

Development of a solvent selection guide for CO₂ spray coating



Yoshiyuki Sato^{a,*}, Tomoki Shimada^a, Kohei Abe^a, Hiroshi Inomata^a, Shin-ichiro Kawasaki^b

^a Research Center of Supercritical Fluid Technology, Graduate School of Engineering, Tohoku University, Aoba 6-6-11-403, Aramaki, Aoba-ku, Sendai 980-8579, Japan

^b Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), Nigatake 4-2-1, Miyagino, Sendai 983-8551, Japan

ARTICLE INFO

Keywords:

Solubility parameter
Phase equilibria
Polymer solution

ABSTRACT

The use of CO₂ for spray coating is a promising technique for volatile organic compound reduction in the paint industry. However, the polymer precipitation might be induced by the addition of CO₂ into solvent, since CO₂ is a poor solvent for most polymer solutions. In this work, a solvent selection guide for CO₂ spray coating is proposed based on the solubility parameter from the viewpoint of avoiding the polymer precipitation. The precipitation tests were carried out for polymer (acrylic resin) + solvent (eight kinds) + CO₂ systems. The solubilities of CO₂ in the polymer + solvent (diethyl ketone, butanol, and methanol) varied from 7 to 33 wt.% CO₂ at 40 °C for pressures from 0.9 to 6.4 MPa. It was found that the solubility parameter of the mixture at the precipitation point had similar values that are due to dissolution of the CO₂ in the solution.

1. Introduction

The paint industry is the largest source of volatile organic compound (VOC) emissions in Japan [1]. It has become an urgent issue to reduce VOC emissions [2]. In 1990, the UNICARB[®] CO₂ spray system [3] was developed by Union Carbide with the aim of reducing the concentration of VOCs in coating formulations. Lewis et al. [4] reported that CO₂ spray systems had technological advantages such as superior leveling compared with conventional ones. Recently, Kawasaki et al. [5] proposed a CO₂ spray system equipped with a micromixer that enables CO₂ to dissolve into organic paint solutions rapidly and homogeneously.

Conventional paint consists of polymer, solvent, and diluents with a large portion being organic solvents. A CO₂ spray coating system is expected to reduce the amount of VOCs as well as energy consumption by using CO₂ as a diluent. However, precipitation of the polymer is induced by CO₂ dissolution into some paints in terms of CO₂ concentration, because CO₂ can act as anti-solvent for a polymer. It is important to prevent precipitation of the polymer in paint solution during mixing of CO₂ with the organic solvent-polymer solution and during transport of the solution to the target surface. Since it is undesirable to replace proven polymers used in coating processes, the solvents should be selected to prevent precipitation in CO₂ spray coating systems. Therefore, development of an effective and practical solvent selection methodology for paint formulations is important.

The solubility parameter [6] is one of the most useful tools for solvent selection. The solubility parameter is originally defined as the

square root of the cohesive energy density. Some researchers [7–9] have applied the solubility parameter to the temperature and pressure ranges including the supercritical region, by using equations of state to calculate the solubility parameter. Williams et al. [9] proposed temperature and pressure effects of the three components of the solubility parameter of Hansen (HSP) [10] and gave CO₂ HSP values as a function of temperature and pressure. On the other hand, it should be noted that solubility parameter of solvents and CO₂ mixtures is important for paint solvent selection in the CO₂ spray coating systems. The solubility parameter of mixtures has been investigated by some researchers [11,12]. Since solubility parameter is based on the cohesive energy density (cohesive energy of unit volume), the volume average solubility parameter is usually used for mixture. However, there have not been reported the effective methods of the solubility parameter evaluation of solvent mixtures containing supercritical fluids, which enable us to design the solvent selection for paint formulations in CO₂ spray coating systems. Some progress has been made in redefining solubility parameters that contain hydrogen bonding effects that are denoted as partial solvation parameters (SPS) [13,14]. This method was considered in this work, but the practical system studied makes application of SPS uncertain. Therefore, a simple approach was taken for the acrylic resin system.

In this work, a solvent selection guide (methodology) for CO₂ spray coating systems is proposed via evaluating the solubility parameters of the solvent + CO₂ mixture and polymer. Acrylic resin was chosen as a polymer component and eight solvents were used. Phase behavior and phase equilibria of polymer + solvent + CO₂ system were

* Corresponding author.

E-mail address: ysato@scf.che.tohoku.ac.jp (Y. Sato).

Table 1
Characteristics and composition of acrylic resin used in this work.

component	fraction [wt%]
acrylic resin	45–55
butyl acetate	45–55
methyl methacrylate	1.0
acid value	3.5 mgKOH/g
hydroxyl number	73.3 mgKOH/g

experimentally studied at 40 °C. Furthermore, the relationship between solubility parameter of the solvent and CO₂ mixtures and the phase behavior was investigated.

2. Experimental

2.1. Sample

Acrylic resin (ACRYDIC 52-666-BA, DIC Corporation, Japan) was used as a polymer component in paints. This polymer is used for isocyanate curing and was supplied as a butyl acetate solution. The number average molecular weight and the weight average molecular weight of the acrylic resin were obtained by SEC with a differential refractive index detector using polystyrene standards and determined to be \bar{M}_n (14.9 kg/mol) and \bar{M}_w (16.8 kg/mol). Characteristics and composition of the acrylic resin obtained by the manufacturer are shown in Table 1. The chemical structure of the polymer was estimated from the information given in Table 1 as shown in Fig. 1. Solubility parameter of the acrylic resin was estimated to be 21.9–23.2 MPa^{0.5} by using Fedors'group contribution method [15].

Eight diluents were used for precipitation tests described below. The data on source, purity, and solubility parameter [10] of the diluents are given in Table 2. The sample (acrylic resin dissolved in butyl acetate) was mixed with one of the diluents (sample/diluent = 5/3 wt.) listed in Table 2. The diluted solutions, which are composed of the polymer sample and a diluent solvent, were prepared so as to have a polymer concentration of 10–20 wt% when CO₂ dissolved into the solution. The diluted solutions were used for precipitation tests and for CO₂ solubility measurements. The CO₂ (purity > 99.5 vol%) was obtained from Showa Denko Gas Products Co., Ltd. All chemicals were used as received.

2.2. Precipitation test

Precipitation of polymer was observed with the phase behavior apparatus shown in Fig. 2. The observation cell, equipped with a cylindrical sapphire window (i.d. ϕ 10, o.d. ϕ 14, length 18 mm) and a test tube (i.d. ϕ 8.3, length 27 mm), was set in a thermostated water bath. Diluted solution (0.3 g) was filled into the test tube. CO₂ was supplied with a regulator (\leq 5 MPa) or a syringe pump ($>$ 5 MPa, ISCO model 260D) and CO₂ pressure was increased at 0.5 MPa interval. When polymer precipitation was observed, the pressure (Krone Corporation, Tokyo, KDM30, accuracy 0.05 MPa) was recorded. A Teflon-coated stirring bar (ϕ 3 \times 8 mm) was used to promote equilibration via a magnetic stirrer that was located under the cell. Equilibration of gas dissolution was confirmed with height change of the liquid meniscus in

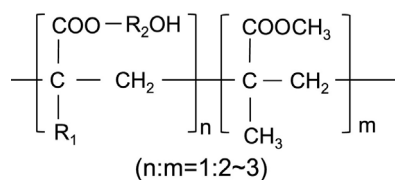


Fig. 1. Estimated chemical structure of the acrylic resin used in the CO₂ spray coating study.

Table 2
Purity and solubility parameter of diluents used in the CO₂ spray coating system. The source of all chemicals was Wako Pure Chemical Industries (Osaka).

Chemical name	Purity (wt%) ^a	Solubility Parameter (MPa ^{0.5}) [10]
<i>n</i> -hexane	96.0	14.9
diisobutyl ketone (DIBK)	90.0	16.9
diethyl ketone (DEK)	98.0	18.2
1-pentanol	98.0	21.6
1-butanol	99.0	23.2
ethanol	99.85	26.5
methanol	99.8	29.6
ethylene glycol	99.5	33.0

^a as reported by the supplier.

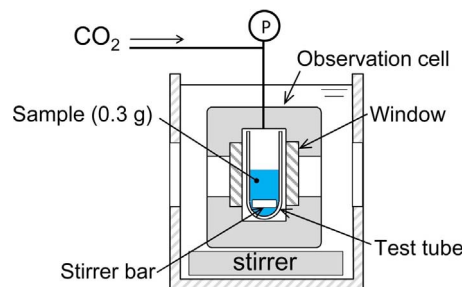


Fig. 2. Phase behavior observation apparatus.

the test tube with a cathetometer. In the experiments, equilibration was generally reached in about 10 min.

2.3. CO₂ solubility measurement

Solubility of CO₂ in the diluted solutions was measured with a synthetic method apparatus for evaluation of the solubility parameter. The apparatus and the details of measuring bubble point pressure (BP) are described in a previous paper [16]. BP was determined from the relationship between the pressure and the inner volume of the cell based on compressibility difference of the liquid phase and the vapor-liquid phase. Estimated uncertainties of temperature and BP are \pm 0.06 K and \pm 0.028 MPa, respectively. A sample of known composition was prepared gravimetrically. Estimated uncertainties of CO₂ weight fraction for the BP experiments are less than 0.0005.

3. Results and discussion

3.1. Precipitation test

Fig. 3 shows examples of the precipitation test. When the diluted solution was homogeneous, the back cell wall behind the test tube could be clearly seen as shown in Fig. 3(a). When polymer precipitation occurred during CO₂ dissolution by pressurization, the solution became cloudy as shown in Fig. 3(b). The images shown in Fig. 3 were typical for all solvent systems.

Experimental results of the precipitation test of the diluted solutions are shown in Fig. 4. Precipitation pressure in the diluted solutions increased as the diluent solubility parameter was close to that of the acrylic resin. It should be noted that the precipitation pressures for DIBK and DEK cases were fairly low compared with those for ethanol and methanol for which the solubility parameter differences from the resin were comparable or slightly larger than those of DIBK and DEK. This is attributed to CO₂ dissolution into the solvent phase. The solubility parameter of CO₂ [9] was calculated as 3.4 MPa^{0.5} at temperature of 40 °C and pressure of 7 MPa so that the solubility parameter of the diluted solution decreased as CO₂ dissolution amount increased. Solubility parameter of the diluents which have a higher solubility

Download English Version:

<https://daneshyari.com/en/article/6477659>

Download Persian Version:

<https://daneshyari.com/article/6477659>

[Daneshyari.com](https://daneshyari.com)