#### THE EFFECT OF INTERFACIAL TENSION IN $\mathrm{CO}_2$ ASSISTED POLYMER PROCESSING

#### DISSERTATION

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By

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#### ABSTRACT

Supercritical fluid technology has made tremendous strides in the past decade in terms of commercial application and fundamental understanding of solution behavior. The addition of small amounts of compressed gases to polymer phases results in substantial and sometimes dramatic changes in the physical properties that dictate processing. These include viscosity, permeability, interfacial tension, and glass transition temperature. By understanding the effects of  $CO_2$  on these properties and developing techniques for incorporating  $CO_2$  in continuous processes, a wide range of opportunities open up for impacting the plastics industry. The products range from foam board insulation and high impact polymer blends to surface-modified biomedical implants and biological micro-electromechanical system (bio-MEMs) devices.

Supercritical  $CO_2$  is a promising solvent for application in polymer blending and foaming. Interfacial tension is a key parameter in determining the bubble nucleation and growth rates, as well as droplet break up in blending. However very limited data on this property is available in the literature for  $CO_2$ -polymer systems.

A novel technique is presented to determine the interfacial tension for the polymer melts and high pressure  $CO_2$  systems by analysis on the axisymmetric pendant drop shape profile, which can simultaneously yield the density, swelling and interfacial tension results. The method avoids the "capillary effect" and the "necking effect" and provides good axisymmetry of the pendant drop, which makes it a suitable method for measuring the interfacial tension for polymer melts under high pressure  $CO_2$  conditions.

In this work, the interfacial tension between polymer melt (PS, PP, PLGA, PMMA) and high pressure CO<sub>2</sub>, and the interfacial tension between polymer melt pairs (PS/PP) saturated with high pressure CO<sub>2</sub> were studied using the pendant drop method in a high pressure, temperature view cell. The effects of CO<sub>2</sub> pressure, temperature and molecular weight on interfacial tension were studied. The interfacial tension between polymer melt and CO<sub>2</sub> was significantly depressed and decreases almost linearly as CO<sub>2</sub> pressure increases in the pressure range up to 100 atm. The interfacial tension between polymer pairs saturated with CO<sub>2</sub> was studied in the CO<sub>2</sub> pressure range up to 100 atm, and was found to decrease significantly with increasing CO<sub>2</sub> pressure and levels off at higher CO<sub>2</sub> pressures.

The linear gradient theory combining with the Sanchez-Lacombe Equation of State was applied in predicting the surface tension or interfacial tensions for polymer melts under high pressure  $CO_2$  conditions, which correctly predicts the depression of interfacial tension by high pressure  $CO_2$  and yields reasonable agreement with experimental data. The temperature effect on the interfacial tension of polymer melts was also correctly predicted using this model.

The role of  $CO_2$  in enhancing the polymer blending process was carried out by combining the interfacial tension depression data with the viscosity reduction data. The capillary number, the most important parameter governing the drop breakage and coalescence in the blending process and thus the morphology of the blends, was used in the analysis. A highly simplified population balance model was applied to calculate the morphology evolution by only considering the droplet breakup during the mixing. The calculated results agree with the experimental data relatively well. Based on the model, the effect of  $CO_2$  on the morphology evolution was also discussed.

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#### **CHAPTER 1**

#### INTRODUCTION

#### 1.1. The production of polymer blends and polymeric foams

The production of polymers is a \$300 billion a year industry in 1995. Polymer blends constitute over 30% wt.% of polymer consumption and exhibits with an annual growth of 9%, which is four times the growth of the plastic industry as a whole[1]. The great majority of polymer blends are immiscible, which is a result of unfavorable thermodynamics caused by low entropies and positive heats of mixing[2].

The current challenge for the polymer blends industry lies in two aspects: the first is to improve production quality; the second is to minimize the environmental impact. Supercritical technology seems to be a promising technology to address this issue because of its non-toxic nature and its transport properties.

The polymeric foam industry is \$2 Billion in 2000 and commonly found in consumer products such as packaging, insulation, cushions, and absorbents as well as "high-tech" applications such as scaffolds for tissue engineering due to the advantages of high strength/weight ratio, insulating properties[3]. Because of the rapid development of these applications, research in foams is drawing increased attention. Since the traditional foaming agents, chlorofluorocarbons (CFCs), have been proven to contribute to the destruction of the ozone layer and will be gradually eliminated in the near future (2010 in US) [4-6], replacement technologies have been under intensive investigation. Supercritical  $CO_2$  is a promising alternative in the application for the polymer foaming process because it is environmentally benign, non-combustible, chemically stable and low-cost.

#### 1.2. Drop break up and coalescence in polymer blending

By blending, desirable properties of different polymers can be combined into single, heterogeneous materials. The details of multiphase domain structures play an important role in the physical properties of polymer blends[7]. Therefore controlling the morphology development during processing is of great importance. During polymer processing, the flow induced changes of structure in two-phase polymer blends are determined by two phenomena: break up and coalescence.

In the blending of polymer melts, the Reynolds number is small so that inertia can be neglected compared to the viscous shear stresses. The buoyancy effects are negligible with respect to interfacial effects since the density difference and hence the Bond number is small. The drop deformation is mainly governed by the capillary number, the ratio of the deforming stress  $\tau$  exerted on the drop by external flow field and the shape conserving interfacial stress  $\frac{\gamma}{R}$ :

$$Ca = \frac{\tau R}{\gamma} = \frac{\eta_m \dot{\gamma} R}{\gamma} \tag{1}$$

with  $\eta_m$  the viscosity of the matrix phase,  $\dot{\gamma}$  the shear rate, *R* is the dimension of the dispersed phase, and  $\gamma$  is the interfacial tension.

Above a critical value  $Ca_{crit}$ , the viscous shear stress overrules the interfacial stress and the drop is stretched and finally breaks into fragments. Taylor [8] and Grace [9] showed that the critical capillary number depends on the flow type and the viscosity ratio p ( $p = \eta_d / \eta_c$ ) between the dispersed and continuous phase. Some important results of their research include:

- It is easiest to deform and break drops around p~1, and impossible to beak drops if p>4 in simple shear because of the rotational character of the flow.
- Elongation flow is more effective than simple shear flow to deform and break drops.

Modeling such results is possible when small deformations are involved [10-12]. Stone gives a nice review concerning this issue[12].

The coalescence phenomenon, driven by interfacial tension, directly in competition with breakup during mixing, is much less understood. Chesters[13] gives a nice review on the understanding of processes of collision and coalescence in liquid-liquid dispersions. The flow driven coalescence in emulsion is usually studied by decoupling the process into an external flow and internal flow. The external flow is the macroscopic flow which brings the droplets together and hence controls the collision frequency, contact force and contact time. The drainage of the fluid film is the critical step in the merging process between two colliding droplets, which constitutes the internal flow. Depending on the interfacial mobility (fully mobile, partially mobile, and immobile interface), three models were developed by Chesters[13] for the film drainage between two colliding droplets. The probability P of the coalescence upon collision of two droplets is expressed as:

$$P = \exp\left(-\frac{t_{drain}}{t_{int}}\right)$$
(2)

where the  $t_{drain}$  is the time required for drainage of the fluid film between droplets, which is a function of viscosity ratio, interfacial tension, droplet size, etc. and  $t_{int}$  is the interaction time during collision, which is determined by the external flow.

From the above review, we can see that by controlling physical properties of the blending system, such as the viscosity ratio and the interfacial tension, we can control the drop breakup and coalescence morphology of the polymer blends. Particularly, the interfacial tension is the key factor to control the morphology and the mechanical properties of the immiscible polymer blends[14]. ScCO<sub>2</sub> technology provides such capability since CO<sub>2</sub> is an effective diluent for polymer melts and improves the ability to process materials through reductions in viscosity and interfacial tension by significantly increasing the free volume.

#### 1.3. Nucleation of bubbles in polymer foaming process

Although some basic principles governing the foaming process are understood, the design of a foaming process is still mainly experimental. As a result, researchers are interested in fully understanding the governing parameters in both foam cell nucleation and growth. According to homogeneous nucleation theory[15, 16], the Gibbs free energy for the formation of a nucleus with critical size is given by

$$\Delta G^*_{\text{hom}} = \frac{16\pi}{3\Delta P^2} \gamma^3 \tag{3}$$

and the homogeneous nucleation rate(  $N_{\rm hom}$  ) , is given by

$$N_{\rm hom} = f_0 C_0 \exp\left(-\Delta G^*_{\rm hom}/kT\right) \tag{4}$$

 $\Delta P$  is related to the supersaturation developed in the polymer and  $\gamma$  is the interfacial tension between polymer and nucleating bubble phases. Either a decrease of interfacial tension or an increase of supersaturation will result in an increase of nucleation rate and the number of bubbles produced.

#### 1.4. Current research status on the CO<sub>2</sub> assisted polymer extrusion process

The interfacial tension has a greater influence on the polymer foaming process due to the cubic power in the free energy term. Although some researchers have pointed out that the interfacial tension in this equation is not precisely the "bulk" interfacial tension, there are no known methods for measuring  $\gamma$  in a nucleating bubble. In fact there are limited data available for the interfacial tension between polymer melts and high pressure CO<sub>2</sub> at conditions relevant to foaming operations.

Supercritical  $CO_2$  is a promising solvent for application in polymer blending process. However limited research has been done on the influence of interfacial tension in the SCF  $CO_2$  assisted polymer-blending process due to the high pressure and temperature. The interfacial tension and viscosity are key parameters in determining the droplet break up and coalescence in blending, and thus the final resulting morphology of processed immiscible blends. Much research has focused on the influence of viscosity on the morphology in the polymer blending process. In polymer blending the domain size of the minor or dispersed phase is at a minimum when the viscosity ratio of the individual polymers is close to one and increases as the viscosity ratio increases [17, 18]. Elkovitch et al. and Lee et al. demonstrate this using batch mixing, single screw extrusion, twin screw extrusion, and tandem extrusion exploiting carbon dioxide's ability in assisting polymer blending[19-27]. When carbon dioxide decreases the viscosity of one component more than the other, the viscosity ratio can be controlled, thus leading to finer dispersed domains and typically improved (e.g. tougher, more flexible, etc.) materials. However the authors did not take into account the factor of interfacial tension, which is another important factor in polymer blending according to the study by Wu[28], who found that the dispersed drop size to be directly proportional to the interfacial tension.

While there exists a substantial body of literature on interfacial tension at high temperature (polymer melts with ambient pressure gases) and high pressure (gases with oligomers or polymer solutions), there is relatively little information available on systems of practical interest (i.e. polymer melts) at high temperature and high pressure. Viscosity reduction of polymer melts by carbon dioxide has been well documented in recent years and is easily correlated via shift factor analysis [24, 29-35]. At the same time little research has been carried out in understanding  $CO_2$  assisted blending processes by combining the effects of both interfacial tension and viscosity.

#### **1.5.** Techniques for the measuring the interfacial tension

Currently only a few methods are available to measure the interfacial tension between polymer melts, due to difficulties of the high temperature involved and high viscosities of polymer melts. Interfacial tension between polymer melts has been studied using both static and dynamic methods. Wu[36] gives a complete review on different techniques to measure the surface tension of polymer melts. The static methods include the pendant drop[37-46], sessile[47-50], spinning drop[29, 51-53], etc, which are based on the analysis of the equilibrium shape of a drop in a forced field (gravitational or centrifugal). The pendant drop is the most commonly used method to measure the interfacial tension for polymer melts and is most promising for simultaneous high pressure and high

temperature application. Harrison, et al. measured interfacial tensions for PS oligomer (Mw=1850)/CO<sub>2</sub> [54] at 45 °C up to 310 bar where  $\gamma$  decreases from 37.4 dyn/cm at 1bar to 1.5dyn/cm at 310 bar. However, no interfacial tension data is currently available for polymer melts under high pressure CO<sub>2</sub>.

Although the time reaching equilibrium is rather long using the pendant drop method due to the high viscosity of polymers which carries the risk of thermal degradation, in the studying of interfacial tension of liquid crystalline polymers (LCPS), with a high viscosity, the pendant drop has been demonstrated to be the only suitable method [44].

#### 1.5.1. Theory of Pendant drop method

The theory of the pendant drop method is based on the balance between gravitational and buoyancy forces. The mechanical equilibrium of a drop of one liquid suspended in another, which is separated by an interface, is given by Laplace's equation:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\Delta P}{\gamma}$$

Where  $R_1$  is the radius of curvature in the plane of Figure 2,  $R_2$  is the radius of curvature in a plane perpendicular to the Figure 2.  $\Delta P$  is the pressure difference across the curved interface and  $\gamma$  is the interfacial tension.



Figure 1.1. Definition of Coordinates for describing Surfaces with an axis of Symmetry

From Figure 2, the relationship between x and  $R_1$  is given by:

$$x = R_1 \sin \phi \tag{1}$$

Because of the symmetry of the interface, both values of R at the apex of the drop are the same, which is characterized as b. At the apex O,

$$\Delta P_0 = \frac{2\gamma}{b} \tag{2}$$

At point S, the pressure  $\Delta P$  can be expressed as

$$\Delta P = \Delta P_0 + \Delta \rho gz \tag{3}$$

Combining equations (1), (2), (3),

$$\frac{\sin\phi}{x/b} + \frac{1}{R_1/b} = 2 + \frac{\Delta\rho g b^2}{\gamma} \frac{z}{b}$$
(4)

 $R_1$  and  $\phi$  can be obtained from geometric consideration and are given below:

$$R_{1} = \frac{ds}{d\phi} = \frac{\left(1 + \left(\frac{dz}{dx}\right)^{2}\right)^{2/3}}{d^{2}z/dx^{2}}$$
(5)

$$\sin\phi = \frac{dz/dx}{\left(1 + \left(\frac{dz}{dx}\right)^2\right)^{1/2}}$$
(6)

#### 1.5.2.Axisymmetric drop shape analysis (ADSA)

The ADSA technique determines the interfacial tension from the shape of an axisymmetric meniscus of a pendant drop. The interfacial tension is calculated by fitting the shape of an experimental drop to the theoretical drop profile according to the Bashforth-Adams equation [55] using a least-squares algorithm with interfacial tension as the adjustable parameter and the drop profile coordinates and the density difference across the interface as the input information. Details of the numerical methods can be found elsewhere [56].

#### 1.6. Summary

The interfacial tension between polymer melts plays a key role in understanding the  $CO_2$  assisted polymer extrusion processing. It is important to establish a reliable technique to measure the interfacial tension under high temperature and high pressure conditions.

#### 1.7.Contents of this thesis

The dissertation attempts to provide the first fundamental understanding of the interfacial behavior between polymer melts and high pressure  $CO_2$  and that between immiscible polymer pairs saturated with high pressure  $CO_2$ . The role of interfacial tension reduction in the blending processes is analyzed to give a fundamental understanding and control these  $CO_2$  assisted processes.

In Chapter 2, the fundamental on the interactions between polymers and  $CO_2$  were briefly reviewed. The addition of small amounts of compressed gases to polymer phases results in substantial and sometimes dramatic changes in the physical properties, such as viscosity, interfacial tension, and glass transition. The fundamental properties of  $CO_2$  / polymer systems are discussed with an emphasis on measurement techniques and available experimental data. The Sanchez-Lacombe EOS is applied in correlating the existing data, which will provide the fundamentals for both the measuring and modeling of the interfacial tensions for polymer melt/CO<sub>2</sub> systems in later chapters.

In Chapter 3, the techniques for measuring the interfacial tension were reviewed. A novel technique is presented to determine the interfacial tension for the polymer melts and high pressure  $CO_2$  systems in a high pressure and high temperature view cell based on the analysis of the axisymmetric pendant drop shape profile (ADSA), which can simultaneously yields the density, swelling and interfacial tension. The method avoids both the "capillary effect" and the "necking effect" and provides good axisymmetry of the pendant drop. The ADSA technique was applied to determine the interfacial tension is calculated by fitting the shape of an experimental drop to the theoretical drop profile according to the Bashforth-Adams equation using a least-squares algorithm with interfacial tension as the adjustable parameter and the drop profile coordinates and the density difference across the interface as the input information. The overall performance of the image acquisition system and the profile analysis software were verified by evaluating the surface or interfacial tensions at both ambient (for water and hexane system) and high pressure (for water  $CO_2$  system) conditions.

In Chapter 4, the interfacial tension measurement results between polymer melt and  $CO_2$  are presented and the effects of pressure and temperature on the interfacial tension are analyzed on three different polymer systems. The dynamic behavior of the interfacial tension evolution is also discussed and the interfacial tension can be obtained based on this transit experimental data, which provides a faster way to make the interfacial tension measurement and avoids the polymer melt degradation.

In Chapter 5, the interfacial tension measurement results between immiscible polymer melt pairs saturated with high pressure  $CO_2$  are presented and the effect of pressure of  $CO_2$  on the interfacial tension is discussed.

In Chapter 6, the theories in predicting interfacial tension are reviewed and the linear gradient theory is discussed and applied in predicting the interfacial tension for small molecule, polymer, polymer/polymer, polymer/CO<sub>2</sub>, polymer/polymer/CO<sub>2</sub> systems.

Chapter 7 discusses the role of  $CO_2$  in depressing the interfacial tension and the implication for the  $CO_2$  assisted polymer blending processes. The capillary number, which characterizes the drop breakage and coalescence, is applied to clarify the effect of interfacial tension reduction in the morphological evolution. A highly simplified population balance model was applied to calculate the morphology evolution by only considering the droplet breakup during the mixing.

Finally Chapter 8 summarizes the results presented in this dissertation and gives suggestions for the future directions of this research. The contributions of this research to the fundamental understanding of polymeric interface under high pressure  $CO_2$ , and the  $CO_2$  aided polymer foaming and blending processes are also briefly mentioned.

#### **CHAPTER 2**

#### PHYSICAL PROPERTIES OF POLYMERS UNDER HIGH PRESSURE CO2

This chapter discusses physical properties (solubility, Tg, Swelling, Density, etc.) of polymers under high pressure  $CO_2$  conditions. The techniques in measuring these properties are briefly reviewed and the experimental data are provided and modeled using the Sanchez-Lacombe Equation of State. The contents of this chapter give the reader the understanding of the interaction between polymer and  $CO_2$ , and also provide fundamentals for the measurement and understanding of interfacial tension for polymer  $CO_2$  systems in the later chapters.

The affinity of  $CO_2$  for a polymer is associated with the interaction between  $CO_2$  and the polymer. Generally the solubility of  $CO_2$  increases with the increasing content of polar groups in the polymer. Berens [57] pointed out that near-critical  $CO_2$  behaves like a polar, highly volatile organic solvent when interacting with polymers. In a recent study, Shieh et. al. [58] reviewed the interactions between  $CO_2$  and polymers and studied the effects of carbonyl group content and crystallinity on the equilibrium solubility of  $CO_2$  in rubbery EVA with different VA(vinyl acetate) content. Their study suggests that the sorption process at or below *Pc* was mainly driven by the carbonyl groups and above *Pc*, by the degree of crystallinity such that the higher the degree of crystallinity, the lower the normalized  $CO_2$  sorption concentration (cm<sup>3</sup> STP  $CO_2$  / mol VA) in the polymer. Several researchers used FTIR (Fourier transformation infrared spectroscopy) to investigate the interaction of  $CO_2$  with polymers. [59-61] found that polymers containing carbonyl groups act as an electron donor and exhibit a specific interaction with  $CO_2$  as an electron acceptor rather than as an electron donor. Mawson et. al. [62] suggest that the interaction of  $CO_2$  with polymers possessing acrylate groups (containing carbonyl groups) may be of a Lewis acid-base nature. Also, the specific interactions between  $CO_2$  and the dipoles of the C-F bonds[63] or fluorine [64] were proposed to explain the increased solubility of  $CO_2$  in fluorine containing polymers. Weak electrostatic interactions were proposed for  $CO_2$  and the  $\pi$  system in PS [[65, 66],

#### 2.1. Plasticization of polymers under high pressure CO<sub>2</sub>

In many of the experimental techniques for studying the glass transition at high pressure, either the thermodynamic state of the polymer-gas system or the glass-to-rubber transition is not well defined[67]. Differential scanning calorimetry (DSC) is the simplest technique to use and provides fast and accurate information on the glass to rubbery transition. For the case of polymer-gas systems, ambient pressure DSC can be used to obtain the plasticized Tg and provides reasonable results provided the loss of gas during sample handling and scanning is minimized. However, it is not a simple task to do so. High pressure cells are available for DSC's with a typical pressure limitation of about 6.9 Mpa (1000 psi). Without elaborate controls, these units also suffer from an increasing pressure in the system during the scan, so it is not possible to define the thermodynamic state of the measurement. Secondly, the baseline stability deteriorates under elevated pressures. [68] In spite of these challenges, DSC remains the best alternative for obtaining  $T_g$ . It should be noted finally that for some systems the  $T_g$  is reduced so far that the apparatus needs to be modified for low temperature scanning.

In this research, the high pressure differential scanning calorimetry (HPDSC) was applied to measure the glass transition temperature (Tg) depression of PS, PMMA and PLGA in situ in the pressure range 1~65 atm.

Figure 2.1 shows the HPDSC cell for measuring the glass transition temperature of polymers under high pressure  $CO_2$ . All the operating procedures are the same as the normal DSC except the following:

- Loading the samples
- □ Purging the gas
- □ Controlling the pressure

Prior to measurement, the HPDSC was calibrated on an empty sample pan at every experimental pressure to determine baseline fluctuations with pressure. For measurements, the polymer sample (~10.0mg) is put into the open pan and loaded into the cell along with the reference pan, the system is purged with  $CO_2$  before the measurement to remove ambient air. The system was then purged with pressurized  $CO_2$  gas at 20 atm for three times. Then  $CO_2$  is introduced into the HPDSC cell at the desired experimental pressure using an ISCO 260D syringe pump operating in constant pressure mode. After 3 hours for equilibration, scanning is initiated ramping from 20°C to 100°C at a rate of  $10^{\circ}$ C/min. After cooling the cell, the scan is repeated until a steady glass transition temperature is obtained.

The glass transition depression under high pressure  $CO_2$  for PS Dow Styron 685D, PMMA and PLGA (75/25) were investigated. For every experimental pressure, the HPDSC was calibrated and used for later glass transition measurement. The polymer sample (~10.0mg) is placed inside the HPDSC cell, and  $CO_2$  is introduced inside the cell to contact with the polymer sample. After 3 hours for equilibration, HPDSC scanning is started, ramping from 30°C to 150°C at a rate of 10°C/min. After cooling the cell, the above scan is repeated until a steady glass transition temperature data is obtained.

Figure 2.2 gives the typical HPDSC scan results of PS under high pressure  $CO_2$ . The drop in Tg can be ascribed to solubilization of  $CO_2$  in the amorphous polymer creating a substantial amount of free volume.

Figure 2.3 gives the give the experimental results of glass transition temperature of PS under pressure CO<sub>2</sub> and comparison with literature data. From the experimental results, we can see that depression of the glass transition temperature of PS under CO<sub>2</sub> is dramatic. There is about a 40°C decrease in the pressure range from 0 to 65 bar or about  $0.695^{\circ} C/bar$ . Figure 2.4 gives the experimental results of glass transition temperature of PMMA under pressure CO<sub>2</sub>. From the experimental results, we can see that the depression of glass transition temperature of PMMA under pressure CO<sub>2</sub>. From the experimental results, we can see that the depression of glass transition temperature of PMMA under CO<sub>2</sub> is at a rate of  $0.723^{\circ} C/bar$ , which is larger than that of PS due to the specific interaction between the carbonyl groups. Figure 2.5 demonstrates the obvious shift in the HPDSC scans for PLGA under CO<sub>2</sub>. Figure 2.6 shows the depression of glass transition temperature of

PLGA (75/25) in the CO<sub>2</sub> pressure range up to 25 bar, with a decreasing rate of  $0.474^{\circ}C/bar$ .



Figure 2.1. Pressure DSC cell



Figure 2.2. HPDSC Scan of PS under Pressure CO<sub>2</sub>



Figure 2.3. Glass transition temperature depression of PS under CO2 and comparison with literature data[67, 69]



# Glass transition depression of PMMA under CO<sub>2</sub>

Figure 2.4. Glass transition temperature depression of PMMA under CO2 [70-73]

Comparison between HPDSC scan of PLGA with and without CO<sub>2</sub>



Figure 2.5. Tg shift for PLGA (75/25) under pressure  $CO_2$ 



Glass transition temperature depression of PLGA under CO<sub>2</sub>

Figure 2.6. Glass transition temperature depression of PLGA (75/25) under CO<sub>2</sub>

# 2.2. Solubility of $\text{CO}_2$ inside polymers and swelling of polymers under high pressure $\text{CO}_2$

Tomasko et al. [3] gives a complete review on techniques for quantitatively measuring the solubility of  $CO_2$  inside polymers. There are three types of methods for quantitatively measuring the solubility of  $CO_2$  inside polymers, each of which can provide data to about 5-7% accuracy.

#### *Barometric (pressure decay) method:*

The mass of gas absorbed by a polymer sample is obtained from the difference between the amount of gas initially contacted with the polymer and the amount remaining in the gas phase after equilibration.

#### *Gravimetric method:*

The simplest method is to study kinetics of desorption by measuring the weight change of a polymer sample after being removed from a high-pressure cell to a microbalance at ambient conditions. However, this method is only limited to low temperature conditions and no occurrence of foaming after release of pressure.

More precisely, the mass of the polymer sample plus  $CO_2$  is directly measured with a sensitive microbalance. The gravimetric method requires an accurate equation of state for the gas phase and some estimate (or measurement) of the swelling of the polymer phase to account for the buoyancy correction.

Several researchers have used an electronic microbalance inside a pressure vessel for insitu measurement at temperatures limited to below 125 °C due to the microbalance operating conditions. It has the advantages of requiring a small sample size (hence short measurement time) and high sensitivity (on the order of micrograms). Y. Kamiya et. al[74] measured the sorption of  $CO_2$  in PMMA at over a temperature range of 35-200°C using this type of microbalance. The other common type of microbalance is the magnetic suspension balance (MSB). [75] This has many advantages similar to the electronic microbalances with the added advantage that the sample and balance are mechanically isolated. The sample is magnetically levitated inside a high pressure vessel while the balance electronics remain at ambient conditions. This makes it suitable for the measurement of gas solubility and diffusivity in polymers at high temperatures and pressures. [76-81] The buoyancy correction is especially important for this type of balance. *Frequency modulation* using a quartz crystal microbalance (QCM) is an accurate and relatively easy technique to measure gas solubility in polymers at high pressures. The QCM is composed of a thin quartz crystal coated with the polymer of interest and sandwiched between two metal electrodes, which establish an alternating electric field across crystal, causing vibrational motion of the crystal at its resonant frequency, f, due to the peizoelectric effect. [82] The resonant frequency decreases linearly as the mass of the coating increases according to the Sauerbrey[83] equation which works very well for small mass gains in well-adhered films. The primary challenge is preparing such well-adhered films on the crystal and this limits somewhat the range of polymers amenable to this technique. Nonetheless, the modulation is reversible and can be used for real-time monitoring of a process.

The solubility of carbon dioxide in the polymer melts must be known in order to understand the factors that influence the interfacial tension in the SCF  $CO_2$  assisted polymer-blending process. Furthermore, the swelling experimental measurement and the solubility data results are essential input parameters for the interfacial tension measurements using the pendant drop method in the later Chapters. In this chapter, this property was studied using the techniques mentioned above.

#### 2.2.1. Solubility of CO<sub>2</sub> in PLGA (75/25)

The simple gravimetric method was applied in measuring the solubility of  $CO_2$  in polymers at ambient temperatures and elevated pressures.

The PLGA(75/25) samples were prepared in thin films with a weight around 100mg. The sorption measurement was carried out in a small high pressure cell immersed in a temperature-controlled water bath. The pressure inside the cell is controlled by an ISCO 260D syringe pump, which operates in constant pressure mode. Before the sorption measurement, the weight of the sample-PLGA thin film was accurately measured by the electro microbalance with an accuracy of 0.1mg. After the sample was loaded inside the cell,  $CO_2$  was introduced and the temperature and pressure were set to the desired value.
After PLGA is equilibrated with CO<sub>2</sub>, the cell was depressurized in 5 s and the sample was then taken out for weight measurement. The weight change of the sample was the intake of the CO<sub>2</sub>, which can be transformed into the weight fraction of CO<sub>2</sub> inside PLGA at the experimental temperature and pressure. Depending on the thickness of the film and operating conditions, different equilibration time may be needed. If different equilibration time (0.5 hours apart) yields almost the same solubility data, the data is the equilibrium solubility of CO<sub>2</sub> inside polymer. For PLGA, 3 hours is enough for the system to equilibrate, as shown in Table 1. Figure 2.7 shows an example of the desorption data, which can be used to obtain the solubility and diffusivity of CO<sub>2</sub> inside PLGA. Figure 2.8 gives the solubility of CO<sub>2</sub> in PLGA in the pressure range 70 bar at 22°C. At 12.4 bar,  $22^{\circ}$ C, the solubility of CO<sub>2</sub> in PLGA is 2.87% and is comparable to the predicted value of the solubility of CO<sub>2</sub> in PMMA, which is possibly due to the specific interaction between CO<sub>2</sub> and the carbonyl groups in polymers, as pointed by Kazarian [65]



Desorption of  $CO_2$  in PLGA at 22°C

Figure 2.7. Desorption of CO<sub>2</sub> in PLGA at 22°C

RUN	Equilibrating time	Weight(g)	Weight(g)	Weight Fraction
	(hours)	(PLGA)	(PLGA+CO <sub>2</sub> )	of CO2
А	4	0.0576	0.0593	2.87%
В	3	0.1644	0.1693	2.89%

Note: Sample A and B has the same thickness.

Table 2.1. Equilibrating time needed for Measuring the Solubility of CO<sub>2</sub> in PLGA



Figure 2.8. Solubility of CO<sub>2</sub> in PLGA (75/25) at 25°C

### 2.2.2. Solubility of CO<sub>2</sub> in PS Dow 685D

The pressure decay method is applied in measuring the solubility of  $CO_2$  inside PS. The experimental setup is shown in Figure 2.9. For measuring the solubility of  $CO_2$  at a given pressure and temperature, about 50g polymer is loaded into the stainless container, which is placed in the oil bath to maintain the desired temperature. Then the  $CO_2$  is pumped into the container by using the syringe pump operating in constant pressure mode. As  $CO_2$  dissolves in the polymer, there is a volume change. Recording this volume change allows one to back-calculate the solubility of  $CO_2$  in the polymer. Figure 2.10 gives the result of the solubility of  $CO_2$  in polystyrene at  $160^{\circ}C$  and  $180^{\circ}C$ , with pressures ranging from

86.2 bar to 155.1 bar. The maximum solubility of  $CO_2$  in PS is about 7% (weight fraction) under these conditions. Some literature data are given for this system for comparison. Our data seems to be slightly higher, which may be due to the different measuring techniques used or the different swelling effect correction.



Figure 2.9. Experimental setup to measure the solubility of CO<sub>2</sub> inside polymers



Figure 2.10. Solubility of CO2 in Polystyrene at 160 °C and 180 °C [78]

## 2.3. The swelling of polymers under high pressure CO<sub>2</sub>

The swelling of polymers are either measured using the techniques mentioned in literature, [84-87] or predicted using the Sanchez-Lacombe equation of state. The basic principle for measuring the swelling of polymers in  $CO_2$  is to determine swelling by measuring the change in one or more dimensions of a polymer sample. However, the pretreatment of the sample and the way in which the sample is prepared (the dimension of the sample) and measured, (either free hanging or lying on a glass plate), can yield different swelling results, which in turn influence the final results of the solubility measurement. Zhang et. al. [88]have investigated the influence of these factors in the solubility measurement in detail.

#### 2.3.1.Swelling of PS Dow Styron 685D

The experiments were carried out in the high pressure high temperature viewcell, which is the same apparatus used to measure the interfacial tension and will be discussed in detail in a later chapter.

Figure 2.11 gives the schematic of experimental set up in measuring the swelling of PS Styron 685D under high temperature, high pressure CO<sub>2</sub> conditions. The sample of PS was filled into a rectangular glass cell with dimension of 12mm x 12mm x 22 mm to a height of around 8mm, as shown in Figure 2.11. Then the glass cell filled with PS was placed inside the vacuum oven and heated to 220°C for 24 hours to remove the bubble inside the melt. After that the sample was slowly cooled down to room temperature and ready for the swelling measurement. The swelling measurements were carried out in the high pressure high temperature view cell, which is the same apparatus used and described in detail in the interfacial tension measurement in the later chapters. Please refer to corresponding chapter for detailed apparatus information. The prepared PS sample were placed inside the view cell, heated to the desired temperature and allowed to reach thermal equilibrium, CO<sub>2</sub> was slowly introduced to view cell. As CO<sub>2</sub> dissolved into PS, the PS sample undergoes one dimension swelling. A CCD camera was used to capture the swelling process. By measuring the relative height change of the PS sample in the glass cell, the swelling of PS under high pressure CO<sub>2</sub> can be determined, as shown in Figure 2.12. Figure 2.13 gives the typical swelling kinetics for PS under high pressure CO<sub>2</sub> conditions. If we define the swelling factor as following[78]:

$$Sw = \frac{v(T, P, s)}{v(T, P)} - 1$$

where S (g-gas/g-polymer) is the solubility, v(T, P) is the specific volume of the pure polymer, v(T, P, s) is the specific volume for the polymer-CO<sub>2</sub> solution,

Figure 2.14 gives the experimental results for the swelling of PS under three temperature:  $120^{\circ}$ C,  $150^{\circ}$ C, and  $180^{\circ}$ C in the pressure range up to 140 atm. Either an increase of

pressure of  $CO_2$  or a decrease in temperature will lead to a higher swelling of PS due to more  $CO_2$  dissolved.



Figure 2.11. Experimental set up for measuring the swelling of polymers under high pressure  $CO_2$ 



Figure 2.12.Typical experimental result for PS swelling measurement under high pressure  $CO_2$ 



Swelling kinetics of PS at 148.5C

Figure 2.13. Swelling kinetics of PS at 148.5°C



Experimental data of Swelling factor of PS under SCF CO<sub>2</sub>

Figure 2. 14. Swelling factor of PS under high pressure CO<sub>2</sub>

### 2.3.2. Swelling of PLGA (75/25)

Recently, Wulf et al. [89] have demonstrated the use of ADSA in simultaneously measuring the polymer density and the surface tension using the sessile drop method. By putting a pallet of known mass on cylindrical holder (which introduces barrier effects and overcomes the limitations of sessile drops, namely the generally low contact angles), the density can be obtained since the volume of the sessile drop can be obtained based on the ASDA analysis, as shown in Figure 2.15. The densities they obtained using this method compared very well to independently obtained literature PVT data. In our experiments, the pendant drop method was used to measure the polymer swelling and interfacial tensions under high pressure  $CO_2$  conditions. Comparing with the sessile drop method,

the time to reach equilibrium for the pendant drop is much shorter, which avoids the risk of polymer degradation at high temperatures.



Figure 2.15. Generalized pendant (a) and sessile (b,c) drop shapes. Sample preparation

## **Experimental procedure**

The experimental set up, the pendant drop formation technique and the experimental procedures are almost the same as those in the interfacial tension measurement, which are described in detail in Chapter 4. The only difference is that sample was weighed using an OHAUS model Galaxy 110 digital balance (with accuracy to 0.1mg) before forming the pendant drop. Once the drop volume is obtained based on the ADSA analysis, the density of the pure polymer can be calculated since the mass is already known. The swelling of polymers by  $CO_2$  can also be obtained based on the volume changes of pendant drop caused before and after the introduction of  $CO_2$ .

Figure 2.16 gives a typical experimental drop profile used to get the density of PLGA and swelling of PLGA under high pressure  $CO_2$  conditions. If the drop is too large and "necking" occurs, a smaller drop should be used.



Figure 2.16 (a) perfect drop profile (b) unusable drop profile

Currently no PLGA density data are reported in literature, but they are essential for the interfacial tension measurement using the pendant drop method. The density results of pure PLGA at ambient pressure using ADSA method are shown in Figure 2.17. A linear dependence on the temperature was observed with a temperature coefficient of  $-7.85 \times 10^{-4} g/cm^{3.°}C$ . Figure 2.18 shows the experimental results of densities of polymer phases under high pressure CO<sub>2</sub> conditions by the ADSA method. If we only calculate the density of PLGA, without considering the dissolved CO<sub>2</sub>, due to the swelling by CO<sub>2</sub>, the density decreased from 1.27 g/cc to 1.15 g/cc as pressure increased to 50 bar. However the density changes for the PLGA saturated with CO<sub>2</sub> are very small. This can be explained by two countering effects: the swelling by CO<sub>2</sub> and the solubility of CO<sub>2</sub> in the polymer matrix, the overall effect is that the density of the PLGA saturated with CO<sub>2</sub> remains relatively unchanged if pressure is not so high. The fact that the density

of PLGA saturated with  $CO_2$  remains relatively unchanged is good for the interfacial tension measurement of polymer under high pressure  $CO_2$ , since limited density under  $CO_2$  conditions are available. We will discuss this fact in detail in a later chapter for the interfacial tension measurement under high pressure  $CO_2$  conditions.

Based on the density of the pure PLGA and the PLGA saturated with  $CO_2$ , the swelling factor of PLGA can be calculated. The swelling results are shown in Figure 2.19.



Figure 2.17 Pure PLGA density results using ASDA method



Figure 2.18. Experimental densities for PLGA/CO<sub>2</sub> system at 22<sup>o</sup>C



Figure 2.19. Swelling factor for PLGA (75/25) under high pressure CO<sub>2</sub>

### 2.4. Sanchez-Lacombe Equation of State

The Sanchez-Lacombe Equation of State [90-92] is perhaps the most widely used model to describe the solubility of  $CO_2$  in polymers[77, 78, 87, 88, 93] due to its simplicity, well defined physical meaning, and the ability to extend available data to high temperature and pressures. It is particularly adept at correlating mixtures containing molecules of widely different size. The equation of state is based on lattice-fluid theory that allows for vacancies in the lattice and assumes the polymer has a flexible liquid structure:

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

Where  $\tilde{P}$ ,  $\tilde{T}$  and  $\tilde{\rho}$  are the reduced pressure, temperature, and density, respectively. *r* represents the number of lattice sites occupied by a molecule composed of *r* segments or "mers". Each molecule in this theory is characterized by 3 parameters ( $T^*$ ,  $P^*$ , and  $\rho^*$ ) that are used as the normalizing constants for the reduced parameters. These characteristic parameters are typically fit to vapor pressure or liquid density data and they are tabulated for several polymers. Typical characteristic parameters for gases and polymers can be found elsewhere[91-93]. Mixtures are handled using volume fraction based mixing rules and an adjustable binary interaction parameter,  $\delta_{i,j}$ , is typically introduced into the mixing rule for P<sup>\*</sup>:

 $P_{ij}^{*} = (1 - \delta_{ij}) (P_{i}^{*} P_{j}^{*})^{0.5}$ 

The adjustable parameter is obtained from a best fit of the equation of state to experimental solubility data. Unfortunately very limited interaction parameter data for  $CO_2$  and polymers are available in literature, and those are in a limited pressure or temperature range [77, 78, 88, 93] .  $\delta_{i,i}$  is expected to decrease with increasing temperature since the specific interactions normally decrease with increasing temperature, however, Kiszka et al. [93] did find negative values of  $\delta_{i,j}$  for the PMMA-CO<sub>2</sub> system that increased with temperature. Compiling values from several sources for the PS-CO<sub>2</sub> system indicates no clear trend with temperature even over a range of temperature exceeding 100 °C. Although the Sanchez-Lacombe equation of state can correlate the solubility of CO<sub>2</sub> in polymers very well, it cannot be relied upon to extrapolate to other temperatures and pressures. Although Kirby et al. [94] has pointed out in their review; "a good representation of the phase behavior is obtained only if the binary mixture parameters are allowed to vary with temperature. The dilemma of this approach is that mixture data are needed to obtain a reasonable estimation of the mixtures, that is, you need to know the answer to get the answer.", the Sanchez-Lacombe EOS allow a reasonably confident prediction of the thermodynamic properties of the mixture under operating conditions.

For application of the Sanchez-Lacombe equation of state to polymer-CO<sub>2</sub> systems, the amorphous polymer above its glass transition temperature can be modeled as a liquid. Polymers below their glass transition temperature have an additional unrelaxed volume and cannot be modeled well by the Sanchez-Lacombe equation of state [93]. Fortunately, as discussed below, the glass transition temperature can often be greatly depressed if sufficient amounts of a high-pressure gas are absorbed in the polymer, which will greatly expand the applicability of the Sanchez-Lacombe equation of state. For example, the glass transition temperature of PMMA is  $105^{\circ}$ C [87], but can be depressed to near ambient temperature at a CO<sub>2</sub> pressure of 70 atm (corresponding to about 25 wt% CO<sub>2</sub> in the polymer).

The following paragraphs describe the application of the Sanchez-Lacombe Equation of State in PS Styron 685D and PLGA (75/25). The pure component characteristic parameters used for SL EOS are listed in the Appendix. These results are essential for application in the interfacial tension measurement under high pressure  $CO_2$  conditions.

#### 2.4.1. SL EOS application for PS Styron 685D

The comparison of the swelling factor between the experimental results and the predicted value at three temperatures: 120°C, 150°C, and 180°C in the pressure range up to 140 atm are shown in Figure 2.20. The predicted value agrees reasonably well with the experimental data by fitting the interaction parameter to the experimental swelling data. The resulting interaction parameters are drawn in Figure 2.21 and compared with the available literature data. We can see that the interaction parameters scattered in temperature range studied. The reason may be the different techniques applied to get the interaction parameters. Our interaction parameter is a little bit higher that those by Sato et al., but falls on the same line with Winssinger et al.'s data.

Using the above obtained interaction parameters from the swelling data, the predicted solubility of  $CO_2$  in PS were shown in Figure 2.22. The predicted results were a little bit lower comparing with the Sato's data.



Correlation of Swelling factor using Sanchez-Lacombe EOS

Figure 2.20. Comparison of swelling factor between experimental and predictions by SL EOS



Figure 2.21. Comparison of the interaction parameters with literature[78, 88, 95, 96]



Prediction of Solubility of CO<sub>2</sub> in PS

Figure 2.22. Predicted solubility of CO<sub>2</sub> in PS using the SL EOS[78]

### 2.4.2. SL EOS application for PLGA (75/25)

Characteristic parameters for pure PLGA we use for PLGA(75/25) are  $T^* = 679.38K$ ,  $P^* = 2602.3bars$ ,  $\rho^* = 1.3525 g/cm^3$ , which were calculated using an iterative method based on the experimental *PVT* data by Alex using Gnomix *PVT* apparatus as described by Zoller et al.

The comparison of the solubility of  $CO_2$  in PLGA between the experimental results and the predicted value at  $22^{\circ}C$  in the pressure range up to 70 atm are shown in Figure 2.23.

The predicted value agrees reasonably well with the experimental data with the interaction parameter  $\delta_{ij} = -0.003$  by fitting to the experimental solubility data. Using the above obtained interaction parameters from the solubility data, the predicted swelling of PLGA is shown in Figure 2.24. The predicted results agree reasonably well with the experimental swelling data.



Figure 2.23. Comparison of solubility between Calculation and Prediction (SL EOS) at  $22^{\circ}C$ 



Figure 2.24. Comparison of swelling factor between Calculation and Prediction (SL EOS) at  $22^{\circ}$ C

# 2.5. Summary

- Experimental techniques to measure the physical properties between polymers and high pressure CO<sub>2</sub> are briefly reviewed. Some of the experimental results are also provided and discussed.
- The Sanchez-Lacombe EOS is briefly reviewed and applied in correlating the experimental data and predicting the physical properties for CO<sub>2</sub> polymer system reasonablely well.
- ADSA method is successfully applied in getting the density measurement and the swelling of polymers under high pressure CO<sub>2</sub>.

• The contents in this chapter provide fundamentals for the future research to measure the interfacial tension between polymer CO<sub>2</sub> systems.

## **CHAPTER 3**

#### INTERFACIAL TENSION MEASUREMENT: APPRATUS VERIFICATION

As discussed in the introduction, the pendant drop method is the most promising method of all the existing techniques in measuring the interfacial tension of polymer melts under high pressure  $CO_2$  conditions. In this chapter, the apparatus in measuring the interfacial tension using pendant drop method based on the ASDA technique is presented and the method is verified.

#### 3.1. High pressure, high temperature view cell

A custom-made high pressure (up to 5000 psi), high temperature (up to 250°C) variable volume view cell (Thar Technologies, Inc.) allowed imaging of the samples as shown in Figure 3.1. The pressure inside the cell is controlled by a syringe pump (ISCO 260D), which operates in a constant pressure mode. The temperature inside the cell is controlled by cartridge heaters and a temperature controller to an accuracy of  $\pm 0.5^{\circ}$ C. Threaded ports were drilled to allow the placement of the drop insertion apparatus, CO<sub>2</sub> injection and thermocouple. Two optical-quality sapphire windows inset perpendicular to the axis of the cell allow the illumination and recording of the drop. A Fiber-Lite model 181-1 gooseneck illumination system (Fisher Scientific) provided uniform lighting, allowing a global thresholding for digitizing the drop image. A CCD camera with an adjustable lens was used to capture the image. The image was then transferred to a monitor for display and recording and finally to a computer system for digitizing.



1. CO<sub>2</sub> cylinder 2.Syringe pump 3.Valve 4. High pressure, high temperature view cell 5. Pressure controller 6. Temperature controller 7.hydraulic pumps 8. Video camera 9.VCR 10.Computer

Figure 3.1 Experimental set up for the pendant drop method

## **3.2.** Apparatus verification

#### 3.2.1. Low pressure verification

The surface tension of water, hexane and acetone were measured at room temperature and atmospheric pressure in order to verify the apparatus. Figure 3.2 gives the comparison between the digitalized pendant drop profile and the theoretical one for the water/air at 24.5 °C based on the analysis. The calculated profile fits the experimental data very well. From the data analysis, we know that the calculated interfacial tension data is not sensitive to the number of data points selected from the experimental profile, but sensitive to the high quality of the selected data points, which will be discussed in detail later in this chapter. The surface tension results are shown in Table 3.1. We can see that, there is a good agreement between the values of surface tension in the literature and those measured in our experiment.

Material	$\Delta \rho(g/cm^3)$	This Work	Literature Values
		(dyne/cm)	(dyne/cm)
Water/Air	0.998	71.15 at 24.5 °C	72.14 at 25 °C [97]
Water/CO <sub>2</sub>	0.998	72.26 at 24.5 °C	72.14 at 25 °C[97]
Hexane/Air	0.6603	18.38 at 22.5 °C	18.4 at 20 °C [98]
Acetone/CO <sub>2</sub>	0.7899	24.25 at 22.5 °C	23.70 at 20 °C[99]

Table 3.1. Comparison between Measured and Reported Surface Tension Value



Figure 3.2. Comparison of the experimental profile (o) and theoretical profile (line) (System: water/air at 24.5 °C)

#### **3.2.2. High pressure verification**

The interfacial tension between water and high pressure  $CO_2$  at room temperature and pressures up to 60 atm was also measured. The drop was produced through tubing with diameter ranging from 1/16'' to 1/8''. By controlling the high pressure hydraulic pump, a desired drop with the right size can be formed. For high pressure conditions, the view cell was purged with  $CO_2$  first to get rid of air inside, then  $CO_2$  was slowly introduced into the view cell to the desired pressure. After the pressure inside the view cell reaches equilibrium, the profile of the pendant drop was captured and digitized every 10 minutes. When consecutive measurements yielded the same interfacial tension data, the drop was considered to have reached equilibrium and the value is reported as the equilibrium interfacial tension.

For the low viscosity water/CO<sub>2</sub> system, the time needed to reach the mechanical equilibrium is very short, on the order of a few minutes, as shown in Figure 3.3, and Figure 3.4. Figure 3.5 gives the experimental results of the interfacial tension of Water/CO<sub>2</sub> in the pressure range up to 70 atm at 24.5 °C. The measured data agree very well with the literature and demonstrate the validity of the experimental apparatus. The interfacial tension decreases as the pressure increase. A simple explanation is as following: as the pressure increases, the density difference decreases, which causes a decrease of the interfacial tension. A detailed discussion will be presented in a later chapter based on the density gradient theory.



Figure 3.3. Evolution of the interfacial tension of water under high pressure CO<sub>2</sub> at 25 °C



Figure 3.4. Development of Drop of water in CO<sub>2</sub> at 24.5°C (Injected with the 1/8" diameter capillary at different time and pressure) (First line: pressure-14.7 psi, Second line: pressure-892psi)



Figure 3.5. Interfacial tension between water and CO2 at 25°C [100]

### 3.3. Summary

From the above experiments, we can see that the pendant drop method is an accurate method for measuring the surface (interfacial) tension. As long as the time is long enough and the final mechanical equilibrium stage is reached, the drop profile can be recorded and digitilized, and the interfacial tension can be accurately calculated. For measuring the interfacial tension in the SCF  $CO_2$  assisted polymer extrusion process, the only adjustments for the apparatus are the installation of a temperature control system and a development of a dropping forming method.

#### **CHAPTER 4**

### SURFACE TENSION OF POLYMER MELTS UNDER HIGH PRESSURE CO2

In this chapter, the surface tensions of polymers (PP, PS, PMMA, PLGA) under high pressure  $CO_2$  were measured using the pendant drop method in a high pressure high temperature view cell based on ADSA analysis.

## 4.1. Experimental

#### 4.1.1. Materials

PL-25: an extrusion grade Poly(methyl methacrylate) (PMMA) with high molecular weight and high heat resistance, supplied by Plaskolite.

Styron 685D: high molecular Polystyrene (PS), with a number average molecular weight of 120,000, supplied by Dow Chemical.

Nova 1037C: low molecular weight PS, supplied by NOVA Chemicals Inc.

Two different molecular weight commercial brands of polypropylene (PP) were also used: PP P4G2Z-011: with a melt index of 12 g/min and PP P4G2Z-026 with a melt index 1.2 g/min (Huntsman Polymers).

PLGA(75/25), (L-lactide 75% + glycolide 25%), provided by Alkermes.

Carbon dioxide was supplied by PRAXAIR at a purity of 99.9%.

### 4.1.2. Experimental set up

The experimental was carried out in the same high pressure high temperature view cell illustrated in Chapter 2, with additions to the apparatus of a temperature control system and a drop forming method as shown in Figure 4.1.



Figure 4.1. Experimental set up for measuring the interfacial tension of polymers under high temperature and under high pressure CO<sub>2</sub>

### 4.1.2.1. Drop formation inside the view cell

A syringe is most commonly used to form a pendant drop. During thermal equilibration, if the drop volume is smaller than a critical value, the drop will retract back into the syringe ("capillary effect" [45]). If the drop is larger than a critical value, it will neck and detach ("necking effect" [45]) For our drop formation method, solid stainless steel rods with diameters varying from 1.0mm to 1.6mm were used. The ends of the rods were polished to give a very smooth and homogeneous bottom surface for good axisymmetry. A filament of polymer sample was weighed (varying from 4.0 to 8.0 mg) and attached to the bottom surface of the rod under high temperature (above 200°C) and placed in a

vacuum oven to form the initial drop. After the bubbles in the PS were removed under vacuum, the rod with the initial drop was taken out of the oven and placed inside the view cell via a bored-through Swagelok fitting. This drop formation technique eliminates the "capillary effect" and by selecting an appropriate size filament, the "necking effect" effect can be eliminated. Figure 4.2 gives an example of the typical necking of drops under high pressure  $CO_2$  conditions due to the reduction of surface tension, which can be avoided by selecting a smaller drop size compared to that without  $CO_2$  conditions. Because the drop mass is known and fixed, this method can in principle simultaneously measure the interfacial tension and density of the polymer phase, as discussed in Chapter 2.



Figure 4.2. Necking of PP drops at 180oC and 131 atm CO<sub>2</sub> pressure (Pictures taken at time 0, 10min, 13min, 15min, 17 min, 18 min in the sequence from left->right, up-> down)

### 4.1.2.2. Experimental procedure

Before an experiment, the polymer samples and the rod are carefully cleaned using ethanol to avoid contamination. After the temperature inside the view cell reached the desired setting, the polymer drop was inserted and  $CO_2$  was introduced into the view cell to the desired pressure. The profile of the pendant drop inside the view cell was captured and digitized every 10 minutes. When consecutive measurements yielded the same interfacial tension data, the drop was considered to have reached equilibrium and the value is reported as the equilibrium interfacial tension. Figure 4.3 gives one typical drop evolution under high pressure  $CO_2$  conditions.



Figure 4.3. PLGA drop evolution at 130°C: at 20min; 40min ; 60min; 100min; 120min; 140min; 150min;

#### **4.1.3. Density determination**

The density difference across the interface is a necessary input for calculating the interfacial tension based on the pendant drop method. The densities of pure polymer PP, PS, PMMA, PLGA as well as those saturated with  $CO_2$  were calculated using the

Sanchez-Lacombe equation of state (S-L EOS) [91, 92, 101, 102]. The characteristic parameters used in the S-L EOS for pure PP, PMMA, PS, PLGA and CO<sub>2</sub> are listed in Appendix. Density data for polymer-CO<sub>2</sub> solutions are also scarce in the literature and so evaluation with the S-L EOS is the best option available. Although the binary interaction parameters for polymer CO<sub>2</sub> systems vary widely based on literature reports, the calculation of density is relatively insensitive to the interaction parameter used in the S-L EOS, which is reasonable considering the low solubility of CO<sub>2</sub> in these polymers. The density of the CO<sub>2</sub> phase is calculated by an accurate modified Benedict-Webb-Rubin (MBWR) equation of state[103].

#### 4.1.3.1. Density of PP:

Zoller [104]used the following equation to evaluate the density of PP (at ambient pressure) and showed that his experimental data and the equation give the same result to within 0.001 g/cm<sup>3</sup>.

 $V(T) = V_0 \exp(\alpha_0 T)$ ,  $V_0 = 1.1606g / cm^3$ ,  $\alpha_0 = 6.7 \times 10^{-4} / cC$ , T is temperature in <sup>o</sup>C. Figure 4.4 shows the calculated pure PP density from the S-L EOS, which agrees very well with Zoller's equation, giving a temperature coefficient  $\frac{d\rho}{dT} = -0.519g / cm^3 K$  The calculated density of the PP phase saturated with high pressure CO<sub>2</sub> at different temperatures is shown in Figure 4.5, which remains relatively unchanged as pressure of CO<sub>2</sub> increases.



Figure 4.4. Comparison of Pure PP density between literature and calculated using SL EOS


Figure 4.5. Calculated density of PP phase saturated with high pressure CO<sub>2</sub>

#### 4.1.3.2. Density of PS

Fox and Flory[105] give empirical equations for calculation of the density of pure PS for molecular weights (Mw) between 3000 and 85,000 and they showed that between 55,000 and 85,000 there is no influence of molecular weight on the density. Ratzsch also showed that the effect of molecular weight on density is almost negligible when Mn is higher that 20,000. The empirical equation for Mw higher than 55,000 is given as following:

 $\rho_{PS} = 1.10 - 0.00068(T - 273)$ 

where  $\rho_{PS}$  is the density in  $g/cm^3$  and T is temperature in K.

Figure 4.6 shows the calculated pure PS density from the S-L EOS, which shows excellent agreement with reported literature data, with a temperature coefficient

 $\frac{d\rho}{dT} = -0.68g/cm^3.K$  The calculated density of PS saturated with high pressure CO<sub>2</sub> at different temperatures is shown in Figure 4.7 and the decrease in density is almost negligible as the pressure of CO<sub>2</sub> increases.



Figure 4.6 Comparison of Pure PS density between literature and calculated using SL EOS



Figure 4.7. Calculated density of PS phase saturated with high pressure CO<sub>2</sub>

## 4.1.3.3. Density of PMMA

For PMMA, Sonani [106] gives the following equation to correlate the experimental data:

$$v_{PMMA} = 0.670 + 5.0 \times 10^{-4} T - \frac{714 \times 10^{-4} T + 4.3}{M_n}$$

where  $v_{PMMA}$  is the specific volume in  $cm^3/g$ , Mn is the number average molecular weight, *T* is the absolute temperature in *K*.

Figure 4.8 shows the calculated pure PMMA density results, which is a little bit higher than the reported literature data, with a temperature coefficient  $\frac{d\rho}{dT} = -0.633g/cm^3.K$ .

The calculated density of PMMA saturated with high pressure  $CO_2$  at different temperatures is shown in Figure 4.9 and again the density change is very small in the pressure range studied.



Figure 4.8. Comparison of Pure PMMA densities between literature and calculated using SL EOS



Figure 4.9. Calculated density PMMA saturated with high pressure CO<sub>2</sub>

From the above discussion, we can see that for all the polymers studied, the calculated densities for the pure polymers using Sanchez-Lacombe EOS agrees very well with the reported literature correlations (which themselves match the experimental data), except in the case PMMA, for which the calculation is a little bit lower than the reported data. The densities of the polymer phases saturated with high pressure  $CO_2$  remain relatively unchanged due to two countering effects: the swelling of polymers by  $CO_2$ , and the dissolution of  $CO_2$  inside the polymer matrix. The fact that the density of polymers saturated with  $CO_2$  remains relatively unchanged is good for the interfacial tension

measurement of polymer under high pressure  $CO_2$ , since limited density data under  $CO_2$  conditions are available.

#### 4.1.4. Drop profile Analysis

SigmaScan Pro, a sophisticated image analysis application that allows you to capture, modify, enhance, and measure digital images, is used to track the edge of the drop, which is. The software has powerful functions for edge tracking with multiple settings for the quality control, such as the stability, threshold setting for the edge detection, density of tracking points, etc.

#### 4.1.4.1 Edge tracking without enhancement

Edge tracking was first performed without picture enhancement using SigmaScan Pro. Figure 4.10 shows a typical tracking result. Overall the tracking is satisfactory although there are some indents for some digitized points. The image can be enhanced using Photoshop software to give a better quality for the later edge tracking.



Figure 4.10. Edge tracking without picture enhancement (PP at 180°C, CO<sub>2</sub> pressure: 56 atm)

#### **4.1.4.2.** Edge tracking with enhancement

Either Photoshop or SigmaScan Pro is used for picture enhancement. In Sigma Scan Pro, if edge tracking fails, one can use edge detection filters and the Histogram Stretch function to improve the contrast of the image, or recapture the image using different contrast settings. For Photoshop, in the Image menu the original image was transformed into Gray Mode first, and then the Brightness/Contrast of the resulted image was adjusted by -20(%) and +80 (%) respectively to enhance the image quality. The resulting enhanced image is shown in Figure 4.11. The edge is much smoother and sharper than that before the enhancement.



Figure 4.11. Edge tracking with picture enhancement (PP at 180°C, CO<sub>2</sub> pressure: 56 atm)

# **4.1.4.3.** Tracking results and comparison of the digitized drop profile between the enhanced and original image

The tracking results for the experimental drop profile with and without photo enhancement are given in Figure 4.12, Figure 4.13 respectively. The digitalized drop profile is much smoother for the enhanced image than that before the enhancement. The comparison of the tracking results is given in Figure 4.14.



Figure 4.12. Digitalized drop profile without enhancement (PP at  $180^{\circ}$ C, CO<sub>2</sub> pressure: 56 atm)



Figure 4.13. Digitalized drop profile with enhancement (PP at 180°C, CO<sub>2</sub> pressure: 56 atm)



Figure 4.14. Comparison of the digitalized results between enhanced and original drop profile (PP at 180°C, CO<sub>2</sub> pressure: 56 atm)

# 4.2. Surface tensions of PP melt under high pressure CO<sub>2</sub>

The effect of  $CO_2$  on the interfacial tension between PP and  $CO_2$  was studied at 180°C, and pressures up to 105 atm. From the results we can see that interfacial tension was

depressed dramatically from around 22 to 12.5 dyn/cm in the pressure range up studied following a linear relation, as shown in Figure 4.15.



Figure 4.15. Interfacial tension between PP and  $CO_2$  at  $180^{\circ}C$ 

#### 4.3. Surface tension of PS melts under high pressure CO<sub>2</sub>

Figure 4.16 shows the measured surface tension for Nova1037C PS at temperatures ranging from 190 to 240°C. The surface tension decreases linearly with an increase in temperature with a temperature coefficient  $\left(-\frac{d\gamma}{dT}\right)$  0.0846 dyn/cm.°C, which is close to

the literature data[36]. The comparison with available literature data is shown in Table 3 and the agreement is excellent considering possible differences in polydisperity and molecular weight.

The effect of  $CO_2$  on the interfacial tension between Nova1037C PS and  $CO_2$  was studied at three temperatures, 210, 220, 230°C, and pressures up to 137 atm. Styron 685D PS and  $CO_2$  was studied at 200°C, in a pressure range up to 103 atm, and results for both polymers are shown in Figure 4.17. From the results we can see that interfacial tension data of both the high (Styron) and low (Nova) molecular weight PS follow exactly the same trend. For Nova1037C PS, we can see that the interfacial tension was depressed dramatically in the pressure range up to 70 atm from around 24 to 14 dyn/cm and then decreased at a much lower rate as the pressure further increased. Also from the experimental results, the interfacial tensions at different temperatures begin to converge at higher pressures. The convergence is due to two counteracting effects. On one hand, increasing temperature drives the interfacial tension down, and on the other hand, the solubility of  $CO_2$  in PS decreases resulting in a higher interfacial tension. These two effects appear to erase the temperature effect on interfacial tension as pressure of  $CO_2$ increases.



Figure 16. Dependence of surface tension for Nova1037C on temperature



Figure 4.17. Interfacial tension between PS and CO<sub>2</sub>

# 4.4. Surface tensions of PLGA under high pressure CO2

The effect of  $CO_2$  on the interfacial tension between PLGA and  $CO_2$  was studied at 40°C, and pressures up to 60 atm, as shown in Figure 4.18. From the results we can see that interfacial tension was depressed dramatically in the pressure range studied from around 43 to 17 dyn/cm following a linear relationship.



Figure 4.18 Interfacial tension between PLGA and  $\text{CO}_2$  at  $40^{\circ}\text{C}$ 





Figure 4.19. Interfacial tension between PMMA and CO<sub>2</sub> at 220°C

The effect of  $CO_2$  on the interfacial tension between PMMA and  $CO_2$  was studied at 220°C, and pressures up to 80 atm, as shown in Figure 4.19. From the results we can see that interfacial tension was depressed dramatically in the pressure range studied from around 29 to 20 dyn/cm following a linear relationship.

#### 4.6. Summary

The pendant drop method was used to study the effect of  $CO_2$  on the surface tension of polymer melts in a high pressure and high temperature view cell. The Sanchez-

Lacombe EOS was successfully used to get the density data of the polymer phase saturated with  $CO_2$ , which is essential for the interfacial tension calculation. A novel pendant drop forming method was used which eliminated the "necking" and "capillary" effects thus allowing the imaging of polymer melts for the long time necessary for equilibration.  $CO_2$  was shown to significantly depress the interfacial tension of all the polymers studied. These data will be modeled and further discussed in a later chapter.

#### **CHAPTER 5**

# INTERFACIAL TENSION MEASUREMENT: IFT BETWEEN POLYMER MELTS UNDER HIGH PRESSURE CO<sub>2</sub>

Although knowledge of the interfacial tension in polymer/polymer systems can provide important information on the interfacial structure between polymers and can help the understanding of such phenomena as polymer incompatibility and adhesion, reliable measurement of interfacial tensions were not reported until 1969[37, 39], because of the experimental difficulties involved due to the high polymer viscosities.

Wu gives comprehensive reviews on the work carried out in the interfacial tension measurements for polymer melts. Generally, the interfacial tension between polymer melts decreases linearly with temperature with a coefficient of 0.01 dyn/cm/°C[36], which is about one half of the value observed for the temperature coefficient for polymer surface tension[36]. The reason lies in the fact that the temperature coefficient of the density difference across the interface,  $\frac{d(\rho_1 - \rho_2)}{dT}$ , is much smaller than the temperature

coefficient of the individual densities,  $\frac{d\rho_i}{dT}$ .

While there exists a substantial body of literature on interfacial tension at high temperature (polymer melts with ambient pressure gases) and high pressure (gases with oligomers or polymer solutions), there is relatively little information available on systems of practical interest (i.e. polymer melts) at high temperature and high pressure  $CO_2$ . In this chapter, the interfacial tensions between PS and PP under high pressure  $CO_2$  were measured using the pendant drop method in a high pressure high temperature view cell based on ASDA analysis.

#### 5.1. Experimental

#### 5.1.1. Materials

In the experiment two different molecular weight commercial brands of polypropylene (PP) were also used: PP P4G2Z-011 with a melt index of 12 g/min and PP P4G2Z-026 with a melt index 1.2 g/min (Huntsman Polymers). All detailed information of the polymers used in the experiments is listed in the appendix.

#### 5.1.2. Experimental set up

The experimental was carried out in almost the same high pressure high temperature view cell illustrated in Chapter 4, except for the installation of the glass cell for one polymer drop forming inside another polymer melt, as shown in Figure 5.1.



Figure 5.1. Experimental set up for measuring the interfacial tension between polymer melts under high temperature and under high pressure CO<sub>2</sub>

#### **5.1.3.** Drop formation inside the view cell

For the drop formation inside another polymer melt, the procedure is similar to that illustrated in Chapter 4. A solid stainless steel rod with diameters varying from 1.0mm to 1.6mm was used. The ends of the rods were polished to give a very smooth and homogeneous bottom surface for good axisymmetry. A filament of polymer sample was weighed (varying from 4.0 to 8.0 mg) and attached to the bottom surface of the rod under high temperatures (above 200°C) and placed in a vacuum oven to form the initial drop. After the bubbles in the Polymer were removed under vacuum, the rod with the initial drop was taken out of the oven for future measurement. For the interfacial tension measurement between polymer melts saturated with CO<sub>2</sub>, a small rectangular glass cell (1.0cm×2.0cm×2.0cm) filled with polymer pellets is heated up in a vacuum oven to degas the melt and is then mounted onto a base inside the high pressure, high temperature view cell. After heating the view cell to the desired temperature, and purging the view cell with CO<sub>2</sub>, the rod with the initial drop was inserted in the PP melt. CO<sub>2</sub> was slowly introduced into the view cell to contact with polymer melts inside. The profile of the pendant drop inside the view cell was captured and digitized every 10 minutes. When consecutive measurements yielded the same interfacial tension data for 2 hours, the drop was considered to have reached equilibrium and the value is reported as the equilibrium interfacial tension. This drop formation technique eliminates the "capillary effect" and by selecting an appropriate size filament, the "necking effect" effect can be eliminated.

#### 5.2. Interfacial tension between PS and PP saturated with CO<sub>2</sub>

The effect of  $CO_2$  on the interfacial tension between two immiscible polymer melts is still not well understood due to the limited experimental data available. In this study, the interfacial tension between PS and PP saturated with  $CO_2$  was studied at 220°C and pressures up to 165 atm for two different molecular weights of PP. Figure 5.2 shows a typical experimental run. The interfacial tension follows an exponential relaxation, similar to that observed by Demarquette[45] in a transient non-equilibrium pendant drop measurement to estimate interfacial tension. They attempted to fit the transient data regarding  $\gamma(t)$  from the pendant drop apparatus to the empirical exponential function given in the following equation:

 $\gamma(t) - \gamma_{\infty} = (\gamma_0 - \gamma_{\infty})e^{-m(t-t_0)}$ 

where  $\gamma_{\infty}$  is the value of  $\gamma(t)$  at infinite time, i.e. the value of interfacial tension,  $\gamma_0$  is the value of  $\gamma(t)$  at  $t_0$  and *m* is a constant.



Figure 5.2. Interfacial relaxation for a typical experimental measurement (PS, P4G2Z-026 saturated with CO<sub>2</sub> at 220°C, 26.4 atm)

This method suggested the possibility of the use of this approach to infer the interfacial tension from the transient drop profile. The advantages of this approach lie in the fact that this can lead to substantial savings in time and efforts, since transient measurements would involve less time than equilibrium measurements. Moreover, the shorter experimental time would diminish degradation problems.

It was observed that at lower temperatures, more time was required to reach equilibrium. Also, smaller drops required shorter times to reach equilibrium than larger drops. This suggests that the time to reach equilibrium might be a function of the viscoelastic properties of polymer melts.

The dependence of interfacial tension on  $CO_2$  pressure is shown in Figure 5.3. From this result we see that for both PP samples, the interfacial tension decreases rapidly in the pressure range up to 50 atm, and then levels off. The interfacial tension decreases by more than 20% in both systems. We suggest that  $CO_2$  may shield the unfavorable contacts between PS and PP segments at the interface.



Figure 5.3. Interfacial tension between PS and PP saturated with CO<sub>2</sub> at 220°C

#### 5.3. Summary

The pendant drop method was successfully used to study the effect of  $CO_2$  on the interfacial tension between polymer melts saturated with high pressure  $CO_2$ . A new pendant drop forming method was used which eliminated the "necking" and "capillary" effects thus allowing the imaging of polymer melts for the long time necessary for equilibration.  $CO_2$  was shown to significantly depress the interfacial tension of between polystyrene and polypropylene to about 20%. In all systems the data show a steep

decrease up to some intermediate pressure followed by a slower decrease at higher pressures.

#### **CHAPTER 6**

# DENSITY GRADIENT THEORY IN CORELATING AND PREDICTING IFT FOR POLYMER/CO<sub>2</sub> SYSTEMS

Theories and advances in predicting interfacial tension of polymer melts were recently reviewed[107]. Two primary theoretical approaches have been developed to predict the interfacial tension between polymer melts. Helfand and Tagami [108-110] formulated a statistical mechanical theory of the interface between immiscible polymers for symmetric systems, which is based on self-consistent field theory. The theory has since been extended to non-symmetric polymer systems[111].

The other common approach is based on the gradient theories(GT) [112-114] combined with the Flory-Huggins expression for the free energy density, or with equations of state, such as the Flory-Orwoll-Vrij model(FOV) [115], or the Sanchez and Lacombe lattice gas model(LF). [91, 92, 101, 102] The latter have had considerable success modeling compressible systems[42, 116-118].

Although conceptually different, the results by Poser and Sanchez [118] give comparable predictions to those of Helfand and Sapse. [119] Sanchez has shown that the gradient theory is "in harmony with the microscopic theory of Helfand and co-workers although the latter treats the polymer interfaces from a different point of view".

In the past two decades, considerable progress has been made in combining the Helmholtz energy of the bulk phases with the gradient theory (GT) of the interface, which has been successfully used for estimating interfacial properties of pure fluids and mixtures[120-129]. The inputs of gradient theory are the free energy of the homogeneous fluid and the influence parameter of the inhomogeneous fluid. The influence parameters can be rigorously related to the mean square range of the direct correlation function of the inhomogeneous fluid.

In this Chapter the gradient model developed by Poser and Sanchez and subsequently modified by Harrison, et al. [54, 130] was used to correlate the interfacial tension. For simplification of the application of GT theory in calculating IFT for polymer/ $CO_2$  polymer/polymer/ $CO_2$  systems, a linear density distribution across the interface is applied. The S-L equation of state is used to determine the polymer phase composition and densities.

#### 6.1. Introduction to density gradient theory

The following is the general interfacial theory developed by Poser and Sanchez[114]. The interfacial tension,  $\gamma$  for a planar interface can be defined as

$$\gamma \equiv \frac{\left(A - A_e\right)}{S_0}$$

where  $S_0$  is the surface area, A is the inhomogeneous system's Hemholtz free energy, and  $A_e$  is the Helmholtz free energy of a hypothetical homogeneous system with the same density and composition. In order to evaluate A, Poser and Sanchez adopted the standard assumption that the entropy of the homogeneous system is only a function of the local density and independent of density gradients. Effects of density gradients on the potential energy E, are evaluated in a mean-field approximation. The potential energy per unit volume, V, and position R, for an n component system with pairwise additive interactions can be written as

$$E(\mathbf{R})/V = \frac{1}{2} \sum_{i}^{n} \sum_{j}^{n} \varepsilon_{ij}(\mathbf{R})$$

where  $\varepsilon_{ij}$  is the interaction energy of component *i* and *j* and is given by

$$\varepsilon_{ij}(\mathbf{R}) = \rho_i(\mathbf{R}) \int \rho_j(\mathbf{R} + \mathbf{s}) \mu_{ij}(\mathbf{s}) d\mathbf{s}$$

where  $\rho_i$  and  $\rho_j$  are the number densities of components of *i* and *j*,  $s = |\mathbf{s}|$  is the intermolecular distance, and  $u_{ij}$  is the intermolecular interaction potential, which is assumed to be spherically symmetric. Expanding  $\rho_j(\mathbf{R} + \mathbf{s})$  around  $\mathbf{s} = 0$ 

$$\rho_j(\mathbf{R} + \mathbf{s}) = \rho_j(\mathbf{R}) + (\mathbf{s} \cdot \nabla)\rho_j + (\frac{1}{2!}(\mathbf{s} \cdot \nabla)^2 \rho_j + \dots$$

which yields the subsequent intergration

$$\varepsilon_{i,j} = -\rho_i(\mathbf{R})\rho_j(\mathbf{R})\kappa_0^{ij} + \rho_i(\mathbf{R})\int \{(\mathbf{s}.\nabla)\rho_j + (\frac{1}{2})(\mathbf{s}.\nabla)^2 \rho_j + ...\}u_{ij}(\mathbf{s})d\mathbf{s}$$
  
with  $\kappa_0^{ij} = -4\pi \int_{\sigma_{ij}}^{\infty} s^2 u_{ij}(s)ds$ 

where  $\sigma_{ii}^{3}$  is the repulsive core volume between components *i* and *j*.

Since  $u_{ij}$  is spherically symmetric, it is an even function of  $s_x$ ,  $s_y$ , and  $s_z$ , so that the integral of the above equation has the following properties:

$$\int (\mathbf{s} \cdot \nabla)^b \rho_j u_{ij} \, \mathrm{d}\, \mathbf{s} = 0 \quad b \text{ odd}$$
$$\int (\mathbf{s} \cdot \nabla)^b \rho_j u_{ij} \, \mathrm{d}\, \mathbf{s} \neq 0 \quad b \text{ even}$$

The integration becomes

$$\varepsilon_{i,j} = -\rho_i(\mathbf{R})\rho_j(\mathbf{R})\kappa_0^{ij} - \rho_i(\mathbf{R})\nabla^2\rho_j(\mathbf{R})\kappa_2^{ij} +$$
  
where  $\kappa_2^{ij} = -\frac{2\pi}{3} \int_{\sigma_{ij}}^{\infty} s^4 u_{ij}(s) ds$ 

Neglecting the fourth and higher order terms in the above equation is the usual gradient approximation. Defining the local Helmholtz free energy density  $a_0(\mathbf{R})$  as

•••

$$a_0(\mathbf{R}) \equiv -\left(\frac{1}{2}\right) \sum_i \sum_j \rho_i(\mathbf{R}) \rho_j(\mathbf{R}) \kappa_0^{ij} - TS(\rho_1, \rho_2, ..., \rho_n)$$

where T is the temperature and S is the entropy per unit volume, results the following expression of the Helmholtz free energy density for an inhomogeneous system:

$$a(\mathbf{R}) = a_0(\mathbf{R}) - \left(\frac{1}{2}\right) \sum_i \sum_j \rho_i(\mathbf{R}) \nabla^2 \rho_j(\mathbf{R}) \kappa_2^{ij}$$

The total Helmholtz free energy for a planar interface of area  $S_0$  and volume  $LS_0$  is given by

$$A = S_0 \int_{-L/2}^{L/2} \left[ a_0(x) + (1/2) \sum_{i} \sum_{j} \rho_i \left( \frac{d^2 \rho_j}{dx^2} \right) \kappa_2^{ij} \right] dx$$

Integration by parts of the second term in the integration leads to futher simplification  $\left(\frac{d\rho_i}{dx} = 0 \text{ as } x \to \infty\right)$ 

$$A = S_0 \int_{-L/2}^{L/2} \left[ a_0(x) + (1/2) \sum_{i} \sum_{j} \kappa_2^{ij} \left( \frac{d\rho_i}{dx} \right) \left( \frac{d\rho_j}{dx} \right) \right] dx$$

The final result for the interfacial tension is

$$\gamma = \int_{-\infty}^{\infty} \left[ \Delta a + (1/2) \sum_{i} \sum_{j} \kappa_{2}^{ij} \left( \frac{d\rho_{i}}{dx} \right) \left( \frac{d\rho_{j}}{dx} \right) \right] dx$$

where 
$$\Delta a \equiv a_0(x) - \frac{A_e}{V} \equiv a_0(x) - \sum_i \rho_i \mu_i^e + P_e$$

 $\mu_i^e$  is the equilibrium chemical potential and  $P_e$  is the external pressure.

Minimization of the above equation yields *n*-coupled differential equations (Euler-Lagrange equations)

$$\frac{\partial \Delta a}{\partial \rho_i} - \left(\frac{1}{2}\right) \sum_j \kappa_2^{ij} \frac{d^2 \rho_j}{dx^2} = 0 \qquad i = 1, 2, \dots n$$

Multiplying the differential equations by  $\frac{d\rho_i}{dx}$  and summing over species *i* yields

$$\frac{d}{dx}\left[\Delta a - (1/2)\sum_{i}\sum_{j}\kappa_{2}^{ij}\left(\frac{d\rho_{i}}{dx}\right)\left(\frac{d\rho_{j}}{dx}\right)\right] = 0$$

which upon integration yields

$$\Delta a = (1/2) \sum_{i} \sum_{j} \kappa_{2}^{ij} \left( \frac{d\rho_{i}}{dx} \right) \left( \frac{d\rho_{j}}{dx} \right)$$

Introducing the simplified notation,  $\kappa_{ij} \equiv \kappa_2^{ij}$ , the equilibrium tension can thus be expressed as

$$\gamma = \int_{-\infty}^{\infty} \sum_{i} \sum_{j} \kappa_{ij} \left( \frac{d\rho_{i}}{dx} \right) \left( \frac{d\rho_{j}}{dx} \right) dx = 2 \int_{-\infty}^{\infty} \Delta a dx$$

The equation was first derived by Bongiorno et al. [112]using a different approach. For a single component, these equations reduce to the well known Cahn-Hilliard equations[113]. The derivation by **Poser and Sanchez**[114] is quite general, and the resulting expression for the interfacial tension can be applied to any mean-field fluid model which provides an expression for the equilibrium potential and a specific form of the intermolecular interaction potential.

Numerical and analytical is facilitated by transforming the expression for interfacial tension from *x* space to  $\rho$  space.

$$\gamma = \int_{\rho_1'}^{\rho_1''} \sqrt{2\Delta a \sum_i \sum_j \kappa_{ij} \left(\frac{d\rho_i}{d\rho_1}\right) \left(\frac{d\rho_j}{d\rho_1}\right)} d\rho_1$$

where *I* and *II* refer to the equilibrium phases.

The above equation can also be written in the following simplified form:

$$\gamma = \int_{\rho_1^{I}}^{\rho_1^{II}} \sqrt{2C\Delta a} d\rho_1$$

where *C* is the influence factor. According to Bongiorno et al. [112],  $\Delta a$  is the "cause of inhomogeneity",  $\rho$  is the "response" and *C* is the "influence factor" which determines how much "response" per unit of "cause". C measures how much extra energy is associated locally with a given density.

#### **6.2. Linear density gradient theory**

The gradient theory (GT) is quite complicated and time-consuming because a set of density profile equations has to be solved by use of numeric methods before calculating IFTs of mixtures and it is difficult to apply to muticomponent mixtures. However in the LGT (Linear Gradient theory), it is assumed that the number density  $\rho_i(Z)$  of component *i* at position *Z* in a *N*-component mixture is linearly distributed across the interface with width L.

$$\frac{d\rho_i(Z)}{dZ} = D_i, \qquad D_i = \frac{\rho_i^{\ I} - \rho_i^{\ II}}{L}$$

where  $D_i$  is a constant for component *i*, *I* and *II* refer to the equilibrium phases.

According to the densities of the equilibrium phases, the density of component i at position Z can be determined. Therefore, it is unnecessary to solve a set of density profile equations. Fleming [131] suggested an interpretation of interfacial phenomena using schematic (linear) density profiles for pure fluids. You-Xiang Zuo[132] used the linear gradient theory (LGT) and successfully predicted the IFTs for a number of mixtures. In

this chapter, the LGT theory was applied in the correlating and predicting the IFTs for polymer/CO<sub>2</sub> systems.

#### 6.3. Application of LGT in the Calculation of IFT for small molecule systems

In order to verify the LGT in calculating the IFT, the LGT combined with PR EOS [133]was applied to calculate the interfacial tension between small molecules and compared with literature data.

The PR EOS has the following form:

$$P = \frac{\rho kT}{1 - \rho b} - \frac{\rho^2 a(T)}{1 + \rho b(2 - \rho b)}$$

where

$$a = \sum_{i}^{N} \sum_{j}^{N} x_{i} x_{j} (a_{i} a_{j})^{\frac{1}{2}} (1 - k_{ij})$$

$$b = \sum_{i}^{N} x_{i} b_{i}$$

$$a_{i}(T) = a_{i}(T_{ci}) \alpha_{i}(T_{Ri}, \omega_{i}), \quad b_{i} = 0.0778 \frac{RT_{ci}}{P_{ci}}$$

$$a(T_{ci}) = 0.45724 \frac{R^{2}T_{ci}^{2}}{P_{ci}}, \quad \alpha_{i}^{\frac{1}{2}} (T_{Ri}, \omega_{i}) = 1 + K_{i} (1 - T_{Ri}^{\frac{1}{2}})$$

$$K_{i} = 0.37464 + 1.54226 \omega_{i} - 0.26992 \omega_{i}^{2}$$

$$T_{Ri} = \frac{T}{T_{ci}}$$

For calculating the IFT using the LGT approach, we need to know the influence factor, which can be obtained by Zuo and Stenby [132]using the following equation:

$$\frac{\kappa}{ab^{\frac{2}{3}}} = A(1 - T_R)^B$$
  

$$A = 0.28367 - 0.05164$$
  

$$B = -0.81594 + 1.0681\omega - 1.1147\omega^2$$

The crossed term of  $\kappa_{ii}$  can be expressed using the following combing rule

$$\kappa_{ij} = \sqrt{\kappa_{ii}\kappa_{jj}}$$

#### 6.3.1. Binary system

LGT model was used to predict the IFTs for two component mixture system Methane-Propane first. Figure 6.1 shows the interfacial tension values predicted by LGT model and the comparison with experimental data at three temperatures. The predicted values agree with reported experimental data[134] very well. As the molar fraction of methane in the liquid phase increases, the IFT decreases. The reason is due to the low surface tension of methane compared with propane. And also at the same Methane molar fraction, the IFTs have lower values at higher temperature due to the reduced molecular interactions under high temperatures.



Figure 6.1. Interfacial tension for Methane-Propane mixtures

Interfacial tension between  $CO_2$  and Decane was also predicted using the LGT theory. Figure 6.2 shows the predicted interfacial tension by LGT model at two temperatures, which agrees with the reported experimental data[135] very well. As the pressure of  $CO_2$ increases, the IFT decreases due to more  $CO_2$  dissolved into the liquid phase, which has a much lower surface tension. At the same pressure, as temperature increases, the surface tension increases. Which can be explained by the following: the pure temperature effect will decrease the IFT, but as temperature increases, the  $CO_2$  dissolved in the liquid phase will also decrease and cause the surface tension to increase. The  $CO_2$  effect dominates and the overall effect is that the IFT decreases. This result can be clearly seen from

Figure 6.3, when the molar fraction of  $CO_2$  is the same, the IFT has a lower value at higher temperatures.



Figure 6.2 . Interfacial tension for  $CO_2$  -Decane mixtures



Figure 6.3 . Interfacial tension for CO<sub>2</sub> -Decane mixtures

## 6.3.2. Ternary Systems

LGT model was used to predict the IFTs for three component mixture system. The interfacial tension between Methane-Propane-Decane at one composition is predicted at three temperatures, as shown in Figure 6.4. The results show satisfactory agreement with reported experimental data[136].



Figure 6.4. Interfacial tensions for Methane-Propane- Decane mixtures (mole Fraction: 0.717+0.209+0.074)

From the above results, we can see that the assumption of linear number density profile across the interface works very well in predicting the IFT combing with the gradient theory. The predicted IFTs agree very well with experimental data away from the critical point.

## 6.4. Application of LGT theory in polymer systems
The Sanchez-Lacombe EOS was used to combine with LGT model in the calculation. For the mer-mer interaction, if we use an-inverse power law for the attractive part,

$$u_{ii} = \infty \qquad s < \sigma_{ii}$$
$$u_{ii} = -\varepsilon_0^{\ ii} \left(\frac{\sigma_{ii}}{s}\right)^m \qquad s \ge \sigma_{ii}$$

The exponential term m depends on the i,j interaction.

Based on Poser and Sanchez's[114] theory, the following results were obtained:

$$\kappa_{ii} = 2\varepsilon_{ii}^{*} \sigma_{ii}^{5} \widetilde{\kappa}_{ii}$$
where
$$\epsilon_{ii}^{*} = P_{i}^{*} v_{i}^{*} = 2\pi \varepsilon_{0}^{ii} / (m-3)$$

$$\widetilde{\kappa}_{ii} = [(m-3)/(m-5)]/6$$

Making the identification of  $\sigma_{ii}^{3} = v_{i}^{*}$ , we get the following results for the influence factor used in the LGT model.

$$\kappa_{ii} = 2P_i^* v_{m,i}^* \overset{\$/_3}{\widetilde{\kappa}}_{ii}$$

For the calculation of mixtures, the geometric mean was used for the cross value:

$$\boldsymbol{\kappa}_{ij} = \left(\boldsymbol{\kappa}_{ii} \boldsymbol{\kappa}_{jj}\right)^{\frac{1}{2}}$$

# 6.3.1. Application of LGT in the Calculation of IFT for pure polymers

The LGT theory was used in predicting the surface tension of pure polymers at different temperatures. The universal pure component factor  $\tilde{\kappa}_{ii} = 0.1238$  was used for all the following pure polymer IFT calculations.

Figure 6.5 gives the calculated surface tension of pure PP in the temperature range from 20°C to 230°C. From the results we can see that the calculated results agree very well with literature data[36]. The LGT model correctly predicts the linear dependence of interface on the temperature with a temperature coefficient of  $-\frac{d\gamma}{dT} = 0.077 dyn/cm.K$ , which is very close to the literature data of 0.076 dyn/cm.K.



Figure 6.5. Surface tension of Pure PP at different temperatures[36].

Figure 6.6 gives the calculated surface tension of pure PMMA in the temperature range from 20°C to 230°C. From the results we can see that the calculated results agree very well with literature data[36]. The LGT model correctly predicts the linear dependence of interface on the temperature with a temperature coefficient of  $-\frac{d\gamma}{dT} = 0.057 dyn/cm.K$ , which is very close to the literature data of 0.056 dyn/cm.K.



Figure 6.6. Surface tension of Pure PMMA at different temperatures[36].



Figure 6.7. Surface tension of Pure PS at different temperatures

Figure 6.7 gives the calculated surface tension of pure PS in the temperature range from  $190^{\circ}$ C to  $240^{\circ}$ C. The calculated results agree relatively well with our experimental data.

# 6.3.2. Application of LGT in the Calculation of IFT between polymer pairs

Some semi-empirical theories of polymeric interfaces have been reported in literature. One most commonly used semi-empirical treatment was to relate the interfacial tension between a pair of incompatible substances to the surface tensions of the pure components. The interfacial tension can be written as the following form:  $\gamma = \sigma_1 + \sigma_2 - W_a$ 

 $W_a$  is the work of adhesion, which is Gibbs free energy decrease (per unit area) when an interface is formed from the two pure component surfaces,  $\sigma$  is the pure polymer surface tension. The interfacial tension can be related to the pure component surface tensions by expressing  $W_a$  in terms of the Good-Girifalco interaction parameter  $\phi_{GG}$  [137-141];

The resulting equation of Good-Girifalco is:

$$\gamma = \sigma_1 + \sigma_2 - 2\phi_{GG}(\sigma_1\sigma_2)^{0.5}$$

The interaction parameter  $\phi_{GG}$ , can be given in terms of molecular constants of individual phases, including polarizabilities, ionization, dipole moments and molar volumes[141]. However the application of this approach is very limited due to the lack of information of those molecular parameters for most polymer systems and the difficulty that a ca. 10% error in  $\phi_{GG}$  will result a ca. 50% error in calculating  $\gamma$ , since for polymers  $\sigma_1 \approx \sigma_2$ .

The semi-empirical theories of polymeric interfaces are very limited in application, especially for muticomponent systems, which have been the advantages of the gradient theory.

In this part the interfacial tensions between polymers pairs are also calculated using the LGT theory. Again the universal constant  $\tilde{\kappa}_{ii} = 0.1238$  was used in the calculation. Figure 6.8 gives the calculated results between PP and PS at different temperatures. There is a linear dependence of dependence of interface on the temperature with a temperature coefficient of  $-\frac{d\gamma}{dT} = 0.009 dyn/cm.K$ , which is much smaller than the reported literature[46]. The reason is that due to the polydispersity of the polymers studied, which makes the coefficient much larger, or the universal constant  $\tilde{\kappa}_{ii}$  varies with temperature.



Figure 6.8. Interfacial tension between PP/PS at different temperatures

# 6.3.3. Application of LGT in the Calculation of IFT between polymer/CO<sub>2</sub>

Figure 6.9 gives the calculated interfacial tension between PS 685D and CO<sub>2</sub> at 200°C and comparison with our experimental data. Figure 6.10 gives the calculated interfacial tension between PS Nova 1037 and CO<sub>2</sub> at three different temperatures and comparison with our experimental data. We can see that as CO<sub>2</sub> pressure increases, the IFT was greatly depressed. The LGT model correctly described the trend of IFT depression by CO<sub>2</sub>, however, the calculated value is a little bit higher which may be due to the lack of accurate SL EOS interaction parameters. One interesting phenomena is the transition of interfacial tension. As the pressure of CO<sub>2</sub> goes high enough, the IFT becomes smaller

for lower temperatures, which is due to two countering effects: the solubility of  $CO_2$  and the temperature.

Figure 6.11 gives the interfacial tension between PP and  $CO_2$  at  $180^{\circ}C$ . The prediction agrees very well with the experimental results.



Figure 6.9. Interfacial tension between PS (Styron 685D)/CO<sub>2</sub> at different temperatures



Figure 6.10. Interfacial tension between PS(Nova 1037)/CO<sub>2</sub> at different temperatures



Figure 6.11. Interfacial tension between PP/CO<sub>2</sub> at 180°C



Figure 6.12. Interfacial tension between PMMA/CO2 at 220oC

Figure 6.12 gives the calculated interfacial tension between PMMA and  $CO_2$  at 220°C. Again although the prediction correctly describes the trend of IFT depression by  $CO_2$ , the calculated value is a little bit higher than the experimental value.

# 6.3.4 Application of LGT in the Calculation of IFT between polymer/polymer saturated with $\ensuremath{\text{CO}}_2$

Figure 6.13 gives the interfacial tension between PP and PS saturated with  $CO_2$  at 220°C and comparison with experimental value. In order for the comparison with the

experimental data, the IFT results were normalized. The figure shows the depression percentage of IFT and comparison with the experimental data. We can see that the prediction correctly predicts the IFT depression by  $CO_2$ , but it fails to correctly describe the trend of IFT depression at high pressure of  $CO_2$ . The reason is still under investigation; probably due to the limitation inherit in the gradient model.



Figure 6.13. Interfacial tension depression between PP/PS at 220°C by CO<sub>2</sub>

Figure 6.14, 6.15 gives the calculated interfacial tension between PMMA and PS saturated with  $CO_2$  in a pressure range up to 200 atm at 220°C. The interfacial tension was depressed as  $CO_2$  pressure increases, and decreases at a much slower rate as higher CO2 pressures, which agrees with the experimental results observed for PS/PP systems.

We also noticed that the depression is much greater than that of the PS/PP system, the reason lies in the fact that  $CO_2$  has a greater affinity with PMMA, and dissolved much more in the polymer matrix of PMMA, and has a greater effect on depressing the interfacial tension.



Figure 6.14. Interfacial tension between PMMA/PS saturated with CO<sub>2</sub>



Figure 6.15. Interfacial tension depression between PP/PS at 220°C by CO<sub>2</sub>

# 6.5. Summary

Using the linear number molecular density distribution across the interface, the density gradient theory combined with S-L EOS was successfully applied to predict the interfacial tension for polymer  $CO_2$  systems. The model correctly predicts the interfacial tension depression for polymers by high pressure  $CO_2$ , which agrees relative well with the experimental data. This model has significance for correlating and predicting the interfacial tensions for polymers saturated with high pressure gases.

# **CHAPTER 7**

# ANALYSIS OF MORPHOLOGY EVOLUTION IN THE CO<sub>2</sub>-ASSISTED POLYMER BLENDING PROCESSES

# 7.1. CO<sub>2</sub> assisted polymer blending

Blending of polymers is an efficient way to produce materials with improved physical properties[1], which are strongly affected by the local morphology. Most polymers are incompatible[2] and the blending process gives rise to a heterogeneous microstructure which can be characterized by the size, shape, and distribution of the constitutional domains. The final morphology of the blends is determined by both the flow conditions applied in the liquid state and the physical properties such as the viscosity and the interfacial tension[142]. In a sufficiently concentrated system, two main flow-induced phenomena control the morphology: one drop can deform and eventually break up into smaller entities; conversely, two or more droplets can collide and eventually coalesce into one larger domain.

Predicting morphology evolution during the processing of polymer blends is challenging and of great importance from both fundamental and industrial points of view. [143]. Extensive research has been carried out in compounders or batch mixers to study the effect of flow and physical properties on the morphology evolution of blends by observing the blend microstructure in the solid state, where there are a lot of techniques are available, such as optical and electron microscopy, and selective etching. Unfortunately the understanding in this area is still far from complete due to the complexity involved in this process and the ill-defined flow conditions. In most cases, only qualitative relations have been proposed between the morphology and the flow parameters, (e.g., shear rate). Grizzuiti et al [144] proposed an experimental technique to perform in situ morphology measurements of polymer blends in well defined flow conditions in a home-made transparent parallel plate device using the optical microscopy technique based on the pioneering work of Taylor. In their study, the distribution of drops and the average size were measured directly during flow at different shear rates and blend compositions. It was found that the average drop size in steady state conditions is a decreasing function of shear rate, and does not depend on blend composition for volume fractions up to 10%.

The Capillary Number, Ca, defined as the ratio of shear stress over the interfacial stress in Chapter 1, was mostly used in the analysis of the average drop size. The breakup of a single droplet is controlled by the balance between viscous and interfacial stresses. There is a critical value Cac, above which viscous stress dominates and causes irreversible deformation and eventually break up of the drops. Below this value the interfacial stress dominates, and there is higher possibility the drops will collide with each other and coalescence into larger drops. Estimates of Cac were first carried out by Taylor[8]. Decades later Grace [9] measured Cac over a wide range of shear rates and viscosity ratios. His results showed that Cac is a strong function of viscosity ratio, p, reaching a minimum at  $p \approx 1$ , later confirmed by other researchers, which means that the most favored conditions for break up are found when the dispersed and the continuous phase have roughly the same viscosity.

The size of the droplets of the dispersed phase is determined by the competition between the break up and coalescence of the droplets. Comparing with the drop break up, the droplet coalescence is much more complex phenomena. Some experiments reported by Elmendorp and VanderVerg [145], Sundararaj and Macosko [146] have shown that in concentrated systems, the average drop sizes increase as a function of concentration in flowing polymer blends. Chesters[13] gives a nice review on the understanding of collision and coalescence in liquid-liquid dispersions. However, up to now, there have been only a few attempts[145, 147-149] to calculate the drop size at steady state based on the assumption of a dynamic equilibrium between these two processes due to the complexity of the processes and lack of experimental data.

By controlling physical properties of the blend system, such as the viscosity ratio and the interfacial tension, we can control the drop breakup and coalescence and thus the morphology of the polymer blends. In particular, the interfacial tension is a key factor to control the morphology and ` this using batch mixing, single screw extrusion, twin-screw extrusion, and tandem extrusion exploiting carbon dioxide's ability in assisting polymer blending[19-27]. By decreasing the viscosity of one component more than the other, the viscosity ratio can be controlled, thus finer dispersed domains and typically improved (e.g. tougher, more flexible, etc.) materials can be obtained. Although the authors pointed out that when the viscosity ratio gets closer to 1, a finer dispersion was achieved, they did not take into account the factor of interfacial tension due to the lack of interfacial tension data and their experimental results lack the comprehensive understanding of relationship between the morphology development and the influential parameters, e.g. the flow conditions and the physical properties.

The blending of PS and PMMA under  $scCO_2$  conditions has been extensively studied in our research group[19-24, 95]. In this chapter, the Capillary number, which combines the effects of interfacial tension and viscosity, was applied in the analysis of morphology development during blending of PMMA and PS under the help of CO<sub>2</sub>, based on the experimental results in both a high pressure batch mixer and twin screw extruder by Elkovitch[21, 22]. The effect of interfacial tension reduction by CO<sub>2</sub> on the morphology was addressed. A population balance model was developed based on the dependence of drop breakup on the Capillary number, which neglects the coalescence of smaller drops in the blending process.

# 7.2. Blend Morphology in Batch Mixing

The morphologies of a 25/75 PMMA/PS blend prepared with a high-pressure batch mixture by Elkovitch[22] are shown in Figure 7.1.





Figure 7.1. TEM Micrograph of 25/75 HMW-PMMA/Polystyrene: Batch Process Morphology Development (Elkovitch, et al, [22])

The average diameter of the drops was determined from the following the relationship according to the author:

$$D_i = 2 \left(\frac{A_i}{\pi}\right)^{1/2}$$
$$D_n = \frac{\sum_{i=1}^n D_i}{n}$$

where Ai is the particle area, and Di is the calculated diameter. Dn is the number average diameter. According to the study, no evidence of coalescence was observed when the batch blending was performed with and without CO<sub>2</sub> due to the low shear rate in the mixing process. Therefore the drop size reduction was due to the breakup of larger droplets. Without CO<sub>2</sub>, the drop size reached 5.7  $\mu m$  after 30 min of mixing and further decreased to 4.2  $\mu m$  and remained relatively unchanged as the mixing happened simultaneously. After 30 min of mixing, about 1.0 wt. % of CO<sub>2</sub> dissolved into the polymer matrix and the drop size reached 3.6  $\mu m$ . After 60 min of mixing, about 1.5% of CO<sub>2</sub> dissolved into polymer matrix and the drop size decreased to 2.8  $\mu m$ . Further increasing the mixing time had no significant effect on the drop size, although the CO<sub>2</sub> continued to dissolve into the polymer because the equilibrium solubility had not yet been reached.

In the above process, there are two questions that need to be clarified. First, for a given weight-fraction of  $CO_2$  in the blend, how much mixing time is needed for the morphology to reach steady state? Second, what is the relationship between the weight-fraction of  $CO_2$  in the polymer blend and the morphology (the steady state average drop size).

In order to better understand the above questions and facilitate the following discussion, the physical properties of blends under different  $CO_2$  weight fractions are listed in Table 7.1.

	Shear	Viscosity	$\eta_1$	$\eta_{1.5}$	$\eta_3$	IFT	IFT	IFT
	rate	$\eta_0$	(1%	(1.5%	(3%	ratio	ratio	ratio
		(No	CO <sub>2</sub> )	CO <sub>2</sub> )	CO <sub>2</sub> )	$(\Upsilon_1/\Upsilon_0)$	$(\Upsilon_{1.5}/\Upsilon_0)$	$(\Upsilon_3/\Upsilon_0)$
		CO <sub>2</sub> )				(1%	(1.5%	(3%
						CO <sub>2</sub> )	CO <sub>2</sub> )	CO <sub>2</sub> )
PS	10.4800	35426	13786	12509	9345	0.90	0.85	0.70
PMMA	10.4800	93456	42981	34900	16487			
Viscosity		3.78	3.11	2.79	1.76			
ratio P								

Table 7.1. Physical properties of blends under different CO<sub>2</sub> weight fractions

The Capillary number was used in the analysis of the morphology development. Due to the complexity of the system involved in the blending process, the following assumptions were made:

- At the same mixing rpm and operating temperature, the flow patterns inside the mixer remain the same under different CO<sub>2</sub> weight fractions.
- The mixing inside the high pressure, high temperature mixer is homogeneous, which means if you sample any part of the blended products for analysis, you always get the same results.
- Under CO<sub>2</sub> conditions, the drop breaks up much easier and faster, i.e. it takes less time for the drop to break up with CO<sub>2</sub>.

Since the shear rate inside the mixer is not well defined, we use the normalized Ca number (based on the Ca number without  $CO_2$ ) for analysis, which eliminates the uncertainty in shear rate, and we can focus our attention on the effect of  $CO_2$  on reducing the interfacial tension and viscosity. Following this approach, a master curve can be created to study the relationship between the equilibrium Ca number and the viscosity ratio. Figure 7.2 gives the relationship between viscosity ratio and  $CO_2$  weight fraction in

the polymer matrix. The viscosity ratio decreases linearly with increasing  $CO_2$  concentration inside the polymer matrix. Figure 7.3 gives the experimental results for the normalized equilibrium Capillary number  $Ca_N$  versus the viscosity ratio. Clearly we can see that  $Ca_N$  (one on one corresponds to the Critical Capillary number  $Ca_{crit}$ ) drops dramatically as the viscosity ratio decreases, which is in good agreement with reported literature data that the  $Ca_{crit}$  reaches a minimum as viscosity ratio gets closer to one. From the results we can explain the second question we mentioned earlier: why further increasing the  $CO_2$  weight fraction does not change the morphology much. The reason lies in the fact that as  $CO_2$  weight fraction increases,  $Ca_{crit}$  remains relatively unchanged, which determines the final equilibrium drop size distribution. We will discuss it in the following modeling part. From this Figure, we can also see the effect of interfacial reduction on the final morphology. The blue line is the calculated Ca number if we don't consider the effect of interfacial tension reduction while keeping other parameters the same. These two lines show the difference of interfacial tension on the steady state morphology of the blends.



Figure 7.2. Viscosity ratio versus the  $CO_2$  weight fraction in the polymer blends



Figure 7.3. Master curve: Normalized Equilibrium Capillary number versus the viscosity ratio

# 7.3. Mathematical Modeling of morphology development in the Mixer

In this study, a simplified steady-state "population balance" model is applied to describe the morphology development during the blending process in the batch mixer, based on the following assumptions:

(1) Homogeneous mixing inside the high pressure, high temperature mixer,

(2) An initial drop size distribution is provided based on experimental measurement.

(3) Only droplet break up is considered. The coalescence of droplets is neglected due to the low concentration of dispersed phase and simplicity of the modeling.

(4) Only binary break up is assumed, meaning that a drop can break into two small droplets. The size of daughter droplets may be different.

The drop size range is divided into n uniform classes, which are

$$d_1 < d_2 < d_3 < \dots < d_{n-1} < d_n$$

According to the population balance model, the volumetric fraction balance for the droplet with diameter di in an elementary time interval  $\Delta t$  can be expressed as follows,

$$F_{k}(i) = F_{k-1}(i) - F_{k-1}(i)p(i) + \sum_{j>i}^{n} F_{k-1}(j)p(j)\beta(d_{j}, d_{i})$$

$$(k = 1, 2, 3 \qquad i = 1, 2, 3, \dots, n)$$
(1)

where Fk(i) is the volumetric fraction of di in elementary time k, Fk-1(i) is the volumetric fraction of di from elementary time k-1, p(i) is the breakage probability of di, and  $\beta(d_j, d_i)$  is the size distribution function of daughter droplets.

The volumetric fraction F(i) is defined as the volumetric fraction of the droplets with the diameter range between  $d(i) \pm \frac{\Delta d}{2}$ ,

$$F(i) = P(d_i)\Delta d \tag{2}$$

where P(di) is the volumetric probability density function.

The breakage probability of di droplet is defined as Equation (3),

$$p(i) = e^{\left(-\frac{C}{Ca(i) - Ca_{crit}}\right)}$$
(3)

where C is a constant and  $Ca_{crit}$  is the critical Capillary number.

To predict daughter drop size distribution, one assumption is suggested that when droplet breakup occurs, the kinetic energy is absorbed as much as possible, then converted to surface energy to form the interface area to the best extent. This means that the volumetric probability density of the daughter droplets follows a trend toward greater the new interfacial area. When a droplet with diameter of d breaks into two droplets with diameter of di and  $d'_i$  respectively, the increment of the surface energy  $\varepsilon_i$  is

$$\varepsilon_i = \pi \gamma (d_i^2 + d_i^2 - d^2) \tag{4}$$

Thus the daughter volumetric probability density function  $\beta(d, d_i)$  is defined as Equation (5).

$$\beta(d,d_i)\Delta d = \frac{\varepsilon_i}{\sum_{\substack{d_i < d}} \varepsilon_j}$$
(5)

Given the initial drop size distribution P(di), and the constant C in equation (3), the drop size distribution and the mean drop diameter evolution during mixing can be calculated by the equation (1)-(5).

The constant C in equation (3) can be evaluated from the experimental data with the following objective function,

$$\min J = \sum (d_{32} \exp - d_{32} cal)^2$$
(6)

where  $d_{32_{exp}}$  is experimental and  $d_{32_{cal}}$  is calculated with equation (7).

$$d_{32}cal = \int_{i=1}^{n} \frac{F_{k}(i)}{d_{i}}$$
(7)

The model was first applied to calculate the morphology in the mixer at  $200^{\circ}$ C without CO<sub>2</sub> conditions. The morphology at 30 min after mixing is used as the initial drop size distribution. A normal distribution of drop size was assumed due to the lack of literature data, as shown in the following equation.

$$P(d) = \frac{1}{\sqrt{2\pi\sigma}} exp\left(-\frac{(d-D_n)^2}{2\sigma^2}\right)$$
(8)

where  $D_n = 5.7 \,\mu m$ ,  $\sigma = 1.6 \,\mu m$ .

Figure 7.4 gives the calculated results for C = 0.8 and comparison with experimental data. The calculated results did a decent job in capturing the morphology evolution.

Based on the model, the calculated results were shown in Figure 7.5 as different initial drop size distributions were given. We noticed that the drop size decreased dramatically in the initial stage, and converged to the same distribution although the initial distributions are different.

For the blending of PS/PMMA under 3wt % CO<sub>2</sub> conditions, the interfacial tension was depressed about 30%. If we only consider the interfacial tension effect on the Capillary number, we get the following calculated morphology evolution based on the population model we developed, as shown in Figure 7.6. From the calculated results, we can see as the interfacial tension was lowered, the morphology evolution was much faster and the equilibrium domain size was smaller, reduced from 3.95  $\mu m$  to 3.16  $\mu m$ . The experimental domain size under 3wt % CO<sub>2</sub> conditions was 2.60  $\mu m$ , which is smaller than the calculated 3.16  $\mu m$ . The difference lies in the fact of the viscosity ratio reduction by CO<sub>2</sub>, as we discussed earlier.



Figure 7.4. Morphology evolution based on the population model



Figure 7.5 Morphology evolutions for different initial drop distributions



Figure 7.6. Comparison of the Morphology evolutions with and with considering the effect of interfacial tension

# 7.4. Blend Morphology in Twin Screw Extrusion and Modeling

Figure 7.7, 7.8 shows the LMW-PMMA/polystyrene blending results at different compositions with and without CO<sub>2</sub> injection in the twin screw extrusion at an average shear rate of 100 s<sup>-1</sup> at 200°C upon injection of 2.0 wt.% CO<sub>2</sub> (Elkovitch, et al [22]). In Figure 7.7, PMMA is the dispersed phase and much smaller domain size was observed with CO<sub>2</sub> conditions. The number average drop size decreased from 1.5  $\mu$ m to 0.48  $\mu$ m with injecting CO<sub>2</sub>. The author attributes this to the viscosity ratio reduction from 1.3 to 0.86 by dissolved CO<sub>2</sub>. The CO<sub>2</sub> lowered the viscosity of LMW-PMMA more than

polystyrene, and the higher viscosity polystyrene can transfer its stress to the LMW-PMMA more effectively, which results a finer dispersion of the LMW-PMMA phase. In Figure 7.8 polystyrene is the dispersed phase. A smaller domain size was observed with  $CO_2$  conditions and the number average drop size decreased from 1.7 µm to 1.2 µm with injecting  $CO_2$ , which is not a significant change. The author thought the result was unexpected since the major phase-LMW-PMMA has a lower viscosity and cannot transfer its stress effectively to disperse the polystyrene. They attributed this to the interfacial tension reduction by  $CO_2$ .

In both experiments carried in Figure 7.7 and Figure 7.8, the interfacial tension between LMW-PMMA and polystyrene saturated with 2% CO<sub>2</sub> was depressed by about 20%., which corresponds to a reduction of drop diameter by 20% for both cases based on the Critical Capillary number. Therefore with injection of CO<sub>2</sub>, if we only consider the effect of interfacial tension reduction, the number average drop size should be decreased from 1.5  $\mu$ m to 1.2 $\mu$ m in Figure 7.7, compared to the experimental value 0.48 $\mu$ m, and from 1.7  $\mu$ m to 1.36 $\mu$ m in Figure 7.8, compared to the experimental value 1.2 $\mu$ m, thus is seems there is a great difference in the above two cases. In order to better understand the phenomena in the above two figures, we use the same analysis based the normalized Capillary number as discussed earlier. Figure 7.9 shows the normalized Capillary number versus the viscosity ratio. From the results, we can see the normalized Capillary number for 25/75 PMMA/polystyrene is smaller that of 75/25 PMMA/polystyrene, which can be used to explain why the number average drop size change under CO<sub>2</sub> conditions are different for two cases of blending. A greater change of Capillary number will result in a larger effect on the morphology of the blends. In this figure, virtual curves are given for the relationship between Capillary number and viscosity ratio, in which the Capillary number reaches minimum as viscosity ratio equals to one. More experimental data needs to be filled in this area in order to generate a master curve for better understanding the droplet breakup and morphology of the blends. In order to do so, different experimental results should be measured by varying the CO<sub>2</sub> concentration.

Figure 7.10 gives the morphology evolution results for 50/50 HMW-PMMA/Polystyrene blend along the length of extruder with and without  $CO_2$  by Elkovitch[22]. For both with and without CO<sub>2</sub>, the morphology evolution can be broken into two stages. In the first, droplet break up dominates after the mixture was fed into the extruder, due to the high Capillary number since the drop diameter is very large. In the second stage, the coalescence of small drops dominates, due to the small Capillary number probably caused by the step down of the shear rate due to the flow channel change. By adding  $CO_2$ , a sharp decrease in the domain size of near the  $CO_2$  injection zone was observed, due to the change of Capillary number caused by the viscosity reduction and interfacial tension reduction. The blending process is very complex considering temperature distribution, the geometry changes of the channel, the diffusion of  $CO_2$  into polymer matrix, etc, which makes the mixing intensity and physical properties vary all along the whole length of the extruder The modeling of such a process is very difficult without making simplifications. The following is one highly simplified model for the blend morphology evolution in the twin screw extruder if we only consider the droplet break up stage (L/D < 22) during the blending process.

Assumptions:

1) No temperature gradient along the entire twin screw extruder.

2) The homogeneous mixing inside the entire twin screw extruder.

3) Plug flow inside the extruder and no geometry change of the flow channel.

4) As CO<sub>2</sub> injected, it will immediately dissolve inside the polymer matrix at the feeding point.

5) Only the droplet breakup is considered. The coalescence of droplets is neglected.

Based on the above assumptions, the same "population balance" model can be developed to describe the morphology development during the blending process. The model is basically the same as the one we used to describe the batch mixing process, by only making the equivalence of  $\Delta t$  (time interval) and  $\frac{\Delta l}{F}$ , where  $\Delta l$  is the interval of flow length and F is the flow rate of the blends. By using the same constant C = 0.8 obtained for the blending in the mixer, the morphology development along the extruder length  $(\frac{L}{D} < 22)$  with and without CO<sub>2</sub> conditions was calculated and compared with the experimental data, as shown in Figure 7.11. The model did a decent job in capturing the morphology evolution. More complicated models can be developed by incorporating the flow inhomogeneity, temperature gradient, diffusion of CO<sub>2</sub>, drop coalescence.

# 7.5. Conclusions

The morphology evolution results in the high pressure, high temperature mixer with and without  $CO_2$  from Elkovitch [23]were analyzed based on the normalized Capillary number, which considered both the effects of interfacial tension and viscosity reduction. The population balance model was applied to calculate the morphology evolution by only considering the droplet breakup during the mixing. The calculated results agree with the experimental data relatively well. Based on the model, the effect of interfacial tension depression by  $CO_2$  on the morphology evolution was also discussed. The initial drop distribution has no effects on the final morphology from the calculated results based on the model. The morphology evolution in the twin screw extruder was also briefly discussed, which is much more complex comparing with that in the mixer.



5 μm	(Mark.D Elkovitch, et al [22])
$D_n = 1.5 \ \mu m$	$D_n = 0.48 \ \mu m$
(a)	(b)

Figure 7.7 TEM Micrographs of Blends of 25/75 LMW- PMMA/Polystyrene Prepared from Twin Screw Extrusion (a) Without CO<sub>2</sub> (b) With CO<sub>2</sub>







Figure 7.9. Master curve: Normalized Equilibrium Capillary number versus the viscosity Ratio



Figure 7.10. Number Average Diameter of 50/50 HMW-PMMA/Polystrene Blend along the Length of Extruder With and Without CO<sub>2</sub>



Figure 7.11. Morphology evolution in the twin screw extruder based on the population model

# **CHAPTER 8**

#### SUMMARY AND FUTURE DIRECTIONS

# 8.1. Summary

The addition of small amounts of  $CO_2$  to polymer phases results in substantial and sometimes dramatic changes in the physical properties, such as viscosity, interfacial tension, and glass transition, which make it a promising solvent for application in polymer blending process. The interfacial tension is the key factor to control the morphology and the mechanical properties of the immiscible polymer blends. However limited research has been done on the influence of interfacial tension in the SCF  $CO_2$ assisted polymer-blending process due to the difficulty of getting the interfacial tension data under high pressure and temperature conditions.

The dissertation attempts to provide the first fundamental understanding of the interfacial behavior for polymer/ $CO_2$ , polymer/polymer saturated with  $CO_2$  systems, and relate this property to the morphology evolution during the  $CO_2$  assisted polymer blending processes. This dissertation addresses the following questions:

- How to measure the IFT for polymer/CO<sub>2</sub> and polymer/polymer/CO<sub>2</sub> systems under high temperature and high pressure effectively and efficiently?
- What is the temperature and pressure effect of CO<sub>2</sub> on IFT for polymer/CO<sub>2</sub> and polymer/polymer/CO<sub>2</sub> systems?
- How to predict the IFT from thermodynamic theories of polymer interfaces?
- How CO<sub>2</sub> affects the morphology in CO<sub>2</sub> assisted polymer blending processes?
Herein we summarize the results of our experimental and theoretical work in an attempt to answer the above questions.

Experimental techniques to measure the solubility and swelling of polymer under high pressure  $CO_2$  were reviewed. The experimental results are provided and correlated using the Sanchez-Lacombe EOS, which can be used to predict the density and swelling of polymers saturated with  $CO_2$  reasonablely well. These results provide fundamentals for the measurement of the interfacial tension between polymer  $CO_2$  systems.

A novel technique is presented to determine the interfacial tension for the polymer melts/high pressure  $CO_2$  systems in a high pressure and high temperature view cell by analysis on the axisymmetric pendant drop shape profile, which can simultaneously yield the density, swelling and interfacial tension results. The method avoids the "capillary effect" [45] and the "necking effect" [45] and provides good axisymmetry of the pendant drop. The ADSA technique [56] was applied to determine the interfacial tension from the shape of an axisymmetric meniscus of a pendant drop. The interfacial tension is calculated by fitting the shape of an experimental drop to the theoretical drop profile according to the Bashforth-Adams equation[55] using a least-squares algorithm with interfacial tension as the adjustable parameter and the drop profile coordinates and the density difference across the interface as the input information. The overall performance of the image acquisition system and the profile analysis software were verified by evaluating the surface or interfacial tensions at both ambient (for water and hexane system) and high pressure (for water  $CO_2$  system) conditions. This reliable technique was used to measure the interfacial tension for polymer melts/high pressure CO<sub>2</sub> systems. For the first time the effect of  $CO_2$  on the interfacial tension for polymer/ $CO_2$  and polymer/polymer/ $CO_2$  systems was studied and clarified in this thesis.  $CO_2$  was shown to significantly depress the surface tension of all the polymers studied. The interfacial tension between polymer-pairs showed a steep decrease up to some intermediate pressure and then followed by a slower decrease at higher pressures of CO<sub>2</sub>. The dynamic behavior of the "interfacial tension evolution" was also discussed and the interfacial

tension data can be obtained based on this transit experimental data, which provides a faster way to make the interfacial tension measurement and avoids the polymer melt degradation.

Current thermodynamic theories in predicting interfacial tension of polymer systems are reviewed. Based on the general interfacial theory developed by Poser and Sanchez[150] and the assumption of linear number molecular density distribution across the interface[151], the linear gradient theory(LGT) combined with Sanchez-Lacombe EOS[91, 102] is applied in correlating and predicting the interfacial tension for the polymer, polymer/polymer, polymer/CO<sub>2</sub>, polymer/polymer/CO<sub>2</sub> systems. The model correctly predicts the interfacial tension depression for polymers by high pressure CO<sub>2</sub>, which agrees relative well with the experimental data. However, it overpredicts the effects of CO<sub>2</sub> on the depression of IFT for polymer-polymer systems. These data have significance for understanding both blending and foaming of polymers using carbon dioxide.

Finally the role of  $CO_2$  in the polymer blending was discussed. The capillary number, which characterizes the drop breakage and coalescence, was used to clarify the effect of interfacial tension reduction in the morphological evolution. The morphology evolution results in a high pressure high temperature mixer, and in a twin screw extruder with and without  $CO_2$  from Elkovitch' results[21, 22] were analyzed based on the normalized Capillary number, which considered both the effects of interfacial tension and viscosity reduction. The population model was applied to calculate the morphology evolution by only considering the drop breakage during the mixing. The calculated results agree with the experimental data relatively well. Based on this model, the effect of  $CO_2$  on the morphology evolution was discussed. A finer dispersed domain was obtained under  $CO_2$  conditions based on this model, which agrees well with the experimental results.

## **8.2. Future Directions**

In this work, the technique to measure the interfacial tension (IFT) for polymer/ $CO_2$ , polymer/ $Polymer/CO_2$  systems under high pressure and temperature has been successfully established. However, due to the sealing problems, the maximum pressure reached during the measurement is only 160 atm. The effect of  $CO_2$  on the IFT at higher pressures needs to be studied in future research. Current measurements only limit to a few polymers or polymer pairs, more experimental measurements on other polymers or polymer pairs of interest to polymer blending or foaming processes should be carried out.

Although foaming with  $CO_2$  is an active area of research and development due to the restrictions imposed by the Montreal Protocol on ozone depleting substances, there are other choice at present, such as hydrogen-containing chlorofluorocarbons/fluorocarbons (HCFC/HFCs), hydrocarbons, and inert gases ( $CO_2$ ,  $N_2$ , argon, or water), which have the highest potential to replace the chlorofluorocarbon (CFC or freon) physical foaming agents (proven to be contributing to the destruction of the Earth's ozone layer and are gradually being eliminated[4-6]). It is necessary to extend our experimental technique to the measurement of the interfacial tension between polymer melts and other high pressure gases used as the foaming agents, since the interfacial tension has a greater influence on the polymer foaming process due to the cubic power in the free energy, according to the traditional nucleation theory[15, 16].

Compatibilizers such as block or graft copolymers can act as interfacial agents in polymer blends[146, 152, 153] by lowering the interfacial tension between immiscible polymer melts and thus stabilize blend morphology and ultimate properties. It would be interesting to study the interfacial tension for the polymer systems with compatibilizers under high pressure  $CO_2$  conditions using the current techniques, and to study the synergistic effects by the compatibilizer and  $CO_2$  on the blending products.

 $CO_2$  plays an important role in determining the final morphology for the polymer blending of PMMA/PS by depressing the interfacial tension and viscosity. In current work, preliminary progress has been made in understanding the morphology evolution during the  $CO_2$  assisted polymer blending process based on the Capillary number analysis, which combines both the effects of IFT and viscosity reduction. However, due to the following limitations of the polymer blending (both mixer and twin screw extruder results) results by Elkovitch[21, 22], the complete understanding of the  $CO_2$  assisted blending process is still very difficult, if not impossible.

- In both the mixer and the twin screw extrusion for the polymer blending, the flow condition is not well defined.
- The morphology measurement during the evolution is ex situ, by freezing sample during blending and analyzing using TEM techniques at a later time. It is hard to say that the measured morphology represents the "true" morphology evolution.
- The blending process was started at the same time as high pressure CO<sub>2</sub> was introduced into the system. This means the physical properties of the system changes with time as CO<sub>2</sub> diffuses into the polymer matrix, which causes the understanding of the blending process much more difficult.

Grizzuti et al[144] did a very good job in studying the morphology evolution *in situ* using the optical microscopic technique in a home made counter rotating parallel plate apparatus, which can produce *well defined* flow of the polymer blends. Modification of this apparatus to operate under high pressure  $CO_2$  conditions can yield results that will greatly simplify the analysis based on the Capillary number. On the other aspect, before each experimental run, making polymer melts equilibrated with  $CO_2$  to keep the viscosity ratio and the IFT constant for the whole blending process will greatly facilate the following analysis.

Currently the population model used did not take into account the influence of coalescence on the morphology evolution during polymer blending. However, the coalescence phenomena did occur and should be considered for concentrated and low Capillary Number systems [144, 145, 154] during polymer blending. The step-down

shear rate experiments can provide such coalescence information, which can be used for the understanding and modeling of the  $CO_2$  assisted polymer blending process. By combining the above well defined experimental results, and also the IFT and viscosity reduction data under high pressure  $CO_2$  conditions, the better and overall understanding of the  $CO_2$  assisted blending process is possible.

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