Abstract

HUSSAIN, YAZAN AHED. Supercritical CO₂ Aided Processing of Thin Polymer Films Studied Using the Quartz Crystal Microbalance. (Under the direction of Christine S. Grant.)

Fundamental and applied aspects of the interactions between carbon dioxide (CO₂) and different polymer systems were investigated to demonstrate the effect and performance of CO₂ during polymer processing. From a fundamental perspective, the sorption of CO₂ into a non-soluble polymer and its dependence on the different system variables were examined. Another fundamental study investigated the dissolution of a fluorinated polymer in CO₂ at different conditions. Finally, the application of supercritical CO₂ for the impregnation of additives into two different polymers was evaluated. These three different studies are connected in two aspects: they all investigate the behavior of polymers under high pressure CO₂ and they all utilize the quartz crystal microbalance (QCM) as the primary analytical technique.

In the first part of this work, the sorption of CO₂ into poly(methyl methacrylate), PMMA, was investigated. The effect of several parameters, including pressure, temperature, film thickness, and polymer state, on the equilibrium and kinetics of the sorption process was studied. The uptake isotherms of CO₂ into PMMA were estimated from the QCM frequency change. This uptake was found to decrease with temperature and to depend on the film thickness. The presence of hysteresis in the sorption-desorption isotherms clearly marked the glass transition which was found to be in good agreement with previously reported values. This glass transition also affected the sorption kinetic. In the glassy state, two-stage sorption curves were observed, whereas in the rubbery stage, Fickian diffusion was evident. The results from this study were utilized to examine the reliability of Sauerbrey equation for mass calculation. By measuring the change in QCM resistance, it was found that both the thickness and the amount of CO₂ dissolved in the polymer can affect the QCM response. However, it was demonstrated that Sauerbrey equation was still applicable for films up to ∼1 µm thick.
In the next part, the dissolution of a fluorinated copolymer poly(dihydroperfluoroctyl methacrylate-\textit{r}-tetrahydropyranyl methacrylate); PFOMA, was studied. The dissolution process consisted of two stages: \textit{CO}_2 sorption and polymer dissolution. The measured frequency was utilized to determine mass changes for both processes. In the sorption stage, the solubility of \textit{CO}_2 into PFOMA was measured at different temperatures and pressures. The solubility was found to depend on both the \textit{CO}_2 density and the temperature. Polymer dissolution started at pressures between 1100 and 1600 psi, depending on the temperature. The dissolution rate was found to increase as the \textit{CO}_2 density increases, but has a possible dependence on the temperature. Finally, the fraction of undissolved polymer after 1 hour of \textit{CO}_2 exposure was estimated. This fraction increased linearly from 20 to more than 90% with \textit{CO}_2 density.

The last part in this work examined the impregnation of ibuprofen (IBU) into two biocompatible polymers: PMMA and poly(vinyl pyrrolidone), PVP. For PMMA, the amount of impregnated IBU decreased as the \textit{CO}_2 density increased. The solubility parameter approach provided a possible explanation for this behavior based on the interactions among PMMA, IBU, and \textit{CO}_2. High partitioning coefficients of IBU between PMMA and \textit{CO}_2 were estimated, indicating a thermodynamically driven impregnation mechanism. A linear increase in the IBU uptake with the initial polymer mass was observed. This behavior could indicate uniform distribution of IBU in the polymer sample. The impregnation rate was found to have a strong dependence on the temperature. Pressure, on the other hand, did not seem to have significant effect. For the impregnation of IBU into PVP, the frequency response was significantly larger than the PMMA case. This unusual behavior can indicate that the PVP films physical properties (\textit{e.g.}, viscoelastic nature of the film or in the film-substrate adhesion) are affected by IBU which might add a non-gravimetric contribution to the frequency change.
SUPERCritical CO$_2$ Aided Processing of Thin Polymer Films Studied Using the Quartz Crystal Microbalance

BY

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Biography

Yazan Ahed Hussain was born in Zarqa, Jordan on the 20th of January, 1978. He is the fifth of four brothers and one sister. He studied the first five years of school in Saudia Arabia, after then he went back to Jordan. In 1995, He joined Jordan University of Science & Technology, where he obtained his B.S. in Chemical Engineering in 2000.

In Fall 2001, he joined the Chemical Engineering Department at NCSU as M.S. student. In the Spring of 2002, he started working on his masters project with Dr. Christine Grant in the MEMS field. On Fall 2003, Yazan obtained his M.S. degree. The next spring, he started working on his PhD with Dr. Grant on the area of polymer processing under supercritical fluids. He defended his PhD thesis on September 8, 2006.
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Chapter 1

Introduction

The research presented in this dissertation aims at studying the behavior of polymers during different supercritical carbon dioxide processing applications. The research also demonstrates the possibilities and challenges of utilizing the quartz crystal microbalance as an analytical tool for real-time studies in these applications.

In this chapter, a general overview of the supercritical fluids technology is given. This field is in a dynamic stage where applications are being introduced and evaluated. Success in commercializing this technology can have a positive impact on the environment by providing an economical alternative to conventional processes. Therefore, large number of studies have focused on supercritical fluids and its applications in order to gain better understanding of the opportunities available from these materials.

1.1 Supercritical Fluids

The interesting physiochemical properties of supercritical fluids (SCF) have received considerable attention as a replacement for traditional solvents in industrial applications [1]. During the 1970’s and early 1980’s, these materials were perceived as having the potential for a new exciting technology offering solutions to both environmental and industrial issues [2]. Initially, supercritical fluids were mainly used for extraction applications, such as caffeine extraction from coffee and tea [1, 2]. During the 1990’s, when the use of chlorocarbons and chlorofluorocarbons (CFC’s) was banned according to the Montreal Protocol, many industries that were relying on these organic materials for cleaning purposes were facing a difficult situation and supercritical fluids were considered as an alternative [3]. Currently, supercritical fluids are being considered in a wide range of applications including reaction, catalysis, polymerization, polymer processing and modification, dry cleaning, and hydrogenation of...
Chapter 1. Introduction

SCF materials are considered to be a “hybrid solvents”—having liquid-like densities and gas-like diffusivities [1], and can dissolve many solids and liquids. Among the interesting characteristics of supercritical materials is the fact that their solvent strength can be easily tuned [2]. Around the critical point, the solvency power of the fluid becomes sensitive to changes in temperature and pressure, a property that has applications in separation technology [7]. Another interesting property of SCF’s is the absence of phase boundary upon transition from liquid or gaseous to supercritical state. By avoiding the phase boundary, problems associated with surface tension are also avoided, which facilitates its penetrations into microporous materials [3] and allows better performance in applications such as microelectronics release [8].

**Figure 1.1:** CO$_2$ density [9] and solubility parameter [10] at different temperatures and pressures. The dotted lines represent the critical conditions ($T_c$ and $P_c$).
Chapter 1. Introduction

By large, carbon dioxide (CO$_2$) is the most common material in supercritical applications. This is mainly due to its easily accessible critical point (31 °C and 1070 psi), chemical inertness, low cost, and environmentally benign nature. As with other supercritical fluids, the properties of CO$_2$ change substantially upon changing the temperature and pressure. Examples of such changes can be seen in Figure 1.1 where the density and solubility parameter are plotted at different temperatures and pressures. Although CO$_2$ may be thought of as an inert medium, under suitable conditions it can dissolve many materials including many vinyl monomers, free-radical initiators, and fluorocarbons [6]. In addition, CO$_2$ can be easily separated and recycled by evaporation.

Polymer processing is one of the major areas where CO$_2$ has potential applications. Indeed, CO$_2$ has been considered as a competitive alternative for other attempts to reduce the environmental impact of industry such as recycling and switching to solvent-free processes [11]. Through proper design, CO$_2$ can be employed in various stages of polymer processing, such as synthesis [12], modification [13], dissolution [14], deposition [15], fractionation [16], and foaming [17].

1.2 Motivation & Objectives

The use of scCO$_2$ in polymer processing is a relatively new subject compared to liquid based processes. While there have been a number of studies on the solvent character of CO$_2$ for many polymers, there is still a need for better understanding of the phenomena involved which can result in a better predictability during processing [6]. Furthermore, performing in-situ studies under high pressure conditions can be challenging and there is a need for analytical tools that can perform such task. The quartz crystal microbalance (QCM) is a technique that has been available for several decades and used in vacuum and liquid environments to perform in-situ, real-time measurements on many systems including polymers. It, therefore, seems promising to adapt the QCM for high pressure gravimetric, and possibly other, measurements on polymeric materials.

The main objective of the work presented in this dissertation is to perform studies on different supercritical polymer processes in order to characterize its equilibrium and dynamic behavior under different pressures and temperatures. These processes include sorption, dissolution, and additive incorporation.
Chapter 1. Introduction

1.3 Outline

This document is divided into seven chapters. In the next chapter, some basics and concepts pertaining to the subjects of this thesis are given including sorption of small molecules into polymers, polymer dissolution, and impregnation of additives into polymers. Chapter 3 discusses different aspects of precision microweighing under high pressures for polymer applications. The complexities associated with piezoelectric-based microweighing in the context of polymer systems under supercritical fluids is discussed. Chapter 4, details the studies on the swelling and sorption of CO$_2$ in a non-soluble polymer. These studies were performed in conjunction with a theoretical interpretation aimed at developing thermodynamic and kinetic models for sorption in polymers under wide range of pressures. Sorption isotherms and kinetics, sorption-desorption hysteresis in glassy polymers, and film thickness effects are among the investigated aspects. The result of the dissolution of a novel CO$_2$-soluble fluorinated polymer in liquid and supercritical CO$_2$ are discussed in Chapter 5. The dissolution was monitored through the QCM frequency which was carefully analyzed to extract information about the different stages of dissolution. In Chapter 6, the incorporation of additives into polymers under supercritical conditions is discussed. This study focused on the impregnation of a therapeutic drug into biocompatible polymers at different conditions. Finally, an overall look at the project and its outcome is presented in Chapter 7 followed by recommendations for possible future research.
Chapter 2

Principles and Concepts

In this chapter, a general background on the subjects relevant to the work in this dissertation is presented. The chapter starts by discussing some general concepts regarding polymers. This will be followed by a description of the sorption process in glassy and rubbery polymers. Polymer dissolution and its mechanism is discussed in Section 2.3, followed by a discussion on the impregnation processes of different additives into polymeric materials. Finally, analytical techniques used for mass change measurements of systems involving polymeric materials under high pressures are reviewed.

2.1 Polymers Characteristics

The macroscopic properties of a polymer are controlled by its chemical structure, chain configuration, and chain conformation. Chain configuration refers to the manner that the successive repeat units are connected to each other in a chain, e.g., head-to-tail versus head-to-head or random versus block. This configuration as well as the chemical structure are usually determined during the course of polymerization [18]. Conformation, on the other hand, refers to the distribution of the chain’s atoms in space resulting from the rotations of its bonds. Due to the large number of bonds that are usually present in the backbone of a polymer chain, the corresponding number of theoretical conformations is enormous. For example, a typical polyethylene chain with 20,000 C—C bonds can have, assuming only three allowable rotational states, \(10^{9540}\) different conformations. While this number might be reduced by certain interactions with the chain’s surroundings, the actual possible number of conformations is still very large [19]. These conformations are responsible for one of polymers most important characteristic, namely, chain entanglements.

Entanglements are the coiling of polymer chains in an amorphous polymer. They can be
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treated as temporary crosslinks and are responsible for holding the polymer together under stress. In the melt state, the entanglements cause a significant increase in the viscosity [20]. In the solid state (and in concentrated solutions) the viscoelastic and rheological properties of the polymer undergo an abrupt transition when the molecular weight exceeds a critical value called the critical entanglement molecular weight [21]. Entanglements are also responsible for some of the unique behaviors observed with polymers. For example, the dissolution mechanism of a polymer is largely controlled by the ability of the polymer chain to disentangle itself from other chains.

Another important characteristic of polymers is the glass transition which indicates its transformation from a glass-like to a rubber-like material. This is usually induced by heating above the glass transition temperature, but can also result from other factors such as the use of plasticizers. Upon transition, polymers experience dramatic changes in their properties such as viscoelasticity and density. The polymer chain molecules in the glassy state are practically frozen in position and cannot move freely. Therefore, the glassy state is said to be in a non-equilibrium state and its response to external stresses cannot be described by equilibrium thermodynamics.

The abrupt change in density, or specific volume, with glass transition is directly related to what is known as the free volume which is the volume in the polymer matrix that is not occupied by the molecules. In the glassy state, the amount of thermal energy available for molecular motion is small, thus the volume occupied is small. In the rubbery state, the motion increases and each molecule will occupy a larger volume. Both the glass transition and free volume are of paramount importance to the diffusion and dissolution processes.

2.2 Sorption of Gases into Polymers

Sorption of low molecular weight components into polymeric materials has been a subject of extensive study for more than sixty years [22, 23] because of its practical importance to many industrial applications such as membrane separations, extraction, drug delivery, and dyeing [24–26]. This is also true at elevated pressures where the sorption process is of interest in applications such as extraction, impregnation, and membrane separation [27].

The sorption process through polymer films is controlled by sorption equilibria at the interfaces, diffusion in the polymer network, and the relaxation of the polymer matrix [28].
These phenomena are affected by the polymer state, \textit{i.e.}, glassy versus rubbery [29]. The relative rate of diffusion compared to the relaxation plays an important role in determining type of the sorption process [30].

Sorption in rubbery polymers

The concentration of the sorbed penetrant in rubbery polymers can be determined by using Henry’s law at low concentrations, whereas the Flory-Huggins theory of polymer solutions or a suitable equation of state can be used for higher concentrations [29]. The kinetics of the sorption process in this state is characterized by a high relaxation rate compared to the diffusion rate. Such process is referred to as Case I (or Fickian) diffusion and can be modeled with the traditional Fickian relationships. For example, for a polymer sheet of thickness \( l \), the mass uptake profile with time can be written as [31]:

\[
\frac{\Delta M}{\Delta M_\infty} = 8 \left( \frac{Dt}{l^2} \right)^{1/2} \left[ \frac{1}{\pi^{1/2}} + 2 \sum_{n=0}^{\infty} (-1)^n \text{erfc} \left( \frac{ml}{4(Dt)^{1/2}} \right) \right]
\]  \hspace{1cm} (2.1)

where \( \Delta M \) is the amount of penetrant uptake at any time \( t \), \( \Delta M_\infty \) is the final penetrant uptake, and \( D \) is the diffusivity. One important assumption in Eq. (2.1) is that \( D \) is constant, \textit{i.e.}, concentration independent [25]. It is sometimes necessary, however, to take into account the dependence of the diffusion coefficient on concentration. One relation that has been commonly used for this purpose is [26]:

\[
D = D_{C_0} e^{\alpha C}
\]  \hspace{1cm} (2.2)

where \( D_{C_0} \) is the zero-concentration diffusivity and \( \alpha \) is the plasticization power [32].

Sorption in glassy polymers

For glassy polymers, both the sorption equilibrium and kinetics phenomena are more complicated. The challenge of modeling gas sorption in this case is due to the nonequilibrium nature of glassy polymers [33]. As nonequilibrium materials, glassy polymers display a strong history dependence in their properties. The history effects in glassy polymers include: thermal and mechanical history, penetrant-induced effects, sample dimension effects, and orientation-induced effects [34, vol. 12]. This dependence on history is manifested by
Chapter 2. Principles and Concepts

the presence of hysteresis between sorption and desorption isotherms and by the anomalous sorption kinetics.

One theory that has been proposed to describe the diverse sorption behavior of glassy polymers is the dual-mode sorption model. This model is one of the simplest and most successful models that has been used to calculate the sorption of small molecules in glassy polymers. The model is expressed as [35]:

\[ C = C_D + C_H = C_D P + \frac{C_H b P}{1 + b P} \]  

(2.3)

This model assumes the existence of two distinct molecular populations of penetrant in the polymer. One population represents the Henry’s law mode \( C_D \) and dissolves directly into the polymer matrix. A second population represents the Langmuir mode \( C_H \) which is sorbed into the microvoids or holes of the polymer. Despite its inflexibility, this model capture the essence of the glassy region, \textit{i.e.}, the coexistence of an equilibrium \( C_H \) and non-equilibrium \( C_D \) contributions to the overall concentration \[24\]. Another approach to model sorption into glassy polymers include the use of the order-parameter concept. Order parameters provides a useful approach to describe non-equilibrium systems with equilibrium thermodynamics [35]. The non-equilibrium nature of the system is accounted for by adding another parameter, or more, to the conventional state variables. The free energy, for instance, can be written as:

\[ dG = -SdT + VdP + \left( \frac{\partial G}{\partial Z} \right)_{T,P} dZ. \]  

(2.4)

The last term in this equation represents the order parameter \( Z \) contribution, which accounts for the departure of the system from the equilibrium state. Example of models that utilized this concept are the model by Wissinger and Paulaitis [35], which uses two order parameters, and that by Doghieri and Sarti [36], which uses the polymer density as an order parameter.

Sorption kinetics in glassy polymers

In the glassy state, deviations from Fick’s law are not uncommon especially above a certain threshold concentration of the penetrant [37]. This complex behavior is mainly due to the
“viscoelastic response of the matrix, the possible glass-rubber transition, and to the coupling effects with the deformation and stress” [38]. The resulting stress generated by the absorbed molecules causes the deformation of the polymer at a certain rate [39]. The relative ratio between the diffusion rate and the deformation rate was found to be directly related to the observed diffusion behavior of the polymer. This ratio was defined by the dimensionless Deborah number, $D_e$, in analogy to the Deborah number used in describing the behavior of viscoelastic flow [40]. The Deborah number is defined as:

$$D_e \equiv \frac{\text{relaxation time}}{\text{diffusion time}} = \frac{t_R}{t_D}$$

(Figure 2.1): General temperature-penetrant concentration diagram. The solid lines represent constant $D_e$ lines. From reference [40].

In Figure 2.1, a general temperature-penetrant diagram proposed by Vrentas et al. [40]
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is presented to demonstrate the dependence of the diffusion process on Deborah number. In Zone I, due to the low temperature and low penetrant concentration, the polymer behaves essentially as an elastic solid (high relaxation time, $De \gg 1$) and the diffusion in this zone is Fickian. $T_E$ on the figure represents the effective elastic temperature limit. In Zone III, the high temperature and/or high penetrant concentration causes the polymer to behave as a viscous fluid and the diffusion is Fickian as well (low relaxation time, $De << 1$). The effective viscous temperature limit is designated as $T_g$. In between these two zones, a non-Fickian diffusion was observed and was referred to as anomalous diffusion.

Figure 2.1 is a simplified presentation of the real situation. Several different diffusion behaviors have been found in the anomalous diffusion regime. A general expression for the mass uptake as a function of time ($t$) is [26]:

$$\frac{\Delta M}{\Delta M_\infty} = kt^n$$  \hspace{1cm} (2.6)

where $k$ is a constant and $n$ depends on the sorption process. The following different behaviors have been observed [26, 32, 41]:

- Fickian: also known as Case I ($n = 1/2$)
- Case II: characterized by a penetrant weight uptake linear with time ($n = 1$) and the existence of a sharp concentration front.
- Anomalous: an intermediate case between Fickian and Case II ($1/2 < n < 1$).
- Supercase II: starts as a Case II or anomalous diffusion but the uptake accelerates as the final equilibrium value is reached ($n > 1$). Usually observable for samples with small thickness.
- Two-stage: two competing processes, Fickian diffusion and polymer relaxation ($De > 1$).

Some examples of these different behaviors are shown in Figure 2.2. The physical mechanism behind the non-Fickian behaviors are not yet complete and might be attributed to the coupling of swelling with the diffusion process or to the presence of inhomogeneity in the glassy sample [26].
Sorption-induced glass transition

In many cases, if sufficient penetrant is absorbed into a glassy polymer, the glass transition temperature ($T_g$) of the polymer will decrease. The prediction of this phenomenon is important for many applications including membrane separation and drug impregnation [42]. When small molecules penetrate the polymer matrix, they will act as a lubricant separating the chains from each other and facilitating its movement, thus lowering the glass transition temperature [19, 20]. The dependence of $T_g$ on the penetrant concentration was expressed as [43]:

$$\ln \left( \frac{T_g}{T_{g0}} \right) = \beta [(1 - \theta) \ln(1 - \theta) + \theta \ln \theta]$$  \hspace{1cm} (2.7)

where $\beta = zR/M_i \Delta C_{pp}$ and $\theta = (V_p/zV_d)\phi/(1 - \phi)$. Here, $z$ is the lattice coordinate number, $R$ is the gas constant, $M_i$ is the molecular weight, $\Delta C_{pp}$ is the excess transition isobaric specific heat of the polymer, $\phi$ is the volume fraction, and $V_i$ is the molar volume.
The subscripts \( p \) and \( d \) refers to the monomer and sorbent, respectively. Using this relation, Chow [43] was able to predict the depression in \( T_g \) for polystyrene by several diluents. A volume fraction of 70% of toluene, for example, reduced the \( T_g \) of polystyrene from 101 to 70 °C.

The plasticizing effect of CO\(_2\) on many polymers is well known and is of great importance in modeling CO\(_2\) sorption in polymers and in the supercritical drug impregnation process. Examples of some measured depression in \( T_g \) induced by CO\(_2\) absorption is shown in Figure 2.3. As can be seen from the figure, significant reduction in \( T_g \) is achieved with only few percents of dissolved CO\(_2\). Depending on the interactions between the polymer and CO\(_2\), four different behaviors of \( T_g \) change with CO\(_2\) content in the polymer was predicted [45]. These behaviors are characterized by the presence of an extremum in the curve describing
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the depends of $T_g$ on the pressure or the composition. One interesting type of $T_g$ behavior is that observed for PMMA-CO$_2$ system. In the pressure-$T_g$ diagram for this system, the $T_g$ will reach a maximum at certain pressure then starts to decrease as the temperature is increased. This phenomenon has been called the “retrograde vitrification” and is caused mainly by the decrease of CO$_2$ solubility in PMMA as the temperature is increased [44, 45].

2.3 Polymer Dissolution

Polymer dissolution is an important phenomenon in many industrial processes including membranes synthesis, plastics recycling, drug delivery applications, and photolithography [46]. In this last application, for example, the dissolution of polymer based films is critical to controlling the ultimate features in the final device. Another potential application of the dissolution of polymers is in scaffolding for tissue regeneration. In this process, cells are grown on polymers that had been shaped into scaffolds that resemble the structure of tissues before dissolving the polymer [47]. In all of the above applications, understanding the mechanism of dissolution is necessary for better processing as well as for theoretical modeling [48].

Two phenomena controls polymer dissolution: solvent diffusion and chain disentanglement [47]. In the more general case of glassy polymers, the dissolution process can be described as follows. The process starts by the diffusion of the solvent molecules into the polymer which causes some morphological change [49]. This process can be described in a similar manner to that discussed in Section 2.2. As the concentration of the solvent increases, the glassy polymer will be plasticized. Upon further increase in the concentration, the polymer chains near the rubbery-solvent interface will start to disentangle from its matrix through a reptation mechanism [50, 51]. The disentangled molecules have high internal mobility which causes the diffusion of these molecules into the solvent and starts the actual dissolution process [49].

As a result of polymer plasticization by the solvent, two distinct fronts are formed: a glassy-rubbery front ($R$) and a rubbery-solvent front ($S$). The sharp differences in the properties (e.g., refractive index, viscosity) between the rubbery and glassy regions make it possible to monitor these two fronts [48] using, for example, FT-IR imaging. At the beginning of the dissolution process, front $R$ will move toward the center of the polymer due
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Figure 2.4: One-dimensional solvent diffusion and polymer dissolution process [46, 52]. See text for details.

to the plasticizing effect of the diffusing solvent. Front $S$ on the other hand, will initially move away from the center due to swelling. Once the dissolution rate exceeds that of swelling, front $S$ will start to move in the opposite direction, i.e., toward the center. The two fronts will then move in the same direction (toward the center) at approximately the same rate, and the gel layer between fronts $S$ and $R$ will have a constant thickness during this stage. Finally, when the whole polymer sample becomes plasticized, front $R$ disappears and front $S$ continues to move toward the center until all the sample has been dissolved [46, 47]. The movement of both fronts is illustrated schematically in Figure 2.4.

The solubility of polymers can be predicted by applying a suitable equation of state to determine the phase behavior of the polymer in different solvents [53]. As for the dissolution kinetics, different approaches have been suggested. For example, a phenomenological model describing the motion of the two fronts was proposed by Tu and Ouano [48]. In this model,
the solvent flux into the polymer and that of polymer into the solvent was used to determine
the swelling and dissolution rates, respectively. Dissolution kinetics can also be obtained
through extending the sorption model with suitable modifications as was done by Peppas
and co-workers [30, 52]. Another approach by Vrentas and Vrentas considered the solvent
and polymer as a single phase, thus avoiding the need to deal with the moving fronts [54]. In
general, there are five approaches to modeling amorphous polymer dissolution as reported
in reference [46]:

1. Phenomenological models with Fickian equations.

2. Models with external mass transfer as the controlling resistance to dissolution.

3. Stress relaxation models and molecular theories.

4. Analysis using transport models for swelling and scaling laws for chain disentangle-

5. Continuum framework models.

2.3.1 Solubility of polymers in CO$_2$

The organic solvents used in the dissolution process have a negative impact on the environ-
ment and have produced pressure on industry to reduce the utilization of these hazardous
materials [5]. In addition, for applications where the polymer is to be used in therapeutic
applications, e.g., drug formulation, it is important to eliminate the residual solvents from
the final product [55]. As a result, attention in the last decade has been given to supercritical
fluids, especially CO$_2$, as a potential replacement for traditional organic solvent processes.
However, there are still some challenges associated with the commercialization of this new
technology.

The poor solvency of CO$_2$ with most polymers had limited the implementation of this
emerging technology [4]. As a result, considerable effort has been made, since the early
1990’s, toward improving polymer solubility in CO$_2$ leading to the modification of fluo-
ropolymers and polyethers to produce highly CO$_2$-soluble polymers [12, 56, 57]. While the
CO$_2$ power as a solvent is complex and cannot be easily predicted from mere consideration
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of chemical structure, the availability of dissolution studies on polymers with different structures in CO₂ can provide a considerable insight into its solvency phenomenon [58]. Previous studies have provided many examples that demonstrate how different chemical and physical properties, such as side chain length, backbone stiffness, and polarity affect the polymer’s behavior in CO₂ [59–61].

2.4 Polymer Impregnation

The impregnation (also termed infusion or incorporation) of additives into polymers is a common process encountered in many industrial applications. In this process, an additive component is made to diffuse inside the polymer matrix to either modify the operation of the polymeric material, as in the case of carbon molecular sieves synthesis [62], or to prepare the polymer to act as a source of an active agent, such as drug-impregnated polymers.

In the impregnation process, it is usually important to ensure proper distribution of the additive inside the polymer. An ideal impregnation, for most applications, will yield a uniformly and stably dispersed additive [63]. In some cases, nevertheless, the uniform distribution is not required and only dispersion of the additive among certain parts is sufficient as in the case of the fabrication of polymer sheets with reflective surfaces.

Conventionally, without utilizing supercritical fluids technology, materials can be dispersed inside polymers via different methods such as solvent evaporation, melt extrusion, and mechanical treatment [64]. In the solvent evaporation method, the material to be impregnated is dissolved in a certain solvent and the solution is brought into contact with the polymer. The solvent is chosen such that it will swell but not dissolve the polymer, thus facilitating the diffusion of the additive material. Finally, the residual solvent is evaporated [65]. Another technique involves the dissolution of both the additive material and the polymer, in predetermined proportions, in a common solvent. The mixture is then dispersed into small particles through mixing with an immiscible solution, such as water [66], or through spray drying. Mechanical treatments include the mixing of the polymer, in solid form, with the additive material, in powder form, using a high speed mixer. The mixer will cause shearing and melting of the polymer thus enhancing the blending process [63].
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2.4.1 Applications

There are many traditional applications in which it is necessary to modify the polymer, via incorporation of additives, to make durable products with the desired properties. These additives can act as [63]:

- Stabilizers: which can have one or more stabilizing functions including thermal, antioxidants, ultraviolet absorbers, fire retardants, and anti-static agents.
- Fillers: used to enhance the chemical and physical properties of the materials and can also be used as cheapners to reduce the cost of some expensive polymers.
- Plasticizers: usually applied to improve the workability of the polymer and to transform rigid polymers into soft materials.
- Colorants: which might be used to produce colored polymers that are either opaque or transparent (dyes).
- Special additives: such as internal lubricants and anti-sticking additives.

In addition to these traditional applications, there are still other areas where the impregnation process is highly attractive. These processes include [55]: (1) organo-metallic complexes impregnation, (2) polymer blends synthesis, and (3) controlled drug release production.

Metal-polymer nanocomposites

In the metal-polymer nanocomposites synthesis process, an organo-metallic compound is first diffused into a polymer and then treated by heat, radiation, or chemical agents to obtain the desired material [55]. The potential of the resulting materials from this process had been recognized for a long time; their applications include: conductive and proactive coatings, high temperature superconductors, metal-polymer hetero-junctions, solar cells, and molecular fillers [67]. Another application where metal-polymer composites can be used is in the preparation of carbon molecular sieves (CMS) which can be used in gas purification processes [55]. For example, Yoda et al. prepared a Ti impregnated silica aerogels which showed an increase in its binding capacity to benzene and can completely decompose the adsorbed benzene to CO$_2$ [68]. The same group also prepared a Pd and Pt impregnated CMS (Figure 2.5) which shows a high selectivity toward hydrogen [62].
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Figure 2.5: TEM photograph of Pd-doped CMS membrane prepared by carbonation of Pd-doped polyimide film. The black dots are the Pd particles dispersed in the membrane [62].

Polymer blends
Polymer blends are another example where the impregnation process can be applied. Blending can be used to achieve some material-related benefits such as [69]:

- Providing materials with a full set of desired properties at the lowest price.
- Extending the engineering resins’ performance.
- Improving specific properties, viz. impact strength or solvent resistance.
- Offering the means for industrial and/or municipal plastics waste recycling.

These blends can be produced in several methods such as mechanical, solution, latex, and fine powder [69]. Impregnation plays a role in producing molecularly dispersed polymer blends. If crosslinking is performed on the blend, the resulting material is called *interpenetrating polymer network* (IPN).¹

The preparation process of polymer blends consists of introducing a solid polymer into a solvent containing the monomer(s) and initiator (plus crosslinker in the case of IPN). After the polymer is impregnated with these materials, the solvent is either removed and the polymerization is initiated or vice versa [71].

Controlled drug delivery
Ensuring proper drug levels in the body is an important issue to be considered when administering drugs to patients in order to achieve the optimum therapeutical effect. One way

¹IPN is “a polymer comprising two or more networks which are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken” [70].
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of achieving this goal is through controlled drug delivery. This technique has been defined as: “the use of whatever means possible, be it chemical, physiochemical, or mechanical, to regulate a drug’s access rate to the body’s central compartment, or in some cases, directly to the involved tissues” [72]. Among the advantages of using drug delivery systems are [73]: eliminating under- and overdosing, maintaining drug levels within a desired range, and the need for fewer administrations. The market for such products is large and promising. For example, in 1997, the sales of advanced drug-delivery systems in the US alone exceeded $13 billion (Table 2.4.1).

Table 2.1: US sales of advanced drug-delivery systems (1996 and 1997) [74].

<table>
<thead>
<tr>
<th>Type of system</th>
<th>1996</th>
<th>1997</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oral</td>
<td>6,066</td>
<td>7,178</td>
</tr>
<tr>
<td>Transdermal</td>
<td>1,525</td>
<td>1,701</td>
</tr>
<tr>
<td>Injectable/implanable polymer systems</td>
<td>856</td>
<td>1,109</td>
</tr>
<tr>
<td>Ocular</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>Liposomes</td>
<td>107</td>
<td>208</td>
</tr>
<tr>
<td>Transmucosal</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>Lung delivery</td>
<td>2,513</td>
<td>2,573</td>
</tr>
<tr>
<td>Nasal delivery</td>
<td>851</td>
<td>994</td>
</tr>
</tbody>
</table>

| Total                                       | 11,965| 13,841|

One form of drug delivery is to load the drug into a certain carrier that can control the rate and manner in which the drug is released. Among the materials that have been considered as drug carriers are liposomes and polymers [72]. The high flexibility of polymeric materials have rendered it of special interest in many drug delivery applications [75]. Through proper choice of materials, polymers can be applied in the drug delivery of high molecular weight drugs, to achieve zero-order release kinetics, and to respond to certain environmental changes (e.g., pH, temperature). Four different polymer-based drug delivery systems have been realized [74]:

- Reservoir system: in which the drug diffuses through a polymer membrane.
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- Matrix system: in which the drug is evenly distributed through a polymer system. In this case, the drug can be released by diffusion through the polymer or by polymer erosion.
- Osmotic system: in which the drug is pumped out through a small hole drilled into the carrier polymer shell.
- Polymer drug conjugates: in which the drug is bonded to the polymer by cleavable bonds.

Several polymers have been examined for drug delivery applications including biocompatible and biodegradable polymers such as poly(methyl methacrylate); PMMA, poly(vinyl pyrrolidone); PVP, and poly(lactide-co-glycolides); PLGA [73]. This last polymer has been a subject to the most active research in the drug delivery field [5]. The release mechanism can also have several forms depending on the polymer system. Polymers available for drug delivery applications can be classified into four major categories [72]:

- Diffusion-controlled systems: which can be either a reservoir or a matrix formulation.
- Solvent-activated systems: where the drug is released by solvent action, i.e., osmotic pressure or swelling.
- Chemically-controlled systems: in which the body enzymes will break the bond between the drug and the polymer, or the polymer will gradually decompose.
- Magnetically-controlled systems: which have been used in cancer chemotherapy to localize the drug action to a specific area.

2.4.2 Supercritical Impregnation

As mentioned in Chapter 1, impregnation is one of the several processes where supercritical CO$_2$ can be used in polymer related applications. A highly attractive aspect of using supercritical fluids, especially in drug delivery applications, is the ability to produce solvent free materials after processing [76]. Avoiding organic solvents in the impregnation process eliminates possible toxic contaminants from the final product and eliminates the drying step which may cause the degradation of thermally labile additives. Supercritical impregnation also allows high control of impregnation by tuning the CO$_2$ properties [5].

The interest in supercritical impregnation was stimulated by the works of Sand [77]
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and Berens [78]. The patent by Sand described a method that can be used to impregnate a thermoplastic polymer with an impregnation material such as a fragrance, pest control agent, or pharmaceutical composition [77]. In a similar patent, Berens et al. described the use of compressed fluids above its critical point to infuse an additive into a polymer at low temperatures [78]. Following these works, several studies have been published on the fundamental and applied aspects of supercritical impregnation [62, 65, 71, 79–83]. A wide range of materials have been impregnated into polymers ranging from dyes, to metal complexes and biological molecules [5].

![Diagram](https://via.placeholder.com/150)

**Figure 2.6**: Interactions in the scCO₂-assisted impregnation system [55].

The role of the supercritical fluid in the impregnation process is twofold [55]. First, it acts as a swelling agent that will plasticize the polymer and opens the way for the solute molecules to diffuse inside the polymer matrix. Second, the supercritical fluid will be the carrier which delivers the solute. These roles are demonstrated in Figure 2.6. In addition to swelling, CO₂ acts as a molecular lubricant that facilitates the diffusion of the additive into the polymer matrix [84]. Two different mechanisms have been proposed for additive loading into polymers using supercritical fluids [64]:

- Additives with high solubility in CO₂ will be deposited inside the polymer matrix upon depressurization. In this case, the polymer will impede the additive
molecules from diffusing out with the CO₂.

- Additives with low solubility in CO₂ are impregnated due to their high affinity to the polymeric material compared to the supercritical fluid; i.e., high partitioning coefficient.

While the first case is advantageous in impregnating additives with low affinity to the polymer, there is a good chance that the additive material will recrystallize upon depressurization. Recrystallization is not favorable since it affects the dispersion of the additive on the polymer matrix and its dissolution rate. On the other hand, the second mechanism can lead to more molecularly dispersed blend but the loading is limited by the solubility of the additive in the supercritical fluid [64].

2.4.3 Impregnation Studies

In this section, the experimental techniques and apparatus usually used to study polymer impregnation in supercritical fluids are discussed. The general procedure for the impregnation process consists of three steps: (1) expose the polymer to the supercritical fluid for certain period of time, (2) introduce the solute-containing fluid to the polymer, and (3) release the fluid in controlled manner to trap the solute in the polymer [5].

**Figure 2.7**: Schematic plot showing the general setup used in impregnation studies. During the equilibration stage only valves 1 and 3 will be open, while in the impregnation stage only valves 2 and 4 will be open.
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A common setup used in the studies of supercritical impregnation of polymers is shown in Figure 2.7. In this setup, the impregnation process is monitored dynamically through measuring the concentration of the additive material in the CO$_2$ stream leaving the setup. The impregnation process starts by saturating the supercritical fluid with the additive material by passing the former through a column containing the additive (saturation column). In the same time, the polymer is swelled with pure CO$_2$ (no additive). After saturating the polymer with the CO$_2$, the path of the fluid leaving the saturation column is changed to pass through the polymer in the impregnation column. The fluid leaving the impregnation column is continuously monitored until no further change in the additive material concentration is observed. Usually, the concentration of the additive in the effluent fluid is detected by a UV/Vis spectrometer. Examples where such setup has been utilized include the impregnation study of several anti-inflammatory drugs in different polymers [85], impregnation of 5-fluorouracil and β-estradiol into PLGA [83], impregnation of cholesterol into PMMA and PMMA/poly(ε-caprolactone) microspheres [66], preparation of Pd and Pt doped CMS from polyimide (Figure 2.5) [62], and the impregnation of ethylcellulose/methylcellulose blends with naproxen [65].

The behavior of polymer films during and prior to impregnation was also investigated via static techniques. Berens et al. [86] used the mass loss analysis technique to determine the CO$_2$ and additive loads into polymers. Direct gravimetric measurements have also been used by Watkins and McCarthy in their novel polymer modification work [71]. Wang et al. [87] used confocal microscopy to perform ex-situ analysis of polypropylene samples impregnated under scCO$_2$ using the dynamic system described above, to examine the uniformity of the areal and depth distribution of a fluorescent probe. The diffusion coefficient of a dyestuff in poly(ethylene terephthalate) films was determined by Sicardi et al. using the film roll method [82]. In this method, a thin polymer film is rolled around a metal rod and fixed with clippers. The setup is then placed inside the supercritical medium that contains the additive material for a specific time. After the impregnation process is finished, the film is unrolled and cut into small pieces at known distances and the concentration in each piece is measured using, e.g., UV/Vis [82, 88].
2.5 Mass Measurements Under High Pressure

Studies that are often performed to characterize the physical and mechanical behavior of polymers include: (1) gravimetric, (2) dilation, (3) phase behavior, (4) morphological, and (5) rheological studies. In this section, the common analytical techniques applied to study the behavior of polymers under high pressures are reviewed. The focus here is on the gravimetric techniques or ones that are used to determine mass changes.

A survey of the current available literature on high pressure studies on polymers show that there are four categories of mass measurement techniques that have been used. These are techniques that are used to measure mass changes in-situ under high pressure. The techniques can be classified as either direct (measure mass change directly) or indirect (the mass is obtained by detecting other changes in the system).

2.5.1 Weighing methods

Weighing techniques are considered the simplest and are based on the direct measurements of the polymer sample mass [25]. These techniques were first used to study the diffusion of organic vapors into polymers. A more accurate version include the suspension of the polymer sample on a spring where the weight can be determined from the spring’s elongation. This system was used, for instance, in determining the diffusion of gases in fluoropolymers [22].

Another way of weighing under high pressures involves the direct measurements using a balance. Two kinds of balances have been used: the electromicrobalance and the magnetic suspension balance. The electromicrobalance (EMB) can be considered as an extension to the spring technique mentioned above. Examples of the use of such technique for high pressure systems can be found in the literature [89–92]. The magnetic suspension balance (MSB) is a widely used setup for high pressure applications. The MSB is similar to the EMB but in this case the sample is held by contactless, magnetic coupling under high pressures. This technique was utilized for studying sorption [93–95] and for adsorption on non-polymeric materials [96]. In both the EMB and MSB cases, it is important to compensate for the buoyancy effects which requires a prior knowledge of the volume changes.

An indirect weighing technique that is worth mentioning here is called the mass loss analysis (MLA). This technique involves equilibrating the polymer with the pressurized fluid for a certain time, rapid release of the pressure, then transferring the polymer sample
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onto a microbalance. The weight of the sample is monitored with time where time zero is
the moment at which the pressure was released. The mass-time curves are then fitted to a
diffusion model, usually Fickian, and the initial mass uptake is determined by extrapolating
the fitted curve to zero time. The MLA technique was utilized to measure CO$_2$ uptake into
several polymers, including PMMA, at different conditions [86, 97, 98].

2.5.2 Pressure decay method

The barometric or pressure decay method is probably the simplest among sorption techniques
in regard of its setup. The principle of this method is to record the pressure change in a
high pressure cell containing the polymer sample. The change in pressure versus time can
be converted to mass change by a proper equation of state or PVT data. The drawback
of this technique is that it requires an accurate equation of state or PVT data to be able
to predict the amount of gas absorbed from the pressure change [5]. This technique is also
sensitive to pressure leaks which might be a challenge especially for slow sorption processes.
Examples of studies that utilized this method are those in references [23, 99, 100].

2.5.3 Chromatographic method

A technique that has been utilized for a while to determine the partitioning coefficient
between a solute and a supercritical fluid is the supercritical fluid chromatography (SFC)
[85, 101, 102]. In SFC, the polymer is used in the chromatograph column and the retention
time of the solute is measured.

In a recent work, a technique was developed to determine the sorption of CO$_2$ into
polymers using gas chromatography (GC) [103]. This was accomplished by mixing a known
amounts of CO$_2$ and a non-absorbable probe (e.g., argon) and equilibrating the mixture with
a certain amount of the polymer. A sample of the fluid phase is then withdrawn from the
mixture and its composition is analyzed using GC. Preliminary results from this technique
were in good agreement with previous studies performed with different techniques.

2.5.4 Frequency modulation methods

Frequency modulation techniques measure mass changes at high pressures by evaluating
changes in the frequency of certain acoustical devices. Two type of devices have been used:
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the vibrating beam technique (VB) and the quartz crystal microbalance (QCM). The latter will be discussed in details in Chapter 3. The VB technique consists of a vibrating beam made of special magnetic material on which the polymer sample is attached to its free end. A magnetic coil is used to excite the beam into vibration. The frequency and amplitude of this vibration are then measured using a strain gauge attached to the beam. From the change in the frequency the change in mass can be extracted [104].

2.5.5 Dissolution measurements

Contrary to sorption, very few kinetic studies have been performed on polymer dissolution in CO$_2$. Most of the available analysis is concerned with determining the phase behavior of polymers under different conditions [53]. The scarcity of kinetic studies is probably due to the low solubility of most polymers in CO$_2$. One study on the dissolution of a fluorinated polymer in CO$_2$ was reported [105]. This study utilized an interferometric dissolution rate monitor technique to measure the change in thickness with time of a spin coated film of a copolymer of tetrahydropyranyl methacrylate and 1H,1H-perfluoroctyl methacrylate. The copolymer was coated on a Si substrate to produce films with $\sim$ 1 $\mu$m thickness. The calculated dissolution rate in this study ranged from $\sim$ 0 to more than 100 nm/s. This rate increased dramatically with pressure. The rate was also found to depend on polymer thickness; thicker films dissolve faster. This dependence on the film thickness was contributed to the large role surface interactions play in the thinner films. Finally, the dependence of the rate on film thickness increased with pressure.
Chapter 3

Quartz Crystal Microbalance

Quartz is one of the ionic crystalline materials with structure lacking a center of inversion [106]. Therefore, a single crystal will possess a polar axis associated with the orientation of atoms in the crystalline lattice [107]. As a consequence, if the crystal is deformed due to a mechanical pressure, an electrical current will be generated. This is the well-known phenomenon of piezoelectricity. Similarly, if an electrical field is applied across the crystal, the polar dipoles will be displaced in a specific direction causing an elastic deformation in the crystal. This phenomenon is known as reverse piezoelectricity.

If a certain potential is applied across two parallel surfaces of a quartz slab, the crystal will deform in a certain direction. If the applied potential polarity is inversed, the crystal will deform in the opposite direction. Hence, an applied AC voltage will cause a periodic deformation in the crystal. The direction of the deformation depends on the angle at which the crystal is cut giving rise to several oscillatory modes such as the thickness shear, the surface acoustic wave, the flexural mode, and the shear horizontal acoustic plate modes as shown in Figure 3.1 [108]. The frequency at which the crystal is made to oscillate is directly related to the applied voltage frequency. By selecting a proper frequency, resonance can be achieved. This frequency is usually called resonance or natural frequency. The sensitivity of the resonance frequency to the surrounding environment is the operation principle of a family of analytical tools called the piezoelectric oscillators.

The Quartz Crystal Microbalance (QCM) is probably the most commonly used member of the piezoelectric oscillators family. The QCM operates under thickness shear mode (TSM) where resonance is achieved when the wavelength is half the thickness of the quartz. The TSM mode is achieved through cutting the quartz crystal at a range of cuts known as the Y-cut family, which includes the AT-cut (at 35° 25′) and BT-cut (at 49° 0′) as shown in Figure 3.2 [109]. Because of symmetry considerations, only the resonance frequency its odd
harmonics can be excited [110]. Due to mechanical losses in quartz, the crystal will oscillate at a spectrum of frequencies instead of one discrete value. The quality factor, $Q$, is used to describe these mechanical losses. $Q$ can be defined as the ratio of the resonant frequency to the full width of frequency at half the maximum amplitude of conductance [111].

### 3.1 Sauerbrey Equation

The resonance frequency of a crystal occurs when the shear wave has a length equal to half the crystal thickness or its odd multipliers. The wave for this case will have a zero amplitude at the crystal’s center, known as the wave’s node, and a maximum at the crystal boundaries,
Chapter 3. Quartz Crystal Microbalance

Figure 3.2: The assignment of axes to a quartz crystal, and different common axes of cut.

know as the anti-nodes. This can be written as:

\[ F_0 = \frac{u_q}{2t_q} \]  

(3.1)

where \( F_0 \) is the resonance frequency, \( u_q \) is the acoustic wave velocity in quartz, and \( t_q \) is the quartz thickness. By simple manipulations, Eq. (3.1) can be used to derive a relation between the change in frequency to the change in thickness (or, in other words, mass if the density is known) as follows:

\[ \Delta F = -\frac{2F_0^2}{\sqrt{\rho_q \mu_q}} \Delta m. \]  

(3.2)

Here, \( \Delta F \) is the change in frequency due to a mass change of \( \Delta m \), \( \rho_q \) and \( \mu_q \) are the quartz density and elastic shear modulus, respectively. This equation is the well-known relation
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derived by Sauerbrey in 1959 and named after him [112]. The main assumptions behind Eq. (3.2) is that the applied mass has negligible thickness with respect to the crystal and that the film has similar acoustic properties to quartz [111]. While such assumptions hold true to many metallic films up to a relatively high thicknesses, non-metallic materials, especially polymers, can show significant deviations. These assumptions and others are discussed in several references [106, 108, 113].

3.2 Electrical Circuit Analogy

In QCM studies, a useful analogy is made between the vibrating quartz crystal and an equivalent electrical circuit. If an ideal crystal, i.e., crystal with no internal friction, is excited by applying a DC voltage for a short time, upon removal of this voltage the crystal will continue to oscillate by virtue of its inertial and elastic energies [107]. This is similar to a swinging pendulum in frictionless surroundings, where the oscillation continues by cyclic transformation of potential and kinetic energies. In electrical circuits, the so called tank circuit shows an identical “swinging” behavior in terms of current and voltage. The tank circuit is composed of an ideal capacitor and an ideal inductor in series. For such circuit, if a voltage is applied for a short period of time, the energy will keep oscillating between the inductor, which stores the energy in the from of magnetic field, and the capacitor, which stores the energy in the from of electrical potential. For a non-ideal crystal, friction imposes a resistance that will cause dissipation of the stored energy. Similarly, in the tank circuit, a resistance can be added in series to the inductor and capacitor, which will cause energy dissipation.

The resulting aforementioned circuit does not represent the QCM system completely; one more component needs to be added. This is due to the piezoelectric nature of quartz, which couples the mechanical and electrical energies through the piezoelectric constant. A brief description of commonly used commercial QCM crystals follows to help explaining this point.

Commercially available QCM crystals are usually made of thin quartz desk with metal electrodes deposited on both sides. The disk is usually half an inch in diameter with portion of the central region fully plated on both sides [114]. Going back to the equivalent circuit representation, the two metal electrodes deposited on both sides of the crystal with the
quartz sandwiched between them will act as a capacitor. Taking into consideration the fact that this is an electromechanical process, it becomes necessary to include this last component, the capacitance, although it does not directly interfere with the motional crystal. Because this capacitance does not depend on the quartz deformation, it should be added to the circuit in parallel. For this reason, the first group of components (the inductor, capacitor, and resistor in series) is called the motional arm, and the second component (the capacitor) is called the static arm. Figure 3.3 is a representation of this circuit, which is also known as Butterworth-Van Dyke (BVD) equivalent circuit for unperturbed quartz microbalance [115].

![Figure 3.3: Butterworth-Van Dyke equivalent circuit for an unperturbed QCM.](image)

This analogy have several advantages [115]. One advantage is that, with only few lumped elements, this model simulates the electrical characteristics of the QCM over a range of frequencies near resonance. Ideally, the model should explicitly relate the circuit elements to physical properties of the QCM as well as surface mass layer and contacting liquid. This allows easier prediction of the QCM behavior. As an example, if the mechanical model for an unloaded QCM is solved and compared to the corresponding circuit model, the following
relations are obtained:

\[ C_0 = \frac{\epsilon_{22} A}{h} \]  
\[ C_q = \frac{8K_0^2 C_o}{(N\pi)^2} \]  
\[ L_q = \frac{1}{(2\pi F_0)^2 C_q} \]  
\[ R_q = \frac{\eta_q}{\bar{c}_{66} C_q} \left( \frac{F}{F_0} \right) \]

where \( \epsilon_{22} \) is the quartz permittivity, \( A \) is the active area of quartz (the area of the smallest electrode), \( h \) is the crystal thickness, \( K_0 \) is a quartz constant related to the electromechanical coupling constant, \( N \) is the harmonic number \((1, 3, 5, \ldots)\), and \( \eta_q \) is an effective quartz viscosity used to take into account any mechanical losses, and \( \bar{c}_{66} \) is the piezoelectrically stiffened quartz elastic modulus [115]. These relations are useful when performing impedance analysis (see next section) on the QCM. Another advantage of the analogy is that standard circuit analysis software can be used to extract information from electrical measurements made on the QCM. This analogy is also useful when the crystal is under external load, \( e.g., \) film deposition or liquid medium [107].

### 3.3 Impedance analysis

The similarity between the QCM and the BVD circuit suggests that electrical circuit measurements can be applied to the QCM. Specifically, the so-called impedance (or network) analysis can be used to determine the values of the circuit components [107]. Impedance analysis involves measuring the current resulting from a certain system at known applied voltage over a specified range of frequencies. In the QCM, this can be done because of the piezoelectric nature. Such analysis can elucidate the properties of the quartz as well as the interaction of the crystal with the contacting medium [107].

The way impedance analysis is performed on QCM is analogous to that for electrical circuits. A certain voltage, having known frequency, is applied to the crystal, the piezoelectric effect will cause the crystal to oscillate and generate an electric current, which is measured. Resonance can be found when the current reaches its maximum, or the impedance reaches
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its minimum. Beside resonance frequency, the magnitude and phase shift of the current are also measured. Knowing the current’s magnitude and phase allows the impedance (or admittance) of the quartz crystal to be calculated.

3.4 Factors Affecting the QCM Behavior

While the high sensitivity of the QCM makes it a unique analytical technique, it imposes a substantial challenges due to the large number of factors that can perturb the QCM operation. Therefore, it is important to comprehensively study the different factors that can affect the QCM operation in order to separate their effects and make correct conclusions. These factors are the subject of this section.

3.4.1 Mass change

Equation (3.2) is the well known Sauerbrey relation that has been applied extensively for mass calculations from frequency data. This equation is usually written as:

\[ \Delta F_m = -C_m \Delta m \]  

(3.7)

where \( C_m \) is the mass sensitivity constant and is equal to 56.6 Hz·µg\(^{-1}\)·cm\(^2\) for a 5 MHz crystal. The advantage of this equation is that it is independent of the deposited mass properties, i.e., \( C_m \) is only a function of quartz properties. However, due to the implied assumptions in this equation, its applicability is limited to frequency changes about 2% of \( F_o \) for rigid films, e.g., metal films. Lu and Lewis [113] presented a more accurate relation, based on the work of Miller and Bolef [116] which can be written as [117]:

\[ \frac{m_f}{m_q} = -\frac{z_f F_o}{z_q \pi F} \tan^{-1} \frac{z_q}{z_f} \tan \frac{\pi F}{F_o} \]  

(3.8)

where \( z_i = \rho_i \nu_i \), and \( c_i \) and \( \nu_i \) are the shear stiffness constant and the wave velocity in the quartz (\( q \)) and film (\( f \)). The validity of this equation has been experimentally justified up to mass loads of 70%, however, it requires the film properties to be known apriori [117].
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3.4.2 Viscous effects

The nature of the medium surrounding the QCM greatly affects its behavior. In fact, it was initially believed that the mechanical losses of the oscillating quartz if immersed in a viscous medium will be very high that the oscillation will cease [110]. Therefore, it is expected that the use of the QCM will be more difficult in viscous media than under vacuum because [118]:

1. The high damping caused by the medium in contact with the quartz surface resulting in a large loss in the quality factor and a decrease in the phase gradient.

2. The observed frequency shift is not only due to mass loading, but also to the viscous coupling with the surrounding medium.

In representing the additional effect of viscous media on the quartz crystal using the analogous electrical components, several analysis were made [110]. Commonly, the viscous medium is assumed to increase the mechanical losses and to introduce an additional mass loading on the crystal surface. This is equivalent to adding a resistor and an inductor in series with the motional arm in the BVD equivalent circuit [107], see page 31. Another effect arises from the parasitic capacitance from the test fixture, which, i.e., the capacitance, arises from the external fields surrounding the QCM. This was accounted for by an additional capacitor in parallel with the motional arm [115].

The effect of viscous coupling on the frequency was quantified by Kanazawa and Gordon [119]. The change in frequency was found to be:

$$\Delta F_\eta = -0.5C_m(\pi F_o)^{1/2}(\rho_f \eta_f)^{1/2}$$

(3.9)

where $\rho_f$ and $\eta_f$ are the density and shear viscosity of the fluid medium surrounding the crystal, respectively. This equation was derived for Newtonian fluids. The same relation was also obtained using a transmission-line model for immersed QCM by Filiâtre et al. [120]. Using this equation, the density-viscosity product for a mixture of ethanol and water was estimated and found to be in good agreement with the tabulated values [119, 120].

When studying polymer films with the QCM, another source of viscous coupling is introduced due to the viscoelastic nature of polymers. This effect from the polymer film must be added to that of the fluid to avoid its incorrect interpretation as mass change [121].
Since Eq. (3.9) was derived for viscous fluids, it cannot be used to account for the viscous contribution from polymer films. As a result, the situation becomes more complex, and large deviations from the ideal behavior may occur depending on the physical properties of the film [122].

An attempt to account for this non-gravimetric effect on the mass calculations was presented by Johannsmann and coworkers [123, 124]. The following relation was proposed:

\[
\frac{\Delta F^*}{F} \approx -\frac{2F_0}{(\rho_q\mu_q)^{1/2}} \Delta m \left[1 + J \frac{4\pi^2 \Delta m^2}{3\rho \mu q} F^2 \right] \tag{3.10}
\]

where \( J = J' - iJ'' = 1/G \) is the shear compliance of the polymer film and \( \rho \) is its density. The change in the complex frequency \( \Delta F^* \) can be written as \( \Delta F + i\Delta \Gamma \) where \( \Delta \Gamma \) is the change in the bandwidth. From Eq. (3.10), a plot of \( \Delta F/F \) versus \( F^2 \) should give a straight line the intercept of which can be used to determine the mass change. It is also possible, using the same plot, to determine the complex compliance of the film using the slope. Unfortunately, this method requires the use of a network analyzer to obtain the necessary frequency and bandwidth changes. It is not possible to obtain such information with the conventional oscillator circuit method [125] which is the technique used in this study.

However, a useful criterion to study viscous coupling is through measuring the QCM resistance. Since viscous coupling affects the mechanical losses experienced by the QCM, both the frequency and resistance will change as a result of this viscous loading. Mass loadings, on the other hand, will only affect the frequency and has negligible effect on the resistance. The relation between crystal resistance and the product of viscosity and density for a QCM at its first harmonic resonance was determined, for a Newtonian fluid, to be [126]:

\[
\Delta R = \frac{\pi}{8K^2 C_o} \left( \frac{\rho_f \eta_f}{\pi F_0 \mu_q \rho_q} \right)^{1/2} \tag{3.11}
\]

where \( K^2 \) is the quartz electromechanical coupling coefficient (\( = 7.74 \times 10^{-3} \)), \( C_o \) is the static capacitance of the crystal (\( = 4.25 \text{ pF} \)). From this relation, the change in the QCM resistance is expected to be linear with the density-viscosity product if the polymer film has no effect on the resistance. As will be seen in the following chapters, this is not always true.
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3.4.3 Temperature

The piezoelectric nature of quartz will be severely affected upon approaching phase transition temperature 573 °C where the quartz loses its piezoelectric nature [127]. Therefore, it is usually not recommended to used the QCM at temperatures above 300 °C.

The advantage of AT-cut quartz crystals is the fact that it has a very small temperature coefficient near room temperature [106]. If large temperature changes are experienced, it becomes necessary to account for this contribution. Rahtu and Ritala [127] presents a method to compensate for such effect using a reference crystal and a modeled baseline. More on the temperature effect can be found in the reference by Wang et al. [128]. It should also be kept in mind that changes in temperature may have an effect on the surrounding medium properties, especially liquids, which will affect the QCM response.

3.4.4 Pressure

Pressure has a compression effect on the QCM, which causes the frequency to increase linearly with increasing pressure. For the case of liquids, where one side of the crystal is exposed to the liquid medium and the other to air, the difference in hydrostatic pressure causes surface stresses, and the relation between the change in frequency and pressure difference is believed to be parabolic [107]. This effect, however, seems not to be very important, since the pressure generally will be constant during the experiment.

For gases, original studies by Stockbridge reported the following relation between the frequency and pressure:

\[
\frac{1}{F_o} \frac{dF}{dp} = 15 \times 10^{-10} \left( 1 - \sqrt{\frac{M}{165}} \right)
\]  

(3.12)

where \(F\) is in Hertz and \(p\) in torr and \(M\) is the gas molecular weight. This relation was proposed for pressures between 100 and 1000 torr. However, Park et al. [129] showed experimentally that a similar relation can still be used for pressures well above 1000 torr. The relation given by Park et al. is written as:

\[
\alpha = \frac{1}{F_o} \frac{dF}{dp} \rightarrow \Delta F_p = \alpha F_o \Delta p
\]  

(3.13)
where the constant $\alpha$ depends on temperature according to:

$$\alpha = 1.095 \times 10^{-5} - 2 \times 10^{-8}T$$ (3.14)

In the above two relations $p$ is given in MPa and $T$ in °C. Wu et al. [130], using the same system as the one used in this work, confirmed that such relations are valid by measuring the change in frequency for adsorbing and non-adsorbing gases.

### 3.4.5 Surface roughness

The issue of surface roughness effect on the frequency response and its interaction with other parameters in the system has been considered for the case of bare [131] and coated [132] QCM crystals in solution. The non-uniform morphology of the surface can affect the frequency in two ways. First, it can result in the entrapment of the fluid within the surface crevices. This factor increases the mass load but will have small effect on energy dissipation. The second factor is the non-shear coupling generated by the movement of the surface asperities in the fluid which will contribute to the energy dissipation [133].

Frequency change due to surface roughness is a function of the fluid properties and surface morphology [131, 134]. The general form of the relation for the change in frequency contributed to the surface roughness was written as [134]:

$$\Delta F_r = \Psi \Delta F_\eta$$ (3.15)

where $\Delta F_\eta$ is defined by Eq. (3.9) and $\Psi$ is a function that depends on the surface morphology. The difficulty in determining an analytical expression for $\Psi$ is highly limiting the use of Eq. (3.15). Attempts to simplify this relation was made by experimentally analyzing the response of QCM crystals with different surface morphologies. Park et al. [129] proposed the following relation:

$$\Delta F_r = -H \cdot \rho_f$$ (3.16)

where $H$ is a constant that depends on the surface roughness. A similar approach was taken by Wu et al. [130] who proposed the following relation:

$$\Delta F_r = -0.5C_mC_r\rho_f$$ (3.17)
where $C_m$ is the constant from Eq. (3.7) and $C_r$ is defined as:

$$C_r = (a + b\delta)\frac{\xi}{\xi_o}$$  (3.18)

The constants $a$, $b$, and $\xi_o$ depend only on the crystal morphology, while $\xi$ depends on the surface morphology and the adsorbed material. $\delta$ is the decay length of the fluid near the QCM surface given by $(\eta_f/(\pi F_o \rho_f))^{1/2}$. While Eqs. (3.16) and (3.17) greatly simplify the expression for $\Delta F_r$, the parameters used within these equations must be experimentally determined.

### 3.5 General Applications of the QCM

The QCM is a very powerful sensor: it responds to extremely small changes in mass, as low as pg/cm²; it can be coated, theoretically, with any material to make it sensitive to specific reagent of interest; it has a very high response time in the order of microseconds; it occupies a small volume and can be used for in-situ measurements; and it is inexpensive. These merits are reflected on the wide range of applications where the QCM has been utilized.

Commercially, the QCM has been used as thickness monitors for vacuum deposition systems. This kind of gravimetric measurements comprises the major section of QCM’s applications. Examples of such applications are: monitoring the detergency process [135], removal of solid organic soils from hard surfaces [136], surfactant adsorption [137], submonolayer deposition [138], biological species adsorption [139–141], and electrochemical processes monitoring [142, 143].

While the main use of the QCM is in gravimetric measurements, other non-gravimetric applications have been performed. For example, Wang et al. used a QCM crystal for pH measurements by coating the crystal with a polymer film that exhibits large changes in frequency upon changing the pH [144]. Another example includes measuring polymers shear modulus. This was done by measuring the change in the QCM current’s amplitude and phase. These changes indicate a change in the physical properties of the film on top of the crystal [145]. QCM was also used as a scanning electrode to determine the surface topography of metal coatings. In this case, a quartz crystal coated with a metal film was actuated using a thin gold wire that scans over the crystal surface. The change in frequency
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from one point to another is then used to determine the local thickness at the scanning point [146].

The QCM was used by the author to study the deposition of self-assembled monolayers (SAM) of an octadecyltrichlorosilane (OTS) on silicon substrates [147]. The OTS is an important surface modification agent that can produce highly hydrophobic surfaces. In this study, deposition of OTS on Si-coated QCM was monitored at different initial OTS concentrations by recording the changes in the QCM frequency and resistance. It was found that a highly viscous layer of crosslinked OTS formed near the Si surface which caused a high increase in the QCM resistance. More details on this study and the obtained results can be found in Appendix D.

3.6 QCM for High Pressure Systems

A similar discussion to that in Section 3.4 can be applied for high pressure systems. In general, for an isothermal system, the overall frequency change can be written as:

\[ \Delta F = F - F_0 = \Delta F_m + \Delta F_\eta + \Delta F_p + \Delta F_r \tag{3.19} \]

The different terms on the RHS of this equation can be estimated using the appropriate equations from Section 3.4. It is, however, commonly accepted that surface roughness contribution (\( \Delta F_r \)) is usually small compared to the other terms. Because of this, and due to the difficulty of its estimation, it has been a common practice to omit the roughness term from the equation. Indeed, all studies reviewed in the next section does not consider the roughness effect. A previous study on the system used in the work presented in this thesis [130] has shown that when a smooth crystal (rms less than 5 nm) is used, the surface roughness effect can be reduced significantly.

3.6.1 Literature review

The number of studies that utilized the QCM under high pressures is limited. These studies can be divided into two categories: fundamental and applied studies. The first category was focused on characterizing the bare QCM behavior under different gases. Examples of such studies are that by Otake et al. who determined the mass of CO\(_2\), N\(_2\) and He adsorbed...
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onto a silver QCM surface at 40 °C and pressures up to 5800 psi [148]. A similar study was published by Tsionsky et al. [149] on the QCM behavior in non-adsorbed gases with emphasis on the effects of surface morphology. Two more studies were published recently dealing with the same subject [129, 130].

Applied studies, on the other hand, involve the use of QCM for microweighing purposes, usually to determine solubility of gases in polymers. The first demonstration of the QCM applicability for such studies was by Bonner and Cheng who studied the sorption of N\textsubscript{2} in polyethylene (PE) at 125 °C and showed a good agreement with literature results obtained by the pressure decay technique [150]. Aubert reported the solubility of CO\textsubscript{2} in a variety of polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and Teflon at 35 and 40 °C and pressures up to 1500 psi using the QCM technique [151]. Miura et al. studied the solubility and adsorption of CO\textsubscript{2} in PS at 40 °C and pressures up to 2500 psi [152]. In their work, the expected amount of CO\textsubscript{2} adsorbed on the surface was estimated by measuring the total solubility of CO\textsubscript{2} at different pressures for three PS films with different initial masses. Zhang et al. studied the sorption of CO\textsubscript{2} into glassy PMMA films at different temperatures [153]. The most recent study to apply the QCM for polymer systems was that by Pantoula and Panayiotou [98, 154]. These authors measured the solubility of CO\textsubscript{2} in PMMA and PS films was measured and compared to results obtained by the mass loss analysis (see page 24) and with literature data. According to the authors, the QCM was only applicable for pressures below the glass transition of the polymer which occurs at about 1000 psi.

Few studies can also be found on non-polymeric systems under high pressures. Guigard et al. evaluated the adsorption of CO\textsubscript{2} on a gold QCM electrode and determined the solubility of bis(acetylacetonato) copper (II) and bis(thienoyl trifluoroacetonnato) copper (II) in CO\textsubscript{2} at 40 °C and 1500 psi [155]. Okahata’s and coworkers used the QCM to investigate the nucleobase molecular recognition in supercritical CO\textsubscript{2} [156, 157]. Other QCM studies include the evaluation of the inclusion behavior of guest molecules to a solid apohost in scCO\textsubscript{2} [158], and probing the phase transition of pure and mixed fluids [159, 160].
3.6.2 Sources of error

Generally speaking, two main challenges largely limit the use of QCM. First, the ability to obtain quantitative information from the QCM is still limited. Second, the reproducibility with this technique is poor due to its high sensitivity and to the large number of variables that can interfere with its operation.

When polymer films are considered, some questions are raised concerning the accuracy of the QCM results. The two main concerns are whether the viscoelastic nature of the film and the stresses due to the sorption-induced swelling will affect the frequency change. The viscoelasticity effect can be caused by polymers with low glass transition or by the plasticization induced by sorption of small molecules. While these issues are applicable to other systems, the following discussion is focused on high pressure studies only.

Due to the above mentioned factors, some researchers were reluctant to apply the QCM for polymeric materials above the glass transition point [98, 161] or to use it at all [162]. Most notably, the report by Banda et al. [162] argued that such effects can cause frequency changes as great as or greater than the frequency change due to the mass uptake itself if the film thickness is large. It is, therefore, necessary to set a limit for the acceptable range of thickness in which the Sauerbrey equation is valid.

As discussed in Section 3.4.1, the Sauerbrey equation is expected to apply up to 2% change in frequency. For a 5 MHz crystal, this is translated into $\sim 7.5 \mu$m for a typical polymer film. Indeed, several analysis had shown that such thickness is still within the range of applicability for the Sauerbrey equation even for soft polymeric films [122, 163, 164]. However, when the absorbtion of a plasticing agent is involved, this range becomes unacceptable. Some authors suggest that the film thickness should not exceed 100 nm [162]. However, it will be shown, in the following chapters, that films up to 1 $\mu$m thick still give satisfactory results.

3.7 QCM Setup

3.7.1 QCM system

The quartz crystals used in this study were 5.00 MHz AT-cut. The crystals, as obtained from International Crystal Manufacturing (Oklahoma City, OK), had a blank diameter of
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8.5 mm and a thickness of 0.25 mm. An Si film (6 mm diameter and 0.1 µm thickness) was vacuum sputtered over an Au electrode; the gold provides the necessary electrical actuation to the quartz. The rms surface roughness for the crystals is less than 10 nm (analyzed using Atomic Force Microscopy [130]). The crystal is connected to an oscillator circuit (Maxtek model PLO-10). This oscillator provides two outputs, frequency and voltage; the voltage reading is inversely proportional to the crystal’s resistance. The oscillator is connected to an Agilent 225 MHz Universal Frequency Counter (model 53131A) to read the frequency of the vibrating crystal. Temperature, pressure, voltage, and frequency readings are acquired using LabView.

![QCM setup diagram](image)

**Figure 3.4:** QCM setup.

3.7.2 Pressure cell and apparatus

The custom built pressure cell was a thick-walled cylinder (I.D. 63.5×200 mm), with a high-pressure electrical feedthrough (Conax Buffalo Technologies) at the top end to drive the QCM. The cell had an inside volume of 25 cm³ and a maximum working pressure of 7500 psi. During an experiment, the crystal was placed into the cell and connected to the oscillator through the electrical feedthrough. A high-pressure thermocouple (Omega) was placed in the cell to indicate any variation in the temperature of CO₂ fluid. The pressure inside the cell was monitored using a pressure transducer (Omega) with an accuracy of
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0.02% of the reading. The whole assembly was then placed in a water bath and controlled to 0.1 °C. The required pressure was achieved via an ISCO pump (model 260D, ISCO, Inc.) which can provide pressures up to 7500 psi. The setup is shown in Figure 3.4.

![Figure 3.4: Schematic diagram of the assembly showing the temperature control and pressure application.](image)

**Figure 3.4:** The frequency components of an uncoated Si QCM at 36 °C. The experimentally measured $\Delta F_T$ represents the raw data. The values of $\Delta F_p$, $\Delta F_\eta$, and $\Delta F_m$ were calculated as discussed in the text.

3.8 Studies on Uncoated QCM in CO₂

3.8.1 Frequency components

To illustrate the use of Eq. (3.19), a sample of the QCM results for an uncoated crystal is shown in Figure 3.5. In this figure, the pressure contribution ($\Delta F_p$) and the viscosity
contribution ($\Delta F_\eta$) were determined using Eqs. (3.13) and (3.9), respectively. The value of $\Delta F_m$ was calculated from:

$$
\Delta F_m = \Delta F_T - \Delta F_p - \Delta F_\eta
$$

(3.20)

Here, $\Delta F_T$ is the experimentally measured frequency change. This is the basic relation used throughout this document to determine the mass change. It can be seen from Figure 3.5 that $\Delta F_\eta$ has a considerably smaller contribution to the total frequency change compared to that of the pressure $\Delta F_p$. This is specially evident in the low pressure regime, i.e., gas phase regime, but slightly increases as the more viscous supercritical phase is approached. It must be noted that $\Delta F_p$ will have a positive value at all pressures, while $\Delta F_\eta$ is always negative. Therefore, as the pressure increases, the total frequency will increase due to the pressure effect while the viscosity will have an opposite effect. The large difference between $\Delta F_T$ and $\Delta F_p$ highlights the tendency of CO$_2$ to adsorb on Si surfaces. For non-adsorbing gases, such as He, the total frequency change was almost identical to that predicted from $\Delta F_p$ and $\Delta F_\eta$ [130].

3.8.2 CO$_2$ adsorption

To demonstrate the extent of CO$_2$ adsorption, the frequency change ($\Delta F_m$) is plotted in Figure 3.6 as function of pressure. The equivalent mass, according to Eq. (3.7) is shown as will. If the CO$_2$ molecule is assumed to have a diameter 4.53 Å [165], the number of theoretically backed monolayers of CO$_2$ molecules can be calculated. For 36 °C and 1500 psi, for instance, the number is about 120 monolayers which corresponds to 55 nm. If the calculation is made based on a liquid like density near the surface (0.77 g/cm$^3$) [166], 78 nm is obtained. These values are considerably higher than previously reported ellipsometry measurements for the adsorption of CO$_2$ onto Si wafers [166] which is believed to be due to the differences in the surface roughness in both cases.

3.8.3 Resistance calibration

As mentioned earlier, the oscillator circuit used in this work can measure the resistance and the frequency of the QCM. While the resistance value is not used for quantitative
measurements, it can be very useful if comparison with a reference state is made or if its general trend is examined. Therefore, the change in resistance was recorded together with the frequency and will be used in the next chapters.

The circuit, as provided by the manufacturer, does not output the resistance values directly. Instead, it measures a DC voltage proportional to the crystal’s conductance (conductance \( \equiv 1/\text{resistance} \)). Therefore, in order to obtain the crystal’s resistance, the voltage reading must be calibrated. The relation between the resistance and voltage given by the manufacturer is:

\[
R = \frac{100}{V} - 20 \tag{3.21}
\]

where the constant 100 is a scaling factor and 20 \( \Omega \) represents the circuit’s internal resistance. This relation was tested by recording the voltage of an uncoated crystal in CO\(_2\).
Equation (3.11) in Section 3.4.2 gives a theoretical expression for the change in the QCM resistance as a function of the density-viscosity product ($\rho \eta$) for a Newtonian fluid. For CO$_2$, the values of $\rho \eta$ can be easily obtained [9] and the expected change in resistance ($\Delta R_{\text{calc}}$) can be calculated. By plotting this resistance change versus the reciprocal of the measured voltage the proposed linear relation between the two values can be checked. This is done in Figure 3.7. The linearity is evident in the figure, confirming the voltage relation to $\Delta R$. The scaling factor, however, was found to be 32 $\Omega \cdot V$. The discrepancy between this value and that provided by the manufacturer might be due the differences between the systems in both cases. The manufacturer value was obtained from measurements in liquids using QCM...
crystals with one exposed face. The internal resistance of the circuit, on the other hand, should not depend on the system. Therefore, the following relation will be used whenever the resistance is to be estimated:

\[
\Delta R = \frac{32}{V} - 20
\]  

\[(3.22)\]

Figure 3.8: Change in resistance \( \Delta R \) as a function of CO\(_2\) properties at different temperatures. The straight line represents Eq. (3.11).

The above calibration was tested against a different set of experiments. In Figure 3.8, \( \Delta R \) was calculated from the measured voltage using Eq. (3.22) and plotted against the square root of the CO\(_2\) density-viscosity product. Good agreement was found for temperatures below and above the critical temperature.
3.8.4 Surface morphology

To demonstrate the effect of surface morphology, experiments were conducted with crystals having different surface finishing. Smooth crystals refer to those that were polished after deposition, while rough refers to crystals that were not polished. The rms roughness of the smooth crystals was measured with atomic force microscopy (AFM) and found to be \( \sim 3 \) nm. The rough crystals have an rms greater than 100 nm.

![Figure 3.9: Comparison between the change in frequency for smooth and rough crystals at 35 °C.](image)

The change in frequency \( (\Delta F_m) \) is shown in Figure 3.9 for both types of crystals at 35 °C. The change in the case of rough surfaces was 2.5 times greater than the smooth ones. As stated in Section 3.4.5, the roughness contribute by trapping CO\(_2\) within the surface crevices and by introducing a non-shear viscous coupling. If significant, the second factor
is expected to affect the crystal’s resistance. A comparison between the measured \( \Delta R \) for both crystals is shown in Figure 3.10. The two crystals show an identical behavior.

![Graph showing comparison between smooth and rough crystals](image)

**Figure 3.10:** Comparison between the change in resistance (\( \Delta R \)) for smooth and rough crystals at 35 °C.

From the above discussion it can be concluded that the difference between the response of the smooth and rough crystals is mainly due to the additional \( \text{CO}_2 \) loading in the later case. This conclusion, however, must be considered with caution. In Section 3.8.2 it was stated that the measured \( \text{CO}_2 \) uptake using the QCM is considerably higher than the reported one. Since the \( \text{CO}_2 \) density near the surface was found to be higher than the bulk value, the larger change in frequency might be due to a higher viscous contribution that was not accounted for by Eq. (3.9).
Chapter 3. Quartz Crystal Microbalance

3.9 Conclusions

The quartz crystal microbalance (QCM) is a highly sensitive technique that can be used in a wide range of applications. While mass measurements is the most common, the QCM can be used, for example, in chemical analysis, determination of the shear modulus of polymers, and detection of phase transition.

Several factors affect the QCM response. Contribution from changes in mass are usually the main factor. Pressure and viscous coupling contributions can be significant and are reasonably estimated with specific analytical expressions. Other factors, such as surface roughness, cannot be estimated readily. For polymer films, the viscoelastic nature of the polymer can contribute to the total frequency change; impedance analysis is require in order to quantify such contribution.

A limited number of studies exist that utilize the QCM in high pressure systems. The majority of these studies examined the sorption of small molecules into polymers. In all of these sorption studies, the relations used to estimate the mass change were those mentioned in Eq. (3.20). Objections on the accuracy of such calculations have been reported. These objections are mainly concerned with the viscoelastic effects of polymers and the swelling-induced stresses which might affect the total frequency change. If such factors are significant, the estimated apparent mass uptake can be higher than the actual uptake. This issue is discussed in more details in the next chapter.

Experiments on the uncoated QCM crystal was presented. The basic relation that will be used to determine the mass uptake was shown. In this relation, the measured frequency is corrected for the pressure and viscosity effects to give the net contribution due to mass changes. The use of this equation was demonstrated on the adsorption of CO$_2$ onto silicon surface.

The relation between the measured QCM resistance and the density-viscosity product was tested. Excellent agreement between the theoretical values and the measured ones where obtained. Although the resistance will not be used for quantitative calculations, the change in the resistance value has proved to be of great importance in examining the QCM behavior, as will be shown in the following chapters.

Finally, the effect of surface morphology on the adsorbed CO$_2$ was presented. It was found that for the rough surface the adsorption was 2.5 times higher that the smooth one.
Chapter 3. Quartz Crystal Microbalance

The resistance, on the other hand, was identical in both cases. This behavior indicates that the higher frequency change in the rough crystal case is mainly due to the higher adsorbed CO$_2$. 
Chapter 4

Sorption and Swelling of Polymers in CO$_2$

Some of the work presented in this chapter also appears in *Macromolecules*; 38(24):10299–10313, 2005 (see Appendix E). Data in Section 4.3.2 is part of a manuscript in preparation (see Appendix F).

4.1 Introduction

As mentioned in Chapter 2, techniques available to study sorption of gases into polymers at elevated pressures are limited. Our previous studies on the utilization of the QCM for gravimetric measurements for polymer dissolution at high pressures was demonstrated (see Chapter 5). The sensitivity and ability to give real time data stimulated interest to utilize the QCM in examining other polymer systems using this approach. This part of the work discusses an evaluation of the sorption of CO$_2$ into poly(methyl methacrylate), PMMA, films under different temperatures and pressures. Several aspects of the sorption process will be discussed including: temperature and pressure effects, interfacial effects, and the kinetics of the sorption process. Finally, the reliability of the QCM results as it interacts with CO$_2$ and the polymer will be discussed.

4.2 Motivation

The studies presented in this chapter are part of a collaborative work$^1$ aimed at the development of theoretical models for the sorption of small molecules into polymeric materials. In order to evaluate the models performance, experimental studies on the sorption and swelling

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$^1$With Dr. Ruben Carbonell from NCSU and Dr. Ferruccio Doghieri from the University of Bologna, Italy.
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of PMMA films were carried out using QCM and high pressure ellipsometry (work done with Jan Genzer group), respectively. This chapter will discuss the studies performed using the QCM to measure CO$_2$ sorption and its kinetics into PMMA films with different thicknesses.

The QCM was applied to measure the sorption of CO$_2$ into PMMA with the following goals in mind:

- Examining different conditions both below and above the critical point of CO$_2$ for glassy and rubbery PMMA.
- Performing measurement on films with different thicknesses to study the effects of film-substrate interactions and surface adsorption on the total measured value of absorbed CO$_2$.
- Performing real-time measurements of the sorption process on glassy and rubbery polymer films under different temperatures.

This chapter will discuss the results from these QCM studies. Before discussing the studies results, an overview of the developed theoretical models is presented.

4.3 Theoretical Models

This section presents a general overview of the developed models with which this work is involved. The objective here is to give a general idea on the subject rather than a detailed description of the models; this can be found in the papers attached in Appendix E and F.

Two of the developed models will be discussed: a thermodynamical model for sorption into bulk films and a kinetics model for the sorption process. A model to describe the behavior of thin films is still under development by Doghieri’s group, therefore, will not be discussed in this section.

4.3.1 Thermodynamics

A model to predict the solubility of small molecules into glassy polymers was developed by Doghieri and Sarti [24]. This model utilized the Sanchez-LaCombe equation of state, SL EoS, and the concept of order parameter to take into account the non-equilibrium nature of the glassy state. The main features of the model, which was called the non-equilibrium lattice fluid, NELF, are:

- SL EoS was used to obtain the Gibbs free energy.
The polymer density was taken as an order parameter the value of which is constant in time but depends on the system’s state. The use of the order parameter is necessary to account for the deviation observed with glassy polymers from the equilibrium behavior. The dependence of the polymer density on the system state allows the prediction of the hysteresis between sorption and desorption. The density was incorporated in the SL expression for the Gibbs free energy by writing the reduced density ($\tilde{\rho}$) as:

$$\tilde{\rho} = \frac{\rho}{\rho^*} \equiv \frac{\rho_2}{\omega_2 \rho^*}$$

where $\rho$ is the total density, $\rho^*$ is the characteristic density in SL EoS, $\rho_2$ is the pure polymer density, and $\omega_2$ is the polymer mass fraction.

In the initial formulation of the model, the change in the order parameter ($\rho_2$) was stated to have the general dependence:

$$\frac{d \rho_2}{dt} = f(T, p, \omega_1, \rho_2)$$  \hspace{1cm} (4.1)

where $\omega_1$ is the sorbent mass fraction. This dependence was to be obtained from a viscoelastic model, e.g., Voigt model. However, in the earlier versions of the model calculations, the density of the glassy polymer was taken to be constant at its initial value while that of the rubbery polymer was calculated from SL EoS [24, 167]. In a later modification to the model, a linear relationship between the system pressure and the density was used based on an extensive examination of available experimental data [168].

The thermodynamic model with which this work is involved was an extension to the NELF model. This model is called the “non-equilibrium thermodynamics for glassy polymers”, NET-GP [169]. The main improvements of the NET-GP over the NEFL model are:

- The plasticization effect of the penetrant molecules on the polymer is predicted using a model derived earlier by Chow [43]. Using this model, the pressure at which the glass-rubber transition occurs can be calculated. At this pressure the polymer is in the rubbery (i.e., equilibrium) state and the EoS can used to estimate its density. Once this and the initial polymer densities are known, the
linear relation between pressure and polymer density can be obtained.

- The NET-GP still utilizes the SL EoS but uses two mixing parameters instead. The use of two parameters gave more accurate predictions of the sorption isotherms.

4.3.2 Kinetics

A model to predict the sorption kinetics of a penetrant into a polymeric matrix was developed by Doghieri and coworkers. The main aspects of this model are:

- The NET-GP model is used to estimate the “equilibrium” sorption values at the interface.
- The free volume theory is used to estimate the diffusivity of the penetrant.
- The coordinate system was transformed from moving- to fixed-boundary using the elongation (\( \lambda \)) defined as \( \partial x / \partial \xi \), where \( x \) is the normal coordinate system and \( \xi \) is the new coordinate system. The value of \( \lambda \) was shown to be equal to the ratio of the initial to the swelled polymer density (\( \rho_p^0 / \rho_p \)) and is a function of time.
- The change in polymer density as a response to the diffusion process is estimated using a rheological model consisting of two Voigt elements in series. Two components were necessary to account for the non-equilibrium swelling behavior in the glassy region. The contribution of each of these two components depends on the state of the polymer with one vanishing as the rubbery state is approached.
- Finally, the polymer bulk viscosity (\( \eta \)) as a function of the penetrant concentration was determined using the relation between the polymer viscosity and the free volume which takes the form: \( \ln \eta \propto 1/\hat{V}_f \).

4.4 Experimental

4.4.1 Materials

Coleman Grade (purity > 99.999%) \( \text{CO}_2 \) was obtained from National Welders. Poly(methyl-methacrylate) having a molecular weight of 72kDa and PDI of 1.08 was obtained from Polymer Source Inc. (Montreal, Canada). Toluene (purity > 99.99%) was obtained from EMD Chemicals (Germany). All materials were used as received.
A PMMA/toluene solution was prepared by mixing the two materials with certain proportions (2–10 wt%), stirring until the solution is clear, then filtering through 0.45 µm filter. PMMA films were prepared by dip coating the QCM crystal into the PMMA solution for a certain period of time (~1 min) then withdrawing the crystal at a controlled rate adjusted to obtain the desired thickness which can be calculated from the frequency change (see Appendix A). The thickness as estimated from SEM images (Figure 4.1) was in good agreement with the calculated one. The film was then dried under vacuum at 80 °C for 1 hour. Following drying, the film was preconditioned in CO₂ for 30 minutes at the maximum pressure of the subsequent experiment. This preconditioning step aims at removing any residual solvent left after vacuum drying and to relax the internal stresses.

4.4.2 Sorption experiments

The sorption experiments, in which the equilibrium concentration of CO₂ in the PMMA film was measured, were performed using the setup described in Section 3.7. A typical run consisted of placing the coated QCM crystal inside the cell under vacuum until the frequency reading was stable within ±1 Hz implying the removal of any remaining residual solvent. Then, the pressure inside the cell was increased to the next desired pressure. In the sorption experiments, the rate at which the pressure was increased was not critical to the results since only equilibrium values were needed. In each of the experiments, the pressure was increased from 0 to 1800 psi in 150 psi steps and decreased to 0 psi again in a similar manner.
4.4.3 Kinetics experiments

Measurements of the diffusion kinetics of CO\textsubscript{2} into PMMA were essentially similar to the sorption measurements. The main difference between the two experiments, however, is in the pressurization rate. In the kinetics experiments, it was desirable to achieve an instantaneous pressure increase while going from one pressure level to the next to minimize the interference between the pressure and sorption effects on the frequency. However, an instantaneous increase is not practically feasible if large temperature changes are to be avoided. In addition, the high pressure pump requires a certain amount of time to attain the set pressure.

To overcome this difficulty, the pressurization procedure needed to be adjusted. For the purpose of achieving fast pressurization, the pump pressure was kept at about 5–10 psi higher (or lower in desorption runs) pressures before connecting the high pressure cell. Once the pump was connected to the cell, the set point was quickly reverted to the required value. This procedure minimizes the time taken by the pump to reach the new set point.

4.5 Results & Discussion

4.5.1 Raw data

An example of the raw data obtained during a typical sorption run for a bulk polymer film is shown in Figure 4.2. The term bulk film refers to films which show a similar behavior to that of bulk material without being affected by the interaction with the substrate. The data reported here considers films with 1 µm or more to be in the bulk region. Thin films, on the other hand, have a thickness of few hundred nanometers as discussed in Section 4.5.4.

Figure 4.2 illustrates the recorded QCM signal (frequency and voltage) and the variations of the controlled variables (temperature and pressure) during a typical pressurization/depressurization cycle. Temperature variations were within ±3 °C and took about 1–2 minutes to return to the set point. For pressure, the overshoot from the pump was about 10–15 psi. As stated earlier, these variations were not a major concern in obtaining sorption isotherms since only equilibrium values were needed.

The data from runs similar to that shown in Figure 4.2 was processed according to the procedure described in Section 3.8.1 (a details example can be found in Appendix A). The frequency was used to calculate the mass change after accounting for the pressure and CO\textsubscript{2}
Figure 4.2: Sample of experimental results showing the pressure, temperature, frequency, and voltage profiles with time from bulk PMMA film at 51 °C.
viscosity effects. The voltage measurements were used to calculate the QCM resistance which was used to evaluate the effect of the change in the viscoelastic properties of PMMA upon absorption of CO$_2$.

4.5.2 Sorption in bulk films

Pressure & temperature effects

In Figure 4.3, the amount of CO$_2$ dissolved in PMMA is shown as a function of pressure at two different temperatures. Pressure has two effects on the polymer. First, the hydrostatic pressure tends to compress the polymer sample, decreasing the free volume and the sorption [170, 171]. On the other hand, as the pressure increases, CO$_2$ density increases dramatically which causes the sorption to increase. For the range of pressures examined in this work, the hydrostatic pressure effect is negligible compared to that of the density, and the net result for increasing the pressure is to increase the CO$_2$ solubility [171].

To examine the temperature effect on CO$_2$ sorption, the data in Figure 4.3 is plotted as a function of CO$_2$ density in Figure 4.4. It is evident from this figure that the temperature effect is not simply on the CO$_2$ density, since there is a significant difference between the sorption at 36 and 51 °C. Such behavior has been observed for many polymers including PMMA [98]. Temperature affects both polymer chain flexibility and intermolecular interactions between the polymer and CO$_2$. As the temperature increases, polymer mobility increases thus increasing the free volume [26]. As for the polymer-CO$_2$ interactions, it has been shown using IR spectroscopy that CO$_2$ acts as an electron acceptor forming a complex with the oxygen on the PMMA’s carbonyl group [172]. Therefore, as the temperature increases, CO$_2$-PMMA interaction decreases yielding lower sorption.

A final observation from Figure 4.3 is on the transition of the polymer state from glassy to rubbery. The transition point, as indicated on the figure, occurs at about 830 and 820 psi for 36 and 51 °C, respectively. To illustrate the difference in sorption behavior between glassy and rubbery polymers, each curve has been divided into two regions. In the lower pressure side, the data has been fitted to a dual-sorption model (Section 2.2) which is the simplest model that takes into account the non-equilibrium nature of this state [24]. In the higher pressures range, Henry’s law has been applied. It should noted that Henry’s law has been used as an illustrative model for an equilibrium thermodynamics relation and might
Figure 4.3: Absorption of CO$_2$ into PMMA film. The arrows indicate the glass-rubber transition as reported in Ref. [44]. The sorption in the glassy region is fitted to the dual-sorption model, while the rubbery region has been fitted to Henry’s law (solid lines).

not be applicable for such high concentrations (> 30% by weight).

Hysteresis
Another distinction between sorption in glassy and rubbery states is the phenomenon of hysteresis. Hysteresis refers to the deviation observed between the amount of CO$_2$ sorbed in glassy polymers during a pressure increase versus a pressure decrease isotherm. This deviation can be attributed to the dependence of the mass uptake on the polymer state which in turn depends on the mechanical and thermal history of the sample. Therefore, and due to the plasticizing effect of the CO$_2$ during sorption, the desorption isotherm is expected to show some variation in the glassy region for both sorption and dilation isotherms [173].
Figure 4.4: CO$_2$ sorption into bulk PMMA films as a function of CO$_2$ density at different temperatures.

Figure 4.5 illustrates the uptake of CO$_2$ into PMMA during a sorption-desorption cycle for two different temperatures. The hysteresis can be clearly seen to start around the glass-rubber transition. It can be also seen from the figure that hysteresis decreases as temperature increase. This is due to the added chain flexibility at higher temperatures which reduces the dependence on the sample history and due to the decrease in the amount of CO$_2$ uptake at higher temperatures.

4.5.3 Sorption Kinetics

The diffusion process in polymers can show different behavior depending on the polymer physical state. During sorption, polymers experience two simultaneous processes: diffusion
and relaxation. The relative rate at which these relaxation and diffusion processes occur is characterized by the diffusion time and relaxation time, respectively. These two quantities are usually compared using the Deborah number ($De$) which is defined as the ratio of the characteristic relaxation time to the characteristic diffusion time. For low Deborah numbers ($De \ll 1$) Fickian diffusion is observed, whereas for large Deborah numbers ($De \gg 1$) a two-stage sorption is observed [174].

Varying the experimental conditions results in changing the polymer properties, namely the diffusion coefficient and viscosity, thus allowing the observation of different sorption behaviors. The results for sorption kinetics measurements are summarized in Figures 4.6 and 4.7. The results shown are for glassy and rubbery PMMA films at different temperatures and pressures for both sorption and desorption steps.
Figure 4.6: Sorption and desorption in glassy polymers at different temperatures. Note that the concentration scales for each sorption step is different from that of the desorption at the same temperature. This can be attributed to the presence of hysteresis in the glassy region.
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Figure 4.7: Sorption of CO₂ in rubbery PMMA at different temperatures. Note that, unlike the glassy case, the concentration scales for each sorption scale is the same as that of the desorption.

From the sorption results in the glassy films in Figure 4.6, the two-stage diffusion can be clearly seen. In this case, the polymer viscosity is high which makes the relaxation process slow compared to the diffusion. When the polymer is plasticized by the presence of sufficient concentration of CO₂ molecules the sorption behavior, as shown in Figure 4.7, becomes Fickian. In this case, relaxation happens rapidly in comparison to diffusion so that the sorption process appears to occur in one step.

The temperature effect on sorption kinetics can be discussed in a similar manner to its effect on sorption isotherms, i.e., in terms of CO₂ density and polymer flexibility. However, the polymer viscosity enters as an additional factor here because of the dynamic nature of the process. As the temperature increases, the diffusion coefficient increases and the viscosity decreases [175] thus the De number decreases. From Figure 4.6 it is seen that the time
taken by the first, diffusion stage of the sorption process tends to shorten as temperature
increases. However, the overall time taken by the whole process does not clearly follow the
same trend which might be due to experimental inaccuracies since changes in the second
stage are not pure gravimetrical. For the rubbery films, Figure 4.7, the temperature effect
on shortening the diffusion time is evident.

Finally, the difference in the mass uptake profiles between sorption and desorption pro-
cess is discussed. For the rubbery state in Figure 4.7 the behavior can be said to be identical
in both cases. This is expected since the rubbery state is an equilibrium one and the polymer
behavior is not expected to depend on the polymer history. The glassy state, on the other
hand, shows a different behavior between sorption and desorption. Namely, the two-stage
features are less evident and the time taken in the desorption process is shorter, an observa-
tion found with other swelling agents [37]. It has been observed that the desorption process
passes through three regions: a short period of high desorption rate that is proportional to
the square root of time followed by intermediate region, and finally an extremely long tail
[37]. Therefore, upon depressurization, the diffusion process starts at a higher concentration
compared to that of the sorption process. Thus, the first, rapid desorption region occurs
while the diffusivity is higher thus shortening the time needed for the desorption process
compared to sorption.

4.5.4 Sorption in thin films

The mechanical, thermal, and other polymer properties depend not only on its chemical and
morphological characteristics but also on its thickness [176]. Examples of polymer properties
that depend on the thickness are the glass transition temperature [177], crystallinity [176],
and small molecules transport behavior [41]. The glass transition temperature, for instance,
has been shown to vary linearly with thickness up to a certain limit [177]. Indeed, this
dependence of \( T_g \) on the thickness can be significant as was shown by studies on supported
PS films which exhibit a depression of more than 40 °C when the thickness is decreased from
1000 to less than 100 Å [178].

The thickness limit by which the polymer sample properties become dependent on its
dimensions is not clearly defined and can vary depending on the measured property. For
example, in the \( T_g \) studies of PS films mentioned earlier [178], it was found that the \( T_g \)
for films with 1000 Å thickness is approximately equal to the bulk $T_g$. Similar observations has been found for PMMA films [179, 180]. Therefore, from the $T_g$ perspective, polymer films with 100 nm or more are considered to lie in the bulk region. Another classification by Frank et al. divides polymer films into ultrathin (< 1000 Å) and thin (1000–10000 Å) based on the characteristic dimension of the polymer (i.e., radius of gyration) [176]. For the work presented in this chapter, the classification criterion is based on the sorption behavior of supercritical fluids into polymer films. Ellipsometric measurements on polymer (PMMA) films with thicknesses up to 325 nm have shown that the sorption isotherm of CO$_2$ into such films exhibits an anomalous behavior [181]. The anomaly is manifested in the presence of a maximum around the critical point of the fluid. Currently, this behavior is not completely understood. Sirard et al. suggested that inhomogeneities in the CO$_2$ concentration inside the film due to polymer/CO$_2$ phase separation might be responsible for such behavior [181]. This conclusion was made based on the observation that the adsorption of CO$_2$ onto Si substrate exhibits a maximum near the critical point which might suggest that the CO$_2$ tends to concentrate near the polymer-substrate interface under such conditions. In this part of the work, the QCM was coated with polymer films having a thickness less than 300 nm, which is within the thin film range.

Pressure & temperature effects

Figure 4.8 summarizes the sorption results of thin PMMA films at two different temperatures. Before discussing the data in this figure, it is important to comment on the glass transition for thin films. The arrows on Figure 4.8 indicates the glass transition pressure ($P_g$) which are the same as those for bulk films shown in Figure 4.5. Although $P_g$ has been shown to depend on the film thickness [179], the films used in this work were large enough that their $P_g$ is not significantly different from the bulk case.

The general behavior of thin films, as shown in Figure 4.8, is similar to that for bulk films, Figures 4.3. Therefore, similar discussion to that in Section 4.5.2 can be made here. One noticeable issue for the thin film case is the effect of surface adsorption on the apparent solubility of CO$_2$. Since the film thickness in this cases is small, the amount of CO$_2$ absorbed into the film is also expected to be small. Therefore, the contribution of adsorbed CO$_2$ on the polymer surface might have a significant effect on the final results. To address this issue, experiments were executed where the initial PMMA mass was varied and the absorption
results were used to extract the expected adsorption at zero polymer mass, as discussed below.

**Adsorption & substrate interactions**

CO$_2$ tends to adsorb and condensate near polymer surfaces causing differences between the bulk and surface layer properties such as the glass transition temperature [182]. As the polymer film thickness becomes smaller, the contribution of this adsorbed CO$_2$ to the total mass change becomes significant. An attempt to account for the adsorbed mass contribution was presented by Miura et al. [152] and is followed here. To estimate the surface adsorption, the CO$_2$ mass uptake was measured at different pressures for films with different initial masses. The absolute CO$_2$ mass uptake was then plotted as a function of the initial polymer mass.
mass as shown in Figure 4.9. The adsorption was calculated by extrapolating the uptake at each pressure to zero polymer mass.

The results for the above calculations are summarized in Figure 4.10. The figure also compares the adsorption between coated and uncoated crystals for both Si and Au substrates. Two observations can be made from this figure. First, the difference between the coated and uncoated crystals is not significant. Second, it is observed that there is a small difference between the Si and Au substrates, whether coated or uncoated, at high pressures. While it is known that the interaction between PMMA and Si substrate is significantly stronger than that with Au substrate [180], the polymer films thicknesses involved in this
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Figure 4.10: Summary of surface adsorption of CO$_2$ onto PMMA coated Si and Au substrates at 36 °C. The Si curve was obtained from the linear fits in Figure 4.9. The Au curve was obtained following a similar procedure (data not shown).

The study are large enough to mask any effect of the substrate. The difference between the adsorption for both substrate can be attributed to the differences in their surface morphology with Au substrate having smoother surface than Si, thus showing lower adsorption.

Finally, in order to correct for the effect of surface adsorption on the total estimated amount of CO$_2$ uptake, the results obtained from Figure 4.10 was used together with the apparent solubility similar to those in Figure 4.8. The expected absorption was calculated by subtracting the adsorbed amount from the total CO$_2$ uptake and the results are shown in Figure 4.11. The figure also presents some literature data for the same system measured using other techniques. The corrected results seems to be in better agreement with that
Figure 4.11: Effect of surface adsorption on the calculated CO$_2$ solubility into thin PMMA films at 36 °C. For comparison, two sets of literature data are shown. The data by Kikic et al. [92] was performed on powder PMMA at ~35 °C using a gravimetric method. The data by Pantoula and Panayiotou [98] was obtained using mass-loss analysis at 35 °C for pellets and film PMMA samples. The vertical line indicates the critical pressure of CO$_2$. 
from literature below the critical point of CO$_2$. Beyond the critical pressure, however, the above procedure seems to overestimate the surface adsorption contribution. The linear fits in Figure 4.9 were observed to show poor correlation above the critical pressure. Similar behavior was observed upon repeating the experiments. The reasons for this is not clearly understood yet, and further studies are needed.

4.5.5 QCM Reliability Assessment

The main emphasis in this part of the work was to obtain reliable CO$_2$ sorption measurements in PMMA using the QCM. It is therefore important to assess the reliability of the QCM results in terms of error sources discussed in Section 3.6.2. This assessment will be done by analyzing the change in the QCM resistance at different conditions.

The mass calculations presented so far utilized the linear Sauerbrey relation between frequency and mass changes (i.e., $\Delta F \propto \Delta m$). For rigid, elastic films, this simple relation is said to be valid for frequency changes up to 2% of the unloaded QCM frequency and can reach 10% for selected films [113]. The crystals used in this work have an initial frequency in the neighborhood of 5 MHz. Thus, the theoretical loading limit is about 100 kHz which corresponds to PMMA films 7.5 $\mu$m thick; much larger than the films examined in this work. When polymer films are considered, however, the viscous nature of these films significantly reduces the applicability limit of the Sauerbrey equation. Polymer films viscoelasticity affects the QCM operation in a manner that might interfere with the mass measurements [121].

To obtain an idea on the effect of the PMMA film on the QCM operation, the change in the resistance ($\Delta R$) of the QCM was analyzed. In Figure 4.12, $\Delta R$ is plotted as a function of CO$_2$ pressure for coated and uncoated crystals. For thin films, the change in the resistance for the coated QCM’s is close to that of the uncoated ones. On the other hand, QCM crystals coated with bulk PMMA films show larger deviations. In all cases, the strong effect of the CO$_2$ viscosity on $\Delta R$ is apparent from the general shape of the curves. As discussed in Section 3.8.3, $\Delta R$ is expected to vary linearly with the square root of the density-viscosity product, $(\rho \eta)^{1/2}$, for Newtonian fluids [126]. The data in Figure 4.12 is replotted as a function of $(\rho \eta)^{1/2}$ for CO$_2$ in Figure 4.13. The linear relation for the uncoated crystals as well as those coated with thin films is evident. Therefore, for thin films it is expected that the mass change results obtained using the Sauerbrey equation to be reliable.
Bulk films, on the other hand, show some deviation for $\Delta R$ compared to the uncoated crystals. At 51 °C, the deviation is lower compared to that at 36 °C, which is contrary to what is expected from the viscoelastic nature of polymers (more viscous at higher temperatures). This can be explained by looking at Figure 4.14 which shows the same data for $\Delta R$ but in this case plotted against the amount of CO$_2$ absorbed. From this figure, it is clear that $\Delta R$ is larger at 51 °C compared to 36 °C for the same amount of CO$_2$ absorbed. Therefore, it can be concluded that the sorption of CO$_2$ into PMMA is what produces the larger changes in $\Delta R$ at the lower temperature as observed in Figure 4.13. In other words, PMMA films up to $\sim 1 \mu$m thickness do not affect the QCM operation significantly at the studied temperatures, but rather the plasticization of these films by the absorption of CO$_2$. The question here is
to what extent will this deviation affect the QCM accuracy?

To answer this question, the analysis introduced by Muramatsu and coworkers is followed [183–185]. This analysis depends on the construction of a frequency–resistance diagram that presents the correlation between these two variables during the process. In this diagram, two limits are defined: the elastic load limit and the viscous load limit. The elastic limit is set by the fact that perfectly elastic films deposited on the QCM surface will cause a change in the frequency only and no change in the resistance. On the other hand, the viscous limit is introduced by the fact that perfectly viscous loadings will affect both the frequency and the resistance. The relation between $\Delta F$ and $\Delta R$ is linear as can be seen from their dependence
Figure 4.14: Change in the resistance of QCM coated with bulk PMMA films at different temperatures as a function of absorption CO\textsubscript{2}. The dots represent the sorption-induced glass-rubber transition taken from Ref. [44].

on the fluid properties. As stated in Section 3.4.2, both $\Delta F$ and $\Delta R$ varies linearly with $(\rho\eta)^{1/2}$ of the fluid, i.e.:

$$
\begin{align*}
\Delta F_{\eta} &\propto -(\rho\eta)^{0.5} \\
\Delta R &\propto (\rho\eta)^{0.5}
\end{align*}
$$

$\implies \Delta R \propto -\Delta F_{\eta}$

From Eqs. (3.9) and (3.11), the proportionality constant is estimated to be equal to $-1.64$. Therefore, the viscous limit is set by the straight line $\Delta R = 1.64 \times \Delta F$. In Figure 4.15, the elastic and viscous limits are those defined by lines $e$ and $v$, respectively. The main conclusion from Muramatsu work is that the Sauerbrey equation gives reliable results if, for
any $\Delta F$, $\Delta R$ is between 0 and a line having a slope equal to $1/8$ of that of the viscous limit line, i.e., a slope of $-1.64/8 \approx 0.2$. In Figure 4.15, this area is that between lines $e$ and $m$. Therefore, if the measured $\Delta F$ and $\Delta R$ are plotted for the different polymers films studied in this work, the reliability of Eq. (3.7) can be evaluated.

To demonstrate the use of the $\Delta F$–$\Delta R$ diagram, the measured $\Delta F$ and $\Delta R$ for the uncoated crystal at different temperatures are shown on the Figure 4.15. For this case, the value of $\Delta F$ was calculated by subtracting the pressure contribution from the measured frequency. As can be seen from the figure, the $\Delta F$–$\Delta R$ lines for the blank crystal deviate slightly from line $v$. This deviation can be attributed to the adsorption of CO$_2$ onto the
surface. Instead of using line \( v \) as a reference, as suggested by Muramatsu, the slope of the blank crystal data was used to estimate the slope of line \( m \). This yielded a narrower range between lines \( e \) and \( m \).

The behavior of thin (\( \sim 200 \) nm) and bulk (\( \sim 1 \mu \)m) are depicted on the same figure. Due to pressure changes during the experiments which causes the density and viscosity of CO\(_2\) to change, the resistance values for the polymer films were corrected for these effects. This was done by subtracting the expected \( \Delta R \) due to changes in CO\(_2\) properties (\( R_{CO_2} \)), as estimated by Eq. (3.11), from the measured resistance (\( R_{exp} \)) to obtain the net resistance change due to CO\(_2\) sorption into the film (\( \Delta R^* \)):

\[
\Delta R^* = R_{exp} - R_{CO_2}.
\]

The frequency change calculations, on the other hand, are similar to the calculations used in the previous sections to estimate the amount of CO\(_2\) absorbed, i.e., using Eq. (3.20).

The thin film behavior, as shown on the figure, seems to resemble that of an elastic material. Only the frequency changed significantly during the course of the sorption process. The resistance can be considered, within experimental accuracy, constant. This can be attributed to the small thickness of these films. Another observation from the above figure, is the sudden increase in the resistance value around \(-900\) Hz. This behavior was seen only for sorption at 25 °C and is expected to be due to the large differences in the CO\(_2\) density and viscosity between the gas and liquid phases which results in a high increase in the absorption.

For bulk films, the change in both the frequency and resistance is much larger than for thin films. This behavior is not unexpected since bulk films can affect the QCM operation more significantly. The effect of the film viscoelasticity can be seen from the two curves at 36 and 51 °C. Although PMMA absorbs more CO\(_2\) at 36 °C, the curve at this temperature is closer to the elastic limit than that at 51 °C. This is an indication that temperature is an important factor when considering the applicability of Sauerbrey equation. The curve also shows that as the CO\(_2\) loading into the polymer increase, the resistance increases and the curve becomes closer to the unreliable limit region. In fact, at 51 °C the point where the polymer has absorbed CO\(_2\) the most is close to line \( m \) that, upon further increase in
Chapter 4. Sorption and Swelling of Polymers in CO₂

CO₂ absorption, the curve will enter the unreliable region. Fortunately, throughout the experiments, the curves remain within the reliable region of the linear mass dependence.

It can be concluded that polymer films, due to their viscoelastic nature, can affect the reliability of the Sauerbrey equation for mass calculations. Several analyses demonstrated that this equation is applicable for polymer films up to 7 µm thickness (for a 5 MHz crystal). In the presence of a strong swelling agent, such as CO₂, this limit is highly reduced. Some authors suggested a maximum limit of 100 nm above which the Sauerbrey equation is not applicable [162]. However, the discussion presented above shows that for the films used in this study, which have a thickness of 1 µm or less, the linear frequency-mass relation is still valid.

4.6 Conclusions

The sorption process in polymers is a complicated phenomenon due to the special characteristics of polymers. Different behaviors can be observed for glassy and rubbery samples of the same polymer. Consequently, the modeling of the two behaviors is expected to be different. In the glassy state, non-equilibrium thermodynamics are needed to model the behavior of the polymer. For rubbery samples, the available equations of state can be used. The transition between glassy and rubbery can be induced by the small molecules diffusion in the polymer matrix. This transition must also be taken into account to correctly model the sorption.

The quartz crystal microbalance was used to determine the sorption isotherms and kinetics for thin and bulk PMMA films at different conditions. The discrepancies between sorption in the glassy and rubbery states as well as the effect of system variables were observed. Namely, the following observations were made: (1) the decrease in sorption upon increasing the temperature, (2) the presence of sorption-desorption hysteresis in the glassy region, (3) the two-stage kinetics of the sorption in the glassy region, and (4) the Fickian kinetics in the rubbery region. The glassy-rubbery transition, as detected by the presence of hysteresis, matches reasonably with reported values for PMMA. In Appendix E and F the results are compared with the developed theoretical models.

The applicability of the Sauerbrey equation was tested using the frequency-resistance diagram. For both thin and bulk films the results were within the reliable region. Thin films
Chapter 4. Sorption and Swelling of Polymers in CO$_2$

did not show significant effect on the QCM operation, while bulk films did. Temperature effect produced higher deviation from the elastic behavior compared to the sorption effect.
Chapter 5

Polymer Dissolution in CO\textsubscript{2}

This chapter is based on a manuscript submitted to the *Journal of Supercritical Fluids* under the title “Dissolution of Polymer Films in Supercritical Carbon Dioxide Using a Quartz Crystal Microbalance”.

5.1 Introduction

Considerable effort has been made since the early 1990’s toward improving polymer solubility in CO\textsubscript{2} leading to the modification of fluoropolymers and polyethers to produce highly CO\textsubscript{2}-soluble polymers [56, 57, 186]. It was shown that fluorinating the backbone or the side-chains of a polymer can significantly change its solubility in CO\textsubscript{2} [59]. A large body of the work in the area of fluorinated polymers solubility under supercritical conditions was done by DeSimone and co-workers [58].

In this part of the work, a copolymer synthesized by the DeSimone group [187], referred to here as PFOMA, is studied in details with respect to its behavior under scCO\textsubscript{2}. The main technique utilized for this study was the quartz crystal microbalance (QCM). The objective is to study the behavior of thin films (in the order of a few hundred nanometers) of this fluorinated copolymer in CO\textsubscript{2} under different temperatures and pressures, with a focus on the mechanisms associated with the adsorption, swelling, and dissolution processes. As will be seen, this copolymer is highly soluble in CO\textsubscript{2} at low temperatures and moderately low pressures.

5.2 Experimental

5.2.1 Materials

A random copolymer of 65 mol\% 1,1-dihydroperfluoroctyl methacrylate (FOMA) and 35 mol\% 2-tetrahydropyranyl methacrylate (THPMA), poly(FOMA-r-THPMA) (Figure 5.1),
was used in this study. PFOMA belongs to a family of fluoropolymers that contain lithographically patternable, photoacid cleavable tetrahydropyranyl (–THP) groups \[188\]. The polymer was synthesized and purified by the DeSimone research group at UNC-Chapel Hill \[187\]. This polymer has a molecular weight of 15k and a $T_g$ of 48 °C in its pure form (no CO$_2$).

Trifluorotoluene (TFT) of greater than 99% purity was purchased from Aldrich Chemical Company and used as received. Coleman grade (purity > 99.99%) CO$_2$ was obtained from National Welders.

![PFOMA structure.](image)

Prior to coating, a clean crystal was put into the pressure cell to determine the fundamental frequency, $F_o$, in vacuum at the experiment temperature. Polymer films were then cast onto the crystal by dipping the crystal into a 2 wt% PFOMA/TFT solution for about 1 min then withdrawing at a controlled speed via a variable speed motor, the speed controls the initial polymer mass on the crystal. The coated crystal was dried at run temperature under vacuum until no frequency change was observed, indicating complete drying. The value of the stabilized frequency of the coated QCM in vacuum ($F_p$) was utilized to calculate the initial total mass of the coated polymer, i.e., $m_o = (F_o - F_p)/C_m$.

5.2.2 Methods

The dissolution experiments were basically performed by placing the QCM inside the high pressure cell and increasing the pressure up to the experimental value at which the dissolution starts. To avoid high mechanical disturbances due to fast pressurization, which can cause instabilities in the QCM signal during the initial stage of dissolution, the pressure was increased in two stages. In the first stage, the pressure was slowly increased to an intermediate value ($P_m$) and allowed to equilibrate at this level. In the second stage, the pressure
was increased rapidly to the final experimental value \(P_{\text{exp}}\). The value of \(P_m\) depended on temperature and was chosen to be below the dissolution pressure \(P_d\) for PFOMA but above the CO\(_2\) critical pressure (1071 psi). Allowing the PFOMA film to equilibrate with CO\(_2\) at \(P_m\) before dissolution minimizes the net contribution of CO\(_2\) absorption to frequency.

The dissolution of the polymer film occurred over a 10 to 60 minute time period depending on the conditions. Following dissolution, the CO\(_2\) was rapidly released out of the cell while the frequency of the crystal was continuously recorded. At the end of each experiment, the QCM was washed with pure TFT solvent and its frequency was measured again under vacuum at the experiment temperature \(F_0'\). This value was found to be within 3.0 Hz of \(F_o\) indicating the ability to close the material balance on the film.

### 5.3 Results and Discussion

The raw frequency data recorded during a typical run is presented in Figure 5.2 to show the different stages (i.e., coating, swelling, dissolution) of the experiment. In the following discussion, the frequency of the coated crystal at a certain pressure \(P_x\) will be designated as \(F_{P_x}\). A full list of the nomenclature is also provided at the end of the chapter.

During the course of the dissolution process several phenomena take place as shown schematically in Figure 5.3. Upon increasing the pressure, CO\(_2\) will adsorb on the polymer film surface; a process that occurs on a short time scale such that its effect on the frequency will be competing with the pressure effect. Therefore, the frequency increase due to the pressure increase, as suggested by Eq. (3.13), will be depressed due to the mass adsorbed on the surface. Following adsorption, CO\(_2\) will start to diffuse inside the polymer film causing the frequency to decrease due to the mass increase. This diffusion process happens on a much longer time scales and can be easily followed by the QCM as discussed below. The sorption process will cause plasticization and relaxation of the polymer thus changing its viscoelastic properties which might affect the QCM response as discussed in the following section. As the CO\(_2\) concentration inside the polymer increases, a critical limit is reached where the polymer chains will have enough mobility to entangle from the network and dissolve into the solution.
Figure 5.2: Frequency of QCM coated with PFOMA film (∼ 0.3 µm) in CO<sub>2</sub> at 37 °C (circles) as a function of time during the pressure cycle (solid line). The run starts by measuring the uncoated crystal frequency in vacuum, 2 dip coating and measuring the coated QCM frequency 3, pressurization slowly up to P<sub>m</sub> and equilibration 4, the pressure was then increased again rapidly to P<sub>d</sub> were dissolution starts and allowed to equilibrate again 5 before CO<sub>2</sub> was released 6. Finally, the QCM was taken out of the cell and cleaned with TFT and the frequency was measured at vacuum 7.
Chapter 5. Polymer Dissolution in CO\textsubscript{2}

Figure 5.3: Schematic showing the different phenomena involved during the dissolution process of polymer films.

5.3.1 Film Viscoelasticity

During the initial stage of pressurization (from vacuum to \(P_m\)), the frequency difference between \(F_{\text{vac}}\) and \(F_{P_m}\) represents all possible contributions to the frequency including pressure, viscous loading from the increase in CO\textsubscript{2} viscosity and density, viscous loading from the change in polymer viscoelasticity due to plasticization, and mass change due to CO\textsubscript{2} uptake. The pressure and CO\textsubscript{2} viscosity effects can be accounted for through the application of proper relations for the frequency change, namely, Eqs. (3.9) and (3.13), respectively. Therefore, mass calculations based on Eq. (3.20) does not account for the viscoelastic effect due to polymer plasticization. To test the extent of the variation in the QCM response due to this viscoelastic effect, a comparison is made between the change in the resistance (\(\Delta R\)) for uncoated and coated crystals. The results are shown in Figure 5.4 for a range of pressures (including the supercritical transition) and temperatures below and slightly above the \(T_g\) of pure PFOMA. As can be seen from part (a) of this figure, \(\Delta R\) for the coated crystals did not show significant deviation from the uncoated ones. The major effect on \(\Delta R\) was the change in CO\textsubscript{2} properties. In Figure 5.4(b), the data in 5.4(a) is represented as a function the CO\textsubscript{2} density-viscosity product represented as \((\rho \eta)^{0.5}\). The linear theoretical relationship suggested by Eq. (3.11) for Newtonian fluids is indeed evident. It is therefore concluded that the viscous coupling is predominately caused by CO\textsubscript{2} and not by the polymer film. Thus, Eq. (3.9) is expected to take into account the nongravimetric contribution to frequency change due to this viscous coupling. This can be attributed to the small thickness of the polymer films studied in this work (\(\sim 0.3 \mu\text{m}\)).
Figure 5.4: Resistance change for bare and PFOMA coated QCM crystals as a function of (a) pressure, and (b) CO$_2$ density-viscosity product.
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Figure 5.5: Frequency change due to absorption of CO$_2$ in polymer film at 1110 psi and 37 °C as a function of initial polymer amount.

5.3.2 Sorption-Dominated Stage

If the frequency change caused by coating the polymer film is designated as $\Delta F_f$; the frequency change due to CO$_2$ absorption into this film will be $S \cdot \Delta F_f$, where $S$ is the solubility in gram CO$_2$/gram polymer. Then, Eq. (3.20) can be rewritten for the interval of CO$_2$ swelling as:

$$\Delta F_T = F_{vac} - F_{Pm} = (S \cdot \Delta F_f + \Delta F_{ads}) + \Delta F_\eta + \Delta F_p$$  \hspace{1cm} (5.1)

Here, the frequency change due to CO$_2$ sorption ($\Delta F_m$) has been split into two contributions: adsorption on the surface ($F_{ads}$), and absorption into the polymer ($S \cdot \Delta F_f$). Therefore, the
slope of the linear plot of $\Delta F_T (= F_{vac} - F_{P_m})$ versus $\Delta F_f$ will give the solubility ($S$) of CO$_2$ in the polymer film. The intercept of this plot reflects the other contributions including the surface adsorption of CO$_2$ which is expected to be independent of the polymer mass. As an example, the data in Figure 5.5 shows the total change in frequency ($\Delta F_T$) at 1110 psi and 37 °C as a function of PFOMA initial mass. From the slope of this figure, the value of $S$ was found to be approximately 0.4 g·g$^{-1}$. Alternatively, the solubility of CO$_2$ in the polymer was evaluated from the frequency shifts at different pressures below the dissolution pressure ($P_d$). The absorbed mass was obtained from Eq. (3.20), the results are shown in Figure 5.6. From this figure, the solubility of CO$_2$ in the polymer at 37 °C and 1100 psi was found to be about 0.48 g·g$^{-1}$. The difference between these two values (0.48 − 0.4 = 0.08) can be attributed to the surface adsorption of CO$_2$ on the polymer which was not accounted for in the later case.

The sorption kinetics of CO$_2$ can be determined since real time data can be easily obtained with the QCM. The frequency data in the initial stage, prior to dissolution, was fitted to a simple Fickian diffusion model (Eq. (2.1)) to obtain the diffusivity of CO$_2$ in PFOMA [31]. As can be seen in Figure 5.7, a good fit was obtained with this model. In this graph, the thickness of the polymer was calculated from $\Delta F_m$ and the bulk polymer density ($\sim 1.1$ g/cm$^3$) [188]. The diffusion coefficient was fitted and found to be on the order of $1 \times 10^{-9}$ cm$^2$/sec. This value is within the reasonable range of diffusivities for CO$_2$ in other polymers such as PTFE [22, 189].

5.3.3 Dissolution-Dominated Stage

Once the CO$_2$ concentration in the polymer reaches a critical value, the chains in the swollen polymer start to disentangle from each other and diffuse out of the network through reptation and dissolution [190]. As can be seen from Figure 5.6, this critical CO$_2$ concentration value ranged between 0.3 to 0.6 mass fraction. For a 15k molecular weight PFOMA sample this is translated into 100 to 200 CO$_2$ molecules per polymer molecule, or 4 to 8 CO$_2$ molecules per repeat unit.

After the steady state frequency at $P_m$ is reached, the CO$_2$ pressure inside the cell was increased to $P_{exp}$ within a short period of time (less than 1 minute). As the pressure increased, more CO$_2$ diffused into the polymer causing the frequency to decrease. At the same
time, polymer dissolution started due to the higher concentration of CO$_2$ which decreases the total mass load on the crystal, thus, raising the frequency. A balance between the absorption of CO$_2$ and dissolution of PFOMA is reached at which point the frequency reaches a minimum, $F_{\text{min}}$ (see Figure 5.2). As shown in Figure 5.7, CO$_2$ absorption takes relatively short times compared to the total dissolution. Therefore, after passing $F_{\text{min}}$, the dissolution rate continues to increase causing an increase in the frequency.

The polymer dissolution stage is defined as starting at $F_{\text{min}}$ and continues until the frequency reaches a new steady state level ($F_{\text{t,exp}}$). It should be noted that, during this stage, pressure and temperature are constant and do not contribute to the frequency shift; the frequency change is due only to mass change on the crystal. As the polymer starts to
dissolve, the absorbed CO\textsubscript{2} will be released. Therefore, the frequency change during the dissolution stage can be written as:

\[
\Delta F = F_{\text{min}} - F_{\text{exp}} = \Delta F_P + \Delta F_{\text{CO}_2} = (1 + S)\Delta F_P
\]  \hspace{1cm} (5.2)

where and $\Delta F_P$ is the mass change due to polymer dissolution, and $\Delta F_{\text{CO}_2}$ is the change in frequency due to the change in the CO\textsubscript{2} mass in the remaining polymer film. As more polymer is removed from the QCM surface, more CO\textsubscript{2} will be released. Therefore, the mass change detected by the QCM at the experimental pressure ($P_{\text{exp}}$) is expected to be larger than the net change in the polymer film mass. To illustrate this point, a comparison is made between the total mass change during the dissolution process ($m_{\text{dis}}$), calculated
Figure 5.8: Comparison between the mass removed as calculated using the frequencies at the experimental pressure ($m_{\text{dis}}$) and the net polymer mass removed calculated using the initial and final frequencies ($m_f$) for PFOMA at 60 °C as a function of pressure. Both values were normalized using the initial, dry polymer mass ($m_o$).

from $F_{\text{min}} - F_{\text{exp}}$, and the polymer mass change ($m_f$) calculated from $F_{\text{vac}} - F_{\text{dis}}$ (refer to Figure 5.2). This is shown in Figure 5.8, where both $m_{\text{dis}}$ and $m_f$ are plotted as a function of pressure. As can be seen from the figure, both values are comparable at low pressures where only a fraction of the polymer is dissolved, and $m_{\text{dis}}$ becomes significantly larger as the pressure increases. This behavior is mainly due to the degree by which the PFOMA dissolves in CO$_2$ at different pressures.
5.3.4 Polymer Dissolution Evaluation

In order to compare the different dissolution isotherms, the real-time dissolution results from the QCM were fitted to a simple dissolution model. The simplification comes from the fact that before dissolution starts, the polymer would have been swelled and plasticized with CO\textsubscript{2} for sufficient time to reach equilibrium. Therefore, modeling the dissolution can be simplified by neglecting the diffusion of CO\textsubscript{2} into the polymer film which allows the use of the quasi-stationary dissolution assumption. As a result, the rate of change on the polymer mass can be written as

\[
\frac{dM}{Adt} = -k(C_e - C)
\]  

(5.3)

where \(M\) is the remaining mass of the polymer, \(t\) is the time, \(A\) is the area, \(k\) is the mass transfer coefficient, \(C_e\) is the dissolved concentration in the liquid side, and \(C\) is the bulk polymer concentration in CO\textsubscript{2}. Writing the concentration as \(C = V(M_0 - M)\), where \(M_0\) is the initial polymer mass and \(V\) is the CO\textsubscript{2} volume, Eq. (5.3) can be solved to give:

\[
\frac{\Delta M(t)}{M_0} = \frac{M_0 - M(t)}{M_0} = A(1 - e^{-\kappa t})
\]  

(5.4)

where \(A = \frac{V C_e}{M_0}\) and \(\kappa = Ak/V\). The exponential coefficient, \(\kappa\), can be used to compare the dissolution rates. The value of \(\Delta M/M_0\) is calculated from the frequency change as:

\[
\frac{\Delta M(t)}{M_0} = \frac{1}{1 + S} \frac{\Delta F_P(t)}{\Delta F_f} = \frac{1}{1 + S} \frac{F_{P_{exp}}(t) - F_{min}}{F_0 - F_{vac}}
\]  

(5.5)

The term \(1 + S\) was used to take into account, in approximate manner, the release of CO\textsubscript{2} as the polymer dissolves into CO\textsubscript{2} as described in Eq. (5.2). The value of \(S\) can be obtained from Figure 5.6. Once \(\Delta M/M_0\) is known as a function of time, the value of \(\kappa\) can be obtained through non-linear regression. Initial calculations with Eq. (5.4) were not able to fit the experimental data accurately. In order to reduce the discrepancy between the calculated and the measured results, Eq. (5.4) was modified as follows:

\[
\frac{\Delta M(t)}{M_0} = A \sum_i (1 - e^{-\kappa_i t})
\]  

(5.6)
Here, the summation was introduced to account for any dispersion in the polymer sample molecular weight. Examples of frequency data manipulated according to Eq. (5.5) and its fit to Eq. (5.6) are shown in Figure 5.9 from which the values of $\kappa_i$ were estimated. In these fits, it was found using three terms in the summation in Eq. (5.6) gave satisfactory fits for all measured data.

![Figure 5.9](image)

**Figure 5.9**: Time profiles for the mass change for PFOMA films at different CO$_2$ densities with comparison to their fits to Eq. (5.6).

Table 5.3.4 summarizes the regressed parameters for different CO$_2$ conditions. These values reflects the dissolution rate. A general trend in the dissolution parameters can be seen from this table. As the CO$_2$ density increases, $\kappa_1$ tends to increase, $\kappa_2$ shows less dependence on the density, and $\kappa_3$ is at least an order of magnitude lower than either $\kappa_1$ or $\kappa_2$. The increase in the dissolution constants with CO$_2$ density can be attributed to the
increase in the solvency power due to the higher concentration of CO\textsubscript{2} molecules around the polymer. It must be noted, however, that temperature seems to play an important role as can be seen from, for instance, the large increase in $\kappa_1$ as the temperature changes from 60 to 70 °C. Temperature might affect the dissolution rate by increasing the mobility of the polymer chains. In addition, temperature plays an important role in the interaction energies between all the molecules (polymer-polymer, polymer-CO\textsubscript{2}, and CO\textsubscript{2}-CO\textsubscript{2}) \[53\]. While no kinetic studies on the dissolution of the PFOMA copolymer exist in the literature, a study by Pham et al. \[105\] on a similar fluorinated copolymer, poly(tetrahydropyranyl methacrylate 1H,1H-perfluorooctyl methacrylate), to the one used in this work confirms the high dependence of dissolution rate on density.

Finally, complete dissolution of the polymer film was not always achieved as can be seen from Figure 5.9. The percentage of the initial mass of PFOMA that was dissolved is plotted in Figure 5.10 as a function of CO\textsubscript{2} density. To obtain this figure, the dissolution curve was truncated after 1 hour; any polymer remaining on the crystal after such time is considered practically insoluble \[105\]. At lower densities only a small fraction of the polymer was removed. The maximum removal shown on this figure is 93% which occurs at 759 kg/m\textsuperscript{3}, corresponding to 40 °C and 2000 psi. Again, the effect of density appears to be the most important in determining the amount of polymer removed.

SEM images of the polymer film before and after dissolution (shown in Figure 5.11) clearly show the non-soluble parts of the PFOMA. This non-soluble portion of the polymer

---

### Table 5.1: Regression parameters for PFOMA at different CO\textsubscript{2} conditions sorted by CO\textsubscript{2} density.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (psi)</th>
<th>$\rho_{CO_2}$ (kg/m\textsuperscript{3})</th>
<th>$\kappa_1 \times 10^3$</th>
<th>$\kappa_2 \times 10^3$</th>
<th>$\kappa_3 \times 10^4$</th>
</tr>
</thead>
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<tr>
<td>40</td>
<td>1300</td>
<td>475</td>
<td>0.60</td>
<td>3.62</td>
<td>1.71</td>
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<tr>
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<td>1600</td>
<td>486</td>
<td>1.05</td>
<td>5.25</td>
<td>5.00</td>
</tr>
<tr>
<td>50</td>
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<td>594</td>
<td>2.43</td>
<td>6.35</td>
<td>3.54</td>
</tr>
<tr>
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<td>2400</td>
<td>652</td>
<td>7.57</td>
<td>2.50</td>
<td>1.10</td>
</tr>
<tr>
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<td>3200</td>
<td>696</td>
<td>47.2</td>
<td>8.11</td>
<td>1.49</td>
</tr>
<tr>
<td>60</td>
<td>2800</td>
<td>712</td>
<td>35.6</td>
<td>5.13</td>
<td>1.06</td>
</tr>
<tr>
<td>40</td>
<td>1800</td>
<td>728</td>
<td>35.9</td>
<td>3.99</td>
<td>1.14</td>
</tr>
<tr>
<td>40</td>
<td>2000</td>
<td>759</td>
<td>62.1</td>
<td>5.65</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Chapter 5. Polymer Dissolution in CO₂

Figure 5.10: Amount (%) of total original mass of PFOMA removed after ~1 hour. The straight line is drawn to show the trend.

might be due, for example, to having a high molecular weight or a high degree of entanglement. This suggests that complete removal of the polymer is not practically achievable. On the other hand, the low removal extent at low CO₂ densities is not due solely to thermodynamic effects; it could be a kinetically limited process.

5.4 Conclusions

In this study, the dissolution behavior of the fluorinated copolymer PFOMA in supercritical CO₂ was investigated using a quartz crystal microbalance (QCM) over a range of pressures and temperatures. To examine the effect of the polymer film viscoelasticity on the QCM
response, the resistance was measured at different temperatures and pressures. The change in the QCM resistance for coated and uncoated crystals were compared. Based on the linear relation between the QCM resistance change versus the CO\(_2\) density-viscosity product it was concluded that the viscous, nongravimetric effect was mainly due to viscous coupling with the surrounding fluid, \textit{i.e.}, CO\(_2\), and not the polymer.

An evaluation of the QCM response as CO\(_2\) pressure was increased indicated that the dissolution process consisted of two stages: an absorption-dominated stage followed by a dissolution-dominated stage. Equilibrium and kinetics data provided insight into CO\(_2\)-polymer interactions and the resulting dissolution.

From the pressure dependent sorption isotherms the polymer was found to absorb up to 60\% of its weight before dissolution commenced. Using Fickian diffusion model the diffusivity of CO\(_2\) into the polymer film was estimated to be in the order of \(10^{-9}\) cm\(^2\)/sec; typical range for rubbery polymers. The PFOMA dissolved in CO\(_2\) at a pressure slightly above the critical pressure at the lowest temperature studied here (40 °C). The dissolution rate and the extent of polymer dissolved depend strongly on temperature and pressure. At low pressures, as little as 20\% of the polymer mass was removed during dissolution. This could be attributed to the presence of insoluble polymer regions due to, for example, the molecular weight distribution or high entanglement density [105]. It is also believed that at low pressures the dissolution process becomes kinetically limited and very long times are required to achieve complete dissolution.

This study is a step toward the understanding and quantification of polymer dissolution

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.11.png}
\caption{SEM images for PFOMA coated QCM’s: (a) before dissolution and (b) after dissolution.}
\end{figure}
Chapter 5. Polymer Dissolution in CO$_2$

in supercritical CO$_2$ which will help in its successful application in different potential applications. Future studies may include the effect of flowing CO$_2$ on dissolution in comparison to static system to elucidate the effect of mass transfer on the dissolution.

Nomenclature

\begin{align*}
T_c & \quad \text{Critical temperature} \\
P_c & \quad \text{Critical pressure} \\
\rho_q & \quad \text{Quartz density} = 2.648 \text{ g cm}^{-3} \\
\eta_q & \quad \text{Quartz shear modulus} = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{s}^{-2} \\
C_m & \quad \text{QCM constant (frequency-mass conversion)} \\
P_{exp} & \quad \text{Pressure at which polymer dissolution start} \\
P_m & \quad \text{Intermediate pressure, before dissolution stage} \\
S & \quad \text{CO}_2 \text{ solubility in polymer} \\
\Delta m & \quad \text{Change in polymer film mass} \\
m_f & \quad \text{Net mass of polymer removed} \\
m_o & \quad \text{Initial mass of polymer on crystal} \\
m_{dis} & \quad \text{Calculated change in mass during the dissolution stage at } P_{exp} \\
r_t & \quad \text{Dissolution rate at time } t \\
t_{exp} & \quad \text{Time taken during the polymer dissolution stage} \\
F_\circ & \quad \text{Frequency of blank crystal} \\
F_x & \quad \text{Frequency at pressure } x \\
\Delta F_m & \quad \text{Change in frequency due to mass change} \\
\Delta F_P & \quad \text{Change in frequency due to pressure change} \\
\Delta F_\eta & \quad \text{Change in frequency due to viscosity change} \\
\Delta F_T & \quad \text{Change in frequency due to temperature change} \\
\Delta F_f & \quad \text{Change in frequency corresponding to } m_f \\
\Delta F_{CO_2} & \quad \text{Change in frequency due to CO}_2 \text{ adsorption}
\end{align*}
6.1 Introduction

Controlled drug delivery provides a mean to control the manner in which drugs are delivered to the body in terms of rate, concentration, and target [72]. This technology can be utilized in the different drug intake routes such as oral, implants, internasal, and transdermal. In many of these routes, utilization is made of a carrier medium in which the drug is either dispersed inside or the carrier forms a shell that encapsulates the drug sample [74]. These carriers can be designed to alter the pharmacokinetics and biodistribution of the drug thus modulating the drug release in a well-defined manner [192]. Two types of carriers are usually used: polymers and liposomes [72]. The use of polymers has certain advantages over other carriers including simplicity, low cost, and high flexibility [34]. Indeed, the wide range of chemistries and configurations that can be obtained with various polymers allows the synthesis of sophisticated drug delivery systems [73]. For example, polymer carriers can be designed to control the delivery rate by either drug diffusion, polymer dissolution, or a combination of both. Polymers can also be designed to target specific cells or tissues, and to be triggered by certain environments or external events, e.g., magnetic or electric stimulation [73, 193].

Several techniques have been used to incorporate drugs into polymers. The choice of the technique depends on the polymer, the drug, and the desired product form. These techniques range from simple mixing, to extrusion, spray drying, solvent evaporation, freeze
spray atomization, and solvent-induced gelation [193]. A relatively new method that is being researched for drug impregnation utilizes the unique properties of supercritical CO$_2$ (scCO$_2$).

Interest in using scCO$_2$ for the impregnation of polymers was first stimulated by Sand who reported on a “method for impregnating a thermoplastic polymer” [77]. Another patent by Berens et al. [78] followed on the use of CO$_2$ to infuse additives into polymers. Many studies followed on the impregnation of various additives (such as dyes, polymer modifiers, and drugs) into polymers using scCO$_2$ [55]. For drug impregnation in polymers, scCO$_2$ offers several advantages besides being an environmentally friendly solvent. These include the elimination of toxic solvent residuals, the ability to operate at low temperatures for thermally labile materials, aiding the extraction of impurities from the polymer (e.g., residual monomer or inhibitor), and providing precise control over the loading level, particle size, porosity, and surface structure [76, 194].

Several studies have been reported on the impregnation process under supercritical conditions. Berens et al. studied the impregnation of different PVC films with dimethyl phthalate (DMP) at 25 °C and pressures up to 950 psi using a simple gravimetric technique [86]. They concluded that DMP uptake decreases as the pressure increases due to the reduced DMP activity at higher CO$_2$ densities. They argued that DMP remains in the polymer after CO$_2$ is released due to polymer deplasticization upon CO$_2$ desorption. As the concentration of CO$_2$ in the polymer decrease, the polymer will return to its glassy state. In this state, the diffusion coefficient in polymers becomes a strong function of the molecular diameter of the diffusant. Since DMP molecules are larger than that of CO$_2$, its desorption becomes kinetically hindered.

Kazarian and coworkers published several spectroscopic studies on supercritical impregnation [64, 79, 195, 196]. Most of these studies focused on the investigation of the interactions between the polymer-CO$_2$-additive materials. For example, they showed that the presence of OH groups on the additive decreased the diffusivity by a factor of 10 compared to the case when such group was absent, which they said to be due to the interactions between the additive and the polymer. An important conclusion from their studies is that the CO$_2$ role in the impregnation process is to act as a “molecular lubricant” [76].
Sicardi et al. presented a study that utilized the film role method to determine the impregnation of two dyes into PET films [82, 88]. They compared their impregnation data for the supercritical case with aqueous impregnation processes and confirmed the high increase in the diffusion coefficient for the former case. Another comparative study was reported by Elvira et al. [66] where PMMA and PMMA/poly(ε-caprolactone) blend microspheres where impregnated with cholesterol using supercritical and dissolution-evaporation techniques. Again, the higher diffusion rate in the supercritical case was observed. They also found that cholesterol crystallized inside the polymer matrix for the case of dissolution-evaporation. Yet, another study compared the supercritical impregnation process to the solution coating and solvent casting techniques [87]. In this work, the authors impregnated a fluorescent probe, 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3-diazole (NBD), into polypropylene films, thickness between 50–90 µm, and used confocal microscopy and UV/Vis spectroscopy to characterize the resulting product. They found an enhanced loading of NBD in the supercritical case compared to the solvent casting technique. Supercritically impregnated NBD showed a uniform distribution throughout the sample thickness.

In this work, the supercritical impregnation of ibuprofen into two different polymer films is investigated. Ibuprofen (IBU), 2-[4-(2-methylpropyl) phenyl] propanoic acid, is a non-steroidal anti-inflammatory drug marketed as a pain-relief product under several commercial names such as Advil and Act-3. IBU was chosen since it is a commonly used drug for impregnation studies. Two commonly used polymers for impregnation studies [73, 76] have been chosen for the current study: poly(methyl methacrylate), PMMA, and poly(vinyl pyrrolidone), PVP. PMMA is a biocompatible polymer that is used for applications in which the drug release mechanism is controlled by diffusion [193]. PVP is used as a biodegradable polymer (water soluble) that can be stabilized by crosslinking with a biodegradable agent [197].

The aim of this study is to investigate the impregnation process of IBU into PMMA films in real-time and in-situ using the quartz crystal microbalance (QCM). Several aspects of the impregnation process will be considered including: the effect of CO₂ density, bulk phase drug concentration, polymer film thickness, and impregnation kinetics. A comparison

\footnote{IBU has two enantiomers, (S)-(+) and (R)-(−)-ibuprofen. While only the (S) enantiomer is biologically active, the (R) enantiomer was found to be converted inside the body into the (S) form through biologically catalyzed enantiomeric interconversion. Therefore, IBU is usually administered as a racemic mixture.}
between PMMA and PVP is also presented.

6.2 Experimental

6.2.1 Materials

Racemic IBU (purity ~98%) was obtained from Sigma. PMMA (molecular weight 72k and PDI 1.08) was obtained from Polymer Source Inc. (Montreal, Canada). PVP (molecular weight ~40k) in powder form was obtained from Fluka. The structures of IBU, PMMA, and PVP are shown in Figure 6.1. Toluene (purity > 99.999%) was obtained from EMD Chemical (Germany). Ethanol (purity ~99.5%) was obtained from Acros Organics (Geel, Belgium). Coleman Grade (>99.999%) CO₂ was obtained from National Welders. All materials were used as received.

![Chemical structures of IBU, PMMA, and PVP.](image)

Figure 6.1: Chemical structures of IBU, PMMA, and PVP.

For the impregnation studies, the polymer films were prepared by the dip coating technique. PMMA films were cast from a solution of 5% by weight in toluene. The PVP films were cast from a 4% solution in ethanol. The solutions were prepared by mixing the materials in the required proportion, stirring till the solution became clear, then filtering through a 0.45 micron filter to remove any impurities or non-soluble materials. After coating, the films were dried under vacuum for 1–2 hours at 85 °C for PMMA and 150 °C for PVP.
Chapter 6. Impregnation of Drugs into Polymers

6.2.2 Setup & Procedures

The setup used for the impregnation experiments is shown in Figure 6.2. The setup consisted of two high pressure cells: the QCM cell and the drug cell. The two cells were connected via a circulation pump as described below.

The QCM cell was a custom made, stainless steel vessel with 31 ml volume. The cell was placed in a water bath where the temperature was controlled to ±0.1 °C. The QCM crystals used were smooth, Au-coated quartz crystals with 5 MHz natural frequency obtained from ICM (Oklahoma City, OK). A high pressure electrical feedthrough (Conax Buffalo Technologies, NY) was utilized to connect the crystal to an oscillator circuit. The circuit used was a voltage-controlled oscillator (Maxtek, model PLO-10, Santa Fe Springs, CA) that provided two outputs, frequency and voltage. The voltage signal can be used to calculate the motional resistance of the QCM. The frequency, voltage, temperature, and pressure readings were all acquired using a data acquisition system (DAQ) connected to a PC.

The drug cell was mounted on a magnetic stirrer and heated using electrical heating tape and a temperature controller (Cole-Parmer, Vernon Hills, IL). A viewing window was installed on the top side of the cell to allow the observation of the drug to visually ensure

Figure 6.2: Schematic illustration of the used setup of impregnation studies.
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complete solubility was achieved before starting the circulation. The pressure in the cell was monitored using a pressure transducer and meter (Omega Engineering, Stamford, CT).

CO\textsubscript{2} was supplied to both cells through a high pressure ISCO pump (ISCO Inc., Lincoln, NE) which was connected to the two cells simultaneously. A check valve was installed to prevent the drug from being carried back to the drug cell to the QCM cell. The two parts of the setup were connected through a circulation loop. The loop consists of a motor-driven, high pressure pump (Micropump Inc., Vancouver, WA) to circulate the CO\textsubscript{2}-drug mixture between the two cells, a switch valve (Vici Valco Instruments, Houston, TX) to direct the circulation, and a high pressure filter (HiP, Eire, PA) to prevent the undissolved drug particles from being entrained into the QCM cell.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.3.jpg}
\caption{A typical impregnation experiment (conditions: 40 °C, 2000 psi, and 0.3 g IBU dissolved in CO\textsubscript{2}). The arrow indicates the point where IBU was introduced into the QCM cell.}
\end{figure}
Chapter 6. Impregnation of Drugs into Polymers

An example of the QCM response during a typical impregnation run is presented in Figure 6.3. Each experiment started by measuring the fundamental frequency, $F_\circ$, of the uncoated QCM at the experiment’s temperature in vacuum (zone I in Figure 6.3). The QCM was then removed and coated with the desired polymer as outlined above. The coated QCM was then put in the QCM cell and preconditioned under CO$_2$ (at the experiment’s temperature and pressure) for about 30 minutes to ensure the removal of the remaining residual solvent (zone II). At the end of the preconditioning step, the QCM cell was flushed with about 1 volume of CO$_2$ before the pressure was released. The base frequency of the polymer-coated QCM was recorded under vacuum, $F_f$ (zone III). The difference between $F_\circ$ and $F_f$ was used to estimate the initial polymer mass.

The impregnation process started by pressurizing the two cells to the required pressure with CO$_2$. The circulation pump was then turned on and the switch valve adjusted so that CO$_2$ was circulated through the QCM cell only (zone IV). In the drug cell, the magnetic stirrer was turned on to dissolve the drug in CO$_2$. Once the frequency of the QCM reached a stable signal, within ±1 Hz for time intervals of about 1 hour, the switch valve was adjusted to allow the circulation through both cells. The circulation was continued until a new stable frequency signal was obtained (zone V). Finally, at the end of the run, the two cells were flushed with ~60 ml of CO$_2$ before the pressure was released (zone VI). All experiments were operated in the homogeneous CO$_2$-IBU phase according to the solubility data reported by literature [198]. This was necessary to avoid blocking the tube lines and to prevent the break down of the circulation pump.

6.3 Results & Discussion

6.3.1 Reliability of QCM results

It was established in Chapter 4 that, in order to obtain reliable results from the QCM, the polymer film thickness must be maintained at a low level to prevent severe non-gravimetric interactions due to the polymer viscoelasticity. Thicknesses in the range of 300 nm were found to give results in agreement with that in literature. The studies performed in this part of the work utilized films having a thickness in the order of ~250 nm which can be considered within the thin film limits for the QCM studies. Therefore, it remains to examine
the effect of IBU loading on the QCM resistance ($R$). In Figure 6.4 a comparison is made between the $\Delta R$ before and after IBU was added. It is evident from the figure that the presence of IBU did not induce any significant changes, within experimental error, on $\Delta R$ compared to the values when only $CO_2$ was absorbed. In addition to the small polymer thickness, this can be attributed to the fact that the IBU will reduce the amount of $CO_2$ absorbed into PMMA due to the high partitioning coefficient of IBU between PMMA and $CO_2$.

**Figure 6.4**: Resistance change in PMMA-coated QCM at different $CO_2$ bulk conditions (i.e., density/viscosity change) upon absorption of $CO_2$ only and $CO_2$+IBU.
6.3.2 IBU-PMMA system

One of the important aspects in the impregnation process is to determine the mass uptake of the drug in the polymer. This is usually done by measuring the concentration of the drug inside the polymer by off-line analysis of the sample [82] or, less frequently, by measuring the concentration in the effluent CO$_2$ [83]. In this work in-situ, gravimetric measurements of IBU uptake at various concentrations in the CO$_2$ phase and different pressures and temperatures were obtained; the results are shown in Figure 6.5. The uptake levels varied with CO$_2$ conditions and IBU concentration from few percents up to 30%. These values are in reasonable agreement with previous supercritical impregnation studies on IBU into PVP.
films where the uptake varied between 10–30% [64]. In comparison with studies on the supercritical impregnation of IBU into PVP, the partitioning coefficient ($K$) of IBU between CO$_2$ and PMMA is also shown in the figure insert. The value of $K$ was obtained from the slope of the straight line fits of the data at each CO$_2$ density. It can be seen from the figure that IBU uptake decreases as CO$_2$ density increases, this can be explained using the solubility parameter approach.

In the solubility parameter approach, the strength of interaction between two components is determined by the difference between their corresponding solubility parameters ($\delta$’s) [199]. A good solvent will have a solubility parameter close to that of the solute [7]. This approach has been used in the literature in attempts to explain the miscibility of solid dispersions of drugs into different carriers [200, 201]. It was suggested that systems with difference between the solubility parameter of the drug and that of the carrier ($\Delta \delta$) smaller than 7.5 MPa$^{1/2}$ show complete miscibility, systems with $\Delta \delta$ between 7.4 and 15.0 MPa$^{1/2}$ show some sign of immiscibility, and those with $\Delta \delta$ above 15.9 MPa$^{1/2}$ show complete immiscibility [200]. The solubility parameters for IBU, PMMA, and CO$_2$ are shown in Table 6.1. The solubility parameter for CO$_2$ depends on its density and was calculated using the Hildebrand-Scott relation given by [202]:

$$\delta = \frac{a^{1/2}}{V}$$

(6.1)

where $\delta$ is the solubility parameter in MPa$^{1/2}$, $a$ is the van der Waals interaction parameter ($=3.64 \times 10^5$ J·cm$^2$/mol$^2$ for CO$_2$), and $V$ is the molar volume of CO$_2$. As can be seen

<table>
<thead>
<tr>
<th>Component</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>19.4</td>
<td>[7]</td>
</tr>
<tr>
<td>IBU</td>
<td>20.9</td>
<td>[200]</td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td>Eq. (6.1)</td>
</tr>
<tr>
<td>$\rho = 0.66$ g·cm$^{-3}$</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>$\rho = 0.76$</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>$\rho = 0.85$</td>
<td>11.7</td>
<td></td>
</tr>
</tbody>
</table>

from Table 6.1, the absolute difference between the solubility parameters of CO$_2$ and both PMMA and IBU, i.e., $|\delta_{CO_2} - \delta_{PMMA}|$ and $|\delta_{CO_2} - \delta_{IBU}|$, decrease with increasing CO$_2$
density. Therefore, the interaction of CO\(_2\) with PMMA and IBU is expected to become stronger as the density increases (i.e., increasing pressure). As a result, the amount of IBU that will mix with PMMA will be negatively affected by its stronger interaction with CO\(_2\) as well as that between PMMA and CO\(_2\). This will yield, as observed, a decrease in the value of \(K\) as the CO\(_2\) density increases (Figure 6.5), a behavior that has been observed for other additive/polymer systems [85, 86, 195, 196].

The dependence of \(K\) on CO\(_2\) density can be discussed from a molecular interaction perspective. For PMMA, the oxygen atom of the carbonyl group has been shown to form an electron donor–acceptor complex with the CO\(_2\) molecule [172]. The strength of this interaction tends to increase as the CO\(_2\) density increases. On the other hand, this oxygen forms an H-bond with the –OH group in IBU [64]. Kazarian and Martirosyan showed that the IBU–PMMA interaction “wins” over that between CO\(_2\)–PMMA which explains the high uptake of IBU at low CO\(_2\) densities [64]. Consequently, it can be concluded that the decrease in the IBU uptake as CO\(_2\) density increases is due to the domination of CO\(_2\)–PMMA interaction over that of IBU–PMMA as the strength of the former increases with CO\(_2\) density which results in a decrease in \(K\) with density.

The large values of \(K\), as shown in Figure 6.5, indicates a thermodynamically driven impregnation mechanism. It has been suggested that the scCO\(_2\)-assisted impregnation into polymeric materials occurs via one of two different mechanisms [76]. The first mechanism is when the additive has low solubility in scCO\(_2\). In this case, the impregnation process is driven by the high distribution coefficient between the additive between CO\(_2\) and the polymer causing more additive to concentrate in the polymer. The second mechanism involves additives with high solubility in the scCO\(_2\) phase. In this case, CO\(_2\) acts as a carrier that delivers the drug into the swollen polymeric matrix. Upon desorption, the CO\(_2\) diffuses at a faster rate compared to the additive material which become entrapped inside the deplasticized polymer. As shown in the insert of Figure 6.5 the value of \(K\) is very high which suggests that the impregnation is most probably driven by the thermodynamical favorability of IBU sorption into PMMA.

Next, the effect of PMMA film thickness on the total amount of IBU absorbed will be examined. The uptake trend as a function of the polymer thickness will be used to evaluate, roughly, the drug distribution uniformity inside the polymer. A linear increase of
the uptake as a function of the polymer thickness indicates that the drug diffuses throughout the polymer and is not concentrated in layer close to the surface. The distribution uniformity criterion is important in drug delivery applications to ensure that the desirable release rate is achieved. If, on the other hand, the drug was concentrated on the area close to the surface, a high initial release rate might result yielding high levels of drug concentration.

In Figure 6.6 the amount of IBU uptake measured at different initial PMMA thickness is shown where the polymer thickness was varied from 25 to 250 nm. These values where determined using the initial change of the QCM frequency upon coating and a PMMA density of 1.19 g/cm$^3$ [203]. The figure shows a linear decrease in IBU uptake with decreasing polymer thickness. The straight line fitted through the data in this figure has a slope of
impregnation of drugs into polymers, slightly higher than the values in Figure 6.6. Therefore, it can be concluded that CO₂ effectively facilitate the diffusion of the drug inside the polymer resulting in a uniformly spatial distribution.

Impregnation Kinetics

The analysis of polymer impregnation kinetics is usually done indirectly by either measuring the concentration of the additive in the CO₂ stream leaving the impregnation cell [83, 85] or by analyzing the final polymer film after being exposed to the supercritical solution for certain amount of time [86, 88]. In few cases, the impregnation was analyzed in real time by measuring the additive concentration inside the polymer through analysis of spectroscopic signal [196, 204]. In this section, the kinetics of IBU diffusion is extracted directly from the QCM measurements and the results are used to estimate the diffusivity of IBU into PMMA.

The kinetics of supercritical impregnation of additives into polymers is commonly described with a Fickian model [83, 88, 196, 204]. In this research, the polymer at the impregnation conditions is in the glassy state and is already swollen by the CO₂. Therefore, it is expected that the change in the polymer density due to IBU sorption will be negligible and the polymer is expected to adhere to Fick’s law. The diffusion process can be expressed for a plane sheet with uniform initial distribution as [31]:

\[
\frac{M}{M_\infty} = 8 \left( \frac{Dt}{l^2} \right)^{1/2} \left[ \frac{1}{\pi^{1/2}} + 2 \sum_{n=0}^{\infty} \left( -1 \right)^n \text{erfc} \left( \frac{ml}{4(Dt)^{1/2}} \right) \right]
\]

where \(M\) is the drug uptake at any time \(t\), \(M_\infty\) is the final drug uptake, \(D\) is the diffusivity, and \(l\) is the film thickness. The value of \(l\) can be estimated from the initial polymer mass and density and the expected swelling at the experimental pressure and temperature as reported previously [169]. For the initial stage of diffusion \((M/M_\infty < 0.6)\), Eq. (6.2) can be approximated as:

\[
\frac{M}{M_\infty} = \frac{8}{\pi^{1/2}} \left( \frac{Dt}{l^2} \right)^{1/2}
\]

From Eq. (6.3), a plot of \(M/M_\infty\) versus \(t^{1/2}\) will give a straight line for the initial impregnation stage.

The QCM frequency change as a function of time was used to calculate the value of
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Figure 6.7: Time profiles for IBU impregnation into PMMA films at 40 °C and 2000 psi for different initial bulk IBU concentrations. The partition coefficient (K) at these conditions is $28 \times 10^3$. The arrow indicates the direction of IBU concentration increase.

$M/M_\infty$ using the following relations:

$$\frac{M}{M_\infty} = \frac{F - F_b}{F_\infty - F_b}$$  \hspace{1cm} (6.4)

In this equation, $F$ is the frequency at any time, $F_b$ is the frequency in CO$_2$ before the introduction of IBU, and $F_\infty$ is the final stable frequency after IBU has been introduced. Some examples of such calculations are plotted as a function of $t^{1/2}$ in Figure 6.7. As can be seen from this figure, the initial part of the curve is not linear. This discrepancy from Fickian diffusion might be due to the presence of other factors that are not accounted
with in Eq. (6.2). One possible factor that might affect the concentration profiles is the effect of mixing between the QCM and the drug cell. The IBU concentration in the QCM cell will not reach its steady state value with the drug cell instantaneously, which can also explain the dependence of the rate on the initial IBU concentration seen in the figure. Other factors intrinsic to the diffusion process might also play a role, e.g., the dependence of $D$ on concentration, although good agreement with Fickian diffusion equations had been reported in the literature but for much thicker films (> 100 µm) [83, 204].

![Figure 6.8](image)

**Figure 6.8:** IBU uptake rate versus initial IBU concentration in CO$_2$ at different temperatures and pressures. The straight lines are drawn to guide the eye.

Nevertheless, qualitative comparisons can still be made between the impregnation rates at different conditions. The results for dissolution rates at different temperatures and pressures are shown in Figure 6.8. The values in this figure were determined from the slope of the $M/M_\infty$ curve at $t_{50}$; the time at which $M/M_\infty = 0.5$. This figure clearly highlights
the effect of the temperature and pressure on the impregnation rate. At 40 °C, the rate isotherms at 2000 and 3000 psi do not show significant differences. This can be explained by considering the behavior of PMMA films with CO$_2$ pressure. The dependence on CO$_2$ pressure of both the swelling and sorption in PMMA films becomes weak at pressures above the critical point [169]. This conclusion reinforces the role of CO$_2$ as a swelling agent in the impregnation process.

Temperature, on the other hand, shows a more drastic effect on the impregnation rate. The rate significantly increases upon raising the temperature by 10 °C. The role of temperature in increasing the diffusivity is well known; the impregnation rate increases as the temperature increases. The dependence of impregnation rate of temperature has been utilized in the dyeing industry to control the kinetics of the process in conjunction with the uptake extent [31].

6.3.3 PVP-IBU system

In this part of the research, preliminary studies on the uptake of IBU in poly(vinyl pyrrolidone), PVP, samples were performed. This system had been examined using IR and Raman spectroscopy by Kazarian and Martirosyan [64]. In their paper, the authors concluded that IBU was molecularly dispersed into the PVP due to the interaction via H-bonding. These interactions also help in preventing the IBU from crystallization. IBU uptake into PVP was found to range from 10–30 wt%.

Before discussing the impregnation results, the behavior of PVP in pure CO$_2$ is presented. PVP is a stiffer polymer than PMMA ($T_g$ about 180 °C) and is known to absorb CO$_2$ to a much lesser extent. In Figure 6.9, our QCM results are compared to literature values in the same system [92]. The literature values were determined using powder PVP samples and the absorption was measured using a conventional microbalance. A good agreement was obtained which highlight the validity of the QCM technique with this polymer.

Our studies on PVP using the QCM showed an unusual behavior. Upon introducing the IBU into the PVP-coated QCM cell, the frequency decreased almost instantaneously, followed by a slow decrease before the frequency reached a new stable level (Figure 6.10). The overall change in the frequency, as shown in Figure 6.11, ranged from 60–220% of the frequency change due to the initial polymer mass. The change was accompanied by a
large decrease in the QCM resistance of \( \sim 200 \, \Omega \). The large changes in the frequency and resistance suggest that the PVP film experiences some physical changes due to IBU presence. Studies on the influence of various drugs on the \( T_g \) of PVP showed that a depression as high as \( 100 \, ^\circ\text{C} \) can result [205, 206]. This depression in \( T_g \), in addition to the fact that CO\(_2\) itself is a strong plasticizer for polymers, might indicate a possibility of large changes in the PVP film viscoelasticity which might contribute to an explanation for the QCM behavior. There is also a possibility of delamination of the PVP film upon exposure to the IBU-CO\(_2\) solution. Further studies are needed on this system to confirm these conclusions.
Chapter 6. Impregnation of Drugs into Polymers

Figure 6.10: Change in frequency of PVP coated QCM upon introduction of IBU (initial concentration in CO\textsubscript{2} $\sim$2.6 mg) at 2000 psi and 40 °C. The arrow indicates the point at which IBU was introduced.

6.4 Conclusions

The utilization of supercritical technology in drug formulation is an exciting field that offers clear advantages over the traditional, aqueous or organic-based techniques. Several studies have been published on the subject since its introduction in the mid 1980s. We believe this study is the first to apply the quartz crystal microbalance technique for \textit{in-situ} characterization of additive impregnation into polymeric films under supercritical conditions. Two systems were studied: PMMA-ibuprofen and PVP-ibuprofen.

The effect of increasing CO\textsubscript{2} density was found to decrease the uptake of IBU into
Figure 6.11: Frequency change due to IBU introduction into the PVP-coated QCM crystal cell as a function of the initial IBU concentration in CO$_2$ at 40 °C and 2000 psi.

PMMA, in agreement with reported studies in literature [85, 86, 195, 196]. This behavior was explained using the solubility parameter approach. Since the solubility parameter for CO$_2$ increases with its density, the interactions between CO$_2$ and both PMMA and IBU strengthen as the density is increased causing the partitioning of IBU in PMMA to decrease. This is also in agreement with the expected molecular interactions between the three components.

An almost linear increase in overall IBU uptake as a function of initial PMMA film thickness was found. This linearity suggests that the IBU was uniformly distributed into the polymer matrix. This is believed to be due to the excellent swelling capacity of the CO$_2$ on PMMA.
Chapter 6. Impregnation of Drugs into Polymers

The impregnation rate was qualitatively investigated for the effect of temperature and pressure. The temperature effect was found to be the most significant as the rate increased by as much as 10 folds upon increasing the temperature by 10 °C. Pressure, on the other hand, had little effect on the rate.

Finally, similar studies to that on PMMA were done using PVP. With this polymer, the QCM response to the introduction of IBU was dramatically different. Very large changes in the frequency and resistance were observed. Possible explanations for such behavior can be that the PVP is experiencing large changes in its viscoelasticity or the delamination of the PVP film. Both of these explanations can have a big effect on the QCM response. Future studies on this system include high pressure, rheological measurements to determine the effect of IBU concentration on the PVP viscosity, and using imaging techniques (e.g., SEM) to examine the state of the film and its adhesion to the substrate. These studies will help in elucidating the causes of the observed behavior with PVP.
Chapter 7

Summary & Future Recommendations

7.1 Overview

The unique role supercritical carbon dioxide can have in polymer processing motivated this research and directed it toward the study of different possibilities in the CO$_2$-polymer processing area. Specifically, CO$_2$ was studied as a simple absorbent and swelling agent for non-soluble polymer, as an agent for supercritical cleaning of soluble polymer films, and as an impregnation agent with a relatively more complex, multicomponent interactions.

In the first part of the research, PMMA, a polymer considered non-soluble in CO$_2$, was used to study the sorption process under high pressures. The sorption of CO$_2$ into the polymer matrix caused an increase in its total mass combined with deformation of the polymer sample. These processes affected the physical properties of the polymer (density and viscoelasticity). In this research, sorption isotherms and sorption kinetics were monitored through mass change measurements. Two distinct regions were observed by these measurements due to the sorption induced glass transition. The distinct diffusion mechanisms and the hysteresis in the sorption-desorption cycles defined the two regions.

The second part of the polymer studies was on polymer dissolution. The good compatibility of fluorinated polymers with CO$_2$ was utilized to provide a suitable system for the studies. A novel copolymer (PFOMA) that belongs to a family of copolymers containing a lithographically patternable, photoacid cleavable tetrahydropyanyl groups was investigated. A protocol for performing these dissolution experiments was first established. Dissolution runs were then carried out at different temperatures and pressures. The dissolution process was analyzed from the initial, sorption-dominated stage and until the dissolution ceases.
The high CO₂-philicity of this polymer was evident from the sorption isotherms (Figure 5.6) which were curved toward the concentration axis. The dissolution rate of the polymer showed a strong dependence on CO₂ density as well as the total dissolvable amount of the polymer.

The final study investigated the impregnation process of additives into polymers. Two biocompatible polymers, PMMA and PVP, were selected. Ibuprofen was selected as the additive material. The effect of bulk concentration, film thickness, temperature, and pressure were examined. The partitioning coefficient and the impregnation rate were determined. The results for PVP impregnation were compared to that of PMMA. CO₂ power as an impregnation agent was a strong function of its density. Less ibuprofen was impregnated as the CO₂ density increased. The possible interactions between the PMMA/ibuprofen/CO₂ mixture can give an explanation for this behavior.

### 7.2 Advanced Microweighing in High Pressures

The overall theme of this research consisted of two intertwined stages. Before the polymer studies mentioned in the previous section was performed, the first stage was to evaluate the use of the quartz crystal microbalance (QCM) under high pressures. In the early stages of this research, a QCM system was constructed and, after several attempts, was successfully operated. The system was then continuously modified to provide a more stable, accurate, and complete information during the process. Following this step, the behavior of the uncoated QCM under high pressures was studied. The effects of pressure, CO₂ physical properties, surface adsorption, and surface roughness were among the tested parameters. These parameters were studied to determine its effect on the QCM response, i.e., frequency and resistance. Once the governing relations for these factors were confirmed, it was possible to pursue with the next stage of polymer studies.

### 7.3 Novelty

The novelty in this research can be summarized in the following points:

- The analysis of the QCM resistance was incorporated to obtain a better estimation of the magnitude of the viscoelastic contribution and the deviations caused by this effect.
Chapter 7. Summary and Recommendations

- The sorption kinetics of CO\textsubscript{2} into PMMA was determined using the QCM frequency change. This is the first report to use the QCM for a detailed kinetics study under high pressures.
- Real-time polymer gravimetric dissolution studies on a novel fluorinated polymer under high pressures.
- Real-time gravimetric measurements of polymer impregnation. This study was the first to investigate the supercritical impregnation of PMMA with ibuprofen.

7.4 Findings

The project findings can be summarized in the following points:

- The QCM is a valuable technique for high pressure studies. However, the effect of polymer viscoelasticity and the film thickness limits must be carefully considered. For PMMA, it was found that a 1 \(\mu\)m thick film is on the limits of Sauerbrey equation applicability. This was confirmed by analyzing the frequency and resistance data and by comparison with other experimental tools [169].
- PFOMA is a highly soluble polymer in CO\textsubscript{2}. The solubility of the polymer is a strong function of CO\textsubscript{2} density. For 40 °C and 2000 psi, about 90% was removed within 15 minutes.
- The maximum ibuprofen uptake in PMMA for the studied conditions was about 26%. The partitioning coefficient of ibuprofen between PMMA and CO\textsubscript{2} was about 50,000 at the lowest CO\textsubscript{2} density studied and decreased as the density increased. A linear increase in ibuprofen uptake was observed as the PMMA thickness increased indicating a uniform distribution of ibuprofen inside the film.

7.5 Recommendations for Future Work

QCM studies

Throughout the course of this work, the QCM has proved to be a powerful technique for high pressure studies. Its use as mass balance for different polymer processes enabled fast and sensitive measurements under such extreme conditions. However, there are two concerns that need to be thoroughly examined. First, the effect of the film properties on the accuracy
of the QCM results must be studied. This might be done by investigating a series of polymers having different viscoelastic properties under different conditions. The variables that must be studied include the effect of film thickness and that of CO₂ sorption and the subsequent film swelling. One important factor that must be taken into consideration is the effect of the QCM frequency on the viscoelastic properties of the polymer film. The high frequencies encountered with the QCM might yield a significant change in the glass transition temperature of polymers [207]. The main output from this study will be an experimentally determined guidelines for the use of the QCM with polymer films under high pressures. These guidelines will indicate the expected error obtained from the linear relation, Sauerbrey equation relating the mass to the frequency as a function of the film thickness and the polymer properties (i.e., T₉, elastic and viscous moduli).

Second, the effect of surface roughness can be investigated. This might be done by coating the QCM with films having a known morphology and measuring the frequency and resistance changes in CO₂. The morphology might be achieved by lithographic, self-organization, or other techniques. The morphology must then be determined using surface microscopy before conducting the experiments. The change in the frequency and resistance can then be determined for different polymers at different temperatures and pressures. The obtained results for polymers with different properties and different surface morphologies can then be used to obtain an empirical relation for the surface roughness effects on the frequency based on the previous works in this field [129, 130].

Impregnation studies

Supercritical impregnation of drugs into polymers is of special interest not only because of the environmentally friendly process, but also for the high control and solvent-free product that it provides. The work reported in this document on the impregnation of polymers under supercritical CO₂ was a preliminary work aimed at identifying the possible opportunities in this area. The results appear to be promising and encourage to continue the investigations. Beside the need to study other polymer/drug systems, two possible subjects can be addressed.

The first subject is regarding the effect of depressurization of CO₂ at the final product. The depressurization process is usually performed by flushing the system with fresh CO₂ at
the experimental pressure, then depressurizing at a certain rate before collecting the final sample. Two undesirable issues can arise during this process: the extraction of the drug from the polymer during the flushing step, and the precipitation of the drug on the polymer surface during the depressurization. Therefore, it is important to perform systematic studies on the effect of the depressurization procedure on the final product in order to determine an acceptable protocol which will give the optimum results. This can be done by studying different flushing/depressurization rate combinations and examine its effect on the final product through \textit{ex-situ} analysis of the drug concentration and surface composition. Another approach is to use the helium displacement process to flush the $\text{CO}_2$ out of the cell before lowering the pressure.

The second subject is the analysis of the products performance by measuring the release rate of the drug in buffered solution. Since the QCM can be used in liquids as well as under high pressures, it is possible to coat one QCM crystal with the desired polymer, perform the supercritical impregnation, and study the release rate. These two steps can be done on the same crystal while measuring the frequency throughout the process.
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2000.


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Appendix
Appendix A

Raw Data Treatment

In this appendix, a numerical example is given on the treatment used to convert the measured frequencies into mass changes. The calculations of the resistance and its change is also demonstrated. The data used in this example are from a run to determine the absorption of CO$_2$ into PMMA-coated, smooth silicon QCM crystal at 36 °C.

An partial example of the raw data as recorded by the data acquisition software is given below. The data recorded includes: pressure (in psi), frequency (in Hz), voltage (in V), temperature (in °C, not shown here), and comments input by the operator. It can be noticed from the data below that there is a difference between the recorded pressure and the pressure set by the pump (as indicated in the comments field). This is due to calibration differences between the pressure transducer of the system and that of the pump. For all calculations, the recorded pressure is used.

**Polymer coating.** The calculations are performed as follows. The mass of the coated polymer is determined from the difference between the coated and uncoated crystals (points 1 and 2) as follows. The frequency change between points 1 and 2:

$$F_2 - F_1 = 4,988,674 - 5,002,072 = -13398 \text{ Hz}$$

The polymer mass can then be calculated using the Sauerbrey equation as:

$$m_{poly} = \frac{-13398}{-56.6} = 237 \text{ µg/cm}^2$$
Appendix A. Raw Data Treatment

Run # 120804-1: CO\textsubscript{2} uptake in thick PMMA films at 36 °C.

<table>
<thead>
<tr>
<th>Pt. #</th>
<th>P (psig)</th>
<th>Frequency (Hz)</th>
<th>Volt. (V)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-14</td>
<td>5,002,072</td>
<td>1.24</td>
<td>clean (vacuum)</td>
</tr>
<tr>
<td>2</td>
<td>-14</td>
<td>4,988,674</td>
<td>0.77</td>
<td>coated (vacuum, after drying)</td>
</tr>
<tr>
<td>3</td>
<td>179</td>
<td>4,987,700</td>
<td>0.50</td>
<td>coated (pump pres. 150 psi)</td>
</tr>
<tr>
<td>4</td>
<td>305</td>
<td>4,987,341</td>
<td>0.43</td>
<td>coated (pump pres. 300 psi)</td>
</tr>
<tr>
<td>5</td>
<td>453</td>
<td>4,986,927</td>
<td>0.36</td>
<td>coated (pump pres. 450 psi)</td>
</tr>
<tr>
<td>6</td>
<td>653</td>
<td>4,986,426</td>
<td>0.30</td>
<td>coated (pump pres. 600 psi)</td>
</tr>
<tr>
<td>7</td>
<td>697</td>
<td>4,986,315</td>
<td>0.29</td>
<td>coated (pump pres. 750 psi)</td>
</tr>
<tr>
<td>8</td>
<td>867</td>
<td>4,985,808</td>
<td>0.23</td>
<td>coated (pump pres. 900 psi)</td>
</tr>
<tr>
<td>9</td>
<td>1051</td>
<td>4,985,074</td>
<td>0.17</td>
<td>coated (pump pres. 1050 psi)</td>
</tr>
<tr>
<td>10</td>
<td>1197</td>
<td>4,984,754</td>
<td>0.10</td>
<td>coated (pump pres. 1200 psi)</td>
</tr>
<tr>
<td>11</td>
<td>1341</td>
<td>4,984,633</td>
<td>0.10</td>
<td>coated (pump pres. 1350 psi)</td>
</tr>
<tr>
<td>12</td>
<td>1485</td>
<td>4,984,534</td>
<td>0.09</td>
<td>coated (pump pres. 1500 psi)</td>
</tr>
<tr>
<td>13</td>
<td>1629</td>
<td>4,984,441</td>
<td>0.08</td>
<td>coated (pump pres. 1650 psi)</td>
</tr>
<tr>
<td>14</td>
<td>1723</td>
<td>4,984,388</td>
<td>0.08</td>
<td>coated (pump pres. 1800 psi)</td>
</tr>
</tbody>
</table>

The thickness (t) can be estimated from this value as follows:

\[
t = \frac{m_{\text{poly}}}{\rho_{\text{poly}}} = \frac{237 \times 10^{-6}}{2 \times 1.15} = 1.03^{-4} \text{ cm} = 1.03 \mu\text{m}
\]

Here, the value of \( m_{\text{poly}} \) was converted to g/cm\(^2\). The factor 2 in the dominator is used because both faces of the QCM are coated.

CO\textsubscript{2} sorption. The change in mass due to CO\textsubscript{2} absorption can be calculated from the differences between the successive points, \( i.e., \) points 2 and 3, 3 and 4, and so on. However, in this case the change in pressure, and CO\textsubscript{2} viscosity and density must be taken into account as described by Eq. (3.7). For example, for points 2 and 3, the total frequency change is:

\[
\Delta F_T = F_3 - F_2 = 4,987,700 - 4,988,674 = -974 \text{ Hz}
\]
Appendix A. Raw Data Treatment

The pressure effect can be calculated using Eq. (3.12). For this specific example, the pressure contribution is:

$$\Delta F_p = 0.34 \times (179 - (-14)) = +66 \text{ Hz}$$

In addition to the pressure contribution, the change in CO\textsubscript{2} physical properties must be taken into account. This is done through Eq. (3.9). The density-viscosity product ($\rho\eta$) of CO\textsubscript{2} at 35 °C and 193 psi (179 + 14 psi) can be found from physical properties tables [9] and is equal to $3.93 \times 10^{-4} \text{ kg.m}^{-4}\cdot\text{s}^{-1}$. The viscosity contribution is then:

$$\Delta F_\eta = -0.5(56.6 \times 10^{-2})(\pi \times 5,002,072)^{1/2}(3.93 \times 10^{-4})^{1/2} = -22 \text{ Hz}$$

The frequency change due to CO\textsubscript{2} mass uptake is then calculated as:

$$\Delta F_m = \Delta F_T - \Delta F_p - \Delta F_\eta$$

$$= (-974) - (+66) - (-22)$$

$$= -930 \text{ Hz}$$

Finally, the mass change can be estimated from $\Delta F_m$ using the Sauerbrey equation:

$$\Delta m_{\text{CO}_2} = \frac{-930}{-56.6} = 16 \mu\text{g/cm}^2$$

The weight fraction of CO\textsubscript{2} in PMMA ($\Omega$) is then:

$$\Omega = \frac{\Delta m_{\text{CO}_2}}{m_{\text{poly}}} = \frac{66}{237} = 0.07$$

**Resistance calculations.** The values of the measured voltage can be used to estimate the change in the QCM resistance. This can be done as follows. The value of the resistance can be calculated using Eq. (3.22). For the uncoated crystal this is equal to:

$$R_o = \frac{32}{1.24} - 20 = 6 \Omega$$

This low value is expected for uncoated quartz. The change in the resistance due to polymer coating (point 2) is:

$$\Delta R_{\text{coat}} = \left(\frac{32}{0.77} - 20\right) - (6) = 15 \Omega$$
Appendix A. Raw Data Treatment

It can be seen here that the polymer layer caused the resistance to increase. This increase, however, is still small. As the pressure increases, the resistance change becomes more significant. For example, the resistance change due to increasing the pressure up to 1650 psi (point 13) is:

\[ \Delta R_{\text{sorp}} = \left( \frac{32}{0.08} - 20 \right) - (6) = 374 \Omega \]

This change is due to two factors. First, the change in the CO\(_2\) properties with pressure. This contribution can be estimated using Eq. (3.11). The value of \((\rho \eta)\) for CO\(_2\) at 36 °C and 1650 psi is \(4.6 \times 10^{-2} \text{ kg}^{1/2} \cdot \text{m}^{-2} \cdot \text{s}^{-1/2}\). Using this value in Eq. (3.11) gives:

\[ \Delta R_{\text{CO}_2} = \frac{\pi}{8(7.74 \times 10^{-4})(4.25 \times 10^{-12})} \times \left( \frac{4.6 \times 10^{-2}}{\pi(4,990,536.9)(2.947 \times 10^{11})(2.651 \times 10^3)} \right)^{1/2} = 250 \Omega \]

The second contribution to \(\Delta R_{\text{sorp}}\) is due to the change in the polymer film properties as the absorbed CO\(_2\) causes the plasticization of the film. This contribution can be estimated from the difference between the \(\Delta R_{\text{sorp}}\) and \(\Delta R_{\text{CO}_2}\):

\[ \Delta R_{\text{film}} = 374 - 250 = 124 \Omega \]

This is equivalent to 33% of the total change in the resistance.
Appendix B

Effect of CO$_2$ Release Rate on Impregnation

One complication of the supercritical impregnation process occurs during the release step of the supercritical fluid. After the polymer film has been kept under the required pressure for certain amount of time, the CO$_2$-drug mixture must be released to collect the final product. It is important to optimize this step to avoid affecting the quality of the final impregnated polymer. On this regard, three issues have been discussed: the precipitation of the solute on the surface, the final state of the drug inside the polymer, and the morphology of the polymer.

A common release protocol is to flush the system with certain amount of CO$_2$ to remove the CO$_2$-drug mixture before depressurizing. Doing so minimizes the precipitation of the drug on the polymer surface resulting in better uniformity by avoiding the presence of excess drug on the polymer surface. However, flushing results in the extraction of the drug from the polymer. The depressurization rate, on the other hand, can affect the polymer morphology. Slow depressurization to remove the supercritical medium prevents polymer foaming [5] but can cause precipitation on the polymer surface. On the other hand, fast depressurization causes polymer foaming while reducing precipitation. Therefore, it is important to optimize the depressurization between these two limits. In this work, preliminary studies on the effect of the release conditions on the extraction of the impregnated ibuprofen from PMMA were performed. The studies consisted of coating the QCM with PMMA film that is already impregnated with ibuprofen and investigate the effect of different release conditions on the amount of ibuprofen extracted.
Appendix B. Effect of CO$_2$ Release Rate on Impregnation

Experimental A mixture of known composition of PMMA and IBU was dissolved in a known amount of toluene. The total concentration of the PMMA-IBU mixture in toluene was 5 wt% and was similar for all experiments. The mass ratio of IBU to PMMA in the mixture ranged from 1:100 to 1:5. The QCM was coated by the dip coating technique as described in Section 6.2. After casting, the films were dried under vacuum for 2 hours at 50 °C.

Three types of experiments were performed. In the first type, the pressure was increased rapidly from 0 to the experiment pressure, and the QCM was left at this condition for long times (> 10 hours). In another experiments set, the pressure was increased stepwise from 0 to the experimental pressure. After each step, the system was allowed several hours before the next step was introduced. Finally, experiments were performed were the cell was pressurized rapidly to the experiment pressure, then the CO$_2$ was flushed through the cell at a controlled rate while maintaining a constant pressure in the cell.

In all experiments, the frequency of coated crystal after drying (in vacuum) and that after the end of the experiment (also in vacuum) was used to calculated the mass change of ibuprofen.

Results & discussion. The net mass change after the end of each experiment is summarized in Figure B.1. In this figure, the total amount of IBU extracted at 40 °C and 2000 psi and different protocols are shown. The different hatchings represent the initial concentration of ibuprofen in PMMA. The different protocols are: static, where the pressure was maintained at 2000 psi for ~9 hours, stepwise, the pressure was increased from 0 to 2000 psi in 500 psi steps, flow, where the system was flushed with ~ 500 ml CO$_2$ at 8, 20, and 60 ml/min.

The initial ibuprofen concentration in PMMA is indicated on this figure by the horizontal dashed lines. One noticeable observation from this figure is that the extraction for both the 10 and 18 wt% samples around or below this initial concentration. The 1 wt% samples, however, the calculated mass change was 6 times greater than the initial concentration. This behavior was seen consistently for all runs. The explanation for this behavior is not yet clear. One possibility is that the amount of residual solvent left in the sample after drying might have a large effect on low concentration in the 1 wt% samples.
Appendix B. Effect of CO\textsubscript{2} Release Rate on Impregnation

It can be seen from this figure that most of the IBU was extracted by CO\textsubscript{2} in both the static and flowing cases. Mass transfer increased dramatically as CO\textsubscript{2} flow rate increased. The amount of IBU extracted after 9 hours at the static conditions is similar to that extracted after 60, 30, and 10 minutes at 8, 20, and 60 ml/min flow rates, respectively. In Figure B.2, the concentration-time profiles for ibuprofen during the static experiments are shown. As can be seen from the figure, the extraction rate was highest for the 1 wt% sample, lowest for the 10 wt% sample, and intermediate for the 18 wt% sample. As mentioned above, the residual solvent in the PMMA sample might cause an erroneous interpretation of the mass change as being ibuprofen extraction. If this is the case, then the extraction rate is expected

Figure B.1: Comparison between different depressurization protocols. See text for details.
Figure B.2: Time profiles for ibuprofen extraction from PMMA films at 40 °C and 2000 psi under static conditions.

to decrease as the initial concentration of ibuprofen increases.

Another possible explanation for the dependence of the extraction rate on the initial concentration might be made on the basis of CO₂ ability to swell the polymer. As discussed in Chapter 6, the PMMA-ibuprofen interactions are said to win over that between of PMMA-CO₂. Therefore, it is expected that the ability of CO₂ to swell PMMA to become slower as the concentration of ibuprofen in the PMMA increases. In terms of the data in Figure B.2, the sample with 1 wt% ibuprofen will be the easiest to swell with CO₂, thus will have a high extraction rate. As the concentration increases, the swelling power of CO₂ becomes hindered by the presence of ibuprofen. At the highest concentration, however, the amount of ibuprofen available becomes large enough that the extraction rate will increase.
Conclusions. The results from this preliminary work demonstrate that bringing fresh CO$_2$ in contact with the ibuprofen-impregnated PMMA can decrease the ibuprofen concentration significantly. The flushing step usually performed in the supercritical impregnation process causes high losses in the impregnated ibuprofen. This loss increases as the flow rate increases. Further studies are needed on this subject, but the importance of the CO$_2$-release step on the final impregnation amount is evident from these studies.
Appendix C

Technical & Experimental Notes

In this appendix, details of some of the technical and experimental issues are presented. The appendix starts with some details about the apparatus, then a description of the experimental procedures for the different experiments, and finally, possible problems and suggested solutions.

C.1 Apparatus

Most of the components in the QCM apparatus do not require frequent replacements. The main three parts that might will need a change on occasions are the QCM crystals and the circulating pump gears.

<table>
<thead>
<tr>
<th>Crystal Spec.</th>
<th>Si</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part no.</td>
<td>131521-5</td>
<td>151630-5</td>
</tr>
<tr>
<td>Frequency</td>
<td>5 MHz</td>
<td>5 MHz</td>
</tr>
<tr>
<td>Blank Diameter</td>
<td>0.340”</td>
<td></td>
</tr>
<tr>
<td>Surface finishing</td>
<td>Polished</td>
<td></td>
</tr>
<tr>
<td>Electrode</td>
<td>Cr/Au/Si</td>
<td>Cr/Au</td>
</tr>
<tr>
<td>Electrode diameter</td>
<td>0.151”</td>
<td></td>
</tr>
<tr>
<td>Other spec.</td>
<td>Mounted and bonded</td>
<td></td>
</tr>
</tbody>
</table>

QCM. The crystals used in this study were obtained from International Crystal Manufacturing Company, Inc. (website: www.icmfg.com). A wide range of crystals are available from this company with different substrate materials, frequencies, and surface finishing. Two type of crystals were mainly used in this study. The specifications for these crystals are shown in
Appendix C. Technical & Experimental Notes

the following table. Si crystals are fabricated upon request and the delivery data for these crystals is long (months).

**Circulation pump.** The circulation pump used in this work was obtained from Micropump Inc. (website: www.micropump.com). The gears used in the pump are made of poly(phenylene sulfide). The gears might break down or wear with time affecting the pump performance. The replacement part number is: SK-GAH.T23.PPS.0 (or SK-L-16687).

### C.2 Materials

The following chemicals were used in this work:

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular formula</th>
<th>CAS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>CH₃COCH₃</td>
<td>67-64-1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>124-38-9</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>67-66-3</td>
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<tr>
<td>Ethanol</td>
<td>C₂H₆O</td>
<td>64-17-5</td>
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<tr>
<td>Ibuprofen</td>
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<tr>
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<td>(C₅O₂H₈)ₙ</td>
<td>9011-14-7</td>
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<tr>
<td>Poly(vinylpyrrolidone)</td>
<td>(C₆H₉NO)ₙ</td>
<td>9003-39-8</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>C₄H₈O</td>
<td>109-99-9</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>108-88-3</td>
</tr>
<tr>
<td>Trifluorotoluene</td>
<td>C₇H₅F₃</td>
<td>98-08-8</td>
</tr>
</tbody>
</table>

### C.3 Procedure

**Coating.** The coating procedure for all the data presented in this work is similar. The procedure steps are as follows:

1. Before using a new crystal, its base frequency must be measured. This value is important for subsequent use of the crystal to determine its cleanliness.
2. Clean the crystal with suitable solvent (e.g., if PMMA was coated on the crystal, toluene or chloroform might be used), rinse with acetone, and dry with nitrogen or Air’it. Check the frequency and compare to the initial value in step 1. Occasionally, ultrasonic cleaning might be needed for some polymer films. In this case, use acetone or other solvent as the cleaning medium.

3. Mount the crystal on the dip coater arm. Ensure the crystal is vertical to obtain uniform coating on both faces.

4. To obtain the desired film thickness, the withdrawal speed and coating solution concentration must be checked. For example, for a 5 wt% of PMMA/toluene solution a withdrawal speed of 95 rpm gave $\sim 1 \ \mu m$ film. The same solution with 20 rpm gave a $\sim 0.2 \ \mu m$ film. These variations in these values can be large ($\pm 0.05 \ \mu m$). Table C.1 shows a series of coatings performed with a similar solution.

<table>
<thead>
<tr>
<th>rpm</th>
<th>Thick. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
</tr>
<tr>
<td>7</td>
<td>170</td>
</tr>
<tr>
<td>14</td>
<td>230</td>
</tr>
</tbody>
</table>

5. The coated QCM can then be placed in the vacuum oven for drying.

6. After the drying step, measure the frequency and resistance of the coated QCM. The resistance will usually have similar value to the uncoated QCM.

Sorption experiments. When the sorption of CO$_2$ into polymer films is to be measured, the following procedure is suggested:

- Prepare the crystal according to the previous section.
- Mount the crystal on the electrical feed through and measure the frequency and resistance. Ensure that the resistance value is normal ($\sim 1$ V for Si crystals and
Appendix C. Technical & Experimental Notes

∼ 2 V for Au crystals). If the voltage is low, or the frequency signal is not in the normal range (∼ 5.00 MHz), there might be a problem with the connect. Try adjusting the connection by firmly pressing the crystal into the mounting pins.

• Unplug the connection from the oscillator circuit and mount the feedthrough on the pressure cell. Replug the connection and test the frequency and resistance.
• Vacuuming the cell is recommended. The frequency usually changes by 10's of Hertz, but the resistance can change significantly which is important for comparison. Vacuuming also removes the water vapor from the cell.
• It is also recommended to precondition the film before starting the experiment. This can be done by increasing the pressure to a certain level (usually same value as the subsequent experiment), hold the pressure for ∼ 30 minutes, flush with 1 cell volume of fresh CO₂, and depressurize. Preconditioning helps in removing the remaining residual solvent and the stresses that raise during coating and drying.
• Once the pressure returns to zero, vacuum the cell again and record the frequency. This value is the one that must be used to calculate the polymer mass.
• After preconditioning, the sorption experiment can be performed. The pressure can be increased in steps. Small steps are preferred to minimize temperature changes.
• At low pressures, the time needed to reach a stable frequency during sorption is large. At higher pressures, the process is much faster.

Impregnation experiments. For the impregnation experiments, the following procedure is suggested:
• Coat and dry the crystal as in the previous section.
• Before putting the crystal into the cell, the system must be cleaned to remove any remaining material from previous experiments. A combination of acetone CO₂ can be used for this purpose. Ensure that all acetone has evaporated before starting.
• Ensure that the valves are adjusted to the required positions.
• Mount the crystal on the feedthrough and attach it to the QCM cell.
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• Vacuum and pressurize the QCM cell as in the previous section. Keep this cell at the desired impregnation pressure.

• Adjust the valves to circulate the CO₂ through the QCM cell only. This step is necessary to eliminate the startup noise of circulation when the impregnation process starts. Continue to monitor the frequency.

• While the CO₂ sorption in the polymer is taking place, prepare the drug cell. Weigh the required amount of the impregnation material and place it in the cell. A stirrer bar might be needed if the material is not highly soluble.

• Once the frequency starts to stabilize, pressurize the drug cell to the same pressure as the QCM cell. This step must not be done too early to minimize additive loss through undetected leakage.

• When the stability of the frequency reaches a satisfactory level, adjust the circulation to pass through both cells.

• Monitor the frequency until a new stable level is reached.

• Flush the system with fresh CO₂ to remove the additive from the cell then depressurize.
Appendix D

OTS Adsorption: A Dynamic Study

This chapter is a manuscript by Yazan Hussain, Jacqueline Krim, and Christine Grant, published under the same title in *Colloids and Surfaces A*, 262:81–86, 2005.

D.1 Abstract

The uptake of octadecyltrichlorosilane (OTS) from an organic solution has been studied in situ and in real time by means of a quartz crystal microbalance (QCM) technique. Changes in both QCM frequency and resistance are reported for a range of OTS concentrations. In addition, the time dependence of OTS uptake has been used to calculate reaction constants. Silicon surfaces overall are characterized by higher levels of material uptake than gold.

D.2 Introduction

Octadecyltrichlorosilane (OTS) can be readily deposited on hydroxylated silicon, which is of particular interest for the fabrication of MicroElectroMechanical System (MEMS) devices. Surfaces coated with OTS exhibit high hydrophobicity and good chemical resistance. Proposed applications of OTS include its use as a self-patterned-mask for etching of SiO$_2$ on Si [1] and as a lubricant and anti-stiction material in MEMS devices [2,3].

Prior experimental characterizations of OTS films have been performed by several techniques including: Atomic Force Microscopy [4,5], contact angle measurements [6], and high-resolution electron energy-loss spectroscopy (HREELS) [7]. A readily available but less widely used technique for surface studies in liquids is the quartz crystal microbalance (QCM). The QCM is highly sensitive to physical properties, particularly mass, of thin films deposited
Appendix D. OTS Adsorption: A Dynamic Study

onto its surface electrode(s). It has been employed for a wide range of studies that include monitoring thin film deposition rates [8–11], polymer dissolution in supercritical CO$_2$ [12], chemical analysis [13], and determination of polymer shear modulus [14]. We employ it here to monitor real-time OTS uptake in situ from a liquid environment.

The QCM operation depends on the sensitivity of its frequency to environmental variables including mass, viscosity of the surrounding medium, temperature, and pressure. The cumulative effect of all of these factors results in the total change in frequency.

For thin rigid films, the mass of the film is ideally related to the frequency change using the Sauerbrey equation:

$$\Delta F = -\left( \frac{2F_o^2}{\sqrt{\rho_q \mu_q}} \right) \Delta m$$

where $F_o$ is the resonance frequency of the unloaded crystal, $\rho_q$ is the density of quartz ($= 2650$ kg/m$^3$), and $\mu_q$ is the elastic shear modulus of quartz ($= 2.947 \times 10^{10}$ kg m$^{-1}$s$^{-2}$). For changes in frequency that are less than 2% of $F_o$, Sauerbrey’s equation is considered highly accurate.

Changes in frequency associated with viscous coupling can be a major component of the overall frequency response in liquid solutions. The viscous coupling may result from the viscoelasticity in the adsorbed material as well as from the surrounding liquid. When an oscillating crystal is in contact with a viscous medium, the shear wave in quartz will propagate through the medium causing high energy dissipation. This dissipation affects the frequency and the quartz quality factor (Q), which can be quantified by measuring the change in the crystal resistance. In addition, changes in bulk and local viscosity can cause frequency changes. The relationship between medium viscosity ($\eta$) and resistance ($R$) was developed by Klavetter et al. [14]:

$$R = \frac{\pi}{8K^2C_o}\left( \frac{\rho \eta}{\pi F_o \mu_q \rho_q} \right)^{1/2}$$

where $K$ is the quartz electromechanical coupling coefficient ($= 7.74 \times 10^{-3}$), $C_o$ is the static capacitance of the crystal ($= 4.25$ pF), and $\rho$ and $\eta$ are the density and viscosity of
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the liquid. Similarly, the relation between the change in viscosity and $\Delta F$ is [15]:

$$\Delta F = -\left(\frac{F_0^3}{\pi \mu q \rho q}\right)^{1/2} (\rho q)^{1/2}. \quad (D.3)$$

A more complete analysis can be attained by measuring the acoustic impedance, which is usually performed by means of a network analyzer. Alternatively, it is possible to estimate the change in the crystal’s impedance through analysis of frequency and resistance measurements. Lucklum and Hauptmann related the frequency shift, $\Delta F$, and resistance shift, $\Delta R$, to the acoustic load impedance using the following approximations [16]:

$$\frac{\Delta F}{F} = -\frac{\text{Im}(Z_L)}{\pi Z_{cq}} \quad (D.4)$$

$$\frac{\Delta R}{2\omega L} = \frac{\text{Re}(Z_L)}{\pi Z_{cq}} \quad (D.5)$$

where $Z_L$ is the acoustic load impedance, $Z_{cq}$ is the characteristic impedance of the quartz, $\omega (= 2\pi F)$ is the radial frequency, and $L$ is the motional inductance of the unloaded crystal in the equivalent circuit. The authors calculated the impedance for different rubbery coatings in liquids with different viscosities. For example, a coating having a storage modulus ($G'$) of $10^6$ Pa, a loss modulus ($G''$) of $10^5$ Pa, and a thickness of 100 nm immersed in 1 cP Newtonian liquid will have an impedance of ca. $8 + j6300$ Pa·s·m$^{-1}$. The acoustic load of the liquid alone is ca. $5600 + j5600$ Pa·s·m$^{-1}$. The value of $L$ for the crystals used in this study was assumed to be 30 mH. Such analysis can be used to study the interfacial slippage of the adsorbed film [17]. Further details on the quartz crystal oscillator and its operation can be found elsewhere [18–20].

No prior studies of OTS uptake by means of QCM were found in literature. The most relevant work is that by Ruehe et al. [21] for the deposition of mono- and dichlorosilanes on Au surfaces. This paper presents a real-time study of OTS deposition from organic solvent onto both Si and metal coated QCM crystals. Both the frequency and resistance changes of the crystal in the liquid phase solution are evaluated. The overall objective is to provide information about the interactions and changes that occur on and close to the surface during uptake on materials of interests to MEMS applications.
Appendix D. OTS Adsorption: A Dynamic Study

D.3 Materials and Method

D.3.1 QCM Apparatus

Polished grade, 5 MHz, AT-cut QCM crystals obtained from Maxtek Inc. were used. A Teflon holder, also obtained from Maxtek, Inc., provided mechanical support and an electrical connection to drive the crystal. The holder allowed only one side of the crystal to be exposed to liquid. The crystals consisted of 2.5 cm diameter quartz disks upon which a thin layer of metal (either 1000 Å Si or 3400 Å Au) was vacuum deposited onto the liquid exposure side (1.3 cm diameter). A gold electrode (0.64 cm diameter), which was not exposed to the liquid, was deposited onto the reverse side of the crystal. A VC oscillator, obtained from Maxtek, was used to drive the crystal. The circuit provides two outputs: frequency and voltage. A frequency counter and a multimeter were used for frequency and resistance measurements. A schematic of the setup is shown in Figure D.1.

Figure D.1: Experimental setup.
D.3.2 Experimental technique and materials

OTS (90+%), chloroform and hexadecane (99+% anhydrous grade), dodecanethiol, and ethanol were obtained from Aldrich. The OTS was stored under vacuum. All materials were used as received without further purification.

Prior to each run, crystals were thoroughly washed with running water then rinsed with DI water, immersed in 0.05 M NaOH solution (∼30 min), treated with UV/O for 30 min, immersed in ethanol (∼30 min), and, finally, treated again with UV/O3. The second UV/O3 treatment is to remove the remaining traces of contaminants and to generate the required hydroxylated surface [22]. This procedure was adopted with modification from previous work by Brzoska et al. [23]

After cleaning, crystals were immediately mounted in the teflon holder and immersed in a solution of hexadecane and chloroform (4:1 by volume, as described in [2])). The solution was placed in a 250 ml Teflon beaker whose temperature was regulated to 20±0.05 °C. Both frequency and voltage were recorded throughout the duration of the experiment. When the frequency signal reached a stable level (within 1–2 Hz as shown in the inset of Figure D.2), between 10 and 6000 µl of OTS was slowly injected into 200 ml solution, yielding a concentration range up to 80 mM. Frequency and voltage shifts were monitored throughout this process, and the run was ended when the frequency reached a new stable level. The difference between the two stable signals before and after injection was taken as ΔF.

D.4 Results & Discussion

A representative plot of the QCM data for the adsorption of OTS on Si is shown in Figure D.2. The figure depicts three characteristic features of the data acquisition and analysis process. First, the frequency signal in the solution was stable to within 1–2 Hz for more than 30 minutes. Second, the frequency decreased almost immediately after OTS injection indicating fast adsorption on the surface. Finally, the frequency limits used to determine ΔF are noted on the figure.

Over the range of OTS concentrations studied, the values of ΔF ranged from 150 to 550 Hz. Using equation (D.1), this corresponds to a mass change of 1 to 5 µg, or 10 to 50 monolayers if a density of 20 Å² per OTS molecule is assumed [24]. Although the OTS
molecules with its inactive methyl endgroup is not expected to form multilayers, physical adsorption on the surface can occur [25,26]. Experimentally these excess deposits are usually removed by rinsing with fresh solvent before analyzing the sample [23]. Physical adsorption will have an effect on the frequency as well as the resistance through energy dissipation, as will be discussed later in this paper.

The high reactivity of OTS can affect the reproducibility of QCM results [21]. Our approach to this issue was as follows. First, the measurements were performed over a wide range of concentrations to observe the general behavior. Second, repetition of a few randomly selected runs was done. Finally, the results from OTS are compared with other
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systems. The systems compared here were selected so that the reactivity of the molecule and the adsorbent-surface interaction were substantially different from the OTS/Si system. They include dodecanethiol (C\text{\textsubscript{12}}H\text{\textsubscript{25}}SH) uptake on Au from ethanol solution and OTS on Au with similar conditions to the OTS/Si system. The results are shown in Figure D.3. For completeness, quantitative results are presented in this paper to compare different substrates and adsorbents in the same experimental system. Any attempt to compare absolute values of frequencies and $\Delta F$ values in another system must take into account differences in the experimental set up.

As can be seen from Figure D.3, using OTS on Si gave higher frequency and resistance changes than thiol and silane on Au surfaces. This is expected since the OTS is more reactive than the thiol. In the thiol-Au system, the interactions occur between the molecules and the surface, unlike OTS where the molecules are highly reactive to each other. Therefore, OTS is expected to cause larger changes in QCM response by forming a complex network on the surface which interacts with the molecules in the solution.

In contrast to the OTS/Si system, the adsorption of OTS on Au gave significantly lower frequency and resistance changes. This is also expected since the Au surface has less active sites (oxygen atoms) due to the inherent instability of the Au oxide layer, in contrast to that of Si (Note: Au–O bond strength is about 222 kJ mol\textsuperscript{−1} compared to 800 kJ mol\textsuperscript{−1} for Si–O [27]). From this observation it can be concluded that that the changes in the solution properties are not the main factor affecting the QCM response.

The frequency change ($\Delta F$) as a function of OTS concentration is shown in Figure D.4. It is interesting to note that at higher OTS concentrations $\Delta F$ tends to decrease instead of reaching a plateau. This may be due to the stronger interaction between OTS molecules at higher concentrations which inhibits its free movement in the solution, causing less interaction with the crystal surface.

The above results suggest that the high affinity of Si surfaces to OTS molecules is inducing large changes in the vicinity of the surface. The nature of these changes and the extent that they interact with the surface are more difficult to address. However, calculating the acoustic impedance of the crystal can be used for this purpose by comparing the magnitudes of the real and imaginary parts of the impedance.
Figure D.3: Comparison of the change in frequency and resistance between: (1) dodecanethiol on Au from ethanol, (2) OTS on Si from C\textsubscript{16}H\textsubscript{34}:CHCl\textsubscript{3}, and (3) OTS on Au from C\textsubscript{16}H\textsubscript{34}:CHCl\textsubscript{3}. All runs were performed at 20 °C.
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Figure D.4: Change in frequency for 5 MHz Si coated crystal upon deposition of OTS film from $C_{16}H_{34}:CHCl_3$ (4:1 by volume) at different OTS concentrations.

Acoustic Impedance

The value of the complex acoustic impedance ($Z_L$) can provide insight into the nature of changes affecting the QCM. Lucklum and Hauptmann [13] theoretically calculated the impedance for a 5 MHz QCM crystal coated with 1 µm polymer films with different shear moduli. Their analysis suggests that a film in the glassy state will have low values for the real and imaginary parts of $Z_L$, whereas in the rubbery state the film will have a significant influence on both parts.

As shown in Figure D.5, both the imaginary and real parts have high values. According to the above discussion, this indicates a high viscous effect from the surrounding medium,
**Figure D.5**: Impedance diagram for the OTS coated crystals as calculated using equations (D.4) and (D.5). OTS concentrations are indicated next to the points.
which is translated into an increase in the viscosity of the region close to surface. This can be concluded by comparing the OTS/Si and OTS/Au systems. It is also evident from Figure D.5 that the imaginary part is slightly larger than the real part. This fact is expected since OTS does form a film on the Si surface.

![Graph showing frequency response for 5 MHz Si QCM crystal after injection of OTS to a final concentration of 1 mM.](image)

**Figure D.6:** Frequency response for 5 MHz Si QCM crystal after injection of OTS to a final concentration of 1 mM.

Adsorption kinetics

The time-dependent frequency data can be used to study the adsorption kinetics. We will assume that the decrease in the resonance frequency represents the adsorption process, an approach that was used previously to study the kinetics of alkanethiols adsorption [28,29].
### Table D.1: Adsorption kinetic and thermodynamic constants for OTS adsorption calculated from the QCM results assuming a Langmuir-type mechanism using equation (D.6).

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{af}$</td>
<td>0.14 mM·s(^{-1})</td>
</tr>
<tr>
<td>$k_{ar}$</td>
<td>0.001 s(^{-1})</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>140 mM(^{-1})</td>
</tr>
<tr>
<td>$\Delta G_{ads}$</td>
<td>-7 kcal/mol</td>
</tr>
</tbody>
</table>

Our evaluation begins with the premise that OTS adsorption follows a Langmuir mechanism. This mechanism involves a two step diffusion-adsorption process, where diffusion is assumed to be the limiting step in the case of OTS [6]. For such a mechanism, the reaction rate can be written as [6]:

$$\phi(t) = \frac{\beta}{\alpha}[1 - exp(-\alpha t)] \quad (D.6)$$

where $\phi$ is the fraction of free active sites on the surface, $\alpha = C_b k_{af} + k_{ar}$ and $\beta = C_b k_{af}$.

The parameters $\alpha$ and $\beta$ can be obtained by fitting the frequency to equation (D.6). An example of QCM data with its theoretical Langmuir fit is shown in Figure D.6. From the relation between $\alpha$ and $C_b$, the values of $k_{ar}$ and $k_{af}$ were determined, see Figure D.7. The results of the reaction rate calculations, the equilibrium constant ($K_{eq} = k_{af}/k_{ar}$), and free energy of adsorption ($\Delta G = -RT \ln K_{eq}$) are shown in Table D.4.

The large scatter in the data in Figure D.7 may be due to two factors. First, the frequency response may not be solely due to the OTS adsorption. It is also possible that the adsorption occurs in a short time interval of the frequency change, while the rest of the changes are due to viscous coupling effects. Second, the ideal assumption of Langmuir adsorption may need to be modified. As can be seen in Figure D.6, the frequency-time relation results in a relatively good fit to the experimental data. However, the behavior of $\Delta F$ with increasing concentration (Figure D.4) does not follow this equation. Therefore, it may be necessary to modify the mechanism to take into account the effect of high OTS bulk concentrations.
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Figure D.7: Determination of rate constants for OTS absorption at 20 °C. The parameter $\alpha = C_b k_{af} + k_{ar}$ was determined by fitting as discussed in the text.

D.5 Conclusions

The adsorption of OTS on Si surface was studied by measuring the change in QCM frequency and resistance, and the results were compared with thiol/Au and OTS/Au systems. The frequency shift associated with OTS adsorption on Si from hexadecane-chloroform solution was greater than 200 Hz. This shift is much larger than that observed with dodecanthiol. This may be explained by the presence of high viscous coupling near the surface, or the attachment of a slippery film of OTS to the surface. This was concluded from the decrease in the frequency shift at higher OTS concentrations. The crystal resistance was coupled
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with frequency change to calculate the impedance of the deposits. The imaginary part of the impedance was comparable to the real part, a situation that can be compared to a rubbery polymer film. Finally, the reaction kinetics were determined by fitting the frequency-time data to Langmuir isotherm. The forward reaction rate constant is four orders of magnitude higher than the reverse constant.

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Appendix E

NET-GP Model

This chapter is a manuscript titled “Nonequilibrium Model for Sorption and Swelling of Bulk Glassy Polymer Films with Supercritical Carbon Dioxide” by Vito Carla, Ke Wang, Yazan Hussain, Kirill Efimenko, Jan Genzer, Christine Grant, Giulio C. Sarti, Ruben G. Carbonell, and Ferruccio Doghieri, published in Macromolecules, 2005, 38, 10299–10313.

This appendix presents a detailed discussion of the non-equilibrium thermodynamics model (NET-GP) as well as a comparison between the experimental results and the model predications.
Appendix E. NET-GP Model

Nonequilibrium Model for Sorption and Swelling of Bulk Glassy Polymer Films with Supercritical Carbon Dioxide

Vito Carla,† Ke Wang,‡ Yazen Hussain,§ Kirill Efimenko,∥ Jan Genzer,¶ Christine Grant,† Giulio C. Sarti,∥ Ruben G. Carbonell,∥ and Ferruccio Doghieri*,‡

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ABSTRACT: A new procedure is introduced for the calculation of solubility isotherms of plasticizing agents in glassy polymer matrices with particular application to the case of absorption of supercritical gases in bulk glassy polymer films. The model presented is an extension of the nonequilibrium thermodynamics for glassy polymers (NET-GP) approach, modified to allow for the calculation of the effects of pressure, temperature, and gas concentration on the glass transition. Mass sorption and one-dimensional swelling behavior are analyzed for the carbon dioxide (CO2)–poly(methyl methacrylate) (PMMA) system at high pressure. A quantitative comparison is presented between the model performance and experimental data measured using quartz crystal microbalance (QCM) and high-pressure ellipsometry (HPE).

1. Introduction

Carbon dioxide in its liquid and supercritical state is an attractive replacement for aqueous and organic solvents in industry primarily because of its tunable solvent properties, low cost, low toxicity, nonflammability, and its ease of recycle.1-6 In addition, carbon dioxide is an excellent plasticizer for polymeric materials;7 it is inert as a reaction solvent, and it has very low surface energy and viscosity, making it ideal for producing thin uniform coatings.7,8 For these reasons, carbon dioxide has been used in several processes, such as polymerization reactions,14 dry cleaning,15 drug formulations,16 foam production,17 metal deposition onto substrates,18 polymer surface modification,19 and microelectronics fabrication,20 and many applications, including polymeric membrane conditioning,21 removal of residual solvents and contaminants from polymeric films,22-24 solute impregnation,25,26 and photore sist development.27-29

In most of the aforementioned industrial applications, the key factor that influences the quality of the final product is the ability to predict sorption and subsequent swelling behavior of the polymer matrix at different operating conditions. Indeed, a reliable thermodynamic model, capable of describing the swelling of glassy polymer systems starting from dry polymeric matrices up to fully plasticized materials, is an essential prerequisite of any good transport model aimed at predicting sorption, desorption, and dissolution kinetics in polymeric films. Because glassy polymers are nonequilibrium systems, the usual thermodynamic models for fluids and amorphous polymers, such as the Sanchez–Lacombe (SL) or the statistical associated fluid theory (SAFT) equation of state, are not directly applicable to these systems.

To fill this knowledge gap, a great deal of work has been done to obtain useful and reliable models for sorption and dilation in glassy polymers. Wissinger and Paulaitis were the first to apply successfully the nonequilibrium thermodynamics concept of an order parameter to an equilibrium lattice model.30 Although their results were in good agreement with their experimental data, they used a constant order parameter with its value fixed at the glass transition conditions so that their model was unable to represent the significant solubility variations and hysteresis behavior associated with sorption–desorption cycles. Soon after their work, several models appeared in the literature based on the same approach but with a different choice of the order parameter.31,32

The Gibbs–DiMarzio criterion, which postulates a loss of configurational entropy at the glass transition temperature, was used by Condo et al. to develop a complete consistent theory for glassy systems through an extension of the classical Sanchez–Lacombe model.33 Because this theory is a direct extension of the Sanchez–Lacombe lattice fluid theory, its predictive power is restricted to systems for which the Sanchez–Lacombe equation of state (EoS) is able to reproduce correctly the mixture behavior in the equilibrium region. However, there exist many real systems of importance for which this is not the case. The main aim of this work is to introduce a new flexible model for mass uptake and swelling of glassy polymer films induced by the sorption of plasticizing agents, with special attention to the case of CO2–polymer systems, over a wide range of pressures. This new model is an extension, to the case of plasticizing solutes, of the nonequilibrium thermodynamic model for solubility in glassy polymers (NET-GP), introduced by Doghieri and Sarti34 and named NELF in its first version.35-37

The NET-GP model extends the free energy mapping for the equilibrium state, which can be obtained from any equations of state, to the nonequilibrium domain of the glassy region using a thermodynamically consistent procedure. The NET-GP approach requires that independent information be available for the mass...
Appendix E. NET-GP Model

density of the polymer in the glassy state since this is used as an order parameter. Therefore, the first assumption of the NET-GP model is that the value of the order parameter, the out-of-equilibrium polymer density, determines the behavior of the system, regardless of the sample history through which this polymer density is achieved. Thus, the NET-GP approach cannot be used as a pure predictive tool because a value of the out-of-equilibrium polymer mass density must be available. It should also be stressed that the latter, being a nonequilibrium property, depends, in the most general case, on the thermal, mechanical, and sorption history of the glassy sample.

This work enhances the predictive capability of the NET-GP model by coupling it with a simple theory capable of estimating the amount of swelling agent necessary to result in a transition from the glassy to the rubbery state based solely on the physical properties of the pure components. As the gas is absorbed, the polymer starts to swell, and eventually, as a result of the augmented free volume, the glass transition temperature is reached until the system crosses the transition point from glass to rubber. While the model obtained this way still requires independent information about the nonequilibrium dry polymer density, it does not make use of any specific adjustable parameter, and only equilibrium binary interaction coefficients need to be determined in order to perform the calculations.

In this paper, the predictions of the new model are compared with mass sorption data collected using a quartz crystal microbalance (QCM) and one-dimensional swelling data recorded using high-pressure ellipsometry (HPE) for PMMA/CO₂ films supported on silicon at two different temperatures and over a wide range of pressures. We also compare the modeling results with other literature data.

An additional significant finding of the present work is the experimental verification of the basic assumption of the NET-GP approach, never done before, which states that two different glassy polymer samples should exhibit the same behavior provided that their initial densities are the same, whatever their thermal, mechanical, and sorption histories.

This was achieved by preparing PMMA films with the same density using two completely different coating and curing techniques. These samples were used to collect sorption and swelling data as a function of pressure at two different temperatures using high-pressure ellipsometry (HPE) and quartz crystal microbalance (QCM) methods. HPE measurements yield data on the film thickness, which can be related to the film dilution through the expression

\[
\% \text{ swelling} = \left( \frac{h - h_0}{h_0} \right) \times 100 \tag{1}
\]

HPE also provides information on the average refractive index of the swollen film, which can be converted into total carbon dioxide mass uptake using the index of refraction of the pure component. In this work, the mass sorption measurements from HPE were compared to the more direct mass sorption data measured with QCM.

In the first part of this paper we describe the experimental procedures utilized in film preparation, sorption, and swelling measurements. This is followed by a description of the NET-GP model, the model used to predict the glass transition point, and the numerical procedure used for carrying out the sorption and swelling calculations. The last section presents the model results of the simulations along with the experimental results. The model performance has been tested at two different temperature, 35 and 50 °C, with pressures ranging from 0 to 1800 psi.

2. Experimental Methods

2.1. High-Pressure Ellipsometry (HPE). 2.1.1. Materials and Sample Preparation. PMMA (M_w = 72 kDa, M_w/M_m = 1.06) was purchased from Polymer Source, Inc., Dorval (Montreal, Canada). Toluene (Fisher) was used as solvent to dissolve PMMA. Silicon wafers (100 mm diameter, a (100) orientation) having ≈1.7 nm thick native oxide films (SiO_x) were purchased from International Wafer Services (Portola Valley, CA). The wafers were cleaned by soaking in a mixture of JTB-111 alkaline–surfactant, hydrogen peroxide, and DI water with a 4.6:1:22.8 volume ratio for 10 min and subsequently rinsed with copious amounts of DI water and dried with nitrogen. PMMA/toluene solutions were spin-coated onto silicon wafers using a HomeWay Research (model 131-024, Indianapolis, IN) spin-coater. The concentrations of the PMMA/toluene solutions and spin rates were varied to obtain films of different thickness. The coated wafers were annealed at 120 °C under vacuum for 3–6 h to remove any residual solvent. After spin-coating and annealing, the film thickness at room pressure was measured by ellipsometry (see below), and the initial mass was measured using a precision lab balance (Mettler Toledo, model AB204, Switzerland). Films of thickness ≈1.2 and ≈1.5 μm were formed with a resulting density of 1.187 g/cm³. The densities of films used for HPE were matched as closely as possible to those used for QCM measurements. As described in detail below, the PMMA films for QCM experiments were formed by dip-coating QCM substrates into PMMA/toluene solution, followed by annealing in a vacuum at 80–90 °C for 1–2 h. The difference in density between the films used in QCM (1.187 g/cm³) and those used in ellipsometry (1.187 g/cm³) was less than 0.2%. The polymer mass per unit area on the QCM substrates was determined by measuring the fundamental frequency difference between the bare crystal and the coated crystal. SEM was used to measure the film thickness.

2.1.2. Ellipsometry Equipment. A variable angle spectroscopic ellipsometer (J.A. Woollam, Inc., Lincoln, NE) with rotating analyzer equipped with a custom-built high-pressure CO₂ cell was used in the HPE experiments. The angle of incidence (with respect to the sample normal) was fixed at 70°, and the wavelength was varied from 500 to 800 nm. The high-pressure cell, constructed of stainless steel, was equipped with three fused silica windows (2.54 cm in diameter and 1.5 cm in thickness, Rohmicon Technology Franklin Park, IL) (cf. Figure 1). The two side windows were fixed at an angle of 110° from vertical in order to obtain normal incidence of the beam with the window to avoid any deviations that can cause a change in polarization of the light and to minimize the uncertainties in the incident angle of the beam on the sample. A custom-made copper sample holder with a spring clip was used to hold the wafer, and it was placed on the bottom of the cell. A torque wrench was used to put an equivalent and minimal amount...
of force to seal the windows to minimize the window birefrin-
gence induced by strain under high pressure. High-purity CO2
gas (Matheson Gas Product, Montgomeryville, PA, purity >
99.99%) was charged to the cell to the desired pressure using
an ISCO pump (model 260D, Isco Inc., Lincoln, NE). The
pressure in the cell was measured using a pressure
transducer (OmegaGardyne, model PX01C1-KG10T, OMEGA
Engineering, Inc., Stamford, CT) controlled to an accuracy
of ±2 psi (0.14 bar). A heating tape was wrapped around the cell
and was connected to a variable autotransformer (model
3PN1010, Staco, Hayward, CA) for temperature control. An
insulation cap was used to cover the entire cell and heating
tapes, except the windows, to obtain a uniform thermal
ellipsometry that was found to be crucial in these experiments,
especially near the critical point of CO2. A custom-built metal
heating plate was placed beneath the supporting stage to
prevent heat losses. An ISCO pump (model 260D, Isco Inc.,
Lincoln, NE) was connected to a heated water bath (model
9110, Poly Science, Niles, IL) to preheat CO2 to the desired
temperature. The temperature inside the cell was measured
by using a thermocouple (OmegaGardyne model HRKQSS-1160-
12-OMEGA Engineering, Inc., Stamford, CT) and was con-
trolled to within ±0.1 °C. The cell was allowed to reach thermal
equilibration at each desired temperature for at least 1 h.
Birefringence of the windows can corrupt the polarization
state of the light, and even nonbirefringent windows can become
birefringent due to pressure-induced window strain.47 This, in
turn, can cause large errors in the calculated properties of the
samples. An experimental procedure developed by J.A. Wool-
lam Co., Inc., was used in this work to account for the effect
of the window birefringence.47

2.1.3. Calibration at High Pressures. To test the ef-
efectiveness of the procedure for correcting induced window
birefringence in the ellipsometric data, a calibration wafer
(made at Triangle National Lithography Center) with a thick
thermal oxide layer (~85 nm) was used for scans at different
pressures and temperatures. A four-layer model was used to
fit the data (cf. Figure 2a). The refractive indices of the silicon
substrate, the Si–SiO2 interface layer, and SiO2 were fixed
using literature values.47 The refractive index of the bulk CO2
atmosphere was given pressure and temperature was also
obtained from literature values.47–49 The ellipsometry data were
fitted to determine the thickness and average refractive index
of CO2 at a given pressure and temperature which was
obtained when the effects of window birefringence were
measured and accounted for in the model calculations. The
maximum deviation of the measured thermal oxide thickness
under pressure from the thickness of the oxide layer measured
in ambient air without windows was found to range between
~1 and +4% over a range of pressures from 0 to 1800 psi.

2.1.4. Swelling Measurements. The PMMA films on the
silicon wafer substrates were introduced into the chamber and
scanned using the ellipsometer described above. The experi-
mental ellipsometric data were fitted using a four-layer model,
shown in Figure 2b, comprising the silicon substrate, a native
oxide layer, a mixed polymer/CO2 layer, and a bulk CO2
medium. The refractive indices at different wavelengths were
adapting literature values47 for silicon substrate, the native
oxide, and the CO2 atmosphere. The fitted parameters for
the swelling experiments were the same as those in the
 calibration scan, with the additional fitting of the refractive
index of the swollen PMMA/CO2 layer. The refractive index
of the swollen PMMA/CO2 layer was modeled as a function of
wavelength by assuming a Cauchy dispersion relationship.47

2.1.5. Mass Sorption Calculations Using Ellipsometry
Data. Ellipsometry measurements provide values of the
thickness and average refractive index of the swollen film.
From this information it is possible to estimate the mass of
gas absorbed given refractive index information for the pure
components. Sirard et al.40 showed that the mass concentration
of CO2 in a PMMA film can be estimated by applying the
Clauss–Masotti equation48,49 to each component in the
swollen film

\[
\left( \frac{n_j^2 - 1}{n_j^2 + 2} \right) = q_j \rho_j, \quad j = \text{CO}_2, \text{PMMA} \tag{2}
\]

where \(n_j\) represents the average refractive index for CO2 and
PMMA in the swollen layer over the wavelength range from
500 to 800 nm, \(R_j\) is the mole refraction, \(M_j\) is the molecular
weight, and \(\rho_j\) is the mass density of the component.40 Equation
2 can be used to calculate values of the ratio \(R_j/M_j\) for each
component in the film, given literature values of the refractive
indices of CO2 and PMMA at the pressure and temperature
in which the measurement is taken. The mass concentration
of CO2 and PMMA in the swollen PMMA film can be calculated
from the measured refractive index \((n)\) of the swollen film
layer through the following mixing rule40,49

\[
\left( \frac{n_j^2 - 1}{n_j^2 + 2} \right) = q_j \rho_j \rho_{\text{PMMA}} + \rho_{\text{PMMA}} \tag{3}
\]

where \(\rho_{\text{CO}_2}\) and \(\rho_{\text{PMMA}}\) are determined from the pure component
refractive index data.

In their analysis of sorption in glassy polymers using simple
interferometry, Fleming and Koester have shown that the linear
mixing rule in eq 3 may fail when the polymer is in the glassy
state because of the difficulty of independently decoupling the
thickness and the refractive index from optical data.48 How-
ever, in our case, with the use of mult,wavelength spectropho-
etic ellipsometry, it is possible to independently determine the
thickness and the refractive index of a thin film, thus avoiding
the aforementioned complications. Using this technique, HPP
has been shown to be able to provide reasonably accurate
estimates of sorption levels in rigid glassy polymers.49

A mass balance on the polymer may be used to be related to
the mass concentration of the polymer in the swollen film to the
measured thickness change of the film upon swelling and the
original polymer density

\[
\rho_j \rho_{\text{PMMA}} \frac{h_j}{h_{\text{PMMA}}} \tag{4}
\]

Using eqs 2–4, the sorption of CO2 can be estimated from
knowing the quantities \(q_j\), \(\rho_j\), \(\rho_{\text{PMMA}}\), and \(h_j\). The mixture
refractive index: The densities of PMMA were calculated, for tempera-
ture higher than the room temperature, using a thermal
expansion coefficient53 of \(5.6 \times 10^{-4} \text{ K}^{-1}\), and the refractive
index of pure PMMA was measured by ellipsometry at 1 atm.
The densities of CO2 were taken44 to be 0.94 at and 0.93 g/cm3
at 35 and 50 °C, respectively. Over the range of pressure of these
experiments, the effect of pressure on the refractive index of
both PMMA and CO2 was negligible.

2.2. QCM Measurements. 2.2.1. Materials and Sample
Preparation. 5.00 MHz AT-cut Si quartz crystals (a blank
diameter of 8.5 mm and a thickness of 0.25 mm) were obtained
from International Crystal Manufacturing (Oklahoma City,
OK). The Si film was vacuum-sputtered over an Au electrode
that provided the necessary conductive path to the quartz.
The rms surface roughness of the crystals used was less than
10 nm (analyzed using AFM). The crystal was connected to a

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Sorption and Swelling of Bulk Glassy Polymer Films 10301
Springs, CA). This oscillator provides two outputs: frequency and voltage. The voltage reading is inversely proportional to the resistance of the crystal. The oscillator is further connected to an Agilent 225 MHz universal frequency counter (model 53131A, Palo Alto, CA) that records the frequency of the vibrating crystal. The time-dependent frequency readings were stored on a computer using Agilent Intuilon Connectivity software.

PMMA films for the QCM experiments were cast onto the surface of the crystal by dip-coating. The crystal was dipped vertically into a 2.4 wt % PMMA/toluene solution, allowed to equilibrate for a specific time, and then was withdrawn from the solution at a controlled rate using a motorized device. The coated crystal was dried under vacuum at 80 °C for 1–2 h. The clean crystal was then placed in the cell under vacuum (0.01 psia), using precision DD-20 Inex Inc. Delray Beach, FL vacuum pump, and the fundamental frequency $F_0$ of the coated crystal was recorded. The stable frequency level is indicative of complete evaporation of the solvent from the polymer during curing. The value of the stabilized frequency of the coated QCM in a vacuum was utilized to calculate the mass of coated polymer by comparing to fundamental frequency of the quartz crystal without polymer. The annealing conditions were chosen so that the density of the films formed for the QCM samples were as close as possible to the density of the films made for the ellipsometry experiments (final measured value 1.187 g/cm$^3$ for the ellipsometry sample and 1.189 g/cm$^3$ for the QCM sample).

2.2.2. High-Pressure QCM Cell. The custom-built pressure cell consists of a thick-wall stainless steel cylinder (63.5 mm i.d. x 200 mm height), with a high-pressure electrical feedthrough (Conax Buffalo Technologies, NY) at the top end to drive the QCM (cf. Figure 3). The cell has an inside volume of 25 cm$^3$ and a maximum working pressure of 7500 psi. The crystal was placed in the cell and connected to the oscillator through the electrical feedthrough during an experiment. A high-pressure thermocouple (Omega, Stamford, CT) was placed in the cell to monitor the temperature of the CO$_2$ fluid. Data acquisition was accomplished via a National Instruments DAQ interface using Labview software. The whole assembly was then placed in a custom-built water bath and controlled to within 0.1 °C.

2.2.1. Mass Sorption Measurements. QCM crystals coated with polymer films were placed in the pressure cell, and the fundamental $F_0$ frequency of the QCM was measured in a vacuum. After a stable signal was achieved, CO$_2$ was slowly introduced into the chamber to increase the pressure. The frequency was then allowed to reach a new stable level and recorded. This procedure was repeated for the third pressure level, and so on. A pressure range from 0 up to 1800 psi was examined in steps of 150 psi. After the time-dependent frequency readings were recorded for each pressure, an analysis was performed in order to obtain the correspondent mass of CO$_2$ uptake vs time behavior.

The frequency of the QCM can be affected by several factors, including the mass adsorbed on the crystal surface ($m$), the pressure ($P$), the properties of the surrounding medium, and the temperature ($T$). Since the temperature was held constant during these experiments, the total change in frequency can be written as the sum of the contributions from mass adsorbed, pressure, and the surrounding medium.

$$\Delta F = F - F_0 = \Delta F_m + \Delta F_P + \Delta F_T$$  \hspace{1cm} (5)

Estimation of the mass effect can be done using the well-known Sauerbrrey equation:

$$\Delta F_m = -2F_0^2 \Delta m / \mu_0 \gamma_0^{1/2} = -C_m \Delta m$$  \hspace{1cm} (6)

where $C_m$ is the mass sensitivity constant (56.6 g/cm$^3$/Hz), $F_0$ is the fundamental frequency of the crystal, $\Delta m$ is the mass per unit area absorbed on the crystal, and the quantities $\mu_0$ and $\gamma_0$ are the shear modulus and density of the quartz, respectively. The equation above represents a simple linear relationship between the change in frequency and the mass uptake. For a crystal coated with a viscoelastic polymer layer this simple relationship may not hold. However, the extent of the deviation from eq 6 depends strongly upon the film thickness. Analysis on this subject in the literature has shown that the linear approximation can be used with confidence only when the load on the QCM is small, i.e., when the film thickness is small (less than a few micrometers). In our experiments, all the film thickness values were on the order of 1 µm, easily justifying the use of eq 6 in calculating the change in frequency due to mass sorption. The QCM sorption data agreed extremely well with prior work in the literature, providing additional proof of the accuracy of eq 6 in this application.

As for the second term, Stockbridge found that the frequency changes linearly with pressure:

$$\Delta F_P = C_P P$$  \hspace{1cm} (7)

where $C_P$ is a constant. This relation has been tested previously and found to be valid for the crystals used in this work. The value of $C_P$ was found to be $-0.14$ Hz/psi in the range of temperature considered here for a 5 MHz quartz crystal.

The viscosity contribution is more difficult to quantify. Kanazawa and Gordon proposed the following equation for the oscillation frequency of a quartz resonator in contact with fluid:

$$\Delta F_T = -F_0^2 \rho_P / \left( \eta P \right) \gamma_0^{1/2}$$  \hspace{1cm} (8)

where $\rho$ and $\eta$ denote the density and shear viscosity of the fluid medium surrounding the crystal. It should also be noted that in these experiments the initial conditions were chosen to be in a vacuum, so that $P$, $\rho$, and $\eta$ are used rather than $\Delta P$, $\Delta \rho$, and $\Delta \eta$.

Although this relation has been used previously to perform similar calculations in the case of bare crystal, it should be recognized that the presence of the polymer film introduces a discontinuity in the viscosity profile in the vicinity of the QCM surface. However, since the polymer film thickness is much smaller than that of the quartz ($\leq 0.1 \mu$), this relation provides a good approximation to account for the viscosity effect.

3. Theory

3.1. The NET-GP Model. This section summarizes the NET-GP model for sorption of gases into glassy polymers for the case of homogeneous, amorphous, and isotropic materials. The model makes use of the well-known concept of order parameter for the description of the nonequilibrium state of the glassy phase at a given temperature, pressure, and composition. This idea provides a useful framework for describing systems that are not at equilibrium and avoids the introduction of mathematically cumbersome memory functions otherwise necessary for dealing with sample histories. The model then assumes that an unambiguous description of the thermodynamic properties of the glassy polymer–gas mixture can be based on a set of state variables
which, along with temperature $T$, pressure $P$, and gas content $\omega_1$, the polymer mass density $\rho_2$ is included as independent variable which measures the volume deformation of the polymer network

$$\Sigma = \Sigma(T, P, \omega_1, \rho_2)$$

(9)

Thus, any specific nonequilibrium function $\Phi_{\text{NE}}$ of the state of the system can be described by an expression of the form

$$\Phi_{\text{NE}} = \Phi_{\text{NE}}(T, P, \omega_1, \rho_2)$$

(10)

With this assumption, polymeric samples below the glass transition temperature have identical thermodynamic properties at given $T$, $P$, and $\omega_1$, provided the order parameter $\rho_2$ is the same, regardless of their thermal, mechanical, or sorption histories. Indeed, while the use of a single order parameter may not be sufficient to describe all the nonequilibrium characteristics of the structure of a glassy polymer mixture, the first-order approximation used in NET-GP addresses the major effect of volume deformation on the properties of the glassy polymeric mixture, and it allows for a quantitative representation of sorption behavior which is satisfactory for most technical purposes.

The thermodynamic analysis of NET-GP model relies on the additional assumption that the order parameter $\rho_2$ is an internal state variable for the system; i.e., its rate of change in time depends strictly on the state of the system:

$$\frac{d\rho_2}{dt} = f(T, P, \omega_1, \rho_2)$$

(11)

While different order parameters can be used to describe the same thermodynamic properties of a glassy-gas–polymer mixture, the assumption of different internal state variables definitely leads to different expressions for the properties in the nonequilibrium states. In this sense, results of the NET-GP model are unique with regard to earlier attempts to describe properties of glassy phases by means of different order parameters.36–42

Given the assumptions of eqs 10 and 11, through the use of well-established tools of thermodynamics of systems endowed with internal state variables, the following conditions hold for the nonequilibrium Helmholtz free energy density $\alpha_{\text{NE}}$ and penetrant chemical potential $\mu_{\text{NE}}$ in the mixture:35–37

$$\alpha = \alpha_{\text{NE}}(T, P, \omega_1, \rho_2) = \alpha_{\text{EQ}}(T, \omega_1, \rho_2)$$

(12)

$$\mu_{\text{NE}} = \frac{\alpha_{\text{NE}}}{\rho_2}$$

(13)

Equations 12 and 13 constitute the key results of the thermodynamic analysis of nonequilibrium states for penetrant–polymer mixtures below the glass transition temperature. They allow for the derivation of expressions for the free energy and solute chemical potential of any nonequilibrium state of a glassy gas–polymer mixture, once reliable expressions for the corresponding equilibrium conditions are known. It is thus possible to calculate the solute solubility in the system, knowing the polymer mass per unit volume, through the classical phase equilibrium condition

$$\mu_{\text{EQ}}(T, P, \omega_1, \rho_2) = \mu_{\text{EQ}}(T, P)$$

(14)

or, equivalently, in terms of fugacities

$$f_{\text{EQ}}(T, P, \omega_1, \rho_2) = f_2(T, P)$$

(15)

In the expressions above, $\mu_{\text{EQ}}$ and $f_2$ are the equilibrium chemical potential and fugacity of a pure penetrant phase, at temperature $T$ and pressure $P$, respectively, and $\rho_2$ is the pseudo-equilibrium polymer density the system reaches under sorption conditions. It is important to stress that $\rho_2$ must be known without using equilibrium arguments in order to solve eqs 14 and 15 for the pseudo-equilibrium gas content $\omega_1$.

In a low-pressure sorption experiment, the swelling induced by the penetrant is negligible, and the pseudo-equilibrium value of the density, $\rho_2^*$, can be approximated by the initial density of the pure polymer $\rho_0^*$. It is useful to remember that $\rho_2^*$ is a nonequilibrium property which depends on the history of the polymeric material, and as such it should be specifically calculated for the case of interest. The problem of representation of solubility isotherms in the low-pressure range has been addressed in previous papers, where numerous examples have been discussed.35–42 However, in the more general case, the polymer density $\rho_2^*$ changes with penetrant pressure $P_g$ in the external phase, and its variation must be considered in order to correctly describe sorption isotherms at moderate and high pressures.

Careful analysis of experimental dilation data for a wide variety of systems indicates that at constant temperature the pseudo-equilibrium polymer density varies linearly with pressure,44 so that it can be adequately represented by an equation of the form

$$\rho_2^*(P) = \rho_2^0(1 - k, P)$$

(16)

where the parameter $k$, is the dilation coefficient of the polymeric material in the gaseous atmosphere. This is also a nonequilibrium variable, which may change according to the thermal and sorption history of the polymeric material, as well as depending on sorption/desorption runs. Figure 4 shows a schematic representation of the density behavior with pressure at constant temperature. An increase in pressure results in a linear decrease in density until a certain pressure $P_g$ is reached at which the amount of solvent absorbed is sufficient to reach the glass transition concentration of which the equilibrium behavior is recovered. The point $(P_g, \rho_2^0)$ is the glass transition point, and for a given mixture it depends only on temperature.

The case of representing sorption isotherms in glassy polymers up to moderate pressures, in which the swelling effect of the penetrant component must be taken into account, has been considered in a previous work through the discussion of several examples.44 However, while the dilation coefficient $k$ has a precise physical meaning, it has been treated in this previous work as an adjustable parameter that needed to be fitted using high-pressure nonequilibrium solubility data. In the following section, an approach is presented that eliminates this shortcoming present in earlier NET-GP theories.

3.2. Model for Plasticization. Using classical and statistical mechanical arguments, Chow36 derived a
Appendix E. NET-GP Model

Table 1. Physical Properties of Un-Cross-Linked and Nonbranched PMMA\(^{65,66}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, (M_n)</td>
<td>100.12 kg/mol</td>
</tr>
<tr>
<td>Molecular weight, (M_d)</td>
<td>44 kg/mol</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>105 °C</td>
</tr>
</tbody>
</table>

relationship expressing the depression of the glass transition temperature of a polymer−solvent mixture (\(T_{g}^\text{mix}\)) by means of liquid plasticizers at low pressures, in terms of the glass transition temperature (\(T_g\)) of the pure polymer, the excess heat capacity, and the mass fraction of solvent inside the polymer. The derivation was based on the application of the Gibbs−DiMarzio criterion, which states that at the glass transition temperature the entropy is zero, to a lattice model. The resulting expression for the glass transition temperature of the polymer−solvent mixture is given by

\[
\ln \left( \frac{T_{g}^\text{mix}}{T_g} \right) = \Psi[(1 - \theta) \ln(1 - \theta) + \theta \ln \theta] \tag{17}
\]

with

\[
\Psi = \frac{2R}{M_n \Delta C_p} \tag{18}
\]

and

\[
\theta = \frac{M_d}{2M_n} \left( 1 - \omega_f \right) \tag{19}
\]

In the equations above, \(T_g\) is the glass transition temperature of the dry polymer, and \(M_n\) and \(M_d\) are the molecular weights of the monomer and solvent, respectively. The quantity \(\Delta C_p\) represents the difference in heat capacity between the supercooled liquid and glass, \(z\) is the lattice coordination number, \(R\) is the ideal gas constant, and \(\omega_f\) is the mass fraction of solvent in the polymer. In Table 1 these parameters, obtained from the literature,\(^{55,56}\) are listed for PMMA.

Chow’s theory requires that the dimensionless parameter \(\theta\) in eq 19 be always less than 0.25 (small concentration limits).\(^{38,6}\) In the present work, the most extreme case has been represented by the lower temperature, where a carbon dioxide mass fraction of 0.146 is needed to lower the glass transition temperature to 35 °C. This, in turn, corresponds to a value of \(\theta = 0.194\), well within the window of applicability of eq 17.\(^{38,6,35}\)

Since eq 17 was developed for calculating the glass transition point in the presence of a liquid plasticizer, it does not have any dependence on pressure. In our case the plasticizer is a high-pressure gas and increases in pressure beyond the critical point may compress the polymer sample, reducing the free volume and increasing its glass transition temperature. However, the effect of pressure on most polymers only becomes important at pressures far above 500 bar,\(^{35}\) significantly above the pressures being considered in this work. As a result, it is reasonable to neglect pressure effects on the glass transition temperature and to use eq 17 in the calculations of the depression of the glass transition temperature for the PMMA/CO\(_2\) system.

A version of the Sanchez–Lacombe equation of state has been developed recently to address the problem of sorption in glassy polymers that also provides a method for estimating the glass transition depression due to sorption.\(^{35}\) Condo et al. have shown that the Chow theory provides a better quantitative agreement with experimental data\(^{38}\) than this new Sanchez−Lacombe theory. Our own calculations (not shown here) have also confirmed the results of Condo et al., showing that the Chow theory led to a much better fit to \(T_g\) data, especially at high solute concentrations. Because of its simplicity and better predictive capability, the Chow model was used here to make all predictions of \(T_g\) values. Just as the NET-GP theory can be used with any equilibrium equation of state, the Chow theory can be readily implemented with any equilibrium thermodynamic model to predict glass transition temperatures.

3.3. Calculation of Solubility Isotherms in Glassy Polymers. Equations 17−19 make it possible to find the value of the penetrant composition that causes the glass transition temperature to drop down to the experimental temperature. Knowing this value, it is possible to calculate, using the equilibrium equation of state, the value of pressure and polymer density at the glass/rubber transition point (\(P_r, \rho_r\)). The assumption that the density variation with pressure is approximately linear up the glass transition point leads to the expression

\[
\rho_r(P) = \rho_f^0 + \frac{P}{P_r} \left( \rho_f^0 - \rho_r^0 \right) \tag{20}
\]

where \(\rho_f^0\) can be evaluated using the equilibrium EoS at \(T, P_r\), and \(\omega_f^0\). Knowing the density at the glass−rubber transition, it is possible to calculate the swelling parameter combining eqs 16 and 20

\[
K_s = \frac{1}{P_r} \left( 1 - \frac{\rho_f^0}{\rho_f^0} \right) \tag{21}
\]

The knowledge of the initial polymer density is crucial for the present model; however, in many cases in the literature this information is not provided, either because it is not deemed to be relevant or because it is difficult to measure the given size or shape of the sample. For those cases in which it is not directly available, we figured out a simple procedure to estimate its value from swelling data.

Taking as example swelling data from the works of Wissinger et al.\(^{36}\) and Zhang et al.\(^{32}\) Figure 5 presents the swelling information as a density ratio (\(\rho_f/\rho_r^0\)) depicting the variation of PMMA density with CO\(_2\) pressure at two different temperatures, 32.7 and 35 °C. From the slope of the line it is possible to evaluate the value of \(K_s\), and then by using eq 21 and knowledge
about the glass transition point \((P_{g}, \rho_{g})\) one can estimate to a good approximation the initial polymer density \(\rho_0\).

A general procedure for the calculation of the pseudoequilibrium penetrant fraction for vapor or gas sorption in glassy polymers at an assigned temperature and pressure can now be stated as follows:

- Choose a model for calculating either the chemical potential or the fugacity of penetrant in the gaseous phase.
- Choose a suitable equation of state (EoS) for the penetrant/polymer pair that provides a successful description of system properties in the melt or rubbery phase.
- Choose a model for calculating either the chemical potential or the fugacity of penetrant in the gaseous phase. In most cases the same model could be conveniently used to represent thermodynamic properties in both the polymeric and gaseous phases.
- If not available, estimate the mass density of the pure polymer at the initial \(T\) and pressure of interest.
- Evaluate the glassy/rubbery transition point \((\rho_{g}, P_{g})\) by taking \(T_{g} = T\) in eq 17 and by solving iteratively for \(\rho_{g}\).
- By using the equilibrium equation of state at constant \(T\), the mixture density and the mass fraction of the penetrant at a given \(P\), \(\rho_{g}(P)\), can be calculated.
- The glass transition pressure is defined as the pressure at which the mass fraction of penetrant becomes equal to \(\rho_{g}\); this fixes the point \((P_{g}, \rho_{g})\).
- Finally, evaluate the polymer density in the penetrant polymer mixture according to whether the pressure is above or below the glass transition pressure

\[
\rho_g = \begin{cases} 
\rho_0 & \text{for } P < P_g \\
\rho_0 \left( \frac{P}{P_g} \right)^{\frac{1}{3}} & \text{from EoS for } P \geq P_g 
\end{cases} \quad (22)
\]

- For each pressure value solve either eq 14 or 15 for the penetrant density in the polymeric mixture.

### 3.4. Equilibrium Equations of State

According to the general procedure described above, different thermodynamic models can be derived for sorption and swelling in glassy polymers using different expressions for the description of polymer/penetrant mixture properties in the melt phase. This makes the NET-GP approach highly flexible since it can be used with any equilibrium EoS capable of describing accurately the melt or rubbery phase.

This work focuses on one of the most successful and frequently used equations of state for polymer solutions, the Sanchez–Lacombe equation of state (SL).\(^{69,71}\) The SL EoS is a lattice-fluid model, in which each component is divided into parts (or “mers”) that are placed into a lattice and are allowed to interact with a mean-field intermolecular potential. In the SL EoS, the reduced density is related to the reduced pressure and temperature according to

\[
\hat{\rho}^2 + \frac{P}{T} + T \ln(1 - \hat{\rho}) - \left[ 1 - \frac{1}{\hat{\rho}} \right] = 0 \quad (23)
\]

The compressibility of the system and the expressions for the fugacity coefficient, derived from the residual Helmholtz free energy\(^{71,72}\), are

\[
Z = \frac{P_0}{T} r 
\]

\[
\ln \psi_i = -\ln Z + (Z - 1) + \left( \frac{\alpha_i^\Gamma(T, V, n)}{n_i} \right) \frac{V}{T} 
\]

\[
\ln \psi_i(T, P, \mu) = -\ln Z + (Z - 1) + \left( -\frac{\hat{\mu}}{\hat{T}} + \left( \frac{1}{\hat{\rho}} + 1 \right) \ln(1 - \hat{\rho}) + 1 \right) + \left[ \frac{Z - 1}{r} \right] \frac{r}{\hat{T}} \left( \frac{\alpha_i^\Gamma}{n_i} \right) \frac{V}{T} \left( \frac{\hat{\mu}}{\hat{T}} \right) \left( \frac{\alpha_i^\Gamma}{n_i} \right) \frac{V}{T} 
\]

In this work two versions of the SL EoS equation of state have been used. The first version (SL-I)\(^{69,71}\) is the classical version with one adjustable binary parameter in the mixing rules, as expressed by eqs 27–29. The second version (SL-II) has two adjustable binary pa-
parameters in the mixing rules as proposed more recently by McHugh and Krunokis, as represented by eqs 29-32. For a complete description of the symbols used above the reader is referred to the notation section at the end of the paper.

In the following section, results from the correlation of experimental sorption and swelling data for the PMMA/CO2 system through use of NET-GP model will be shown in detail, using both the SL-I and SL-II equations of state. The pure component parameters for CO2 and PMMA for use in the SL-I and SL-II equations of state were obtained from the literature and are tabulated in Table 2. The critical point for carbon dioxide predicted using these parameters is (42 °C, 75 bar), which means that the model overestimates the critical temperature by about 11 °C and overestimates the critical pressure by only 20 psi. In the case of the CO2–PMMA system, the critical temperature by about 11 °C and overestimates the critical pressure by only 20 psi. In the case of the CO2–PMMA pair, the predicted swelling coefficients are all within 1–4% of the experimental values, indicating that the procedure is indeed capable of making reasonable extrapolations of the density variations with pressure at constant temperature.

Solubility data obtained for CO2 in PMMA at 50 °C as measured by both the HPE and QCM techniques in sorption/desorption experiments are compared in Figure 6a, where the quantity Δ CO2 represents the ratio of grams of CO2 absorbed per gram of polymer (g CO2/g polymer).

The two series of measurements are in very good agreement with each other, except for a few scattered points at low pressures. At this relatively high temperature there is very little hysteresis in the CO2 isotherm as the pressure is decreased. As discussed in the experimental description, films prepared for QCM and HPE followed two completely different preparation histories but have nearly identical densities. The excellent agreement between the sorption data for both samples shown in Figure 6a indicates not only that the two measurement techniques are highly consistent but also that glassesy polymer films prepared according to two completely different protocols exhibit similar sorption behaviors, provided they are characterized by the same polymer mass density. This result provides experimental verification of one of the basic assumptions in the development of NET-GP models, namely, that the glass polymer density can be used as a single order parameter to determine swelling and sorption, and as a consequence, samples with the same initial density are expected to exhibit similar sorption and swelling behavior regardless of their past histories. This is the first experimental verification of the suitability of this assumption.

HPE can provide a prompt measurement for the glass transition pressure, i.e., the pressure required to have sufficient amount of CO2 absorbed into the polymer matrix necessary to lower the glass transition temperature to the experimental temperature. To determine the glass transition pressure, we measured the ellipsometric angle \( \psi \) as a function of CO2 pressure at different wavelengths (from 500 to 800 nm) for both sorption and desorption isotherms. Figure 6b shows a plot of the average \( \psi \) values as a function of pressure along with straight line fits to point out the difference in slopes before and after the critical pressure. The pressure at which the change in curvature occurs is

### Table 2. Pure Component Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CO2</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_c [kPa] )</td>
<td>263</td>
<td>696</td>
</tr>
<tr>
<td>( P^* [kPa] )</td>
<td>659</td>
<td>503</td>
</tr>
<tr>
<td>( \rho^* [g/cm^3] )</td>
<td>1.62</td>
<td>1.269</td>
</tr>
</tbody>
</table>

### Table 3. Interaction Parameters for Both Versions of the SL Equation of State

<table>
<thead>
<tr>
<th>Binary Parameters</th>
<th>SL-II</th>
<th>SL-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k^0_{ij} )</td>
<td>0.1246</td>
<td>-0.044</td>
</tr>
<tr>
<td>( \varepsilon^0_{ij} )</td>
<td>0.033</td>
<td>0.1161</td>
</tr>
<tr>
<td>( \varepsilon^*_{ij} )</td>
<td>-0.015</td>
<td>0.044</td>
</tr>
</tbody>
</table>

* Parameters fit to sorption data above 100 bar at two temperatures, 35 and 50 °C.
Appendix E. NET-GP Model

Figure 6. (a) Solubility isotherm for CO2 in PMMA at 35 °C from sorption and desorption experiments as measured by QCM and high-pressure ellipsometry. (b) Ellipsometric angle ψ as a function of CO2 pressure at 35 and 50 °C. The CO2-induced glass transition pressure, \( P_g \), is identified as the pressure at which the slope of the \( ψ \)-pressure curve changes.

Figure 7a shows experimental data for CO2 solubility in PMMA at 50 °C measured from QCM sorption experiments. Superimposed on the data in Figure 7a are the predictions of the NET-GP model using the SL-I and SL-II equations of state. The interaction parameters used in the SL-I and SL-II models fitted to the sorption data for pressures greater than 100 bar are listed in Table 3. According to the Chow theory in eq 17, the CO2 concentration at the glass transition point should correspond to a value of \( P_g \). The \( P_g \) values estimated from the presence of hysteresis in dilation during the sorption and desorption cycles.

identified as the \( P_g \), i.e., \( P_{35} = 64 \) bar and \( P_{50} = 58 \) bar, which are in very good agreement with previous measurements.74,75 The beginning of the hysteresis in the dilation data upon sorption and desorption cycles has been often associated with the glass transition pressure.39,40 The data in Figure 6a,b indicate that the \( P_g \) values estimated from the change in slope of the ellipsometric angle agree quite well with \( P_g \) values estimated from the presence of hysteresis in dilation during the sorption and desorption cycles.
Appendix E. NET-GP Model

Figure 7. (a) Solubility isotherm for sorption of CO$_2$ in PMMA at 50 °C: comparison between experimental data and fitting results using NET-GP SL-I [thin solid line] and NET-GP SL-II [thick solid line]. (b) Volume swelling isotherm for sorption of CO$_2$ in PMMA at 50 °C: comparison between experimental data and predicted results using NET-GP SL-I [thin solid line] and NET-GP SL-II [thick solid line].

Solubility results obtained with NET-GP and the SL-II equation of state exhibit a clear representation of all features shown by experimental data over the entire pressure range, including a slight change in the slope at the glass transition pressure. A less accurate picture of solubility and pseudo-solubility data is obtained by means of NET-GP with the SL-I equation of state, although the qualitative variation of the solubility isotherm with pressure range is correctly represented.

Figure 7b shows % swelling or dilatation data using HPE during sorption at 50 °C for PMMA at CO$_2$ pressures corresponding to the sorption data shown in Figure 7a. The predicted % swelling results from the NET-GP model using SL-I and SL-II parameters shown in Table 3 are superimposed on the experimental results. The swelling calculations shown in this figure did not require any additional fits of
parameters, only a direct application of the parameters fitted in the high-pressure regime with sorption data shown in Figure 7a. As was the case with the sorption data, the results from the NET-GP approach with the SL-II model provide a more accurate representation of the swelling experimental data. Considering that all the model results in Figure 7b were complete predictions, even the less accurate NET-GP SL-I model resulted in an impressively good comparison with the % swelling experimental results. The linear behavior assumed for volume swelling below $P^*_{\text{CO}_2}$ in eq 16 is clearly visible in the model predictions, and it is substantially confirmed by the experimental data.

Having established that the NET-GP SL-II model clearly offers a more accurate representation of the experimental results for the PMMA/CO$_2$ system, only the results of this model will be presented in subsequent discussions.

Figure 8. (a) Solubility isotherm for sorption–desorption cycle of CO$_2$ in PMMA at 50 °C: comparison between experimental data and fitting results using the NET-GP SL-II theory. (b) Volume swelling isotherms for sorption–desorption cycle of CO$_2$ in PMMA at 50 °C: prediction using the NET-GP SL-II theory.
Appendix E. NET-GP Model

Figure 8a shows QCM sorption data measured at 50 °C during both sorption and desorption cycles as the pressure is increased to 135 bar and then decreased to the atmospheric pressure. The results are compared to the predicted gas solubility calculated using NET-GP SL-II. Even though the hysteresis in CO₂ solubility for sorption–desorption cycles in this system is not very large, the model is able to represent it through the use of a different swelling coefficient (k′) for the desorption leg. The extra information needed for calculating the desorption curve in the glassy region has been retrieved here through the use of a fitting procedure for the swelling coefficient.

The corresponding HPE swelling data during the sorption and desorption cycle at 50 °C are shown in Figure 9.

Table 4. Comparison of Experimental64 and Calculated Swelling Coefficients for Several Polymer–Gas Pairs at 35 °C

<table>
<thead>
<tr>
<th>system</th>
<th>(k_s) [MPa⁻¹]</th>
<th>exp.</th>
<th>calc.</th>
<th>error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA–CO₂</td>
<td>(1.85 \times 10^{-3})</td>
<td>1.80 \times 10^{-3}</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>PC–CO₂</td>
<td>(1.14 \times 10^{-3})</td>
<td>1.18 \times 10^{-3}</td>
<td>3.51</td>
<td></td>
</tr>
<tr>
<td>PC–C₂H₄</td>
<td>(1.20 \times 10^{-3})</td>
<td>1.21 \times 10^{-3}</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>PS–CO₂</td>
<td>(1.21 \times 10^{-3})</td>
<td>1.23 \times 10^{-3}</td>
<td>1.65</td>
<td></td>
</tr>
</tbody>
</table>

* The data needed for the calculations have been taken from the literature.64,65

Figure 8a shows QCM sorption data measured at 50 °C during both sorption and desorption cycles as the pressure is increased to 135 bar and then decreased to the atmospheric pressure. The results are compared to the predicted gas solubility calculated using NET-GP SL-II. Even though the hysteresis in CO₂ solubility for sorption–desorption cycles in this system is not very large, the model is able to represent it through the use of a different swelling coefficient (k′) for the desorption leg. The extra information needed for calculating the desorption curve in the glassy region has been retrieved here through the use of a fitting procedure for the swelling coefficient.

The corresponding HPE swelling data during the sorption and desorption cycle at 50 °C are shown in...
Appendix E. NET-GP Model

Figure 8b. For comparison, Figure 8b also shows the % swelling predictions using the NET-GP SL-II. The hysteresis in the measured system volume between sorption and desorption below $P_g$ is clearly evident in the experimental data. The model is able to obtain a fairly accurate quantitative comparison on the magnitude of the % swelling hysteresis, at least close to the glass transition, but it is not able to predict very well the values at lower pressure.

This large disparity between the model and the experimental data at low pressures is probably due to the assumption of linearity of polymer density with pressure in desorption as well as sorption. Whereas this assumption, based on experimental evidence, has been useful for modeling sorption, apparently it does not hold true in desorption for the entire pressure range. It seems to be reasonable approximation near the glass transition point, but it does not carry forward as the pressure goes to atmospheric. This assumption is also responsible for the predicted nonzero value of the swelling at zero pressure.

Figure 9a shows the measured solubility of carbon dioxide by QCM in terms of grams of CO$_2$ absorbed per gram of polymer (gCO$_2$/g) during a sorption—desorption cycle at 35 °C, a temperature just above the critical temperature for CO$_2$. Also shown are the comparisons to calculated values using the NET-GP SL-II model with parameters fit with solubility data during the sorption step above 100 bar at 35 °C. The binary interaction parameters for both the SL-I and SL-II models at this temperature are also shown in Table 3. Chow’s theory in eq 16 predicts that the CO$_2$ mass density at the glass transition point corresponds to a value of $\Omega_{CO_2} = 0.171$. Using the NET-GP SL-II model, the value of the glass transition pressure at 35 °C was estimated to be $P_g^{35} = 62$ bar, very close to the measured value. In the figure the sorption isotherm for CO$_2$ in PMMA at 35 °C has been predicted by means of the equilibrium SL-II equation of state $P_g^{35}$ and the NET-GP SL-II model below that limit. A comparison of the experimental and predicted results reveals that the model provides an accurate representation throughout the whole pressure range, as the polymer changes from glassy to rubbery and the penetrant transits from vapor to a supercritical fluid.

Figure 9b shows the corresponding % swelling of PMMA measured by HPE during the sorption—desorption cycle at 35 °C, together with the NET-GP SL-II predictions. The linear volume dilation below the glass transition pressure is evident as well as the hysteresis in measured film thickness below $P_g$ during sorption and desorption runs. The results from the NET-GP SL-II model provide a good representation of the complex swelling behavior of this system for sorption process in the whole pressure range and for desorption process as long as the pressure is above 20 bar, the point below which the linear density variation with pressure assumption during dilation apparently fails in reproducing the experimental results, as discussed above.

Finally, in Figure 10 a comparison is shown between the predictions of the NET-GP SL-II model and swelling data for CO$_2$ sorption in PMMA measured by Wissinger and Paulaitis. The binary interaction parameters for this calculation were estimated by fitting the swelling data at high pressure, and the results are summarized in Table 5. The initial densities of the polymer samples used in the NET-GP SL-II calculations were not reported by Wissinger and Paulaitis, but they were estimated by the procedure described in the model.

### Table 5. Interaction Parameters for the SL-II Model

<table>
<thead>
<tr>
<th>Binary Parameters</th>
<th>SL-II</th>
<th>SL-II</th>
</tr>
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<tbody>
<tr>
<td>$k_{ij}$</td>
<td>0.099</td>
<td>0.091</td>
</tr>
<tr>
<td>$\ell_{ij}$</td>
<td>-0.080</td>
<td>-0.161</td>
</tr>
<tr>
<td>$k_{ij}^{T}$</td>
<td>0.078</td>
<td>0.077</td>
</tr>
<tr>
<td>$\ell_{ij}^{T}$</td>
<td>0.161</td>
<td></td>
</tr>
</tbody>
</table>

* Parameters fit to data above 80 bar for each temperature.
Appendix E. NET-GP Model

This work describes an extension of the nonequilibrium thermodynamics of glassy polymer (NET-GP) model for swelling and sorption to the case of a high-pressure plasticizing penetrant. The theory of Chow is used to estimate the penetrant concentration at the glass transition point, which can then be used to estimate the pressure at the glass transition point using the equilibrium equation of state for the rubber phase. By assuming there is a linear relation between the glassy polymer density and the pressure below the glass transition pressure, it is possible to estimate the dilatation or swelling coefficient for the polymer–penetrant system. This facilitates the calculation of the sorption and swelling behavior by modeling the system using NET-GP below the glass transition pressure and the equilibrium equation of state above the glass transition pressure. The NET-GP approach can be used with any equilibrium equation of state that is capable of predicting the behavior of the system in the rubbery state. As a result, this is a very flexible approach that can be used for any equation of state regardless of its complexity. Use of the theory relies on knowledge of the initial density of the glassy polymer prior to solvent penetration. For cases, in which the initial polymer density is not known or is not provided, a procedure is described that facilitates its estimation based on the magnitude of the swelling coefficient.

The new model was applied to the interpretation of experimental data collected for sorption/desorption processes of CO$_2$ in PMMA films at different temperatures and for a wide range of CO$_2$ pressures. Swelling of PMMA was measured using high-pressure ellipsometry (HPE) and mass absorption was measured directly by use of a quartz crystal microbalance (QCM). The mass of absorbed CO$_2$ was also determined indirectly from the measured refractive index of the swollen film resulting from the ellipsometric analysis.

One of the major experimental findings of this work is that the sorption and swelling behaviors of two samples of a glassy polymer are the same as long as their densities are the same, even though their histories can be significantly different. To the best of our knowledge, this is the first experimental verification of the basic assumption of the NET-GP model, namely, that the glass polymer density can be used as order parameter to describe the nonequilibrium thermodynamic state of the system.

Through the use of a nonequilibrium version of the Sanchez–Lacombe lattice fluid model with two binary interaction parameters (NET-GP SL-II model), gas solubility and volume dilution were correctly represented at all experimental conditions. The model was able to provide a remarkably good agreement with the swelling hysteresis observed experimentally upon sorption and desorption of the gas, except for pressures close to atmospheric in desorption runs, where there is an apparent breakdown in the assumption of linearity of density with pressure.

The model also was able to provide an accurate description of the glass transition pressure variation with temperature as well as of the amount of gas absorbed in the glassy polymer phase. The work presented here can serve as the basis for future development in the study of the dynamic and equilibrium properties of high-pressure gas–polymer systems.

Acknowledgment. The authors thank the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing at NC State University and the University of Bologna for their funding of this work. This work was also supported in part by the Italian Ministry (MIRST) and the STC Program of the National Science Foundation under Agreement CHE-9876674.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Helmholtz free energy density (kcal kg$^{-1}$)</td>
</tr>
<tr>
<td>$C_n$</td>
<td>QCM mass coefficient</td>
</tr>
<tr>
<td>$C_f$</td>
<td>QCM pressure coefficient</td>
</tr>
<tr>
<td>$\Delta g$</td>
<td>constant pressure specific heat (J kg$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$f$</td>
<td>fugacity</td>
</tr>
<tr>
<td>$F$, $F_0$</td>
<td>QCM frequencies (MHz)</td>
</tr>
<tr>
<td>$\Delta F_0$</td>
<td>mass contribution to the frequency (MHz)</td>
</tr>
<tr>
<td>$\Delta F$</td>
<td>pressure contribution to the frequency (MHz)</td>
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<tr>
<td>$\alpha$</td>
<td>viscosity contribution to the frequency (MHz)</td>
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<tr>
<td>$h$, $h_0$</td>
<td>sample thickness ($\mu$m)</td>
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<tr>
<td>$k_b$</td>
<td>binary energetic interaction parameter</td>
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<tr>
<td>$k_0$</td>
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</tr>
<tr>
<td>$\Delta m$</td>
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</tr>
<tr>
<td>$M_w$</td>
<td>molecular weight (kg kmol$^{-1}$)</td>
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<tr>
<td>$n_j$</td>
<td>refractive index</td>
</tr>
<tr>
<td>$n_{ij}$</td>
<td>mixture refractive index</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure (bar)</td>
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<td>HPE coefficient (cm$^3$ g$^{-1}$)</td>
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<td>$R$</td>
<td>gas constant (J mol$^{-1}$ K$^{-1}$)</td>
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<tr>
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<td>$v^*$</td>
<td>Sanchez–Lacombe volumetric parameter (cm$^3$)</td>
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<td>$c^*$</td>
<td>Sanchez–Lacombe energetic parameter (J mol$^{-1}$)</td>
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<td>volume fraction</td>
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<tr>
<td>$\gamma$</td>
<td>fugacity coefficient</td>
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<td>$\eta_0$, $\eta_j$</td>
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<td>binary volumetric interaction parameter</td>
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<td>chemical potential (J mol$^{-1}$)</td>
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<td>$\theta$</td>
<td>Chow’s theory parameter</td>
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<td>$\rho_0$, $\rho_j$, $\rho$</td>
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</tr>
<tr>
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<td>state</td>
</tr>
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<td>$\omega$</td>
<td>mass fraction</td>
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<tr>
<td>$\Omega$</td>
<td>mass ratio</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Chow’s theory parameter</td>
</tr>
</tbody>
</table>

Subscripts

- $i$, $j$ = generic component in the mixture
- 1, CO$_2$ = carbon dioxide
- 2, PMMA = polymer
- mix = mixture
- $m$ = mass
- $P$ = pressure
- $q$ = quartz
References and Notes


Appendix E. NET-GP Model
Appendix F

Model for Sorption Kinetics

This chapter is essentially a manuscript titled “Modeling Sorption Kinetics of Carbon Dioxide in Bulk Polymeric Films Using the Non-Equilibrium Thermodynamics Approach” in preparation by Vito Carla, Yazan Hussain, Christine Grant, Giulio C. Sarti, Ferruccio Doghieri, and Ruben G. Carbonell.

Abstract

The Non-Equilibrium Thermodynamics of Glassy Polymers (NET-GP) approach [Macromolecules, 2005, 38, 10299] is applied to the development of a one-dimensional transport model aimed at describing the kinetics of sorption and dilation of supported polymeric films in supercritical carbon dioxide. The NET-GP model has been combined with the free volume theory to estimate the diffusive flux, and with a simple rheological constitutive equation to model relaxation behavior, to build a sorption-diffusion-relaxation model to describe mass uptake and swelling kinetics of polymeric films in contact with carbon dioxide over a wide range of pressures and temperatures. The model calculations are compared to real-time mass sorption data of CO\textsubscript{2} in poly(methylmetacrylate) (PMMA) taken using a high-pressure Quartz Crystal Microbalance (QCM) in both rubbery and glassy polymer regimes.

F.1 Introduction

Carbon dioxide is gaining increasing interest as a solvent for industrial applications because of its unique characteristics, such as non-flammability, low toxicity, natural abundance, low cost, and environmental compatibility [1, 2]. As a supercritical fluid, CO\textsubscript{2} has a gas-like viscosity, a low surface energy and a liquid-like density, allowing it to penetrate into small gaps and to exhibit enhanced solubility and transport properties. In addition, the solvent power of CO\textsubscript{2} can be easily tuned by small changes in temperature and pressure.
Appendix F. Model for Sorption Kinetics

As a result, there is a wide range of applications in which CO\(_2\) could replace traditional aqueous and organic solvents, from the food industry to coatings in the automotive and furniture industries, and polymer production and processing [3]. The latter is of particular interest due to the ability of carbon dioxide to easily swell and plasticize many polymers, making it ideal for manipulating polymer physical properties, enhance diffusion of small molecules and as foaming agent [4, 5].

Modeling the transport of solvents, including CO\(_2\) at high pressure, in polymeric materials is of paramount importance in processes such as drug impregnation and photolithography. Such models would eventually allow for process optimization and facilitate extension to other desired systems and applications. However, the mathematical description of solvent mass sorption in polymers is a difficult challenge since several different types of transport behaviors have been observed experimentally over the years for various polymer-solvent pairs at different operating conditions [6-12]. The penetration of small molecules into polymer films causes significant changes in the polymer structure, enhancing the free volume of the system and the mobility of the polymer chains, thus lowering the glass transition temperature and allowing the matrix to relax and swell [13]. In turn, these factors affect strongly the additional adsorption and diffusion of penetrant molecules.

The aim of the present work is to introduce a new sorption-diffusion-relaxation model for studying mass uptake and swelling kinetics of polymeric films brought in contact with CO\(_2\) over a wide range of pressures and temperatures. It is a direct application of the Non-Equilibrium Thermodynamics of Glassy Polymers (NET-GP) approach, initially developed by Doghieri and Sarti [14,15] for the study of sorption in glassy polymers at low pressures, and recently extended by Carla et al. [16] to high-pressure regions.

The NET-GP approach consists of extending any suitable equilibrium model applicable in the rubbery region over into the non-equilibrium glassy region by means of an order parameter, the polymer density. This parameter is considered to be not only a function of thermodynamic variables, i.e., temperature, pressure, and composition, but also of the thermal, mechanical, and sorption history of the sample.

In our previous work [16], the pseudo-equilibrium density of the polymer was estimated by means of a linear relationship between the density and the pressure below the glass transition point. While this was sufficient for calculating the sorption isotherms, in order
Appendix F. Model for Sorption Kinetics

to describe the kinetics of the relaxation process by means of which the out-of-equilibrium degree of the system changes in a sorption process, an evolution equation for the polymer density must be considered. This has been accomplished using a mechanical model that provides information on the polymer density change with time through a stress-strain relationship.

The use of a mechanical model to describe the polymer density raises the need to define the stress (or driving force) that causes the swelling. Indeed, there have been several different attempts to describe this force. Sarti [17] used the difference in the chemical potential between the pure polymer and the swollen polymer as the driving force for polymer swelling. Sarti and Apicella revised this approach by considering the non-equilibrium state of the glassy polymer, adding an excess term to the equilibrium driving force [18]. A similar expression for the chemical potential was used by Bisschops et al. [19] and its gradient was used as the driving force for swelling.

Instead, the mechanical model introduced here has been developed starting from a force balance on a volume element of the film and it is written in terms of isotropic pressures, so that the driving force for swelling ends up being the difference between the actual system pressure and the equilibrium pressure calculated for that particular volume element.

Several studies have been published over the years on modeling the diffusion of small molecules in polymers and some of the milestones achieved in the past will be briefly discussed here to put our work in perspective. Much more complete summaries of this field have been recently published by Frish [11] and by Vrentas and Duda [20].

Vrentas and Duda [12] studied the diffusion of small molecules in amorphous polymers through a re-examination of the free volume theory and were able to explain successfully the change in diffusion behavior with molecular size. Unfortunately, the quantitative comparison of their model with experiments gives good results only at low pressures. Durning and Tabor [21] investigated the problem of mutual diffusion of small molecules in concentrated polymeric solutions under small driving forces. Their analysis took into account the deformation of the polymer caused by the solvent and their work included a memory integral contribution from transient network theory and the reptation model. However, Durning and Tabor model is limited to incompressible systems with small deformation. Peppas and coworkers developed a more complete model for describing sorption and dissolution kinetics.
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but their approach makes use of the Flory-Huggins theory for the chemical potential, thus neglecting the non-equilibrium nature of the glassy system [22, 23].

In the aforementioned models, one of the major shortcomings arises from the absence of a reliable thermodynamic model valid over a wide range of pressures, from the glassy state up to fully plasticized rubbery state. In our previous work [16], a new procedure was introduced to calculate solubility isotherms for gas sorption in bulk films; in the present work we utilize that procedure in conjunction with the free volume theory and a simple rheological model for polymer deformation to describe the mass transport of CO$_2$ in PMMA.

In the following sections, the various aspects of this new transport model are described. A finite element discretization procedure was used to obtain a numerical solution to the set of coupled partial differential equations describing solute transport and polymer deformation. The resulting concentration profiles of penetrant molecules inside the polymer under both glassy and rubber conditions were integrated over the film thickness to predict the kinetics of mass sorption and desorption of CO$_2$ in supported films of PMMA at two different temperatures and under a wide range of pressures. These theoretical results are compared to real-time mass sorption data taken with a high-pressure Quartz Crystal Microbalance (QCM). It is demonstrated that the model provides an excellent description of the mass sorption and desorption rates in both the glassy and rubbery polymer regimes.

F.2 Theory

This section describes the formulation of a one-dimensional mass transport model for diffusion of a mobile solvent species into a polymeric film using the NET-GP approach. The continuity equations for the solvent ($s$) and polymer ($p$) species take the form,

$$\frac{\partial \rho_s}{\partial t} = \nabla \cdot \left( \rho_s \frac{\nabla p}{\rho_s} + j_s \right)$$  \hspace{1cm} (F.1)

$$\frac{\partial \rho_p}{\partial t} = \nabla \cdot \left( \rho_p \frac{\nabla p}{\rho_p} \right)$$  \hspace{1cm} (F.2)

where $j_s$ is the solvent diffusive flux,

$$j_s = \rho_s \left( \nabla s - \frac{\nabla p}{\rho_s} \right)$$  \hspace{1cm} (F.3)

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Here \( v_s \) and \( v_p \) are the local mass velocities of the solvent and polymer respectively, and \( \rho_s \) and \( \rho_p \) are the corresponding mass densities. The mass diffusive flux for the mobile species can be calculated using a generalized Fickian constitutive equation where the driving force is the gradient in the chemical potential of the solvent in the polymer,

\[
\dot{j}_s = -D^* \nabla \mu_s \tag{F.4}
\]

The quantity \( D^* \) is a generalized diffusion coefficient for the solvent transport in the polymer which will be described in additional detail later.

The solvent chemical potential in the equation above can be determined using the NET-GP approach modified for high pressures [16], which provides an expression for the solvent chemical potential under non-equilibrium (glassy) conditions:

\[
\mu_{s}^{\text{NE}} = \mu_{s}^{\text{NE}} (T, P, \omega_s, \rho_p) \tag{F.5}
\]

The expression for the non-equilibrium equation of state is obtained through the proper extension of any well-established equilibrium equation of state (EoS) for fluid systems, by assuming the polymer density is an order parameter for the system that can be treated as an internal state variable. The NET-GP approach requires an evolution equation for the mass density that describes the polymer volume relaxation to its final value,

\[
\frac{d\rho_p}{dt} = f(T, P, \omega_s, \rho_p) \tag{F.6}
\]

In this work, the evolution equation will take the form of a mechanical constitutive equation to determine the kinetics of this relaxation process.

For the case of one-dimensional transport along the \( x \)-axis, the continuity equation for the mobile species (\( \text{CO}_2 \)) in lab-fixed coordinates reduces to the form,

\[
\left( \frac{\partial \rho_s}{\partial t} \right)_x = -\left( \frac{\partial}{\partial x} (\rho_s v_{px} + j_{px}) \right) \tag{F.7}
\]

This coordinate system is illustrated in Figure F.1 for the case of a polymer film coated on a hard substrate. At the \( \text{CO}_2 \)-polymer interface \( x = \delta \) at \( t = 0 \) and \( x = \delta + \Delta \delta \) at
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Figure F.1: Schematic illustration of the relationship between the lab-fixed and polymer-fixed coordinate systems.

\[ t = \Delta t \] it will be assumed that the chemical potential of the external fluid is the same as the chemical potential of the solvent in the polymer. It will also be assumed that the substrate is impervious to solvent transport so that at \( x = 0 \) the flux of solvent is zero.

In lab-fixed coordinates, the swelling of the polymer during solvent diffusion gives rise to a mathematically difficult moving boundary problem since the polymer film thickness \( \delta \) will be time-dependent. In order to avoid this complication, it is useful to define a polymer-fixed coordinate \( \xi \) in which the spatial domain of the solvent continuity equation has fixed, time independent boundaries so that \( 0 < \xi < \delta(0) \) (see Figure F.1). Dependent variables expressed in polymer-fixed coordinates will be designated with the superscript \( P \) in the following development.

It is possible to rewrite the solvent continuity equation, Eq. (F.7), in terms of these new coordinates by defining a quantity we shall call elongation, \( \lambda \), which serves to relate the lab-fixed to the polymer-fixed coordinates,

\[ \lambda = \left( \frac{\partial x}{\partial \xi} \right)_t \] (F.8)

By definition, the velocity of the polymer at a given time along the \( x \) direction is equal to the time rate of change in the spatial position \( x \) for a fixed value of the polymer-fixed...
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coordinate,
\[
\left( \frac{\partial x}{\partial t} \right)_\xi = v_{px} \tag{F.9}
\]

Chain differentiation of the left hand side of Eq. (F.7) results in the expression,
\[
\left( \frac{\partial \rho_s}{\partial t} \right)_x = \left( \frac{\partial \rho_s}{\partial t} \right)_\xi + \left( \frac{\partial \rho_s}{\partial \xi} \right)_t \left( \frac{\partial \xi}{\partial t} \right)_x = \left( \frac{\partial \rho_s}{\partial t} \right)_\xi - \frac{v_{px}}{\lambda} \left( \frac{\partial \rho_s}{\partial \xi} \right)_t \tag{F.10}
\]
while expanding the derivative of the right hand side in Eq. (F.7) leads to relationship,
\[
\frac{\partial}{\partial \xi} (\rho_s v_{px} + j_{sx}) \frac{1}{\lambda} = \left( v_{px} \frac{\partial \rho_s}{\partial \xi} + \rho_s \frac{\partial v_{px}}{\partial \xi} + \frac{\partial j_{sx}}{\partial \xi} \right) \frac{1}{\lambda} \tag{F.11}
\]

Substitution of Eqs. (F.8)–(F.11) in Eq. (F.7), results in an alternative form of the continuity equation for solvent,
\[
\lambda \frac{\partial \rho_s}{\partial t} + \rho_s \frac{\partial \lambda}{\partial t} = - \frac{\partial j_{sx}}{\partial \xi} \tag{F.12}
\]
that can be written in the simpler form,
\[
\left[ \frac{\partial}{\partial t} (\rho_s \lambda) \right]_\xi = - \left[ \frac{\partial j_{sx}}{\partial \xi} \right]_t \tag{F.13}
\]

The diffusive flux of solute in the equation above also needs to be expressed in the polymer-fixed system, in which, by definition, the polymer velocity is zero,
\[
j_{sx}^P = \rho_s^P \left( v_{sx}^P - v_{px}^P \right) = \rho_s^P v_{sx}^P \tag{F.14}
\]

It is also necessary to recognize that the specific density of the polymer is coordinate dependent. In fact, the volume of the polymer sample changes in the lab-fixed system but it remains constant in the polymer-fixed coordinates (see Figure F.1). In order to express the solute density in the polymer-fixed coordinate system, it is useful to refer to the determinant of the displacement gradient tensor [24],
\[
\det F = \frac{V}{V_0} = \frac{\rho_s^P}{\rho_s} \tag{F.15}
\]
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The displacement gradient tensor, \( F \), can be easily obtained from the relationship between the two systems of coordinates, and, for the particular case of one dimensional diffusion in a polymer film in rectangular coordinates, is given by the expression,

\[
F = \begin{pmatrix}
\lambda & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] (F.16)

From the definition of \( \lambda \) in Eq. (F.8) and the ratio of densities in Eq. (F.15) we have,

\[
\rho_s^P = \lambda \rho_s
\] (F.17)

After accounting for the unit vector difference between the systems, i.e., \( \xi = \lambda^{-1} \xi^P \), it is clear that \( u_{s\xi}^P = \lambda^{-1}(u_{sx} - v_{px}) \) and finally \( j_{s\xi}^P = j_{sx} \), which means that for the particular geometry considered the solute flux in the polymer fixed coordinate system is the same as that in fixed laboratory coordinates. As a result, the solvent continuity equation in the polymer-fixed coordinates, Eq. (F.13), takes the form,

\[
\left( \frac{\partial \rho_s^P}{\partial t} \right)_\xi = - \left( \frac{\partial j_{s\xi}^P}{\partial \xi} \right)_t
\] (F.18)

In a completely analogous manner, it is possible to derive the continuity equation for the polymer in a polymer-fixed frame, which takes the form,

\[
\left( \frac{\partial \rho_p^P}{\partial t} \right)_\xi = - \left( \frac{\partial \rho_p \lambda}{\partial \xi} \right)_\xi = 0
\] (F.19)

Eq. (F.19) implies that \( (\rho_p \lambda)_\xi \) is constant in time. Since, by definition, at the beginning of the diffusion process the elongation is equal to unity, this equation also indicates that \( \lambda \) is equal to the ratio of the initial polymer density to the polymer density at a given time,

\[
\lambda = \frac{\rho_0}{\rho_p}
\] (F.20)
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Using the above equation, it is possible to evaluate the elongation once the *evolution expression* for the polymer density is provided. It should be noted that Eq. (F.20) could also have been derived from Eq. (F.15) and Eq. (F.16), thus validating the mathematical consistency of the present formulation.

Eqs. (F.18) and (F.20) can be used for calculating the penetrant and polymer density profiles inside the polymer matrix with time, resulting in a description of the kinetics of mass sorption and volume dilatation. In order to complete the model description, constitutive equations are needed for the diffusive flux in Eq. (F.18) and the evolution equation for the polymer density, Eq. (F.6). In addition, the initial and boundary conditions must be considered for the particular case chosen.

Constitutive equation for the diffusive flux

The generalized Fickian expression for the diffusive flux, Eq. (F.4), can be written in the form [25],

\[
J_{s\xi} = -\left(\frac{L_s \rho_s \omega_p}{RT}\right) \frac{\partial \mu_N^E}{\partial x} \tag{F.21}
\]

where the driving force has been expressed as a chemical potential gradient and the diffusivity \(L_s\) has been taken from the free volume theory of Vrentas and Duda [20] in the form,

\[
L_s = L_s^0 \exp \left[ -\frac{\gamma (\omega_s V_s^* + \omega_p \zeta V_p^*)}{V_{mix}^*} \right] \tag{F.22}
\]

In the above and throughout this work, the free volume term has been calculated according to the expression [26],

\[
V_{mix}^* = V_p - \frac{1}{\rho_{mix}^*} \tag{F.23}
\]

where \(V_p\) is the polymer molar volume obtained from a force balance acting upon the sample, as shall be shown later, and \(\rho_{mix}^*\) is the *closed packed density* of the mixture, which can be evaluated from the thermodynamic model.

Writing Eq. (F.21) in the polymer-fixed system we have,

\[
J_{s\xi}^P = -\left(\frac{L_s (\lambda \rho_p^* \omega_p)}{RT}\right) \frac{\partial \mu_N^E}{\partial \xi} \frac{\partial \xi}{\partial x} = \left(\frac{L_s \rho_p^* \omega_p}{RT}\right) \frac{\partial \mu_N^E}{\partial \xi} \tag{F.24}
\]

By considering the explicit functional form of the non-equilibrium chemical potential of the
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solute, the total differential change in chemical potential for a process takes the form,

$$d\mu_{s}^{NE} = \frac{\partial \mu_{s}^{NE}}{\partial T}dT + \frac{\partial \mu_{s}^{NE}}{\partial P}d\omega_{s} + \frac{\partial \mu_{s}^{NE}}{\partial \rho_{p}}d\rho_{p} \tag{F.25}$$

In the case of uniform temperature and pressure fields, and when the composition, \(\omega_{s}\), is written in terms of solvent density, Eq. (F.25) becomes,

$$d\mu_{s}^{NE} \bigg|_{T,P} = \frac{\partial \mu_{s}^{NE}}{\partial \rho_{s}^{P}}d\rho_{s}^{P} + \left( \frac{\partial \mu_{s}^{NE}}{\partial \rho_{p}} - \frac{\partial \mu_{s}^{NE}}{\partial \rho_{s}^{P}} \frac{\rho_{s}^{P}}{\rho_{p}^{P}} \right) d\rho_{p}^{P} \tag{F.26}$$

This equation can be more conveniently written in the form,

$$j_{s}^{P} = -L_{ss}^{P} \frac{\partial \rho_{s}^{P}}{\partial \xi} - L_{sp}^{P} \frac{\partial \rho_{p}^{P}}{\partial \xi} \tag{F.27}$$

where

$$L_{ss}^{P} = \left( \frac{L_{s}^{P} \omega_{p}^{P}}{RT} \right) \frac{\partial \mu_{s}^{NE}}{\partial \rho_{s}^{P}} \tag{F.28}$$

and

$$L_{sp}^{P} = \left( \frac{L_{s}^{P} \omega_{p}^{P}}{RT} \right) \left( \frac{\partial \mu_{s}^{NE}}{\partial \rho_{p}^{P}} - \frac{\partial \mu_{s}^{NE}}{\partial \rho_{s}^{P}} \frac{\rho_{s}^{P}}{\rho_{p}^{P}} \right) \tag{F.29}$$

The first terms in the parentheses in Eqs. (F.28) and (F.29) represent the free volume contributions to the diffusion coefficient, while the terms involving gradients of the non-equilibrium chemical potential represent the thermodynamic contribution. The expression for the non-equilibrium chemical potential is derived in the work of Carla et al. [16], based on an expression for the non-equilibrium Helmholtz free energy of the system,

$$\mu_{s}^{NE} = \left( \frac{\partial a^{NE}}{\partial n_{s}} \right)_{T,P,n_{p},\rho_{p}} \tag{F.30}$$

where \(n_{s}\) is the number of moles of the penetrant species. The NET-GP model modified for high pressures [16] was used to estimate the solute chemical potential in the non-equilibrium glassy state for the solute-polymer mixture. The Sanchez-Lacombe (SL) two binary parameter equation of state (EoS) was used to represent the thermodynamic properties in the equilibrium (rubbery) states. The SL EoS was also used to model the thermodynamic properties.
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properties external phase (pure CO\textsubscript{2}).

Evolution equation for the polymer density
According to one of the assumptions of the NET-GP approach, the polymer density is treated as the order parameter that provides the out-of-equilibrium degree of the system, so that a non-equilibrium argument is required for calculating its value.

The development of an evolution equation for the density can be approached through the use of a rheological constitutive equation that provides the force balance acting upon each element of the sample, thus relating the stress resulting from solvent penetration and the corresponding strains due to polymer relaxation.

![Figure F.2: Voigt rheological model and physical interpretation of its components.](image)
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It is clear from a careful analysis of the data available in the literature that an accurate description of the viscoelastic behavior of a polymer is only made possible by accounting for more than a single relaxation time for the material [27], due to the distribution of strengths of polymer chain entanglements, which ultimately are strongly dependent upon the thermo-mechanical history of each sample. As an approximation of the real behavior, we adopt a simple rheological model, shown in Figure F.2, to describe the stress-strain relationship of the polymeric material. The mechanical model involves two Voigt elements, each having its own stress-free equilibrium length, modulus and viscosity. The two Voigt elements share the same overall forces that can be written in the form of sum of elastic and viscous contributions, as follows,

\[ F = k \left( \frac{x - x^0}{x^0} \right) + \vartheta \frac{d}{dt} \left( \frac{x - x^0}{x^0} \right) \]  

(F.31)

where \( k \) represents the modulus, \( x^0 \) and \( x \) are the initial and final length, and \( \vartheta \) has the meaning of a viscosity.

For a given deformation, the resulting force acting upon each element at equilibrium is balanced only by the contribution of the spring (elastic contribution) and can be written as \( F^{eq} = k(x - x^0)/x^0 \). Eq. (F.31) can then be rewritten in the form,

\[ F - F^{eq} = \vartheta \frac{d}{dt} \left( \frac{x - x^0}{x^0} \right) \]  

(F.32)

in which the elastic term is incorporated in the equilibrium resulting force acting upon the element.

Eq. (F.32) can be written in terms of pressure and derivatives of the volume or density, by adopting the following formal equivalences,

\[ F - F^{eq} \Leftrightarrow P - P^{eq} \]  

(F.33)

\[ \frac{d}{dt} \left( \frac{x - x^0}{x^0} \right) \Leftrightarrow \frac{1}{V} \frac{dV}{dt} = -\frac{d \ln \rho}{dt} \]  

(F.34)

\[ \vartheta \Leftrightarrow \eta \]  

(F.35)

Note that in this particular mechanical model, the driving force for evolution of the polymer density is the difference between the actual pressure exerted upon the polymeric
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sample and the corresponding pressure in the equilibrium system. The constitutive equation
for the polymer density then takes the simple form,

\[
\frac{\partial \rho_p}{\partial t} = -\rho_p \frac{(P^{eq} - P)}{\eta}
\]  \hfill (F.36)

When the time rate of change of the polymer density goes to zero, the expression above
gives rise to the equilibrium polymer density,

\[
\frac{\partial \rho_p}{\partial t} \rightarrow 0 \quad \rightarrow P \rightarrow P^{eq} \equiv - \left( \frac{\partial a}{\partial V} \right)_T
\]  \hfill (F.37)

Under these conditions the formalism is consistent with the equilibrium equation of state.
With this picture in mind, the volume deformation of the polymer can be thought as being
made up of two contributions, one from each Voigt element, with a suitable weighting factor,

\[
V_p = \chi V_p^A + (1 - \chi) V_p^B
\]  \hfill (F.38)

Here \(\chi\) represents the weight of Voigt element \(A\) in the set, and \(V_p^A\) and \(V_p^B\) are the two
measures of volume deformation associated with each Voigt element which can be calculated
using evolution equations analogous to Eq. (F.36),

\[
\frac{1}{V_p^A} \frac{\partial V_p^A}{\partial t} = \frac{P^{eq}(T, V_p^A, \mu_s) - P}{\eta_A}
\]  \hfill (F.39)

and

\[
\frac{1}{V_p^B} \frac{\partial V_p^B}{\partial t} = \frac{P^{eq}(T, V_p^B, \mu_s) - P}{\eta_B}
\]  \hfill (F.40)

In the equations above, \(\mu_s\) is the CO\(_2\) chemical potential in the external phase. Eqs. (F.38)–
(F.40) represent the evolution law for the polymer volume, to be solved along with the
pertinent initial conditions,

\[
V_p^A(t = 0) = V_p^{A0} = V_{eq}(T, P, \omega_s)
\]  \hfill (F.41)

\[
V_p^B(t = 0) = V_p^{B0} = \frac{V^0 - \chi V_p^{A0}}{1 - \chi}
\]  \hfill (F.42)
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In the simplified picture of the polymer rheology considered here, the intent is to have Voigt element A represent short time relaxation phenomena, so that steady-state conditions can be reached, i.e., \( P = P^{eq}(T, V_p^A, \mu_s) \), in the pseudo-equilibrium state. More specifically, the short term relaxation phenomena refers to the first time constant in a two-stage sorption process often exhibited during solute adsorption in polymers close to the glass transition. On the other hand, element B is intended to represent the long time relaxation response of the polymer and it is supposed to reach the equilibrium state on an appreciable time scale only above the glass transition point, in the rubbery region.

Since the main interest in this work is in the representation of short time relaxation phenomena, the following assumptions will be made for the characteristic viscosities of the Voigt elements A and B,

\[
\eta_A = \begin{cases} 
\eta_A(T, P, \omega_s) & T \leq T_{gmix}(\omega_s) \\
0 & T > T_{gmix}(\omega_s)
\end{cases}
\]  

\( F.43 \)

\[
\eta_B = \begin{cases} 
\infty & T \leq T_{gmix}(\omega_s) \\
0 & T > T_{gmix}(\omega_s)
\end{cases}
\]  

\( F.44 \)

where \( T_{gmix}(\omega_s) \) is the glass transition temperature of the mixture during sorption. In essence, Voigt element A has a finite viscosity below the glass transition temperature, while the volume of Voigt element B is thought to be 'frozen' at its initial volume evaluated through Eq. \( (F.42) \). Both Voigt elements A and B are assumed to have zero viscosity in the rubbery region, which implies that they are thought to react instantaneously to any force applied to them, thus behaving like an elastic solid. The overall polymer density, needed by the thermodynamic model, can be calculated from the expression,

\[
\rho_p = \frac{1}{V_p}
\]  

\( F.45 \)

where the partial mass volume of the polymer is calculated using Eqs. \( (F.38)-(F.40) \).

As for the bulk viscosity of element A below the glass transition that appears in Eq. \( (F.43) \), there is a simple treatment in the literature given by Royer et al. [28]. They have developed a correlation to take into account the effects of temperature, pressure and \( \text{CO}_2 \).
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concentration on the shear viscosity of polymers,

\[ \ln \left( \frac{\eta_A(T, P, \omega_s)}{\eta_A^0} \right) = \frac{C_1 \cdot (T - T_{g_{mix}})}{C_2 + (T - T_{g_{mix}})} - \frac{C_1 \cdot (T - T_{g_{mix},P})}{C_2 + (T - T_{g_{mix},P})} \]  

(F.46)

This expression follows the Williams-Landel-Ferry (WLF) equation [28, 29], in which the viscosity shifts are related to the change in the free volume of the mixture through the glass transition temperature change upon sorption, which in turn can be calculated using a simple model such as the Chow’s theory of glass transition depression [13].

However, since the free volume of the mixture upon sorption can be estimated through Eq. (F.23), it was preferable to utilize the more fundamental Doolittle’s equation [28],

\[ \ln \eta_A = \ln A + \frac{B}{V_{f_{mix}}} \]  

(F.47)

The WLF equation can be derived from Eq. (F.47) once a linear expression for the free volume change with temperature has been assumed. It can be assumed, as was done deriving the WLF equation, that the same functional relationship is valid through the glass transition point. This results in the expression,

\[ \ln \eta_A^0 = \ln A + \frac{B}{V_f^0} \]  

(F.48)

where \( \eta_A^0 \) and \( V_f^0 \) are the bulk viscosity and the free volume of the pure polymer at the glass transition, respectively.

Subtracting Eq. (F.48) from Eq. (F.47) results in,

\[ \ln \eta_A - \ln \eta_A^0 = B \left( \frac{1}{V_{f_{mix}}} - \frac{1}{V_f^0} \right) \]  

(F.49)

where the constant \( B \) can be calculated either from WLF material parameters as \( B = \alpha C_1 C_2 \) [28] or from the Vrentas-Duda parameters as \( B = \gamma V_p^* \) [30]. Both approaches are equivalent but the second approach has been chosen for these calculations, and with a little algebra it
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is possible to obtain the final shifting expression,

$$\ln \left( \frac{\eta_A}{\eta_A^0} \right) = \frac{\gamma V_p^* (V^0 - V_p)}{(V^0 - 1/\rho_p^*) (V_p - 1/\rho_{\text{mix}}^*)}$$  (F.50)

In this way the only material parameter involved in the viscosity equation that needs to be estimated from the experimental data is the dry bulk viscosity of the polymer at the glass transition point, $\eta_A^0$, that is strongly dependent upon the thermo-mechanical history of the sample.

Whereas the bulk viscosity has a well-known physical meaning, and the values fit to the experimental data, as shall be shown later, are safely within the range of the literature reported values [27], a more detailed discussion is needed for $\chi$. The value of $\chi$ represents the relative contributions of element $A$ to the real system behavior. This parameter is used to account for the mechanical behavior of the out-of-equilibrium polymer density in the glassy state so that the magnitude of $\chi$ depends on the degree of deviation from the equilibrium (rubbery) state. For a rubbery material the value of $\chi$ is unity.

For the case of a glassy polymer, the values of $\chi$ are retrieved from experimental sorption data, whereas for the case of a rubbery polymer $\chi$ is simply set to be 1. However, it is possible to develop a simple procedure that enables a rather good a-priori estimation of $\chi$.

Taking the derivative with pressure of both sides of Eq. (F.38) results in the expression,

$$\frac{dV_p}{P} = \chi \frac{dV_p^A}{P} + (1 - \chi) \frac{dV_p^B}{P}$$  (F.51)

By considering the assumption associated with Eq. (F.41), i.e., $\tau_B \rightarrow \infty$, in the short time scale, at the glass transition temperature it is possible to make the approximation,

$$\frac{dV_p}{dP} \bigg|_{T_g^-} \cong \chi \frac{dV_p^A}{dP} \bigg|_{T_g^+}$$  (F.52)

The glass transition for the element $A$ can be approached from above or below $T_g$, but the left hand side of the above equation can only be approached from below $T_g$. Eq. (F.52) can
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be divided on both sides by the specific volume,

\[
\left( \frac{1}{V_p} \frac{dV_p}{dP} \right)_{T_g^-} = \chi \left( \frac{1}{V_p} \frac{dV_p^A}{dP} \right)_{T_g^+} \tag{F.53}
\]

By noticing that the expression in parenthesis is nothing but the definition of the isothermal bulk compressibility, it can be seen that the value of \( \chi \) can be related to the ratio of the isothermal bulk compressibility above and below the glass transition temperature,

\[
\chi = \frac{\left( \frac{1}{V_p} \frac{dV_p^A}{dP} \right)_{T_g^+}}{\left( \frac{1}{V_p} \frac{dV_p}{dP} \right)_{T_g^-}} = \frac{k_{T_g^+}}{k_{T_g^-}} \tag{F.54}
\]

Using experimental values for the isothermal compressibility PMMA [31] in the rubber and glassy states yields an estimate of \( \chi \), \( 2.8 \times 10^{-4} \text{MPa}^{-1}, 0.63 \).

Initial and boundary conditions

The initial conditions can be written assuming a uniform distribution of concentration for both species at the beginning throughout the film thickness. The interfacial boundary condition derives from the phase relation and allows for the calculation of the solvent solubility, for a given temperature, pressure and polymer density. Finally, at the non-permeable substrate, the flux is taken equal to zero.

\[
t = 0 \quad \rho_s = \rho_s(\xi, 0) = \rho_s^0 \\
= 0 \quad \rho_p = \rho_p(\xi, 0) = \rho_p^0 \\
\xi = \delta(0) \quad \mu_{s}^{NE} = \mu_{s}^0 \\
\xi = 0 \quad j_{s \xi}(0, t) = 0 \tag{F.55}
\]

The above set of equations was solved numerically and compared to real-time mass absorption data for CO\(_2\) diffusion into PMMA films taken at two temperatures and over a wide range of pressures with a high-pressure Quartz Crystal Microbalance (QCM). The section that follows describes the details of these measurements.
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F.3 Experimental

Materials. Coleman Grade (purity > 99.999%) CO₂ was obtained from National Welders. Poly(methyl-methacrylate) having a molecular weight of 72kDa and PDI of 1.08 was obtained from Polymer Source Inc. (Montreal, Canada). A 5 wt% PMMA solution in Toluene (Fisher) was used for film preparation by dip coating. All materials were used as received.

QCM system. The quartz crystals, obtained from International Crystal Manufacturing and used in this study as received, were 5.00 MHz AT-cut Si with a blank diameter of 8.5 mm and a thickness of 0.25 mm. The rms surface roughness for the crystals used was less than 10 nm (analyzed using AFM). A voltage-controlled oscillator was used (Maxtek model PLO-10) to provide both frequency and voltage outputs. The voltage reading is inversely proportional to the resistance of the crystal. An Agilent 225 MHz Universal Frequency Counter (model 53131A) was used to read the frequency.

Pressure cell and apparatus. The custom-built pressure cell consisted of a thick-wall cylinder (63.5 mm I.D. × 200 mm height), with a high-pressure electrical feedthrough for QCM connections. A high-pressure thermocouple (Omega) was used to measure the cell temperature, and a pressure transducer, (Omega, part No. PX 302), was used to measure the pressure. The whole assembly was then placed in a water bath and controlled to ±0.1 °C. Data acquisition of the four readings was done using LabView [16].

Polymer film preparation. After measuring the fundamental frequency of the clean crystal in vacuum, $F_0$, the crystal was dipped vertically into the PMMA solution in toluene for 1 minute and withdrawn from the solution at a controlled rate. The coated crystal was then dried under vacuum at 76 °C for approximately 1 hour. The frequency was measured after drying; a constant stable frequency level was an indication of sufficient solvent removal. The value of the stabilized frequency of the coated QCM in vacuum was used to calculate the initial total mass of coated polymer, and this mass was in turn used with the bulk polymer density [16] to estimate the film thickness, which was found in all cases to be close to 1 µm. Cross-sectional SEM images of the coated QCM crystals support this estimation. The film roughness, as measured by AFM for samples before and after treatment with CO₂,
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was about 5 nm. After a stable signal was realized in vacuum, the pressure was increased to its initial value. The frequency was then allowed to reach the new stable level; the procedure was then repeated for the second pressure level, the third pressure level, and so on. The pressures studied in this work ranged from 0 up to 1800 psi. Runs during which sudden pressure changes were achieved at uniform temperature were used for comparison between theory and experiment.

![Graph showing concentration profiles of the penetrant species in the polymer at different times for De << 1 (a), De ~ 1 (b), and De >> 1 (c).](image)

**Figure F.3:** Concentration profiles of the penetrant species in the polymer at different times for De << 1 (a), De ~ 1 (b), and De >> 1 (c).

F.4 Results and Discussion

The sorption process resulting from a relatively small increase in the solute fugacity in the external phase is the combination of several elementary phenomena. The model developed
Appendix F. Model for Sorption Kinetics

above addresses the kinetics of two of these elementary phenomena, solute molecular diffusion and volume swelling of the polymer matrix. The Deborah number $De$, defined as the ratio of the characteristic time for polymer relaxation $\tau_R$ to the characteristic time for diffusion $\tau_D$ [32],

$$De = \frac{\tau_R}{\tau_D} = \frac{\eta/k}{l/D^2} \quad (F.56)$$

Here $\eta$ and $k$ are the effective bulk modulus and the viscosity of the polymeric matrix respectively, $D$ represents the mean diffusion coefficient of solute in the polymeric mixture and $l$ indicates the characteristic dimension of the polymer sample. For those cases in which $De \ll 1$ ($\tau_R \ll \tau_D$), the polymer relaxation phenomenon is fast when compared to solute molecular motion from the boundary to the core of the sample and diffusion process occurs in a fully relaxed matrix. These conditions give rise to the case of Fickian diffusion processes, typical of equilibrium fluid or solid phases. On the other hand, for those cases in which $De \approx 1$ ($\tau_R \approx \tau_D$) the diffusion and relaxation occur on the same time scale and the resulting rate of overall mass uptake, which has very different features from those of classical Fickian processes, is often referred to as anomalous sorption kinetics. Finally, when $De \gg 1$ ($\tau_R \gg \tau_D$) the relaxation is relatively slow and a first sorption stage, in which solute molecules diffuse in an unswollen matrix, is expected to be followed by a second relaxation-driven sorption step. In these cases, at longer times, the volume relaxation phenomenon generates an enhanced diffusive flux caused by the increase in the polymer free volume without any change in the solute fugacity, as can be expected by the second term in Eq. (F.27), which descends directly from the NET-GP approach. Higher solute mobility allows the sorption in this second step to occur without significant concentration gradients within the sample. The latter situation is known as two-stage sorption kinetics. Examples of typical solute concentration profiles for sorption processes in a polymeric sample are given in Figure F.3 for the three different cases. The experiments analyzed below are in the category of both small and large Deborah numbers, and the model developed is meant to test to what extent such complex diffusion phenomena can be modeled using relatively simple concepts of the polymer swelling mechanics and diffusive fluxes.

This section presents the analyses of several experimental results for sorption-desorption processes of CO$_2$ in PMMA films, using the sorption-diffusion-relaxation model described
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previously. By means of comparisons between model prediction/correlation and experimental results obtained for both rubbery and glassy polymeric phases, the capability of the model and the role of model parameters on determining the kinetics of sorption are discussed.

Table F.1: Parameters used in SL thermodynamic model [16].

<table>
<thead>
<tr>
<th>Pure Component</th>
<th>CO₂</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T^* ) [K]</td>
<td>283</td>
<td>696</td>
</tr>
<tr>
<td>( P^* ) [MPa]</td>
<td>659</td>
<td>503</td>
</tr>
<tr>
<td>( \rho^* ) [g/cm³]</td>
<td>1.62</td>
<td>1.27</td>
</tr>
<tr>
<td>Mix</td>
<td>35 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>( k_{ij} )</td>
<td>0.1246</td>
<td>0.1161</td>
</tr>
<tr>
<td>( \eta_{ij} )</td>
<td>0.033</td>
<td>-0.015</td>
</tr>
</tbody>
</table>

Pure component characteristic temperatures, pressures and densities for the SL EoS were obtained after analysis of experimental data for vapor pressure and saturated liquid density for CO₂, and of experimental data for specific volume as function of temperature and pressure for PMMA and they are shown in Table F.1. Temperature dependent binary parameters were fitted by analysis of high-pressure solubility and swelling data determined in a previous work [16]. Parameters for the free volume expression of solute mobility used in this work were obtained from the literature [26, 30] and are listed in Table F.2 (column labeled "Rubber").

Table F.2: Parameters used in free volume model for mobility coefficient in rubbery states [26, 32].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Glass</th>
<th>Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_0 ) [cm²/s]</td>
<td>( 6.7 \times 10^{-11} )</td>
<td>( 7.9 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>( \zeta V_p^* ) [cm³/g]</td>
<td>0.1214</td>
<td></td>
</tr>
<tr>
<td>( V_s^* ) [cm³/g]</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

Model results shown below were obtained through the numerical solution of a set of PDE's in the polymer fixed frame for the solute concentration and the volume swelling resulting from Eqs. (F.18), (F.27), (F.38)–(F.40). The equations were discretized by the
application of a control volume formulation [33].

Figure F.4: Solute content in PMMA film for CO$_2$ sorption from 1650 to 1750 psi and corresponding desorption at 35 °C, experimental data and model prediction.

Figure F.4 and Figure F.5 show the experimentally measured mass of CO$_2$ in PMMA films as a function of time in terms of the mass ratio for sorption processes taking place at 35 and 50 °C. Sorption measurements resulting from a step increase in CO$_2$ pressure from 1650 to 1750 psi are shown as full symbols while corresponding desorption results are shown as open symbols. In the same figures, model predictions (lines) are compared with experimental data.

It should be noted that model results in Figure F.4 and Figure F.5 were obtained through pure predictive procedures, using parameters for thermodynamic and transport properties obtained from the literature, taking as initial values of CO$_2$ mass fraction those measured
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Figure F.5: Solute content in PMMA film for CO$_2$ sorption from 1650 to 1750 psi and corresponding desorption at 50 °C, experimental data and model prediction.

experimentally. There were no adjustable parameters used in these computations. The rheological properties of the polymer discussed above do not play any role in the simulations in Figure 4 and Figure F.5 since at these pressures and temperatures the solvent concentration keeps the material in the rubbery region, well above the critical value for glass transition. As expected, under such conditions the NET-GP simply becomes the SL EoS.

It is interesting to note that the long time concentrations predicted by the model in both sorption and desorption processes compare well with experimental data, as a result of the SL EoS ability to accurately represent the thermodynamic properties for the CO$_2$-PMMA system, with the binary interaction parameters indicated in Table F.1. The agreement between experimental and predicted kinetics of both sorption and desorption processes is
Figure F.6: Solute mass uptake for CO₂ in PMMA film for sorption step from 1650 to 1750 psi at 35 and 50 °C, experimental data and model results.

also remarkable, verifying the Fickian nature of the observed transport phenomenon and the validity of the pertinent free volume model parameters obtained from the literature and listed in the column labeled “Rubber” in Table F.2. In Figure F.6, the sorption data already shown in Figure F.4 and Figure F.5 are plotted on a logarithmic scale in terms of CO₂ mass uptake along with the model prediction illustrating the Fickian-like sorption behavior (slope $\sim 1/2$) discussed above.

Figure F.7 shows a comparison between experimental data and model calculations for CO₂ mass uptake in a PMMA film for the case of a sorption experiment run at 50 °C for a jump in pressure from 370 to 450 psi. The solute content in this case is well below the critical value for glass transition so the material is always in the glassy state. As a result,
the measured sorption data shows a two-stage sorption behavior that is commonly observed during diffusion processes in such systems. Two different steps in mass uptake, characterized by rather different time scales and kinetic orders are evident in the experimental data.

Model predictions for sorption kinetics are compared with experimental data in Figure F.7, as obtained for different values of the characteristic initial viscosity $\eta_0^\alpha$. Results for these model calculations were obtained in this case after accounting for measured values of the initial polymer density ($\rho_p^0 = 1.1344 \text{ g/cm}^3$) and CO$_2$ content ($\rho_s^0 = 0.0598 \text{ g/cm}^3$). While the same thermodynamic parameters listed in Table F.1, and most of the free-volume parameters ($\gamma$, $\zeta V_p^*$, $V_s^*$), already considered in simulations above $T_g$, were used for model
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calculations shown in Figure F.6, an exception has been made for the value of the characteristic penetrant mobility \( L_s^0 \). Given the glassy nature of the system, an adjustment of the mobility value was needed to obtain a correct time scale for the first sorption stage, as listed in the column labeled “Glass” in Table F.2.

Table F.3: Mechanical model parameters (\( \eta_0^A \) and \( \chi \)) values for the glassy polymer case.

<table>
<thead>
<tr>
<th>Case</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Bulk Viscosity [MPa·s]</td>
</tr>
<tr>
<td>( \eta_0^A ) (Sorption)</td>
<td>( 1 \times 10^6 )</td>
</tr>
<tr>
<td>( \eta_0^A ) (Desorption)</td>
<td>( 2 \times 10^5 )</td>
</tr>
<tr>
<td>Voigt Fraction</td>
<td></td>
</tr>
<tr>
<td>( \chi ) (Sorption)</td>
<td>0.60</td>
</tr>
<tr>
<td>( \chi ) (Desorption)</td>
<td>0.42</td>
</tr>
</tbody>
</table>

It is evident from the comparison between the model and experiments in Figure F.7 that the kinetic order of the experimental data (slope \( \sim 1 \)) for the first sorption stage is definitely different from that obtained from the model calculation. The non-Fickian nature of the experimental diffusion kinetics observed in this case for short times cannot be represented well with the model using the diffusive flux from of Eq. (F.27), which is always Fickian in nature. However, the model can account for the solute content reached in the polymeric sample at the end of the first short time step. This corresponds to the pseudo equilibrium conditions attained in the unswollen PMMA for the assigned value of CO\(_2\) fugacity, and the result demonstrates the capability of the NET-GP model to describe this condition.

The Voigt model parameters \( \chi \) and \( \eta_0^A \) were used to fit the observed kinetics of the second stage sorption step and are listed in Table F.3 (50 °C, Sorption). The pseudo equilibrium solute content predicted by the model at the end of the second stage only depends on the parameter \( \chi \) and a value 0.68 was obtained from the best fit procedure, a value which is not too far from the theoretically predicted value of 0.63 discussed previously. The sensitivity of the predicted characteristic time for the relaxation stage to the value of \( \eta_0^A \) is illustrated in Figure F.7 in which several plots are shown. The best fit was obtained for a value of
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\( \eta_0 = 0.8 \times 10^6 \) MPa·s which has the same order of magnitude as bulk viscosity values in the literature for PMMA in the glassy region [27]. For the sake of clarity, Figure F.8 is a plot of the same experimental data shown in Figure F.7, this time on a linear scale, and compares it to the best fit of the parameters for the model. This figure makes it very clear that the first non-Fickian diffusion step lasts less than 60 seconds, and the model does an excellent job of representing the CO\(_2\) absorption data through most of the mass absorption process. Using the parameters estimated through the fitting procedure, values for the characteristic
diffusion and relaxation times in the sorption process analyzed above can be calculated and a Deborah number can be estimated, for the conditions of the experiments shown in Figure F.7, as \( De \approx 2 \times 10^3 \gg 1 \). The large value of the Deborah number in this case indicates that relaxation is much slower than diffusion, which is consistent with the observed two-stage
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sorption behavior.

![Diagram of CO2 content in PMMA film for sorption step from 370 to 450 psi at 50 °C, experimental data and best fit results from model.](image)

**Figure F.9:** CO2 content in PMMA film for sorption step from 370 to 450 psi at 50 °C, experimental data and best fit results from model.

In Figure F.9 and Figure F.10 results are compared for solute content measured in a sorption experiment for CO2 pressure jump from 370 to 450 psi at 35 °C and in a corresponding desorption step, together with the best fit from the model calculations. Thermodynamic and transport parameters in Table F.1 and values from the “Glass” column in Table F.2 were used in all calculations. The model results shown in Figure F.9 and Figure F.10 were obtained with parameters \( \chi \) and \( n_0 A \) estimated from a fitting procedure and these are listed in Table F.3 (35 °C, Sorption and Desorption). It is interesting to observe that good estimates were obtained for the solute concentration level reached at the end of the first sorption or desorption step in both cases and that is remarkable, as the values at this time do not depend on fitting parameters. Reasonable representations of sorption levels attained at longer times.
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and the kinetics of the second step in the sorption/desorption processes were obtained in these cases through the use of convenient values for model parameters $\chi$ and $\eta_0^A$, respectively.

In Figure F.11, data are shown for solute content measured during a desorption process of $\text{CO}_2$ in a PMMA film from 450 to 370 psi at 50 °C. The parameters used to fit this data with the model are shown in Table F.3 (50 °C, Desorption). In this case a two-step desorption processes is not evident from the experimental observations, at least for the time interval examined. This is evident by making a direct comparison of the results in Figures F.10 and F.11. The long time decay to equilibrium exhibited in the desorption step data at 35 °C in Figure F.10 is not present in the desorption data at 50 °C shown in Figure F.11. Analysis of the experimental data in Figure F.11 through the use of the model

Figure F.10: $\text{CO}_2$ content in PMMA film for desorption step from 450 to 370 psi at 35 °C, experimental data and best fit results from model.
that some volume relaxation process took place in the PMMA sample during the desorption experiment, as indicated by non negligible values of the $\chi$ parameter obtained from the fitting (Table F.3). On the other hand, the relaxation time is very short in this case, with respect to the diffusion time, to allow the model to evaluate a characteristic viscosity and indeed the sorption results can be satisfactorily interpreted in terms of a negligible value of $\eta_A^0$. This difference in behavior between the desorption steps in Figures F.10 and F.11 are a reflection of the difference between the temperature of the experiment and the glass transition temperature of the polymer under the corresponding operating conditions.

The fit of the adsorption and desorption kinetic data presented above for systems in the rubbery and glassy state is highly dependent on the relationship between the viscosity of the
material in the presence of CO\textsubscript{2} as represented by Eq. (F.50). This expression is taken to be valid through the glass transition point and it is of interest to examine the predictions of this equation for the viscosity variation of PMMA with temperature and as a function of the CO\textsubscript{2} concentration. Figure F.12 illustrates the viscosity shift of PMMA upon sorption at 35 and 50 °C over a wide range of CO\textsubscript{2} concentration, as predicted by Eq. (F.50). Unlike Eq. (F.46), our treatment of the viscosity does not require a different value of the \( C_2 \) parameter above and below the glass transition point, and our results compare quite well with Eq. (F.46) in the rubbery region [28]. The methodology for calculating the polymer viscosity in both the glassy and rubbery states is a direct advantage of the NET-GP theory, which is able to account for the behavior of the system in the out of equilibrium state.

Figure F.12: Viscosity shift upon sorption at 35 and 50 °C as predicted by model.
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The model introduced here interprets the relaxation process in solute sorption kinetics in terms of the volume dilation of the polymer matrix and it would be interesting to compare the time dependent swelling predicted by the model with experimental swelling rate data. Unfortunately, the experimental procedure used in these experiments did not allow for continuous measurements of film thickness to evaluate swelling kinetics. However, a few data points at relatively long sorption times were obtained using ellipsometry in a previous work [16] and a comparison is possible for these data with the swelling values estimated by the model presented here. Figure F.13 compares the time dependent swelling predicted with the present kinetic model with measured data for sorption steps at 35 and 50 °C in the glassy state. It is relevant to observe that the measured swelling values at long time are consistent...
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with those described by the model used in the analysis of the solubility measurements.

F.5 Conclusion

The NET-GP model has been shown to provide a good quantitative prediction of the isothermal sorption data in a wide range of pressures in both the glassy and rubbery regions [16]. By coupling this reliable model with the free volume theory for the diffusive part, and a simple rheological equation for the relaxation part, this work has proven the applicability of our approach to represent the kinetics of differential sorption/desorption experiments in glassy as well as rubbery polymeric systems. The model performance in different operating conditions, namely different temperatures and pressures for both sorption and desorption, was satisfactory and it allowed for a description of both Fickian and two-stage type sorption behavior and to account for the transition from one to another by changes of temperature and solute pressure.

Several examples of the application of model results to the analysis of differential sorption/desorption experiments for CO$_2$ in PMMA were considered. In all cases good results were obtained, confirming the validity of the approach used in representing thermodynamic properties, in both equilibrium and non-equilibrium conditions. Relaxation steps during sorption/desorption cycles were described in this context in terms of volume relaxation of polymer samples with two adjustable model parameters: the characteristic bulk viscosity and the weight for Voigt elements in the rheological model. Characteristic viscosity values obtained from analysis of sorption data are in the expected order of magnitude [27], while values of the weighting factor $\chi$ for the rheological model confirm the rough estimation performed on volumetric properties of pure polymeric species. A novel feature of the model, made possible by the ability of the NET-GP model to predict behavior in both glassy and rubbery systems, is that bulk viscosity values of the sample could be derived from knowledge of the molar volume of the non-equilibrium system.

The rheological model parameters retrieved from sorption steps were different from those obtained through analysis of corresponding desorption runs. This is not surprising as the nonlinear character of bulk rheology of glassy polymers is well documented and a comprehensive representation of details in their volume swelling cannot be obtained in the simple terms discussed here. The aim of this work was to provide a meaningful combination of mass
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transport and volume relaxation models that may prove or disprove the validity of the basic idea used to represent relaxation phenomena induced by solute sorption in glassy polymers. One major advantage of this approach consists in its simplicity and capability of being extendable, in a straightforward manner, to multi-component systems and multi-dimensional transport problems.

F.6 Acknowledgment

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F.7 Notation

\( t \) Time
\( \dot{j} \) Diffusive flux
\( D^* \) Generalized diffusion coefficient
\( T \) Temperature
\( P \) Pressure
\( x \) Spatial coordinate in the lab-fixed system
\( V \) Volume
\( F \) Displacement tensor
\( \hat{e} \) Unit vector
\( L \) Diffusivity
\( \hat{V}^* \) Specific critical hole free volume
\( \dot{v} \) Local mass velocity \([\text{cm} \cdot \text{s}^{-1}]\)
\( V_{f}^{\text{mix}} \) Mixture free volume
\( a \) Helmholtz free energy
\( n \) Number of moles
\( F \) Force
\( \hat{V}_p^A, \hat{V}_p^B \) Contribution of Voigt element \( A/B \) to the total deformed volume of the polymer
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\( T_g \) Glass transition temperature
\( k \) Isothermal bulk compressibility, polymer elastic modulus
\( De \) Deborah number
\( A, B, C_1, C_2 \) Constants

**Greek Symbols**

\( \rho \) Density \([\text{g}\cdot\text{cm}^{-3}]\)
\( \rho_{\text{mix}}^* \) Mixture closed packed density
\( \mu^{NE} \) Chemical potential
\( \omega \) Mass fraction
\( \delta(0) \) Initial film thickness
\( \xi \) Spatial coordinate in the polymer-fixed system
\( \lambda \) Elongation
\( \zeta \) Ratio of the critical molar volume of the solvent to that of the polymer
\( \vartheta \) Polymer viscosity
\( \eta_A \) Bulk polymer viscosity of Voigt element \( A \)
\( \eta_A^0 \) Initial bulk polymer viscosity of Voigt element \( A \)
\( \chi \) Weight of Voigt element \( A \) to the total polymer volume
\( \tau_R \) Characteristic relaxation time
\( \tau_D \) Characteristic diffusion time
\( \Omega \) Mass ratio \((\text{g CO}_2/\text{g PMMA})\)

**Subscripts and superscripts**

\( s \) Penetrant \((\text{CO}_2)\)
\( p \) Polymer \((\text{PMMA})\)
\( \text{mix} \) Polymer-CO\(_2\) mixture
\( x \) With respect to lab-fixed system
\( \xi \) With respect to polymer-fixed system
\( 0 \) Initial value
\( P \) In the polymer-fixed system
\( NE \) Non-equilibrium
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$EQ$  
Equilibrium

$A, B$  
Element $A/B$ in the mechanical model

$-$  
Vector

F.8 References


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