [127-129, 132-134, 137, 168, 169, 171, 175, 237, 245], the interaction of the polymer and the gas molecules in the presence of nanoparticles should be studied. The amount and dispersion of nanoparticles are expected to influence the swelling behaviors of a nanocomposite/gas mixture.
In this study, my efforts are focused on the effects of the nanoparticles on the \( PVT \) and solubility behaviors.

### 6.3 Modeling of Organoclay Nanocomposite Fully-Exfoliated Case

![Illustration of different states of dispersion of organoclays in polymers with corresponding WAXS and TEM results](image)

Paul at el. [161] explained various structure formations of nanocomposite materials due to the inclusion of nanoparticles (Figure 6.1). It is well-known that the structure of nanocomposites might be either exfoliated or intercalated if the nanoparticles are compatible with polymer. After determination of the \( PVT \) and solubility behaviors of HDPE-PNC, a model was adopted to explain the phenomenon. The model is based on the work by Utracki et al. [53].

Israelachvili et al. [261] and Horn and Israelachvili [163] measured the viscosity of a PS/mica solution by using a surface force analyzer (SFA). They noted that the area just above the
platelet polymer behaves like a solid (2-9 nm thick surface layer), and then the viscosity progressively decreases. They found that the average bulk solution viscosity is 100-120 nm away from the solidified polymer. Motivated by these findings, Utracki et al. [53] investigated the PVT behavior of the nanocomposites of PP. According to them, without counting the transition section, the nanocomposites consist of mainly two sections: (1) a hard section, which comprise nanoparticles wrapped with solidified polymer; and (2) a soft section, which is like the regular polymer. The model assumes a reduction of molecular mobility near a crystalline surface (here clay) and this is defined as “solidified polymer”.

![Figure 6.2 Modeling of organoclay PNC system without gas (fully exfoliated case)](image)

The solubility of a BA in PNC would depend on how the BA interacts with the hard and soft sections. The solubility of CO₂ in various HDPE-PNC samples (with compatibilizer) was determined at various temperatures and pressures. The model (Figure 6.2) developed by Utracki and Simha [53] was adopted to determine the solubility of the BAs in nanocomposites.
According to the model, the nanocomposite consists of two sections: (a) a hard section, and (b) a soft section. They assumed that the inorganic platelets are coated with 6 nm thick solidified PP (hard section) and dispersed into the PP matrix.

The assumptions of this modeling for solubility measurement are as follows:

1. Gas will only dissolve in the soft section.

2. The hard section does not change in terms of mass and volume in the composite during gas dissolution in the PNC.

3. Only the soft section will swell due to gas dissolution.

The composition of the hard section in the mixture is determined by the organoclay content (K is the number of MMT platelets with a thickness of 0.96 nm, K=1 for exfoliated case) and its distribution in the PNC system (Figure 6.3).
6.4 Solubility Determination of PNC System

There are three major issues when calculating the solubility of BAs in nanocomposite melts. They are as follows:

i. the \( PVT \) behavior of the soft section,

ii. the solubility behavior of the soft section, and

iii. the swelling behavior of the soft section.

According to research work by Utracki and Simha [18], the \( PVT \) behavior of the soft section is exactly the same as that of neat polymer. Therefore, depending on the soft section behavior, the determination of the solubility of BAs in a PNC system can be divided into 3 major ways: (1) purely theoretical, (2) semi-empirical, and (3) purely experimental approach.

6.4.1 Purely Theoretical Approach

Once the amount of soft or hard section is known, the solubility of a PNC system can be theoretically determined from the solubility information of neat polymer and the EOS. If the solubility behavior of the soft section is the same as that of neat polymer (\textit{Approach 1}), its solubility can be theoretically determined from the solubility of the neat polymer and the solidified polymer amount. On the other hand, if the solubility behavior is different than that of neat polymer, the solubility can be theoretically determined by using an EOS (\textit{Approach 2}).

6.4.2 Semi-Empirical (Semi-Experimental + Semi-Theoretical) Approach

The solubility of the PNC system can also be determined by using the MSB and theoretically calculating the swollen volume. According to Equation 6-3, once the apparent solubility is calculated from the MSB, the only unknown parameter is the swollen volume (\( V_3 \)).
This swollen volume can be calculated by two approaches. If the swelling behavior of the soft section is the same as the neat polymer (Approach 3), the swollen volume can be calculated from the neat polymer swollen information and vol% of soft section. On the other hand, if the swelling behavior is different from that of the neat polymer, the swollen volume can be calculated using SS-EOS and hence the solubility (Approach 4) can also be determined.

6.4.3 Purely Experimental Approach

In recalling Equation 7-3, solubility can be purely experimentally measured if the swollen volume or polymer/gas density can be experimentally determined (Approach 5). This is the most accurate approach. The determination of the PVT behavior of a polymer/gas mixture by using a visualization system is one of the current research activities that I and my colleagues have undertaken in the laboratory at the University of Toronto. Once the PVT properties of the PNCs are directly measured, anyone will be able to evaluate the validity of the other 4 approaches (1-4). It also helps to compare all of the PVT and solubility data predicted by the EOS and evaluate the validity.

6.5 Experimental

6.5.1 Materials

The HDPE/clay nanocomposites used in this study are listed in Table 6-1. In this study, HDPE (2607; Nova Chemicals, Calgary, Canada) with a density of 0.947 g/cm³ and a melt flow index (MFI) of 5.0 g/10 min (ASTM D 1238) and HDPE-g-maleic anhydride (PE-g-MAn, Fusabond MB-100D, MFI 2.0 g/10min; DuPont Canada, Kingston, Canada) were used. An organoclay, a natural montmorillonite layered silicate modified with dimethyl dehydrogenated tallow alkyl ammonium (Cloisite 20A; Southern Clay Products, Gonzales, TX), was utilized as the filler. The details of the sample preparation were discussed in a journal article by Lee [262].
Carbon dioxide (Coleman grade, 99.99% purity, Linde Gas/BOC Canada) and all other materials were used as received.

### Table 6-1 HDPE-PNC used in this study

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<td>5</td>
<td>HDPE-3-MA</td>
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### 6.5.2 Experimental Procedure

Gas solubility was determined by empirically measuring gas uptake with an MSB. The swelling was analyzed by using a laboratory developed PVT apparatus for high temperatures and pressures.

As mentioned in the previous chapters, a gravimetric method that utilizes an MSB from Rubotherm GmbH, Germany, was used to measure the sorption of CO₂ in polymer melts. A detailed description of the experimental apparatus and procedures is available in prior publications [124, 137], and a brief summary of the procedure is described below.

Before beginning the sorption experiment, a precisely weighed polymer sample was placed in a sealed absorption chamber, degassed in the vacuum chamber, and preheated to a designated temperature. The balance readout at vacuum P~0 and temperature T for the polymer
sample without any dissolved gas was recorded as \( m(0,T) \). This value reflects the weight of the vacuum.

High-pressure gas was subsequently charged into the chamber, and sorption took place. When the saturation stage was reached, the sorption ceased, and the weight readout from the balance was recorded as \( m(P,T) \) at pressure \( P \) and temperature \( T \). Hence, the mass gained \( (m_g) \) from the dissolved gas in the polymer was calculated as follows in Equation 6-1:

\[
m_g = m(P,T) - m(0,T) + \rho_{gas} (V_B + V_P + V_S)
\]

where \( \rho_{gas} \) is the density of the gas inside the chamber at temperature \( T \) and pressure \( P \), which can be measured in situ by the MSB and \( V_B, V_P \), and \( V_S \) are the volumes of the sample holder (i.e., the sample container and all measuring load coupling devices) and pure polymer at temperature \( T \) and pressure \( P \), and the swollen volume of the polymer due to gas dissolution, respectively. \( V_B \) is usually determined in advance with a blank experiment. \( V_P(P,T) \) can be typically determined by using Tait’s equation [160, 161] for each polymer.

By ignoring the swollen volume \( (V_S) \) of the polymer in Equation 1, the measured weight gain of the \( m_g \) of the polymer with a mass \( m \) at STP can be transformed as follows to the apparent solubility of Equation 6-18, \( X_{apparent} \), which is less than the actual solubility:

\[
X_{apparent} = \frac{m(P,T) - m(0,T) + \rho_{gas} (V_B + V_P)}{m}
\]

The \( X_{apparent} \) was calculated by using an MSB. As shown in Equations 6.1 and 6.2, it is impossible to accurately measure gas solubility in the polymer melt without considering the swollen volume \( (V_S) \). To accurately determine solubility, correction of the buoyancy effect on the apparent solubility data is essential, especially in a high-pressure condition where gas density (i.e., \( \rho_{gas} \)) is high and swollen volume (i.e., \( V_S \)) is large.
The swollen volume was then measured by using an in-situ visualization system [185, 202] and coupled in the following equation to determine the exact solubility:

$$X_{corrected} = X_{apparent} + \frac{\rho_{gas} \times V_r}{m}$$  \hspace{1cm} 6-3

It should be noted that the determined solubility of the PNC is only the solubility of the neat polymer, and not the overall solubility of the PNC.

### 6.5.3 PVT Data of Neat HDPE

The PVT data for pure HDPE were obtained through the use of a Gnomix PVT apparatus from McGill University. The PVT equation (Tait’s equation) was then derived based on the measurement data. The PVT equation is listed below for HDPE (Equation 6-4).

$$v_{p, \text{pure}} = (1.1488 + 9.7005 \times 10^{-4} T) \times (1 - 0.089 \ln(1 + \frac{P}{197.17 \exp(-5.1317 \times 10^{-3} T)}))$$  \hspace{1cm} 6-4

where the specific volume $v_{p, \text{pure}}$ is in cc/g, the temperature $T$ is in °C and pressure $P$ is in MPa.

Furthermore, the PVT data of this pure material were used to derive the corresponding characteristic parameters: $P^*$, $V^*$, $T^*$ for the SS-EOS. All of the characteristic parameters are listed in Table 6-2. The specific volumes determined by the SS-EOS and experimental data were compared, see Figure 6.4. It was found that the SS-EOS is well capable of determining the PVT behavior of neat HDPE.

<table>
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<th>Substance</th>
<th>$P^*/$MPa</th>
<th>$V^*/$(cm$^3$/g)</th>
<th>$T^*/$K</th>
<th>$M_*$/(g/mole)</th>
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</tbody>
</table>

Table 6-2 Scaling parameters for SS-EOS for HDPE
Figure 6.4 Comparison of specific volume of the neat HDPE between experimental and theoretical (SS-EOS) calculation

### 6.5.4 PVT Data of HDPE Nanocomposites

The PVT data for pure HDPE-polymeric nanocomposites (HDPE-PNCs) were obtained through the use of a Gnomix PVT apparatus from McGill University. The PVT equations (Tait’s equations) were then derived based on the measurement data. Furthermore, the PVT data of this

<table>
<thead>
<tr>
<th>Substance</th>
<th>$P^*/$MPa</th>
<th>$V^*/$(cm$^3$/g)</th>
<th>$T^*/$K</th>
<th>$M_*/$(g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE-00-MA</td>
<td>623.9</td>
<td>1.1779</td>
<td>10684</td>
<td>40.3</td>
</tr>
<tr>
<td>HDPE-0.05-MA</td>
<td>620.9</td>
<td>1.1679</td>
<td>10584</td>
<td>40.3</td>
</tr>
<tr>
<td>HDPE-0.5-MA</td>
<td>640.3</td>
<td>1.1585</td>
<td>10412</td>
<td>38.9</td>
</tr>
<tr>
<td>HDPE-3-MA</td>
<td>631.5</td>
<td>1.1452</td>
<td>10492</td>
<td>40.2</td>
</tr>
</tbody>
</table>
pure material was used to derive the corresponding characteristic parameters: $P^*$, $V^*$, $T^*$ for the SS-EOS. All the characteristic parameters are listed in Table 6-3. The specific volume determined by SS-EOS and experimental data were compared (Figure 6.5). It is obvious that SS-EOS is well capable to determine the $PVT$ behavior of HDPE-PNC. It is to be noticed that infusion of nanoparticles decreases the specific volume of the polymer.

![Graph showing comparison of specific volume of Neat HDPE and HDPE-PNC between experimental and theoretical (SS-EOS) calculation](image)

Figure 6.5 Comparison of specific volume of the neat HDPE and HDPE-PNC between experimental and theoretical (SS-EOS) calculation

6.6 Results and Discussion

6.6.1 Swelling Behavior of HDPE Nanocomposites in Presence of CO$_2$

As illustrated in all of the previous chapters, the swelling of a polymer/gas mixture due to the dissolution of gas is unavoidable during solubility measurement. The amount of the total volume swelling is determined as the product of the total mass and the specific volume of the polymer/gas mixture. Therefore, swelling and solubility are coupled with each other.
Section 3.2.1.1 has outlined the detailed procedures for the calculation of $V_s$. The swelling ratios of the HDPE-PNC samples were measured at temperatures from 423K to 493K (150°C to 220°C), and pressures up to 21 MPa by using a PVT apparatus. The swelling behaviors of the HDPE-PNC samples are shown in Figures 6.6. It can be observed that the swelling ratio decreases as the temperature and the amount of nanoparticles increase for all PNC systems. Since the nanoparticles decrease free volume and thereby the swelling as discussed above, the capacity of the PNC for accommodating gas will be decreased with the nanoparticles. It can also be noticed that grafted-maleic anhydride (HDPE-g-MA) decreases the swelling of HDPE.
polymer. To decouple the effect of g-MA and to determine the effect of nanoparticles only, the comparison was made between the HDPE-g-MA and HDPE-PNC. It is clearly shown that infusion of nanoparticles significantly decreases the amount of swollen volume.

### 6.6.2 Solubility of CO$_2$ in HDPE Nanocomposites

![Figure 6.7 Solubility of CO$_2$ in HDPE-PNCs](image)

The solubility of CO$_2$ in the HDPE-PNC samples was measured at temperatures from 423K to 493K, and pressures up to 25 MPa by using an MSB. The solubilities determined from fully experimental approach are shown in Figures 6.7. It can be observed that the solubility of CO$_2$ decreases as the temperature and the amount of nanoparticles increase for all of the PNC
Figure 6.8 Effect of nanoparticles on solubility of CO$_2$ in HDPE-PNCs systems. Since the nanoparticles decrease free volume [17, 18] and thereby the swelling as discussed above, the capacity of PNC for accommodating gas will be decreased with the nanoparticles (Figure 6.8). It can also be noticed that grafted-maleic anhydride (HDPE-g-MA) decreases the solubility of CO$_2$ in polymer. However, to decouple the effect of g-MA and to determine the effect of nanoparticles only on solubility, the comparison was made between the HDPE-g-MA and HDPE-PNC. Moreover, to describe this kind of phenomenon a model was adopted and described in the next following sections. It is obvious that infusion of organoclay nanoparticles in polymer decreases the solubility of gas in polymers. It is believed that infusion
of nanoparticles generates significant quantity of solidified polymer near its surface (interfacial zone). Since solid like polymer absorbs a few or very less amount of gas, the total absorption capacity of the system decreases. However, the amount of absorption of gas fully depends on exfoliation percentage. Nonetheless, it is also believed that the solubility behavior of polymeric composites fully depends on the interaction or affinity between fillers (micro or nano) and gas. In other words, if the nanoparticles (such as CaCO$_3$, aluminum oxide, tin oxide) or fillers (such as carbon black, zeolites, silica gel) are highly polar and/or porous, over all sorption (absorption + adsorption) might increase due to adsorption phenomenon.

6.7 Comparison of All Approaches to Determine Solubility

As mentioned above, all the five approaches were applied to determine the solubility of CO$_2$ in HDPE-PNC system. The solubilities of CO$_2$ in the HDPE-PNC samples were determined/predicted at temperatures from 423K to 493K, and pressures up to 21 MP. The solubilities determined from the different approaches are shown in Figures 6.9. The fully experimental approach (approach 5) indicates that infusion of nanoparticles might generate significant amount of solidified-polymer which may reduce total absorption capacity of the polymer. It is also clear that approach 1 and 4 gives very close prediction for low loading nanoparticles. However, for 0.5% nanoparticles, approach 1 and 3 provide better prediction. It is also obvious that fully experimental approach-5 has the lowest solubility for all cases. The interaction parameters for all 3 temperatures are given in Table 6-4.
Table 6-4 Interaction parameters for HDPE-PNC+CO₂

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>HDPE+CO₂</th>
<th>HWC-0.05+CO₂</th>
<th>HWC-0.5+CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>δₑ</td>
<td>1.3004</td>
<td>1.2955</td>
<td>1.2951</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7213</td>
<td>0.7215</td>
<td>0.7216</td>
</tr>
<tr>
<td>463</td>
<td>δₑ</td>
<td>1.3061</td>
<td>1.3001</td>
<td>1.2981</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7184</td>
<td>0.7211</td>
<td>0.7201</td>
</tr>
<tr>
<td>493</td>
<td>δₑ</td>
<td>1.3201</td>
<td>1.3020</td>
<td>1.3011</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7172</td>
<td>0.7105</td>
<td>0.7103</td>
</tr>
</tbody>
</table>
Figure 6.9 Comparison of all approaches to determine the solubility of CO$_2$ in HDPE-PNC
6.8 Determination of Solidified Polymer Thickness (t) of PNC

After determining the solubility of HDPE-PNC the thickness of the solidified polymer was determined. Full exfoliation of clay/high density polyethylene (HDPE) nanocomposites was successfully achieved with the aid of maleated HDPE (PE-g-MAn), by melt blending in a twin-screw extruder employing a long residence time configuration. The detail could be found in journal [262]. The morphology of the composites was determined using wide-angle X-ray diffraction and transmission electron microscopy [262]. Figure 6.10 shows that in the case of HWC1.0, there were no characteristic clay peaks, indicating that an exfoliated structure was achieved. For HWC3.0 and HWC5.0, there was a substantial reduction in the intensity of the diffraction peak, which is shifted at a lower angle than that of pure clay, suggesting a mixture of intercalated and exfoliated clay. It is apparent therefore that, under the same processing conditions, clay concentration affects the degree of the exfoliation. No evidence of a peak was seen at clay loadings below 1 wt%. The successful generation of exfoliated structures is attributed largely to the chosen screw configuration, which ensured increased residence time and moderately high shear intensity inside the extruder, thereby facilitating the diffusion of polymer into the clay galleries. In addition to the choice of suitable processing conditions, increasing the compatibility between the matrix and the organoclay by adding PEg-MAn is necessary to facilitate delamination of clay platelets [262].
Figure 6.10 X-ray diffraction patterns of HDPE-PNC composites: (a) HWC0.05 (b) HWC0.5 (c) HWC1.0 (d) HWC3.0 (e) HWC5.0 (f) pure clay (Cloisite 20A) [262]

The model is based on fully exfoliated case where only one MMT wrapped-up with solidified polymer on both sides as shown in Figure 6.2. If the total number of MMT amount is N, then the total solidified-polymer, \( V_{\text{solidified-polymer}} \) amount would be

\[
V_{\text{solidified-polymer}} = 2N\pi r_{\text{MMT}}^2 t_{\text{solidified-polymer}}
\]  

For MMT particles, the total volume is \( NV_{1\text{-MMT}} \) (in m\(^3\)). If the corresponding MMT mass is \( X_{\text{MMT}} \) (in g), and density is \( \rho_{\text{MMT}} \) (2.3 x10\(^6\) g/m\(^3\)) [53] then it can be written as:

\[
X_{\text{MMT}} = \rho_{\text{MMT}} \times NV_{1\text{-MMT}} = \rho_{\text{MMT}} \times N\pi r_{\text{MMT}}^2 t_{\text{MMT}}
\]
where \( t_{\text{MMT}} \) is the thickness (0.96x10\(^{-9}\) m) and \( r \) is the radius (100x10\(^{-9}\) m) \([53]\) of the MMT particle respectively. It is to be noted that once \( X_{\text{MMT}} \) is known, the total number of MMT, \( N \) can be determined by using Equation 6-6. By putting the value of \( N \) in Equation 6-5,

\[
V_{\text{solidified-polymer}} = \frac{2X_{\text{MMT}}t_{\text{solidified-polymer}}}{\rho_{\text{solidified-polymer}}^M M T}
\]

6-7

Afterward, the total mass of the solidified polymer, \( m_{\text{solidified-polymer}} \) was determined by using the following formula:

\[
m_{\text{solidified-polymer}} = \rho_{\text{solidified-polymer}} \times V_{\text{solidified-polymer}}
\]

6-8

where \( \rho_{\text{solidified-polymer}} \) is the density of the neat polymer (0.947x10\(^6\) g/m\(^3\)). Now, once the \( m_{\text{solidified-polymer}} \) is known, the thickness of the solidified-polymer, \( t_{\text{solidified-polymer}} \) can be determined by using the Equation 6-9.

\[
m_{\text{solidified-polymer}} = \rho_{\text{solidified-polymer}} \times V_{\text{solidified-polymer}} = \rho_{\text{solidified-polymer}} \times \frac{2X_{\text{MMT}}t_{\text{solidified-polymer}}}{\rho_{\text{solidified-polymer}}^M M T}
\]

6-9

It is obvious that to determine the thickness of solidified-polymer, \( t_{\text{solidified-polymer}} \) and the total number of MMT particles, \( N \) the amount of MMT particles, \( X_{\text{MMT}} \) should be known first. The amounts of the MMT particles were determined from the TGA analysis and are shown in Table 6-4. Meanwhile the thickness of solidified-polymer was also determined from the experimental solubility data and using SS-EOS. In this case, Equation 6-9 was also used to predict the \( t_{\text{solidified-polymer}} \).

As a case study HDPE-0.05-gMA is explained here. The amount \( N \) was determined using equation 6-6 and TGA data as follows:

\[
N = X_{\text{MMT}} \left( \frac{\rho_{\text{MMT}} \times \pi r^2 t_{\text{MMT}}}{2.3 \times 10^6 \times 3.14 \times (100 \times 10^{-9})^2 \times 0.96 \times 10^{-9}} \right) = 0.0347 \left( \frac{2.3 \times 10^6 \times 3.14 \times (100 \times 10^{-9})^2 \times 0.96 \times 10^{-9}}\right)
\]

6-10

\[
N = 5 \times 10^{14}
\]
Afterward, using the solubility data, $N$ and SS-EOS, $t_{\text{solidified-polymer}}$ was determined. It was found that the solidified thickness is around 2-4nm range and it is independent of temperature.

Table 6-5 TGA results of HDPE-PNCs

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Onset Temperature (°C)</th>
<th>Peak Temperature (°C)</th>
<th>Final Temperature (°C)</th>
<th>Weight percentage of MMT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat HDPE</td>
<td>470.7</td>
<td>499.6</td>
<td>518.8</td>
<td>0</td>
</tr>
<tr>
<td>HWC-0.0</td>
<td>481.5</td>
<td>508.5</td>
<td>530.9</td>
<td>0</td>
</tr>
<tr>
<td>HWC-0.05</td>
<td>487.3</td>
<td>508.9</td>
<td>-</td>
<td>0.0347</td>
</tr>
<tr>
<td>HWC-0.5</td>
<td>487.3</td>
<td>508.9</td>
<td>-</td>
<td>0.247</td>
</tr>
<tr>
<td>HWC-3.0</td>
<td>483.6</td>
<td>500.7</td>
<td>-</td>
<td>1.728</td>
</tr>
</tbody>
</table>

Table 6-6 Determination of thickness $t_{\text{solidified-polymer}}$ of HDPE-PNCs from solubility data

<table>
<thead>
<tr>
<th>Sample name</th>
<th>MMT, X wt%</th>
<th>Total number of Platelets, N</th>
<th>Thickness, t (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T=453 K</td>
</tr>
<tr>
<td>HWC-0.05</td>
<td>0.0347</td>
<td>$5 \times 10^{14}$</td>
<td>2.72</td>
</tr>
</tbody>
</table>
6.9 Verification of Solidified Polymer Thickness (t) of PNC by Using Solubility Data

After determining the thickness of the solidified polymer, the solubility data was used to verify it. In this case HDPE-g-0.5 PNC was taken into account and taking 3nm as solidified polymer thickness. The Figure 6.11 shows the solubilities determined by SS-EOS using the thickness of the solidified polymer and the experimental data. It is clear that solubility predicted by the SS-EOS is very close to the experimental data. This indicates that the thickness amount is quite accurate and has significant effect on solubility.

Figure 6.11 Verification of thickness of solidified polymer of PNC by using solubility data
6.10 Determination of Diffusivity of HDPE-PNC

In this study, the diffusivity of supercritical carbon dioxide in high density polyethylene (HDPE) and HDPE/Organoclay polymeric nanocomposite (HDPE-PNC) melts were investigated. The diffusivities were determined by using sorption curves of HDPE-PNC using a magnetic suspension balance (MSB). Diffusivities of CO$_2$ in the samples were determined using the following equation for Fickian diffusion through a flat plate[200, 201]:

$$\frac{M_t}{M_\infty} = 4\left(\frac{D}{\pi L}\right)^{0.5} \left(\frac{t}{L}\right)^{0.5}$$

where $M_t$ is the mass gain by the sample at time $t$, $M_\infty$ is the maximum mass gain, $D$ is the diffusivity of CO$_2$ in the polymer, and $L$ is the thickness of the sample. $M_\infty$ is the equilibrium solubility of CO$_2$ at the conditions of the experiment. The diffusion coefficient of CO$_2$ in sample was obtained from the slope of $M_t/M_\infty$ plotted against $t^{0.5}/L$ at 7 MPa and various $T$ for all samples. The following four assumptions were used during the diffusivity determination.

- Assuming Fick's second law.
- Assuming one-dimensional diffusion into polymer sample sheet with all diffusion substances entering through a single face plane.
- Treating the diffusion coefficient $D$ as being independent of gas concentration during each stepwise gas sorption process.
- Assuming the thickness of the polymer disk, $L$, to be constant during sorption (non swelling effect. Therefore only the sorption data at low pressure were used for extraction of the diffusivity).

As expected that nanocomposites would exhibit low diffusivities because of the nature of their gas barrier properties as reported by others [202, 263], the addition of clay reduced the
diffusivity slightly (Table 6-7). It is believed that the fully exfoliated nano clay particles will decrease the diffusivity because of the increased tortuous path, and decreased mobility of the polymer molecules due to huge number of MMT platelets \(10^{14}\). It was also noticed that diffusivity increases with increasing temperature.

Table 6-7 Determination of diffusivity of HDPE-PNCs from solubility data at 7 MPa

<table>
<thead>
<tr>
<th>Sample name</th>
<th>MMT, X wt%</th>
<th>Total number of Platelets, N</th>
<th>Diffusivity D, cm(^2)/s x 10(^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=423 K</td>
<td>T=463 K</td>
<td>T=493 K</td>
</tr>
<tr>
<td>Neat HDPE</td>
<td>-</td>
<td>-</td>
<td>8.10</td>
</tr>
<tr>
<td>HWC-0.05</td>
<td>0.0347</td>
<td>5\times10^{14}</td>
<td>7.31</td>
</tr>
<tr>
<td>HWC-0.5</td>
<td>0.247</td>
<td>35.6\times10^{14}</td>
<td>6.12</td>
</tr>
</tbody>
</table>

6.11 Summary

In this study, the solubilities of supercritical carbon dioxide in high density polyethylene (HDPE) and HDPE/Organoclay polymeric nanocomposite (HDPE-PNC) melts were investigated. The solubilities were determined by using a magnetic suspension balance (MSB) and by measuring the swollen volume using a PVT apparatus. It was found that infusion of nanoparticles decreases both the solubility and the swelling of the polymer. It was also noticed
that at a same temperature and pressure, fully exfoliated HDPE composites swell less and absorbs less CO$_2$ compared to intercalated samples. Afterward, a model was adopted to describe the pressure-volume-temperature ($PVT$) behaviors of HDPE nanocomposites with and without gas dissolution. According to the model, a nanocomposite consists of two sections: a hard section (a nanoparticle and solidified polymer surrounding the nanoparticle) and a soft section (neat polymer). It is believed that infusion of nanoparticles generates significant amount of solidified polymer and thus decreases both the solubility and swelling by decreasing the total absorbing capacity of the system. Finally, the amount of solidified polymer was also determined by using the model, fully exfoliated solubility and $PVT$ data. However, it is also believed that the solubility behavior of polymeric composites fully depends on the interaction or affinity between fillers (micro or nano) and gas. In other words, if the nanoparticles (such as CaCO$_3$, aluminum oxide, tin oxide) or fillers (such as carbon black, zeolites, silica gel) are highly polar and/or porous, over all sorption (absorption + adsorption) might increase due to adsorption phenomenon. Through the solubility, $PVT$ and modeling of nanocomposites, this research has advanced the understanding of the effect of nanoparticles on solubility that governs different physical phenomena (such as cell nucleation and, cell growth) during plastic foaming.
CHAPTER 7. EFFECTS OF INTERCALATED NANOPARTICLES ON THE PVT AND SOLUBILITY BEHAVIORS OF POLYMER

7.1 Introduction

There is a vast amount of literature on PE/clay nanocomposites. However, in most cases, attempts to achieve fully exfoliated clay nanocomposites by adding a small amount of clay (<3 wt %) have not been successful due to the lack of favorable interactions between polymers and the clay surface, which result in clay particle aggregation. Different microstructures, including intercalated, mixed intercalated, exfoliated, and ordered and disordered exfoliated, may be obtained depending on the clay content, with the latter being favored as the clay content decreases. In intercalated nanocomposites, most clay exists in layered stacks; therefore, the polymer–clay has a reduced actual interfacial contact area, whereas a completely exfoliated structure ensures maximum interfacial contact due to its extremely fine dimensions (high aspect ratios over 200). The large surface area of fully exfoliated clay nanoparticles, and intimate contact between particles and polymer matrix may notably improve physical and mechanical properties, as well as other performance characteristics of their composites, such as flame retardancy, without substantially affecting their processability and cost, even at very low clay contents of less than 1.0 wt %.

In Chapter 6, the PVT and solubility behaviors of fully exfoliated nanocomposites were elucidated. In this chapter, the main focus is on the PVT and solubility behaviors of intercalated nanocomposites which are mostly common cases. In this study, the effect of nanoparticles on the PVT and solubility behaviors of polypropylene nanocomposites (PP-PNCs) is investigated.
7.2 Modeling of Organoclay Nanocomposite for Intercalated Case

As mentioned in Chapter 6, Utracki et al. [53] investigated the PVT behavior of PP nanocomposites. They indicated that without counting the transition section, the nanocomposites mainly consist of two sections: (1) a hard section, which comprise nanoparticles wrapped with solidified polymer; and (2) a soft section, which is like regular polymer. The solubility of a BA in PNC would depend on how the BA interacts with the hard and soft sections. The model developed by Utracki et al. [53] was adopted to determine the solubility of BAs in nanocomposites. According to the model, nanocomposites consists of two sections: (a) a hard section, and (b) a soft section. The assumptions for this type of modeling for solubility measurement were described in Chapter 7. The composition of the hard section in the mixture is determined by the organoclay content ($K$ is the number of MMT platelets with a thickness of 0.96x K nm).

![Diagram of organoclay PNC system with gas (intercalated case)](image)

Figure 7.1 Modeling of organoclay PNC system with gas (intercalated case)
0.96 nm, \( K=1 \) for exfoliated case) and its distribution in the PNC system (Figure 7.5). For intercalated cases, \( K \) might be any number higher than 1 and to be determined. As described in previous chapter (equation 6-5), the total number of particle and \( K \) is related by as follows:

\[
V_{\text{solidified-polymer}} = 2N'\pi r_{\text{MMT}}^2 \frac{t_{\text{solidified-polymer}}}{N'N'K} \quad 7-1
\]

As \( K=1 \), \( N' = N \).

7.3 Experimental

7.3.1 Materials

Polypropylene/clay nanocomposites used in this study are listed in Table 7-1. The organoclay is montmorillonite (MMT) intercalated with 0.78 mmol/g of dimethyl dihydrogenated tallow ammonium chloride (Cloisite 15A from Southern Clay Products, Gonzales, TX; (d001) 2.96 nm; abbreviated as C15). All of the samples were obtained from the National Research Council Canada (NRCC), Industrial Materials Institute, QC, Canada. Details on the sample preparation have been discussed in a journal article by Utracki et al. [53].

Table 7-1 PP-PNC used in this study

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Neat Polymer, (wt%)</th>
<th>Organoclay (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>PP-2</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>PP-4</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>
7.3.2  

**PVT Behavior of PP Nanocomposites**

The PVT behaviors of the PP-PNCs are shown in a journal paper by Utracki et al. [53]. Utracki et al. measured the PVT behavior of PP and its nanocomposites by using a Gnomix machine. It was found that the infusion of organoclay decreases the specific volume of the PP polymer [53]. After measuring the PVT, they extracted the scaling parameters of the SS-EOS for the PP and PP-PNC systems. The scaling parameters are shown in Table 7-2. The SS-EOS was used to predict the swelling and solubility of PP-PNCs.

Table 7-2 SS-EOS parameters for the PP-PNC used in this study [53]

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$P^*$ (MPa)</th>
<th>$V^*$ (cc/g)</th>
<th>$T^*$ (K)</th>
<th>$M_s$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>572.7</td>
<td>1.1728</td>
<td>10449</td>
<td>43.1</td>
</tr>
<tr>
<td>PP-2</td>
<td>516.9</td>
<td>1.1874</td>
<td>10712</td>
<td>48.4</td>
</tr>
<tr>
<td>PP-4</td>
<td>502.8</td>
<td>1.1857</td>
<td>10917</td>
<td>50.7</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>954.2</td>
<td>0.5860</td>
<td>2,960</td>
<td>44.01</td>
</tr>
</tbody>
</table>

7.4 Results and Discussion

7.4.1  

**Swelling Behavior of PP Nanocomposites in Presence of CO$_2$**

As illustrated in all of the previous chapters, the swelling of a polymer/gas mixture due to the dissolution of gas is unavoidable during solubility measurement. The amount of the total volume swelling is determined as the product of the total mass and the specific volume of the polymer/gas mixture. Therefore, swelling and solubility are coupled with each other. Section 3.2.1.1 outlined the detailed procedures for the calculation of $V_s$. The swelling ratios of the PP-PNC samples were measured at temperatures from 453 K to 493 K (180°C to 220°C), and pressures up to 21 MPa by using a PVT apparatus. The swelling behaviors of the PP-PNC samples are shown in Figure 7.2. It can be observed that the swelling ratio decreases as the
temperature and the amount of nanoparticles increase for all of the polymer nanocomposite (PNC) systems. Since the nanoparticles decrease the free volume [17, 18] and thus the swelling as discussed above, the capacity of the PNCs to accommodate gas will be decreased with the nanoparticles. It is clearly shown that the infusion of nanoparticles significantly decreases the amount of swollen volume. To illustrate this phenomenon, a model was adopted and described in the modeling section (Section 7.1). Since swelling only takes places in the soft section, a reduced soft section by the introduction of nanoparticles may significantly affect the overall swelling behaviors if the nanoparticles are well dispersed. The hard section might also affect the degree of swelling in the soft section by acting as a structure constraint. However, the effect of the hard section on the degree of swelling has not yet been determined.
Figure 7.2 Swelling behavior of PP-PNCs in presence of CO₂
7.4.2 Solubility of CO\textsubscript{2} in PP Nanocomposites

The solubility of CO\textsubscript{2} in the PP-PNC samples was measured at temperatures from 423 K to 493 K, and pressures up to 21 MPa by using an MSB. The solubilities determined from a fully experimental approach are shown in Figure 7.3. It can be observed that the solubility of CO\textsubscript{2} decreases as the temperature and the amount of nanoparticles increase for all of the PNC systems. Since the nanoparticles decrease the free volume [17, 18] and thus the swelling as discussed above, the capacity of PNCs to accommodate gas will be decreased with the nanoparticles (Figure 7.2). However, in order to describe this kind of phenomenon, a model was adopted, and is described in Section 7.1.
It should be noted that solubility is defined not in the overall composite, but rather, only in the polymer. It is obvious that the infusion of organoclay nanoparticles in the polymer decreases the solubility of gas in polymers. It is believed that the infusion of nanoparticles generates a significant quantity of solidified polymer near its surface (interfacial zone). Since solids like polymers absorb little or very small amounts of gas, the total absorption capacity of the system decreases. However, the amount of gas absorption fully depends on the exfoliation percentage. Nonetheless, it is also believed that the solubility behavior of polymeric composites fully depends on the interaction or affinity between fillers (micro or nano) and gas. In other
words, if the nanoparticles (such as CaCO$_3$, aluminum oxide, tin oxide) or fillers (such as carbon black, zeolites, silica gel) are highly polar and/or porous, the overall sorption (absorption + adsorption) might increase due to an adsorption phenomenon. In intercalated nanocomposites, most clay exists in layered stacks; therefore, polymer–clay has a reduced actual interfacial contact area and smaller amounts of solidified polymer generated. As a result, unlike exfoliated cases, solubility and swelling might not significantly decrease compared to neat polymers.

7.5 Comparison of All Approaches to Determine the Solubility

As mentioned above, all of the five approaches were applied to determine the solubility of CO$_2$ in PP-PNC systems. The solubilities of CO$_2$ in the PP-PNC samples were determined/predicted at temperatures from 453 K to 493 K, and pressures up to 21 MP. The interaction parameters are given in Table 7-3. The procedures to determine the solubilities from the different approaches are discussed in detail in Chapter 6.

The solubilities determined from the different approaches are shown in Figure 8.4. It has been observed that the solubility of CO$_2$ decreases as the temperature and the amount of nanoparticles increases for all PP-PNC systems. Since the nanoparticles decrease the free volume [4,5] and thereby swelling as discussed above, the capacity of the PNCs to accommodate gas will be decreased. It has been noticed that only Approach 1 shows a decreasing trend in solubility compared to the others, and Approaches 2-4 show the same trend. This theoretically means that solubility decreases with the infusion of nanoparticles which produces a larger hard section in PNCs. In Approaches 2 and 4, it is observed that the swelling ratio decreases as the amount of nanoparticles increases. However, both approaches show a very similar solubility for any particular nano loading. The experimental approach (Approach 5) which is quite reliable, provides strong support for the fact that the infusion of nanoparticles decreases the solubility of PBA in PNC systems.
Table 7-3 Interaction parameters for PP-PNC+CO₂

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Interaction Parameters</th>
<th>PP+CO₂</th>
<th>PP-PNC-2 +CO₂</th>
<th>PP-PNC-4 +CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>453</td>
<td>δₑ</td>
<td>2.1164</td>
<td>2.0151</td>
<td>2.1218</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7495</td>
<td>0.7765</td>
<td>0.7740</td>
</tr>
<tr>
<td>473</td>
<td>δₑ</td>
<td>2.0083</td>
<td>1.9398</td>
<td>2.0081</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7772</td>
<td>0.7988</td>
<td>0.8034</td>
</tr>
<tr>
<td>493</td>
<td>δₑ</td>
<td>1.9796</td>
<td>1.8812</td>
<td>1.9997</td>
</tr>
<tr>
<td></td>
<td>δᵥ</td>
<td>0.7870</td>
<td>0.8164</td>
<td>0.8086</td>
</tr>
</tbody>
</table>
Figure 7.5 Comparison of all approaches to determine the solubility of CO$_2$ in PP-PNC
7.6 Determination of Number of Platelets, $K$ for Intercalated Case

The solubility of CO$_2$ in various PP-PNC samples (without a compatibilizer) was determined at various temperatures and pressures. Since PP-PNCs are intercalated cases, the number of MMTs, $K$ was determined by using the solubility data of PP-PNC-2 and listed in Table 7-3.

Table 7-4 Prediction of $K$ for the PP-PNC systems at various temperatures, $T$

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Number of MMTs, $K$</th>
<th>$T=453$ K</th>
<th>$T=473$ K</th>
<th>$T=493$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-PNC-2</td>
<td></td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

It is obvious from Table 7-3 that unlike HDPE-PNCs, there might be 4 to 5 MMTs wrapped with solidified polymer in intercalated PP-PNCs. It is also clear that temperature and pressure do not have an effect on the number of MMTs. Afterwards, the solubility of PP-PNC-4 was determined by using this $K$ value to check the validity. The solubilities determined by using this $K$ value are shown in Figure 7.6. It is obvious that these solubilities are very close to those from the experimental data. This validates the number of MMTs, $K$ for the PP-PNC systems. In other words, PP-PNCs are not fully exfoliated and there might be at least 4-5 MMTs wrapped with solidified polymer.
7.7 Determination of Diffusivity of PP-PNC

In this study, the diffusivity of supercritical carbon dioxide in PP and PP/Organoclay polymeric nanocomposite (PP-PNC) melts were investigated. The diffusivities were determined by using sorption curves of PP-PNC using a magnetic suspension balance (MSB). Diffusivities of CO$_2$ in the samples were determined using the following equation for Fickian diffusion through a flat plate[200, 201]:

$$\frac{M_t}{M_\infty} = 4(D/\pi)^{0.5}(t/\pi L)^{0.5}$$ \hspace{1cm} (7-2)

where $M_t$ is the mass gain by the sample at time $t$, $M_\infty$ is the maximum mass gain, $D$ is the diffusivity of CO$_2$ in the polymer, and $L$ is the thickness of the sample. $M_\infty$ is the equilibrium
solubility of CO$_2$ at the conditions of the experiment. The diffusion coefficient of CO$_2$ in sample was obtained from the slope of M$_t$/M$_\infty$ plotted against t$^{0.5}$/L at 7 MPa and various $T$ for all samples.

As expected that nanocomposites would exhibit low diffusivities because of the nature of their gas barrier properties as reported by others [202, 263], the addition of clay reduced the diffusivity slightly (Table 7-4). It is believed that the fully exfoliated nano clay particles will decrease the diffusivity because of the increased tortuous path, and decreased mobility of the polymer molecules due to huge number of MMT platelet. It was also noticed that diffusivity increases with increasing temperature. It was also noticed that diffusivity of PP polymer is lower than HDPE polymer.

Table 7-5 Determination of diffusivity of PP-PNCs from solubility data at 7 MPa

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Diffusivity D, cm$^2$/s x 10$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=453 K</td>
</tr>
<tr>
<td>Neat PP</td>
<td>7.20</td>
</tr>
<tr>
<td>PP-2</td>
<td>5.22</td>
</tr>
<tr>
<td>PP-4</td>
<td>4.89</td>
</tr>
</tbody>
</table>
7.8 Summary

A model is adopted to describe the intercalated PVT behavior of PP-PNCs and measure the solubility of blowing agents in PNCs. From the modeling, five possible approaches are used to determine the solubility of blowing agents in PNCs. Approach 5, which utilizes a fully experimental approach, indicates that the infusion of nanoparticles might decrease the swollen volume and solubility behaviors of polymers. It is obvious that the infusion of nanoparticles significantly increases the hard sections which will, in turn, decrease the swelling and solubility of PNCs. Also, the validity of the above 4 approaches is verified with Approach 5. For intercalated cases, a model is developed and the number of MMTs is predicted and verified. It is shown that the PP-PNCs in this study are not fully exfoliated and there might be at least 4-5 MMTs wrapped with solidified polymer. In intercalated nanocomposites, most of the clay exists in layered stacks; therefore, the polymer-clay has a reduced actual interfacial contact area and smaller amounts of generated solidified polymer. As a result, unlike exfoliated cases, solubility and swelling might not significantly decrease as compared to neat polymers. It is obvious that infusion of nanoparticles decreases the diffusivity of PP.
CHAPTER 8. CONCLUSIONS AND FUTURE WORK

8.1 Summary

A comprehensive effort has been made to understand the phase equilibrium of polymer/gas, polymer/gas blends and polymeric-nanocomposite/gas systems. First, a general methodology for the phase equilibrium/solubility study is proposed by using a sorption experimental apparatus based on the gravimetric method. Then, various thermodynamic models developed by Li [8] are employed to accurately correct experimentally measured data. Finally, all of the models are verified by using fully experimental data. A thorough study has therefore been conducted using various thermodynamic models for the phase equilibrium and solubility investigations. Finally, a systematic study has been carried out to obtain the solubility data of physical BAs and their blends in polymers and PNC melts, which play a very important role in developing and selecting the next generation of BAs for plastic foam processing.

8.2 Key Contributions from this Thesis Research

In summary, the theoretical work, computer simulation, and experimental work conducted in this study have lead to the following contributions and conclusions:

1) Technically sound, experimental approaches and thermodynamic models for the \( PVT \), solubility and diffusivity behaviors of polymer nanocomposites/gas systems.

2) Investigation of the validity and suitability of EOS. Since various EOS have been used to determine the swollen volume and solubility of polymer/gas mixtures, the accuracy should be justified. It has been noticed that swollen volumes and solubilities determined by using various EOS in the literature are not the same. With the help of fully experimental data, it is now possible to verify EOS. It
could be concluded that the SS-EOS is able to predict the PVT and the solubilities of polymer/gas, polymer/gas-blends and polymer nanocomposite/gas mixtures fairly accurately and it is reliable.

3) In the case of polymer/blend mixtures, the overall solubility of the BA blends as well as that of each individual component in the polymer is obtained. The solubility data and thermodynamic properties will be very helpful for evaluating new BA blends in plastic foaming processes. Theoretical data for each gas component in polymer indicate that less soluble gas might help to further dissolve more soluble gas than polymer melts.

4) The effect of nanoparticles on PVT and solubility behaviors is also revealed. All the possibilities (approaches) to determine the PVT and the solubility of polymer nanocomposite/gas mixtures are evaluated. A fully experimental approach (which is more reliable) indicates that infusion of organoclay nanoparticles in polymers might decrease the swollen volume and the overall capacity of the gas absorption of the polymers. A model is also adopted to describe this kind of phenomenon. It is demonstrated that the infusion of nanoparticles significantly increases the hard sections (nanoparticle wrapped with solidified polymer) which will, in turn, decrease the total gas absorption capacity of the system. Although the thickness of the solidified polymer is on a nanoscale (3-10 nm), the total number is significant ($10^{15}$ - $10^{17}$ range). As a result, both the swollen volume and the solubility of the polymer nanocomposites are affected and considerably decrease. However, it is considered that the solubility behavior of polymeric composites fully depends on the interaction or affinity between fillers (micro or nano) and gas. In other words, if the nanoparticles (such as CaCO$_3$, aluminum oxide, tin
oxide) or fillers (such as carbon black, zeolites, silica gel) are highly polar and/or porous, the overall sorption (absorption + adsorption) might increase due to the adsorption phenomenon.

8.3 Recommendations and Future Work

The following suggestions are made for future research on the study of phase equilibrium or solubility for polymer/supercritical fluid systems.

I. For polymer/blend gas systems, the theoretical data of each gas component dissolved in polymer indicate that N\textsubscript{2} might help to dissolve more CO\textsubscript{2} in polymer. However, due to the lack of experimental data, this theoretical data cannot be verified and should be done so in the future.

II. More comprehensive investigation on the solubility study is suggested. For example, the solubility of gases in polymer blends will be another very exciting topic.

III. SL-EOS estimation might be also verified using gas blend data.

IV. For nanocomposite systems, the amount of thickness in solidified polymer should be experimentally verified by using an SFA or any other method.

V. The solubility of gas blends in nanocomposites might be another interesting topic.

VI. Furthermore, more detailed studies should be carried out to understand the effect of the polymer chain chemical structure on solubility, i.e., molecular weight and molecular weight distribution.

VII. For PVT studies, the accuracy of the edge detection of polymer and tip should be studied in more detail.

VIII. Swelling behavior of polymers due to BAs sorption below critical pressure might be very interesting topic.
REFERENCES


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APPENDIX

APPENDIX 1

Image Movement Input Algorithm

%---------------------------------------------------------------
%---------------------------------------------------------------

%%%% This program is used for the image reconstruction based on
the X-Y |
%%%% stage movement and the calibration, using all the image
taken |
%%%% By Hongbo Li, Gary Li |
%---------------------------------------------------------------
%---------------------------------------------------------------|
%%%% define the movement distance in terms of pixel from
calibration %%%
Dy=[0, 115.91, 316.59, 432.5, 432.5, 316.59, 115.91, -115.91, -316.59
-432.5, -432.5, -316.59, -115.91 ]';
Dx=-[0, 435.25, 318.603, 116.647, -116.647, -318.603, -435.25, -435.25
-318.603, -116.647, 116.647, 318.603, 435.25 ]';
%%%% save the image file name based on the number sequence %%
filenames={'p1.tif' 'p2.tif' 'p3.tif' 'p4.tif' 'p5.tif' 'p6.tif'
'p7.tif' ...
'p14.tif'
'p15.tif'...
'p22.tif' 'p23.tif' 'p24.tif' 'p25.tif' 'p26.tif' 'p27.tif'
'p28.tif'
'p29.tif'...
'p30.tif' 'p31.tif' 'p32.tif' 'p33.tif' 'p34.tif' 'p35.tif'
'p36.tif'
'p37.tif'...
'p38.tif' 'p39.tif' 'p40.tif' 'p41.tif' 'p42.tif' 'p43.tif'
'p44.tif'
'p45.tif'};

%%% Important Note %%%

%%% Vertical movement using the x directional pixel movement values

%%% Horizontal movement using the y directional pixel movement values

%%% Remember: New Program there is no sign changes;
Image Reconstruction Algorithm

%%% Edge Reconstruction %%%
clear; close all; clc;
B=[ ];
C=[ ; ; ];

%%% Load the stage step movement and all the images file %%%%
%%% Movement: Dx, Dy in the unit of pixies based on calibration
%%% Image Files: "bmp" format, or "Tif" format in the sequence taken %%%%
Image_Movement_Input;
volume_cylinder=0;
DX_total=0; DY_total=0;
for i=1:length(Dx)
    image_file = uigetfile('*.tif;*.bmp','Choose image file');
    image_file=char(filenames(i));
    I = imread(image_file);
    figure(1); hold;
imshow(I);

%%%possible thresholding/smoothing and edge detection routine
%%%
%%% use the canny edge detection algorithm to obtain the edge coordinates %%

%%% threshold value and sigma can be changed%

BW1 = edge(I,'canny',0.1,1);
figure(2);
imshow(BW1);

drop_edge = bwmorph(BW1,'remove',3);

[X Y]= find(drop_edge);
X=X+Dx(i); Y=Y+Dy(i);

DX_total=DX_total+Dx(i);DY_total=DY_total+Dy(i);
X=X+DX_total; Y=Y+DY_total;

%%% Put the X and Y coordinates into a matrix %%
A=[X,Y];
B=[B; A];

%%% Plot the constructed image%%%%
figure(3);

plot(B(:,1),B(:,2),'b.');
end ;
Axialsymmetric Volume Integration Algorithm

%------------------------------------------------------------------------------------------------------------------

%Combine cropping and volume calculation script this program crops droplet
%image in half by finding profile maximum and spline the boundary
%calculate partial volumes separately using curve fitting and integration
%Script features cropping routines and edge detection and volume calculation
%routines that can be used separately
%For spline fit function checkxy is used for removing duplicates and noise,
%checkxy MUST be in the workin directory!
%------------------------------------------------------------------------------------------------------------------

clc;
cla;
clf;
syms s;
v_left=0;
v_right=0;
v_total=0;
V_final=0;

image_file = uigetfile('*.tif;*.bmp','Choose image file');
I = imread(image_file);
%%%%possible thresholding/smoothing routine here%%%%
BW1 = edge(I,'canny',0.1,1);
drop_edge = bwmorph(BW1,'remove',3);
[X,Y] = find(drop_edge);
%%%% plot to check for artifacts %%%%
figure(1); plot(X,Y,'b.');
%%%%Find the highest point of the drop or the apex of the drop%%%%
%%%%that is the smallest value for x %%%%
minX = min( X );
index = find( X==minX );
centerY = mean( Y(index) );
%%%%2048- centerY image width, modify for larger images%%%%
%%%%480 - image height, modify for actual image%%%%
width=2048-centerY;
Image_right = imcrop(BW1, [centerY 0 width 2048]);
figure(2);
imshow(Image_right);
imwrite(Image_right,'right_part.tiff','tif','Compression','none','WriteMode','overwrite');  
figure(3);  
imshow(Image_left);  
imwrite(Image_left,'left_part.tif','tif','Compression','none','WriteMode','overwrite');  
Image_left = imcrop(BW1, [0 0 centerY 2048]);  
%%%%calculate the right part volume%%%%  
right_image_file = imread('right_part.tif');  
drop_edgeR = bwmorph(right_image_file,'remove',3);  
[X1,Y1] = find(drop_edgeR);  
figure(4);  
plot(X1,Y1,'ro');  
%removing duplicates, function checkxy MUST be in the working directory!  
[xx1,yy1] = checkxy(X1,Y1,'R');  
xx_right=xx1'; yy_right=yy1';  
ymin=min(Y1);  
yyy_right=yy1-ymin;  
%%%% Volume Integration Calculation %%%%  
pp=spline(xx_right,yy_right);  
[B,c,L,K,D]=unmkpp(pp);
x_max=max(xx_right);
x_min=min(xx_right);
%ymin=min(yy_right);
ymin=min(Y1);
NT=10000;
xright=linspace(x_min,x_max,NT);
yright=ppval(pp,xright);
figure(5); hold;
plot(xright,yright,'o');
volume=0;
for i=1:length(xright)-1
if xright(i)<= 996
v_right=v_right+1/3*pi*(abs((xright(i+1)-xright(i)))*((yright(i)-ymin)^2+(yright(i)-ymin)*(yright(i+1)-ymin)+(yright(i+1)-ymin)^2);
elseif xright(i)>= 996
volume=0;
else
end;
end;

%%%left part volume calculation%%%
left_image_file = imread('left_part.tif');
drop_edgeL = bwmorph(left_image_file,'remove',3 );
[X2,Y2] = find(drop_edgeL);
figure(6);
plot(X2,Y2,'bd');
% removing duplicates, function checkxy MUST be in the working directory!
[xx2,yy2] = checkxy(X2,Y2,'L');
xx_left=xx2'; yy_left=yy2';
ymax=max(Y2);
yyy_left=abs(yy2-ymax);
figure(7); hold;
plot(xx_left,yy_left,'rd');
volume = 0;
%%%%Calculate volume integrals %%%%
pp=spline(xx_left,yy_left);
xmax=max(xx_left);
xmin=min(xx_left);
%ymax=max(yy_left);
ymax=max(Y2);
NT=10000;
xleft=linspace(xmin,xmax,NT);
yleft=ppval(pp,xleft);
figure(8);
plot(xleft,yleft,'*');
for i=1:length(xleft)-1
if xleft(i) <= 986
v_left = \frac{1}{3} \pi (|x_{left(i+1)} - x_{left(i)}|) (y_{left(i)} - y_{max})^2 + |y_{left(i)} - y_{max}| |y_{left(i+1)} - y_{max}| + (y_{left(i+1)} - y_{max})^2; \\
\text{elseif } x_{left(i)} \geq 986 \\
\text{volume} = 0; \\
\text{end}; \\
\text{end}; \\
\text{%%%Total volume by combining the } v_{left} \text{ and } v_{right} \text{ together%%%}
\text{v_total} = (v_{right} + v_{left}) / 2; \\
\text{step_size} = 0.5; \ % \text{ the XY stage step size is 0.5 \, \mu m \text{ per step} } \\
\text{cal_factor} = 0.187329365; \ % \text{ the calibration factor is pixel/step} \\
\text{vol_conversion_factor} = \left(\frac{\text{step_size}}{\text{cal_factor}} \times 10^{-4}\right)^3; \\
\text{v_final} = \text{v_total} \times \text{vol_conversion_factor}; \\
\text{format long} \\
\text{date_time} = \text{fix(clock)}; \\
\text{V} = [\text{date_time}, \text{v_final}]; \\
\text{%%%saving file and appending data to existing values%%%} \\
\text{fid} = \text{fopen('volume data.txt', 'a+', 'n')}; \\
\text{fprintf(fid, '%12.0f %9.2f\n', V);} \\
\text{fclose(fid);}
Function “checkxy” Algorithm

function [x,y] = checkxy(x,y,Ntest)

%CHECKXY check the given data
x = x(:).'; y = y(:).';
NT=length(x);
if any(diff(x)<0), [x,index] = sort(x); y = y(index); end
if (Ntest=='R')
    %[b0,indx]=min(y); a0=x(indx);
    a0=x(NT);b0=y(NT);
else
    if (Ntest=='L')
        %[b0,indx]=max(y); a0=x(indx);
        a0=x(NT);b0=y(NT);
    else
        error('wrong input')
    end
end

%% Note, here we must keep the highest value of Y, since it is sensitive to
%% the final volume;
%% Depending on which part of the image, the extreme value y (at the end)
%% has to be selected

mults = knt2mlt(x);
if any(mults) % remove repeat sites, averaging the corresponding values
for j=find(diff([mults,0])<0)
    y(j-mults(j)) = mean(y(j-mults(j):j));
end
repeats = find(mults);
x(repeats) = [];
y(repeats) = [];
%temp = warndlg(...
%'Data has been modified', ...
% 'Repeated values found ...');
%waitfor(temp)
end
n0=length(x);
if a0==x(n0)
x(n0)=a0; y(n0)=b0;
end
if a0 ~=x(n0)
x(n0+1)=a0; y(n0+1)=b0;
end
lx = length(x);
if lx<2
    error('There should be at least two data points.')
end

if lx~=length(y)

error(['The number ',num2str(lx),' of data sites should match',...
' the number ',num2str(length(y)),' of data values.'])

End
Asymmetric Volume Calculation Algorithm (Fortran)

C THIS ALGORITHM IS DEVELOPED TO SPLINE THE PRIMETER OF EACH
C LAYER OF THE DROP AND THEN USE SIMPSON’S RULE TO INTEGRATE
C TO COMPUTE THE VOLUME OF ASYMMETRIC DROP SHAPE
C THIS IS TO CALCULATE THE VOLUME OF SESSILE DROP

PROGRAM VOLUME CALCULATION OF A SESSILE DROP

PARAMETER (IMAX=560) ! TEMP=150
C PARAMETER (IMAX=570) ! TEMP=200
C PARAMETER (IMAX=506) ! TEMP=250

PARAMETER (KMAX=100)
PARAMETER (PAI=3.1415926)

REAL RL(0:KMAX,0:IMAX),RR(0:KMAX,0:IMAX)
REAL THETAL(0:KMAX), THETAR(0:KMAX)
REAL TOT(0:IMAX)
REAL AREA(0:KMAX,0:IMAX)
REAL TEMP

C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C DATA INPUT

TEMP=150.
C TEMP=200.
C TEMP=250.
IF (TEMP .EQ. 150.) THEN
OPEN (2, FILE='E:\3\SPLINE150L.DAT',STATUS='OLD')
READ (2,*) (THETAL(K),K=1,KMAX)
DO I=1,IMAX
READ (2,*) (RL(K,I), K=1,KMAX)
ENDDO
CLOSE (2)
OPEN (4, FILE='E:\3\SPLINE150R.DAT',STATUS='OLD')
READ (4,*) (THETAR(K),K=1,KMAX)
DO I=1,IMAX
READ (4,*) (RR(K,I), K=1,KMAX)
ENDDO
CLOSE (4)
ENDIF
IF (TEMP .EQ. 200.) THEN
OPEN (12, FILE='E:\3\SPLINE200L.DAT',STATUS='OLD')
READ (12,*) (THETAL(K),K=1,KMAX)
DO I=1,IMAX
READ (12,*) (RL(K,I), K=1,KMAX)
ENDDO
CLOSE (12)
OPEN (14, FILE='E:\3\SPLINE200R.DAT',STATUS='OLD')
READ (14,*) (THETAR(K),K=1,KMAX)
DO I=1,IMAX
READ (14,*) (RR(K,I), K=1,KMAX)
ENDDO
CLOSE (14)
ENDIF

IF (TEMP .EQ. 250.) THEN
OPEN (22, FILE='E:\3\SPLINE250L.DAT',STATUS='OLD')
READ (22,*) (THETAL(K),K=1,KMAX)
DO I=1,IMAX
READ (22,*) (RL(K,I), K=1,KMAX)
ENDDO
CLOSE (22)
OPEN (24, FILE='E:\3\SPLINE250R.DAT',STATUS='OLD')
READ (24,*) (THETAR(K),K=1,KMAX)
DO I=1,IMAX
READ (24,*) (RR(K,I), K=1,KMAX)
ENDDO
CLOSE (24)
ENDIF

DO K=1,KMAX
RL(K,0)=0.
RR(K,0)=0.
ENDDO

C CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C VOLUME CALCULATION
VOL=0.

DO I=1,IMAX
  TOT(I)=0.
  C DO K=1,KMAX-1
  C AREA(K,I) =
    C & PAI*((RL(K,I)+RL(K+1,I)+RL(K,I-1)+RL(K+1,I-1))/4.)**2
    C & *(THETAL(K+1)-THETAL(K))/360.
    C & +PAI*((RR(K,I)+RR(K+1,I)+RR(K,I-1)+RR(K+1,I-1))/4.)**2
    C & *(THETAR(K+1)-THETAR(K))/360.
    C TOT(I)=TOT(I)+AREA(K,I)
  C ENDDO

DO K=1,KMAX-1
  AREA(K,I)=1./3.*PAI*(
    & (( RL(K,I-1)+RL(K+1,I-1) )/2.)**2
    & +(( RL(K,I-1)+RL(K+1,I-1) )/2.)*(( RL(K,I)+RL(K+1,I) )/2.)
    & +(( RL(K,I)+RL(K+1,I) )/2.)**2
    & )* (THETAL(K+1)-THETAL(K))/360.
    & +
    & 1./3.*PAI*(
      & (( RR(K,I-1)+RR(K+1,I-1) )/2.)**2
      & +(( RR(K,I-1)+RR(K+1,I-1) )/2.)*(( RR(K,I)+RR(K+1,I) )/2.)
      & +(( RR(K,I)+RR(K+1,I) )/2.)**2
      & )* (THETAR(K+1)-THETAR(K))/360.
    TOT(I)=TOT(I)+AREA(K,I)
ENDDO

TOT(I)=TOT(I)*(2.6953E-4)**2

VOL=VOL+TOT(I)*1.*(2.6803E-4)

ENDDO

IF (TEMP .EQ. 150) THEN

ERR=(VOL-0.014416)/0.014416 ! T=150 DEGREE C
WRITE(*,*) 'VOL=', VOL, ' CC'
WRITE(*,*) (VOL-0.014416)
WRITE(*,*) 'ERR=', ERR*100, ' %'
ENDIF

IF (TEMP .EQ. 200) THEN

ERR=(VOL-0.014848)/0.014848 ! T=200 DEGREE C
WRITE(*,*) 'VOL=', VOL, ' CC'
WRITE(*,*) (VOL-0.014848)
WRITE(*,*) 'ERR=', ERR*100, ' %'
ENDIF

IF (TEMP .EQ. 250) THEN

ERR=(VOL-0.01528)/0.01528 ! T=250 DEGREE C
WRITE(*,*) 'VOL=', VOL, ' CC'
WRITE(*,*) (VOL-0.01528)
WRITE(*,*) 'ERR=', ERR*100, ' %'
ENDIF

OPEN (6, FILE='AREA.DAT', STATUS='UNKNOWN')

DO I=1,IMAX
  WRITE (6,*) I, TOT(I)
ENDDO

CLOSE (6)

END
APPENDIX 2

Calibration is carried out in vacuum condition at the experimental temperature prior to each experiment. The calibration is done at all the levels across the sample horizontally in X direction and vertically in Y direction. The following graphically illustrates how the calibration is determined in both directions. The number of levels is determined to cover the whole drop.

Calibration in X direction
At level 1, the edge point on the X axis at pixel coordinate $X_I$ of the drop is moved across the lens (or the screen) to a new location at $X_{I,N}$ with the stage moved N step towards right (or left) direction as illustrated as following two pictures.

During the N step movement, the number of pixel is determined as: $X_{I,N} - X_I$

Since each step of the stage is 0.5μm, the pixel size (in cm) at level 1 can be determined as:

$$\frac{0.00005 \times N}{X_{I,N} - X_I}$$

Similarly, the pixel size at all other levels could be determined.

**Calibration in Y direction**
At level 1, the edge point on the Y axis at pixel coordinate $Y_I$ of the drop is moved across the lens (or the screen) to a new location at $Y_{I,N}$ with the stage moved N step in upward (or downward) direction as illustrated as following two pictures.

During the N step movement, the number of pixel is determined as: $Y_{I,N} - Y_I$

Since each step of the stage is 0.5μm, the pixel size (in cm) at level 1 can be determined as:
Similarly, the pixel size at all the levels could be determined. Since the pixel is not a perfect square pixel, the pixel size would be averaged in both X and Y directions to be as the calibration factor. This calibration factor is used as the conversion factor for the volume conversion from pixel to metric unit.

The following Table shows the calibration results from one of the experiments.

![Table](image-url)

\[
\frac{0.00005 \times N}{Y_{1-N} - Y_1}
\]
APPENDIX 3

MSB Absorption Test for Saturation Time Determination

1) Linear PP/CO₂ at 180°C
2) Branched PP/CO$_2$ at 180°C
180°C Branched PP/CO₂ Saturation

Weight (g)

Time (min)

90 95 100 105 110 115 120 125 130 135 140 145 150 155 160

14.44

14.42

14.41

14.40
APPENDIX 4

1. Supporting Information for PP

The solubilities of CO$_2$ in linear and branched polypropylene (PP) were measured at temperatures from (453 to 493) K and at pressures of up to 31 MPa using a magnetic suspension balance (MSB) and a $PVT$ apparatus. The experimental results are presented in Tables 1 to 6.

Table 1. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in branched PP at (453.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>452.9</td>
<td>6.970</td>
<td>0.0454</td>
<td>0.0483 ± 0.0006</td>
</tr>
<tr>
<td>453.0</td>
<td>10.441</td>
<td>0.0645</td>
<td>0.0745 ± 0.0009</td>
</tr>
<tr>
<td>453.1</td>
<td>13.945</td>
<td>0.0807</td>
<td>0.1044 ± 0.0017</td>
</tr>
<tr>
<td>453.2</td>
<td>17.434</td>
<td>0.0929</td>
<td>0.1338 ± 0.0011</td>
</tr>
<tr>
<td>453.2</td>
<td>20.916</td>
<td>0.1011</td>
<td>0.1605 ± 0.0024</td>
</tr>
<tr>
<td>453.2</td>
<td>24.384</td>
<td>0.1059</td>
<td>0.1845 ± 0.0025</td>
</tr>
<tr>
<td>453.2</td>
<td>27.892</td>
<td>0.1079</td>
<td>0.2071 ± 0.0026</td>
</tr>
<tr>
<td>453.2</td>
<td>31.382</td>
<td>0.1080</td>
<td>0.2273 ± 0.0035</td>
</tr>
</tbody>
</table>

Table 2. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in branched PP at (473.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>473.0</td>
<td>7.018</td>
<td>0.0426</td>
<td>0.0437 ± 0.0004</td>
</tr>
<tr>
<td>473.1</td>
<td>10.472</td>
<td>0.0606</td>
<td>0.0664 ± 0.0010</td>
</tr>
<tr>
<td>473.1</td>
<td>13.960</td>
<td>0.0762</td>
<td>0.0913 ± 0.0021</td>
</tr>
<tr>
<td>473.1</td>
<td>17.446</td>
<td>0.0885</td>
<td>0.1171 ± 0.0026</td>
</tr>
<tr>
<td>473.0</td>
<td>20.932</td>
<td>0.0976</td>
<td>0.1421 ± 0.0032</td>
</tr>
<tr>
<td>473.0</td>
<td>24.420</td>
<td>0.1037</td>
<td>0.1645 ± 0.0010</td>
</tr>
<tr>
<td>473.0</td>
<td>27.911</td>
<td>0.1073</td>
<td>0.1836 ± 0.0031</td>
</tr>
<tr>
<td>473.1</td>
<td>31.399</td>
<td>0.1089</td>
<td>0.2001 ± 0.0043</td>
</tr>
</tbody>
</table>
Table 3. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in branched PP at (493.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>493.1</td>
<td>7.011</td>
<td>0.04054</td>
<td>0.0409 ± 0.0007</td>
</tr>
<tr>
<td>493.1</td>
<td>10.469</td>
<td>0.05776</td>
<td>0.0620 ± 0.0009</td>
</tr>
<tr>
<td>493.2</td>
<td>13.959</td>
<td>0.07304</td>
<td>0.0847 ± 0.0012</td>
</tr>
<tr>
<td>493.2</td>
<td>17.443</td>
<td>0.08563</td>
<td>0.1081 ± 0.0014</td>
</tr>
<tr>
<td>493.1</td>
<td>20.924</td>
<td>0.09579</td>
<td>0.1318 ± 0.0011</td>
</tr>
<tr>
<td>493.2</td>
<td>24.420</td>
<td>0.10278</td>
<td>0.1536 ± 0.0021</td>
</tr>
<tr>
<td>493.2</td>
<td>27.905</td>
<td>0.10757</td>
<td>0.1724 ± 0.0023</td>
</tr>
<tr>
<td>493.2</td>
<td>31.398</td>
<td>0.11184</td>
<td>0.1874 ± 0.0029</td>
</tr>
</tbody>
</table>

Table 4. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in linear PP at (453.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>452.8</td>
<td>6.931</td>
<td>0.0484</td>
<td>0.0518 ± 0.0010</td>
</tr>
<tr>
<td>452.9</td>
<td>10.449</td>
<td>0.0698</td>
<td>0.0818 ± 0.0021</td>
</tr>
<tr>
<td>453.0</td>
<td>13.924</td>
<td>0.0876</td>
<td>0.1134 ± 0.0027</td>
</tr>
<tr>
<td>453.0</td>
<td>17.405</td>
<td>0.1016</td>
<td>0.1452 ± 0.0030</td>
</tr>
<tr>
<td>453.0</td>
<td>20.904</td>
<td>0.1119</td>
<td>0.1763 ± 0.0032</td>
</tr>
<tr>
<td>453.1</td>
<td>24.400</td>
<td>0.1186</td>
<td>0.2056 ± 0.0043</td>
</tr>
<tr>
<td>453.1</td>
<td>27.873</td>
<td>0.1221</td>
<td>0.2320 ± 0.0042</td>
</tr>
<tr>
<td>453.1</td>
<td>31.378</td>
<td>0.1233</td>
<td>0.2535 ± 0.0034</td>
</tr>
</tbody>
</table>
Table 5. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in linear PP at (473.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>473.0</td>
<td>6.996</td>
<td>0.0464</td>
<td>0.0484 ± 0.0003</td>
</tr>
<tr>
<td>473.1</td>
<td>10.456</td>
<td>0.0664</td>
<td>0.0748 ± 0.0010</td>
</tr>
<tr>
<td>473.2</td>
<td>13.942</td>
<td>0.0839</td>
<td>0.1034 ± 0.0013</td>
</tr>
<tr>
<td>473.2</td>
<td>17.426</td>
<td>0.0984</td>
<td>0.1324 ± 0.0020</td>
</tr>
<tr>
<td>473.3</td>
<td>20.912</td>
<td>0.1096</td>
<td>0.1600 ± 0.0012</td>
</tr>
<tr>
<td>473.3</td>
<td>24.400</td>
<td>0.1179</td>
<td>0.1851 ± 0.0014</td>
</tr>
<tr>
<td>473.3</td>
<td>27.897</td>
<td>0.1234</td>
<td>0.2071 ± 0.0014</td>
</tr>
<tr>
<td>473.3</td>
<td>31.374</td>
<td>0.1265</td>
<td>0.2274 ± 0.0027</td>
</tr>
</tbody>
</table>

Table 6. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ in linear PP at (493.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>493.0</td>
<td>7.009</td>
<td>0.0432</td>
<td>0.0445 ± 0.0010</td>
</tr>
<tr>
<td>493.1</td>
<td>10.462</td>
<td>0.0620</td>
<td>0.0685 ± 0.0013</td>
</tr>
<tr>
<td>493.2</td>
<td>13.955</td>
<td>0.0787</td>
<td>0.0936 ± 0.0024</td>
</tr>
<tr>
<td>493.2</td>
<td>17.441</td>
<td>0.0926</td>
<td>0.1190 ± 0.0024</td>
</tr>
<tr>
<td>493.2</td>
<td>20.924</td>
<td>0.1036</td>
<td>0.1440 ± 0.0022</td>
</tr>
<tr>
<td>493.3</td>
<td>24.412</td>
<td>0.1122</td>
<td>0.1682 ± 0.0034</td>
</tr>
<tr>
<td>493.3</td>
<td>27.909</td>
<td>0.1182</td>
<td>0.1894 ± 0.0013</td>
</tr>
<tr>
<td>493.3</td>
<td>31.403</td>
<td>0.1223</td>
<td>0.2052 ± 0.0033</td>
</tr>
</tbody>
</table>
2. Supporting Information for LDPE

The solubilities of CO\(_2\) in low density polyethylene (LDPE) were measured at temperatures from (383 to 493) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. The experimental results are presented in Tables 7 to 9.

Table 7. Solubility, \(X\) (g-gas/g-polymer) of CO\(_2\) in LDPE at 383 K (\(P\), pressure of CO\(_2\) and \(T\), temperature)

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(P/\text{MPa})</th>
<th>(X_{\text{apparent}})</th>
<th>(X_{\text{corrected}})</th>
<th>(S_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>382.9</td>
<td>6.99</td>
<td>0.0514</td>
<td>0.0607</td>
<td>1.0654</td>
</tr>
<tr>
<td>383.0</td>
<td>10.45</td>
<td>0.0699</td>
<td>0.0908</td>
<td>1.0901</td>
</tr>
<tr>
<td>383.1</td>
<td>13.94</td>
<td>0.0792</td>
<td>0.1183</td>
<td>1.1148</td>
</tr>
<tr>
<td>383.1</td>
<td>17.44</td>
<td>0.0793</td>
<td>0.1434</td>
<td>1.1397</td>
</tr>
<tr>
<td>383.1</td>
<td>20.94</td>
<td>0.0741</td>
<td>0.1677</td>
<td>1.1645</td>
</tr>
</tbody>
</table>

Table 8. Solubility, \(X\) (g-gas/g-polymer) of CO\(_2\) in LDPE at 423 K (\(P\), pressure of CO\(_2\) and \(T\), temperature)

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(P/\text{MPa})</th>
<th>(X_{\text{apparent}})</th>
<th>(X_{\text{corrected}})</th>
<th>(S_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.8</td>
<td>6.95</td>
<td>0.0432</td>
<td>0.0500</td>
<td>1.0549</td>
</tr>
<tr>
<td>422.9</td>
<td>10.45</td>
<td>0.0607</td>
<td>0.0765</td>
<td>1.0813</td>
</tr>
<tr>
<td>422.9</td>
<td>13.93</td>
<td>0.0736</td>
<td>0.1029</td>
<td>1.1076</td>
</tr>
<tr>
<td>423.0</td>
<td>17.42</td>
<td>0.0818</td>
<td>0.1291</td>
<td>1.1338</td>
</tr>
<tr>
<td>423.0</td>
<td>20.90</td>
<td>0.0853</td>
<td>0.1549</td>
<td>1.1601</td>
</tr>
</tbody>
</table>

Table 9. Solubility, \(X\) (g-gas/g-polymer) of CO\(_2\) in LDPE at 463 K (\(P\), pressure of CO\(_2\) and \(T\), temperature)

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(P/\text{MPa})</th>
<th>(X_{\text{apparent}})</th>
<th>(X_{\text{corrected}})</th>
<th>(S_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>462.9</td>
<td>7.00</td>
<td>0.0389</td>
<td>0.0442</td>
<td>1.0475</td>
</tr>
<tr>
<td>463.0</td>
<td>10.45</td>
<td>0.0550</td>
<td>0.0678</td>
<td>1.0746</td>
</tr>
<tr>
<td>463.1</td>
<td>13.94</td>
<td>0.0686</td>
<td>0.0926</td>
<td>1.1019</td>
</tr>
<tr>
<td>463.1</td>
<td>17.42</td>
<td>0.0792</td>
<td>0.1180</td>
<td>1.1291</td>
</tr>
<tr>
<td>463.1</td>
<td>20.91</td>
<td>0.0867</td>
<td>0.1439</td>
<td>1.1564</td>
</tr>
</tbody>
</table>
3. Supporting Information for PS

The solubilities of CO₂ and N₂ in polystyrene (PS) were measured at temperatures from (403 to 463) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. The experimental results are presented in Tables 10 to 15.

Table 10. Solubility, \( X \) (g-gas/g-polymer) of CO₂ in PS at 403 K (\( P \), pressure of CO₂ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>402.9</td>
<td>7.044</td>
<td>0.0339</td>
<td>0.0385</td>
<td>1.0440</td>
</tr>
<tr>
<td>402.9</td>
<td>10.468</td>
<td>0.0454</td>
<td>0.0574</td>
<td>1.0730</td>
</tr>
<tr>
<td>402.9</td>
<td>13.884</td>
<td>0.0521</td>
<td>0.0759</td>
<td>1.1019</td>
</tr>
<tr>
<td>402.9</td>
<td>17.299</td>
<td>0.0543</td>
<td>0.0942</td>
<td>1.1308</td>
</tr>
<tr>
<td>402.9</td>
<td>20.700</td>
<td>0.0528</td>
<td>0.1130</td>
<td>1.1595</td>
</tr>
</tbody>
</table>

Table 11. Solubility, \( X \) (g-gas/g-polymer) of CO₂ in PS at 423 K (\( P \), pressure of CO₂ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.8</td>
<td>7.041</td>
<td>0.0291</td>
<td>0.0331</td>
<td>1.0406</td>
</tr>
<tr>
<td>422.8</td>
<td>10.451</td>
<td>0.0396</td>
<td>0.0494</td>
<td>1.0649</td>
</tr>
<tr>
<td>422.9</td>
<td>13.933</td>
<td>0.0473</td>
<td>0.0662</td>
<td>1.0896</td>
</tr>
<tr>
<td>422.9</td>
<td>17.424</td>
<td>0.0511</td>
<td>0.0826</td>
<td>1.1144</td>
</tr>
<tr>
<td>422.9</td>
<td>20.924</td>
<td>0.0525</td>
<td>0.0997</td>
<td>1.1393</td>
</tr>
</tbody>
</table>

Table 12. Solubility, \( X \) (g-gas/g-polymer) of CO₂ in PS at 463 K (\( P \), pressure of CO₂ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>463.0</td>
<td>6.959</td>
<td>0.0242</td>
<td>0.0271</td>
<td>1.0335</td>
</tr>
<tr>
<td>463.1</td>
<td>10.452</td>
<td>0.0345</td>
<td>0.0421</td>
<td>1.0563</td>
</tr>
<tr>
<td>463.1</td>
<td>13.937</td>
<td>0.0427</td>
<td>0.0571</td>
<td>1.0790</td>
</tr>
<tr>
<td>463.1</td>
<td>17.417</td>
<td>0.0488</td>
<td>0.0724</td>
<td>1.1017</td>
</tr>
<tr>
<td>463.2</td>
<td>20.898</td>
<td>0.0528</td>
<td>0.0879</td>
<td>1.1245</td>
</tr>
</tbody>
</table>
Table 13. Solubility, $X$ (g-gas/g-polymer) of $\text{N}_2$ in PS at 403 K ($P$, pressure of $\text{CO}_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
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<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>402.9</td>
<td>7.026</td>
<td>0.0031</td>
<td>0.0034</td>
<td>1.0041</td>
</tr>
<tr>
<td>402.8</td>
<td>10.457</td>
<td>0.0044</td>
<td>0.0049</td>
<td>1.0061</td>
</tr>
<tr>
<td>402.9</td>
<td>13.874</td>
<td>0.0054</td>
<td>0.0063</td>
<td>1.0080</td>
</tr>
<tr>
<td>402.8</td>
<td>17.297</td>
<td>0.0063</td>
<td>0.0076</td>
<td>1.0100</td>
</tr>
<tr>
<td>402.9</td>
<td>20.709</td>
<td>0.0071</td>
<td>0.0090</td>
<td>1.0120</td>
</tr>
</tbody>
</table>

Table 14. Solubility, $X$ (g-gas/g-polymer) of $\text{N}_2$ in PS at 423 K ($P$, pressure of $\text{CO}_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
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<tr>
<td>423.0</td>
<td>6.946</td>
<td>0.0031</td>
<td>0.0034</td>
<td>1.0050</td>
</tr>
<tr>
<td>423.0</td>
<td>10.456</td>
<td>0.0045</td>
<td>0.0051</td>
<td>1.0076</td>
</tr>
<tr>
<td>423.1</td>
<td>13.941</td>
<td>0.0057</td>
<td>0.0068</td>
<td>1.0101</td>
</tr>
<tr>
<td>423.1</td>
<td>17.421</td>
<td>0.0069</td>
<td>0.0085</td>
<td>1.0126</td>
</tr>
<tr>
<td>423.1</td>
<td>20.904</td>
<td>0.0078</td>
<td>0.0100</td>
<td>1.0152</td>
</tr>
</tbody>
</table>

Table 15. Solubility, $X$ (g-gas/g-polymer) of $\text{N}_2$ in PS at 463 K ($P$, pressure of $\text{CO}_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
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<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
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</thead>
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<td>462.8</td>
<td>6.971</td>
<td>0.0032</td>
<td>0.0035</td>
<td>1.0061</td>
</tr>
<tr>
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<td>10.461</td>
<td>0.0049</td>
<td>0.0056</td>
<td>1.0091</td>
</tr>
<tr>
<td>462.9</td>
<td>13.947</td>
<td>0.0062</td>
<td>0.0074</td>
<td>1.0121</td>
</tr>
<tr>
<td>462.9</td>
<td>17.425</td>
<td>0.0075</td>
<td>0.0093</td>
<td>1.0152</td>
</tr>
<tr>
<td>462.9</td>
<td>20.909</td>
<td>0.0085</td>
<td>0.0110</td>
<td>1.0182</td>
</tr>
</tbody>
</table>
4. Supporting Information for PS and CO$_2$/N$_2$ Blend

The solubilities of CO$_2$/N$_2$ blends in polystyrene (PS) were measured at temperatures from (403 to 463) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. The experimental results are presented in Tables 16 to 24.

Table 16. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 25:75 in PS at (403.15 ± 0.2) K ($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>402.9</td>
<td>6.995</td>
<td>0.0106</td>
<td>0.0115</td>
<td>1.0135</td>
</tr>
<tr>
<td>402.9</td>
<td>10.422</td>
<td>0.0147</td>
<td>0.0172</td>
<td>1.0255</td>
</tr>
<tr>
<td>402.9</td>
<td>13.849</td>
<td>0.0180</td>
<td>0.0228</td>
<td>1.0375</td>
</tr>
<tr>
<td>402.9</td>
<td>17.263</td>
<td>0.0206</td>
<td>0.0285</td>
<td>1.0494</td>
</tr>
<tr>
<td>402.9</td>
<td>20.709</td>
<td>0.0228</td>
<td>0.0343</td>
<td>1.0615</td>
</tr>
</tbody>
</table>

Table 17. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 25:75 in PS at (423.15 ± 0.2) K ($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.9</td>
<td>6.964</td>
<td>0.0095</td>
<td>0.0102</td>
<td>1.0106</td>
</tr>
<tr>
<td>422.8</td>
<td>10.521</td>
<td>0.0132</td>
<td>0.0153</td>
<td>1.0216</td>
</tr>
<tr>
<td>422.8</td>
<td>13.941</td>
<td>0.0162</td>
<td>0.0202</td>
<td>1.0322</td>
</tr>
<tr>
<td>422.9</td>
<td>17.358</td>
<td>0.0186</td>
<td>0.0251</td>
<td>1.0428</td>
</tr>
<tr>
<td>422.9</td>
<td>20.769</td>
<td>0.0204</td>
<td>0.0300</td>
<td>1.0534</td>
</tr>
</tbody>
</table>

Table 18. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 25:75 in PS at (463.15 ± 0.2) K ($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>462.8</td>
<td>6.970</td>
<td>0.0095</td>
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<td>1.0074</td>
</tr>
<tr>
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<td>0.0144</td>
<td>1.0156</td>
</tr>
<tr>
<td>462.8</td>
<td>13.854</td>
<td>0.0161</td>
<td>0.0188</td>
<td>1.0237</td>
</tr>
<tr>
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<td>17.286</td>
<td>0.0186</td>
<td>0.0231</td>
<td>1.0318</td>
</tr>
<tr>
<td>462.9</td>
<td>20.702</td>
<td>0.0207</td>
<td>0.0273</td>
<td>1.0399</td>
</tr>
</tbody>
</table>

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Table 19. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 50:50 in PS at (403.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
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</thead>
<tbody>
<tr>
<td>402.9</td>
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<td>1.0200</td>
</tr>
<tr>
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<td>0.0296</td>
<td>1.0352</td>
</tr>
<tr>
<td>402.9</td>
<td>13.885</td>
<td>0.0310</td>
<td>0.0387</td>
<td>1.0505</td>
</tr>
<tr>
<td>402.9</td>
<td>17.294</td>
<td>0.0352</td>
<td>0.0477</td>
<td>1.0657</td>
</tr>
<tr>
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<td>20.697</td>
<td>0.0385</td>
<td>0.0567</td>
<td>1.0808</td>
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</table>

Table 20. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 50:50 in PS at (423.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
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<th>$X_{\text{apparent}}$</th>
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<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.8</td>
<td>7.077</td>
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<td>0.0181</td>
<td>1.0153</td>
</tr>
<tr>
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<td>0.0263</td>
<td>1.0289</td>
</tr>
<tr>
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<td>0.0282</td>
<td>0.0344</td>
<td>1.0427</td>
</tr>
<tr>
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<td>17.302</td>
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<td>0.0426</td>
<td>1.0564</td>
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<td>20.712</td>
<td>0.0358</td>
<td>0.0510</td>
<td>1.0702</td>
</tr>
</tbody>
</table>

Table 21. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 50:50 in PS at (463.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
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<th>$T$/K</th>
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<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
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<td>0.0232</td>
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</tr>
<tr>
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<td>13.891</td>
<td>0.0254</td>
<td>0.0299</td>
<td>1.0333</td>
</tr>
<tr>
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<td>17.311</td>
<td>0.0290</td>
<td>0.0362</td>
<td>1.0432</td>
</tr>
<tr>
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<td>20.713</td>
<td>0.0324</td>
<td>0.0428</td>
<td>1.0531</td>
</tr>
</tbody>
</table>
Table 22. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 75:25 in PS at (403.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
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<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
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</thead>
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<td>402.9</td>
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<td>1.0289</td>
</tr>
<tr>
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<td>0.0334</td>
<td>0.0400</td>
<td>1.0494</td>
</tr>
<tr>
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<td>0.0389</td>
<td>0.0518</td>
<td>1.0700</td>
</tr>
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<td>17.283</td>
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<td>1.0907</td>
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<td>0.0749</td>
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</table>

Table 23. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 75:25 in PS at (423.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
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</tr>
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<td>0.0371</td>
<td>1.0392</td>
</tr>
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<td>0.0482</td>
<td>1.0574</td>
</tr>
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<td>0.0422</td>
<td>0.0588</td>
<td>1.0755</td>
</tr>
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<td>20.724</td>
<td>0.0449</td>
<td>0.0697</td>
<td>1.0936</td>
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</tbody>
</table>

Table 24. Solubility, $X$ (g-gas/g-polymer) of CO$_2$/N$_2$ blend of 75:25 in PS at (463.15 ± 0.2) K
($P$, pressure of CO$_2$/N$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
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<td>1.0169</td>
</tr>
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<td>10.470</td>
<td>0.0264</td>
<td>0.0301</td>
<td>1.0312</td>
</tr>
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<td>0.0410</td>
<td>1.0454</td>
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<td>17.269</td>
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<td>1.0595</td>
</tr>
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<td>20.721</td>
<td>0.0452</td>
<td>0.0625</td>
<td>1.0738</td>
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</table>
5. Supporting Information for HDPE-PNC (Exfoliated Cases)

The solubilities of CO\textsubscript{2} in HDPE-PNC were measured at temperatures from (423 to 493) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. The experimental results are presented in Tables 25 to 38.

Table 25. Solubility, $X$ (g-gas/g-polymer) of CO\textsubscript{2} of in neat HDPE at (423.15 ± 0.2) K ($P$, pressure of CO\textsubscript{2} and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X$\textsubscript{apparent}</th>
<th>$X$\textsubscript{corrected}</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
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<td>0.0230</td>
<td>1.0177</td>
</tr>
<tr>
<td>423.1</td>
<td>8.35</td>
<td>0.0496</td>
<td>0.0582</td>
<td>1.0570</td>
</tr>
<tr>
<td>423.1</td>
<td>10.47</td>
<td>0.0602</td>
<td>0.0746</td>
<td>1.0742</td>
</tr>
<tr>
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<td>13.95</td>
<td>0.0729</td>
<td>0.1008</td>
<td>1.1024</td>
</tr>
<tr>
<td>423.2</td>
<td>17.43</td>
<td>0.0808</td>
<td>0.1269</td>
<td>1.1306</td>
</tr>
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<td>423.3</td>
<td>20.92</td>
<td>0.0841</td>
<td>0.1531</td>
<td>1.1589</td>
</tr>
</tbody>
</table>

Table 26. Solubility, $X$ (g-gas/g-polymer) of CO\textsubscript{2} of in neat HDPE at (463.15 ± 0.2) K ($P$, pressure of CO\textsubscript{2} and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X$\textsubscript{apparent}</th>
<th>$X$\textsubscript{corrected}</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>462.3</td>
<td>3.51</td>
<td>0.0221</td>
<td>0.0230</td>
<td>1.0182</td>
</tr>
<tr>
<td>462.6</td>
<td>8.38</td>
<td>0.0429</td>
<td>0.0501</td>
<td>1.0537</td>
</tr>
<tr>
<td>462.7</td>
<td>10.48</td>
<td>0.0541</td>
<td>0.0659</td>
<td>1.0690</td>
</tr>
<tr>
<td>462.8</td>
<td>13.94</td>
<td>0.0635</td>
<td>0.0855</td>
<td>1.0943</td>
</tr>
<tr>
<td>462.8</td>
<td>17.43</td>
<td>0.0759</td>
<td>0.1116</td>
<td>1.1198</td>
</tr>
<tr>
<td>462.9</td>
<td>20.93</td>
<td>0.0786</td>
<td>0.1312</td>
<td>1.1453</td>
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</tbody>
</table>

Table 27. Solubility, $X$ (g-gas/g-polymer) of CO\textsubscript{2} of in neat HDPE at (493.15 ± 0.2) K ($P$, pressure of CO\textsubscript{2} and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X$\textsubscript{apparent}</th>
<th>$X$\textsubscript{corrected}</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>492.8</td>
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<td>0.0367</td>
<td>1.0389</td>
</tr>
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<td>493.0</td>
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<td>0.0479</td>
<td>0.0583</td>
<td>1.0645</td>
</tr>
<tr>
<td>493.0</td>
<td>13.98</td>
<td>0.0586</td>
<td>0.0781</td>
<td>1.0895</td>
</tr>
<tr>
<td>493.0</td>
<td>17.40</td>
<td>0.0669</td>
<td>0.0983</td>
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<tr>
<td>493.0</td>
<td>20.83</td>
<td>0.0727</td>
<td>0.1187</td>
<td>1.1396</td>
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</tbody>
</table>
Table 28. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPE-g-MA at (423.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.2</td>
<td>3.53</td>
<td>0.0228</td>
<td>0.0235</td>
<td>1.0118</td>
</tr>
<tr>
<td>423.1</td>
<td>8.39</td>
<td>0.0489</td>
<td>0.0567</td>
<td>1.0521</td>
</tr>
<tr>
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<td>0.0582</td>
<td>0.0715</td>
<td>1.0694</td>
</tr>
<tr>
<td>423.2</td>
<td>13.96</td>
<td>0.0700</td>
<td>0.0965</td>
<td>1.0983</td>
</tr>
<tr>
<td>423.3</td>
<td>17.45</td>
<td>0.0774</td>
<td>0.1220</td>
<td>1.1273</td>
</tr>
<tr>
<td>423.3</td>
<td>20.94</td>
<td>0.0796</td>
<td>0.1469</td>
<td>1.1563</td>
</tr>
</tbody>
</table>

Table 29. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPE-g-MA at (463.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>462.0</td>
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<td>0.0194</td>
<td>0.0201</td>
<td>1.0130</td>
</tr>
<tr>
<td>462.8</td>
<td>8.39</td>
<td>0.0433</td>
<td>0.0499</td>
<td>1.0488</td>
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<td>10.47</td>
<td>0.0517</td>
<td>0.0626</td>
<td>1.0639</td>
</tr>
<tr>
<td>463.0</td>
<td>13.96</td>
<td>0.0639</td>
<td>0.0848</td>
<td>1.0894</td>
</tr>
<tr>
<td>463.0</td>
<td>17.45</td>
<td>0.0725</td>
<td>0.1067</td>
<td>1.1149</td>
</tr>
<tr>
<td>463.1</td>
<td>20.95</td>
<td>0.0796</td>
<td>0.1305</td>
<td>1.1404</td>
</tr>
</tbody>
</table>

Table 30. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPE-g-MA at (493.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
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<td>492.8</td>
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<td>0.0452</td>
<td>0.0545</td>
<td>1.0588</td>
</tr>
<tr>
<td>492.8</td>
<td>13.88</td>
<td>0.0556</td>
<td>0.0734</td>
<td>1.0838</td>
</tr>
<tr>
<td>492.9</td>
<td>17.30</td>
<td>0.0632</td>
<td>0.0923</td>
<td>1.1088</td>
</tr>
<tr>
<td>492.9</td>
<td>20.72</td>
<td>0.0683</td>
<td>0.1114</td>
<td>1.1337</td>
</tr>
</tbody>
</table>
Table 31. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.05\%) at $(423.15 \pm 0.2)$ K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.9</td>
<td>7.14</td>
<td>0.0439</td>
<td>0.0499</td>
<td>1.0483</td>
</tr>
<tr>
<td>422.8</td>
<td>10.56</td>
<td>0.0599</td>
<td>0.0740</td>
<td>1.0732</td>
</tr>
<tr>
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<td>13.99</td>
<td>0.0708</td>
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</tr>
<tr>
<td>422.9</td>
<td>17.41</td>
<td>0.0761</td>
<td>0.1184</td>
<td>1.1232</td>
</tr>
<tr>
<td>422.9</td>
<td>20.83</td>
<td>0.0773</td>
<td>0.1395</td>
<td>1.1482</td>
</tr>
</tbody>
</table>

Table 32. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.05\%) at $(463.15 \pm 0.2)$ K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>462.9</td>
<td>7.14</td>
<td>0.0382</td>
<td>0.0425</td>
<td>1.0378</td>
</tr>
<tr>
<td>462.9</td>
<td>10.56</td>
<td>0.0527</td>
<td>0.0634</td>
<td>1.0617</td>
</tr>
<tr>
<td>462.8</td>
<td>13.99</td>
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<td>0.0842</td>
<td>1.0857</td>
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<tr>
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<td>17.41</td>
<td>0.0725</td>
<td>0.1051</td>
<td>1.1097</td>
</tr>
<tr>
<td>464.0</td>
<td>20.67</td>
<td>0.0783</td>
<td>0.1250</td>
<td>1.1325</td>
</tr>
</tbody>
</table>

Table 33. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.05\%) at $(493.15 \pm 0.2)$ K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>492.9</td>
<td>7.13</td>
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<td>0.0358</td>
<td>1.0327</td>
</tr>
<tr>
<td>492.9</td>
<td>10.56</td>
<td>0.0445</td>
<td>0.0536</td>
<td>1.0567</td>
</tr>
<tr>
<td>492.9</td>
<td>13.99</td>
<td>0.0543</td>
<td>0.0716</td>
<td>1.0807</td>
</tr>
<tr>
<td>492.9</td>
<td>17.41</td>
<td>0.0613</td>
<td>0.0895</td>
<td>1.1047</td>
</tr>
<tr>
<td>492.9</td>
<td>20.69</td>
<td>0.0655</td>
<td>0.1067</td>
<td>1.1276</td>
</tr>
</tbody>
</table>
**Table 34. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.5%) at (423.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)**

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>423.0</td>
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<td>0.0217</td>
<td>0.0228</td>
<td>1.0172</td>
</tr>
<tr>
<td>423.1</td>
<td>8.36</td>
<td>0.0478</td>
<td>0.0556</td>
<td>1.0513</td>
</tr>
<tr>
<td>423.2</td>
<td>10.48</td>
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<td>0.0704</td>
<td>1.0661</td>
</tr>
<tr>
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<td>13.97</td>
<td>0.0691</td>
<td>0.0938</td>
<td>1.0906</td>
</tr>
<tr>
<td>423.3</td>
<td>17.45</td>
<td>0.0764</td>
<td>0.1168</td>
<td>1.1149</td>
</tr>
<tr>
<td>423.3</td>
<td>20.93</td>
<td>0.0783</td>
<td>0.1384</td>
<td>1.1393</td>
</tr>
</tbody>
</table>

**Table 35. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.5%) at (463.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)**

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<td>8.38</td>
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<td>0.0490</td>
<td>1.0440</td>
</tr>
<tr>
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<td>10.46</td>
<td>0.0515</td>
<td>0.0616</td>
<td>1.0581</td>
</tr>
<tr>
<td>462.9</td>
<td>13.95</td>
<td>0.0636</td>
<td>0.0829</td>
<td>1.0818</td>
</tr>
<tr>
<td>463.0</td>
<td>17.44</td>
<td>0.0724</td>
<td>0.1040</td>
<td>1.1056</td>
</tr>
<tr>
<td>463.0</td>
<td>20.93</td>
<td>0.0778</td>
<td>0.1248</td>
<td>1.1293</td>
</tr>
</tbody>
</table>

**Table 36. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (0.5%) at (493.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)**

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
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<td>0.0352</td>
<td>1.0299</td>
</tr>
<tr>
<td>492.9</td>
<td>10.47</td>
<td>0.0440</td>
<td>0.0526</td>
<td>1.0532</td>
</tr>
<tr>
<td>492.9</td>
<td>13.89</td>
<td>0.0538</td>
<td>0.0703</td>
<td>1.0765</td>
</tr>
<tr>
<td>492.8</td>
<td>17.30</td>
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<td>0.0881</td>
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</tr>
<tr>
<td>492.9</td>
<td>20.73</td>
<td>0.0650</td>
<td>0.1050</td>
<td>1.1230</td>
</tr>
</tbody>
</table>
Table 37. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (3%) at (423.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>422.8</td>
<td>3.50</td>
<td>0.0214</td>
<td>0.0224</td>
<td>1.0114</td>
</tr>
<tr>
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<td>8.39</td>
<td>0.0480</td>
<td>0.0552</td>
<td>1.0432</td>
</tr>
<tr>
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<td>10.47</td>
<td>0.0550</td>
<td>0.0666</td>
<td>1.0567</td>
</tr>
<tr>
<td>423.3</td>
<td>13.96</td>
<td>0.0660</td>
<td>0.0882</td>
<td>1.0794</td>
</tr>
<tr>
<td>423.3</td>
<td>17.45</td>
<td>0.0721</td>
<td>0.1087</td>
<td>1.1021</td>
</tr>
<tr>
<td>423.3</td>
<td>20.94</td>
<td>0.0737</td>
<td>0.1280</td>
<td>1.1248</td>
</tr>
</tbody>
</table>

Table 38. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in HDPNE-PNC (3%) at (463.15 ± 0.2) K ($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.0201</td>
<td>1.0136</td>
</tr>
<tr>
<td>462.9</td>
<td>8.36</td>
<td>0.0426</td>
<td>0.0490</td>
<td>1.0432</td>
</tr>
<tr>
<td>462.9</td>
<td>10.46</td>
<td>0.0511</td>
<td>0.0614</td>
<td>1.0560</td>
</tr>
<tr>
<td>463.0</td>
<td>13.95</td>
<td>0.0635</td>
<td>0.0824</td>
<td>1.0773</td>
</tr>
<tr>
<td>463.0</td>
<td>17.44</td>
<td>0.0726</td>
<td>0.1029</td>
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<tr>
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<td>20.92</td>
<td>0.0785</td>
<td>0.1228</td>
<td>1.1198</td>
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</table>
Fig 1: Gnomix data for HDPE-PNC (exfoliated cases)
Comparison of Isobaric Plot of Neat HDPE and HNC
(ALL Runs)

Fig 2: Gnomix data for HDPE-PNC (intercalated cases)
6. Supporting Information for PP-PNC

The solubilities of CO$_2$ in PP-PNC were measured at temperatures from (423 to 493) K and at pressures of up to 21 MPa using a magnetic suspension balance (MSB) and a PVT apparatus. The experimental results are presented in Tables 39 to 47.

Table 39. Solubility, \( X \) (g-gas/g-polymer) of CO$_2$ of in Neat PP at (453.15 ± 0.2) K (\( P \), pressure of CO$_2$ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>452.9</td>
<td>8.36</td>
<td>0.0527</td>
<td>0.0624</td>
<td>1.0706</td>
</tr>
<tr>
<td>453.0</td>
<td>10.46</td>
<td>0.0640</td>
<td>0.0800</td>
<td>1.0915</td>
</tr>
<tr>
<td>453.1</td>
<td>13.96</td>
<td>0.0801</td>
<td>0.1106</td>
<td>1.1266</td>
</tr>
<tr>
<td>453.1</td>
<td>17.44</td>
<td>0.0921</td>
<td>0.1418</td>
<td>1.1614</td>
</tr>
<tr>
<td>453.1</td>
<td>20.93</td>
<td>0.1001</td>
<td>0.1739</td>
<td>1.1963</td>
</tr>
</tbody>
</table>

Table 40. Solubility, \( X \) (g-gas/g-polymer) of CO$_2$ of in Neat PP at (473.15 ± 0.2) K (\( P \), pressure of CO$_2$ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
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<td>0.0576</td>
<td>1.0595</td>
</tr>
<tr>
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<td>0.0602</td>
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<td>1.0775</td>
</tr>
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<td>472.9</td>
<td>13.95</td>
<td>0.0751</td>
<td>0.0995</td>
<td>1.1073</td>
</tr>
<tr>
<td>473.0</td>
<td>17.43</td>
<td>0.0869</td>
<td>0.1265</td>
<td>1.1372</td>
</tr>
<tr>
<td>473.0</td>
<td>20.92</td>
<td>0.0953</td>
<td>0.1537</td>
<td>1.1670</td>
</tr>
</tbody>
</table>

Table 41. Solubility, \( X \) (g-gas/g-polymer) of CO$_2$ of in Neat PP at (493.15 ± 0.2) K (\( P \), pressure of CO$_2$ and \( T \), temperature)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( P/\text{MPa} )</th>
<th>( X_{\text{apparent}} )</th>
<th>( X_{\text{corrected}} )</th>
<th>( S_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>492.7</td>
<td>8.35</td>
<td>0.0471</td>
<td>0.0535</td>
<td>1.0507</td>
</tr>
<tr>
<td>492.8</td>
<td>10.44</td>
<td>0.0571</td>
<td>0.0678</td>
<td>1.0674</td>
</tr>
<tr>
<td>492.8</td>
<td>13.96</td>
<td>0.0722</td>
<td>0.0928</td>
<td>1.0955</td>
</tr>
<tr>
<td>492.9</td>
<td>17.44</td>
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<td>0.1179</td>
<td>1.1232</td>
</tr>
<tr>
<td>492.9</td>
<td>20.93</td>
<td>0.0934</td>
<td>0.1431</td>
<td>1.1511</td>
</tr>
</tbody>
</table>
Table 42. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (2wt%) at (453.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (MPa)</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>452.9</td>
<td>8.37</td>
<td>0.0544</td>
<td>0.0616</td>
<td>1.0433</td>
</tr>
<tr>
<td>453.0</td>
<td>10.46</td>
<td>0.0662</td>
<td>0.0787</td>
<td>1.0619</td>
</tr>
<tr>
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<td>13.95</td>
<td>0.0829</td>
<td>0.1075</td>
<td>1.0927</td>
</tr>
<tr>
<td>453.1</td>
<td>17.44</td>
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<td>0.1366</td>
<td>1.1236</td>
</tr>
<tr>
<td>453.2</td>
<td>20.93</td>
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</tbody>
</table>

Table 43. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (2wt%) at (473.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (MPa)</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>472.9</td>
<td>8.35</td>
<td>0.0513</td>
<td>0.0573</td>
<td>1.0366</td>
</tr>
<tr>
<td>472.9</td>
<td>10.47</td>
<td>0.0624</td>
<td>0.0726</td>
<td>1.0517</td>
</tr>
<tr>
<td>473.0</td>
<td>13.95</td>
<td>0.0784</td>
<td>0.0978</td>
<td>1.0765</td>
</tr>
<tr>
<td>473.0</td>
<td>17.44</td>
<td>0.0911</td>
<td>0.1229</td>
<td>1.1012</td>
</tr>
<tr>
<td>473.1</td>
<td>20.94</td>
<td>0.1005</td>
<td>0.1477</td>
<td>1.1261</td>
</tr>
</tbody>
</table>

Table 44. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (2wt%) at (493.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (MPa)</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>492.7</td>
<td>8.36</td>
<td>0.0471</td>
<td>0.0521</td>
<td>1.0311</td>
</tr>
<tr>
<td>492.7</td>
<td>10.49</td>
<td>0.0575</td>
<td>0.0663</td>
<td>1.0469</td>
</tr>
<tr>
<td>492.8</td>
<td>13.96</td>
<td>0.0718</td>
<td>0.0893</td>
<td>1.0726</td>
</tr>
<tr>
<td>492.9</td>
<td>17.45</td>
<td>0.0841</td>
<td>0.1132</td>
<td>1.0984</td>
</tr>
<tr>
<td>492.9</td>
<td>20.94</td>
<td>0.0924</td>
<td>0.1360</td>
<td>1.1242</td>
</tr>
</tbody>
</table>
Table 45. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (4wt%) at (453.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>453.0</td>
<td>8.36</td>
<td>0.0536</td>
<td>0.0591</td>
<td>1.0228</td>
</tr>
<tr>
<td>453.0</td>
<td>10.46</td>
<td>0.0656</td>
<td>0.0755</td>
<td>1.0392</td>
</tr>
<tr>
<td>453.0</td>
<td>13.94</td>
<td>0.0827</td>
<td>0.1027</td>
<td>1.0665</td>
</tr>
<tr>
<td>453.1</td>
<td>17.43</td>
<td>0.0957</td>
<td>0.1297</td>
<td>1.0939</td>
</tr>
<tr>
<td>453.1</td>
<td>20.94</td>
<td>0.1045</td>
<td>0.1562</td>
<td>1.1213</td>
</tr>
</tbody>
</table>

Table 46. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (4wt%) at (473.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>472.7</td>
<td>8.34</td>
<td>0.0495</td>
<td>0.0548</td>
<td>1.0233</td>
</tr>
<tr>
<td>472.8</td>
<td>10.46</td>
<td>0.0598</td>
<td>0.0689</td>
<td>1.0387</td>
</tr>
<tr>
<td>472.9</td>
<td>13.94</td>
<td>0.0749</td>
<td>0.0930</td>
<td>1.0639</td>
</tr>
<tr>
<td>472.9</td>
<td>17.43</td>
<td>0.0865</td>
<td>0.1167</td>
<td>1.0892</td>
</tr>
<tr>
<td>472.9</td>
<td>20.92</td>
<td>0.0953</td>
<td>0.1406</td>
<td>1.1145</td>
</tr>
</tbody>
</table>

Table 47. Solubility, $X$ (g-gas/g-polymer) of CO$_2$ of in PP-PNC (4wt%) at (493.15 ± 0.2) K
($P$, pressure of CO$_2$ and $T$, temperature)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$P$/MPa</th>
<th>$X_{\text{apparent}}$</th>
<th>$X_{\text{corrected}}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>492.7</td>
<td>8.40</td>
<td>0.0476</td>
<td>0.0513</td>
<td>1.0131</td>
</tr>
<tr>
<td>492.7</td>
<td>10.47</td>
<td>0.0583</td>
<td>0.0652</td>
<td>1.0274</td>
</tr>
<tr>
<td>492.8</td>
<td>13.98</td>
<td>0.0706</td>
<td>0.0851</td>
<td>1.0516</td>
</tr>
<tr>
<td>492.8</td>
<td>17.47</td>
<td>0.0838</td>
<td>0.1087</td>
<td>1.0756</td>
</tr>
<tr>
<td>493.0</td>
<td>20.94</td>
<td>0.0949</td>
<td>0.1328</td>
<td>1.0996</td>
</tr>
</tbody>
</table>