Property Prediction of Poly(propylene) Plasticized by CO_2

Hiroshi Inomata[1)*], **Yusuke Koizumi**[1)], **Kohtatsu Hirose**[1)], **Yoshiyuki Sato**[1)], **Hideo Ohyabu**[2)]

1) Tohoku University, Research Center of Supercritical Fluid Technology
Aoba 6-6-11, Aramaki, Aoba-ku, Sendai 980-8579, JAPAN
2) Japan Chemical Innovation Institute, AIST Tohoku Center,
Nigatake 4-2-1, Miyagino-ku, Sendai 983-8551, JAPAN
* Corresponding author, TEL : +81-22-795-7283, FAX: +81-22-795-7282 , e-mail : inomata@scf.che.tohoku.ac.jp

ABSTRACT

We have measured the P-V-T at molten state and swelling ratio at solid state under pressurized CO_2 for poly(propylene) and re-determined the parameters of Sanchez-Lacombe (S-L) EOS by using the measured data. The prediction methodology for predicting various thermodynamic properties by using the S-L EOS with appropriate theory was presented. A comparison of prediction accuracy between the parameter sets indicated that the parameter set representing the P-V-T behavior well can predict the other properties such as viscosity, solubility and surface tension.

Keywords CO_2, Sanchez-Lacombe EOS, P-V-T, MCP

1. INTRODUCTION

Micro-cellular plastic (MCP) producing using supercritical CO_2 has attracted much attention due to its environmentally friendliness and also excellent material features such as low density, low heat conductivity, etc[1~4)]. The supercritical CO_2 MCP equipments are composed of an extruder, a supercritical CO_2 feeder, and a molding/injection unit. The extruder is the most important unit that achieves various important phenomena in this technique; melting polymer, dissolving CO_2 into melt polymer, mixing for homogenous solution and phase separation leading to forming. Designing the above mentioned processes requires quantitative information under these phenomena in accordance with the physical-chemical properties of the polymer mixtures involving CO_2.

There have been proposed a lot of equation of states (EOS) with the aim of accurately calculating the equilibrium and also transport properties. Among proposed EOSs, the Sanchez-Lacombe (S-L) equation[5,6)] has been widely used for calculating physical properties of polymers under supercritical CO_2 because of its applicability to both CO_2 and polymers. However, the calculation accuracy by S-L equation is strongly dependent on the EOS parameters which are normally determined from the experimental P-V-T data. For polymers whose PVT data sometimes do not cover the temperature range of MCP processing, the EOS parameters used may provide insufficient results.

In this work, we have measured the P-V-T of molten polymer and swelling ratio under pressurized CO_2 for poly(propylene) (PP) and determined three sets of EOS parameters of the Sanchez-Lacombe (S-L) EOS with the measured data. By comparing the three sets, the effect of the parameter values on the prediction ability of the EOS was discussed against P-V-T, viscosity, glass transition temperature and surface tension. Through these calculations, the descriptions of each property by S-L EOS was presented and an attempt was made to estimate the degree of crystalline of polymer+CO_2 mixtures from S-L EOS.

2. EXPERIMENT

2.1 P-V-T

A bellows-type dilatometer (Fig.1), which was developed by Sato et al[7]., was used for measuring the pressure - volume - temperature (PVT) properties of melt polymers with changing temperature and pressure. A calibration of the device was performed by measuring PVT of mercury and water. The experimental uncertainty of specific volumes was estimated to be within ±0.2%, while that of temperatures was within ±0.1 K below 300°C, and that of pressures ±0.1 MPa below 100 MPa. The PVT properties of polypropylene and polycarbonate were measured by the apparatus.

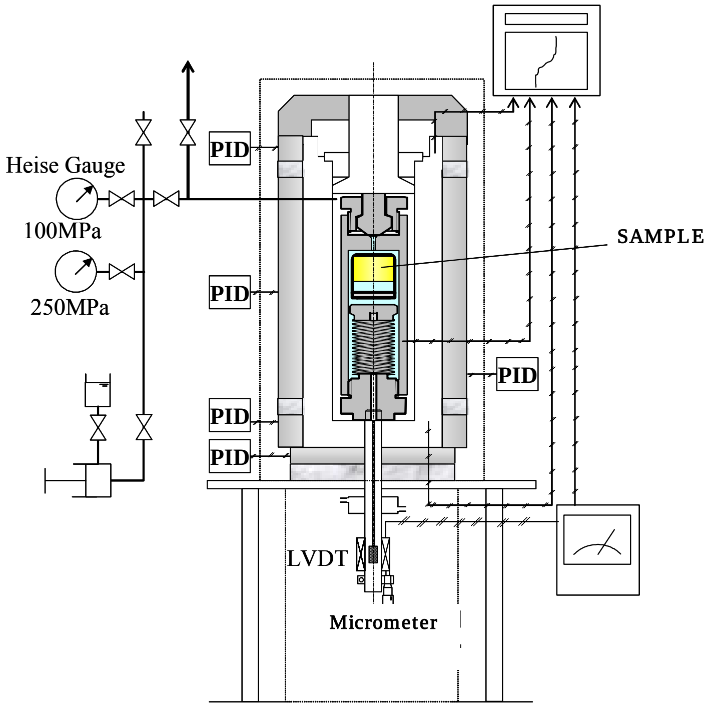

Fig.1 Apparatus of PVT measurements

2.2 SWELLING

Figure 2 shows the apparatus built for measuring the swelling behavior of polymers. The sample polymer whose shape was conditioned as cylindrical cone was set to the high pressure cell equipped with optical windows and then contacts with CO_2 at a desired pressure. The swelling ratio is determined by direct observation via CCD scope which enables us to follow the volume change with time. The equilibrium volume is converted to swelling ratio with using a digital imaging utility.

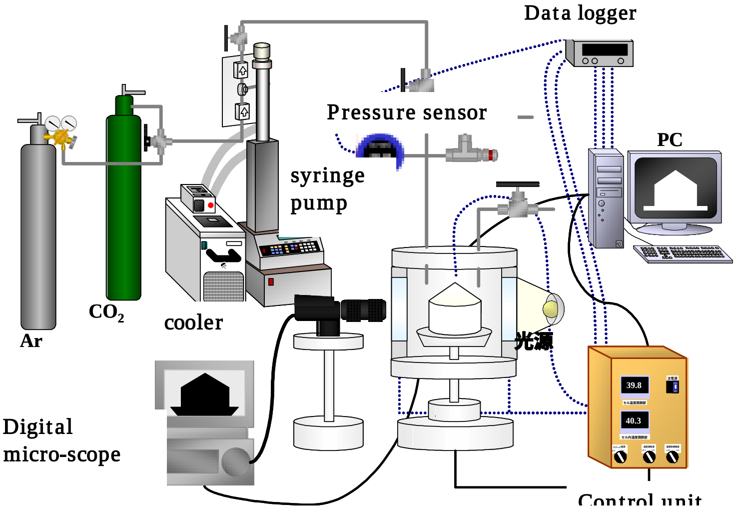

Fig.2 Apparatus of Swelling Measurements

2.3 Material

Poly(Propylene), product PF-814 from Montell was used as received. The average molecular weigh was $\overline{M}_n$ =8.5×10^4, and $\overline{M}_w$ =9.85×10^5. Other properties of the sample are as follows; T_g=2.45°C, T_m=159°C and the degree of crystalline is estimated as X_c=62.8wt%.

3. EXPERIMENTAL RESULTS

Figure 3 shows the P-V-T data for poly(propylene) measured in this work. The transition observed at about 430 K (~160C) represents the melting of PP sample. The data clearly indicate the temperature and pressure dependence of PVT.

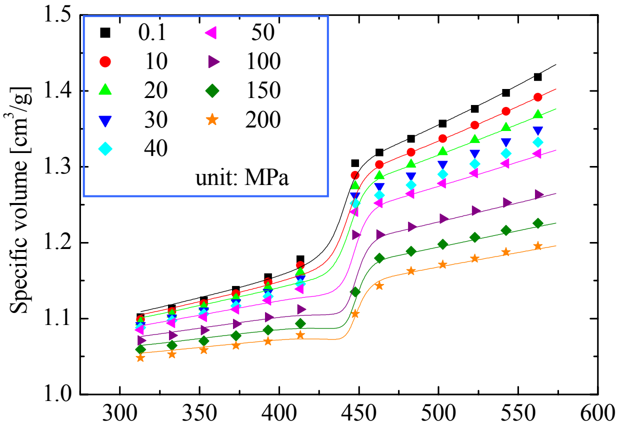

Fig.3 PVT behaviors of PP

These data were subjected to the determination of the equation of state parameters, which should be applied to the prediction of various thermo-physical properties of the polymer.

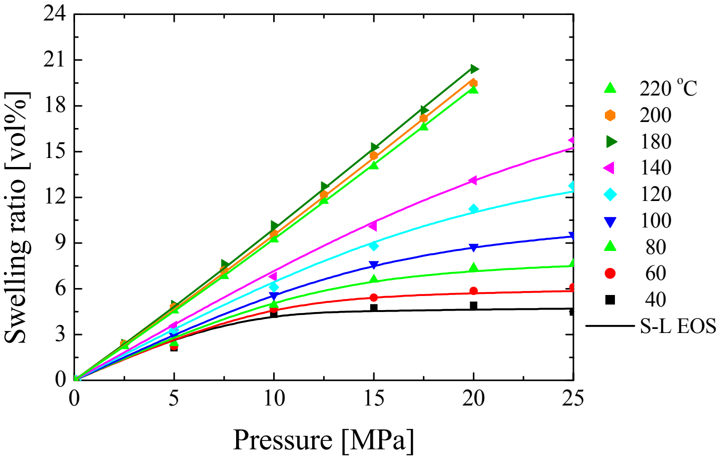

Fig.4 Swelling behaviors of PP with dissolved CO_2

Figure 4 shows the swelling ratios of PP in the temperature range of 40C to 220C. The data indicate the polymer swells with increasing pressure, which may be induced by the increase in free volume by CO_2 dissolution under pressure. At higher temperatures, PP sample is melt and changes its volume in proportional to the pressure, indicating dissolving CO_2 in terms of the Henry's law. Whereas, at lower temperatures, solid PP is swollen by dissolving CO_2 and the swelling ratio firstly increases with pressure and approaches a certain plateau value. This may be attributed to the elasticity contribution of solid polymer matrix.

4. DISCUSSIONS

4.1 Sanchez-Lacombe equation of state

Among the numerous equations of state, the Sanchez-Lacombe equation of state was adopted for correlating the PVT and swelling data and also for predicting other various properties related to MCP processes.

The Sanchez-Lacombe equation of state(S-L EOS) is expressed as follows; [5,6)]

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

$$\tilde{P} = \frac{P}{P*}, \tilde{\rho} = \frac{\rho}{\rho*}, \tilde{T} = \frac{T}{T*}, r = \frac{MP*}{RT*\rho*} \qquad (2)$$

Characteristic parameters, P^*,ρ^*, and T^* for mixture were evaluated with the following mixing rules.

$$P* = \sum_i \sum_j \phi_i \phi_j P^*_{ij} \qquad \phi^0_i = \frac{(\phi_i P^*_i / T^*_i)}{\sum_j (\phi_j P^*_j / T^*_j)}$$

$$P^*_{ij} = (1-k_{ij})(P^*_i P^*_j)$$

$$T^* = P*\sum_i \frac{\phi^0_i T^*_i}{P^*_i} \qquad \phi_i = \frac{(w_i/\rho^*_i)}{\sum_j (w_j/\rho^*_j)} \qquad (3)$$

$$\frac{1}{r} = \sum_i \frac{\phi^0_i}{r^0_i}$$

In Eqs. (3), $T^*{}_i$,$P^*{}_i$,$\rho^*{}_i$, and $r^0{}_i$ refer to the characteristic parameters of component *i* in the pure component and k_{ij} is a binary interaction parameter determined by fitting the calculated values to the experimental data. The pure component parameters determined with PVT data and used in this work are given in Table 1. Para1 focuses on PVT behavior severely and Para2 does on PVT briefly and critical point.

Table 1 Sanchez-Lacombe Eq. parameter sets

	P^* [MPa]	ρ^* [kg/m^3]	T^* [K]
Para1	421.4	1.408	340.49
Para2	307.6	1.116	329.85
Wang para	720.3	1.58	208.9 + 0.459T- 0.000756T^2

Wangpara is from ref(8)

4.2 Prediction of Thermo-Physical Properties by S-L EOS

This study aims at the goal to propose a general methodology which enables us to predict various properties with a single EOS and corresponding theory. The concept to this end is schematically shown in Fig.5. Most important issue is the selection of EOS, S-L equation in this work. We have made an attempt through discussing the prediction performance of each property by the approach shown in Fig.5.

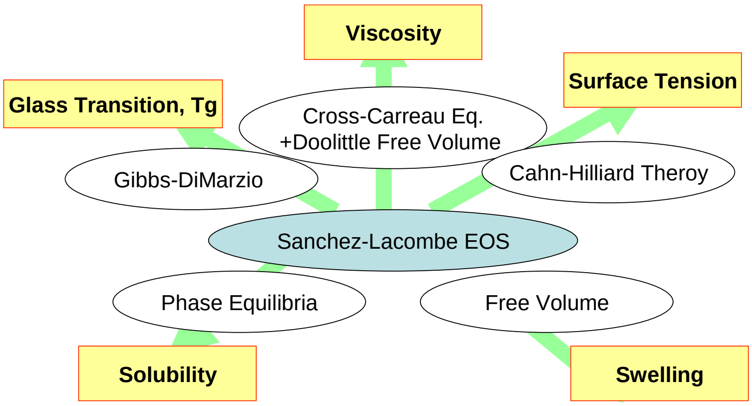

Fig.5 Concept of proposed prediction method

1) Swelling (solubility)

Swelling ratio of PP was calculated from the following equation and the volume of polymer phase calculated by S-L equation. Since the swelling is the property of mixture, PP+CO_2, the interaction parameter, k_{ij}, was handled as a fitting parameter to represent the experimental data. The correlation result was fairly good as shown in Fig.4 (lines). In calculation, it was assumed that the swelling takes place only in amorphous phase and the CO_2 content was calculated from vapor-liquid equilibrium between amorphous-CO_2 vapor phases.

$$S_w = \left(1 - \frac{v_{mix}(P,T,w)}{(1-w)\cdot v_2(P,T,0)}\right)\times 100$$

S_w[vol%]:swelling ratio, w[g-CO_2/g-Polymer+CO_2]:CO_2 weight fraction ,
$v_{mix}(P,T,w)$[cm^3/g-Polymer+CO_2]:Polymer+CO_2 specific volume,
$v_2(P,T,0)$[cm^3/g-Polymer]:Polymer specific volume

It was found that the k_{ij} is strongly dependent on the temperature, especially at lower temperatures. We supposed that this might be attributable to the crystalline-amorphous ratio change with temperature. Namely the k_{ij} values reflect the ratio and we calculated the crystallinity from the k_{ij} value againt the k_{ij}^{amo} extrapolated to the completely melting temperature.

$$X = 1 - {k_{ij}^{amo}}\big/{k_{ij}}$$

The results almost agreed with those estimated from PVT data as shown in Fig.6, which suggesting the validity of the approach mentioned above.

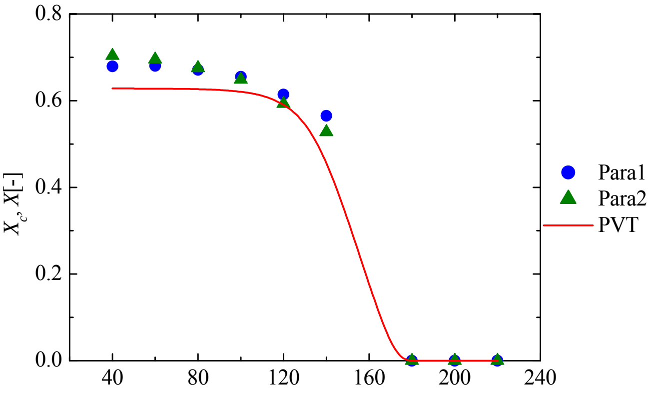

Fig.6 Estimated Crystallinity of PP against T

2) Viscosity

The viscosity change of melt polymer dissolving CO_2 was calculated with using the Cross-Carreau[9,10] theory together with Doolitte free volume theory[11].

$$\eta = \frac{\eta_0}{\left\{1+\left(\frac{\eta_0\dot{\gamma}}{\tau}\right)^{a}\right\}^{\frac{1-n}{a}}} \qquad \tau = \frac{1}{C^{1/1-n}} \qquad \eta_0 = A\exp\left(\frac{B}{f}\right)$$

η_0: zero shear rate viscosity, n: shear rate sensitivity parameter, a, C: B: constants

η_0 is based on the Doolittle equation with the free volume fraction, f;

$$f = \frac{V - V_0}{V_0}$$ V_0: polymer core volume

$$f(T,P,w) = f(T_r,P_r,w_r) + \left.\frac{\partial f}{\partial T}\right|_{P_r,w_r}(T-T_r) + \left.\frac{\partial f}{\partial P}\right|_{T_r,w_r}(P-P_r) + \left.\frac{\partial f}{\partial w}\right|_{T_r,P_r}(w-w_r)$$

$$= f(T_r,P_r,w_r) + \boldsymbol{\alpha}(T-T_r) - \boldsymbol{\beta}(P-P_r) + \boldsymbol{\phi}(w-w_r)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{、} \quad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

By using the measured swelling ratio data, free volume fraction, *f*, could be finally represented as follows;

$$f(T,P,w) = 5.6958\times10^{-4}T - 4.8098\times10^{-4}P + 1.2446\times10^{-2}w + 0.025$$

T[°C]: Temperature, *P*[MPa]: Pressure, *w*[wt%]: CO_2 concentration

The viscosity calculated using these equations was compared with the experimental data12) as shown in Fig.7. The calculation could represent the tendencies of experimental behaviors at different pressures and CO_2 concentrations; viscosity reduction by dissolving CO_2 and slight increase in viscosity with pressure. We applied this method to other polymers and it worked.

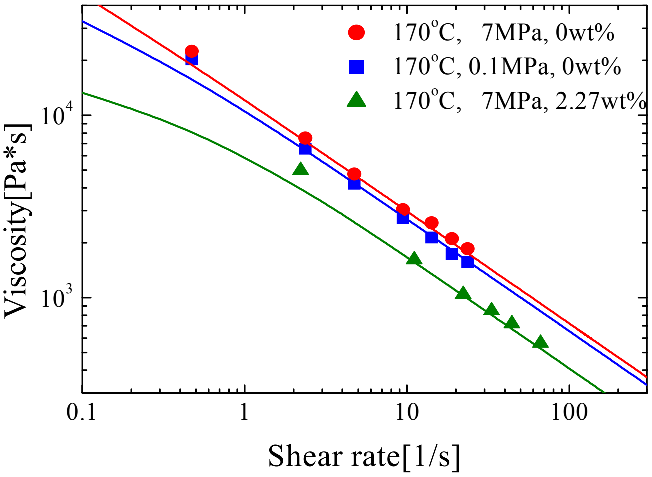

Fig.7 Viscosity of PP melt containing CO_2

3) Tg

Tg of polymers can be calculated by using Gibbs-DiMarzio theory 13) which assumed the Tg as a second order transition where conformal entropy is zero. From this theory, we can calculate Tg by solving the following conformal entropy from S-L EOS.

$$-\frac{S^C}{krN} = (\tilde{v}-1)\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r} + \left(\frac{\phi_1}{r_1}\right)\ln\left(\frac{\phi_1}{r_1}\right) + \left(\frac{\phi_2}{r_2}\right)\ln\left(\frac{\phi_2}{r_2}\right) + 1 + \frac{\ln(2/z)-1}{r}$$
$$+\left(\frac{\phi_1}{r_1}\right)(r_1-2)\left[\ln(1-f_1) - f_1\frac{\Delta\varepsilon_1}{kT}\right] + \left(\frac{\phi_2}{r_2}\right)(r_2-2)\left[\ln(1-f_2) - f_2\frac{\Delta\varepsilon_2}{kT}\right]$$

$$f_i = \frac{(z-2)\exp(-\Delta\varepsilon_i/kT)}{1+(z-2)\exp(-\Delta\varepsilon_i/kT)}$$

S^C : configuration entropy, k : Boltzmann constant, f : occupancy, z : coordination number,
$\Delta\varepsilon$: internal energy change by flexibility, i : component i

Figure 8 shows the comparison of calculated and experimental Tg under pressurized CO_2. The parameter set of Para1 for S-L EOS was used in this calculation. It was clearly revealed that Tg is largely decreased with pressure trough CO_2 penetrating the polymer matrix and its plasticizing effect. The calculation is strongly dependent on the parameter values and k_{ij}. As can be seen, an accurate prediction is possible by knowing the adequate kij value from solubility data. It should be also noted that similar results could be obtained for other polymers such as PP, PC and PE.

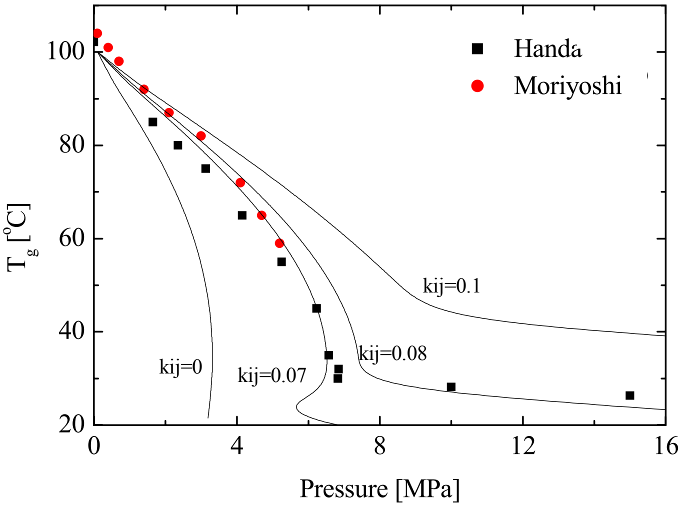

Fig.8 Tg of Poly(styrene) under pressurized CO_2

4) Surface tension

Poser and Sanchez[14)] applied the Cahn-Hilliard theory[15)] to express the concentration/density fluctuation of Gibbs energy and derived the expressions for calculating the surface tension from Sanchez-Lacombe EOS.

$$\gamma = 2^{1/2}\frac{\left\|\left[\kappa_{11}^{1/2}+\kappa_{12}^{1/2}\left(\Delta\rho_2/\Delta\rho_1\right)\right]\right\|}{v_{m,1}^*}\int_{\phi_1^1}^{\phi_1^2}\tilde{\rho}\Delta a^{1/2}d\phi_1\ , \quad \Delta a = \tilde{\rho}\left[g-\left(\frac{\phi_1}{v_{m,1}^*}\right)\mu_1^e-\left(\frac{\phi_2}{v_{m,2}^*}\right)\mu_2^e\right]$$

$$g = -\tilde{\rho}P^* + P/\tilde{\rho} + kT\left[\frac{\left(1/\tilde{\rho}-1\right)\ln\left(1-\tilde{\rho}\right)}{v_0^*}+\frac{\ln\tilde{\rho}}{v^*}+\frac{\phi_1\ln\phi_1}{v_1^*}+\frac{\phi_2\ln\phi_2}{v_2^*}\right], \qquad \kappa_{ii} = 2P_i^* {v_{m,i}^*}^{8/3}\tilde{\kappa}_{ii}$$

γ[mN/m]:surface tension, κ_{ij}[-]:interaction parameter、$\Delta\rho_i$[g/cc]:density difference, $v^*_{m,i}$[cc/mol]:monomer volume、Δa: free energy difference at interface、g:Gibbs free energy

Figure 9 shows the prediction results for PP under CO_2. It would be noted that there is no fitting parameter in this calculation. It can been seen that Para1 and Para2 could represent well the experimental data, suggesting the possible accurate prediction of surface tension with

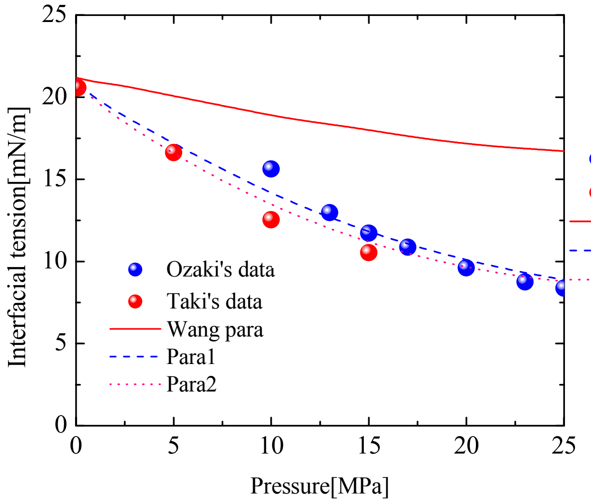

Fig.9 Surface tension of PP and CO_2

the parameter which is capable of representing volumetric properties well.

5. CONCLUSION

The P-V-T relations of melt poly(propylene) (PP) and the swelling of PP in CO_2 have been measured with the originally designed apparatus. The measured data were used to determine the characteristic parameters of Sanchez-Lacombe EOS. Three parameter sets were used to examine the prediction performance of S-L EOS for viscosity, Tg change, solubility and surface tension. The parameter set, which was determined in order to accurately represent the volumetric behavior in the target temperature range, was revealed to provide the satisfactory prediction for viscosity, surface tension, etc, suggesting the importance of how to determine the equation parameter values for accurate property prediction. If one can have a good parameter set, it is quite possible to predict various thermodynamic properties by using related thermodynamic relationship.

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