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POLYMER IMPREGNATION AND SURFACE
MODIFICATION USING SUPercritical FLUIDS

DISSERTATION

Presented in Partial Fulfillment of the Requirement for the Degree
of Doctor of Philosophy in Chemical Engineering in the Graduate
School of The Ohio State University

By

Yiqing Wang, B. S.

*****

The Ohio State University
2001

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ABSTRACT

Incorporation of functional modifiers into polymers is one way to change the polymer properties. The high solubility, diffusivity and plasticizing behavior of CO₂ in polymers makes it a unique temporary plasticizer to accelerate the sorption of additives into polymers.

The impregnation of a fluorescent probe (4-hexadecylamino-7-nitrobenz-2-oxa-1,3-diazole or NBD) into polypropylene from supercritical carbon dioxide is presented. Confocal microscopy was combined with traditional thermodynamic and spectroscopic studies to demonstrate distinct differences between supercritical fluid impregnation, solution coating, and solvent casting. The results show improved partitioning and distribution of the solute from supercritical solutions relative to conventional techniques.

Kinetic studies show that the solute diffusivity in CO₂-swollen polymers is two orders of magnitude larger than in the same polymers at ambient conditions. Polymer properties have significant impact on the modifier loading and distribution. An efficient loading of modifiers into polymers is usually related to large amorphous areas, large free volumes and favorable interactions between modifier and polymer molecules.
After supercritical fluid impregnation, NBD has a high concentration at the edge and on the surface of bubbles in foamed poly(methylmethacrylate) (PMMA) while it distributes evenly in semi-crystallized polypropylene.

To demonstrate a potential application, commercial surfactant poly(ethylene terephthalate)/poly(oxyethylene terephthalate) (PET/POET) copolymer was coated to polyester fabrics to make it wettable. In the process of trying to characterize this system, \textit{in-situ} spectroscopic investigation demonstrates that the fluorescence emission of dimethyl terephthalate, the model compound for PET/POET, is completely quenched in SC-CO$_2$ due to the small dielectric constant.
To my parents and Chao
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FIELDS OF STUDY

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CHAPTER 1

INTRODUCTION

The demand for new polymeric materials comes from areas as diverse as consumer products and aerospace equipment. Besides synthesis from novel monomers, incorporating new functional modifiers into commercial polymers is another way to produce polymers with specific properties. In the past decade, supercritical fluid aided polymer impregnation, as a novel technique, has gained significant attention in both academic research and industrial application.

A supercritical fluid (SCF) is simply a substance above its critical point, which is the highest temperature and pressure at which it can exhibit vapor/liquid equilibrium. One of the most promising features of a supercritical fluid is its dramatic density change with just small changes in the temperature and applied pressure. This sensitivity leads to a "tunable" control of the solvent power. The viscosity of a supercritical fluid is less than typical liquids and the diffusivities of solutes are closer to those of gases. Subsequently, mass transfer in a SCF should be significantly improved. The motivation of using supercritical fluids in material processing initially comes from environmental considerations. Supercritical carbon dioxide (SC-CO$_2$), the most widely used...
supercritical fluid, is relatively cheap, nontoxic, and nonflammable. Moreover, the fact that CO₂ is a gas under ambient conditions makes it easily removable after processing.

The unique properties of SCFs bring several advantages to polymer processing. Supercritical CO₂ can reversibly swell glassy and rubbery polymers, which will facilitate the impregnation of solutes into the polymer matrix or the extraction of monomer or other additives from the polymer matrix. SC-CO₂ can reduce the viscosity of polymer melts by up to an order of magnitude, which will aid polymer extrusion and blending (Elkovitch et al 1998, Gerhardt et al 1992, Khan et al 1998, Wisssinger and Paulaitis, 1987, Zhang et al 1997). Maintaining conditions above the critical temperature avoids creation of a vapor-liquid interface upon the release of pressure. As a result, no capillary forces are present to distort the substrate allowing greater control over the modification process. Because the solvent power of SCFs is much lower than that of typical liquid swelling agents, the partitioning of modifiers to the polymer is several orders of magnitude compared to a liquid solvent that swells the polymer substrate a comparable amount.

In this work, SC-CO₂ will be employed as the solvent and carrier for the modifier and a swelling agent for the polymer. The significance of this approach is the possibility to incorporate desirable functions into the polymer without changing its original properties such as mechanical strength. We are especially interested in surface modification for applications involving wetting, adhesion, and biocompatibility.

Polymers have been impregnated using SC-CO₂ include polystyrene (Berens et al 1992), poly (methyl-methacrylate) (PMMA) (West et al 1998), poly (vinyl chloride) (Muth et al 2000, Berens et al 1992), polyethylene (Ma and Tomasko 1997, Cooper et al

We investigated the impregnation of a surfactant-like probe molecule into polypropylene and PMMA films. Quantitative and qualitative studies on both the equilibrium and kinetics of the process are presented.

Chapter 2 is a brief review of related work in literature, including SC-CO₂/polymer interactions, solute solubility in SC-CO₂, SCF impregnations and potential applications of polymer surface modification using SCF.

Chapter 3 focuses on the equilibrium distribution of modifiers between the fluid phase and the polymer phase. A comparison between SCF impregnation and other traditional solvent methods is presented. The distribution of modifiers in polymer films after impregnation was studied using a confocal scanning microscope.

Chapter 4 reports the diffusivity of solute in CO₂-swollen polymers. The durability of modifiers on polymer surface is investigated via two-step solvent extraction. The impact of polymer properties on modifier distribution is studied by comparing the polypropylene and PMMA impregnation.
In chapter 5, a polymeric surfactant was attached to polymer surfaces to change the wettability. In situ spectroscopic analysis was used to characterize the surfactant and its model compound in SC-CO$_2$.

Finally, a brief conclusion is presented. Recommendations are made for future research on SCF aided polymer impregnation.
CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Using supercritical carbon dioxide as the solvent and carrier to modify polymer properties is a relatively new area. Beren (1992) first showed the advantages of SCFs when used to infuse or deposit additives dissolved in a SCF into a polymer matrix. Since then, extensive research has been done to incorporate various solutes into different polymers. Generally, the process contains three main features. The first is to dissolve the functional modifiers in SC-CO$_2$ to form a homogeneous solution. The second is the interactions between CO$_2$ and the polymer matrix under supercritical conditions. The third is the partitioning of the modifiers between the fluid phase and the polymer phase. In this chapter, literature related to each feature is reviewed.

The polymer surface modification is based on the same principles and follows a similar process as polymer impregnation while focusing on the surface properties. Some potential applications of the surface modification will be reviewed at the end of this chapter.
2.2 Solubility of substances in supercritical fluids and the modeling

There are two mechanisms for measuring solubility in supercritical fluids, using either the static or dynamic technique. Dynamic systems apply a slow fluid flow through a cell containing the solute. The fluid is then depressurized through a restrictor into a trapping device. The extracted solute is usually measured by gravimetric, spectrophotometric, or chromatographic techniques. The gas coming out of the restrictor is measured by a flow meter to determine the fluid quantity and calculate the solubility. A modification for this technique is to place an inline sampling valve before the restrictor and pass the sampled solute directly into a HPLC or supercritical fluid chromatographer to analyze (Hansen and Bruno 1993). The challenge with these techniques is that they rely on the rapid approach of equilibrium between the solute and the fluid flowing through the chamber.

The static method includes two main categories: one is to observe phase transition between the solute and the fluid and the other is to perform the in-situ spectrometric measurement of the dissolved solute. The phase transition method uses a variable volume cell with a movable piston and a viewing window. A known amount of solute and fluid are placed in the cell at a known temperature, and the pressure is increased by moving the piston until the system becomes single phase. (Costa et al 1996) The in-situ spectrometric method uses a high-pressure view cell to allow measurement by UV-VIS or IR spectrometry. (Hansen et al 1994, Jackson et al 1995) A careful calibration of the spectral information is the key step for this technique.

The enhancement factor is a dimensionless measure of solvent power, defined as the measured solubility of a solute divided by the ideal gas solubility. The enhancement
factors for SCFs range from $10^3$ to $10^6$ or even $10^8$. In CO$_2$, solubilities are governed by solute vapor pressure and solvent density and only secondarily by solute-solvent interactions in the SCF phase. As a result, the enhancement factor is relatively insensitive to the solute structure but very dependent on the polarity and density of the solvent. (Brennecke and Eckert 1989, Johnston et al 1989)

The solutes generally fall into two classes. The first comprises a series of simple, mostly aromatic hydrocarbons. The solubility data from this class are used extensively for developing models and improving understanding of the SCF extraction behaviors. The second is a wide variety of solutes of practical importance. For example, Nalesnik (1998) and coworkers investigated the solubility of taxol in SC-CO$_2$ using a high-pressure UV-visible-light-transmission static cell at pressures from 3000 psia to 7000 psia and temperatures from 35°C to 45°C. The solubility of taxol increases by a factor of seven from $0.7 \times 10^{-7}$ to $5.0 \times 10^{-7}$ mole fraction from 3000 psia to 7000 psia. Bristow et al (2001) applied both dynamic and static methods to measure the solubility of drug compounds including paracetamol (acetaminophen), o-, m-, and p-hydroxybenzoic acid and isomers of methoxybenzamide in SC-CO$_2$. They reported that the dynamic online method turned out to be the most effective, rapid, accurate, and reproducible technique applicable to small amount of sample (ca. 25 mg). Lee and his colleagues (1999, 2001) measured solubility of several dispersed dyes in SC-CO$_2$.

There are three aspects of SCF behavior that make phase equilibrium modeling or prediction especially difficult. (1) The fluid is highly compressible, which leads to solvent condensation or clustering about the solute. Figure 2.1 is the pure component phase diagram in the vicinity of its critical point. The slope of the density-pressure plot
is very high, which indicates a large compressibility. (2) SCF solutions are usually highly asymmetric due to the large differences in both size and force constant of the molecules involved. (3) The vapor pressure that is the most important indicator of solubility is often not available for relatively nonvolatile solids.

For a system consisting of a solid phase in equilibrium with a SCF, the fugacity is given by

\[ f_i^* = P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[ \frac{v_i^f (P - P_i^{\text{sat}})}{RT} \right] \]

where \( P_i^{\text{sat}} \) is the sublimation pressure, \( \phi_i^{\text{sat}} \) is the fugacity coefficient at saturation, and \( v_i^f \) is the molar volume.

Models for supercritical phase equilibria fall into several categories depending on how the fugacity in SCF phase is calculated. The most common model treats the SCF phase as a compressed gas and uses an equation of state to calculate the fugacity coefficient of the solute in the fluid phase. The fugacity in SCF is given by:

\[ f_i^{fr} = y_i \phi_i^{fr} P \]

where \( y_i \) is the mole fraction of component \( i \).

Other models treat the SCF phase as an expanded liquid. (Mackay and Paulaitis, 1979) The fugacity is given by:

\[ f_i^L = x_i \gamma_i(P^0, x_i) f_i^{0L}(P^0) \exp \left\{ \int_0^{P^0} \frac{v_i}{RT} dP \right\} \]

where \( \gamma_i(P^0, x_i) \) is the activity coefficient at the reference pressure, and \( f_i^{0L}(P^0) \) is the reference liquid fugacity. Since there are few techniques have been developed to calculate the reference fugacity, this model is adopted much less than the compressed
gas model. Computer simulation is another approach to modeling solute solubility in SCFs. (Nouacer and Shing 1989, Panagiotopoulos et al 1986)

Many equations of state have been used to calculate the fugacity coefficient. The Peng-Robinson equation gives a good qualitative picture of all types of SCF-phase behaviors (Hong and Modell 1983) and reasonably good quantitative fits for a wide variety of systems. Perturbation equations that incorporate the Carnahan-Starling (1972) repulsive term significantly improve the quantitative modeling. (Johnston and Eckert 1981, Mart et al 1986) The use of lattice models is a different approach, which is based on the idea of the distribution of molecules over the sites in a three-dimensional lattice. The strength of lattice models is their ability to account for mixtures with large size differences. (Leblans-Vinck 1985, Van der Haegen et al 1988, Kumar et al 1987)

The goals of the modeling efforts are both to correlate existing data and to attempt prediction of phase equilibria. So far, the overwhelming majority of work falls in the correlation category, which contains a varying amount of theoretical basis and a large number of regressed parameters. The prediction models should have minimum numbers of parameters and link those parameters to real physical properties. The hard-sphere expansion theory incorporated with a Kirkwood-Buff (1951) fluctuation integral has been recommended as a prediction model (Kwon and Mansoori 1993). The model fits solubility data with one dimensionless parameter and two molecular-size parameters. Another prediction model is developed by Bush and Eckert (1998) based on linear solvation energy relationship. It is a type of expanded liquid model. It can be used to predict solubility on the basis of available pure component properties or extrapolating limited solubility data.
2.3 Polymer substrate and SC-CO$_2$ interactions

It is a fact that CO$_2$ can diffuse into a polymer matrix under pressure. The sorption of CO$_2$ in polymers is mainly determined by the density of CO$_2$ and the properties of the polymer. The solubility of CO$_2$ in polymers generally increases with CO$_2$ pressure and the sorption in amorphous polymers is much higher than in crystalline polymers because CO$_2$ is believed to absorb primarily in the amorphous regions of the material and not in the crystalline regions. The sorption of CO$_2$ into polymers results in their swelling and increases their segmental and chain mobility. An important effect for glassy polymers subjected to SC-CO$_2$ is plasticization, which includes the reduction of the glass transition temperature (Tg). (Wissinger and Paulatis, 1987, Shieh et al 1996, Chang et al 1998, Condo et al 1992, Goel and Bechman 1993, Zhang et al 1997). The volume change of some common polymers when exposed to CO$_2$ is shown in figure 2.1. At room conditions, the glass transition temperatures for PMMA and polystyrene are approximately 105°C and 100°C respectively. It can be seen that Tg for both polymers is significantly decreased under CO$_2$ pressure.

It is the interactions between CO$_2$ and the basic units in polymer molecules that result in the plasticization effect. For example, the interaction between CO$_2$ and the carbonyl groups has been suggested to be of the Lewis acid-base type. (Kazarian et al 1996) As a result, the solubility of SC-CO$_2$ in PMMA could be up to 25 wt% at certain conditions (Wissinger and Paulatis 1987, Liau and McHugh 1985. Miyoshi and coworkers (1997) reported that in polystyrene the phenyl ring motion induced by CO$_2$ was observed via NMR. The CO$_2$–fluorine interactions in solutions of fluoroacrylates dissolved in SC-CO$_2$ were observed via different methods. (Kazarian, 1996, Dardin, et
al., 1997, 1998) Koros (1985) found that the solubility of CO$_2$ increases in various compounds with increased concentration of carbonyl or sulfone groups. As a comparison, the solubility of methane in those compounds remains constant because methane molecules lack of the ability to form specific interactions with those functional groups.

The solubility of CO$_2$ in polyolefins is reported to be very low. Shieh and coworkers (1996) found that HDPE, LDPE and polypropylene films (thickness < 1mm) treated with CO$_2$ at elevated pressure and temperature change weight up to 0.3%. Presumably, this low amount is due to the lack of specific interactions between CO$_2$ and the polymer chains.

Some common polymers could be listed according to their decreasing compatibility with CO$_2$: poly(dimethylsiloxane) (PDMS), perfluoroalkyl ethers and acrylates, poly(methyl methacrylate) (PMMA), poly(vinylchloride) (PVC), polystyrene (PS), poly(ethylene terephthalate) and polyolefins.

It was also demonstrated that after exposure to SC-CO$_2$, polymers could experience a secondary crystallization process. (Chiou et al 1985, Shieh et al 1996) The plasticization increases the rate of polymeric segmental motions and makes the formation of small crystals kinetically possible. The observation of secondary crystallization is delayed for several weeks after the treatment. The crystallization and other rearrangement of the polymer chains will affect the long-term modification effect using SCF.

The plasticization of polymers induced by SC-CO$_2$ has motivated research in different polymer processing operations. These include polymer extrusion and blending.
with viscosity reduction, polymer solid-state impregnation and extraction, polymer morphology changes due to induced crystallization and foaming of polymers.

In recent years, the thermodynamics of polymer-SCF interactions and the theory of glass transition in polymers under high-pressure have received much attention. Sanchez and Lacombe (1977, 1978) developed an equation from Flory-Huggins lattice fluid theory that is the most widely used model in polymer/supercritical fluid systems. The equation recently has been applied to modeling of solute partitioning between cross-linked polymers and supercritical fluid phases. (Brantley et al. 1999, West et al. 1998, Condo et al. 1996) Dong and Fried (1997) developed a statistical thermodynamic approach to account for the mixing of polymers, small molecules and holes. They indicated that polymer-plasticizer interactions and plasticizer size determine the plasticizing efficiency. Therefore, CO$_2$ is expected to be a good plasticizer due to its small size even though its interactions with polymers may be weak.

2.4 Polymer impregnation

The high diffusivity, low surface tension, plasticizing behavior in polymers and the easy solvent recovery makes CO$_2$ a unique temporary plasticizer to accelerate the absorption of additives into polymers. The idea is to expose the polymer substrate to CO$_2$ saturated with the additive under high pressure. The CO$_2$ can diffuse into the polymer and swell it, then facilitate the absorption of the additive. In the process of decompression, the CO$_2$ can diffuse out of the polymer quickly. The polymer recovers from plasticization and the diffusivity of the additive decreases. Some of the additive will be left in the polymer and desorb at a very slow rate. From kinetic studies, it is
suggested that the major effect of CO\textsubscript{2} is not to dissolve the additive, but to accelerate the additive absorption by plasticizing the polymer. (Khan et al 1998, Sahle-Demessie et al 1998, Shieh et al 1996)

Several impregnation examples exist in the literature. Kazarian and co-workers performed dye impregnation into PMMA using SC-CO\textsubscript{2}. (Kazarian et al 1997, 1998) Howdle and co-workers introduced CpMn(CO)\textsubscript{3} into polyethylene films and powders. (Howdle et al 1994) Berens and his colleagues reported kinetic and equilibrium data for the polyvinylchloride/dimethyl phthalate/CO\textsubscript{2} system. (Berens et al 1992) Our research group investigated the process to introduce N,N-Dimethyldodecylamine N-oxide into non-woven polyethylene. The results showed that the surfactant is present both as impregnated and adsorbed modifier. The supercritical coated material gives a much more uniform coating with smaller crystallites of surfactant and a larger and more permanent decrease in the contact angle than aqueous coating. (Ma and Tomasko, 1997)

Kazarian (2000) pointed out that there are two different mechanisms of supercritical fluid impregnation of additives into polymers. The first is a simple deposition of the additive into the polymer matrix. The second mechanism involves specific interactions between the solutes and certain polymer units, which could result in a preferential partitioning of a solute into the polymer phase. Most of the polymer dyeing applications using supercritical fluids belongs to the second category.

In addition to these two mechanisms, there are some new approaches developed from the basic impregnation operations. Perman and co-workers (1994) invented a method to impregnate additives such as dyes, monomer, and drugs into polymers. They exposed to a supercritical fluid the polymeric material, a carrier liquid that can
completely or partly dissolve the additive, and the additive in a pressure vessel for sufficient time to swell the polymeric material, such that an additive that is even incompatible with the polymer can infuse into it. Another interesting application is to modify polymers by adding a monomer and an initiator into a CO2-swollen polymer matrix with a subsequent in-situ polymerization. Watkins and McCarthy (1994) synthesized a variety of polymer blends by infusion of styrene monomer and an initiator into polyethylene, nylon 66, poly(oxymethylene) and some other polymers. Muth and coworkers (2000) recently demonstrated that the polymerization could be controlled within certain penetration depth, which could benefit surface modification.

The quantitative measurement of diffusion or mass transfer of solutes in polymer matrices under SC-CO2 conditions is one of the most challenging problems in the polymer impregnation research. Berens et al. (1992) demonstrated that the kinetically-limited incorporation of an additive into a glassy polymer matrix is accelerated by SC-CO2 plasticization. They found that the solute diffusivity increases 5-6 orders of magnitude with the presence of subcritical CO2. Cotton (1993) reported a diffusivity enhancement of 2-3 orders of magnitude in the extraction of solutes from polypropylene using SC-CO2. Chapman and coworkers (1996) have shown that the enhancement in solute diffusion cannot be accounted for exclusively by the reduction of Tg in polystyrene. They suggested that solute-CO2 interactions may play a role. Kazarian et al. (1998) compared the diffusion of a dye in CO2-swollen PMMA with the diffusion in heated polymer. Vincent and coworkers (1997) made a comparison of the diffusion of water between CO2-swollen PMMA and lyophilically-swollen PMMA. Both experiments suggested that it is not only the swelling effect of CO2 that facilitated the
diffusion but also its ability to solvate the solutes. “Molecular lubricant” is used to describe the role of CO₂ in this process. (Kazarian et al 1997)

2.5 Potential applications of SCF technology in polymer surface modification

Wettability of polymers plays an important role in many technological fields. Good contact between a liquid and a solid is required in gluing, painting and washing. On the other hand, the application of polymeric fibers in clothes, tents and outdoor products require a water-repellent surface. The surface tensions of some common polymers are listed in figure 2.2. (Garbassi et al 1998) It is clear that most of them are neither hydrophilic enough for a complete wetting by water nor hydrophobic enough to promote a rolling away of water. Thus, it is necessary to hydrophilically or hydrophobically modify these common polymer surfaces for certain applications.

Ma and Tomasko (1997) modified the high-density polyethylene surfaces with a surfactant (N, N-Dimethylhexylamine N-oxide) using SCF technique. The contact angle with water is a measurement of the surface wetting ability. A larger contact angle corresponds to a more hydrophobic surface. The results (Figure 2.3) showed that SCF treatment decreases the contact angle and the effect is more significant than aqueous coating treatment. Rajagopalan and McCarthy (1997) converted PTFE (Polytetrafluoroethylene) to a PTFE/polystyrene blend by polymerizing styrene in SC-CO₂-swollen PTFE. They found that sulfonating the polystyrene enhances the wettability of the surface.

The potential applications of polymer films with highly reflective metallized surfaces in aerospace devices stimulated interest in coating organometallic compounds
onto polymer surfaces. Rosolovsky et al (1997) infused silver complexes from SC-CO$_2$ solution into polyimide films and then thermally cured them at 300°C. Highly reflective silver surfaces were formed on both sides of the films.

Tribological applications of polymeric materials attracted more and more attention in recent years because of their low density and interfacial adhesion energy compared with metals. However, their low thermal durability and consequences of viscoelastic and plastic deformations limit the application. Surface modification is required to improve the tribological performance of friction and wear-loaded parts. Glass or carbon short fibers, metal powders and microparticles have been added to polymer matrices to reinforce the material. Popov and his colleagues (1998) obtained an improved tribological behavior of polyacrylate by impregnating copper (II) hexafluoroacetylacetonate to the polymer in SC-CO$_2$ environment.

The application of polymer materials in the biomedical device manufacture is developing fast in the last decade. It is known that when the biomaterials contact blood, plasma proteins adsorb to the surface very rapidly and may lead to mural thrombus formation. Protein adsorption regulation by surface modification could improve the biocompatibility of polymer materials. (Garbassi et al 1998, Horbett and Brash, 1995) It has been shown that coating the surface with a layer of pendant polyethyleneoxide (PEO) chains can lower the tendency of protein adsorption. Prevention of protein adsorption also has a huge market in the contact lenses industry. The inclusion of large amounts of PEO units in contact lenses is reported to greatly reduce protein adsorption and allow extended wear. (Froix 1990)
In textile and detergent industry, it has been proved that polyesters can be hydrophilically modified by polyethylene terephtalate/polyoxyethylene terephtalate (PET/POET) and other polyester surfactants to improve the surface wettability and the oil release process (Yang and Rathman 1996, Grosslink et al 1988, Robertson et al 1969) and nylon surfaces can be hydrophobically modified by fluoro-chemicals. (Livama et al 1990)

Recently, using polymeric materials to make micro scale reactors have received much attention. Since the tunnels have a very small size, fluids may not be able to get through due to a large surface tension of the polymers. Therefore, a more hydrophilic polymer surface is crucial for this application.

The applications listed above are only a few examples of polymer surface modification that could employ SCF technology. More applications could be explored to give polymers desirable properties by taking advantages of this technique.
Figure 2.1 Pure component phase diagram in the vicinity of its critical point
Figure 2.2 Volume change of polymers when swollen by CO₂
Figure 2.3 The surface tension of some common polymers
Figure 2.4 The advanced contact angle of PE films impregnated with DDAO
CHAPTER 3

SUPERCRITICAL FLUID IMPREGNATION OF SURFACTANT-LIKE PROBE INTO POLYPROPYLENE

3.1 Introduction

Interest in supercritical fluid aided polymer processing has been growing rapidly in recent years. The high solubility, diffusivity and plasticizing behavior of CO₂ in polymers makes it a unique temporary plasticizer to accelerate the sorption of additives into polymers. It has been reported that polymer surface wettability can be modified by supercritical fluid impregnation with surfactant (Ma and Tomasko, 1997) or by SCF aided grafting. (Rajagopalan and McCarthy, 1997) Kazarian and co-workers impregnated dyes into PMMA using SC-CO₂. (Kazarian et al 1997, 1998) Berens and his colleagues reported kinetic and equilibrium data for the polyvinylchloride/ dimethyl phthalate/ CO₂ system. (Berens et al 1992) Kinetic studies suggest that the major effect of CO₂ is not to dissolve the additive, but to accelerate the additive absorption by plasticizing the polymer. (Shieh et al 1996, Khan et al 1998, Sahle-Demessie et al 1998)

The studies cited above also confirm the advantages of a supercritical fluid to provide appropriate plasticization of polymer substrate and appropriate solvent power for the modifier. The “pressure tuning” of these two properties ensures that the
distribution coefficient of the modifier strongly favors the polymer phase over the supercritical phase. Therefore, the supercritical solvent is much more efficient than most liquid solvents for impregnation because less modifier remains in the solvent. This will have substantial implications for applications involving high-value or hazardous modifiers.

The partitioning of a solute between CO$_2$ and a polymer substrate under supercritical conditions has been quantified and modeled by several researchers. Johnston and coworkers (1989) quantified the distribution of toluene between CO$_2$ and silicone rubbers and the partitioning of naphthalene, benzoic acid, phenanthrene, 2-naphthol, and pyrene between CO$_2$ and poly (dimethylsiloxane) (PDMS). Brantley and his colleagues (1999) reported the partitioning of deuterated methanol, deuterated propanol, naphthalene, 2-naphthol and acridine between CO$_2$ and PDMS or poly (cyanopropylmethylsiloxane). The system we quantified and modeled is significantly different in two aspects. First, polypropylene was used as the substrate instead of siloxane-based polymers. The volume of PDMS (silicone rubber) could increase approximately 60% when contacting CO$_2$ at 40°C and 100 bar. (Shim and Johnston, 1989) The uptake of CO$_2$ by polypropylene is less than 5 wt% under similar circumstance. Also, it is believed there are specific interactions between CO$_2$ and some chain sites in siloxane-based polymers, which is not possible for polypropylene. The different CO$_2$/substrate interactions are expected to induce different impregnation mechanisms and different partitioning. The second difference is that a surfactant-like dye molecule with much larger molecule weight (Mw 404.55) was used as the solute. The modeling of cosolvent and small molecule partitioning has fundamental
significance. However, in many applications such as dyeing and drug impregnation, the distribution quantification of large molecules is more desirable.

The purpose of this study is to conduct a fundamental investigation into the modifier/SCF/polymer interactions and equilibrium sorption in the modification process. Compared with previous impregnation studies, this work explored two new approaches: 1) we focus not only on the loading of modifiers in polymers but also their spatial distribution; 2) A careful comparison between supercritical fluid impregnation and conventional solution methods was conducted. A spectroscopically active probe molecule was chosen as the modifier and UV-VIS and fluorescence spectroscopies were employed. The binary systems SC-CO$_2$/modifier and SC-CO$_2$/polymer substrate were first investigated, followed by subsequent studies of SCF modification of the substrate. These results were compared with conventional solution impregnation methods using solvents that also swell the substrate. The results indicate that the SCF method favors the partitioning of the modifier into the polymer phase and yields a much higher loading of modifiers in polymers than solution methods. Using confocal microscopy, we also have found that the SCF modification provides more uniform distribution of the modifiers in the polymer substrate than the solution method. Further, the contact time with the SCF solution and the storage time after processing affect the conformation and distribution of the modifiers.
3.2 Experiment

3.2.1 Materials

Two types of polypropylene films were used as received. Type II films (McMaster-Carr 8742K111) were used specifically for a CO\textsubscript{2} solubility study. Type I (Blueridge Films Inc.) was used for all of the modification experiments. The cast polypropylene films were made from polypropylene pellets (Aldrich, 42788-8). Some important properties of the polymers are listed in table 3.1. The modifier, 4-hexadecylamino-7-nitrobenz-2-oxa-1,3-diazole (NBD) (see figure 3.1), was purchased from Molecular Probes, Inc.(Portland, Oregon) and used as received.

3.2.2 Binary system study

The procedure of Berens and Huvard (1989) was followed for the measurement of CO\textsubscript{2} solubility in polypropylene. The film was loaded in a small vessel that was then pressurized with pure CO\textsubscript{2} (bone dry, 99.99%, Liquid Carbonic). The vessel was kept at a given temperature and pressure for at least 8 hours for the absorption of CO\textsubscript{2} to reach equilibrium. At the end of the experiment, the vessel was opened, the sample was quickly brought to an electronic digital balance (Mettler AT400, accuracy 0.0001g) The desorption of CO\textsubscript{2} as a function of time was recorded starting approximately 25 seconds after the vessel was vented. According to Fick's law of diffusion, at the initial stage of the desorption, the sample weight and the square root of desorption time should be linear. Therefore, solubility data were obtained by extrapolating the curve back to zero time. Figure 3.2 is an example of the desorption curve. Compared to Type I films, Type II films with larger thickness dissolve more CO\textsubscript{2} and give a more accurate result from the gravimetric measurement.
The solubility of NBD in CO$_2$ was measured using the impregnation apparatus (figure 3.3) but bypassing the polymer sample vessel. Since the solubility of NBD in CO$_2$ is very low, the traditional weight change measurement of the valve and the filter cannot accurately determine the amount of NBD dissolved. Instead, the collected NBD was washed off the metering valve, the filter and connecting tubing with a known amount of methanol and the concentration of the NBD solution was determined using a UV-VIS spectrophotometer (Varian, Cary 100). The solubility of NBD was then determined from the mass of NBD and the mass of CO$_2$ measured by a mass flow sensor (Brooks, 5860E).

3.2.3 Three modification methods

(1) Supercritical fluid modification The procedure for SCF treatment is similar to the solubility measurement. The solvent was pumped through the extraction vessel containing the modifier. And then the saturated supercritical solution went through the sorption vessel containing the polymer film. In the sorption vessel the modifier distributed between the SC-CO$_2$ phase and the polymer phase. Supercritical solution was continuously pumped through the sorption vessel until the exiting concentration was constant, indicating sorption equilibrium between the polymer substrate and the fluid phase. Then the flow was switched to pure CO$_2$ bypass line to replace the supercritical solution in the sorption vessel with pure CO$_2$. One vessel volume of pure CO$_2$ was passed through before depressurizing in order to avoid precipitation on the sample during depressurization.

Using this apparatus, polypropylene films were treated with NBD/SC-CO$_2$ solutions at 60°C and different pressures. Every run takes about 3 hours.
(2) **Solution coating** We also treated the polymer films by solution coating which is a traditional modification method. In this treatment, modifiers were dissolved in a typical solvent. The polymer films were kept in the solution at ambient pressure for 24 hours and then removed and air-dried for two days. Toluene was selected as the solvent to treat polypropylene because it is one of the best swelling solvents for this polymer (approximately 21 vol%).\(^{15}\) The coating temperature for polypropylene is 60°C, which is identical to the SCF treatment temperature.

(3) **Solvent casting** Polypropylene pellets (Aldrich 42788-8) and NBD were dissolved in hot xylene and the solution was cast onto a hot casting mold to make a film. The film was peeled off the plate very soon after a film was formed to let the solvent evaporate from both sides of the film.

Following spectroscopic studies on all the films, the NBD was re-extracted with pure toluene to quantify the uptake of NBD by the films.

### 3.2.4 Confocal laser scanning microscopy

Confocal laser scanning microscopy (CLSM, Bio-Rad MRC-600) with fluorescence and reflected light detection was applied to collect images of polypropylene films after different treatments. This system allows axial focus adjustment, to observe different layers inside an object. Fluorescent confocal microscopy was used to determine the distribution of NBD within the films. The magnification is 20× and the excitation wavelength is 488nm.
3.3 Results and discussion

3.3.1 CO\(_2\) solubility in polypropylene

At a given temperature, the solubility of CO\(_2\) in polypropylene increases with increasing pressure. After a turning point, the solubility levels off (Figure 3.4 a). At 40°C, the solubility of CO\(_2\) in polypropylene films could be up to 5.5 wt%. Figure 3.4 b is the CO\(_2\) density calculated with a modified BWR equation of state. The software was developed by Dr. David Bush in Georgia Institution of Technology. It is obvious that CO\(_2\) solubility in polypropylene is closely related to its density.

3.3.2 NBD solubility in SC-CO\(_2\)

As shown in Figure 3.5, the solubility of NBD in CO\(_2\) increases with increasing pressure. The effect of temperature on the solubility is more complicated. At a certain pressure, a higher temperature corresponds to a lower CO\(_2\) density. On the other hand, the vapor pressure of the solid NBD will increase with increasing temperature. In Figure 3.5, in the low pressure region, the density effect is dominant which gives a lower solubility at 60°C than at 40°C. In the high pressure region, the effect of increased NBD vapor pressure is more significant which gives a much higher solubility at 60°C. The increase of solubility at high temperature could also be caused by the melting of the material. The result from differential scanning calorimetry (DSC) shows that the melting point of NBD at ambient is 110°C. Visual observation of NBD in a view cell indicates that NBD does not melt under experimental conditions.

A lattice fluid model was used to correlate the binary solubility data, which is discussed in more detail in the modeling section.
3.3.3 SCF modification versus solution coating

For both SC-CO$_2$ and toluene treatments, the uptake of NBD by polypropylene films increases with increasing NBD concentration in the fluid phase. However, the partitioning behavior of NBD between the fluid and polymer phases heavily depends on the solvent properties. $K_D$ is defined as the concentration of the solute in the fluid phase divided by the concentration of the solute in the substrate phase, and is a function of solvent quality, modifier and substrate properties. Wasting functional modifier in solvent is not desirable for the purpose of polymer modification. Therefore, the key to improving the efficiency of a modification process is to decrease $K_D$.

$K_D$ was calculated from the experimental data according to the following formula:

$$K_D = \frac{\text{[gNBD/gFluid]}}{\text{[gNBD/gPolypropylene]}}$$

Calculated values of $K_D$ from SC-CO$_2$ and toluene treatments are shown in Figure 4. A Log scale was used since the quantities from two methods are very different. $K_D$ from CO$_2$ treatment is $1.5 - 2$ orders of magnitude smaller than from the toluene treatment. These results can be explained in terms of the interactions between molecules. Toluene is an excellent swelling solvent for polypropylene but because it is simultaneously a good solvent for the modifier only modest impregnation takes place. On the other hand, the solvent power of CO$_2$ for the modifier is not very strong, so the modifiers tend to escape from the CO$_2$ phase and partition into the polymer phase. The data from literature and our experiments imply that CO$_2$ is not as good a swelling agent as toluene for polypropylene. However, the comparatively weak solvent power of CO$_2$ gives the modifiers a tendency to partition into the polymer phase. The unique balance of
equilibrium contributes to the small $K_D$ of SCF modification. Other investigators also reported this unique partitioning behavior. (Shim and Johnston 1989, West et al 1998)

These results suggest that we can use a smaller amount of modifier to achieve a higher degree of impregnation using SCF technology. In other words, although CO$_2$ is not as good a solvent as toluene for NBD, it is much better for loading NBD onto polymer substrates.

### 3.3.4 Distribution of modifier in films

In some applications, it is desirable to load the modifiers to a certain place in the polymers, either on the surface or in the bulk. One example could be to impregnate drugs into biodegradable polymers in order to control the drug release. Therefore, it is important to understand where the modifiers reside in the substrate and how to control their distribution by changing operational conditions. We took images of polypropylene samples treated with various methods and different system conditions and studied the effect of different methods, contact time and storage time on the modifier distribution.

1. **The effect of different methods**

Figure 5 shows images of a polypropylene film treated with CO$_2$ at 190 bar, 60°C for 15 minutes. The images were taken the next day after treatment. Z indicates the distance down from the surface. The black area in the upper left corner of the $Z=0$ image is caused by the slightly curled up corner of the sample.

When 488nm light hits a blank polypropylene film, the image is completely dark because there is no fluorescent emission. The white area in the images indicated the location of NBD molecules.
As shown in the figure, NBD is both adsorbed on the surface and absorbed in the bulk. Also, it is quite uniformly distributed in the polypropylene films. On the up and bottom surfaces, there are small bright spots which represent small NBD crystals. Since we flush through one vessel volume of pure CO\textsubscript{2} after the impregnation, it is unlikely that the crystals were formed during the pressure release process through precipitation. A better explanation is that the defects on polymer surfaces offer nuclei sites for NBD molecules. Since SC-CO\textsubscript{2} solution is saturated with NBD, NBD molecules have a good tendency to leave CO\textsubscript{2} phase and crystallize on the solid NBD phase. The loading of NBD in polypropylene films coated from toluene solution is too small to give a clear image.

Figure 6 contains the images taken for a film cast from polypropylene, NBD and xylene solution. NBD molecules stay in the bulk rather than on the surface and instead of being uniformly distributed, they group together in a honeycomb-like pattern.

The reason for the modifiers staying in the bulk could be related to the solvent evaporation process. After the solution was cast into the mold, the solvent close to the surface leaves and causes a comparatively low-toluene surface region. The NBD molecules have more affinity for toluene than polypropylene, and as a result, NBD molecules move to the toluene-rich middle region of the film. As the toluene escapes from the polymer matrix, the NBD molecules crystallize before the polymer chains are frozen.

(2) The effect of contact time

Figure 7 is the surface image from a film treated with SC-CO\textsubscript{2} solution at 2800psi and 60°C for 8 hrs. It can be seen that after a long time of contact between the SC-CO\textsubscript{2}
solution and the polymer, there are more crystals on the surface and some of them have a fairly large size. The large crystals are partly buried in the inside layers. The images collected from inside of the film indicate there is no small crystal. There are two reasons that could contribute to the crystal formation on surface rather than in the bulk: one is that the nucleation sites of NBD are located on the surface; the other is that the NBD concentration inside the polymer is lower than the saturated value.

By controlling the contact time, we can control the loading and the conformation of the modifiers on polymer surface.

(3) The effect of storage time

We kept a polypropylene film for one year after treatment and collected the images. The film originally treated with SCF method at 2800 and 60°C for 3 hrs was observed after 1 year of storage at room temperature and pressure (Figure 8). It can be seen that after one year the NBD molecules migrated to the surface and left the middle region almost completely void of NBD. This phenomenon is quite common in polymer applications. Polymer molecules tend to exclude small incompatible molecules out from their matrix by chain relaxation. The NBD molecules group together at the polymer surface in a fiber like structure. This is evidence that the NBD and polypropylene mixtures are metastable.

This result demonstrated that SCF modification could add modifiers into the polymer matrix even when the system is not thermodynamically stable. Although the modifiers will exude eventually, the slow rate of migration will allow us to use this technique in most of the possible applications. For example, biocompatible modifiers will remain in place long enough for cell attachment and growth in biomedical devices.
3.4 Modeling

3.4.1 Thermodynamic modeling with equation of state

Thermodynamic modeling could improve understanding of the fundamentals of the modification process and provide predictive information for scaling up the process. The Sanchez-Lacombe (S-L) equation of state (Sanchez and Lacombe 1976, 1978) is one of the most common equations of state for polymer solutions:

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

(1)

where \( \tilde{\rho} \) is the reduced density, \( \tilde{P} \) is the reduced pressure, \( \tilde{T} \) is the reduced temperature, and \( \tilde{r} \) is the number of lattice sites occupied by a chain molecule (r-mer).

In the S-L equation, a pure component is described with three characteristic parameters: \( T^* \), \( P^* \) and \( \rho^* \). The parameters are typically obtained from pure component data such as vapor pressure or liquid densities. The characteristic parameters required for polypropylene and \( \text{CO}_2 \) were obtained from the literature and are listed in Table 3.2. (Pottiger, M. T.; Laurence 1984, Kiszka et al 1988) Since the PMMA modification experiments are only used to give a qualitative comparison, we did not model the process. The crystal density of NBD estimated through a group contribution method (Van Krevelen and Hoftyzer 1976) was used as \( \rho^* \). The characteristic temperature and pressure of NBD were then found via fitting the experimental solubility data in \( \text{CO}_2 \) through an optimization procedure. They were then used to model the phase behavior of the ternary system. The mixing rules outlined by Xiong and Kiran (1993) were applied for the binary and ternary systems.
(1) CO\textsubscript{2}/Polypropylene Binary System

From Figure 2, it is clear that the S-L equation fits the CO\textsubscript{2} solubility data very well with a reasonably small binary interaction parameter $\delta_{ij} = 0.107$. The CO\textsubscript{2}/polypropylene binary experimental data was obtained at 40°C, but the ternary system was studied under 60°C. Theoretically, $\delta_{ij}$ is a temperature dependent parameter, however, since the temperature difference is small, we assume that $\delta_{ij}$ is constant over the temperature range from 40°C to 60°C.

(2) CO\textsubscript{2}/NBD Binary System

The solid NBD was assumed to be pure since the SC-CO\textsubscript{2} solubility in the solid phase is negligible. In order to avoid direct calculation of the chemical potential for the solid, a reference state was chosen and departure functions of chemical potential from the reference state for both phases were calculated. (You and Lee, 1993) For this system, the subcooled pure liquid at operating temperature and pressure was chosen as the reference state ($\mu_{i}^{ref}$). At equilibrium, the chemical potential of a component in each phase is equal:

$$\mu_{i}^{L} - \mu_{i}^{ref} = \mu_{i}^{SCF} - \mu_{i}^{ref}$$

(2)

As discussed by Prausnitz et al (1986), the left side of the equation can be replaced by the calculation of the ratio of fugacity and its pressure correction:

$$RT \ln \left( \frac{f_{i}^{ref}}{f_{i}^{L}} \right) = RT \ln \left( \frac{f_{i}^{ref}}{f_{i}^{S}} \right)^{sat} + V_{i}^{L} (P - P^{sat}) - V_{i}^{S} (P - P^{sat})$$

(3)
$\nu^l$ and $\nu^S$ are the molar volumes of the solute in the subcooled liquid and solid states. They are expected to be roughly similar and as an approximation, the second and the third terms on the right side cancel out in our calculation.

$$\Delta \mu_i^s = \mu_i^s - \mu_i^{ref} = -RT \ln \left( \frac{f_i^{ref}}{f_i} \right)$$

(4)

The fugacity difference between the subcooled liquid and pure solid at saturated conditions can be calculated through a reversible thermodynamic path (Prausnitz et al, 1986):

$$\ln \left( \frac{f_i^{ref}}{f_i} \right)^{sat} = \frac{\Delta h_i^f}{RT_m} \left( \frac{T_m}{T} - 1 \right) - \frac{\Delta c_p}{R} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta c_p}{R} \ln \frac{T_m}{T}$$

(5)

where $\Delta c_p = c_p(liquid) - c_p(solid)$ and $\Delta h_i^f$ is the heat of fusion at the melting point ($T_m$). $T_m$, $\Delta c_p$ and $\Delta h_i^f$ were measured using differential scanning calorimetry (DSC).

$\mu_i^{SCF}$ and $\mu_i^{ref}$ on the left hand side of the equation (2) are calculated separately using Sanchez-Lacombe equation. $\mu_i^{ref}$ is obtained by setting the mass fraction of component $i$ equal to 1.

Since NBD is a specialty chemical, no phase equilibrium data is available for this compound. There are three parameters need to be identified: $T^*$, $P^*$ and the binary interaction parameter $\delta_y$. For the NBD-CO$_2$ system, the binary interaction parameter $\delta_y$ was set to zero, while $T^*$ and $P^*$ of NBD were adjusted to minimize the deviation of the calculated solubility data from the experimental data. It is theoretically incorrect to assume that $\delta_y$ is zero for molecules with big differences like NBD and CO$_2$. However, the errors could be partially compensated by fitting $T^*$ and $P^*$ to the experimental data.
Figure 3 shows the model calculation to be in good agreement with experiment. The optimized $T^*$ and $P^*$ of NBD are given in Table 3.2. The value of $T^*$ is 1655.6°K, which is much higher than the values for some typical alkanes. (Sanchez and Locombe, 1976) There are two reasons that could contribute to such a high $T^*$: First, the Sanchez-Lacombe equation of state was developed to describe phase behavior of classic fluids and fluid mixtures. It is not surprising to see unusual characteristic parameters for NBD since it is crystalline at ambient conditions. Secondly, the polar group on the NBD makes a simple comparison with alkanes unsuitable.

(3) CO$_2$/NBD/Polypropylene Ternary System

The fluid phase was modeled as a binary phase since the solubility of polypropylene in SC-CO$_2$ is negligible. In the polymer phase, SC-CO$_2$ swelling and NBD sorption were considered simultaneously. The interaction parameter $\delta_y$ between polypropylene and NBD was adjusted to 0.068 to give the best correlation. As shown in Figure 13, the Sanchez-Lacombe equation of state successfully describes the NBD partitioning between the SCF and polymer phases. The modeling also shows that the uptake of NBD by polypropylene does not increase as significantly as the solubility of NBD in SC-CO$_2$ when the pressure increases. The results imply that higher pressure prefers higher uptake of modifiers by substrates but does not benefit $K_D$. Suitable operating conditions can be chosen depending on specific requirements of a process.

3.4.2 Molecular modeling and Langmuir adsorption analysis

The Langmuir isotherm is developed for the adsorption of a surface-active solute from dilute solution to a substrate surface. The equation is written as:
\[ \frac{c}{n^* / w} = mc + b \]  

(5)

where \( m \) and \( b \) are constants, \( c \) is the concentration of the solute in the fluid phase, \( n^* / w \) is the maximum number of moles of solute adsorbed per unit weight of substrate. (Hiemenz, 1986) In these experiments, \( n^* / w \) will be a function of \( T \) and \( P \) because the loading depends on these conditions.

The SCF modification experimental data were fitted with equation (5) and the constant \( m \) was found to be \( 1.233 \times 10^6 \). The physical significance of \( m \) is as follows:

\[ m = \frac{N_A \sigma^0}{A_{sp}} \]  

(6)

where \( N_A \) is the Avogadro's number, \( \sigma^0 \) is the area occupied per molecule. \( A_{sp} \) is the specific area of the substrate. \( A_{sp} \) measured by \( N_2 \) adsorption BET is 0.05 m\(^2\)/gram, which implies that polypropylene films are nonporous. \( 1/(mN_A) \) is the solute loading on the substrate surface, which has units of molecules per gram of substrate. The value of \( 1/(mN_A) \) obtained from our data is listed in Table 3.3.

Table 3.3 also lists \( \sigma^0 \) calculated using Hyperchem. In this approach, \( \sigma^0 \) was estimated for NBD molecules in different configurations. The NBD loading on polypropylene surface was obtained by dividing \( A_{sp} \) with \( \sigma^0 \). From Table 3.3, it is clear that the NBD loading on polypropylene films analyzed from experimental data is much higher than from the molecular modeling, which indicates that the solute is not only adsorbed on the surface but also impregnated into the bulk of the polymer. This agrees with our observation from confocal scanning microscopy.
The experiments on PMMA films are used as a qualitative comparison to polypropylene modification. No further modeling was applied.

3.5 Conclusion

Polymer modification using supercritical fluid as the only solvent was investigated. The solubility data show SC-CO$_2$ can penetrate into polypropylene films and act as a carrier for the modifier in modification process. Although the solubility of NBD in SC-CO$_2$ is low, the loading of the NBD molecules onto polymers is significantly improved compared with solution coating. SC-CO$_2$ offers a unique balance in impregnating modifiers into polymers by swelling the matrix and maintaining relatively weak solvent power for the modifier. Supercritical modification gives a uniform modifier distribution in polymers even though the modifier/polymer interactions are not favorable. Slow migration to the surface was observed for polypropylene and NBD system after SCF modification.
<table>
<thead>
<tr>
<th></th>
<th>Polypropylene Film Type I</th>
<th>Polypropylene Film Type II</th>
<th>Polypropylene Cast Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Mn</td>
<td>97,000</td>
<td>108,000</td>
<td>67,000</td>
</tr>
<tr>
<td>Average Mw</td>
<td>440,000</td>
<td>586,000</td>
<td>250,000</td>
</tr>
<tr>
<td>Melt flow index (230°C/2.16kg ASTM D1238)</td>
<td>1.5 g/10min</td>
<td>0.5 g/10min</td>
<td>12 g/10min</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>12 g/10min</td>
<td>50 - 60 %</td>
<td>50 - 60 %</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.90</td>
<td>0.90 - 0.91</td>
<td>0.9</td>
</tr>
<tr>
<td>Tm (DSC, peak) (°C)</td>
<td>164</td>
<td>163</td>
<td>164</td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td>90 ± 10</td>
<td>1588 ± 76</td>
<td>90 ± 15</td>
</tr>
</tbody>
</table>

[1] The data was collected using X-Ray Diffraction.
[2] The data were obtained from reference (Brandup et al 1999).
[3] The data were collected using differential scanning calorimetry (DSC).
All of the other data were from the manufactures.

Table 3.1 Polymer Properties
Table 3.2. S-L EOS characteristic parameters and other physical properties used in modeling

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>NBD</th>
<th>Polypropylene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mw (g/mol)</strong></td>
<td>44.01</td>
<td>404.55</td>
<td>440000</td>
</tr>
<tr>
<td><em><em>P</em> (bar)</em>*</td>
<td>5745.1</td>
<td>2592.5</td>
<td>2811</td>
</tr>
<tr>
<td><em><em>T</em> (K)</em>*</td>
<td>305</td>
<td>1655.6</td>
<td>770.9</td>
</tr>
<tr>
<td><em><em>ρ</em> (g/cm³)</em>*</td>
<td>1.51</td>
<td>1.18</td>
<td>0.852</td>
</tr>
<tr>
<td>Δ(h_f) (J/mol)</td>
<td>_</td>
<td>72172</td>
<td>_</td>
</tr>
<tr>
<td>Δ(c_p) (J/mol)</td>
<td>_</td>
<td>68.7</td>
<td>_</td>
</tr>
<tr>
<td>Molecule configuration</td>
<td>Area occupied by a single molecule $\sigma^0$ (Å²)</td>
<td>NBD loading on polypropylene films (molecules/g)</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Flat</td>
<td>792</td>
<td>6.31E+15</td>
<td></td>
</tr>
<tr>
<td>vertical via tail</td>
<td>118</td>
<td>4.23E+16</td>
<td></td>
</tr>
<tr>
<td>vertical via head</td>
<td>236</td>
<td>2.12E+16</td>
<td></td>
</tr>
<tr>
<td>Langmuir analysis of experimental data</td>
<td>–</td>
<td>4.88E+17</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3. Molecular modeling results of NBD sorption into polypropylene
Figure 3.1 The structure of 4-hexadecylamino-7-nitrobenz-2-oxa-1,3-diazole (NBD)
Figure 3.2 The desorption of CO\textsubscript{2} from polypropylene
Figure 3.3 The apparatus for polymer impregnation using SCF
Figure 3.4 (a) CO₂ solubility in polypropylene films at 40°C; (b) Pure CO₂ density at 40°C
Figure 3.5 NBD solubility in SC-CO$_2$
Figure 3.6 Partitioning coefficients of NBD from SCF modification and solution coating at 60°C
Figure 3.7 NBD distribution in a polypropylene film (thickness = 80 μm) from SCF modification at 60°C and 190 bar for 15 minutes
Figure 3.8 NBD distribution in polypropylene film
(thickness = 90 μm) from solvent casting
Figure 3.9 NBD distribution in a polypropylene film (thickness = 90 μm) from SCF modification at 60°C and 190bar for 8 hours
Figure 3.10 NBD distribution in a polypropylene film (thickness = 100\textmu m) after one year storage at room conditions. (The sample was originally treated with SCF solution at 60°C and 190 bar for 3 hours).
<table>
<thead>
<tr>
<th><strong>Experimental Data</strong></th>
<th><strong>Fitted parameter</strong></th>
<th><strong>Assumptions</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ solubility in polypropylene</td>
<td>( k_y (\text{CO}_2/\text{PP}) )</td>
<td>( k_y ) is a constant over ( T = 40^\circ\text{C}-60^\circ\text{C} )</td>
</tr>
<tr>
<td>NBD solubility in CO₂</td>
<td>( T^<em>, P^</em> ) and ( \rho^* )</td>
<td>Fluid phase: a binary phase (neglect the solubility of polypropylene in CO₂)</td>
</tr>
</tbody>
</table>
| NBD partitioning (\( K_D \)) between CO₂ and PP | \( k_y (\text{NBD}/\text{PP}) \) | • NBD phase: a pure solid.  
• Reference state = the subcooled pure liquid at operating \( T, P \)  
• \( k_y (\text{NBD}/\text{CO}_2) = 0 \) |

Figure 3.11 The procedure of modeling using Sanchez-Lacombe equation of state
Figure 3.12 Partitioning coefficients ($K_d$) of NBD from SCF modification at 60°C
CHAPTER 4

KINETICS OF POLYMER IMPREGNATION USING SUPERCRITICAL CO₂ AND THE IMPACT OF POLYMER PROPERTIES ON MODIFIER DISTRIBUTION

4.1 Introduction

While CO₂ and polymer interactions have been extensively investigated, quantification of the polymer impregnation process is lacking. The challenges come from three aspects. First, it is a multi-component system which includes SCF, modifier and polymer substrate. Secondly, the dimension change in polymers when swollen by CO₂ increases the complexity for modeling. Finally, since the modifier loading in polymers is usually a small amount, a sensitive analytical method is required to monitor the process.

The investigation on CO₂/polymer interactions has revealed that the swelling effect of high pressure CO₂ should aid the mass transfer of modifiers in polymers. The research on determining diffusivities can be divided into two categories based on experimental methods.

The first category involves post-treatment analysis of the loading. Usually, the polymer is treated under SCF conditions for a certain period of time. Then the system is
vented and the loading of the modifier is quantified. Berens et al. (1992) measured the weight change of poly (vinyl chloride) (PVC) after impregnation with dimethyl phthalate in CO₂. West et al. (1998) re-extracted dispersed red I into methylene chloride from PMMA after SCF dyeing and analyzed the solution via UV-VIS. Sicardi et al. (2000) transferred the “film roll method” from a water impregnating system into the SCF system. They wrapped 25 layers of PET films on a big roll and impregnated it with disperse blue or disperse yellow in SC-CO₂. The films were unrolled after dyeing and the dye concentration in each layer was quantified using UV-VIS. The concentration was plotted versus distance to obtain the diffusivity.

The other category includes analysis under high pressure. Kazarian and coworkers (West et al. 1998, Brantley et al. 1999) monitored the UV absorption of dye in polymers in SC-CO₂ atmosphere and converted the absorption intensity to dye concentration. Schnitzler and Eggers (1999) used a magnetic microbalance to measure the weight change of poly (ethylene terephthalate) when impregnated with disperse dye in SC-CO₂. A view cell was mounted to the balance system and a CCD camera was used to record the volume change of the polymer. The UV-VIS method requires a subtraction of the absorption from the fluid phase while the gravimetric method needs a consideration of the CO₂ absorption in polymers.

Table 4.1 lists the solute diffusivities reported in the cited work. It is hard to make a simple comparison between them because the data were collected from different systems and the experimental conditions are different. There is a clear trend that the diffusivity increases with increasing pressure or temperature.
Diffusivity of additives in polymers was also obtained by investigating the supercritical fluid extraction process. Cotton et al (1993) investigated the diffusion of additives in polypropylene during the supercritical fluid extraction process. In their work, polypropylene pellets originally contained known amounts of additives. After extraction, SC-CO\textsubscript{2} was released from a fused silica restrictor and the additive was dissolved in a solvent. The quantity of solute was measured using capillary supercritical fluid chromatography. Chapman and his colleagues (1996) applied forced Rayleigh scattering technique to study the diffusivities of \textit{cis} and \textit{trans} azobenzene isomers. This work is unique because it is the first time that the diffusivity is not correlated from the adsorption curve but directly calculated from the dye concentration decay caused by diffusion. On the other side, this technique has strict limitations on the substance. The polymer must be transparent and the additive must have a \textit{cis} and \textit{trans} transition when shined by light. Table 4.2 lists the solute diffusivity measured from the supercritical fluid extraction process.

In this chapter, methods from both categories were applied to find the mass transfer properties of the modifier. The experiment in the first category employs a series of operations: impregnation, depressurization, re-extraction and quantification. The most questionable and hard-to-repeat step is the depressurization. We investigated the impact of the pressure release on both the polymer morphology and the modifier distribution. \textit{In-situ} UV-VIS and front surface fluorescence were employed to monitor the process and their applicability is discussed.

The polymer used for SCF impregnation in the cited work includes PDMS, PMMA, PVC, and PET. Most are amorphous polymers and interact well with CO\textsubscript{2}. Much less
work has been done on polyolefin impregnation although there are many application opportunities for modifying these materials. We impregnated polypropylene with NBD and compare it with PMMA impregnation in terms of polymer morphology change, partitioning coefficient, modifier uptake and modifier distribution in polymers.

4.2 Experimental

4.2.1 Re-extraction of SCF treated polymer films in solution

It is expected that when the film is exposed to the modifier and SC-CO$_2$ solution, both adsorption on the surface and impregnation will occur. This experiment was designed to test the swelling effect on modifier loading and find the durability of modifiers loaded on the surface, which is very important for tailoring the surface properties.

The films were treated with the same apparatus and the same procedure as described previously. NBD impregnated polymer film was tethered to the cap of a quartz cuvette. The cuvette was filled with a pure solvent. The cap was then fit on top of the cuvette and the film was fully soaked in the liquid. The fluorescence emission from the solution was recorded versus time. The solution was stirred at a well-controlled rate. If the rate is too slow, the kinetics curve would have sharp peaks or valleys; if the rate is too fast, it would generate much heat and cause solvent vaporization. Figure 4.1 is a schematic diagram of the experimental setup.

Methanol and toluene were chosen as the re-extraction agents for polypropylene. Methanol cannot swell polypropylene while toluene can swell it up to 21 vol%. (Sammes et al. 1994) Hexane was used to wash off NBD “sitting” (physically adsorbed
not impregnated) on the PMMA surface while methanol was used to extract NBD from PMMA matrix. For fluorescence analysis, the excitation wavelength was 440nm and the emission was collected at 490nm, 500nm and 530nm for hexane, toluene and methanol solutions respectively. As shown in Figure 4.26, the wavelength is where the maximum emission in the solvent is located.

4.2.2 Kinetics of polymer impregnation

The films were impregnated with NBD for different periods of time in SC-CO$_2$ followed by a fast pressure release. The system conditions were different for different polymers (Table 4.3). Type II polypropylene and PMMA have the same dimension and they will be used for comparison. It has been shown that NBD solubility increases with increasing temperature. Since the interaction between polyolefin and CO$_2$ is much less than that between PMMA and CO$_2$, higher NBD solubility is necessary to achieve a similar impregnation. Therefore, 60°C was chosen for type II polypropylene and 40°C for PMMA. In order to have the same CO$_2$ density, 162 bar was chosen for the 60°C treatment and 102 bar was the pressure for 40°C system.

After impregnation, the film was soaked in a pure solvent and NBD was re-extracted into the solution. NBD concentration in solution was quantified using fluorescence or UV absorption. Since we are working with dilute solutions, there is a linear relationship between intensity and concentration for both methods. A standard curve of intensity versus concentration was obtained from a series of NBD solutions with known concentration. Concentration of the sample solution was then calculated from the spectroscopic intensity based on this linearity.
In a departure from the quantification in previous work (West et al 1998), the re-extraction was conducted in two steps. The solvents used for polypropylene and PMMA have been discussed above. Films impregnated longer than 5 hours could not be completely re-extracted even after a couple of days at room temperature. Therefore, in order to speed up the re-extraction, the temperature of the solvents was kept at 35-40°C.

4.2.3 Polymer impregnation with fast and slow pressure release

When pressure is released at the end of the impregnation experiment, CO$_2$ escapes from the polymer matrix and the swollen polymer should experience a relaxation back to its original shape. Both processes should have an impact on the modifier loading and distribution in the polymers.

The apparatus is shown in Figure 4.2. Chamber I and II were loaded with the same type of polymer films. The valve between the two chambers was open during the process. The procedure is the same as the impregnation: pressurized CO$_2$ dissolved NBD and contacted the polymer films in chamber I and II. At the end of each trial, 6-8 ml pure CO$_2$ (at the system conditions) was run through to avoid precipitation of NBD from the fluid phase. Then the shut-off valve between the two chambers was closed. Pressure was released through the metering valve. The film in chamber II underwent "fast" pressure release. Chamber I that remaining at high pressure was directly connected to the pump. The pump was then slowly refilled at a rate of 0.05 - 0.2 ml/min to provide a controlled withdrawal of CO$_2$ and hence a controlled depressurization. The film in chamber I is the sample referred to as "slow" pressure release. Images of polymers containing NBD were taken using SEM (XL-30 FEG) and confocal laser scanning microscopy (CLSM, Bio-Rad MRC-600).
4.2.4 Steady-state fluorescence emission

The steady-state emission spectra of NBD in treated films were collected with a fluorescence spectrometer (Photon Technology International, Model QM-1). The film was fixed on a custom designed sample holder and the excitation beam (440 nm) hit the front surface of the film at a 30° input angle to minimize noise in the spectra due to reflected light. A detector collected the fluorescence emission at a 90° angle to excitation beam.

4.2.5 In-situ UV absorption of NBD

A high-pressure view cell was built and mounted to the UV absorption compartment (see chapter 5.3.2 for details). The NBD spectrum in CO\textsubscript{2} under high pressure was collected.

In order to monitor the impregnation process, PMMA film was placed in the middle of the view cell. PMMA is transparent and absorption free in the NBD absorption range. An excess amount of NBD was loaded in the bottom of the cell. The cell was pressurized with CO\textsubscript{2} and kept at a constant pressure and temperature. UV absorption was recorded versus time. The absorption signal collected was the combination from that of the CO\textsubscript{2} phase and the polymer phase. Since NBD dissolved in CO\textsubscript{2} relatively quickly and the fluid phase was saturated with NBD during the experiment, the fluid phase absorption was a constant and could be subtracted.

4.2.6 In-situ front surface fluorescence of the PMMA film

A high-pressure view cell was attached to the fluorescence spectrophotometer. A special tool was designed to hold a polymer film in the view cell (see chapter 5.3.2 for details). The excitation light could hit the film surface at 30° to the normal of the
surface. The emission was collected at 90° to the input light. NBD was loaded in another vessel and CO$_2$ saturated with NBD was run through the view cell during the impregnation.

4.3 Results and Discussion

4.3.1 Re-extraction kinetics and surface characterization

A sample of type I polypropylene film (thickness 0.004”) was treated with SCF impregnation for 40 minutes. The film was then soaked in methanol for re-extraction. Figure 4.3 is the NBD concentration in methanol versus time. The concentration was calculated from fluorescence intensity based on the standard curve. Methanol can dissolve NBD well. Although the solubility data is not available, it is observed that a solution with $1.0 \times 10^{-5}$ mol/l concentration could be made at room conditions. From the figure, it can be seen that methanol extracted NBD from the film but the curve leveled off quickly. After the extraction, the film was air dried for three hours and weighed on a balance to make sure that the weight did not change anymore to confirm the absence of residual methanol. The polypropylene film still appeared yellow (solid NBD is orange), which indicated the existence of NBD.

Since methanol cannot swell polypropylene films, it is hypothesized that methanol can only wash away NBD physically adsorbed on the surface. This experiment confirms that the swelling effect of CO$_2$ on polypropylene films benefits the loading of NBD into the polymer matrix. There is NBD remaining in the film even after rinsing with methanol. Figure 4.4 shows the fluorescence images of polypropylene films after SC-
CO₂ impregnation. Figure 4.5 shows the images of the same film washed in methanol for 1 hour.

When collecting images using the confocal scanning microscope, a big challenge is to define the surface. Some of the small bright spots shown in the photo appear in focus first. However, this is not the film surface but particles slightly higher than the surface. Then, when the z-direction motor goes down about 5 μm to focus on different layers, an image with some surface structure appears. This is defined as the film surface. The images in Figure 4.4 and Figure 4.5 do not have much difference, which implies that methanol cannot desorb all of the NBD on polypropylene surfaces. In other words, some of the NBD on surface is attached to the film in a more durable manner than simple physical adsorption.

The film was then put in pure toluene for the second step re-extraction. Figure 4.6 shows the kinetics of the process. A qualitatively different desorption behavior is observed. At the beginning the NBD concentration does not increase dramatically, apparently because the surface of the film lacks of NBD. After 10 minutes, the slope of the curve becomes steep which represents a faster extraction. This occurs when toluene penetrates into the film, swells it, and increases the diffusion of NBD. The curve levels off when the film is depleted of NBD. After toluene extraction, the film turns semi-transparent with no color, identical to the control sample. The film is soft and slightly curled when taken out of toluene while it looks the same after soaking in methanol.

This experiment confirms that NBD is not only adsorbed on the surface but also impregnated in the bulk of polypropylene films. It is entangled with the polymer chains and is only released upon the generation of free volume by a swelling agent.
Hexane is used to extract NBD from PMMA surfaces. NBD solubility in hexane is unknown but a $1.0 \times 10^{-5}$ mol/l solution can be made at room conditions. As shown in Figure 4.7 (a), the dissolution curve is very noise and the concentration is very low which challenges the sensitivity of the fluorescence analysis. The low concentration is either because there is no NBD adsorbed on surface or NBD is firmly bonded. Previous experiments have shown that NBD has a better affinity for PMMA than polypropylene. Therefore, it is more likely that NBD is entangled in the PMMA matrix even for the surface layer. Air-dried PMMA was then soaked in methanol to measure the kinetics of re-extraction. As shown in Figure 4.7 (b), there is a slight delay before the concentration begins to increase.

4.3.2 Kinetics of impregnation

(1) Polypropylene (0.004")

Figure 4.8 is the total amount of NBD versus impregnation time for type I polypropylene film. It is the sum of NBD extracted by methanol and toluene. The data are scattered in a certain range. The possible reason could be found from the confocal images in Figure 4.4. The quantity to the tail of small crystals on the surface is a very random factor, which is suggested to be related to the surface morphology. Since the film is thin ($\leq 100 \mu m$), the contribution from NBD on surface is significant to the total quantity. Therefore, we can only quantify a range of loading.

Figure 4.9 demonstrates the percentage of NBD in films washed off by methanol, i.e. the NBD adsorbed on the surface. The percentage is somewhat scattered as well but is in a reasonable range. For this film, about 5-20 % NBD was “sitting” on the surface.
For type II polypropylene film with a much large thickness (1/16"), the total NBD loading increases with contact time (Figure 4.10). The larger thickness allows us to measure more accurately the time dependence of the impregnation and analyze the data for the diffusion coefficient, $D$, of the modifier in the polymer film.

The data was modeled with a relationship that describes one-dimensional diffusion of a component through a finite plate (see the following equation).

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left\{ -\frac{D(2n+1)^2 \pi^2 t}{l^2} \right\}$$

where $M_t$ is the total amount of solute in the plate at a given time. $M_\infty$ is the equilibrium loading. $D$ is the diffusivity, $l$ is the thickness of the film and $t$ is time. The series was truncated at $n = 8$, which provides enough detail to fit the data accurately. (Crank, 1975)

In order to apply this equation to our system, several assumptions need to be made:

a) The diffusivity is a constant during the process and throughout the polymer.

b) The polymer dimension does not change. Since less than 5 wt% of CO$_2$ adsorbed in polypropylene, it is reasonable to neglect the volume change.

c) The NBD concentration in the CO$_2$ phase is a constant. This assumption should hold well because there is excess NBD loaded in the cell. Also NBD dissolution into CO$_2$ is expected to be much faster than its diffusion into polymers.

d) The diffusion from the edge is neglected. Only one-dimensional diffusion is considered.

The impregnation did not reach equilibrium for this sample. The solubility of NBD in polypropylene has been measured in last chapter and the value is used as $M_\infty$. The
NBD diffusivity in polypropylene under 162 bar and 60°C CO₂ atmosphere is calculated to be $9 \times 10^{-13}$ m²/s. Table 4.4 lists the diffusivity of various solutes in polypropylene reported in literature. As can be seen, the diffusivities at similar temperature are approximately 2 orders of magnitude smaller than that we measured for NBD. It therefore appears that CO₂ swelling increases the solute diffusivity in semi-crystallized polypropylene.

Figure 4.11 is the quantity of NBD washed by methanol. Except for 2 points, most of the data are in a narrow range ($1.0 - 5.0 \times 10^7$ gNBD/gpolypropylene), which is less than 5% of the total loading.

(3) PMMA

Figure 4.12 is the uptake of NBD by PMMA films. $M_{\infty}$ is determined from the impregnation of a thinner PMMA film made of same materials. According to Wissinger’s measurement (Figure 2.1), the volume of PMMA changes about 27% at the experimental conditions, which makes assumption (b) questionable. It could be solved as a moving boundary problem that requires a numerical solution. Knowledge of CO₂ absorption kinetics in polymers is necessary.

We employed the above equation to estimate the NBD diffusivity in PMMA at 102 bar and 40°C. If the original size is used, $D$ is $6 \times 10^{-13}$ m²/s. If the equilibrium size (e. g. the swollen size) is used, $D$ is $7 \times 10^{-13}$ m²/s. Figure 4.13 shows that less than 3% of NBD adsorbed on the surface of PMMA films.
4.3.3 NBD distribution in polymers

(1) PMMA films

PMMA is a glassy polymer at room conditions and it reaches or gets close to its glass transition point under CO₂ pressure. (see Figure 2.1) SEM pictures in Figure 4.14 show the cross section of PMMA films treated for 6.8 hours. 4.14 (a) is the sample after fast pressure release while (b) is treated with slow pressure release. Both films are foamed by CO₂. The mechanism of foaming has been well documented. (Goel and Beckman 1995, Parks and Beckman, 1996) It could be described as a three-step process. First, high pressure CO₂ penetrates into the polymer matrix to swell it and form a homogeneous phase. When the pressure is released, CO₂ near the surface has the largest pressure gradient. It escapes from the polymer quickly and the surface layer goes back to its original shape. CO₂ absorbed inside the polymer cannot leave the polymer phase quickly enough and some nuclei are formed at sites within the polymer. CO₂ diffuses to the nuclei and forms bubbles. This phenomenon is called foaming. A small portion of CO₂ desorbs from the polymer at a very slow rate that may take several days at room conditions. In Figure 4.14 (a), we refer to the solid structure near surface as “skin”. The center of the polymer is foamed by CO₂. The size of the bubbles depends on several operational parameters, among which pressure release rate is a very important one. When the pressure is released slowly under a good control, the foaming could be minimized. As shown in Figure 4.14 (b), the foaming is significantly reduced. There are only several big bubbles in the center. The slow release allows CO₂ to escape before the polymer recovers from the swollen state. It is believed that foaming happens in the batch technique near the point where CO₂ density changes dramatically with pressure.
Therefore, if the release rate is slow enough near the critical point, it is possible to avoid foaming. It is desirable in some impregnation applications to take advantage of the plasticization but avoid foaming.

Figure 4.15 (a) is the fluorescence emission from the PMMA film cross section. The sample was treated for 6.8 hours followed by fast pressure release. A large amount of NBD accumulates near the surface. The width of the bright band is measured from the photo to be 108 μm. From edge to center, the NBD concentration dropped very fast. Figure 4.15 (b) is the SEM picture focused on the skin area of the same sample. The width of the skin is about 100 – 130 μm. Therefore, all of the bright band falls in the skin area. The center area of the film is not free of NBD but the amount is very small. The formation of the uneven distribution of NBD in the film could happen either during the impregnation process or the pressure release process. It is unlikely to be the former because after 6.8 hours, CO₂ and PMMA should have formed a homogeneous phase. The SEM picture in Figure 4.14 (a) could be taken as evidence that CO₂ has penetrated well into PMMA. The diffusion of NBD from edge to center in a homogeneous phase should be a continuous process, which should generate either a uniform NBD distribution or a smooth concentration gradient. Therefore, it is suggested the high NBD concentration in skin is primarily caused by the pressure release.

When the system is vented, there is a competition between NBD diffusion and polymer relaxation. Which phenomena dominates depends on the polymer properties and CO₂/polymer interactions. From Liao and McHugh’s data (1985), it is estimated that 25 wt% of CO₂ dissolved in the film. In addition, PMMA is well plasticized and close to its glass transition state. When pressure is released, we hypothesize that NBD
was carried by CO₂ escaping from the polymer matrix. The frozen polymer chains in the skin trapped NBD to build a high concentration band.

A similar bright band was observed in the PMMA film experienced slow pressure release (Figure 4.16 (a)). This photo better demonstrates that the bulk phase of the film contains small amount of NBD. Another comparatively high NBD concentration appears around the big bubbles. This is also evidence that CO₂ carries NBD around when the pressure is released. When CO₂ diffuses out of the film into the bubbles, NBD is precipitated on the bubble walls. Figure 4.16 (b) is the photo taken in the confocal microscopy with reflected light. It is exactly the same spot as Figure 4.16 (a). The reflection from transparent objectives such as this PMMA film usually gives strong black and white contrast. It is hard to identify any surface structure but we are able to see the two bubbles.

Figure 4.17 also show the fluorescence emission from PMMA films with slow pressure release. It is another sample but treated under the same conditions as the film in Figure 4.16. In Figure 4.17, (a) and (b) are basically from the same spot with (b) focused on the center while (a) includes the bright band. It is clear that NBD concentration is high around bubble areas.

An interesting phenomenon was observed when we look at the bubbles from the top surface. Figure 4.18 (a) is the photo of a bubble in PMMA taken using light microscope. It seems there is some crystal-like structure in the bubble. Figure 4.18 (b) is the fluorescence emission from this sample on a different spot. The motor was focused on the layer 160 μm beneath the surface. Since the crystal-like stuff is fluorescent, it is highly possible that NBD has crystallized on the bubble walls.
Another interesting observation is the "growth" of the bright band versus contact time with CO$_2$. Figure 4.19 is the fluorescence emission from PMMA films for different period of time followed by fast pressure release. It can be seen that the width of the bright band is increasing with contact time. If we consider the two SEM photos in Figure 4.20, we find that the skin thickness of the PMMA film does not change with contact time. Therefore, the growth in the bright band should be primarily due to NBD concentration in the film.

(2) Polypropylene films

Polypropylene has different properties from PMMA. It is a rubbery polymer at ambient and experimental conditions. Polypropylene has 50 -60 % crystallinity while PMMA is primarily amorphous. The carbonyl groups in PMMA have a favorable interaction with CO$_2$ while polypropylene units are relatively inert to CO$_2$. Figure 4.21 shows the absorption of CO$_2$ in polypropylene and PMMA. Polypropylene can absorb about 5.5 wt% of CO$_2$ while PMMA absorbs 27 wt% of CO$_2$ under the experimental conditions studied here.

Figure 4.22 shows polypropylene films treated with CO$_2$ and NBD solution for 17.8 hours: 4.22 (a) is the sample with a fast pressure release while the sample in 4.22 (b) is treated with well controlled slow release. No foaming happens to the films. It is because polypropylene is a rubbery polymer and the comparatively mobile chains relax well when CO$_2$ leaves the matrix.

Figure 4.23 shows the fluorescence images from the cross section of polypropylene films after SCF impregnation. Differently from PMMA, there is no high NBD concentration near the surface for samples with fast or slow pressure release. Instead,
NBD is evenly distributed. Because the film is broken in liquid nitrogen, the cross section surface is not smooth. Some area on the photo is comparatively dark because that part is slightly out of focus.

Figure 4.24 is the confocal fluorescence images taken from the surface of the film. The sample is treated for 17.8 hours with fast pressure release. It is clear that NBD is evenly distributed. The film with controlled pressure release was observed using the confocal scanning microscopy as well. It has been shown in Figure 4.25 that NBD is allover the film. In both photos, NBD forms honeycomb structure. The patterns in the sample with slow pressure release (Figure 4.25) seem to be better developed than the patterns in the sample with fast pressure release (Figure 4.24). This reminds us that in chapter 3 (Figure 3.8), much larger honeycomb structures were seen in cast polypropylene film. Both of them should be caused by the unfavorable NBD and polypropylene interaction. The polar NBD and nonpolar polypropylene are not thermodynamically compatible. NBD has a tendency to crystallize and build its own phase to minimize the contact with polypropylene. It is highly possible that NBD molecules only distribute in the amorphous area in the polymers. The crystallized polymers appear dark in the photos because of lacking of NBD. SCF dyeing combined with confocal fluorescence microscopy could be an inexpensive way to configure the amorphous and crystallized polymer structures.

Since polypropylene is at its rubbery state and less than 5wt% of CO₂ dissolved in the polymer, the polymer morphology does not change much. When the system is vented, the polymer chains feasibly relax. CO₂ carries out some NBD but for the well-
developed crystals, CO$_2$ has no power to bring them out. Therefore, an even distribution of NBD in polypropylene was observed in previous confocal photos.

4.3.4 Steady-state fluorescence of NBD in films

Fluorescence emission is very sensitive to the environment of the excited molecule and has been applied extensively in SCFs to investigate interactions between molecules. (Brennecke et al 1990, Sun et al 1992, Ryan et al 1997) Figure 4.26 compares the spectra of NBD in different solvents. The spectrum in supercritical carbon dioxide (163bar, 40°C) was collected using the high-pressure view cell. When the polarity of the solvent increases, the peak of the spectra shifts to longer wavelengths because the polar solvents have a greater ability to stabilize the excited state molecules. This in turn lowers the excited state energy and causes an emission of photons with less energy. In general, a more polar environment causes a longer wavelength emission band.

Figure 4.27 shows the front-surface NBD spectra of polypropylene films. The NBD spectra of the SC-CO$_2$ treated film has a peak at 525nm, and as a comparison, the NBD band of solution coated film is located at 500nm. There are several reasons that could account for this difference. The first possibility is solvent residue in the films. Because CO$_2$ is a gas at room temperature and atmospheric pressure, it leaves the substrate very quickly and cleanly when the system pressure is released. Further, the use of the supercritical state ensures that CO$_2$ does not enter the vapor-liquid two-phase region so no interfacial capillary forces are created. It is these capillary forces that are usually responsible for the inability to completely remove a liquid solvent from a substrate by heating alone. For the solution treated films, we try to minimize this possibility by drying the films. Since toluene is a more polar molecule than polypropylene, any
toluene residue should have caused a band around 508nm instead of 500nm, which is what we observed in Figure 10. A second possibility includes structural property changes after different treatment, such as morphology, crystallinity and chain alignment. However, the results from DSC did not show any significant change in crystallinity of the films. Finally, relating the NBD band location to its concentration in films, we find that longer wavelength bands always accompany higher NBD concentration. Thus, we suggest the band location difference is a concentration effect. A high NBD concentration increases the possibility for two molecules to pack together, or have one sitting right above the other. Their π-electron clouds are then partially or completely overlapped. This stacking phenomenon affects not only the ground state energy of the molecule but also the excited state energy. Following this hypothesis, the spectra reveal that the stacking lowers the excited state energy level more than the ground state energy level, which causes an emission band located at longer wavelength. Qian (1988) observed a similar phenomenon for the fluorescence emission spectra of PET in solution and in the solid state. He found the solid state PET band was located at longer wavelengths than in CF$_3$COOH solution. He suggested that this was because the excimer sites are pre-formed since the backbone chain motions are frozen in the glassy state. The concept of "pre-formed excimer site" has the same meaning as the term "π-stacking" used here.

Dipole-dipole interactions may also explain the concentration effect. NBD has a larger dipole moment than polypropylene molecules and the dipole-dipole interactions between two NBD molecules is expected to be stronger than the dipole-induced dipole interactions between an NBD molecule and a polypropylene segment. Therefore, when
the concentration is high, one NBD molecule can "feel" not only polypropylene molecules but also other NBD molecules. This stronger interaction between NBD molecules in close proximity to each other at high concentration may serve to stabilize the excited state resulting in a shift in the emission similar to that seen in solvent relaxation. (Lackowicz 1983)

These explanations are consistent with the results from confocal microscopy.

Figure 4.28 shows the NBD spectra of PMMA films. The band from SC-CO$_2$ treated film is red-shifted approximately 6nm from the solution treatment band. A similar concentration and band location relation, longer wavelength band corresponding to higher concentration, is observed for this system.

The polypropylene and PMMA films have different structure and properties which also play an important role in the modification. In order to add comparable amounts of modifier, PMMA requires much less time in both SCF and solution coating methods and requires lower density of SC-CO$_2$ in SCF treatment. One reason is that the repeat unit of PMMA (methyl methacrylate) shows an affinity for the solvents while the propylene unit is quite inert. The other reason is that the crystallinity of solid PMMA is generally lower than the crystallinity of polypropylene. The large fraction of amorphous volume will increase the solvent swelling effect, which increases the loading of modifier in the films. (Shieh et al 1996, Wissinger and Paulaitis 1987)

Band shifts are used to relate the band location to the modifier concentration and the film structure. We set the position of the maximum in the NBD spectra at dilute concentration as the reference position, and measure the shift in nm of the peak maximum. Figure 4.29 describes the relation between the band shift and the NBD
concentration for both PMMA and polypropylene films. The shift in polypropylene is more significant than in PMMA films implying that it is easier to see a band shift caused by the concentration effect in polypropylene films. In other words, a NBD molecule "feels" a more polar local environment in polypropylene than in PMMA. These observations may be explained by considering the interactions between modifier and polymer molecules. Since PMMA is more polar and has more amorphous volume than polypropylene, the NBD molecules will favorably interact and mix with PMMA therefore diluting themselves relative to the polypropylene case. For polypropylene, the NBD molecules tend to stay on the surface and group together rather than penetrating into the bulk phase because of the relatively unfavorable interactions between polymer and modifier molecules. The structural properties of the films could also contribute to the distribution of the modifier molecules but the mechanism has not been completely verified.

$$K_D$$ is defined in Chapter 3, which is the modifier concentration in the fluid phase divided by the modifier concentration in the polymer phase. Figure 4.30 shows $$K_D$$ of NBD in PMMA/CO$_2$ and polypropylene/CO$_2$ systems respectively. It is obvious that $$K_D$$ for PMMA is smaller than $$K_D$$ for polypropylene, which confirms that it is easier to add NBD into PMMA.

### 4.3.5 In-situ UV absorption of NBD

Figure 4.31 shows the UV absorption scan versus time. PMMA film is placed in the middle of the cell while excess NBD is on the bottom. When the cell is pressurized, initially the UV absorption is from the fluid phase. Then after NBD adsorbed or absorbed into PMMA, the spectrum should be a combination of the information from
the fluid phase and the solid phase. Since the fluid phase NBD concentration is low and
does not change versus time, for a longer contact time, the spectrum contains
information primarily from the polymer phase.

It can be seen from the figure, the band shifts to longer wavelength during the
impregnation process. Usually, the changes in the surrounding circumstance such as
polarity could cause a band shift. The spectrum of pure NBD in CO$_2$ has a peak at
424nm. When NBD is adsorbed onto PMMA surface or impregnated, the molecules are
in a completely different environment than the fluid phase. It can be seen from the
figure that NBD has a maximum absorption at 452nm in PMMA. The fluid phase
absorption is a constant and could be subtracted from the total absorption. Figure 4.32 is
the polymer phase UV absorption versus time.

As cited in the introduction part of this chapter, Karazian and coworkers (Kazarian
et al. 1998, Brantley et al. 1999) used this method to quantify several SCF impregnation
processes. They converted the absorption intensity to solute concentration based on
Beer’s law. The absorptivity was determined by measuring respectively the absorption
of the solute in CO$_2$ or polymer at known concentration. They reported the kinetics of
PMMA film dyeing and also the partitioning of small molecules such as naphthalene in
poly (dimethylsiloxane) and poly (cyanopropylmethylsiloxane). However, it is
questionable to relate the absorption to solute concentration in polymers. Beer’s law is
developed for dilute or medium concentration homogeneous solution. It needs to be
proved that it would still hold in polymer/solute solution. Using this method to quantify
the diffusion is risky because during the impregnation process, CO$_2$ will penetrate into
the polymer to change its volume and possibly some optical properties. On the other

hand, the solute will first adsorb on polymer surface and then penetrate into the bulk. It is unlikely that Beer’s law would hold or the absorptivity would be a constant during this process. Therefore, it is not appropriate to draw any quantitative conclusion from this figure.

4.3.6 In-situ front surface fluorescence of the PMMA film

Figure 4.33 shows the fluorescence emission of NBD versus contact time. Since the solubility of NBD in CO$_2$ at 102 bar and 40°C is very low (approximately 0.7 ppm), the fluorescence is primarily from NBD on PMMA surface. This method is not quantitative because there is no simple linear relationship between the fluorescence emission and the probe concentration on surface. The emission at 508nm was plotted versus time (the second figure on that page). It qualitatively describes that the adsorption happened spontaneously as the CO$_2$ and NBD solution contacts the polymer.

4.4 Conclusion

The durability of modifiers on polymer surface after SCF impregnation was investigated via two-step re-extraction. The result shows that modifiers on surface are not physically adsorbed but entangled with polymer chains. Kinetics study gives the diffusivity of the modifier in polypropylene and PMMA. It is confirmed that CO$_2$ swelling facilitates the modifier diffusion. Images taken with confocal scanning microscope show that modifiers distribute evenly in semi-crystallized polypropylene while they accumulate on the edge and in the foamed bubble walls in PMMA. Post-treatment front surface fluorescence study suggests that the modifier has more affinity to polar PMMA than nonpolar polypropylene.
<table>
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<tr>
<th>Solute</th>
<th>Polymer</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>D (m²/s)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Dimethyl phthalate</td>
<td>PVC</td>
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<td>Berens et al, 1992</td>
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<td>Disperse yellow</td>
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<td>220</td>
<td>1.4×10⁻¹⁴</td>
<td>Sicardi et al, 2000</td>
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<td></td>
<td>110</td>
<td>250</td>
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<td></td>
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<td>220</td>
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<td>88</td>
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<td>West et al, 1998</td>
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<td>Disperse orange</td>
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<td>120</td>
<td>300</td>
<td>1.93×10⁻¹¹</td>
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Table 4.1 Solute diffusivities in polymers in SC-CO₂ atmosphere
<table>
<thead>
<tr>
<th>Solute</th>
<th>Polymer</th>
<th>$P$ (bar)</th>
<th>$T$ (°C)</th>
<th>$D$ (m$^2$/s)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Irogafos 168 *</td>
<td>Polypropylene</td>
<td>405</td>
<td>50</td>
<td>$(1±0.5)\times10^{-11}$</td>
<td>Cotton et al, 1993</td>
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<tr>
<td>Irganox 1010 **</td>
<td>Polypropylene</td>
<td>405</td>
<td>50</td>
<td>$(8±4)\times10^{-12}$</td>
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<tr>
<td>Azobenzene (cis)</td>
<td>Polystyrene</td>
<td>42</td>
<td>35</td>
<td>$3\times10^{-17}$</td>
<td>Chapman et al, 1996</td>
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<td>$1\times10^{-15}$</td>
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<td></td>
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<td>85</td>
<td>35</td>
<td>$1.2\times10^{-14}$</td>
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<td></td>
<td>85</td>
<td>35</td>
<td>$6\times10^{-15}$</td>
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Note: * Irogafos indicates tris-(2,4-ditertiarybutyl phenyl) phosphite  
** Irganox indicates pentaerythritol tetrakis-[3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate]

Table 4.2 Solute diffusivities in polymers in SC-CO$_2$ extraction process
<table>
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<th>Polymer</th>
<th>P (bar)</th>
<th>T (°C)</th>
<th>CO₂ density (g/ml)</th>
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<td>0.712</td>
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<tr>
<td>Type II polypropylene</td>
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<td>0.651</td>
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<tr>
<td>PMMA</td>
<td>102</td>
<td>40</td>
<td>0.652</td>
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Table 4.3 Impregnation conditions for different polymers
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<th>$T , (^\circ\text{C})$</th>
<th>$D , (m^2/s)$</th>
<th>Reference</th>
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<tr>
<td>2,4-Dihydroxybenzophenone</td>
<td>75</td>
<td>1.9×10^{-13}</td>
<td>Westlake and Johnson, 1975</td>
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<td>2-Hydroxy-4-octoxybenzophenone</td>
<td>44</td>
<td>1.7×10^{-14}</td>
<td>Johnson and Westlake, 1975</td>
</tr>
<tr>
<td>2-Hydroxy-4-octoxybenzophenone</td>
<td>75</td>
<td>4.7×10^{-13}</td>
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<tr>
<td>Didodecyl, 3,3-thiodipropionate (DLTB)</td>
<td>56</td>
<td>(5.4±0.4)×10^{-14</td>
<td>Jackson et al, 1968</td>
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<td></td>
<td>78</td>
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<tr>
<td></td>
<td>96</td>
<td>(1.9±0.2)×10^{-12}</td>
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<tr>
<td></td>
<td>100</td>
<td>(2.1±0.2)×10^{-12}</td>
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<td></td>
<td>135</td>
<td>(1.89±0.15)×10^{-11}</td>
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<td>1,3,5-tris (3,5-di-tert-butyl-4-hydroxybenzyl) mesitylene (Irganox 1330)</td>
<td>80</td>
<td>1.4×10^{-14}</td>
<td>Schwarz et al, 1989</td>
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Table 4.4 Solute diffusivities in polypropylene
Figure 4.1 The setup for re-extraction kinetics study
Figure 4.2 The apparatus for impregnation with fast and slow pressure release

1. Syringe pump
4. 3/8" tubing loaded with NBD
8. Shut off valve

2. Pressure gauge
5. Filter
9. Metering valve

3. heating coil
6. Polymer chamber I
10. Filter

7. Polymer chamber II
11. Water bath
Figure 4.3 The re-extraction kinetics of NBD by methanol from polypropylene
Figure 4.4 Fluorescence image of polypropylene after SCF impregnation: (a) 5 μm above the surface (b) surface
Figure 4.5 Fluorescence image of polypropylene after SCF impregnation and 1 hour extraction in methanol: (a) 5 μm above the surface (b) surface
Figure 4.6 The re-extraction kinetics of NBD by toluene from polypropylene (after methanol extraction)
Figure 4.7 The re-extraction kinetics of NBD from PMMA
Figure 4.8 The kinetics of SCF impregnation for type I polypropylene film (190 bar, 60°C)
Figure 4.9 Percentage of NBD washed off by methanol from type I polypropylene surface
Figure 4.10 The kinetics of SCF impregnation for type II polypropylene film (162 bar, 60°C)
Figure 4.11 NBD washed off by methanol from type II polypropylene surface
Figure 4.12 The kinetics of SCF impregnation for PMMA (102 bar, 40°C)
Figure 4.13 Percentage of NBD washed off by hexane from PMMA
Figure 4.14 PMMA after SCF impregnation for 6.8 hours:
(a) fast pressure release (b) slow pressure release
Figure 4.15  PMMA after SCF impregnation with fast pressure release (a) fluorescence; (b) SEM
Figure 4.16 PMMA after SCF impregnation with slow pressure release (a) fluorescence; (b) reflection
Figure 4.17 PMMA after SCF impregnation with slow pressure release
Figure 4.18 Bubbles in PMMA (a) light microscope; (b) confocal fluorescence (the focus is 160 μm beneath surface)
Figure 4.19  The effect of contact time on band width in PMMA
Figure 4.20 Skin of PMMA after exposed to CO$_2$
Figure 4.21 The adsorption of CO₂ in PMMA and polypropylene
Figure 4.22 Polypropylene after SCF impregnation for 17.8 hours:
(a) fast pressure release (b) slow pressure release
Figure 4.23 Fluorescence images of polypropylene after SCF impregnation
(a) fast pressure release; (b) slow pressure release
Figure 4.24 Surface fluorescence images of polypropylene after SCF impregnation with fast pressure release
Figure 4.25 Surface fluorescence images of polypropylene after SCF impregnation with slow pressure release
Figure 4.26 Spectra of NBD in different solvents
Figure 4.27 Spectra of NBD in polypropylene films
Figure 4.28 Spectra of NBD in PMMA films.
Figure 4.29 Spectral shift ($\Delta\nu$) vs. NBD concentration

**NBD concentration (10^{-4} \text{ mol/kg})**
Figure 4.30 $K_p$ for PMMA and polypropylene
Figure 4.31 *In-situ* UV absorption of NBD in PMMA impregnation
Figure 4.32 *In-situ* UV absorption of NBD in PMMA impregnation versus time
Figure 4.33 In-situ PMMA front-surface fluorescence emission
(Time in minutes was labeled in the upper figure)
CHAPTER 5

SPECTROSCOPIC CHARACTERIZATION OF POLY (ETHYLENE TEREPTHALATE)/POLY (OXETHYLENE TEREPTHALATE) AND ITS MODEL COMPOUND AS SURFACE MODIFIERS

5.1 Introduction

Most commercial polymers are hydrophobic, such as polyolefins, acrylic and polyesters. However, in some applications, a hydrophilic surface, i.e. a lower surface tension is desirable. Coating surfactant onto polymer surfaces using supercritical fluids as the solvent and carrier is one way to achieve a more wettable surface.

In order to monitor the surface modification process, it is required to apply a modifier that is detectable using some analytical method. Poly (ethylene terephthalate)/poly (oxyethylene terephthalate) (PET/POET) shown in figure 5.1 is a polymeric surfactant that is used in both detergent and textile industries as a surface modifier to enhance surface wettability and impart oily soil release to polyester fabrics. PET/POET is also spectroscopically active. In aqueous solution, PET/POET absorbs at 244nm and 295nm and has emission bands at 334nm and 386nm (Figure 5.2). UV absorption and fluorescence emission/excitation spectroscopy will be used to monitor molecular interaction and surface adsorption. The use of fluorescence and UV
absorption spectroscopy to study structure and interactions in SCFs is well documented (Brennecke et al 1990, Sun et al 1992, Ryan et al 1997, Zagrobelny et al 1992) These techniques require a spectroscopically active probe as well as some knowledge of the environmental response of that probe. The latter is usually obtained from studies in liquid solutions. Aqueous solution structures of the PET/POET polymeric surfactants have been investigated by Yang and Rathman (1996) via neutron scattering as well as fluorescence spectroscopy. PET/POET forms intramolecular excimers between adjacent phenyl rings at lower concentrations (under 100 ppm), which indicates that the polymer chain adopt a cis configuration in between terephthalate groups. In aqueous-based applications, the PET/POET polymer distribution responsible for the excimer formation adsorbs preferentially onto the polyester fabric. The addition of ionic surfactant affects the polymer solubility, the chain conformation, and also the surface adsorption in sequence. In order to do the modification in SC-CO$_2$, it is important to understand the solubility and solution structure of PET/POET in SC-CO$_2$.

One of the disadvantages of using this surfactant is that it is a polymeric material with a molecular weight distribution. The non-uniform molecular weight makes it difficult to experimentally and theoretically quantify the process. For example, polymeric molecules of different sizes have varying solubilities in a solvent, including SC-CO$_2$. We did a parallel study of dimethyl terephthalate (DMTE), the model compound of PET/POET. DMTE has the same structure as the unit on PET/POET (Figure 5.1). They should have similar spectroscopic behaviors, which could help us to identify the spectra and understand the structure of the solutes in SCFs.
An *in-situ* high-pressure fluorescence view cell was built to get qualitative information on the SC-CO$_2$/polymeric surfactant interactions. Based on the information from aqueous solution application, the purpose of the investigation is to determine whether the same structural parameters (PET/POET ratio and PEG length) are important for excimer formation and ultimately whether the structure of PET/POET in aqueous solutions can be duplicated and exploited in the CO$_2$-based process.

PET/POET does dissolve in SC-CO$_2$ but the solubility is fairly low. However, even with this low solubility, SC-CO$_2$ impregnation could make polyester fabric (which is otherwise hydrophobic) wettable. DMTE could dissolve very well in SC-CO$_2$ and has an absorption peak at 237nm and 295nm. The surprising result is that DMTE becomes non-fluorescent in SC-CO$_2$. A systematic study of DMTE fluorescent behaviors in solutions indicates that the dielectric constant dramatically changes the fluorescence intensity of DMTE.

5.2 Background

The application of spectroscopic analysis improved our understanding of fluid properties and molecular interactions between SCFs and other substances. Several literature studies using fluorescence and UV absorption spectroscopy in SCF research will be introduced.

Johnston (Kim and Johnston 1987) investigated the local composition of SC-CO$_2$ and a cosolvent about a solute at infinite dilute solutions. They reported that solvent molecules accumulate around solute molecules and the clusters of solvent about the solute are enriched in cosolvent.
Brennecke and coworkers (1990) investigated the naphthalene/triethylamine exciplex and pyrene excimer formation in supercritical solutions using in-situ high-pressure fluorescence spectroscopy. Pyrene forms excimers even in very dilute SCF solutions in SC-CO$_2$, whereas in aqueous solution it occurs at much higher concentration. According to the general rule that intermolecular excimer formation is diffusion controlled, this observation confirms the dramatically increased diffusivity in the immediate vicinity of the critical point.

Tomasko and his colleagues (1993) investigated the structure and interactions in cosolvent-modified supercritical fluid. They used solutes that exhibit well-characterized spectral responses to an organized, hydrogen-bonded solvent environment in liquids. The band shift and spectral intensity change was recorded to reveal the microenvironment of cosolvent-modified supercritical fluids. They found that when cosolvent is added, the governing reason for solubility enhancement in SCF is not the hydrogen bonding which has been frequently observed in liquid solvents. It is due to density or dielectric enhancement.

Niemeyer et al (1997, 1998) report quantitative data on the local microenvironment surrounding pyrene dissolved in water and several supercritical alkanes (n-pentane, n-hexane, n-heptane, n-octane). Steady-state fluorescence measurements indicate that there is an increase in local fluid density surrounding the pyrene molecules relative to the fluid bulk density. The maximum relative local density augmentation increases with increasing alkane chain length.
Kazarian and coworkers (West et al. 1998, Kazarian et al. 1997, 1998, Brantley, 1999) applied UV absorption spectroscopy to quantify the polymer dyeing process. The details of the experiment have been discussed in chapter 4.

Carbon dioxide in the liquid and supercritical fluid states is a possible replacement for toxic organic solvents. However, nonvolatile hydrophilic substances such as proteins, ions, and most catalysis are insoluble. The formation of aqueous microemulsion droplets in a carbon dioxide-continuous phase with a surfactant could overcome this limitation. (Johnston et al 1996) The reverse micelles are micro reactors. Spectroscopic methods are extensively used to study the formation of reverse micelles in CO$_2$ and the microenvironment inside the micelles. Clarke et al (1997) have shown that an aqueous solution of potassium permanganate (KMnO$_4$) could be dispersed in SC-CO$_2$ when water/SC-CO$_2$ microemulsions stabilized by an ammonium carboxylate perfluoropolyether (PFPE) surfactant. Bright and coworkers (Kane et al 2000) investigated enzyme-induced reaction within the water core of reverse micelles that have been formed in SC-CO$_2$. Fulton and his colleagues (Ji et al 1999) applied UV-VIS to study the synthesis and disperse of silver nanoparticles in water-in-CO$_2$ microemulsion.

All of the cited research indicates that fluorescence and UV absorption are powerful tools for investigating SCF systems.
5.3 Experimental

5.3.1 Materials

Dimethyl terephthalate is from Aldrich (18512-4) and used as received. PET/POET was originally from Dupont (Zelcon 4780) and purified and characterized by Dr. Chihae Yang.

5.3.2 Build the high pressure view cell

The design of the view cell is from Dr. Joan Brennecke at the University of Notre Dame. The cells were built by Senior Instrument Maker Paul Green in our department. The design of the cell is shown in Figure 5.3.

Three faces of the cell can hold 1/4" thick and 1/2" diameter quartz windows. Modification made to the original design are that only two faces of our cells are packed with quartz discs and the third one holds a hex-head plug. The plug is a stainless steel threaded high-pressure fitting sealed by a rubber o-ring. The quartz windows are sealed with brass and lead rings. Details about how to seal the window can be found in Appendix A.3. While the quartz windows are packed permanently, the plug can be removed, which makes cleaning the cell very convenient. The plug has some space on the inner side that can hold a piece of polymer fabric.

One side of the cell contains a 1/8" threaded hole designed for placing a resistance temperature detector (RTD). The top face contains two 1/16" threaded holes, which are the inlet and outlet for the fluids.

The system to which the cell is attached to consists of the high-pressure view cell, the digital pressure gauge, 1/16" and 1/8" O.D. stainless steel tubing and several valves. The temperature is controlled using a Dwyer temperature controller equipped with
Tapco cartridge heaters. The temperature controller is modified with a big relay to protect it from sudden voltage changes. The cartridge heaters are placed in the holes at the four corners of the cell. A ground wire is added to the heater for a safety precaution. The temperature is measured with a platinum resistance thermometer in direct contact with the fluid inside the cell. The temperature is maintained to ±0.1°C.

Figure 5.4 is the apparatus for in-situ UV absorption measurement. The regular front wall on the spectrophotometer is replaced with a special box with some expanded volume for the compartment. The regular cuvette holder is replaced with a custom one that can hold the cell in place (see Figure 5.5). The view cell is placed in the compartment and sitting in the middle of the light path. A piece of rubber and some dark colored tape are used to seal the hole on the special box where the tubing and cables pass through. It is hard to seal the fittings connected to the view cell which include two 1/16” fittings on the top and one 1/8” fitting on the side. Therefore, the system is designed to avoid removing them frequently.

For the fluorescence system, there are access holes on the front and the left side of the compartment. The covers on the holes are removed and the tubing and cables can go through. A customer-designed holder (Figure 5.6) is used to replace the regular cuvette holder. The positions of two convex mirrors in the compartment need to be adjusted to maximize the fluorescence intensity. For the in-situ front surface fluorescence experiment reported in chapter 4, a small holder is designed to hold the polymer films in the view cell and expose the surface of the film 30° to the input light (Figure 5.7).

The volume of the entire cell system is calibrated to be 4.7 ml for the UV system and 4.5 ml for the fluorescence system. The calibration process is as follows: first
evacuate the cell and connect it to a syringe pump that is filled with liquid acetone; run the pump at a very slow flow rate (e.g. 1ml/min) and watch the outlet of the cell system; when the first liquid drop appears, stop the pump. The volume change on the pump is the volume taken up by the cell system. This volume includes the inner volume of the cell, the volume taken up by the length of 1/16” tubing and the dead volume of the pressure gauge.

Between different runs, the cell can be taken away from the spectrophotometer by disconnecting the 1/16” fittings on the inlet and outlet line and pulling off the cartridge heaters from the holes. The RTD is connected to the cell all the time and its cable can be disconnected from the temperature controller.

Parts for building the view cell and the control system are listed in the appendix (Table A.1).

5.3.3 PET/POET solubility in SC-CO$_2$

The apparatus in Figure 3.3 and the same procedure for NBD solubility measurement was used to measure the solubility of PET/POET in SC-CO$_2$. The only difference is that the quantity of PET/POET dissolved in SC-CO$_2$ was measured directly from the weight change of the metering valve and the filter before and after the experiment.

5.3.4 Polyester fabric surface modification

The same apparatus and procedure used in NBD impregnation experiment was applied. Since the fabric is soft, it tends to stick to the wall. A small tool made of stainless steel wire was used to hold the fabric in place.
The contact angle was measured as follows: a water drop with approximately 10\(\mu\)l volume was placed on the fabric surface using a syringe; a picture was taken with a CCD camera (Cohu, model 4915-2000/0000) and the contact angle was calculated by analyzing the water drop.

5.3.5 *In-situ* UV absorption and fluorescence spectroscopy

DMTE and PET/POET were dissolved in dichloromethane respectively to make solutions. A certain amount of the solution was loaded to the view cell and the solvent was evaporated. Then, the cell was pressurized with CO\(_2\) to make a supercritical solution. The spectra were collected using the spectrophotometers.

In fluorescence studies, the cell was purged with nitrogen to remove oxygen before pressurization. An oxygen trap (Alltech Associates, Inc., U8115) was attached to the bone-dry CO\(_2\) cylinder to get rid of any trace amount of oxygen.

The dissolution of PET/POET into SC-CO\(_2\) could be monitored using the kinetics function on the UV/VIS spectrophotometer. In order to observe the pressure effect on solubility, an excess amount of PET/POET was loaded in the view cell. The cell was kept at a certain temperature but the pressure was changed after the dissolution curve leveled off at one pressure.

5.3.6 Kinetics of polymer surface adsorption

A known amount of polymer film or fabric was loaded in the hex-head plug. DMTE or PET/POET was loaded at the bottom of the cell (Figure 5.8). The cell was then pressurized with CO\(_2\) and the UV absorption of the fluid phase was recorded versus time.
5.4 Results and discussion

5.4.1 PET/POET solubility in SC-CO$_2$

The solubility of PET/POET has been shown in Figure 5.9. The solubility of PET/POET in CO$_2$ is very low which is not surprising because PET/POET is a polymeric material with a molecular weight around 2400.

After the solubility measurement, PET/POET collected from the metering valve and the filter (hereafter referred to as the “extract”) was dissolved in water to make a solution. The fluorescence emission of this aqueous solution is in Figure 5.10. There are two peaks in the original PET/POET aqueous solution. The peak located at 320nm is the monomer peak and the peak at 380 is the excimer peak. It is primarily intramolecular excimers because the terephthalate rings separated by ethylene or oxyethylene groups could entangle with each other. In the spectrum of the extract, it is obvious that the excimer peak disappeared and the monomer peak is dominant. This implies that CO$_2$ preferentially dissolved the low molecular weight PET/POET and left the high molecular weight molecules that are responsible for excimer formation in the vessel.

5.4.2 Polyester fabrics surface modification

PET/POET was applied as the modifier to change the wettability of polyester fabric. Figure 5.11 is the SEM picture of the fabrics. The contact angle was measured to be 130°. After impregnated with PET/POET/CO$_2$ solution at 35°C and 170 bar for 1 hour, the fabric became wettable. When a water drop was put on the surface, it spread spontaneously.
5.4.3 UV absorption of DMTE and PET/POET in SC-CO$_2$

Figure 5.12 shows the UV absorption of DMTE in hexane, CO$_2$ and water. The intensity is an arbitrary scale. There are two absorption bands. One has a peak at 236nm and the other one is located around 285-290nm. The intensity of the 236nm peak is much higher than the other peak. The two bands correspond to different configurations of DMTE molecules. Specifically, they represent different orientations of the carbonyl bond relative to the π ring surface within a DMTE molecule. There is a slightly red shift in the 236nm peak when the solvent has a larger polarity.

Beer’s Law ($I = εbc$) describes the linear relationship between absorption and solution concentration. It holds for many solutions at a certain concentration range (but not usually hold for condensed solution). ε is the molar absorbtivity which is a function of solute properties, solvent properties and the wavelength. DMTE was dissolved in SC-CO$_2$ at different concentrations and the absorption was measured. From Figure 5.13, it can be seen that the absorption of DMTE in CO$_2$ obeys Beer’s Law. At a certain concentration, changing the pressure does not affect the intensity very much.

Figure 5.14 is the absorption of PET/POET in CO$_2$ and in water. The bands are located at the same positions as DMTE and show similar red shift.

The dissolution of PET/POET into CO$_2$ can be monitored by collecting the UV absorption versus time. Figure 5.15 shows the PET/POET concentration change in CO$_2$ after the cell is pressurized. If the same experiment is repeated at different pressure, the pressure effect on solubility can be demonstrated. Figure 5.16 is the raw data. One stage is corresponding to one pressure. Figure 5.17 summarizes the data from Figure 5.16. We can see a clear trend of increase in absorption with increasing pressure. Since the
solubility of PET/POET is low, even at equilibrium state, the absorption should still follow Beer's Law. Therefore, figure 5.17 could be considered as the relative solubility at different pressures. In order to find the absolute value of PET/POET solubility in CO$_2$, the absorption needs to be calibrated. It is a very difficult job if not impossible because it is hard to find of the PET/POET quantity in CO$_2$ phase. The method used for loading certain amount of DMTE does not work for PET/POET because no matter how much is loaded in the cell, there is always some high molecular weight PET/POET left on the bottom.

5.4.4 Fluorescence of DMTE in SC-CO$_2$

Figure 5.18 is the emission and excitation spectra of DMTE in methanol. The excitation spectrum is similar to the UV absorption spectrum but the intensity ratio of the two peaks is reversed. The molecule shows fluorescence at 320nm.

Surprisingly, DMTE is not fluorescent when dissolved in CO$_2$. In order to find the reason for this interesting phenomenon, DMTE was dissolved in three solvents with different dielectric constant and viscosity. The concentration of each solution was kept the same (1.0e-5 mol/l). Figure 5.19 shows the fluorescence emission. It can be seen that the band position keeps the same for different solutions. When the intensity is drawn versus the dielectric constant of each solvent (Figure 5.20), it is obvious that as the dielectric constant of the solvent decreases, the emission intensity decreases dramatically. We suggest that the small dielectric constant of CO$_2$ causes fluorescence disappeared. In Chapter 3, the effect of dielectric constant on band shift has been discussed. For NBD, the emission red shift was observed when dielectric constant increases. For DMTE, the solvent dielectric constant does not affect the band position.
but the band intensity. This phenomenon is not expected but understandable because of the complexity of the interactions between a fluorophore and its surrounding environment.

5.4.5 Kinetics of polymer surface adsorption

The DMTE concentration in CO$_2$ was collected versus time with the presence of a piece of polyester fabrics in the view cell. It is expected that the dissolution of DMTE into CO$_2$ is much faster than the adsorption onto polymer surface. Therefore, the UV absorption increases fast upon pressurization. As adsorption onto the fabric surface occurs, the concentration in the fluid phase is expected to decrease. However, the results in Figure 5.21 did not show any apparent change in the UV absorption. Since we are monitoring the depletion of DMTE in the fluid phase, if the quantity of DMTE adsorbing onto the surface is very small, the concentration change in the fluid phase would be undetectable.

In order to increase the DMTE quantity adsorbed, more polyester fabric was loaded into a vessel and the vessel was attached to the view cell. The diffusion of DMTE from the cell to the vessel was tested before loading any fabrics. It turned out that since the outlet tubing is only 1/16” O.D., the diffusion of DMTE from the cell to the vessel is very slow. No further adsorption experiments were conducted.

5.5 Conclusion

Fluorescence and UV-VIS spectroscopy appear to be powerful tools for SCF process investigation. It allows us to monitor the process on-line. However, the complexity of spectral phenomena brings some uncertainty to the application of these
methods. Usually, a careful study of the spectral behaviors of a fluorophore is performed in typical solvents before applying it in a SCF system. Our result in DMTE and some previous work have shown that the behaviors of the fluorophore in SCFs could be completely different from its liquid solutions. The key problem of using these analytical methods is to find an appropriate probe molecule that is spectroscopically active in a supercritical fluid environment.

Beer's law holds for SCF solution. The absorption can be converted to concentration and UV-VIS can be applied to measure the solubility of some compounds in SCFs. The challenge is to calibrate the relationship between the absorption and the concentration.

Finally, CO$_2$ preferentially extracts low molecular weight polymer, which makes the quantification of the process difficult. The polymeric surfactant could be applied successfully in tailing polymer wettability but not as a probe for theoretical study.
Figure 5.1 The structure of poly (ethylene terephthalate)/poly (oxyethylene terephthalate) and dimethyl terephthalate
Figure 5.2 PET/POET fluorescence emission in aqueous solution
(PET/POET concentration = 56ppm)
Note: The double lines represent stainless steel tubing and the single line are cables.

**Figure 5.3 The setup for *in-situ* UV-VIS**
Figure 5.4 View cell design
Figure 5.5 The holder for the UV-VIS view cell

Note: 1) All dimensions are in inches
2) Material: sheet iron. Thickness: 0.04 inch
3) Two bolts go through the 0.18 inch diameter holes. Cartridge heaters inserted to the cell go through the 0.27 inch diameter holes.
Note: 1) All dimensions are in inches
2) Material: aluminum painted black
3) A bolt was used to screw the two walls together in order to hold the cell

Figure 5.6 The holder for the fluorescence view cell
Note: 1) All dimensions are in inches.
2) Material: aluminum painted black

Figure 5.7 The holder inserted into the fluorescence view cell for front-surface study
Figure 5.8 The diffusion path of modifier in UV-VIS cell for the surface adsorption study
Figure 5.9 The solubility of PET/POET in CO₂ at 40°C
Figure 5.10 Fluorescence spectra of PET/POET before and after CO₂ extraction
Contact angle = 130°

Figure 5.11 SEM of polyester fabrics and its contact angle
Figure 5.12 UV spectra of DMTE
Figure 5.13 UV absorption intensity versus the concentration of DMTE in CO$_2$
Figure 5.14 UV spectra of PET/POET
Figure 5.15 Dissolution of PET/POET into CO₂
Figure 5.16 PET/POET dissolution curve (The pressure in bar is labeled)
Figure 5.17 PET/POET solubility versus pressure
Figure 5.18 DMTE fluorescence spectra in methanol
Figure 5.19 DMTE fluorescence emission in different solvents (with N₂ purge).
Figure 5.20  Fluorescence intensity of DMTE versus dielectric constant of the solvent
Figure 5.21 DMTE concentration in CO$_2$ during the adsorption process
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Using SC-CO$_2$ as the only solvent to incorporate surfactant-like probe molecules or polymeric surfactant into polymers has been investigated. The solubility data show SC-CO$_2$ can penetrate into polypropylene and PMMA films and act as a carrier for the modifier in modification process. Semi-crystallized polypropylene can absorb CO$_2$ up to 5.5 wt% while amorphous PMMA can take up 25 wt% of CO$_2$ under experimental conditions.

Although the solubility of NBD in SC-CO$_2$ is low, the loading of NBD molecules onto polymers is significantly improved compared with solution coating. The partitioning coefficient from SCF modification is 1.5 – 2 orders of magnitude smaller than the solution coating, which indicates a more effective process. SC-CO$_2$ offers a unique balance in impregnating modifiers into polymers by swelling the matrix and maintaining relatively weak solvent power for the modifier. Kinetic studies confirm that the diffusivity of the modifier in polymers is improved by CO$_2$ swelling. The solute diffusivity in CO$_2$-swollen polypropylene is $9 \times 10^{-13}$ m$^2$/s from our work while it is approximately $1 - 6 \times 10^{-14}$ m$^2$/s in polypropylene at ambient conditions.
Post-treatment characterization of the polymers using microscopy techniques reveals that the distribution of modifiers highly depends on the polymer properties and polymer/CO₂ interactions. Supercritical modification gives an even modifier distribution in polypropylene even though the modifier/polymer interactions are not favorable. In glassy polymers like PMMA, the polymer morphology and the modifier distribution are determined not only by the impregnation process but also the pressure release rate. The plasticization of PMMA by CO₂ generates an uneven distribution of modifiers with high concentrations at the edge and in the foamed bubbles. Since there are favorable interactions between the modifier molecule and PMMA chain units, the modifier partitioning to PMMA is much higher than polypropylene.

Two-step re-extractions of impregnated polymers with a non-swelling solvent and a swelling agent imply that SCF impregnation provides a tailored surface with good modifier durability. Slow migration to the surface on the order of months was observed for polypropylene and NBD system after SCF modification.

In-situ spectroscopic methods are good tools for investigating systems under supercritical conditions. The UV-VIS absorption of spectroscopically active compounds in SC-CO₂ follow Beer’s law and the pressure has little effect on the absorptivity of NBD at working conditions (100 – 200 bar). The solubility of the compound can be quantified using UV-VIS with careful calibration. Fluorescence of solutes in SC-CO₂ could demonstrate completely different behaviors from typical solvents. One example in this work is the complete absence of fluorescence emission from dimethyl terephthalate that is fluorescent efficiently in liquid solvents. The small dielectric constant is suggested to be responsible for the significant quenching. When applied to
solid phase, data from both spectroscopic methods provide good qualitative information about the molecular interactions but lack quantitative meaning.

This study demonstrated the principle of a new process to coat and impregnate synthetic materials using a supercritical solvent and investigated different factors that contribute to the final distribution of modifiers in the materials.

6.2 Recommendations

After nearly 10 years of investigation, researchers have demonstrated the promising features of supercritical fluids as applied to polymer impregnation. There is rapidly growing interest in its applications grows fast in various fields with a trend recently toward biomedical materials. Still, there is room for fundamental and practical research on this subject.

The high-pressure environment of supercritical fluids makes most analytical methods that work well under ambient conditions unavailable. Modification of the instruments or development of new quantification methods is required. *In situ* UV-VIS and *in situ* FTIR could be two examples. Therefore, the challenge in doing experimental research on supercritical fluids comes from the necessity of exploring an appropriate analytical method and investigating the supercritical system at the same time.

Some fundamental problems about this technique have been investigated but far less than well solved. One example is how the structure and size of the solute molecule affect its equilibrium and kinetic behaviors. One approach to this problem could be the use of a series of compounds with similar structures and various sizes or slightly
different functional groups as the modifiers. A good reference with similar consideration in experimental design was published by Brantley in 1999.

Another interesting fundamental problem is the solute diffusivity in polymers in supercritical atmosphere. It could be seen from table 4.1 and 4.2 that the data are different by several orders of magnitude. A homogeneous phase is necessary for the constant diffusivity assumption in Fick's law. However, the fact is CO₂ takes time to penetrate into polymers and changes polymer morphology, which challenges this assumption. All of the post-treatment quantification methods neglect this problem. West (1998) tried to solve this problem by maintaining the cell loaded with polymer at 75 bar for 3 hours before any impregnation took place. However, the CO₂ adsorption in polymers may change much when the system is pressurized to 100 or 200 bar. There is another problem neglected by almost everyone about applying Fick's law. When the solute concentration on the polymer surface is different from the fluid phase concentration, there should be a coefficient that accounts for this deviation. Therefore, the boundary condition at x=0 should be C₀=kC_fluid. In all cited works, C₀ is set to be equal to C_fluid. Therefore, the diffusivity correlated is not the true D. If there are favorable interactions between the solute and the polymer, this problem will be severe. This might be one of the reasons that the diffusivities in literature are so much different. In table 4.1 and 4.2, it seems that diffusivities measured by on-line methods (West et al 1998, Chapman et al 1996) are much smaller than diffusivities from off-line methods.

A possible experiment is to use the microbalance in our lab to measure the loading of modifiers on line. Since the sensitivity of the balance is much less than the fluorescence spectrophotometer, molecules with good solubility in CO₂ should be used.
A view cell could be attached to the system and the dimension change of the polymer could be recorded and analyzed. Von Schnitzler and Eggers (1999) have published a paper using similar apparatus. Another diffusivity measurement is to use UV-VIS or fluorescence to monitor the extraction of solutes by CO\textsubscript{2} from polymers. This is a more sensitive method than the gravimetric measurement.

What does the impregnation process look like? A complete dynamic model of the impregnation process has not been developed. There are several questions involved: 1) How does the dye diffuse into the polymer? Do they accumulate at the surface to reach a constant concentration first or they are carried by CO\textsubscript{2} and diffuse into the bulk right after pressurization? 2) Are the solutes bonded to the polymer chains or they are floating in the polymer/CO\textsubscript{2} phase? 3) What happens when the pressure is released? Will the solute be carried around by CO\textsubscript{2} or trapped by the polymer matrix spontaneously upon pressure release. Chapter 4 partially answered the third question. Thermodynamics modeling or computer simulation could be applied to describe this process. Some related work has been published recently. Kumar and Colby (1996) developed a concentration fluctuation model to predict the impact of concentration heterogeneities that are present in any mixture on dynamic properties such as viscosities and diffusion coefficients. Hofmann et al (2000) utilized Monte Carlo method to predict the small molecule diffusion in dense amorphous polysiloxanes and polyimides. Smith and coworkers (2000) combined neutron scattering studies and quantitative atomistic molecular dynamics simulations to describe the melt dynamics of polyethylene and polybutadiene. Nauman et al (2001) reported a simulation method to predict the nonlinear diffusion and phase separation in binary and ternary polymer systems.
Compared with thermodynamics modeling, computer simulation usually requires few adjustable parameters. However, the complexity in developing a simulation method makes it not feasibly accessible. It is suggested as a possibility to describe the polymer impregnation process but not recommended as a near future project in our group.

The research in polymer impregnation using supercritical fluids seems quite experimentally concentrated in academia. More generous models need to be developed to correlate or predict the solute partitioning or diffusivity in polymers. It is suggested for our research group that the S-L equation be re-written with a user-friendly interface. Then everyone could have an easy access to it and work on more advanced modeling.

With respect to applications, SCF impregnation could be used to incorporate small drugs into polymers. The key problem is to dissolve the solute in SC-CO$_2$. Cosolvents may be used if necessary. It is suggested to investigate the solubility of the drugs in CO$_2$ first. *In-situ* UV-VIS or fluorescence spectrophotometers could be used as a screening technique to understand the solute solubility in CO$_2$ or the cosolvent system. No calibration is necessary. The spectral intensity should be proportional to the solubility.

In some applications, it is desirable to incorporate protein with active functions into polymer matrix. Even with the aid of cosolvent, protein is not soluble in most supercritical fluids. One approach to solve this problem has been discussed in our group. The idea is to dissolve the protein in water and use SC-CO$_2$ as a swelling agent only. The protein aqueous solution is placed in a cell connected to another cell where the polymer is loaded. The two cells are mounted in the water bath vertically with the protein cell on the top. The temperature of the bath is well controlled. At the beginning, the valve between the protein cell and the polymer cell is closed. After the system is at
SC-CO₂ atmosphere, the aqueous solution is allowed to flow into the polymer cell by gravity to contact the CO₂-swollen polymer. Presumably, the protein could be infused into the polymer. Upon depressurization, CO₂ and water would escape from the polymer substrate at different rates while the protein is trapped in the polymer matrix. It is questionable what would happen when the swollen polymer contact the aqueous solution. It is unlikely that the aqueous solution can tunnel into the swollen polymer because of the large surface tension of water. It is possible that the solution will diffuse into the matrix but the morphology of the polymer soaked in the aqueous solution is unknown.

Microemulsions in SCFs could be applied to solvate proteins into SCFs. Gale et al. (1987) first reported that an anionic surfactant, bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) could form micelles in various compressed-gas solvents near their critical point. Since then, extensive research has been done to describe phase behaviors of these systems and explore the potential applications. Bartscherer et al (1995) wrote a review on this topic with great details. It has been demonstrated that these solutions could accommodate significant amounts of water and solubilize polar solutes and even high molecular weight proteins. (Smith et al 1990, Johnston et al 1996, Jackson and Fulton, 1996) It is worth a try to deliver proteins solubilized in SCF/microemulsion solutions to porous or well-swollen polymers.
APPENDIX A

MIXING RULES FOR SANCHEZ-LACOMBE EQUATION

1. The basic equation of state is given by:

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

2. The reduced parameters for a pure substance are defined as:

\[ \bar{P} = \frac{P}{P^*} \]
\[ \bar{T} = \frac{T}{T^*} \quad T^* = \frac{P^* v_0}{R} \]
\[ \bar{\rho} = \frac{\rho}{\rho^*} \quad \rho^* = \frac{M}{v^*} \]
\[ \bar{v} = \frac{v}{v^*} \quad \bar{v} = 1/\bar{\rho} \]

\( R \) is the gas constant. \( v_0 \) is the volume of a lattice site. \( v^* \) is the hard-core molecular volume. \( M \) is the molecular weight. The size parameter \( r \) is related to the equation-of-state by:

\[ r = \frac{v^*}{v_0} \quad r = \frac{P^* v^*}{RT^*} \]

Thus, a pure component is completely characterized by three parameters \( P^*, T^* \) and \( \rho^* \).

3. For multi-component mixtures, these parameters are determined from pure-component parameters using the following mixing rules:
(1) The mixing rule for is based on the assumption that the closed-packed molecular volume of each component is conserved. Therefore:

\[ \frac{1}{v^*} = \sum_i \frac{\phi_i}{v_i^*} \]

\(\phi_i\) represents the closed-packed volume fraction of the \(i\)th component in the mixture at the incompressible state. It’s given by:

\[ \phi_i = \frac{m_i / \rho_i^*}{\sum_i m_i / \rho_i^*} \]

where \(m_i\) is the mass fraction of the component \(i\).

(2) \(P^*\) for the mixture is given by:

\[ P^* = \sum_i \phi_i P_i^* - RT \sum_i \sum_j \phi_i \chi_{ij} \]

where \(\chi_{ij}\) counts for the interactions between \(i\) and \(j\) molecules. It is given by:

\[ \chi_{ij} = \frac{P_i^* + P_j^* - 2(P_i^* P_j^*)^{1/2}(1 - \delta_{ij})}{RT} \]

\(\delta_{ij}\) is the interaction parameter which is usually a small quantity.

(3) \(T^*\) is given by:

\[ T^* = \frac{P^* v_o}{R} \]

where \(v_o\) is calculated from the following equation:

\[ \frac{1}{v_o} = \sum_i \phi_i \left( \frac{P_i^*}{RT_i^*} \right) \]

4. The chemical potential of component \(i\) in a multi-component system is calculated using the following equation:
\[
\frac{\mu}{RT} = \ln \phi + (1 - \frac{v_i^*}{v_i^*}) + \tilde{\rho} v_i^* \left( \sum_j \phi_j \chi_j - \sum_i \sum_j \phi_j \chi_j \right) \\
+ r_i \left\{ \frac{-\tilde{\rho} + \tilde{P} \tilde{v}}{\tilde{T}} + \tilde{v} \left[ (1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho} \ln \tilde{\rho}}{r_i} \right] \right\}
\]

where \( \tilde{T} = T / T_i^* \), \( \tilde{P} = P / P_i^* \) and \( r_i = P_i^* v_i^* / RT_i^* \).
APPENDIX B

FORTRAN PROGRAMS

1. Program to determine $t^*$ and $p^*$ from nbd solubility data (optimizetp.for)

The core of this program is to calculate the NBD concentration in the fluid phase at a given temperature and pressure. An optimization program in the software package (Microsoft Visual Fortran) is fit outside of the core. The program applies simplex method to optimize the parameters. Some variables (FJAC(LDFJAC,N), FSCALE(M), FVEC(M), IPARAM(7), and RPARAM(7)) in the main program are parameters for the optimization program. They are not defined or used in the subroutines.

Here is a brief explanation of the subroutine functions:

FCN(M,N,X,F)

Compare the calculated solubility with experimental data. The main program will use this result to improve the values of the fitted parameters.

SOLIDINS(CF(STAR,PPRED,YPRED,NICOUNT)

Determine the NBD solubility in SCF phase by calculating the chemical potential

SLPOTREF(T,P,AMW,PS,TS,RHOS,POTREF)

Calculate the reference state chemical potential of NBD

POT(SOLID(T,POTS)
Calculate the chemical potential of NBD in the solid phase

**SLCHEMPOT(T,P,Y,POT2,DEN,NNN)**

Calculate the chemical potential of a component in a fluid phase

**CONVERT(NTYPE,X,AMW)**

- NTYPE=1, convert mass fraction to mole fraction;
- NTYPE=2, convert the mole fraction to mass fraction.

**GETRHO (T, P, R, RHO, NNN)**

Calculate \( \tilde{\rho} \) from given \( \tilde{T} \), \( \tilde{P} \) and \( r \) using Sanchez-Lacombe basic equation of state.

There are sometimes 3 roots. If NNN=1, this subroutine will return the maximum root.

If NNN=0, it will return the minimum root.
Define variables

Input the parameter \((T^*, P^*, \rho^*)\) initial values

Input the parameter \((T^*, P^*, \rho^*)\) high and low limit

Call the optimization program "BCLSF" and "UMACH" to find optimized parameters

Output

Figure B.1 Flow chart of the main program in Optimize.for
Get initial values of the parameters (\(T^*, P^*, \rho^*\)) from the main program

Define variables

Input the experimental data: pressure (\(P\)) and NBD solubility in CO2 (\(Y\))

Call subroutine SOLIDINSCF to calculate the NBD solubility in CO\(_2\) and get a series of \(P\) and the corresponding predicted \(Y\)

Calculate the NBD solubility at experimental pressure by linear interpolation of the predicted \(Y\)

Calculate the difference (\(F\)) between the experimental \(Y\) and the predicted \(Y\) for each experimental pressure

Return \(F\) to the main program. The main program will calculate the total deviation and generate the improved \(T^*, P^*\) and \(\rho^*\)

Figure B.2 Flow chart of subroutine FCN in Optimize.for
Get NBD parameters ($T^*$, $P^*$, $p^*$) from subroutine FCN

Input $T^*$, $P^*$, $p^*$ of CO$_2$, $\delta_{ij}$, pressure range ($P_{\text{low}}$, $P_{\text{high}}$) and $T$

Give initial NBD mass fraction $Y(2)$

Call subroutine POTSOLID to calculate the NBD chemical potential in solid state

$P = P_{\text{low}}$

Call subroutine SLPOTREF to calculate the NBD potential at reference state

$J\text{FLAG}=1$

$J\text{FLAG} < 2000$

$Y(1) = 1 - (Y(2))$

Call subroutine SLCHEPOT to calculate NBD chemical potential in SCF

$\frac{\mu_{\text{SCF}} - \mu_{\text{Solid}}}{\mu_{\text{SCF}}} < 1e^{-4}$

$\mu_{\text{SCF}} - \mu_{\text{Solid}} < 0$

Figure B.3 Flow chart of subroutine SOLIDINSCF in Optimize.for
OptimizeTP.for

PARAMETER (LDFJAC=4, M=4, N=3)
REAL FJAC(LDFJAC,N), FSCALE(M), FVEC(M), IPARAM(7), RPARAM(7), X(N), XGUESS(N), XLB(N), XS(N), XUB(N)
EXTERNAL BCLS,F,UMACH
DATA XGUESS/860.5650.0,1.18/, XS/3.0E0/, FSCALE/4.0E0/
DATA XLB/200.0,1000.0,0.8/, XUB/2000.0,20000.0,2.0/
ITP = 0
IPARAM(1) = 0
CALL BCLS (F, M, N, XGUESS, ITP, XLB, XUB, X, FSCALE, IPARAM, RPARAM, X, FVEC, FJAC, LDFJAC)
CALL UMACH (2, NOUT)
WRITE (NOUT,99) X, FVEC, IPARAM(3), IPARAM(4)
99 FORMAT (' The solution is ', 3F9.4, //, ' The function ', & evaluated at the solution is ', /, 18X, 4F9.4, //, & ' The number of iterations is ', 10X, I3, '/., ' The ', & ' number of function evaluations is ', 13, /)
OPEN(UNIT=16,FILE='TEMP.OUT')
WRITE(16,99) X, FVEC, IPARAM(3), IPARAM(4)
END

SUBROUTINE FCN(M,N,X,F)
PARAMETER(MM=4,NN=3)
DIMENSION X(NN),F(MM), YEXP(MM), YCAL(MM), PPRED(50), YPRED(50)
DATA YEXP/140.2393574,154.3046617,182.4352702,209.255875/
CALL SOLIDINS CF(X,PPRED,YPRED,NICOUNT)
NPOINT=1
DO 20 I=1,MM
DO 30 J=NPOINT,NICOUNT
IF(PPRED(J).GE.PEXP(I),AND.PPRED(J).LT.PEXP(I)) THEN
SLOPE=(PEXP(J)-PPRED(J))/((PPRED(J)+1)-PPRED(J))
YCAL(I)=YPRED(J)+(YPRED(J+1)-YPRED(J))*SLOPE
GOTO 33
ENDIF
30 CONTINUE
33 NPOINT=J
IF(YCAL(I).EQ.0) THEN
WRITE(*,*) DID NOT FIND YCAL'
ENDIF
F(I)=SQRT(ABS(YEXP(I)-YCAL(I)/YEXP(I))
WRITE(*, '(F10.8,I0.1,2X,F10.8)') PEXP(I),YEXP(I),YCAL(I)
20 CONTINUE
END
SUBROUTINE SOLIDINSCF(STAR^PRED,YPREDJflCOUNT)
PARAMETER(N=^,NN=3)
DIMENSION AMW(N),TS(N),PS(N),RHOS(N),Y(N),SL(N,N)
DIMENSION PPRED(50),YPRED(50),STAR(NN)
COMMON AMW,TS,PS,RHOS,SL
DATA AMW/44.01,404.55/,TS(1)/305/,PS(1)/5745.1/,RHOS(1)/1.51/
DATA SL/4*0.0/,PLOW/120/,PHIGH/220/,PINC/20/
GASR=83.14
TS(2)=STAR(1)
PS(2)=STAR(2)
RHOS(2)=STAR(3)
T=333.15
Y(2)=2.0E-9
CALL POTSOLID(T,POTS)
P=PLOW
DO 30 ICOUNT=1,100
   CALL SLPOTREF(T,P,AMW(2),PS(2),TS(2),RHOS(2),POTREF)
   JFLAG=1
   JFLAGLIMIT=2000
   DO WHILE (JFLAG.LT.JFLAGLIMIT)
      Y(1)=1-Y(2)
      CALL SLCHEMPOT(T,P,Y,POT2,DEN,0)
      POTSCF=POT2-POTREF
      DIFF=POTSCF-POTS
      ERROR=ABS(DIFF/POTSCF)
      IF(ERROR.LT.1E-4) GOTO 50
      IF (DIFF.LT.0) THEN
         Y(2)=Y(2)*(1+0.9/JFLAG)
      ELSE
         Y(2)=Y(2)*(1-0.9/JFLAG)
      ENDIF
      JFLAG=JFLAG+1
   ENDDO
   50 IF(JFLAG.GE.JFLAGLIMIT) THEN
      WRITE(*,*) 'DID NOT CONVERGE'
   ELSE
      WRITE(*,*) 'REACH EQUILIBRIUM'
   ENDIF
   PPRED(ICOUNT)=P
   YPRED(ICOUNT)=Y(2)
   WRITE(16,200) ICOUNT,PPRED(ICOUNT),YPRED(ICOUNT),DEN,JFLAG
   IF (P.GE.PHIGIÔ GOTO 40
   P=P+PINC
30 CONTINUE
40 NCOUNT=ICOUNT
   WRITE(*,*) 'UPPER PRESSURE HAS BEEN REACHED'
RETURN
END
SUBROUTINE SLPOTREF(T, AMW, PS, TS, RHOS, POTREF)
GASR = 83.14
TR = T/TS
PR = P/PS
VO = GASR*TS/PS
VS = AMW/RHOS
RSIZE = VS/VO
CALL GETRHO(TR, PR, RSIZE, RHO, I)
VR = 1/RHO
POTREF = -RHO/TR + PR*VR/TR + (VR-1)*LOG(1-RHO) + LOG(RHO)/RSIZE
POTREF = GASR*T*RSIZE*POTREF
RETURN
END

SUBROUTINE POTSOLID(T, POTS)
HMELT = 72172.5
DELTCP = 68.7
TMELT = 384.15
GASR = 83.14
GASRI = 8.314
FTEMP = HMELT/GASRI/TMELT*(TMELT/T-1) - DELTCP/GASRI*(TMELT/T-1)+DELTCP/GASRI*LOG(TMELT/T)
POTS = -GASR*T*FTEMP
RETURN
END

SUBROUTINE SLCHEMP0T(T, P, Y, POT2, DEN, NNN)
PARAMETER (N = 2)
DIMENSION AMW(N), TS(N), PS(N), RHOS(N), CHEMP(N), SL(N, N)
DIMENSION Y(N), RSIZE(N), VO(N), VS(N), PHI(N), XP(N, N)
COMMON AMW, TS, PS, RHOS, SL
GASR = 83.14
SUMPHI = 0
SUMVS = 0
SUMVO = 0
SUMXP = 0
SUMAMW = 0
PSMIX = 0
CALL CONVERT(1, Y, AMW)
DO 5 I = 1, N
  5 SUMAMW = SUMAMW + AMW(I)*Y(I)
CALL CONVERT(2, Y, AMW)
DO 10 I = 1, N
  10 VO(I) = GASR*TS(I)/PS(I)
  VS(I) = AMW(I)/RHOS(I)
  RSIZE(I) = VS(I)/VO(I)
CONTINUE
DO 20 I = 1, N
  20 SUMPHI = SUMPHI + Y(I)/RHOS(I)
DO 30 I = 1, N
  30 PHI(I) = Y(I)/RHOS(I)/SUMPHI
SUMVS = SUMVS + PHI(I)*VS(I)
SUMVO = SUMVO + PHI(I)*VO(I)
CONTINUE
VSMIX=1/SUMVS
VOMIX=1/SUMVO
RHOSMIX=SUMAMWA^SMIX
DO 40 I=1,N-1
   DO 50 J=I+1,N
      XPIJ(J,J)=(PS(I)+PS(J)-2*SQRT(PS(I)*PS(J))*(1-SL(I,J)))/GASR/T
      XPIJ(J,I)=XPIJ(I,J)
      SUMXP=SUMXP+PHI(I)*PHI(J)*XPIJ(I,J)
   CONTINUE
50 CONTINUE
40 CONTINUE
DO 70 I=1,N
70 PSMIX=PSMIX+PHI(I)*PS(I)
PSMIX=PSMIX-GASR*T*SUMXP
TSMIX=PSMIX*VOMIX/GASR
RMIX=VSMIX/VOMIX
TR=T/TSMIX
PR=P/PSMIX
CALL GETRHO(TR,PR,RMIX,RHO,NNN)
VR=1.0/RHO
DEN=RHO*RHOSMIX
DO 80 I=1,N
   SUM1=0
   DO 85 J=1,N
      IF(J.NE.I) SUM1=SUM1+PHI(J)*XPIJ(I,J)
50      TEMP1=LOG(PHIG)+(1-VS(I)/VSMIX)
      TEMP2=RHO*VS(I)*(SUM1-SUMXP)
      TEMP3=-RHO*LOG(1-RH0)+RHO*LOG(RHO)/RSIZE(I)
      TEMP3=RHO*LOG(RHO/PS(I))/GASR/T(SMIX)+VR*TEMP3
      CHEMP(I)=GASR*T*(TEMP1+TEMP2+TEMP3)
   CONTINUE
80 CONTINUE
POT2=CHEMP(2)
RETURN
END

SUBROUTINE CONVERT(NTYPE,X,AMW)
PARAMETER (N=2)
DIMENSION X(N), AMW(N)
SUMX=0
IF(NTYPE.EQ.1) THEN
   DO 10 I=1,N
      SUMX=X(I)/AMW(I)+SUMX
   DO 20 I=1,N
      X(I)=X(I)/AMW(I)/SUMX
   ELSE
      DO 30 I=1,N
         SUMX=X(I)*AMW(I)+SUMX
      DO 40 I=1,N
         X(I)=X(I)*AMW(I)/SUMX
      ENDIF
   RETURN
END
Subroutine GETRHO (T, P, R, RHO, NNN)
Dimension ROOT(3)
RHO=0.001
STEP=0.0001
TOL=0.00001

DO 20 IJ=1,3
   ROOT(IJ)=0
DO 10 I=1,10001
   IF(RHO.LE.1.0) THEN
      F=RHO**2+P+T*(LOG(1.0-RHO)+(1.0-1.0/R)*RHO)
      IF(ABS(F).GE.TOL) THEN
         IF(((IJ.EQ.1).OR.(IJ.EQ.3)).AND.(F.LT.0)).OR.((IJ.EQ.2)
            + .AND.(F.GT.0))) THEN
            RHO=RHO-STEP
            STEP=STEP*0.1
            RHO=RHO+STEP
         ELSE
            RHO=RHO+STEP
         END IF
      ELSE
         ROOT(IJ)=RHO
         STEP=0.001
         RHO=RHO+STEP
      ENDIF
   ELSE
      ROOT(IJ)=RHO
      STEP=0.001
      RHO=RHO+STEP
   ENDIF
10 CONTINUE
5 CONTINUE
20 CONTINUE

IF(NNN.EQ.1) THEN
   DO 30 I=1,3
      IF(ROOT(I).GT.1.0) ROOT(I)=-1.0
      RHO=AMAX1(ROOT(1),ROOT(2),ROOT(3))
   ELSE
      RHO=AMIN1(ROOT(1),ROOT(2),ROOT(3))
      IF(RHO.GT.1.0) RHO=-1.0
   ENDIF
30 RETURN
END
2. Program to determine the carbon dioxide solubility in polypropylene (co2polymer.for)

This program is used to predict solubility of CO$_2$ in polypropylene when the interaction parameter is known. If the interaction parameter needs to be fit from the experimental data, the optimization program used in "OptimizeTP.for" can be attached outside of this program.

Both the SCF phase and the polymer phase are considered as a binary phase. It makes the program to converge faster than considering the SCF phase as a single-component phase. The solubility of polymer in the SCF phase is very small. In order to focus on the CO$_2$ solubility, the variable named POLYFLAG is used to control the calculation. When the polymer concentration (Y2) in SCF phase is very small, POLYFLAG equals 1. The following calculation will keep Y2 a constant and improve CO$_2$ solubility value.

A series of pressures and corresponding solubility could be calculated. They are compared with the experimental data.
Figure B.4 Flow chart of the main program in CO2polymer.for
Input Data File for CO2polymer.for (PP.dat)

******************************************************************************
*                                                                      *
44.01
305  5745.1  1.51
586000
770.9  2811  0.852
0.103
40
10  260  10

******************************************************************************
*                                                                      *
The values are corresponding to:

CO\textsubscript{2} molecular weight (g/mol)
$T^*$(K) $P^*$ (bar) $\rho^*$ (g/cm$^3$) ------ CO\textsubscript{2}

PP molecular weight (g/mol)
$T^*$ (K) $P^*$ (bar) $\rho^*$ (g/cm$^3$) ------ Polypropylene

Interaction parameter ($\delta_\eta$)

Temperature (°C)

Low pressure limit (bar) high pressure limit (bar) interval
PARAMETER(N=2)
DIMENSION H(N,1000),Q(N,1000),POTV(N),POTL(N),TEST(N)
DIMENSION AMWN(N),TS(N),PS(N),RHOS(N),X(N),Y(N),U(N),V(N),
+ SL(N,N),RSIZE(N)
DIMENSION PRESSURE(106),XCO2(100)
COMMON/SANCHEZ/AMW,TS,PS,RHOS,RSIZE,SL
OPEN(UNIT=15,FILE='PP.DAT',STATUS='OLD')
OPEN(UNIT=16,FILE='TEMP.OUT')
GASR=83.14

DO 10 I=1,N
   READ(I5,*)AMW(I)
   READ(I5,*) TS(I),PS(I),RHOS(I)
10 CONTINUE

DO 50 I=1,N-1
   DO 60 J=I+1,N
      READ(15,*)SL(I,J)
      SL(J,I)=SL(I,J)
60 CONTINUE
50 CONTINUE

READ(I5,*)T
READ(15,*) PLOW,PHIGH,PINC
T=T+273.15
WRITE(16,*) T=', T, 'K', SL(1,2)

WRITE(*,12)
WRITE(*,13)
WRITE(16,12)
WRITE(16,13)
12 FORMAT(//,1X,'X(1)',8X,'Y(2)',8X,'PRESSURE',6X,
+ 'DEN LIQUID',5X,'DEN VAPOR',2X,'#ITERATIONS')
13 FORMAT(24X,'(bar)',8X,'(g/cc)',4X,'(g/cc)')

H(1,1)=20.0
H(2,1)=0.005
P=PLOW
DP=PINC

Do 20 I=1,100
   DO 30 J=1,2000
      X(2)=(1.0-H(J,FLAG))/(H(2,JFLAG)-H(1,JFLAG))
      X(1)=1.0-X(2)
      IF((X(1).LT.0).OR.(X(1).GT.1))GOTO 115
      Y(1)=H(J,FLAG)*X(1)
      Y(2)=1.0-Y(1)
      IF(Y(2).LE.5.E-4)POLYFLAG=1
      CALL SLCHEMPOT(T,P,Y,POTV,DENV,0)
      CALL SLCHEMPOT(T,P,X,POTL,DENL,1)
      Q(J,FLAG)=EXP((POTL(1)-POTV(1))/(RSIZE(1)*GASR*T))
      Q(2,FLAG)=EXP((POTL(2)-POTV(2))/(RSIZE(2)*GASR*T))
      Q(2,FLAG)=EXP((POTL(2)-POTV(2))/(RSIZE(2)*GASR*T))
115  
20 CONTINUE
TEST(1)=ABS(Q(1,JFLAG)-1.0)
TEST(2)=ABS(Q(2,JFLAG)-1.0)
IF(POLYFLAG.EQ.1) TEST(2)=0
IF(TEST(1).GE.1.E-4.OR.TEST(2).GE.1.E-4) THEN
   H(1,JFLAG+1)=H(1,JFLAG)*Q(1,JFLAG)
   H(2,JFLAG+1)=H(2,JFLAG)*Q(2,JFLAG)
   IF(POLYFLAG.EQ.1) H(2,JFLAG+1)=H(2,JFLAG)
ELSE
   GOTO 35
ENDIF
30 CONTINUE
WRITE(*,*) THE TIE LINE DID NOT CONVERGE!
GOTO 115
35 DPOLD=DP
DP=PINC
IF(P.LE.50.0) THEN
   DP=10
ELSE
   IF(H(2,JFLAG).GT.0.4) DP=5.0
   IF(H(2,JFLAG).GT.0.6) DP=3.0
   IF(H(2,JFLAG).GT.0.8) DP=1.0
   IF(H(2,JFLAG).GT.0.95) GOTO 75
ENDIF
SS2=X(2)+DP*(X(2)-U(2))/DPOLD
TT2=Y(2)+DP*(Y(2)-V(2))/DPOLD
IF((ICOUNT.EQ.1) TT2=Y(2)
IF((ICOUNT.EQ.1) SS2=X(2)
TT1=1.0-TT2
SS1=1.0-SS2
H(1,1)=TT1/SS1
H(2,1)=TT2/SS2
U(1)=X(1)
U(2)=X(2)
V(1)=Y(1)
V(2)=Y(2)
WRITE(16,85) X(1),Y(2),P,DENL,DENV,JFLAG
85 FORMAT(1X,F8.6,F8.6,4X,J?82,5X,F9.3,5X,F9J,6X,I5)
IF(P. GE. PHIGH) THEN
   WRITE(*,*) UPPER PRESSURE BOUND REACHED'
   GOTO 115
ENDIF
PRESSURE(ICOUNT)=P
XCO20COUNT)=X(l)
P=P+DP
20 CONTINUE
75 WRITE(*,*) NEAR THE MIXTURE CRITICAL POINT'
115 WRITE(*,116) THE PROGRAM IS COMPLETED'
116 FORMAT(///,8X,'THE PROGRAM IS COMPLETED')
WRITE(16,77)
77 FORMAT(///,1X,P(bar),5X,'Xexp(wf)',4X,'Xcal(wf)'),
CALL COMPARE(PRESSURE,XCO2,ICOUNT,ERROR)
173
SUBROUTINE COMPARE(PRESS,XCO2,ICOUNT,ERROR)
DIMENSION PRESS(100),XCO2(100),XDATA(20),PDATA(20),XPRED(20)
OPEN(UNIT=12,FILE='EXPERIMENT.DAT',STATUS='OLD')
READ(12,*) NDATA
DO 10 I=1,NDATA
   READ(12,*) PDATA(I),XDATA(I)
10 CONTINUE
NPOINT=1
ERROR=0
DO 20 I=1,NDATA
   DO 30 J=NPOINT,ICOUNT
      IF(PRESS(J+I).GE.PDATA(I).AND.PRESS(J).LT.PDATA(I)) THEN
         SLOPE=(PDATA(I)-PRESS(J))/(PRESS(J+I)-PRESS(J))
         XPRED(I)=XCO2(J)+(XCO2(J+I)-XCO2(J))*SLOPE
         GOTO 33
      ENDIF
30 CONTINUE
33 ERROR=ERROR+ABS(XPRED(I)-XDATA(I))*2/(XPRED(I)+XDATA(I))
   NPOINT=J
20 CONTINUE
ERROR=ERROR/NDATA
DO 40 I=1,NDATA
40 WRITE(16,88) PDATA(I),PDATA(I),XPRED(I)
88 FORMAT(F6.2,4X,F8.6,4X,F8.6)
RETURN
END

SUBROUTINE SLCHEMPOT(T,P,Y,CHEMP,DEN,NNN)
PARAMETER (N=2)
DIMENSION AMW(N),TS(N),PS(N),RHOS(N),CHEMP(N),SL(N,N)
DIMENSION Y(N),RSIZE(N),VO(N),VS(N),PHI(N),XPJ(N,N)
COMMON/SANCHEZ/AMW,TS,PS,RHOS,RSIZE,SL
GASR=83.14
SUMPHI=0
SUMVS=0
SUMVO=0
SUMXPS=0
SUMAMW=0
PSMX=0
CALL CONVERT(1,Y,AMW)
DO 5 I=1,N
   SUMAMW=SUMAMW+AMW(I)*Y(I)
5 CALL CONVERT(2,Y,AMW)
DO 10 I=1,N
   VO(I)=GASR*TS(I)/PS(I)
   VS(I)=AMW(I)/RHOS(I)
10 RETURN
END
RSIZE(I)=VS(I)/VO(I)
10 CONTINUE
DO 20 I=1,N
20 SUMPHI=SUMP+Y(I)/RHOS(I)
DO 30 I=1,N
PHI(I)=Y(I)/RHOS(I)/SUMP
SUMVS=SUMVS+PHI(I)/VS(I)
SUMVO=SUMVO+PHI(I)/VO(I)
30 CONTINUE
VSMIX=1/SUMVS
VOMIX=1/SUMVO
RHOSMIX=SUMAMW/VSMIX
DO 40 I=1,N-1
DO 50 J=I+1,N
XP1(I,J)=(PS(I)+PS(J)-2*SQR(P(I)*P(J))*(1-SI(I,J)))/GASR/T
XP1(I,J)=XP1(I,J)
SUMXP=SUMXP+PHI(I)*PHI(J)*XP1(I,J)
50 CONTINUE
40 CONTINUE
DO 70 I=1,N
70 PSMD(P)=PSMD(P)+PHI(P)*P(I)
PSMIX=PSMD(P)*GASR/T*SUMXP
TSMIX=PSMIX*VOMIX/GASR
RMIX=VSMIX/VOMIX

TR=T/TSMIX
PR=P/PSMIX
CALL GETRHO(TR,PR,RMIX,RHO,NNN)
VR=1.0/RHO
DEN=RHO*RHOSMIX
DO 80 I=1,N
SUM1=0
DO 85 J=1,N
85 IF (J.EQ.I) SUM1=SUM1+PHI(J)*XP1(I,J)
TEMP1=LOG(PHI(I)+(1-1/VS(I)/VSMIX)
TEMP2=RHO*VS(I)*(SUM1-SUMXP)
TEMP3=(1-RHO)*LOG(1-RHO)+RHO*LOG(RHO)/RSIZE(I)
TEMP3=RSIZE(I)*(-RHO+P/PS(I)*VR/TTS(I))+VR*TEMP3
CHEMP(I)=GASR*T*(TEMP1+TEMP2+TEMP3)
80 CONTINUE
RETURN
END

SUBROUTINE CONVERT(NTYPE,X,AMW)
PARAMETER (N=2)
DIMENSION X(N), AMW(N)
SUMX=0
IF(NTYPE.EQ.1) THEN
DO 10 I=1,N
10 SUMX=X(I)/AMW(I)+SUMX
DO 20 I=1,N
20 X(I)=X(I)/AMW(I)/SUMX
ELSE

175
DO 30 I=1,N
   SUMX=X(I)*AMW(I)+SUMX
DO 40 I=1,N
   X(I)=X(I)*AMW(I)/SUMX
ENDIF
RETURN
END

SUBROUTINE GETRHO (T, P, RHO, NNN)
DIMENSION ROOT(3)
RHO=0.001
STEP=0.0001
TOL=0.00001

DO 20 IJ=1,3
   ROOT(IJ)=0
DO 10 I=1,10001
   IF(RHO.LE.1.0) THEN
      F=RHO**2+P*T*(LOG(1.0-RHO)+(1.0-1.0/R)*RHO)
      IF(ABS(F).GE.TOL) THEN
         IF(((IJ.EQ.1).OR.(IJ.EQ.3)).AND.(F.LT.0)).OR.((IJ.EQ.2)
+ .AND.(F.GT.0))) THEN
            RHO=RHO-STEP
            STEP=STEP*0.1
            RHO=RHO+STEP
         ELSE
            RHO=RHO+STEP
         ENDIF
      ELSE
         ROOT(IJ)=RHO
         STEP=0.001
         RHO=RHO+STEP
         GOTO 5
      ENDIF
   ELSE
      ROOT(IJ)=RHO
      STEP=0.001
      RHO=RHO+STEP
      GOTO 5
   ENDIF
END IF
ELSE
   ROOT(IJ)=RHO
END IF
END

IF(NNN.EQ.1) THEN
   DO 30 I=1,3
      IF(ROOT(I).GT.1.0)ROOT(I)=1.0
      RHO=AMAX1(ROOT(1),ROOT(2),ROOT(3))
   ELSE
      RHO=AMIN1(ROOT(1),ROOT(2),ROOT(3))
      IF(RHO.GT.1.0) RHO=-1.0
   ENDIF
RETURN
END

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3 Program to calculate the partitioning of nbd between co2 and polypropylene
(partitioning.for)

The SCF phase is considered as a binary phase (CO2 and NBD) The polymer phase is treated as a three-component phase (CO2, NBD and polypropylene).

The SCF phase is saturated with NBD. Therefore, the solubility of NBD at the given temperature and pressure is calculated based on the fact that NBD in SC-CO2 is in equilibrium with solid NBD. The mass fraction of NBD in polypropylene is then calculated to make its chemical potential to be equal to the chemical potential in the SCF phase. The CO2 concentration in polypropylene is calculated simultaneously.
Define variables

Input $T$, and pressure range ($P_{\text{low}}$, $P_{\text{high}}$)

Guess the partitioning coefficient for $CO_2$ ($H_1$) and NBD ($H_2$) and $Y_2$

Output "Did not converge"

$P = P + \Delta P$

Do $\text{INUMBER} = 1, 100$

Call subroutine SCF to calculate the mass fraction and the chemical potential for $CO_2$ and NBD in SCF phase

SCF phase converge

Do $\text{JITEM} = 1, 500$

$X_1 = \frac{Y_1}{H_1}, X_2 = \frac{Y_2}{H_1}, X_3 = 1 - X_1 - X_2$

H1 = H1*Q1, H2 = H2*Q2

Calculate the chemical potential differences between SCF and PP phase

$Q_1 = \exp\left(\frac{\mu_1^{PP} - \mu_1^{SCF}}{r_1RT}\right), Q_2 = \exp\left(\frac{\mu_2^{PP} - \mu_2^{SCF}}{r_2RT}\right)$

$\text{test1} = |q_1 - 1|, \text{test2} = |q_2 - 1|$

Figure B.5 Flow Chart of the Main Program in Partitioning, for
PARAMETER(N=3)
DIMENSION H(2,1000),Q(2,1000)
DIMENSION POTL(N),POTV(N),Y(2),X(N),RSIZE(N)
DATA PLOW/90.0/,
HIGH/300.0/,
PINC/20.0/
OPEN(UNIT=16,FILE=TEMP.OUT)
WRITE(16,77)
77 FORMAT('P(bar)',3x,'XC02',6x,'YNBD',8x,'XNBD',7x,'XDRY',18x,'KD')
GASR=83.14
T=333.15
P=PLOW
IWARN=0
YINITIAL=2.2E-9
H(1,1)=20
H(2,1)=0.01
DO 10 INumber=1,100
 CALL SCF(T,P,YINITIAL,Y,POTV,DENV,IWARN)
 IF(IWARN.EQ.1) GOTO 115
 DO 30 JITEM=1,100
 X(1)=Y(1)/H(1,JITEM)
 X(2)=Y(2)/H(2,JITEM)
 X(3)=1-X(1)-X(2)
 CALL SLCHEMPOT(T,P,X,POTL,RSIZE,DENL,3,1)
 Q(1,JITEM)=EXP((POTL(1)-POTV(1))/(RSIZE(1)*GASR*T))
 Q(2,JITEM)=EXP((POTL(2)-POTV(2))/(RSIZE(2)*GASR*T))
 TEST1=ABS(Q(1,JITEM)-1.0)
 TEST2=ABS(Q(2,JITEM)-1.0)
 IF(TEST1.LE.1.E-5.AND.TEST2.LE.1.E-5) GOTO 35
 H(1,JITEM+1)=H(1,JITEM)*Q(1,JITEM)
 H(2,JITEM+1)=H(2,JITEM)*Q(2,JITEM)
30 CONTINUE
 WRITE(*,*) 'THE TIE LINE DID NOT CONVERGE!'
 GOTO 115
35 WRITE(*,*) 'MODIFIER IN EQUILIBRIUM'
 XDRY=X(2)/(1-X(1))
 WRITE(16,85) P,X(1),Y(2),X(2),XDRY,DENV,DENL,Y(2)/XDRY
85 FORMAT(F5.1,2X,F8.6,2X,E9.3,2X,F9.7,2X,F8.6,2X,F5.3,2X,
 + F5.3,2X,E8.3)
 IF(P.GE.PHIGH) THEN
   WRITE(16,*)'UPPER PRESSURE BOUND REACHED'
 GOTO 115
 ENDIF
 H(1,1)=H(1,JITEM)
 H(2,1)=H(2,JITEM)
 P=P+PINC
179
CONTINUE

WRITE(16,116)
WRITE(*,116)
FORMAT(///,8X,'THE PROGRAM IS COMPLETED')
END

SUBROUTINE SLCHEMPOT(T,P,Y,CHEMP,RSIZE,DEN,N,NNN)
PARAMETER (K=3)
DIMENSION AMW(K),TS(K),PS(K),RHOS(K),CHEMP(K),SL(K,K)
DIMENSION Y(K),RSIZE(K),VO(K),VS(K),PHI(K),XPIJ(K,K)
DATA AMW/44.01,404.55,58600/,
TS/305.1655.59,770.9/,
PS/5745.1,2592.5,2811/,
RHOS/1.51,1.18,0.852/
DATA SL/9*0.0/
GASR=83.14
SUMPHI=0
SUMVS=0
SUMVO=0
SUMXP=0
SUMAMW=0
PSMIX=0

SL(1,3)=0.107
SL(2,3)=0.068
DO 2 I=1,N-1
DO 3 J=I+1,N
   SL(I,J)=SL(I,J)
   \CONTINUE
2 CONTINUE

CALL CONVERT(1,Y,AMW,N)
DO 5 I=1,N
   SUMAMW=SUMAMW+AMW(I)*Y(I)
   CALL CONVERT(2,Y,AMW,N)
   DO 10 I=1,N
      VO(I)=GASR*TS(I)/PS(I)
      VS(I)=AMW(I)/RHOS(I)
      RSIZE(I)=VS(I)/0(I)
   10 CONTINUE
   DO 20 I=1,N
      PHI(I)=Y(I)/RHOS(I)/SUMPHI
      SUMVS=SUMVS+PHI(I)/VS(I)
      SUMVO=SUMVO+PHI(I)/VO(I)
   30 CONTINUE
   VSMIX=1/SUMVS
   VOMIX=1/SUMVO
   RHOSMIX=SUMAMW/VSMIX
   DO 40 I=1,N-1
   DO 50 J=I+1,N
      XPIJ(I,J)=(PS(I)+PS(J)-2*SQR(PS(I)*PS(J)))/(1-SL(I,J)))/GASR/T
   40 CONTINUE
   50 CONTINUE
   CONTINUE

10 CONTINUE

WRITE(16,116)
WRITE(*,116)
FORMAT(///,8X,'THE PROGRAM IS COMPLETED')
END
SUBROUTINE SCF(T,P,YINITIAL,Y,POTV,DENV,IWARN)
PARAMETER(N=2)
DIMENSION Y(N),POTV(N),RSIZE(N)
GASR=83.14
Y(2)=YINITIAL
CALL POTSOLID(T,P,POTS)
CALL SLPOTREF(T,P,POTREF)
JNUM=1
JNUMLIMIT=500
DO WHILE (JNUM.LT.JNUMLIMIT)
  Y(1)=1-Y(2)
  CALL SLCHEMPOT(T,P,Y,POTV,RSIZE,DENV,2,0)
  POTSCF=POTV(2)-POTREF
  DIFF=POTSCF-POTS
  ERROR=DIFF/ABS(POTSCF)
  IF(ABS(ERROR).LT.1E-5) THEN
    WRITE(*,*) 'VAPOR PHASE REACH EQUILIBRIUM'
    GOTO 50
  ENDIF
  Y(2)=Y(2)*(I-ERROR)
  JNUM=JNUM+1
ENDDO
WRITE(16,*) Y(2), Y(2)*(I-ERROR)
JNUM=JNUM+1
END

SUBROUTINE SCF(T,P,YINITIAL,Y,POTV,DENV,IWARN)
IWARN=1
50 RETURN
END

SUBROUTINE SLPOTREF(T,P,POTREF)
GASR=83.14
AMW=404.55
TS=1655.59
PS=2592.5
RHOS=1.18
TR=T/TS
PR=P/PS
VO=GASR*TS/PS
VS=AMW/RHOS
RSIZE=VS/VO
CALL GETRHO(TR,PR,RSIZE,RHO,1)
VR=1/RHO
POTREF=-RHO/TR+PR*VR/VR+(VR-1)*LOG(1-RHO)+LOG(RHO)/RSIZE
POTREF=GASR*T*RSIZE*POTREF
RETURN
END

SUBROUTINE POTSOLID(T,POTS)
HMELT=72172.5
DELTCP=68.7
TMELT=384.15
GASR=83.14
GASR1=8.314
FTEMP=HMELT/GASR1/TMELT*(TMELT/T-1)
+DELTCP/GASR1*(TMELT/T-1)+DELTCP/GASR1*LOG(TMELT/T)
POTS=-GASR*T*FTEMP
RETURN
END

SUBROUTINE CONVERT(NTYPE,X,AMW,N)
PARAMETER (K=3)
DIMENSION X(K), AMW(K)
SUMX=0
IF(NTYPE.EQ.1) THEN
DO 10 I=1,N
10 SUMX=X(I)/AMW(I)+SUMX
DO 20 I=1,N
20 X(I)=X(I)/AMW(I)/SUMX
ELSE
DO 30 I=1,N
30 SUMX=X(I)*AMW(I)+SUMX
DO 40 I=1,N
40 X(I)=X(I)*AMW(I)/SUMX
ENDIF
RETURN
END

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SUBROUTINE GETRHO (T, P, R, RHO, NNN)
DIMENSION ROOT(3)
RHO=0.001
STEP=0.0001
TOL=0.00001

DO 20 IJ=1,3
   ROOT(IJ)=0
DO 10 I=1,10001
   IF(RHO.LE.1.0) THEN
      F=RHO**2+P-T*(LOG(1.0-RHO)+(1.0-1.0/R)*RHO)
      IF(ABS(F).GE.TOL) THEN
         IF(((I.EQ.1).OR.(I.EQ.3)).AND.(F.LT.0)).OR((I.EQ.2) .AND.(F.GT.0))) THEN
            RHO=RHO-STEP
            STEP=STEP*0.1
            RHO=RHO+STEP
         ELSE
            RHO=RHO+STEP
         END IF
      ELSE
         ROOT(IJ)=RHO
         STEP=0.001
         RHO=RHO+STEP
      END IF
   ELSE
      ROOT(IJ)=RHO
      STEP=0.001
      RHO=RHO+STEP
   ENDIF
10 CONTINUE
5 CONTINUE
20 CONTINUE

IF(NNN.EQ.1)THEN
   DO 30 I=1,3
30      IF(ROOT(I).GT.1.0)ROOT(I)=-1.0
      RHO=AMAX1(ROOT(1),ROOT(2),ROOT(3))
   ELSE
      RHO=AMIN1(ROOT(1),ROOT(2),ROOT(3))
      IF(RHO.GT.1.0) RHO=1.0
   ENDIF
RETURN
END
APPENDIX C

HOW TO SEAL THE VIEW CELL WINDOWS

To seal a window is a job that needs great patience and care. Initially, the cavity where the window will sit should be well cleaned. Usually a scratched or broken quartz window is the reason to repack the window. Punch the broken window with a sharp-head screwdriver and a hammer. The window turns into powders (For safety reasons, goggles and gloves should be worn). Then a screwdriver and a pair of tweezers can be used to pull out the brass and lead rings. It is easy to remove the brass rings but a bit more tough to handle the soft lead because they packed very tight in place. Great care should be taken to avoid scoring the inside of the cell with the tools.

The brass rings are available commercially (Phoenix Specialty Meg. Co., Inc.) but the lead rings are made by hand. They are punched off a thin lead sheet (Mcmaster-Carr). A rubber-head hammer and several circular punches are the implements. Three types of lead ring with the same O.D. but different I.D.s need to be punched. The O.D. of these rings is the diameter of the cavity wall. Lead ring #1 is packed between the quartz disc and the cavity wall. Therefore, the I.D. of ring #1 is the same as the O.D. of the quartz disc. Ring #2 whose I.D. is a little bit larger than ring #1 is packed on the bottom of the cavity. Ring #3 has about a $\frac{1}{4}''$ I.D. It sits on the top of the disc and contacts the holder. It is hard to keep the two circles punched concentric. A slight
deviation is tolerable because the lead is squeezed later during the packing process. However, a good shape ring is helpful for a good packing and quick seal.

Ring #2 is placed in the window cavity first. The I.D. of this ring cannot be too small. Otherwise, the lead squeezed to the center because of packing may block the light path. Then a brass ring and a quartz window are placed in the window cavity. The brass ring centers the window in the hole. A #1 lead ring is then carefully placed around the window. A custom tool is used to carefully push down the lead ring (see Figure A.6). This tool can screw into the cell cavity and has a circular extension the same diameter as the brass ring. A wrench may be necessary to screw this tool down. Special care must be taken when using this tool to pack the rings. If the quartz disc is not well centered but a large force is exerted on the wrench, the tool would break the disc. Then brass rings and #1 lead rings are placed around the quartz discs alternatively until the ring level is equal to the top of the window. Every time when a ring is fit in, the tool is used to tighten the rings. The window holder is used to press the quartz discs down to the bottom during the packing process. Hand tight or slight wrench tight are suggested. The reason to do that is because packing of the rings may push up the quartz discs in the center. Finally, lead ring #3 is placed on the top of the window and the holder is then screwed on to the top of the lead ring.

Now, the window has been seated in the cavity. The cell is fixed on the vice and connected to a syringe pump. A safe precaution would be to use water instead of carbon dioxide to seat the window. A protective shield is suggested, especially when testing pressure higher than 3000psi.
Initially, the cell is pressurized to 20 psig and hold for 5 minutes. If it does not hold this pressure, vent the cell and tighten the window holder a little bit. A 1 1/8” wrench is used to tighten the window holder. It is suggested to put your hand close to the end of the handle and hold it. Then put your thumb on the head of the wrench. Then your hand can feel how hard it is to tighten the holder and you can well control the force exerted on the holder. Once the cell holds the initial 20 psig pressure, vent the cell and slightly tighten the holder. Continue this process of pressurizing, venting and tightening in ca. 50psi increments until 300 psig has been approached. The press should hold at each increment. Then increase 100 psig every time and repeat the process. It is important to remember that the high pressure pushes the windows against the wall and squeezes the rings. The fact is that the high pressure itself seals the window and the wrench tightening close the gap created by compressing the lead from the inside water. Therefore, turn the wrench hard will not seal the window but break it. Whenever tightening the holder, a minimal amount of force should be applied. Pay close attention to the windows when let it sit at a certain pressure. If water leaks from the center or the outside edge of the holder, vent the cell immediately and tighten the holder and pressurize it again. If it still does not hold the pressure, try to hold at a lower pressure for a while and repeat the venting, tightening and pressurizing. Don’t let the cell leak for a long time because the fluid will carve tunnels in the lead, which makes it very difficult to seal.

During the compressing process, the lead will be squeezed to the center of the window and block it. Once the cell holds the required pressure (3500 psig in our case),
this extra bit of lead should be removed. It can be scraped away with a small spatula or screwdriver. Avoid scratching the quartz windows.

The window is sealed at this moment. However, after being used for a while, the window may start to leak. It is suggested to tighten the holder once a while.
<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
<th>Manufacture</th>
<th>Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz windows</td>
<td>Fused Silica Windows</td>
<td>Dynasil</td>
<td>Ph: (856) 767-4600 Fax: (856) 767-6813 <a href="mailto:dynasil@aol.com">dynasil@aol.com</a></td>
</tr>
<tr>
<td></td>
<td>Diameter: 0.500&quot; (+/-0.005) Thickness: 0.260&quot; (+/-0.005) Commercial 80/50 Polish</td>
<td>Dynasil 385 Cooper Rd. West Berlin, NJ 08091</td>
<td></td>
</tr>
<tr>
<td>Lead O-ring</td>
<td>Lead Sheet 1/24&quot; thick, 12&quot;x12&quot;, Part #: 9032 K111</td>
<td>McMaster-Carr Company 200 Aurora Industrial Pkwy Aurora, OH 44202</td>
<td>Ph: (330) 995-5500 Fax: (330) 995-9600 <a href="mailto:la.sales@mcmaster.com">la.sales@mcmaster.com</a></td>
</tr>
<tr>
<td>Brass O-ring*</td>
<td>Diameter: 0.62&quot; Item: P×5766</td>
<td>Phoenix Specialty Meg. Co., Inc. P.O. Box 418 Hwy. 301 South Bamberg, SC 29003-0418</td>
<td>Ph: (803) 245-5161</td>
</tr>
<tr>
<td>Hex-head</td>
<td>Type 316 SS Threaded High-Pressure Fitting Hex-head plug, 3/4&quot;-16 Straight Thread, Part # 51205 K418</td>
<td>McMaster-Carr</td>
<td></td>
</tr>
<tr>
<td>Temperature Controller</td>
<td>Item#: D16A2-110</td>
<td>Dwyer Instruments, Inc. P.O. Box 373 Michigan City, IN 46361</td>
<td>Ph: (219)-879-8000 Fax: (219) 872-9057</td>
</tr>
<tr>
<td>RTD probe</td>
<td>Item#: 56141-1221-030-000-000-48</td>
<td>Dwyer Instruments, Inc.</td>
<td></td>
</tr>
<tr>
<td>Cartridge Heater**</td>
<td>Item#: C2A5 Diameter: 1/8&quot; Watts: 100</td>
<td>Tapco Products, Inc. P. O. Box 42395 Cincinnati, OH 45242</td>
<td>Ph: (614)-464-2292 Fax: (513)-683-7675</td>
</tr>
</tbody>
</table>

Table C.1 Parts for the high-pressure view cell
Note: 1) All dimensions are in inches. 2) Material: stainless steel

Figure C.1 Sealing tool for quartz windows
APPENDIX D

SEVERAL IMPORTANT THINGS ABOUT THE FLUORESCENCE SPECTROPHOTOMETER

The instrument is from Photon Technology International. The model is QM-1. The contact technician in the company is Mr. John Cook (Phone: 713-329-0910 ext. 117).

1 The lamp voltage

The standard lamp for this model is 75 Watts Xenon lamp. We use 150 Watts lamp since lots of compounds have low solubility in carbon dioxide. Therefore, when the lamp is ignited, the voltage should be kept between 140 – 150 Watts. In all of the manuals, 70 – 75 Watts are suggested but it is not the right choice for our system.

2 The lamp cooling

For the standard lamp (75 Watts), cooling water is not necessary. However, for our 150 Watts, cooling water MUST be run through the cooling pipe. Inefficient cooling will lead to a lamp explosion. If there is no cooling, the lamp will explode within 10 minutes after it is turned on. The lamp is very hot at working conditions. If tap water is used, the calcium in water will precipitate in the pipe around the cathode and block the flow. Therefore, distilled water should be used. The cooling system used in my work is described in Figure A.7. It can also serve as a syringe pump cooling.
3 The lamp explosion

If for some reasons the lamp is exploded, the first thing to do is to calm down. Since the lamp is filled with high pressure Xenon, it is harmless. When the lamp housing is opened, wrecks of the lamp could be seen on the reflector and a quartz disc. The function of the quartz window is to stop small particles from entering the compartment when explosion happened. Don’t touch the reflector with hands because it will scratch the reflecting surface. Use air to blow away the dust. Although there are some melted small pieces of glass on the surface now, the reflector should still work fine. The quartz disc should be replaced with a new one.

After the parts are changed and put back into the housing, the voltage may indicate zero (the normal value is 004 before ignition) when the lamp is turned on. It is because the lamp fuse was burned when the lamp exploded. The fuse is located inside the ignition control box. It is highly recommended that you call the company before you open the box.
1. Fluorescence spectrophotometer lamp housing  
2. Pump  
3. Bath with water/ice mixture  
4. Bottle with distilled water  
5. Pump  
6. Syringe pump  
Note: Don't use tap water as the lamp cooling water because the calcium will precipitate in the pipe and block the flow.

Figure D.1 Cooling system for fluorescence study
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