Interfacial Tension Measurements of Polymer/$scCO_2$ Systems by the Pendant Drop Method

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Abstract: For the interfacial tension (IFT) measurements of polymer/supercritical carbon dioxide ($scCO_2$) systems, high-pressure pendant drop apparatus was constructed. Melt polymer phase was pressurized into a high-pressure vessel that has two sapphire windows through a capillary to form a polymer drop on the capillary tip. The drop image was recorded by a CCD camera, and the IFT was calculated by the Axisymmetric Drop Shape Analysis (ADSA) method. Reliability of the apparatus was confirmed by the IFT measurements of poly (styrene) (PS)/$scCO_2$ system. The IFT of poly (methylmethacryrate)/$scCO_2$ system with and without aliphatic carboxyl acids was measured.

I. Introduction

Recently, global scale environmental damage such as warming, ozone layer depletion, and acid rain becomes large problem. Therefore, the severe pollution control had begun to carried out in many countries worldwide, and the conversion of conventional industrial process to more environmentally friendly process have been required. Volatile organic solvents (VOS) are one of the causes of the photochemical smog with the hydrocarbons that are included in the automotive exhaust gas of the automobile. The regulation for the effluent of VOS will become more severe in the near future.

As an alternative to the VOS, many researchers are looking forward to supercritical carbon dioxide ($scCO_2$). $ScCO_2$ is non-toxic, inflammable, and environmentally benign fluid. One of the most promising industrial processes for the utilization of $scCO_2$ is a polymerization process. As the CO_2 is chemically stable, it is inert for radicals, and need no drying process because it is a gas under the ambient condition. Unfortunately, $scCO_2$ does not dissolves most polymers except for high pressures and temperatures [1]. To utilize the SC-CO_2 as an alternative solvent in the polymerization process, effective surfactant must be developed to overcome this low solubility. In the present stage of the study, only polymers which contain perfluoroalkyl side chains, or their block copolymers are the most effective surfactant for dispersion polymerization [2]. Unfortunately, compounds which consist perfluoroalkyl group are expensive.

In our previous study [3-7], it was found that carboxyl acid vinyl monomers such as acrylic acid and methacrylic acid work as surfmers (surfactant + monomer), and that aliphatic carboxyl acids have surfactant like natures in $scCO_2$. In this study, for the quantitative understanding of the surface activity of the carboxyl acid group, interfacial tension (IFT) measurements of polymer/myristic acid/$scCO_2$ systems were conducted.

II. Experimental

Materials: polystyrene (PS, Mw=309,312, Mw/Mn=1.804) and polymethyl methacrylate

(PMMA, Mw=89,230, Mw/Mn=2.302) were purchased from Wako Pure Chemical Co. Ltd., and used after freeze-comminution. Myristic acid was also supplied from the Wako Pure Chemicals Co. Ltd., and used without further treatment.

Apparatus and procedures: For the IFT measurements, pendant drop method [8] was employed. **Figure 1** shows a schematic representation of the experimental apparatus constructed in this study. The apparatus consists of mainly four parts, variable volume view cell (Tama Seiki Co. Ltd.) constant temperature air bath (Yamato DN410H), CO_2 feed system, and image analysis system. Inner volume of the view cell is 48 cm^3.

In experiments, polymer powder was placed in the cylinder, and evacuated. Temperature was raised to the experimental condition, and drop of melt polymer was formed at the tip of the capillary. The image of the drop was taken by a CCD camera, and analyzed by the selected plane (SP) method [8] and axysymmetric drop shape analysis (ADSA) method [9].

In the case of the SP method, IFT g is given as follows:

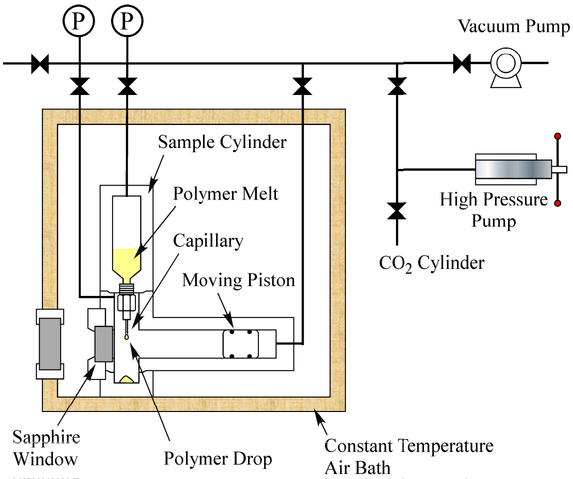

Figure 1. Schematic representation of experimental apparatus.

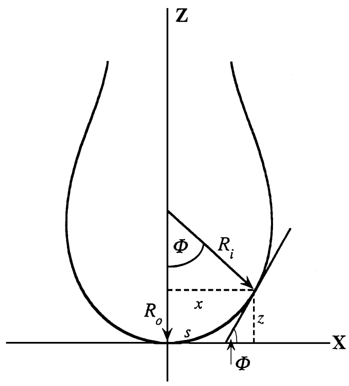

Figure 2. Representation of the drop profile coordinate system.

$$g = \frac{\Delta r g (de)^2}{H} \quad , \quad H = func(S) \quad , \quad S = \frac{de}{ds}$$

where de the maximum (equatorial) diameter of the pendant drop, and ds the diameter of the pendant drop in a selected plane at a distant de from the apex of the drop, g the gravity acceleration, and Δr the density difference across the interface. The de and ds could be obtained from the image of the pendant drop.

For the case of ADSA method, shape of the pendant drop is expressed as a set of three first-order differential equations with the drop profile coordinate system (**Figure 2**):

$$\frac{dx}{ds} = \cos f \ , \ \frac{dz}{ds} = \sin f \ , \ \frac{df}{ds} = \frac{2}{R_0} + \left(\frac{\Delta r g}{g}\right) z - \frac{\sin f}{x}$$

where x and z are the X and Z coordinate of a point on a drop profile, R_0 the radius of curvature at the apex, and f the turning angle at the point.

As could be seen from both equations, the Δr must be known for the calculation of IFT. In this study, Δr was calculated by Sanchez-Lacombe equation of state [10-12] with k_{ij} s determined from the experimental data [13]. IFT calculated by the SP method and ADSA method well coincided within several % in all experiments.

III. Results and Discussion

At first, to confirm the reliability of the apparatus, IFT of PS/scCO_2 system was measured. In the pendant drop measurements, IFT is calculated from the drop shape, and the drop should be just before the dropping from the capillary tip. At that condition, IFT is under equilibrium with the gravitational force. **Figure 3** shows IFT of PS and images of the pendant drop taken at various stage of drop falling at 42.15K and 30MPa. In this study, IFT was measured from the drop just before the falling (image 3 or 4 of Figure 3).

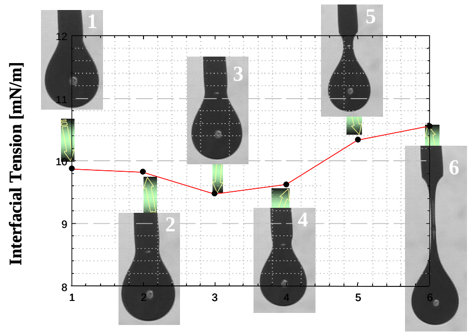

Figure 3. Formation of a PS drop from a steel capillary at 423.15K, 30MPa.

Figure 4 shows IFT of PS/scCO_2 system. In the figure results of Harrison (Mw=1,500) [14] and Jaeger *et al.* (Mw=150,000) [15] are also shown for comparison. It could be seen from the figure, our results agreed well with Jaeger *et al.* except for low temperature region. As their results don't smoothly connect to the IFT under ambient conditions, our date would be justified to be more accurate. Extremely low IFT of Harrison will be attributed to the low molecular weight of the PS sample they used.

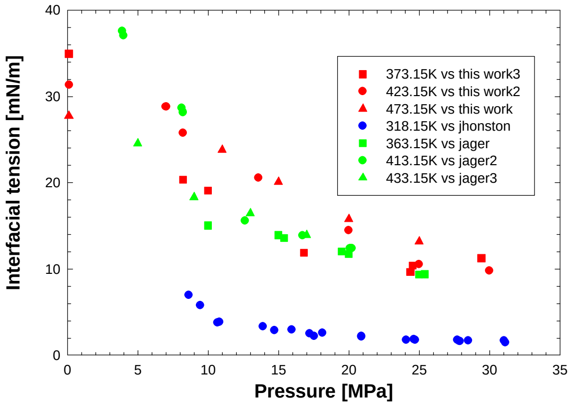

Figure 4. Interfacial tension of PS/scCO_2 system.

Physical properties of supercritical fluid systems often depend on its density, not on pressure. **Figure 5** shows the solubility dependence of the IFT of PS/scCO_2 systems. In the figure, line is for the eye. As could be seen, all data obtained in this study are fell over one universal line.

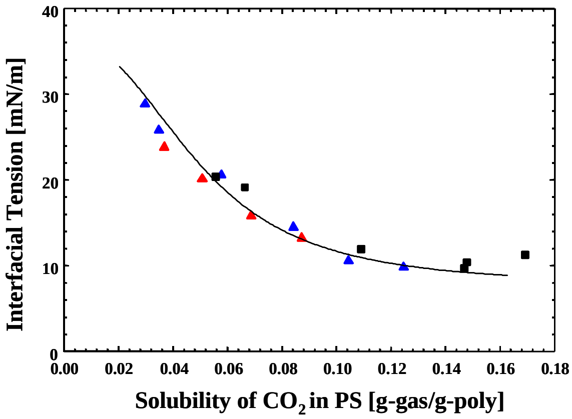

Figure 5. Solubility dependence of the IFT of PS/scCO_2 system.

As described above, it would appear that the reliability of the apparatus is proved. Then the IFT of PMMA/scCO_2 and PMMA/myristic acd/scCO_2 were measured.

Figure 6 shows the IFT of PMMA/scCO_2 systems with and without myristic acid at 90°C. In the figure, theoretical IFT of PMMA/scCO_2 system calculated by Goel and Beckman [16] is also shown for comparison. It is clear from the figure that the theoretical calculation by Goel and Beckman is not sufficient for the evaluation of IFT. It presumably due to the fact that their theory does not include the effect of solubility of CO_2 to PMMA properly.

From the figure, it is also clear that existence of the myristic acid lowers the IFT of PMMA/scCO_2 system to sum extent. The degree of the lowering of the IFT is comparable to the PS/Ps-b-PFOR systems [14]. The surface activity of aliphatic carboxyl acids in the polymer/scCO_2 system was experimental proved at the first time in the world.

IV. Conclusion

Apparatus for the IFT measurements of polymer/scCO_2 systems was constructed. Reliability of the apparatus was confirmed by the IFT measurements od PS/scCO_2 system. The IFT of PMMA/scCO_2 systems with and without aliphatic carboxyl acids was conducted. The surface activity of aliphatic carboxyl acids in the polymer/scCO_2 system was experimental proved at the first time in the world. With this knowledge, it would be possible to build the polymerization process that uses scCO_2 as an alternative solvent without expensive fluorinated surfactants. At the same time, existence of the universal relationship between solubility of CO_2 and IFT was also suggested. It will be important for processes such as supercritical foaming process and other polymer processing processes that uses CO_2.

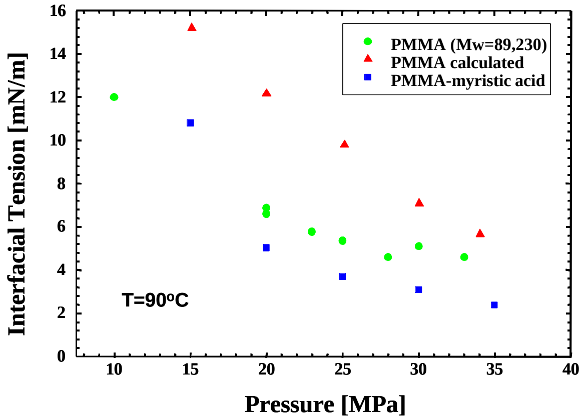

Figure 6. IFT of PMMA/scCO_2 systems with and without myristic acid.

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