A Study of Solubility of an Organic EL Compound by Means of Supercritical Carbon Dioxide

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Abstract: This study relates to the cleaning and reuse of metal masks used in the process of manufacturing organic EL displays, which belong to the next-generation display. Supercritical carbon dioxide was used as the solvent to wash those masks. In this study, the solubility of organic compound by supercritical carbon dioxide was measured, and modeling of solubility was completed. Focusing attention on the fact that the solubility is almost at the same level as that of RED60 dye, which is under development toward practical application, it was verified whether it was possible to thoroughly wash the mask, using mimic metal masks.

(Received 3 September, 2004; Accepted 30 November, 2004)

1. Introduction

Organic EL displays, which draw people's attention as a next generation display, involve various problems in mass manufacture although they are viable to become really a next generation display.

One of such problems is the treatment of metal masks, which are used in selective painting of pixels with organic compound as luminescent material in the organic EL display manufacture process, as shown in Fig. 1. Those metal masks, treated with precision processing, are discarded after a single use because it is difficult by washing to thoroughly clean deposited organic compounds.

Hence, we tried to wash metal masks with supercritical carbon dioxide as solvent in order to make them reusable as refreshed masks.

Use of supercritical carbon dioxide involves several advantages:

- (1) Kinematic viscosity is low, causing little stress
 - (2) Excellent in permeability into micro-structure
 - (3) Can control the solubility via the pressure and temperature
 - (4) Low in environmental load because it is a component of atmospheric air
 - (5) It is inert, nonflammable, nontoxic and odorless
 - (6) Needs no drying process after washing metal masks
- Therefore, the solubility of organic compound into supercritical carbon dioxide was measured, and estimation of solubility was modeled. This

solubility-estimating expression will be effective when we are designing a washing apparatus in the near future.

Further, mimic metal masks were created for confirming the actual washing condition, and washing situation was observed when supercritical carbon dioxide was used, which was compared with washing with ethanol.

Fig. 1 Process of manufacturing organic EL display.

2. Experiment

2.1 Solubility measurement experiment

The organic compound used in the experiment was anthracene-based substance (hereafter referred to as “EL 1”) with purity of 99.9%. The solubility of this material was measured by the experiment apparatus as shown in Fig. 2. The abovementioned organic compound was accreted on silica, which was dissolved into supercritical carbon dioxide in a column. For determination of solubility, two types of dissolved organic compounds were used: (1) those collected by double trap, and (2) those deposited inside the tubing upstream of the trap. Organic compounds deposited inside tubing were collected by washing the tube with solvent in the line-washing syringe. Both types of organic compounds collected by (1) and (2) were measured for solubility by a spectrophotometer.

The carbon dioxide used was of 99.9% or higher purity, and supplied from a siphoned cylinder. PU-980 by JASCO Inc. was used as the carbon dioxide pump, and CB-Jr by Iuchi Inc. was used as the cooler to chill the carbon dioxide pump so that the temperature of -6°C would be attained, and GC-12A by Shimadzu Inc. was used as the thermostatic chamber to keep the column at a constant temperature. Structure was arranged such that the flow rate regulation valve would be opened and closed repeatedly for a certain volume by a stepping motor in order to prevent reduction of opening degree of valves due to sticking organic compound. Two cold traps were provided in tandem to collect dissolved organic compound. In addition, the flow rate of carbon dioxide used for dissolution was read from the gas flow meter.

Fig. 2 Apparatus of solubility experiment.

2.2 Metal mask washing experiment

Further, EL 1 was deposited by evaporation onto mimic metal masks, having various shapes of opening, as shown in Fig. 5, and also an experiment of washing with supercritical fluid was performed by placing mimic metal masks in the column of apparatus. Result was compared with the experiment of washing with ethanol at room temperature.

3. Correlation

In our solution model, the solubility of compound is given by the following equation because the supercritical fluid is taken as an expanded liquid:

$$y_2 = \frac{1}{\gamma_2^\infty} \frac{f_2^{OS}}{f_2^{OL}} \quad (1)$$

where the infinite dilution activity coefficient γ_2^∞ can be calculated by using the regular solution theory, which is conjugated by the Flory-Huggins theory, and the fugacity ratio can be determined by using the fugacity expression, given by Prausnitz et al., induced from the solid-liquid equilibria, both of which are expressed as follows [1,2,3]:

$$\ln \gamma_2^\infty = \frac{v_2}{RT} \left(\delta_1 - \sqrt{\frac{\Delta U_2}{v_2}} \right)^2 + 1 - \frac{v_2}{v_1} + \ln \frac{v_2}{v_1} \quad (2)$$

$$\ln \frac{f_2^{OS}}{f_2^{OL}} = \frac{\Delta H_2^m}{RT} \left(\frac{T}{T_m} - 1 \right) \quad (3)$$

Equations 1 to 3 brings us a solubility correlation equation as expressed below:

$$\ln y_2 = \frac{\Delta H_2^m}{RT} \left(\frac{T}{T_m} - 1 \right) - \left[\frac{v_2}{RT} \left(\delta_1 - \sqrt{\frac{\Delta U_2}{v_2}} \right)^2 + 1 - \frac{v_2}{v_1} + \ln \frac{v_2}{v_1} \right] \quad (4)$$

where σ_1 was calculated using the method of Gidding et al.[4], and ΔH_m and T_m are heat of fusion and melting point of dissolved substance, respectively, and they were 29.4 kJ/mol and 291.2°C as measured using a differential scanning calorimeter (DSC). ΔU_2 was calculated using the Fedors' atom group contribution method [5,6]. Further, it was considered that v_2 varies under the effects of fluid density. Taking into account the fluid density-dependence, therefore, this was calculated by Equation 5 [7,8]:

$$\ln v_2 = \alpha \ln \rho_1 + \beta \quad (5)$$

where α and β are fitting parameters, and thus the parameters were optimized so that the error between the

result of solubility measurement and the result of estimation would be the smallest in order to minimize the absolute average relative dispersion (AARD).

4. Result and discussion

4.1 Solubility measurement result

The density and the solubility of EL 1 when temperature and pressure are changed are shown in Table 1, and the density and the solubility are plotted in a graph as shown in Fig. 3. The diagram indicates that the fluid density changes along with the altering pressure at fixed temperature levels, and as a result, the solubility is changed in a wide range. The solubility is improved as the fluid density becomes greater at each temperature level. The result tells us that the higher the temperature is, the greater the solubility is improved. In addition, the effect of flow velocity was not noticed.

Table 1 EL1 solubility with changing temperature and pressure.

40°C P(MPa)	$\rho / \text{g ml}^{-1}$	Mole fraction($\times 10^{-6}$)
30	0.9107	2.81
60°C P(MPa)	$\rho / \text{g ml}^{-1}$	Mole fraction($\times 10^{-6}$)
15	0.6061	0.06
20	0.7248	0.17
25	0.7871	0.33
30	0.8301	0.94
80°C P(MPa)	$\rho / \text{g ml}^{-1}$	Mole fraction($\times 10^{-6}$)
15	0.4276	0.02
20	0.5959	0.14
25	0.6873	0.44
30	0.7460	0.83
120°C P(MPa)	$\rho / \text{g ml}^{-1}$	Mole fraction($\times 10^{-6}$)
15	0.2801	0.02
20	0.4013	0.12
25	0.5065	0.59
30	0.5860	1.66

Fig. 3 Apparatus of solubility experiment.

Solubility of RED60, which is a disperse dye, is added for reference [9]. When it is considered that the data of Red60 is 40°C, the solubility of EL1 is a little smaller than that of Red60.

4.2 Correlation result

Fig. 4 shows the correlation between the solubility measured in the experiment and the values calculated by Equation 4. An excellent correlation with AARD of 16.8% resulted from the assumption of letting α and β of EL 1, used in our study, be -1.39 and 1.26 .

The above result enables us to estimate solubility at pressure and temperature, at which solubility was not

Fig. 4 Correlation between EL1 solubility and solubility correlation equation.

measured in our experiment. Further, this equation of solubility will be useful for deciding the liquid flow rate, working pressure and temperature when some installation is designed in practice.

4.3 Metal mask washing experiment result

Fig. 5 Shape of mimic metal mask.

Next, whether EL 1 having solubility of the same level as that of RED60, which is now under development toward practical application, can thoroughly clean the mimic metal masks will be verified.

For comparison, mimic metal masks washed with supercritical carbon dioxide (ethanol was added by 5%

Fig. 6 Result of ethanol washing at room temperature(left) and result of washing with supercritical carbon dioxide(right).

mole fraction as an entrainer) at 60°C and under 30MPa and those washed with ethanol at the room temperature are shown by SEM photographs in Fig. 6. The photographs evidently show that ethanol washing failed to fully clean the compound deposits on irregular surfaces of opening section, while washing with supercritical carbon dioxide was successful in washing away foreign matters sticking to irregular parts of various shapes of metal masks.

Fig. 7 shows schematic diagrams for washing with solvent and washing with supercritical carbon dioxide. In solvent washing, the surface tension of solvent hinders the solvent from washing away foreign matters sticking to minute holes and parts of precision processing, but in supercritical carbon dioxide washing, gas molecules are ready to be diffused to wash and clean even minute holes, which is considered to have made the difference demonstrated in this study.

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Fig. 7 Schematic diagram of washing.