Impregnation of fluorescence dyes into polymer optical fibers

using carbon dioxide fluids

（二酸化炭素流体を用いるプラスチック光ファイバーへの
蛍光色素の注入に関する研究）

2011 年 3 月

趙 川
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Chapter 1  General introduction

1.1 Optical polymer functional materials

Transparent polymer materials are used in many optoelectronics applications. Polymers have become one of the most promising candidates for new materials with excellent optical performance and functionality. Their physical chemical properties can be varied by doping various molecular compounds, for example, optical amplifiers and generators, medical sensors, memory cells and others.

Among these organic materials, compared with other materials, polymeric materials have several advantages. First, the properties of polymers can be widely tuned by chemically modifying the structure of the monomer, the functional groups, or the polymer backbones. Second, compared to fragile glass fiber and expensive semiconductor chips, polymeric materials provide for easy, low-cost, and reliable fabrication of optical devices. Third, functional polymeric materials also provide an excellent platform for integrating several diversified materials with different functions. [1-3].

In 1993, Yasuhiro Koike was the first to report the possible application of rhodamine 6G doped polymer optical fibers (POFs). By doping the dye in the POFs, the high optical gain was observed with the POFs [4]. Subsequently, POFs doped with several types of fluorescent dyes have been extensively studied. Many research groups observed that incorporating the fluorescent dyes into POFs, resulted in highly efficient lasing properties and optical parametric amplification. By experiment, scholars have shown that the Rhodamine B doped step-index POF provides very good prospects for optical amplification of high gain and high efficiency. Compared with other doped materials,
dye-doped optical fiber has its obvious advantages such as low-cost and high
conversion efficiency for a variety of applications, which require tunable high-power
pulsed beams. With a specific dye, narrow line width laser output tunable in a range of
tens of nanometers with high efficiency can easily be obtained [5–12]. These properties
are desirable for application in the field of fiber laser and local communication systems.

In most cases, the conventional methods to prepare dye-doped polymer optical fiber
has one drawback, the preparation of dye-doped POFs requires the use of a radical
polymerization process. To fabricate dye-doped POFs, the first step of this process
consisted of the fluorescence dye dissolved in a methyl methacrylate (MMA) monomer
and polymerization can be induced by using either azobisobutyronitrile or benzoyl
peroxide as a radical initiator. Because many fluorescence dyes do not dissolve well in
nonpolar MMA solution, additives such as ethyl alcohol and dimethyl sulfoxide are
added to the reagents [14]. Second step, free radical polymerization of MMA must take
place at approximately 90°C for 24 h and 110°C for 40 h to complete polymerization,
the dye-doped perform PMMA rod obtained by this polymerization process. Finally, at a
stable temperature of 200°C, 600 and 1000 µm diamond polymer optical fiber was
drawn at this performing rod. The shortcoming is fluorescence dye has a low thermal
stability, decomposition of dye occurred during the high temperature polymerization
process, it has led to degradation of the dyes as a gain medium. HIGUCHI reported that
rhodamine 6G in PMMA to decompose at about 70°C is shown in Fig. 1.1 [13]. Another
group has reported that during polymerization approximately 37-56 % of the dye is lost,
as determined monitoring changes in dye absorption intensity [8]. Extreme example,
laser dye O4PC has poor solubility in MMA and almost all (nearly 100%) doped O4PC
molecules decompose in the polymerization process. This method limits the use of dyes
with poor thermal stability.

Fig. 1.1 Typical absorption spectra of rhodamine 6G/PMMA at different heating times.

Initial rhodamine 6G concentration: $7.1 \times 10^{-5}$. Heating temperature: 73°C.

Heating time: Curve 1, 0h; 2, 88 h; 3, 242 h and 4, 352 h.

To overcome this problem, an efficient and mild method for doping dyes into POFs at a lower temperature is required.

1.2 Supercritical and subcritical carbon dioxide fluid

Carbon dioxide is non-toxic, non-flammable, chemically inert, and inexpensive, supercritical conditions are easily achieved: $T_c = 304$ K and $P_c = 7.38$ MPa. A supercritical carbon dioxide fluid is defined as a substance for which both pressure and
temperature are above the critical values, Fig. 1.2.

![Phase diagram of a pure substance](image)

**Fig. 1.2** Phase diagram of a pure substance

Supercritical carbon dioxide fluids (scCO₂) have interesting properties. The properties are said to supercritical fluids are compressed gases which can display properties between those of liquids and gases. The special combination of gas-like viscosity and liquid like-density of supercritical fluid results in it has being an excellent solvent. This means that it can tuned by adjusting the fluid parameters such as pressure and temperature.

1.3 **Application of carbon dioxide fluids**

In literature it is known that supercritical CO₂ and subcritical (liquid or gaseous) are able to dissolve a number of low molecular compounds, it can be used as a solvent. To
date, it has successfully been used as a solvent in the processing of various organic compounds such as extraction and purification, dyeing, polymer modification, formation of polymer composites, microcellular foaming, impregnation and polymerization [15-21].

Recently, to prepare a functional polymer, the impregnation of molecular into the polymer by the supercritical dyeing method using a complex has been researched. [22] The supercritical carbon dioxide impregnation method is based on the use of a supercritical/subcritical solvent, carbon dioxide or CO₂ + cosolvent mixtures, as a carrier for the molecular which also impregnation the polymeric matrix, thus facilitating the diffusion of the molecular. The depressurization step results in retaining the molecular inside the polymer. Small amounts of cosolvent can improve the polarity of CO₂ solvent. Therefore, the amount of impregnated/dispersed molecular can be controlled by changing the operational pressure and temperature process conditions, as well as by choosing the appropriate cosolvent and varying the overall solvent mixture composition.

This technique it is known as supercritical solvent impregnation and it already proved its advantages for the development of drug impregnated polymeric materials which can be used as for many biomedical applications. CO₂ fluids impregnation method allows the drug impregnation dispersion of most polymeric and, when properly employed, without altering and damaging their physical, chemical, and mechanical properties and without degrading their constituent drugs, additives and polymers [23-30].

1.4 Aim and outline of this thesis

The aim of this thesis is to investigate a subcritical/supercritical level of CO₂ fluid
impregnation method as an alternative to the conventional free radical polymerization method to prepare fluorescence dyes doped POFs. The solubility of rhodamine dyes in CO₂ fluids was measured, and then the impregnation effect of various factors, such as organic cosolvent, pressure, temperature and time of the impregnation process was also investigated.
1.5 Reference


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Chapter 2  Solubility of Rhodamine 6G and Rhodamine B in Carbon Dioxide Fluids

2.1 Introduction

To use of carbon dioxide fluids in impregnation, the solubility of dyes in carbon dioxide fluids is fundamentally important in the development and design of carbon dioxide impregnation processes. Generally speaking, a dye may be incorporated into a polymer by first dissolving it in a carbon dioxide solvent, then, allowing the dye to diffuse along with the CO$_2$ fluids into the polymers, which become swollen with the CO$_2$ fluids. During the decompression process, CO$_2$ gas leaves the polymer, but the dye remains mostly confined within the polymer. Therefore, the dissolution rate of a dye, or rate in which the dye goes into solution, is an important parameter for determining how much dye is dissolved in CO$_2$ solvent. If a dye is difficult to get into solution, then the amount of dye available for absorption may be small and thereby present difficulties in achieving the desired effect.

Supercritical/subcritical CO$_2$ is a good solvent for many non-polar dyes. By contrast, water-soluble polar dyes such as acidic dyes and reactive dyes do not dissolve in nonpolar supercritical CO$_2$, and few relevant data are yet available. Therefore, designing and developing this process for doping rhodamine dyes within a polymer optical fiber, will require a large body of solubility data pertaining to the rhodamine dyes.

From a general point of view, experimental techniques for solubility evaluation can be divided in ‘static’ and ‘dynamic’. The ‘flow method’, is the most used in the literature [1-3] and consists of an extractor containing the dyes crossed by the
supercritical fluid; the flow rate is set to a value that guarantees the saturation of the fluid with the solute and the dye concentration can be measured or through on-line spectroscopy or by recovering the solid in a trap with organic solvent after an expansion valve.

In this work, the measurement and correlation of the solubility of the fluorescent dyes rhodamine 6G and rhodamine B in supercritical/subcritical carbon dioxide with or without a cosolvent were determined. The results were obtained using a flow-type apparatus, at 293.15, 308.15 and 318.15 K, in a pressure range 8.0 - 24.0 M. The effect of adding methanol as a cosolvent was investigated under the same conditions. The flow type apparatus used for solubility measurements is briefly described and the experimental procedure presented. Solubility data were correlated with the Chrastil and Sovova density-based equations.

2.2. Experiment
2.2.1 Materials

Rhodamine 6G and rhodamine B are the standard among fluorescence dyes, and any dye claiming good performance should be compared with it. Rhodamine dyes that are used in laser dyes as a gain medium are promising candidates for high-power light amplification because of extremely large absorption and emission cross sections. Rhodamine dye is a xanthene derivative and is ionic and highly polar. It is soluble in most polar solvents including water, alcohols and methanol [4-6].

The rhodamine 6G and B dyes used in this study were purchased from Kanto Chemical Co., Inc., and their chemical structures are shown in Table 2.1. Carbon
dioxide gas (99.5% purity) was provided by Uno Sanso Co., Ltd.. The methanol used for modifying the solubility properties of CO₂ fluids is in guaranteed-grade reagent form and was used without further purification.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Molecular structure</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine 6G</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>479</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>479</td>
</tr>
</tbody>
</table>

**Table 2.1** Molecular structure and weight of Rhodamine dyes

### 2.2.2 Solubility Experiments Measuring Device and Method

To measure the solubility of dyes in carbon dioxide fluids, a flow-type apparatus was used [7]. A schematic diagram of the apparatus is shown in Fig. 1. It was constructed in a gas chromatography oven, the temperature of which could be easily controlled. Before the experiment, the dyes were spread on the Celite beads with a weight ratio of dyes to beads of about 1:10. Then approximately 5g of dyes and beads were charged in a stainless steel extraction cell fixed to the chromatography oven. The extraction cell was 0.6 cm in diameter, and both ends of the cell were filled with glass.
wool. To get a smooth stream of supercritical carbon dioxide fluid with a constant temperature, a capillary 3 meter long was set in front of the dye (saturation) cell. The temperature of the capillary and cell was controlled within ±0.1K in the oven. The carbon dioxide pressure was controlled using a backpressure valve. The exact pressure was measured using a pressure transducer and an indicator. When the experiment was conducted with a cosolvent, the cosolvent was mixed with CO₂ fluid through high pressure solvent metering pump, after which the mixed fluids would flow through the capillary. The well-mixed CO₂ and cosolvent then entered into the extraction cell. The dye-containing fluids flowed through a two-step acetone trap where the dissolved dye was separated from the carbon dioxide fluids. A wet-type flow meter was used to measure the volume of the released CO₂. Finally, the solubility of the dyes in CO₂ was determined by measuring the concentration of dyes in the acetone solution. These values were measured with SHIMADZU UV-1700 UV-VIS Spectrophotometer.

![Diagram](image)

**Fig. 2.1** Schematic diagram of experimental apparatus
2.3. Results and discussion

2.3.1 Solubility in the carbon dioxide fluids

In this work, the solubility of rhodamine in carbon dioxide fluids with or without a cosolvent was measured at 293.15, 308.15 and 318.15 K, from 8.0 to 24.0 MPa. The experimental results are listed in Table 2.2. The mole fraction of dye (y_2) is used in this paper to describe the solubility of the dyes. These data show that rhodamine 6G and rhodamine B is a xanthene derivative and is ionic and highly polar, it is very difficult soluble in pure carbon dioxide fluids. Over the entire experimental conditions, mole fractions of the dyes are in the range of 10^{-9} to 10^{-12}, which are far lower than disperse dye in the scCO_2. Since carbon dioxide is nonpolar, the solubility behavior may be governed mainly by the physical interactions between carbon dioxide and the dye molecules. The rhodamine dyes is its extremely low solubility in pure CO_2, the results support the view that the non-polar disperse dyes are easily soluble in the supercritical CO_2, on the contrary, the solubility of water soluble polar dyes scCO_2 is rather low.
<table>
<thead>
<tr>
<th>T(K)</th>
<th>P/MPa</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>Rhodamine 6G $y_2 \times 10^9$</th>
<th>Rhodamine B $y_2 \times 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Methanol concentration</td>
<td>Methanol concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0% mol</td>
<td>5% mol</td>
</tr>
<tr>
<td>293.15</td>
<td>8</td>
<td>827.67</td>
<td>0.309</td>
<td>5.512</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>878.55</td>
<td>0.629</td>
<td>8.781</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>912.06</td>
<td>0.736</td>
<td>11.664</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>937.78</td>
<td>0.953</td>
<td>14.593</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>958.94</td>
<td>1.290</td>
<td>16.173</td>
</tr>
<tr>
<td>308.15</td>
<td>8</td>
<td>425.77</td>
<td>0.066</td>
<td>1.792</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>767.61</td>
<td>0.904</td>
<td>7.603</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>827.66</td>
<td>1.390</td>
<td>13.178</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>866.33</td>
<td>2.064</td>
<td>17.594</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>895.60</td>
<td>3.021</td>
<td>19.601</td>
</tr>
<tr>
<td>318.15</td>
<td>8</td>
<td>240.59</td>
<td>0.008</td>
<td>0.384</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>659.01</td>
<td>1.254</td>
<td>17.280</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>760.83</td>
<td>1.755</td>
<td>17.552</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>813.27</td>
<td>2.439</td>
<td>19.232</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>849.98</td>
<td>3.552</td>
<td>24.917</td>
</tr>
</tbody>
</table>

**Table 2.2** Solubilities of Rhodamine 6G and Rhodamine B in carbon dioxide fluids with or without methanol
Fig 2.2 Solubility of rhodamine 6G in the pressure range of 8–24 MPa and temperatures of 293.15K (▲), 308.15K (○), and 318.15K (■).

Fig 2.3 Solubility of rhodamine B in the pressure range of 8–24 MPa and temperatures of 293.15K (▲), 308.15K (○), and 318.15K (■).
2.3.2 Effect of pressure on the solubility of rhodamine

Fig 2.2 and Fig 2.3 show the relationship between the solubility of the rhodamine dyes and the fluids pressure of CO\textsubscript{2} at a series of temperatures. It is observed that, the solubility increases with an increase in the pressure of carbon dioxide. The influence of pressure on the solubilities is more pronounced at high temperatures. This may be due to the increased density of CO\textsubscript{2} at increased pressure because the CO\textsubscript{2} density is directly related to its dissolving power. Carbon dioxide density increases, resulting in a decrease in the average distance between the molecules, and an increase in the interaction force between molecules of the solute and the solvent, such that the solubility is increased accordingly.

2.3.3 Effect of temperature on the solubility of rhodamine

The solubility isotherms have a crossover at pressures around 8 to 24 MPa as shown in Figure 2.2 and 2.3, indicating that the rhodamine dyes solubility increases by approximately 200 times as pressure changes from 8 to 24 MPa at 318.15 K, is as sensitive to temperature over the investigated conditions. Below the crossover pressure, the solubility decreases with increasing temperature, whereas an opposite trend was exhibited at pressures higher than the crossover pressure. The crossover phenomena could be attributed to the competitions between solute’s vapor pressure and solvent’s density, whose temperature dependences are in opposite directions. This is because the temperature influence on the dye solubility in supercritical CO\textsubscript{2} primarily affects dye saturation and vapor pressure, CO\textsubscript{2} density, and the intermolecular interactions in the fluid phase. At different pressure range, these factors have different effects. In the low-pressure area, when the temperature is high, the solute solubility is smaller, it’s the
density which plays a dominant role, dye solubility decreases with rising temperature. In the high-pressure area, temperature takes the dominant position in affecting the saturated vapor pressure and the intermolecular interactions, when the temperature increases, the saturation vapor pressure of the solute increases, interaction between fluid enhanced increases, and the dye solubility increases.

2.3.4 Solubility in supercritical/subcritical CO$_2$ with methanol

While supercritical fluids have been widely investigated as replacement to volatile organic solvents in extraction and impregnation, it has limited solvent power for most polar dyestuffs because it is nonpolar and is unable to form hydrogen bonds with these polar molecules. In literature it was described that disperse dye solubility range is $10^{-6}$ – $10^{-7}$ mole fraction [8-10]. The previous experimental data shows that, for rhodamine dyes having high molecular masses and polarity, the magnitude of solubility in pure supercritical CO$_2$ fluid remains at $10^{-9}$ to $10^{-12}$ mole fraction, far less than the solubility of the general disperse dyes in CO$_2$ fluid. To improve polarity and solubility, as evidenced from experimental results [11-15], the solubility of solutes in supercritical fluids can be greatly enhanced by addition of a small amount of cosolvent, usually a polar solvent such as acetone, ethanol and methanol. The solubility enhancement by adding cosolvent may be attributable to an increase of scCO$_2$ polarity, modification of phase behavior, and generation of additional intermolecular interactions between cosolvent and solute molecules. Methanol is one of the few organic solvents considered suitable as a cosolvent.

In this experiment, the effect of methanol as a cosolvent on the solubility of
rhodamine dyes in CO$_2$ fluids was studied at 293.15, 308.15 and 318.15 K, from 8.0 to 24.0 MPa with a methanol concentration of 5.0 mol %. The results obtained are shown in Table 2. Fig. 2.4, 2.5, 2.6 and 2.7 show the cosolvent effect for rhodamine at 3.08.15K and 318.15K with 5.0 mol% methanol loading. These enhancements can be important for the process design since, at constant temperature, solubility obtained at 8–24 MPa in presence of methanol can be up to 25 times larger than in pure CO$_2$. This means that the process could be carried out at milder conditions, keeping the same rhodamine dye solubility in the CO$_2$ solvent and, thus, the same driving force for the mass transfer in the fluid phase.

This improvement is a result of the molecular interactions between the solute and the cosolvent, in which the attractive force between molecules is the main factor determining the solubility of the material. Intermolecular interactions between the dye and cosolvent molecules may involve physical forces and specific chemical forces. The physical interactions between polar rhodamine molecules and the polar cosolvent molecules of methanol should include electrostatic, induction, and dispersion forces [16-17]. The molecular structure of rhodamine contains a carbonyl group, whereas methanol can be both a hydrogen bond acceptor and a donor, thus intermolecular interactions exist between methanol molecules. The hydrogen bonds between supercritical CO$_2$ and methanol can be formed in a variety of ways. In addition, the induction effect of the methanol to supercritical CO$_2$ increases the polarity of the fluid. All these factors contribute in the increase of the intermolecular forces between rhodamine and carbon dioxide molecules, and promote the dissolution of rhodamine in supercritical CO$_2$. Table 2 shows the solubility of rhodamine dyes is much higher than in pure supercritical CO$_2$. 
**Fig 2.4** Solubility of rhodamine 6G in the pressure range of 8–24 MPa and temperatures of 308.15K, with (■) and without (▲) methanol

**Fig 2.5** Solubility of rhodamine 6G in the pressure range of 8–24 MPa and temperatures of 318.15K, with (■) and without (▲) methanol
**Fig 2.6** Solubility of rhodamine B in the pressure range of 8–24 MPa and temperatures of 308.15K, with (■) and without (▲) methanol

**Fig 2.7** Solubility of rhodamine B in the pressure range of 8–24 MPa and temperatures of 318.15K, with (■) and without (▲) methanol
2.4 Correlation of experimental solubility data

The dye solubility data should be accurately modeled for effectively designing any supercritical fluid impregnation process. To predict supercritical solubility behavior, many models have been developed to correlate the experimental solubility data. These models help to explain the relationship between the solubility of the solute and the solvent density. Density-based approaches show their outstanding simplicity in correlating the solute solubility and only use readily available independent variables (pressure, temperature and density of carbon dioxide fluids). They do not require physical properties. In this work, the Chrastil equation s and Sovova equations were used to correlate the solubility of dyes in supercritical fluids in both the presence and the absence of methanol.

2.4.1 Correlation model under pure carbon dioxide conditions

According to the association theory, Chrastil holds the view that, in the supercritical fluid and solute system, an association reaction occurs between the solute molecules and supercritical fluid molecules, thus producing a solvent based association complex [18]. According to the relationship between the solute and the solvent concentrations, the semi-empirical solubility association equation is as follows:

\[ C = \rho^k \exp\left[\frac{a}{T} + b\right] \quad (1) \]

Rearranging, the equivalent from results:

\[ \ln c = k \ln \rho + a/T + b \quad (2) \]

where \( c \) is the solubility of the solute in the supercritical solvent (g/L), \( \rho \) the density of the pure solvent (g/L) and \( k \) (association number) is the number of molecules in the solvate complex. Parameter \( a \) is dependent on the total heat of reaction and \( b \) is
dependent on the molecular weights of the solute and solvent and the association constant. The experimental solubility data is fitted using Chrastil empirical equation. Thus, the solubility equations based on the Chrastil equations for rhodamine 6G (equation 2) and rhodamine B (equation 3) are as follows:

\[
\ln c = 4.848 \ln \rho - \frac{11313.772}{T - 10.206}
\]

\[
\ln c = 4.937 \ln \rho - \frac{14801.373}{T + 0.8102}
\]

The Chrastil expression gives \( \ln c \) linear in \( \ln \rho \), and the plot of \( \ln c \) vs. \( \ln \rho \) are shown in Fig. 2.6 and Fig. 2.7.

![Graph](image)

**Fig. 2.8** Correlated results from Chrastil equation for Rhodamine 6G in compressed CO\(_2\)
Correlated results from Chrastil equation for Rhodamine B in compressed CO$_2$

Chrastil’s equation has some limitations. It is not valid over a wide range of temperatures. However, the temperature range of this study is as narrow as 30 K. Within this temperature range, the isotherms are apparently parallel as shown in the graphs; i.e. the association number can be assumed as a constant for each investigated system. The average absolute relative deviation (AARD%) is calculated according to following equation:

$$\text{AARD} = \frac{1}{n} \sum_{i=1}^{n} \frac{|c_{\text{cal}} - c_{\text{exp}}|}{c_{\text{exp}}}$$  \hspace{1cm} (4)

In this equation, $c_{\text{cal}}$ represents the calculated value and $c_{\text{exp}}$ represents the experimental value, with smaller AARD values indicating better correlation. The AARD
values of rhodamine 6G and rhodamine B are 25.66% and 31.05 %, respectively. The test results are satisfactory.

2.4.2 Correlation model under cosolvent conditions

For the calculation of the solubility of a solid in the scCO$_2$ with cosolvent, Sovova also presented a new density-based model for cosolvent ternary systems [19].

\[ S_c - S = K\omega_{et}^m S^n \]  \hspace{1cm} (5)

In this equation, $S_c$ is the mass fraction solubility in SCCO$_2$ containing cosolvent, $S$ is mass fraction solubility in pure SCCO$_2$, and $\omega_{et}$ is the component mole fraction of the cosolvent in the mixed solvent, and k, m, and n are parameters to be determined. In this experiment, $\omega_{et}$ is given by a certain value (mole fraction is a constant of 0.05), therefore, at constant mole fraction of cosolvent, the new parameters $R$ is defined.

\[ R = \ln(k\omega_{et}^m) \]  \hspace{1cm} (6)

As a result, eq 5 transforms into eq 6

\[ S_c - S = \exp(R) \times S^n \]  \hspace{1cm} (7)

The Sovova model was expressed as equation (8)

\[ \ln(S_c - S) = R + n \ln S \]  \hspace{1cm} (8)

The results based on correlating this moldel are presented in Table 2.3. The calculated solubility value and the average absolute relative error AARD of the experimental data were calculated according equation 4. The AARD values of rhodamine 6G and rhodamine B are 11.58% and 15.78% respectively.
Table 2.3 Correlated parameters for equation 6 for Rhodamine 6G and Rhodamine B in scCO$_2$ with methanol

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>n</th>
<th>AARD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine</td>
<td>-2.462</td>
<td>0.667</td>
<td>16.72%</td>
</tr>
<tr>
<td>6G</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhodamine</td>
<td>-0.973</td>
<td>0.729</td>
<td>13.35%</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5. Conclusion

The solubility of rhodamine 6G and rhodamine B in SCCO$_2$ was measured at various pressures (8.0–24.0 MPa) and temperatures (293.15, 308.15 and 318.15 K) with or without methanol. The solubility of the dye was found to increase with increasing pressure. These results indicate that methanol can significantly increase the dyes’ solubility in supercritical fluids. Relatively good fits are obtained using Chrastil and Sovova equations. Well-correlated results were obtained between the calculated and experimental solubilities based on all fitted models. The solubility results clearly indicate the feasibility of processing this dye, and possibly rhodamine dyes, using modified supercritical/subcritical fluid technologies and processes, for example, with optical polymers.
2.6 Reference


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Chapter 3  Impregnation of rhodamine dyes into POF

3.1 Introduction

In the earlier days, supercritical/subcritical CO₂ were mainly used in extraction applications. Recently, supercritical fluid impregnation offers tremendous potential for effectively treating a variety of polymer materials with modifiers. The modifiers molecules, which are dissolved in the CO₂ fluids and impregnated into the polymer [1], the modifiers molecules could also are a dye or a drug, which can chemically modify polymers without melting the polymer, this is shown in Fig 3.1.

![Diagram of Dyeing Process](image)

**Fig. 3.1** Interactions between the supercritical CO₂ impregnation systems

In this work, the authors introduced a subcritical level of CO₂ fluid impregnation method as an alternative to the conventional free radical polymerization method to prepare fluorescence dyes doped polymer optical fiber. The solubility of rhodamine
dyes in CO$_2$ fluids was measured, and then the impregnation effect of various factors, such as organic cosolvent, pressure, temperature and time of the impregnation process was also investigated.

3.2. Experimental

3.2.1 Materials

An optical fiber is a transparent thin fiber, usually made of glass or polymer, for transmitting light [2]. According to raw materials, optical fiber is basically classified into two materials, silicate glass and polymer. Silicate glass is the most transparent material as known and optical glass fibers with extremely low attenuation of light transmission and high bandwidth have been developed. These optical glass fibers have been used for long distance telecommunications. Recently there has been considerable interest in the development of Polymer Optical Fibers. The ductility of polymers is an important advantage and confers on POF easy processing, easy handling, low costs and large core diameter (The large core diameter, up to 1 mm or more). Furthermore, because polymers have low densities they are light-weight. To date, POF have an extended applicability, such as in computer networks, local area networks, data links, optical sensors, lighting and so on.

Optical fiber is a cylindrical structure that transmits light along its axis. Light can be transmitted through transparent media by means of total internal reflection, which is possible in a core-cladding configuration. In large-diameter fibers, the core that allows the transmission of light, and the cladding must have a lower refractive index than the core. Typically, uses PMMA or PS, a general resin as the core material, and fluorinatated polymers for the clad material. The structure of the polymer optical is shown in Fig. 3.2.
Among the known polymers, Poly (methyl methacrylate) (PMMA) has been used in optical devices, such as an optical fiber, and exhibits outstanding chemical and thermal stability. In this work, polymer optical fiber CK30 used was provided by MITSUBISHI RAYON CO.LTD. The POF has a step index (SI) profile which is composed of fluorinated polymer for cladding and poly (methyl methacrylate) for core. The average diameter of the core is about 738 μm and the outside diameter is about 750 μm, 97% of the volume of the POF is made from PMMA. Rhodamine is the most widely used and studied as the fluorescence dye. Rhodamine 6G and B were purchased from KANTO CHEMICAL CO, INC. The structures of the rhodamine 6G and rhodamine B are shown in Table 2.1.

**Fig. 3.2** The cross-sectional drawing of the polymer optical fiber CK30
Carbon dioxide gas used was provided by Uno Sanso Co., Ltd. (99.5% purity). Methanol is also used for modifying the solubility property of CO$_2$ fluids. It is guaranteed-grade reagent form and was used without further purification.

3.2.2 Impregnation apparatus and procedures

A particular apparatus designed for the impregnation using CO$_2$ fluids is shown in Fig.3.4 and Fig.3.6. The temperature in the bath can be controlled within ±1 °C by the temperature sensor (6). A specially designed stainless steel pipeline (5) is a spiral form and its inner diameter is 5 mm, which makes it possible to contain the original polymer optical fiber with a length of approximately 80 cm is shown in Fig.3.5. Through a circulation pump (4), CO$_2$ fluids circulate in the stainless steel pipeline so that impregnation experiments can be done up to 20 MPa.
Fig 3.4 Supercritical dyeing machine

Fig. 3.4 Schematic diagram of the impregnation experimental apparatus

(1) CO₂ cylinder, (2) high-pressure pump, (3) valve, (4) circulation pump, (5) stainless steel pipeline, (6) temperature sensor, (7) needle valve, (8) solvent

Fig. 3.5 A spiral form stainless-steel high-pressure column
In a typical impregnation process, a blank POF with certain length is fixed in the stainless steel pipeline by one end and the dye with a ratio between 0.05 and 1.5% owf (i.e. % weight of dye per weight of POF) is used. For the carbon dioxide fluids/cosolvent experiments, all the dyes were previously dissolved in organic solvent, and then the solvent enters into steel pipeline. When the system reaches the desired temperature, the CO$_2$ is injected into the pipeline by a high-pressure pump (2) at a given

Fig. 3.6 Supercritical impregnation apparatus
pressure to obtain CO$_2$ fluids, and the circulation pump makes the CO$_2$ fluids circulating within pipeline through the impregnation process. After a specified period of impregnation time, to avoid foaming, the system is very slowly ventilated by a valve and a needle valve (7).

At the end of the impregnation experiment, when the system had reached to atmospheric pressure, the impregnated POF was extracted from the stainless steel pipeline. A digital optical microscopy was used to evaluate the form and dye diffusion area within the treated POFs. The dye concentration absorbed on the POFs was measured spectrophotometrically after the extraction of the dye with chloroform and posterior measurement of dye absorption intensity. These values were measured with SHIMADZU UV-1700 UV-VIS Spectrophotometer. To understand degree of swelling, diameter change data for POFs were measured by micrometer after the treatment process for 48 h.
3.3 Results and Discussion

3.3.1 Impregnation in pure supercritical

Experiments were carried out to investigate whether impregnation of rhodamine dyes are feasible for POF in pure carbon dioxide fluids. The experiment was conducted with CO$_2$ over a pressure ranging from 10 - 20 MPa at temperatures from 30 - 80 °C, and with contact time ranging of 30 to 180 min. The experimental results show that under these conditions, impregnating POF with a rhodamine dyes was not obtained. Even spending longtime in high-pressure and high temperature, dyes were scarcely doped in POF, show in Fig. 3.7.

The result is consistent with a general view that the impregnation process is feasible when the dye is soluble in the CO$_2$ fluids [3-5].

Fig. 3.7 Polymer optical fiber was impregnated at scCO$_2$ at pressure 10 MPa, 40 °C and 2h

3.3.2 Cosolvent choice

To increase the polarity of scCO$_2$, the addition of a polar additive is frequently
applied. In literature it was described that 3 to 10 mole % of a polar additive is already sufficient [4,5]. In this study, rhodamine dyes was impregnated using pure scCO₂ or modified ones with several solvents (methanol, ethanol, water, acetone, chloroform, Dimethyl Sulphoxide, formyl, acetic acid and so on) and their efficiencies were performed, respectively.

A great lot of experiments show that among the modifiers employed, methanol was found to greatly enhance the impregnation efficiency without any cracks for polymer optical fiber under proper conditions.

The chapter 2 solution data indicate that methanol can significantly increase the dyes’ solubility in supercritical/subcritical fluids.

![Fig. 3.8](image)

**Fig. 3.8** Solubility of rhodamine 6G in CO₂ fluids without (▲) or with 5 % methanol (■) at temperature 293.15 K
Fig. 3.9 Solubility of rhodamine B in CO₂ fluids without (▲) or with 5 % methanol (■) at temperature 293.15 K

From Fig.3.8 and 3.9, we can conclude that the solubility of rhodamine dyes in carbon dioxide solvent increases with the increase of the mole fraction of methanol in the mixture at fixed temperatures and pressures. This result is due to the strong molecular interactions between the solute and the cosolvent.

In this impregnation experiment show that if methanol is added 4-6 mol% to the CO₂ fluids, rhodamine dyes can be impregnated POF despite the fact that rhodamine dye has low affinity for PMMA, is shown in Fig.3.10. The results are understandable from the solubility enhancement by methanol.

It is a generally accepted view that the impregnation process is feasible when the dye is soluble in the CO₂ fluids, and the polymer material is swollen by the CO₂ fluids and the dye molecular impregnation inside the polymer matrix with the CO₂ fluids.
When the system is depressurized, CO\textsubscript{2} leaves the polymer materials, leaving the dye molecule trapped POF.

Fig. 3.10 Blank Optical Fiber (right) and rhodamine 6G impregnated POF (left)

Studies conducted by the previous scholar show the impregnation into polymers is influenced by a variety of factors. In this study, several parameters, such as system pressure, temperature and contact time for CO\textsubscript{2} fluids must be optimized to get a successful impregnation [6-11].
3.3.3 Effect of pressure

Generally speaking, solubility increases as the CO\(_2\) density increases under pressure, and the high density is conducive to the completion of the impregnation process. The experimental conditions are as follows: the pressure ranges from 2 to 12 MPa, contact time is 36 hrs and the constant temperature is 20 °C. Fig.3.11 shows the experimental data, from which it is clear that different pressure can lead to very different dyes concentration in the POFs.

![Graph showing the effect of CO\(_2\) pressure on rhodamine 6G concentration](image)

**Fig. 3.11** The effect of CO\(_2\) pressure on the rhodamine 6G concentration absorbed in the POF, T=20 °C

Our experimental results can be ascribed the increase in solubility of the dye in the CO\(_2\) due to pressure. In this experiment, the density of the CO\(_2\) at different pressure conditions, which is shown in Table 3.1, was calculated by using the Ely-Haynes-Bain equation. The density of the fluid grows steadily with increasing pressure at a given
temperature, while the solubility depends strongly on the density, if pressures ranging from 5 MPa to 6 MPa, the density of CO\textsubscript{2} increases rapidly and the subcritical fluids begin to act like liquid solvents. Therefore impregnation experiments are generally suitable to operate over a pressure range of 6MPa to 8MPa.

<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>Density, g/cm\textsuperscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.09753</td>
</tr>
<tr>
<td>5</td>
<td>0.14073</td>
</tr>
<tr>
<td>6</td>
<td>0.78265</td>
</tr>
<tr>
<td>7</td>
<td>0.80847</td>
</tr>
<tr>
<td>8</td>
<td>0.82767</td>
</tr>
</tbody>
</table>

Table 3.1 Carbon dioxide density at 20°C

On the other hand, it is known that the swelling of PMMA with the presence of scCO\textsubscript{2} increased in direct proportionally with pressure, the swelling enhances the mobility of the polymer chains and changes the polymer properties, however, excess swell is undesirable specially for the optical fiber. To understand the degree of swelling, diameters POFs were measured by micrometer after the treatment process for 48 hrs. The results showed that the diameter changes were less than 2% when the pressure was less than 8 MPa, and POFs retained their initial shape, which followed in the required tolerance. Therefore, in this experiment, 6-8 MPa is considered appropriate to be for impregnation.

3.3.4 Effect of temperature and impregnation time

As light is transmitted in the core of optical fiber, the poured-in dyes should be
distributed evenly throughout the inside POF to guarantee the well function. Fig 3.12 shows dye concentration in POF under the same impregnation condition for a different period of time. Clearly, the dye concentration in POF increases with impregnation time and reaches a plateau after 30hrs. Moreover, microscopic observation revealed that at the beginning stage the dyes stay on the surface of POF and form a dye layer, afterwards they gradually move towards the core of POF, after 36h they are evenly distributed throughout the inside of POF is shown in Fig 3.13. The dye diffusion is very slow. The reason may be the poor affinity and poor interaction between rhodamine dyes and PMMA. Furthermore, in this experiment is operating beneath the critical temperature, and rhodamine molecule is large, the diffusion rates is comparatively slow and needs a long period under lower temperature conditions.

![Absorption intensity vs Impregnation time](image)

**Fig. 3.12** The effect of time on the rhodamine 6G concentration absorbed in the POF,
T=20 °C, P=8 MPa

**Fig. 3.13** Rhodamine 6G distribution in the POF vs. impregnation time, experiments carried out at 8MPa and 20°C.

In the dyeing process, dye diffusion rate increases with temperature at the same pressure. At low temperature in selected impregnation range (temperature below 10–15 °C), a very low diffusion rate of dyes in POF is observed by digital microscope. On the other hand, higher temperature is not absolutely beneficial to the impregnation. The author observed that when the impregnation temperature is higher than 22 °C, it can easily lead to irreversible structural changes in the POFs, and the structure change of POFs is undesirable in optical fibers. Judicious selection of conditions makes it possible to avoid changes in the structure of POFs. The great amount of experimental results
suggests that the impregnation temperature between 18 °C to 20 °C is appropriate.

**Fig 3.14** Due to the impregnation less than 40°C, the structure of polymer optical fiber was changed

The swelling and foaming behavior of PMMA films in presence of scCO₂ have been widely described [12-14].

To investigate whether there exists foaming in treated POFs, a digital optical microscopy was used to evaluate the form of the treated POFs. In addition, Scanning Electron Microscopy (SEM) was conducted by HITACHI S–2600HS to observe the cross-section of samples [15,16]. Fig.3.15 (a) shows foaming bubbles in a POF is observed by optical microscopic. Nevertheless, optics applications wish to avoid foaming, experiments have been performed to confirm the excite beam could hardly be detected through the POF with few bubbles. Fig.3.14 (b) shows the SEM image of the cross-sectional of dye doped sample. Image exhibited no detectable micro porous structure, which suggests that impregnation method can provide effective
process of the POF with gentle nonfoaming products. It is possible that low-pressure subcritical CO$_2$ is of lower swelling than scCO$_2$, and at the end of impregnation period, by carefully control the ventilation time (more than 4 hours), foaming during pressure release is not a problem [17,18].

![Fig. 3.15 POFs was examined by optical microscopy and SEM.](image)

(a) Microscopy images shows the bubble occurred in the POF (diameter 0.75 mm), (b) A cross-sectional SEM image of dye impregnated POF
3.4. Conclusions

In this study, a method using subcritical levels of modified carbon dioxide fluids (20 °C and 8 MPa with 5 mol % methanol) to successfully impregnate rhodamine dyes in POFs is introduced. Rhodamine solubility is very low in pure CO₂, but increases by adding a small amount of methanol. In this work, in order to avoid swelling the impregnation in polymer optical fiber with rhodamine dyes was performed in near critical carbon dioxide. The designation ‘near critical’ means at 20°C and 80 bars one is operating beneath the critical temperature but still in the critical region. In this critical region, CO₂ fluids become liquid-like and the CO₂ begin to act like liquid solvents.

Under optimized impregnation condition (18-20 °C, 8 MPa and impregnation time of 36 hrs), the authors are able to produce homogeneously impregnated POFs with dye concentrations ranging from 50 to 3000 ppm.

Compared with the conventional drop process, one very important advantage of this method is that it allows the fluorescence dyes to be poured into the POF without decomposition. These results provide a new way to prepare POFs doped with thermally lower stable molecules and expand the field of application of compressed CO₂ fluids technology.
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Chapter 4 Measurement and stability analysis

4.1 Rhodamine doped POF emission spectrum

For the fluorescence spectrums measurements, the action of dye doped POF was pumped at 532 nm with a frequency-doubled Q-switched Nd:YAG laser [1-5]. A schematic of the experimental setup to characterize the dye-doped polymer optical fiber as an optical medium is given in Fig. 4.1. The pump source for the measurement is a doubled Q-switched Nd:YAG laser at 532nm, and two 15cm-long POFs with a diameter of 780 μm, one with rhodamine dyes concentration of approximately 2000 ppm were used in this experiment, another is blank polymer optical fiber. Pump light was guided into POF by a microscope objective lens, and an optical spectral analyzer was used to measure fluorescence spectrum at the output end of POF. The spectral profiles are presented in Fig. 4.2. The emission spectrum of blank polymer optical fiber was 532 nm with a 3.4 nm bandwidth, on the other hand, the rhodamine 6G and rhodamine B impregnated POF showed a emission spectrum with a peak at around 600 nm and 620 nm, which is obviously different from the typical Nd:YAG lasing at 532 nm. These results are consistent with the theory that fluorescence dyes have strong absorption in the visible portion and exhibit strong fluorescence, thus it can be concluded that dye molecules are indeed in the core region of optical fiber.
Fig. 4.1 Measurement set-up of optical properties of POF

Fig. 4.2 Comparison of emission spectra from Rhodamine 6G doped POF (peak at 596nm) and blank POF (peak at 532nm).
Fig. 4.3 The emission spectra from Rhodamine B doped POF of approximately 2000 ppm

Fig. 4.4 The emission spectra from Rhodamine 6G doped POF of approximately 2000 ppm
4.2 The effect of CO₂ fluids processing on dyes decomposition

In the last few years, dye-doped polymer optical fibers have achieved significant potential as suitable optical amplifiers. They have relatively compact, maintenance free and low cost gain media. However fluorescence dyes lasers have a serious problem of low thermal stability of the dyes. The decomposition of the dye molecule can be achieved by radical polymer process of dye-doped polymer optical preparation. To understand the effect of CO₂ fluids processing on fluorescence dye decomposition, experiments were carried out for rhodamine 6G solution in methanol (1.25×10⁻³ mol mL⁻¹) at 25 °C and 10 MPa for 36 hours. The degradation ratio was estimated from absorbance of the rhodamine 6G methanol solution. The absorption spectrum of the treated and the untreated samples were analyzed by a UV-VIS spectrophotometer. The result was shown in Figure 4.5. It was clear that only a slight difference in spectrums intensity was observed among the spectrum of rhodamine 6G samples. Compared with the dye loss of approximately 37-56 % in the polymerization methods reported in literature [6], this result implied that lower pressure and lower temperature impregnation process had little negative effects on the performance of fluorescence dyes.
Fig. 4.5 Absorption spectrum of rhodamine 6G, original sample is shown by solid line and treated is shown by a dashed line.
4.3 Reference


Chapter 5  Conclusions

Coming to the end of this thesis the results will be put into perspective. The aim of this research was impregnation of fluorescence dyes rhodamine 6G and rhodamine B into polymer optical fiber using super/sub-critical CO$_2$ fluids.

An overview of supercritical/subcritical carbon dioxide fluids processes in the presence of organic material and polymer has been presented. The use of carbon dioxide fluids in polymerization and polymer modification has several advantages compared to more conventional techniques such as melt and solution modification. A few examples of commercial scale applications are the supercritical extraction, supercritical dyeing of PET and the polymerization of some polymers in supercritical fluids.

Fluorescence dyes are a coherent source of radiation with a wide tuning range and find many applications in various fields. At present, there are a number of materials which have been used as solid hosts for laser dyes such as polymers, porous glasses, and organically modified silicates. Fluorescence dyes based on polymer optical fiber have been reported extensively in literature, but the problems of as the polymer optical fiber materials polymerize, the result shows that dye decomposes when the temperature is above 70°C. In this study, rhodamine dyes was impregnated using pure CO$_2$ or modified ones with cosolvent and their efficiencies were compared with that of the conventional method. Based on of these results, subcritical impregnation would be considered as a novel doped method for optical fiber to substitute the sol-gel method.

In this work, first, the solubility of rhodamine 6G and rhodamine B in scCO$_2$ was measured at various pressures (8.0–24.0 MPa) and temperatures (293.15, 308.15 and
318.15 K) with or without methanol. The solubility of the dye was found to increase with increasing pressure. These results indicate that methanol can significantly increase the dyes’ solubility in supercritical fluids. Relatively good fits are obtained using Chrastil and Sovova equations. Well-correlated results were obtained between the calculated and experimental solubilities based on all fitted models. The solubility results clearly indicate the feasibility of processing this dye, and possibly rhodamine dyes, using supercritical/subcritical fluid technologies and processes, for example, with optical polymers.

Secondly, depending on a variety of factors, such as the polarity of the fluids, the temperature, pressure and time, which are with carbon dioxide fluids dyes impregnation in the polymer, have been discussed in detail.

Finally, in laser characteristic experiment, the results presented indicate that using a super/critical fluids technique, we have produced that is to our knowledge the first fluorescence dyes doped polymer optical fiber, and the dyes have a uniform distribution doping in POF.

In this work, carbon dioxide fluids impregnation is a useful method for the polymer procedure. We have developed a novel method of rhodamine dye doped polymer optical fiber preparation. This method allows us to add functions dye to polymers while retaining the initial shapes. Furthermore, the characteristics of the polymers can also be controlled. In this method, the molecules of the dye are dispersed into the polymer. This method enables us to prepare a polymer optical fiber in which functional organic molecules without altering and damaging their physical, chemical, and mechanical properties.
発表論文

レフェリー制のある学術雑誌

(1) Impregnation of fluorescence dyes into polymer optical fiber using carbon dioxide fluid

Chuan Zhao, Satoko Okubayashi, Takayuki Suzuma, Kazumasa Hirogaki, Isao Tabata, Teruo Hori

繊維学会誌 Vol.67, No.2 (2011) p 34-39

(2) Supercritical Dyeing of Polyester Fibers in a Mini-Plant Possessing Internal Circulator

Satoko Okubayashi, Takayuki Suzuma, Chuan Zhao, Keisuke Miyazak, Kazumasa Hirogaki, Isao Tabata, Teruo Hori

繊維学会誌 Vol.67, No.2 (2011) p 27-33

(3) A Novel Method of Modifying Poly(ethylene terephthalate) Fabric Using Supercritical Carbon Dioxide

Ma, Wen-Xiao, Zhao, Chuan, Okubayashi, Satoko, Tabata, Isao, Hisada, Kenji, Hori, Teruo

JOURNAL OF APPLIED POLYMER SCIENCE  2010, 117, 1897-1907
Acknowledgments

I would like to express my appreciation to various kind people I have met. At first, I want to acknowledge with thank Prof. Dr. Teruo Hori of University of Fukui, for his knowledge transference and advantageous assistant in this research, I’m grateful for his kindness, patience, and wisdom. My heartfelt thanks are also given to Assistant Prof. Dr. Satoko Okubayashi of Kyoto Institute of Technology, Assistant Prof. Dr. Kenji Hisada and Mr. Isao Tabata of University of Fukui. Also, I am very grateful to Prof. Dr. Takao Kobayashi and Dr. Yasufumi Enami for guidance of the laser experiments and offering apparatus. Finally, I thank my family and my friends for their support and encouragement.

Zhao Chuan
2011/01/10