

MASS TRANSFER OF NEAR CRITICAL CARBON DIOXIDE IN POLY(METHYL
METHACRYLATE)

A Thesis

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By

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ABSTRACT

Supercritical carbon dioxide has gained popularity in recent decades in a wide variety of fields. From Supercritical Fluid Extraction (SFE) to 'Green Chemistry', supercritical carbon dioxide has been shown to be a non-toxic, non-flammable, and inexpensive alternative to traditional hazardous or undesirable chemicals. One of the most promising applications of supercritical carbon dioxide is in polymer processing.

Although there has been much research on carbon dioxide polymer processing, one commonly overlooked characteristic has been the effect carbon dioxide at its critical temperature (30.98°C) and pressure (7.38 MPa) on polymer matrixes. This tends to be hard to characterize because of the inherent high variability at the critical point. However, recent research has shown that polymers display 'anomalous' behavior at this point that may be useful for polymer processing. This study helps to try to characterize this 'anomalous' behavior by measuring the carbon dioxide solubility and diffusivity near its critical point.

Samples of Poly(methyl methacrylate) (PMMA) were exposed to carbon dioxide at various conditions between 30°C to 70°C and 548 psia to 1520 psia. The solubility was extrapolated from sample desorption using the Gravimetric Mass Balance method. The diffusivity coefficient was calculated from a time-dependent sorption curve.

Solubility and diffusivity measurements matched well with data from the literature. Although no 'anomalous' behavior was observed around the critical point, solubility information suggested that there was a distinct change in carbon dioxide and PMMA interactions. Furthermore, setting polymer processing conditions at the critical temperature and pressure of carbon dioxide appears to give an optimum amount of dissolved carbon dioxide for the lowest temperature and pressure. Additional research should be conducted to see whether this 'anomalous' behavior is distinguishable for a wider range of diffusivities or for thinner polymer films.

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1. INTRODUCTION

1.1 Supercritical Fluids

The past couple of decades have seen a steady increase in the number of processes using supercritical fluids. This state arises when a

compound is heated and pressurized past its critical temperature and pressure.

Figure 1.1 shows the location of the supercritical fluid state in relation to the three most common physical states; solid, liquid, and gas.

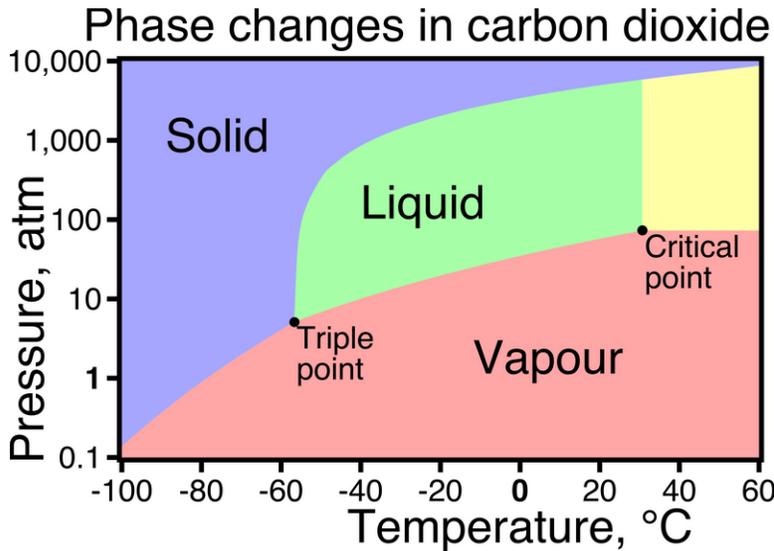


Figure 1.1: A phase diagram of Carbon Dioxide [1]

What makes the supercritical phase unique is that the distinction between the liquid and gas phases disappear. A liquid cannot be produced by increasing the pressure and a gas cannot be formed by raising the temperature. These supercritical fluids have a solvent strength comparable to its liquid phase while retaining the superior mass transfer abilities of its gaseous phase. A visual representation of this transition to the supercritical state for carbon dioxide is shown in Figure 1.2.

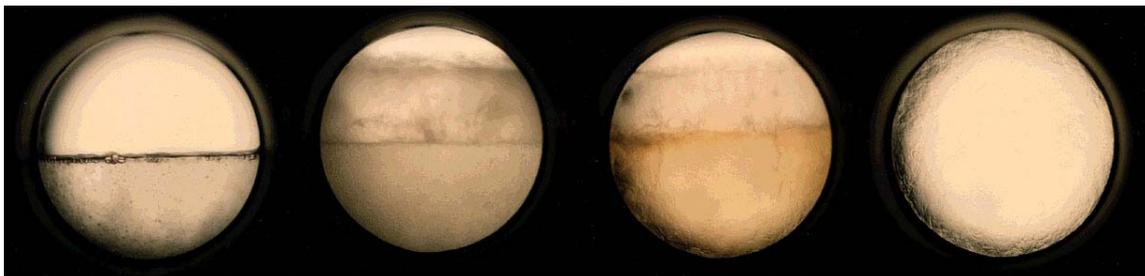


Figure 1.2: A visual representation of Carbon Dioxide in the two phase region (Left Picture) reaching a supercritical state (Right Picture) with increasing temperature and pressure. [2]

1.2 Supercritical Carbon Dioxide

One of the most promising supercritical fluids is supercritical carbon dioxide with a critical temperature and pressure of 30.98°C and 7.38 MPa (1,070 psi), respectively. This is easily attainable in a laboratory or industrial setting. Since it is generally chemically inert it has proven useful as a solvent for a wide range of reactions. Many food and pharmaceutical companies are considering the use of carbon dioxide because it is non-toxic, non-flammable, inexpensive, and easy to remove from final products.

1.3 Applications

By far the most widespread use of supercritical carbon dioxide is in Supercritical Fluid Extraction (SFE). Some common examples include the decaffeination of coffee and tea, the processing of hops, tobacco extraction, creation of spice extracts, and the extraction of fats and oils. Nearly all industrial uses of supercritical carbon dioxide are via SFE [3].

Supercritical Fluid Chromatography (SFC) using carbon dioxide has recently gained popularity. Similar to traditional liquid chromatographic separation, SFC replaces liquid solvents with supercritical carbon dioxide. Although it's mainly used as an analytical technique, it has been demonstrated on an industrial scale by the fractionation of essential oils and fats [3].

Many chemists have also been turning to supercritical carbon dioxide as a reaction medium. Supercritical carbon dioxide's unique solvent capabilities have proven useful in the pharmaceutical industry where traditional reaction processes may not be suitable for delicate pharmaceutical compounds. The relative safety and effectiveness of supercritical carbon dioxide has led to a natural incorporation into the field of 'Green Chemistry' [4].

Another emerging application is in supercritical particle formation. Recent research has indicated that supercritical carbon dioxide can be used to form micro or nano-sized homogenous particles. This would be a boon for improving inhalable medications, such as insulin. The two most promising methods are the Rapid Expansion of Supercritical

Solutions (RESS) technique for non-polar molecules and the Supercritical Antisolvent Crystallization technique for polar molecules [3].

Many companies specializing in coating are beginning to study supercritical carbon dioxide application techniques. These coatings range from metal primers to biomedical devices to glass coatings. There has even been interest in using supercritical carbon dioxide to remove existing coatings. The flexibility of supercritical carbon dioxide has allowed for its application in a variety of situations [5].

One of the most promising applications of supercritical carbon dioxide has been in polymer processing. Carbon dioxide has some unique effects on polymer matrixes. In most polymers it acts as a plasticizer, lowering the polymers glass transition temperature and viscosity. This is useful in several polymer processing techniques such as extrusion mixing or foaming. Supercritical carbon dioxide has also demonstrated an ability to increase mass transport of large molecules into the polymer matrix, a useful property for the pharmaceutical industry. Carbon dioxide has also been used as a suitable substitute for traditional foaming agents such as Chlorofluorocarbons (CFC's) because of its ability to increase polymer molecular mobility while retaining the polymer's physical durability [6].

1.4 Poly(methyl methacrylate) (PMMA)

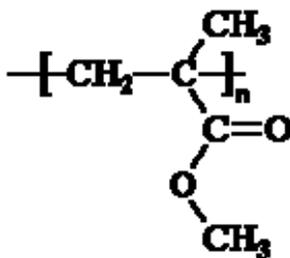


Figure 1.3: Structure of PMMA [8]

Poly(methyl methacrylate) (PMMA), more commonly known as acrylic, is sold under several tradenames such as Plexiglas® or Lucite®. The structure of PMMA is shown in Figure 1.3. It has gained popularity in numerous industries due to its impact resistance and high transparency. The most notable is as a substitute for glass in aquariums, hockey stadiums, and motorcycle helmets visors. PMMA is also extensively utilized in acrylic

paints. Since it is biocompatible, it is used in many medical applications including dentures, hard contact lenses, and orthopedic bone cement [7].

2. BACKGROUND

2.1 Motivation

Much research has been conducted to obtain a theoretical understanding of supercritical carbon dioxide. However, there exist several deficiencies in some fundamental areas. For

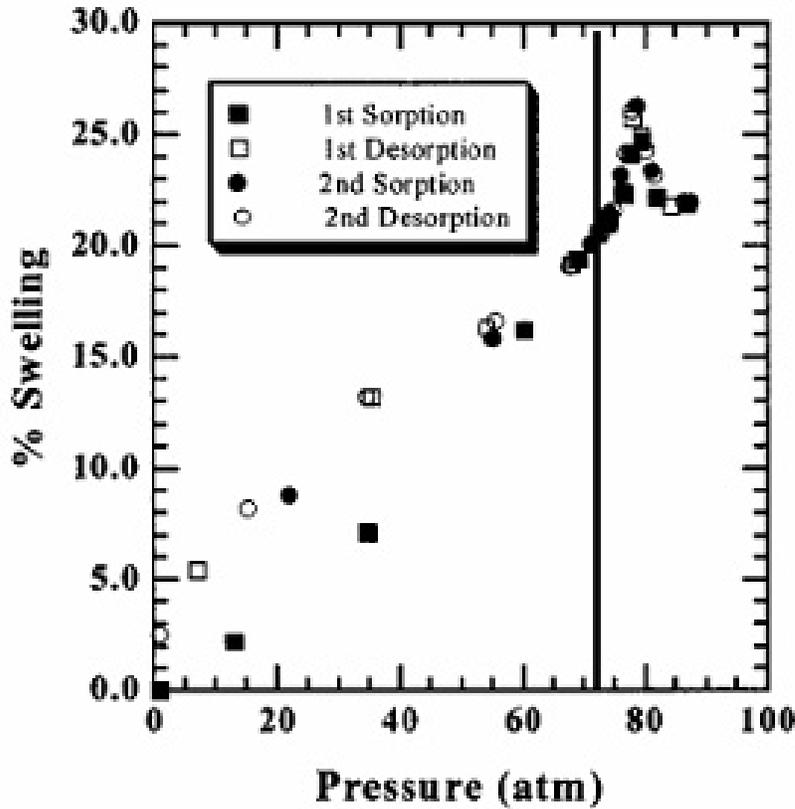


Figure 2.1: Swelling Isotherm of PMMA/CO₂ at 35°C. The critical pressure of CO₂ is shown by the vertical line [9].

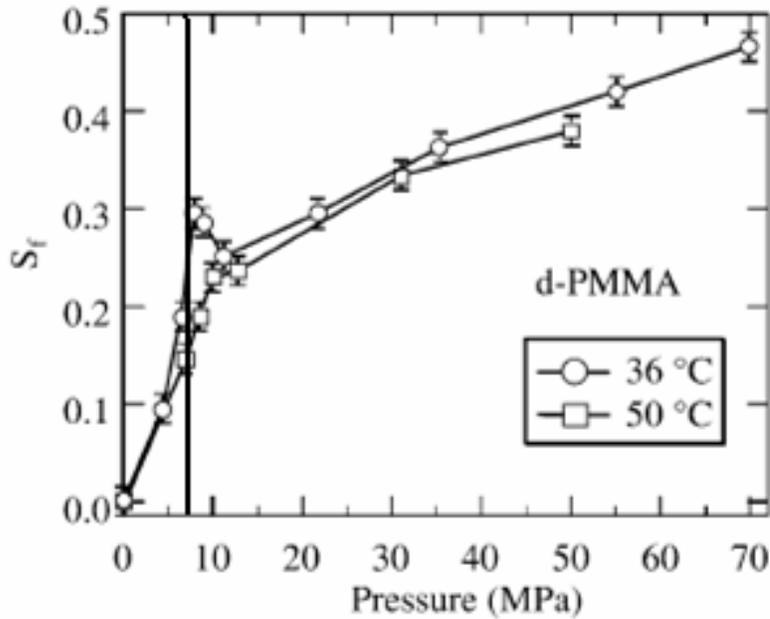
appeared to be some ‘anomalous’ swelling near the critical point of carbon dioxide. This phenomenon was further confirmed by Koga et. al. [10], as shown in Figure 2.2, using a similar swelling experiment.

The requirement of pressurized equipment remains the largest deterrent for widespread adoption of supercritical carbon dioxide in industrial application. Sufficient industrial conditions may require pressures upwards of 100 atm; an achievable but undesirable

example, little research has been directed towards understanding the dynamics of near critical carbon dioxide on the polymer matrix, although recent advances have shown promising results.

Sirard et. al. [9] performed an experiment to study the swelling of thin PMMA films using carbon dioxide as the swelling agent; shown in Figure 2.1. The team discovered that their

pressure. The research by Sirard et. al. [9] and Koga et. al. [10] suggests that some of the



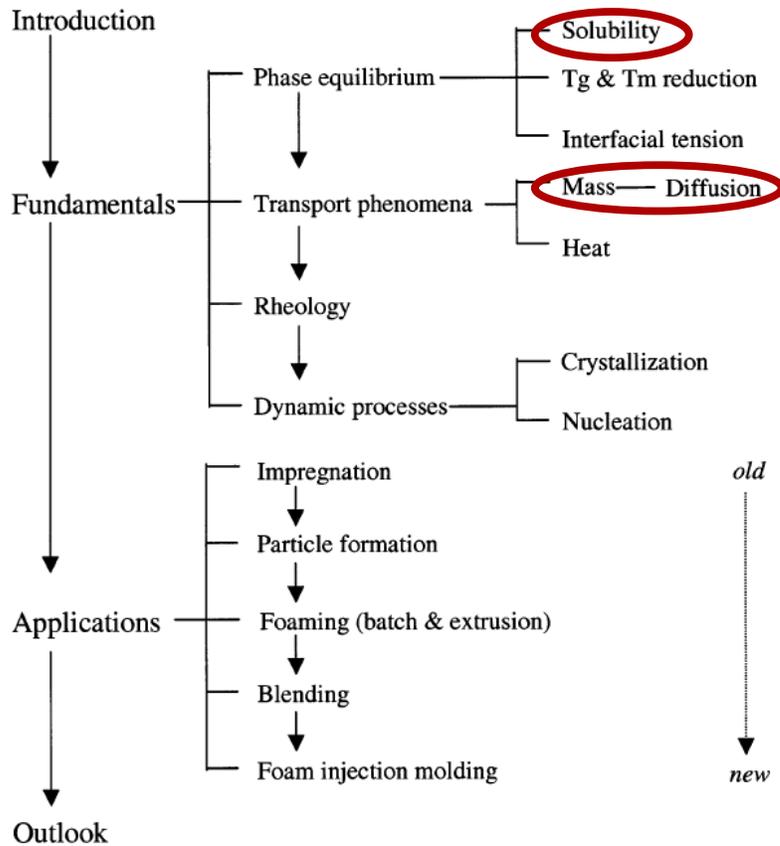
benefits of supercritical carbon dioxide may be achievable at more modest pressures. If proven true, this would help reduce the overall cost of supercritical carbon dioxide applications and make the process more viable on an industrial scale.

Figure 2.2: Swelling Isotherm of CO₂ and PMMA. The critical pressure of CO₂ is noted by a vertical line [10].

2.2 Fundamentals

The studies by Sirard et. al. [9] and Koga et. al. [10] focused solely on carbon dioxide induced swelling of thin PMMA films. However, it is unclear whether this behavior extends to thicker PMMA samples where surface conditions play less of a role. Even though polymer swelling may be useful in some industrial applications, most potential users are interested in two questions; how fast and how much? Both of these can be answered by investigating the diffusivity and solubility of carbon dioxide in PMMA.

The solubility provides a quantitative answer to the amount of carbon dioxide that is absorbed. This is useful for determining the swelling of a polymer foam or the amount of carbon dioxide needed to get a viscosity reduction. The diffusivity can prove useful in determining the time needed to get the expected result. This is an important consideration since many companies have adopted continuous processing equipment, such as extruders,



to improve processing time and efficiency.

An unexpected increase in either attribute near the critical point of carbon dioxide would prove invaluable to the adoption of supercritical carbon dioxide processes. Figure 2.3 shows how these two parameters relate to current carbon dioxide and polymer research.

Figure 2.3: Description of how this research fits into Carbon Dioxide - Polymer research [6]

2.3 Experimental Techniques

There are three major categories of experimental techniques that can be used to measure the solubility or diffusivity of a gas. They are Gravimetric, Barometric, and Frequency Modulation methods [6].

The gravimetric method is by far the most prevalent due to its simplicity and economical price. The common characteristic between all gravimetric methods is that they rely on measuring the weight of a polymer sample before and after exposure to carbon dioxide. The difference represents the mass of carbon dioxide absorbed into the polymer matrix.

The primary distinguishing factors between the designs are where and how this weight is measured. The most simplistic approach is to weight the sample on a common electronic microbalance before and after exposure to carbon dioxide. This is done by quickly transferring the polymer from its sample container to a microbalance at ambient conditions. The desorption of carbon dioxide can be determined by the steady decrease in

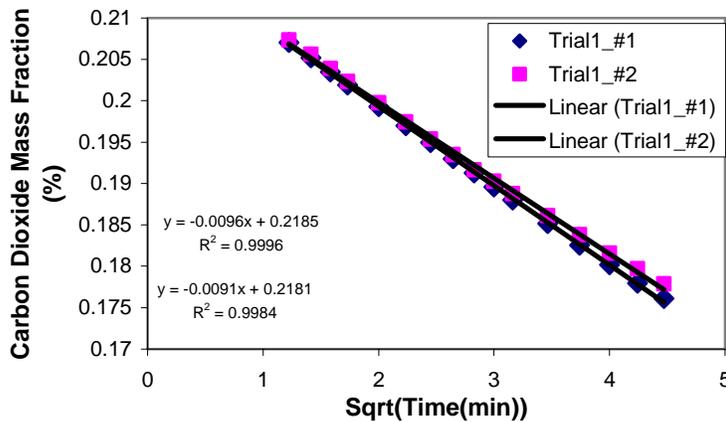


Figure 2.4: Extrapolation of desorption data to obtain carbon dioxide solubility.

the polymer's weight. By extrapolating this desorption curve to the time of sample container depressurization, the original amount of absorbed carbon dioxide can be determined [11], [12]. An example of this extrapolation and desorption curve is shown in Figure 2.4.

This design has two notable disadvantages. Polymer samples must be quickly transferred from their experimental container to the microbalance to ensure that the measured curve will be in the linear desorption region. Also, there must not be any significant swelling or

deformation that would cause a nonlinear release of carbon dioxide from the polymer matrix. Either problem will cause the extrapolation to be difficult or inaccurate.

Several researchers have improved upon this basic technique by placing the microbalance in situ. This allows for faster and more accurate weight measurements over a more continuous range. There are usually two in situ microbalance designs that dominate. The first is the inclusion of a microbalance inside the pressurized volume where the polymer sample is in direct contact with the microbalance. The second design, usually called the Magnetic Suspension Balance, uses a series of magnets to separate the polymer sample from direct contact with the balance. Although the later tends to be more complicated and expensive, it allows for testing a greater range of temperatures and pressures without damaging the microbalance [6], [11], [12].

Although all the gravimetric methods can be used to measure the diffusivity, the in situ designs provide greater flexibility and ease of use. The change in polymer mass can be measured continuously as experimental conditions are modified. The first gravimetric method requires that the carbon dioxide solubility be measured at increasing exposure times to produce a similar sorption curve. This is much more intensive and time consuming, as it requires at least a half dozen solubility measurements to get the same results as the in situ methods.

The Barometric Method is another commonly used technique for determining carbon dioxide solubility and diffusivity. This method utilizes a pressure gauge to measure the drop in carbon dioxide pressure as a fixed volume of carbon dioxide is absorbed into the polymer sample. The mass of absorbed carbon dioxide can be determined from this pressure change via the carbon dioxide volume and density [6].

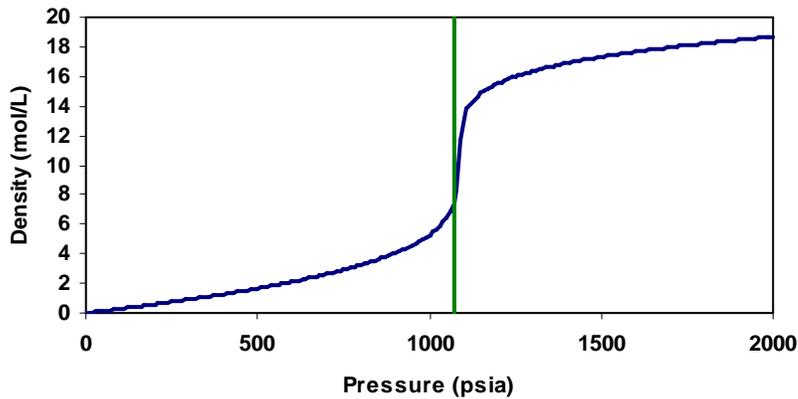


Figure 2.5: Diagram of Carbon Dioxide density versus pressure at 31.2°C. The critical pressure is noted by a vertical line.

Although useful for determining both the solubility and diffusivity of carbon dioxide, this method requires a significant pressure change to obtain accurate results.

Figure 2.5 helps illustrate why this is difficult as carbon dioxide temperature

and pressure approach its critical point. For both low and high pressure carbon dioxide, large changes in density correlate to large changes in pressure. As carbon dioxide approaches its critical pressure, this effect weakens requiring larger and larger changes in density to achieve significant pressure changes. This can be achieved by either increasing the size of the polymer sample or decreasing the available carbon dioxide volume. Either situation is too difficult to achieve while still getting accurate measurements [6].

Frequency Modulation is one of the newer and more exotic methods of carbon dioxide measurement, involving the use of a Quartz Crystal Microbalance (QCM). In this technique, a quartz crystal is coated with a thin film of polymer. Due to the unique piezoelectric characteristics of quartz, the vibration of this crystal can be measured as the polymer film absorbs carbon dioxide by applying an electric current. This allows for continuous measuring of both the solubility and diffusion of carbon dioxide into a polymer [6].

3. EXPERIMENTAL

3.1 Materials

The polymer Poly(methyl methacrylate) (PMMA) was obtained from Plaskolite, Inc. in pellet form under the trade name Acrylic PL-25. It has an average molecular weight of 125,000, density of 1.19 g/mL, melt temperature of 157.2°C, and glass transition temperature of 110°C. The carbon dioxide used in this experiment was Grade 3.0 (>99.9% purity) supplied by Praxair.

3.2 Sample Preparation



Figure 3.1: PMMA Bars

that the pellets had sufficiently melted. Then the hydraulic jack was used to apply and release pressure on the samples five times. On the final press, the pressure from the hydraulic jack was held and the mold was heated for an additional four hours. Once the mold had naturally cooled to room temperature it was removed and the PMMA bars extracted.

The PMMA pellets were formed into bars, shown in Figure 3.1, of approximate dimensions 60 mm by 9.25 mm by 1.75 mm via compression molding. This was accomplished by the attachment of a Craftsman 8-Ton Hydraulic Press to a metal-framed press built by Carver Laboratory. Heating of the sample was accomplished by an Omega Temperature gauge and controller. This setup is shown in Figure 3.2.

After the custom-manufactured metal mold had been filled with PMMA pellets, it was loosely placed within the press and heated to approximately 200°C. This was done for about one



Figure 3.2: Compression Molding Setup

3.3 Exposure to Carbon Dioxide

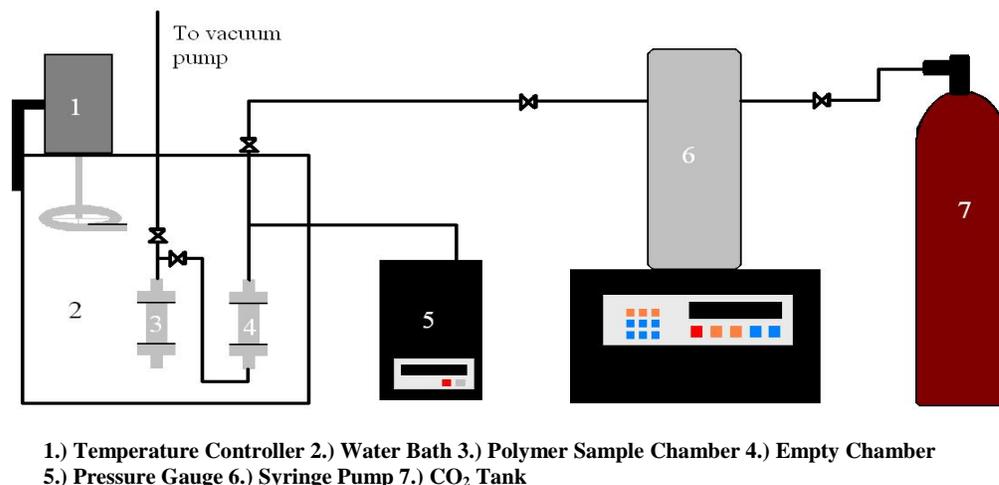


Figure 3.3: Diagram of the experiment Gravimetric Mass Balance Method

An experimental apparatus was constructed to expose the PMMA samples to carbon dioxide. This setup is shown in Figure 3.3. A high pressure tank of carbon dioxide was connected to an ISCO 260D Syringe Pump with a SFX 200 Controller Unit, shown in

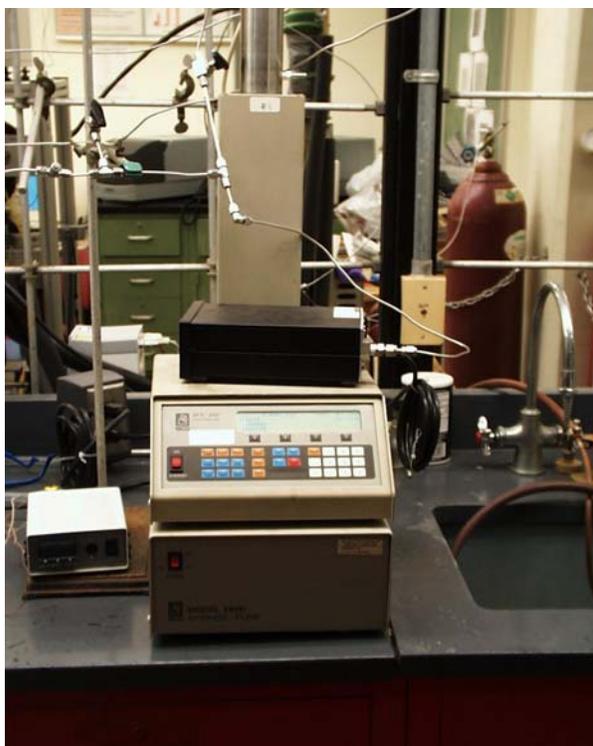


Figure 3.4: ISCO Carbon Dioxide Syringe Pump

Figure 3.4. This pump supplied carbon dioxide to two custom made vessels, one as a carbon dioxide reserve and one as a polymer sample container, located in a water bath. Appropriate temperature and circulation was provided by a Fisher Scientific Isotemp Immersion Circular (Model 730). This setup is shown in Figure 3.5. The pressure and temperature were measured by a Sensotec GM Electronic Pressure gauge and an Omega DP-25-TH Temperature gauge. All pressurized valves, fittings, and tubing were supplied by Swagelok.

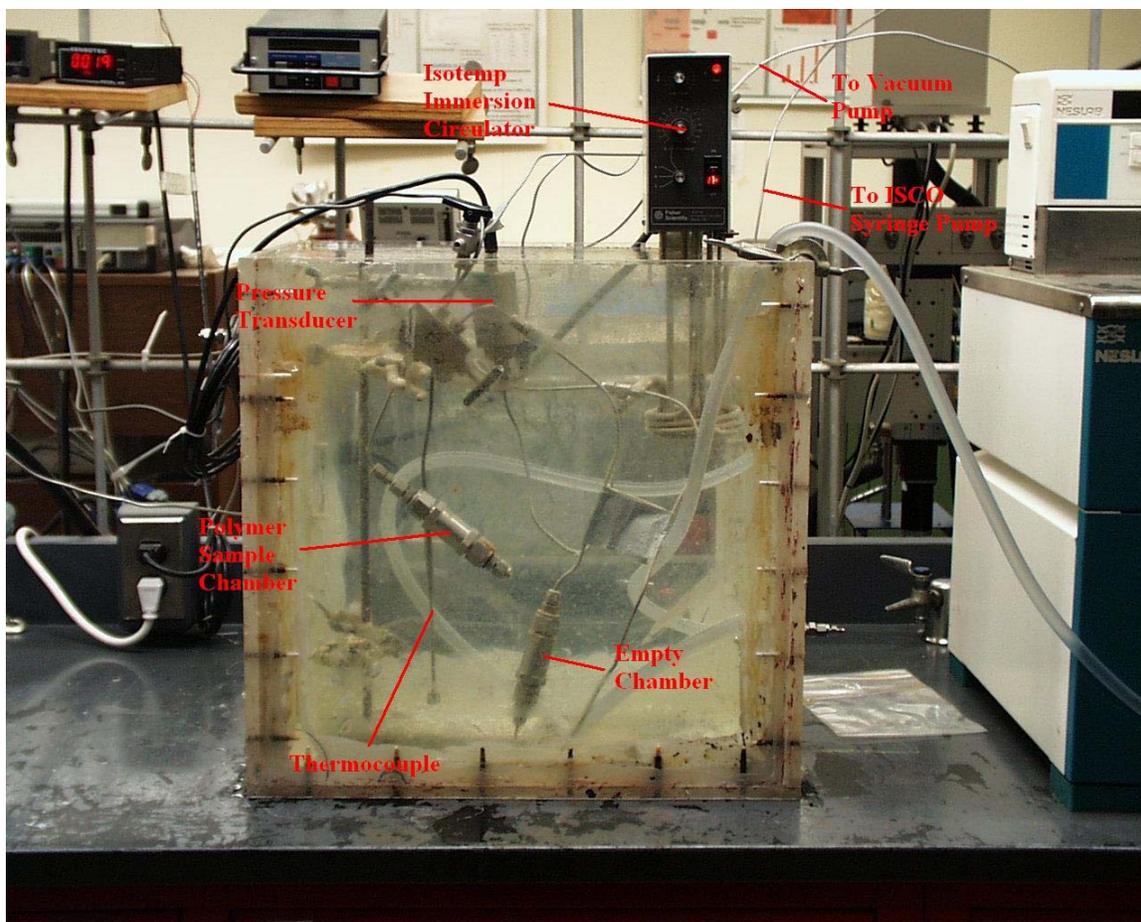


Figure 3.5: Water Bath Experimental Apparatus

Two PMMA bars were placed in the sample vessel separated by a piece of aluminum foil. Although not shown in this setup, an additional polymer sample chamber could be added to double the number of tested samples at one time. The air was removed from these vessels via a Franklin Electric Welch Duo-seal Vacuum pump for approximately 30 minutes. During this time the vessels were submerged in the water bath and heated to the desired temperature, which varied from 30°C to 70°C. The ISCO Pump was used to set the carbon dioxide pressure, which ranged from 548 psia to 1520 psia. The polymer samples were then exposed to the carbon dioxide at the desired temperature and pressure for times ranging between 30 minutes to 7 days.

3.4 Microbalance at Ambient Conditions

Two mass balances were used to obtain the mass change of the PMMA samples during carbon dioxide desorption; an Ohaus Galaxy 110 and a Mettler AT400 electronic microbalance. Once the desired exposure time had been reached, the samples were quickly transferred from their vessels to the microbalances. This was accomplished within 2-3 minutes of depressurization.

The samples were then weighed at regular, increasing intervals for 20 minutes. Those intervals are shown in Table 3.1. When more than two samples were tested at one time, they were weighed on the mass balances via a rotating schedule.

Table 3.1:
Sample Measurement Interval

Time Period (min)	Time Interval (min)
0 - 3	0.25
3 - 5	0.5
5 - 10	1
10 - 20	2

4. ANALYSIS

4.1 Solubility

The initial PMMA weight decrease due to carbon dioxide desorption is linear with time [13], as shown in Figure 2.4 above. This data can be extrapolated back to the depressurization of the samples to get the mass fraction percent of carbon dioxide in PMMA at the experimental conditions prescribed.

4.2 Diffusivity

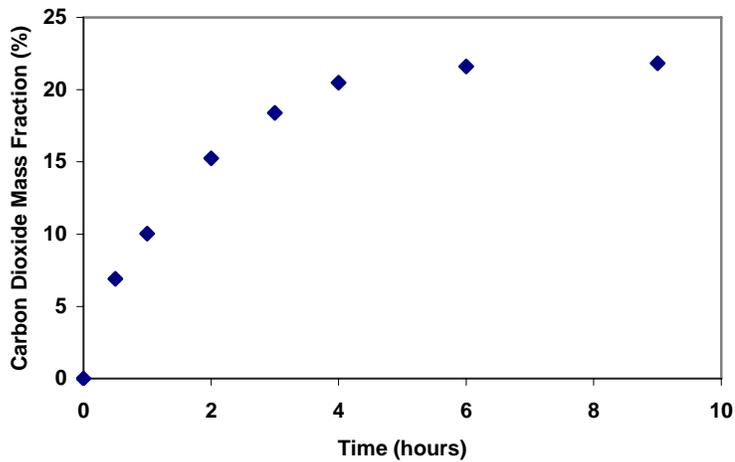


Figure 4.1: Absorption of carbon dioxide into PMMA at 40°C and 1,265 psia for diffusivity calculations.

Unfortunately, this gravimetric technique cannot directly measure the diffusion of carbon dioxide into PMMA. Instead, the solubility of carbon dioxide is measured at specific exposure durations. A sample of this curve is shown in Figure 4.1.

In general, the one dimensional, non-steady state diffusion can be described by Fick's Second Law of Diffusion, Equation (1).

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) \quad (1) [14]$$

Where D is diffusion coefficient, C is the concentration of the diffusion substance, x is the coordinate perpendicular to the plane, and t is the time. One solution that satisfies this differential equation for a plane is given by Equation (2).

$$M(t) = \frac{8M_{\infty}}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 Dt}{L^2}\right) \quad (2) [14]$$

Where $M(t)$ is the mass of diffusing substance at time, t , M_∞ is the equilibrium sorption attained theoretically after an infinite time, and L is the thickness of sample. This can be modified, via a Laplace transformation, to Equation (3).

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{L^2}\right) \quad (3) [15]$$

This form of the solution is useful because it can be simplified to linear equations. Neglecting the higher order terms, Equation (3) can be separated into early and late stage solutions. When $M(t)/M_\infty < 0.6$ then Equation (3) can be simplified to Equation (4).

$$\frac{M(t)}{M_\infty} \approx 2 \left(\frac{D}{\pi L^2} \right)^{1/2} t^{1/2} \quad (4) [16]$$

The diffusion coefficient can be obtained by plotting the $M(t)/M_\infty$ versus $t^{1/2}$. When $M(t)/M_\infty > 0.6$ then Equation (3) can be simplified to Equation (5).

$$\ln\left(1 - \frac{M(t)}{M_\infty}\right) \approx \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D}{4L^2}\right)t \quad (5) [16]$$

Here, the diffusion coefficient can be obtained by plotting $\ln(1 - M(t)/M_\infty)$ versus t .

5. RESULTS AND DISCUSSION

5.1 Solubility – Experimental Results



Figure 5.1: PMMA Samples after desorption from lower (left) to higher (right) temperature and pressure

The solubility of carbon dioxide in PMMA was qualitatively determined by the visual characteristics of the samples after exposure. This classification is shown in Figure 5.1, where the samples became more visibly affected with increasing temperature and pressure. The solubility of carbon dioxide in PMMA was quantitatively measured as the

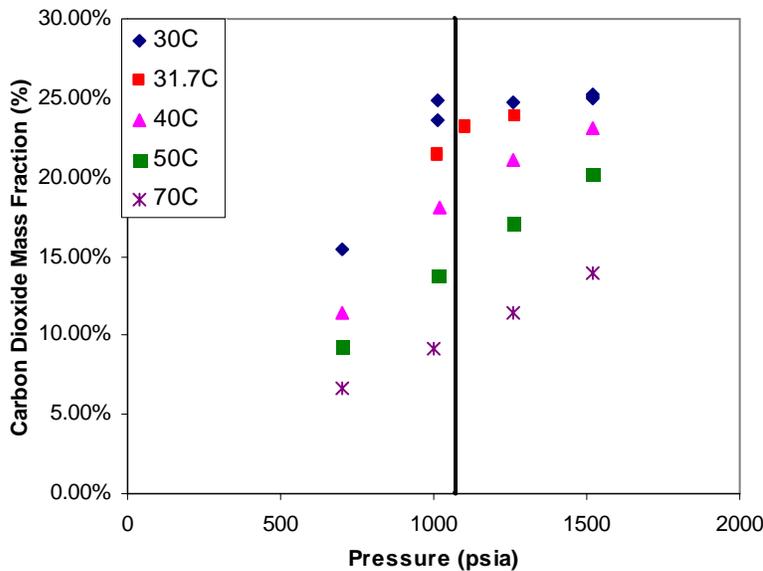


Figure 5.2: Experimental values of carbon dioxide solubility in PMMA. The critical pressure is indicated by a vertical line.

percentage mass fraction of carbon dioxide, on a gram for gram basis, which was absorbed into the polymer matrix. These results are shown in Figure 5.2. The temperatures ranged from 30°C to 70°C while the pressures ranged from 700 psia to 1520 psia. The critical pressure of carbon

dioxide is noted by the vertical line.

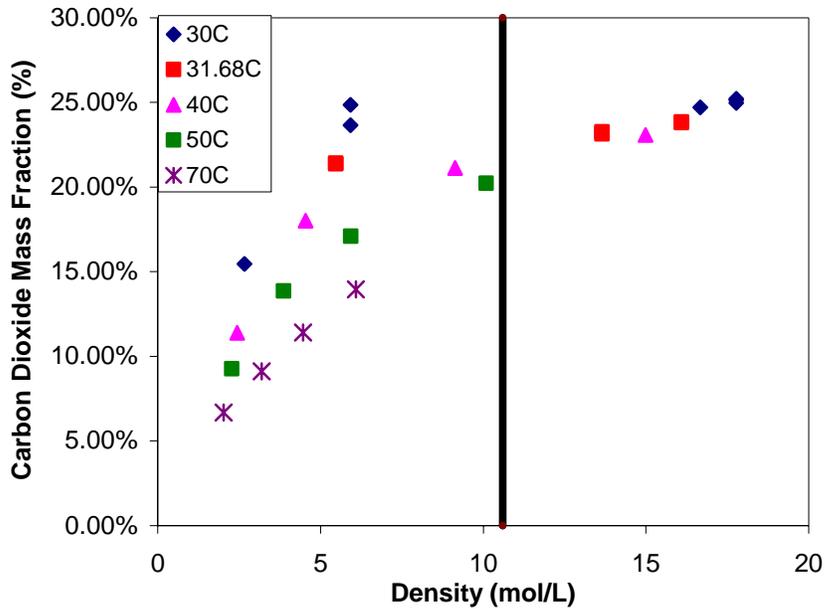


Figure 5.3: Experimental values of carbon dioxide solubility in PMMA. The critical density is indicated by a vertical line.

Several notable trends emerge in the carbon dioxide solubility. First, the solubility increases with increasing pressure. This is not unexpected since higher pressures indicate a higher carbon dioxide density and therefore increased carbon dioxide

concentration. The second trend is that the solubility decreases with increasing temperature, from about 25% for 30°C to about 10% for 70°C. This suggests that PMMA loses some of its sorption capability as it gets closer to its glass transition and melting point. This is also not unexpected since increasing temperatures decrease carbon dioxide's thermodynamic favorability to stay dissolved in PMMA.

The most interesting development is results near the critical point of carbon dioxide. As the temperature and pressure approach the critical point, the rate of change in the solubility slows drastically causing the solubility to 'plateau'. Interestingly, this effect appears when the carbon dioxide mass fraction percent is plotted versus carbon dioxide density instead of pressure, as shown in Figure 5.3. If this 'plateau' effect was due to the sharp change in carbon dioxide density as it crosses into the supercritical phase region, then this behavior would disappear when the mass fraction was plotted versus the density. The fact that it does not indicate that this 'plateau' effect may arise from the interaction of carbon dioxide with the polymer matrix rather than the physical characteristics of carbon dioxide change into a supercritical fluid.

5.2 Solubility – Comparison to the Literature

Literature values for carbon dioxide solubility in PMMA were found for the temperatures 30°C, 40°C, 50°C, and 70°C. The comparison of these values to the experimental results is shown in Figure 5.4 through Figure 5.7 and Table 5.1. The experimental values match well with the literature, usually falling within a couple of percentage points. This is especially true for the higher temperatures where the values are almost indistinguishable.

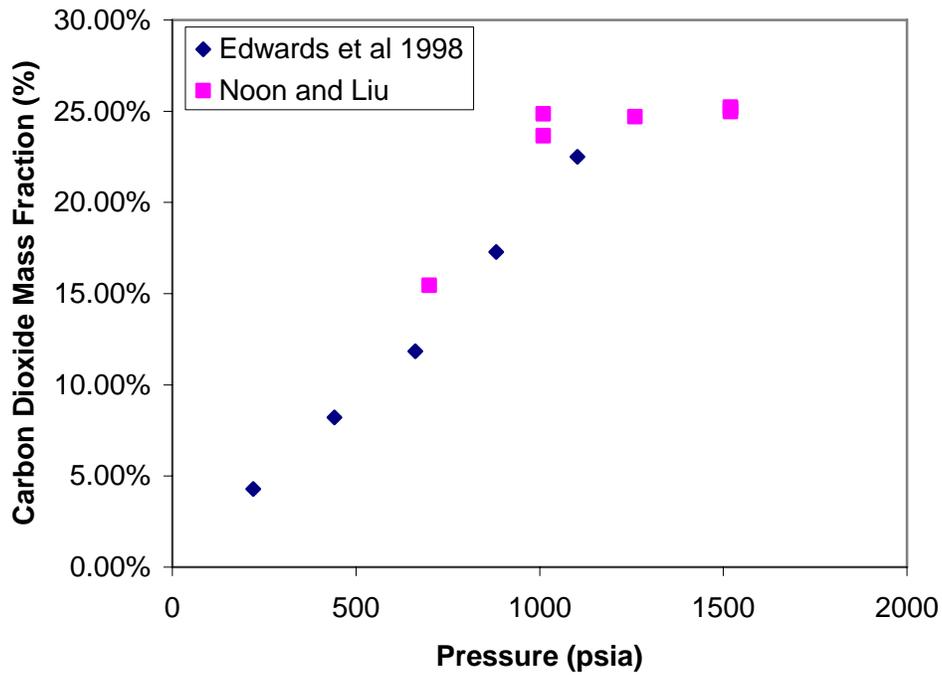


Figure 5.4: Comparison of experimental Solubility to literature values for 30°C for carbon dioxide in PMMA.

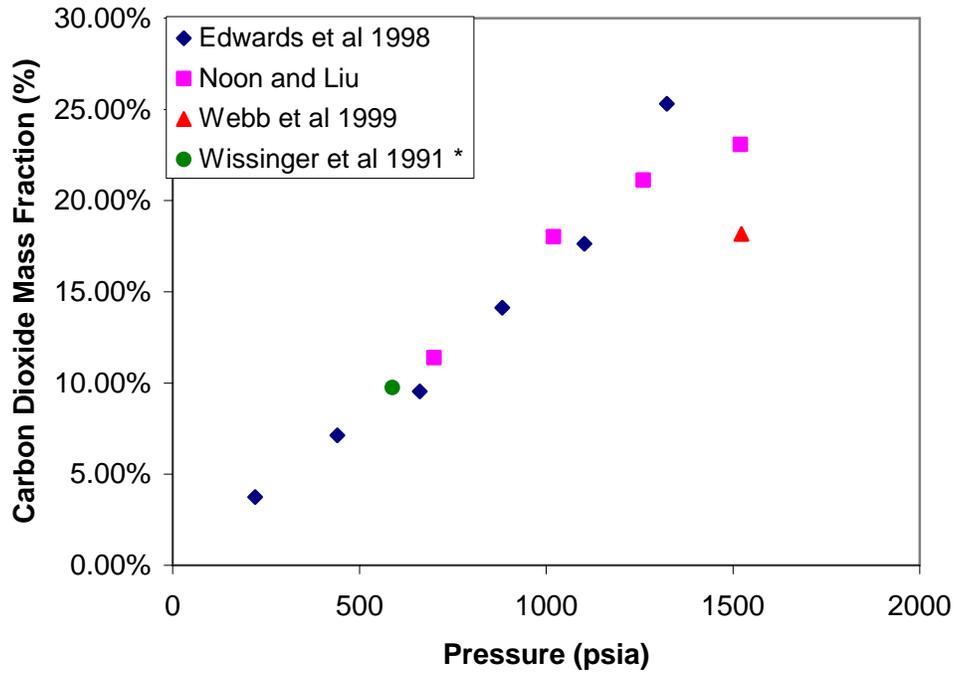


Figure 5.5: Comparison of experimental Solubility to literature values for 40°C for carbon dioxide in PMMA. (* The data for Wissinger et al 1991 [18] was obtained at 42°C)

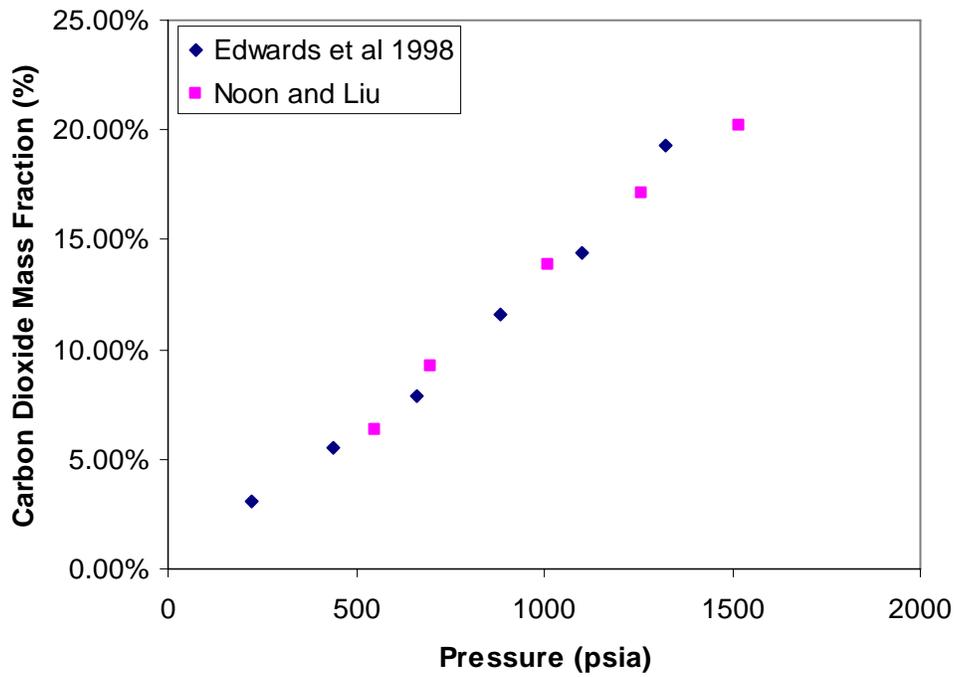


Figure 5.6: Comparison of experimental Solubility to literature values for 50°C for carbon dioxide in PMMA.

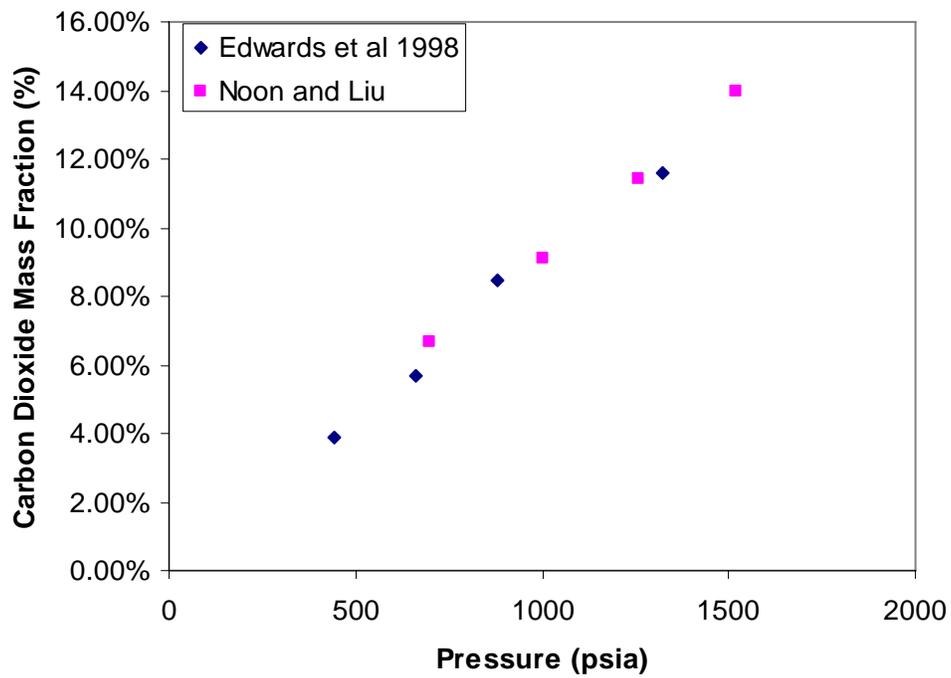


Figure 5.7: Comparison of experimental Solubility to literature values for 70°C for carbon dioxide in PMMA.

Table 5.1: Solubility from the Literature

Temperature (°C)	Pressure (psia)	Solubility		Source
		(cm ³ STP/g-Polymer)	Mass Fraction (%)	
30	220.5	22.00	4.29%	Edwards et al 1998
30	441	42.10	8.21%	Edwards et al 1998
30	661.5	60.70	11.84%	Edwards et al 1998
30	882	88.60	17.28%	Edwards et al 1998
30	1102.5	115.30	22.49%	Edwards et al 1998
30	700	79.25	15.46%	Noon and Liu
30	1010	121.23	23.65%	Noon and Liu
30	1010	127.43	24.86%	Noon and Liu
30	1260	126.61	24.70%	Noon and Liu
30	1520	128.00	24.97%	Noon and Liu
30	1520	128.92	25.15%	Noon and Liu
30	1520	129.28	25.22%	Noon and Liu
40	220.5	19.20	3.75%	Edwards et al 1998
40	441	36.60	7.14%	Edwards et al 1998
40	661.5	48.90	9.54%	Edwards et al 1998
40	882	72.40	14.12%	Edwards et al 1998
40	1102.5	90.40	17.64%	Edwards et al 1998
40	1323	129.70	25.30%	Edwards et al 1998
40	700	58.39	11.39%	Noon and Liu
40	1020	92.37	18.02%	Noon and Liu
40	1260	108.26	21.12%	Noon and Liu
40	1520	118.31	23.08%	Noon and Liu
40	1522.92	93.14	18.17%	Webb et al 1999
42	588	50.00	9.75%	Wissinger et al 1991
50	220.5	15.60	3.04%	Edwards et al 1998
50	441	28.20	5.50%	Edwards et al 1998
50	661.5	40.60	7.92%	Edwards et al 1998
50	882	59.30	11.57%	Edwards et al 1998
50	1102.5	73.70	14.38%	Edwards et al 1998
50	1323	99.10	19.33%	Edwards et al 1998
50	548	32.29	6.30%	Noon and Liu
50	700	47.47	9.26%	Noon and Liu
50	1010	71.10	13.87%	Noon and Liu
50	1260	87.66	17.10%	Noon and Liu
50	1520	103.70	20.23%	Noon and Liu
70	441	19.90	3.88%	Edwards et al 1998
70	661.5	29.20	5.70%	Edwards et al 1998
70	882	43.50	8.49%	Edwards et al 1998
70	1323	59.30	11.57%	Edwards et al 1998
70	700	34.24	6.68%	Noon and Liu
70	1000	46.75	9.12%	Noon and Liu
70	1260	58.49	11.41%	Noon and Liu
70	1520	71.56	13.96%	Noon and Liu

5.3 Diffusivity – Experimental Results

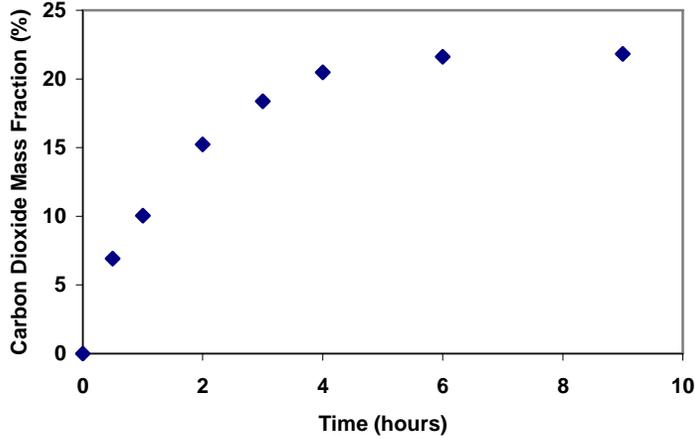


Figure 5.8: Absorption of carbon dioxide into PMMA at 40°C and 1,265 psia for diffusivity calculations.

The gravimetric mass balance method was used to get the solubility of carbon dioxide in PMMA over time durations ranging from 30 minutes to 9 hours. This was done at 40°C and 1,265 psia. The resulting sorption curve is shown in Figure 5.8.

The diffusivity was then calculated by averaging the results of the early and late

stage equations (Equation 4 and 5). Those values are shown in Table 5.2. As shown, the results from both the early and late stage equations were relatively accurate, being within a 25% of each other.

Table 5.2: Diffusivity Experimental Values

Temperature (°C)	Pressure (psia)	Method	Diffusivity x 10 ⁸ (cm ² /s)
40	1,265	Early Stage	27
40	1,265	Late Stage	49
40	1,265	Average	38

5.4 Diffusivity – Comparison to the Literature

The diffusivity coefficient calculated from the sorption curve was compared to values in the literature. This comparison is shown in Figure 5.9 and Table 5.3. The diffusion coefficient of $4 \times 10^{-7} \text{ cm}^2/\text{s}$ measured in this research shows good correlation with the literature values. However, there are two noticeable trends.

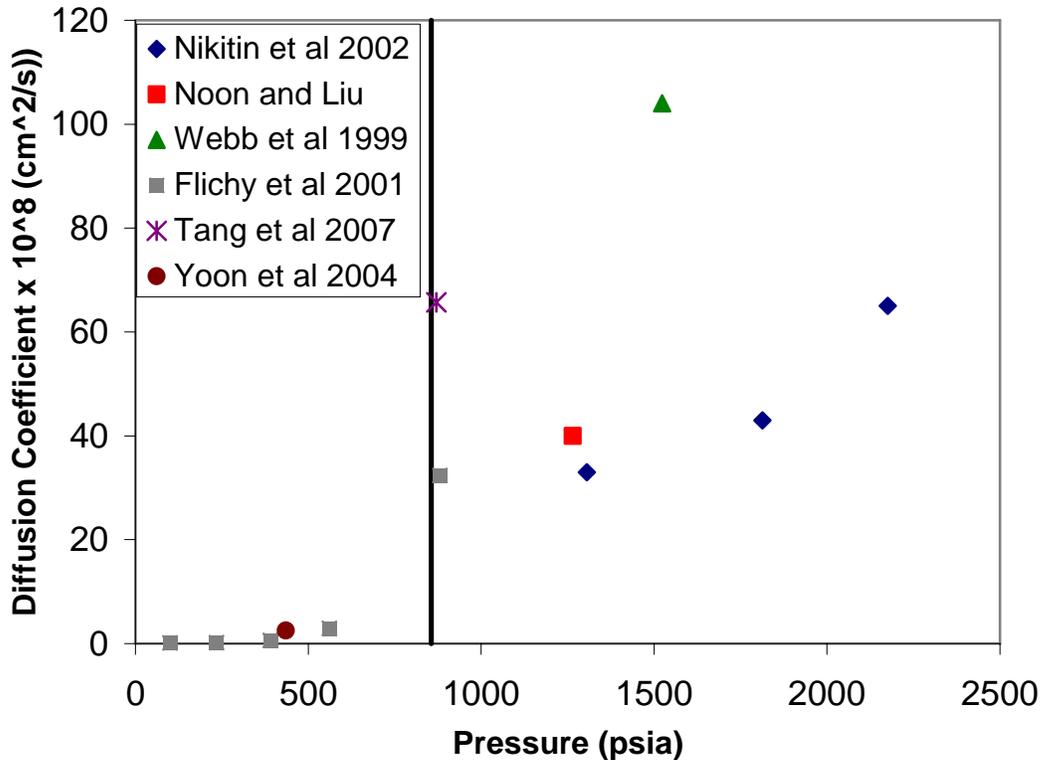


Figure 5.9: Comparison of experimental Diffusion Coefficient to literature values for 40°C for carbon dioxide in PMMA. (* The data for Nikitin et al 2002 [19] was obtained at 38°C). The vertical line indicates the pressure at which PMMA transfers from a glassy to rubbery polymer. [24]

First, is that there is substantial variability of the diffusion coefficient in the literature itself. A possible explanation for this variations could be the type of PMMA used. Although the chemical structure is the same, different studies had different sources of PMMA. The molecular weight and density of PMMA is related to how it was created and can have a considerable affect on the bulk polymer properties. Since no two PMMA chains are the same, most of the time only the average molecular weight is given. This can be even harder to determine for those whole synthesize their own PMMA. This

difference in molecular weight could account for the small variations in diffusion coefficient values shown in Figure 5.9.

Second, there is a large jump in the diffusivity coefficient between 600 psia and 800 psia. This can be explained by the state of the PMMA. At 40°C, PMMA transforms from a solid, glassy polymer to a more fluid, rubbery polymer around 855 psia [24], which is indicated by the vertical line in Figure 5.9. This change, called the glass transition, causes PMMA to become less viscous and more easily able to absorb carbon dioxide. This would correspond with a sudden rise in diffusivity, which is seen in Figure 5.9.

Table 5.3: Diffusion Coefficients from the Literature

Temperature (°C)	Pressure (psia)	Diffusion Coefficient x 10 ⁸ (cm ² /s)	Source
25	15	0.24	Huguchi et al 1996 [23]
25	1,523	17	Berens et al 1992 [11]
30	870	65.9	Tang et al 2007 [21]
38	1,305	33	Nikitin et al 2002 [19]
38	1,813	43	Nikitin et al 2002 [19]
38	2,176	65	Nikitin et al 2002 [19]
38	2,901	60	Nikitin et al 2002 [19]
38	3,626	64	Nikitin et al 2002 [19]
38	13,054	33	Nikitin et al 2002 [19]
38	36,260	64	Nikitin et al 2002 [19]
40	100	0.12	Flichy et al 2001 [20]
40	235	0.21	Flichy et al 2001 [20]
40	390	0.62	Flichy et al 2001 [20]
40	435	2.5	Yoon et al 2004 [22]
40	556	2.95	Flichy et al 2001 [20]
40	870	65.7	Tang et al 2007 [21]
40	880	32.36	Flichy et al 2001 [20]
40	1,265	40	Noon and Liu
40	1,523	104	Webb et al 1999 [13]
50	1,813	44	Nikitin et al 2002 [19]
60	435	3.6	Yoon et al 2004 [22]
60	870	68.6	Tang et al 2007[21]
65	1,813	50	Nikitin et al 2002 [19]
80	870	71.9	Tang et al 2007 [21]

6. CONCLUSIONS

The gravimetric mass balance method has been validated as a suitable method to measure the solubility of carbon dioxide in PMMA. A reduction in the rate of the solubility change due to increasing pressure was confirmed by the data. The utilization of the gravimetric mass balance method to obtain sorption curves and diffusivity coefficients was also demonstrated. The resulting values for both solubility and the diffusivity coefficient were reasonably close to the corresponding literature values, although the diffusivity coefficient measurement is less accurate than it would be if done via another method.

Although a change in carbon dioxide – PMMA dynamics was displayed by the experimental results, this data does not seem to confirm the ‘anomalous’ behavior of carbon dioxide near its critical point. Of the numerous possibilities for this, the most likely is that this phenomenon is limited to thin films on a micro or nano scale. The rapid density change of carbon dioxide near its critical point means that small fluctuations in pressure can cause drastic changes in density. This may cause a rapid increase in swelling of thin films that do not appear in bulk polymer samples. Further investigation is needed to see what sample thickness is required to observe this ‘anomalous’ effect.

Although the results did not confirm the ‘anomalous’ swelling at the critical point, the solubility data indicates that this would be an optimum processing condition. Increasing operating temperature actually decreases the sorption capacity of PMMA. While increasing operating pressure past the critical pressure makes only modest gains. This research indicates that to optimize the solubility of carbon dioxide in PMMA, the operating conditions should be as close to the critical point as possible. This allows for the highest solubility’s of carbon dioxide that still has most of the benefits of supercritical carbon dioxide at the lowest temperature and pressure.

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