

High-pressure rheology of polymer melts containing supercritical carbon dioxide

Sang Myung Lee, Jae Ho Han, Kyung Yi Kim, Young Joon Ahn and Jae Wook Lee*

Applied Rheology Center, Dept. of Chemical Engineering, Sogang University,
1 Shinsu-Dong, Mapo-Gu, Seoul 121-742, Korea

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Abstract

Supercritical carbon dioxide (scCO₂) has advantages of being incorporated in polymer with high solubility and of being recovered easily by depressurizing. ScCO₂ reduces the viscosity of polymer melt and it is expected to be used as a plasticizing agent. In this work, we studied on the effect of scCO₂ on the rheological properties of polymer melts during extrusion process. Slit die attached to twin screw extruder was used to measure the viscosity of polymer melts plasticized by supercritical CO₂. A gas injection system was devised to accurately meter the supercritical CO₂ into the extruder barrel. Measurements of pressure drop within the die, confirmed the presence of a one phase mixture and a fully developed flow during the measurements. The viscosity measurement of polypropylene was performed at experimental conditions of various temperatures, pressures and CO₂ concentrations. We observed that melt viscosity of polymer was dramatically reduced by CO₂ addition.

Keywords : rheology, supercritical fluid, extruder, solubility, polypropylene

1. Introduction

Supercritical fluid is defined as a fluid that is above its critical temperature and pressure. Supercritical fluids have characteristics such as gas-like diffusivity and viscosity and liquid-like density. In particular, supercritical CO₂ has a wide range of applications due to environmentally friendliness, lower critical point, relatively low cost, non-toxicity and non-flammability compared to other supercritical fluids. Viscosity reduction of polymers has been of great interest in the realm of polymer processing because high viscosity is a major obstacle for the processing of high molecular weight polymers or complex mixtures of particle filled polymers or pastes. Usually, this problem is resolved by increasing the temperature or by the addition of plasticizing agents. However, increasing the temperature requires higher energy consumption and may lead to thermal degradation. Added plasticizers usually remain in the product, thus affecting its properties and performance. Supercritical CO₂ can be used as plasticizing agent that lowers the viscosity of various polymer melts (Chiou *et al.*, 1985; Lee *et al.*, 1999; Lee *et al.*, 2000). The method of removal of carbon dioxide used as a plasticizer from the polymeric product is simple, economic and safe compared to the conventional plasticizer removal methods such as costly drying and hazardous solvent removal processes,

which is very important in the processing of polymer-based materials. Upon release of pressure from various processes the CO₂ will dissipate as a gas and only the final product will remain. Recently, supercritical CO₂ has been applied to the plastics industry such as synthesis, foaming and blending due to its various advantages.

To apply supercritical CO₂ in polymer processing applications, it is essential to know the physical properties of polymer/CO₂ system. This study is focused on the measurement of rheological properties of CO₂-plasticized polymer melts.

2. Theory

2.1. Method of viscosity calculation

In capillary die flow, the melt viscosity can be determined from the measured pressure drops, ΔP and volumetric flow rate of the polymer in a slit die, Q , using the following equations;

$$\eta = \tau_w / \dot{\gamma}_w \quad (1)$$

τ_w denotes the shear stress at the slit die wall which is defined by

$$\tau_w = \frac{H}{2(1+H/W)} \frac{dP}{dx} \quad (2)$$

where x is the length of the die, H is the slit height and W is the slit die width. $\dot{\gamma}_w$ is the wall shear rate, which is converted from the apparent shear rate, $\dot{\gamma}_{ap}$, by the Rabinow-

*Corresponding author: jwlee@sogang.ac.kr
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itsch correction.

$$\dot{\gamma}_w = \frac{\dot{\gamma}_{ap}}{3} \left(2 + \frac{d \ln \dot{\gamma}_{ap}}{d \ln \tau_w} \right) \quad (3)$$

The apparent shear rate is given by

$$\dot{\gamma}_{ap} = 6Q/WH^2 \quad (4)$$

Q denotes the volumetric flow rates of the neat molten polymer or polymer/CO₂ solutions. Dividing the mass flow rate of the polymer by its density gives the value of Q .

It is important to note that the density of polymer/CO₂ solution is a function of temperature, pressure and concentration of dissolved CO₂. An appropriated correction of the volumetric flow rates is needed to calculate accurate viscosities in consideration of temperature, pressure and CO₂ dissolution effects. The equation of state was used to calculate the densities of both neat polymer and polymer/CO₂ solutions. In this study, the Sanchez-Lacombe equation of state (S-L EOS) was employed (Sanchez *et al.*, 1978; Lacombe *et al.*, 1976). S-L EOS is used with the mixing rules and it will be introduced to Section 2.2. The equation of state for polymer alone is derived by fitting S-L EOS to a PVT data of the neat polymer. To calculate the characteristic parameters and derive the equation of state for polymer/CO₂ solutions, the binary interaction parameter, k_{12} , between the polymer and CO₂ is required. The interaction parameter was obtained through data of CO₂-solubility into the polymer.

2.2. Sanchez-Lacombe Equation of State (S-L EOS)

The Sanchez-Lacombe equation of state is given by:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] = 0 \quad (5)$$

where $\tilde{\rho}$, \tilde{P} and \tilde{T} are reduced density, pressure and temperature, respectively. The reduced variables are defined in terms of characteristic parameters:

$$\begin{aligned} \tilde{T} &= \frac{T}{T^*} & T^* &= \varepsilon^*/R \\ \tilde{P} &= \frac{P}{P^*} & P^* &= \varepsilon^*/v^* \\ \tilde{\rho} &= \frac{\rho}{\rho^*} & \rho^* &= M/(rv^*) \end{aligned} \quad (6)$$

where T^* , P^* and ρ^* are characteristic temperature, pressure and density, respectively. The parameter ε^* is the interaction energy, v^* is the characteristic volume of a lattice site and r is the number of lattice sites occupied by a molecule of molecular weight M . In the Sanchez-Lacombe theory, T^* , P^* and ρ^* are derived from ε^* , v^* and r , as shown in Eq. 6. In application of the S-L EOS, however, T^* , P^* and ρ^* are

often determined directly as the pure component parameters by an optimization procedure.

The EOS for the mixture is formally identical to that of a pure component. However, mixing rules are employed for calculating the characteristic parameters and r of the mixture. In formulating the mixing rules, two material balance equations for the close-packed molecular volume of each component and can be expressed as $r_i v^* = r_i^o v_i^*$. This relationship guarantees that an i molecule occupying r_i^o sites of volume v_i^* in its pure state will occupy the same volume, r_i sites of volume v^* in the mixture. The second rule keeps the total number of pair interactions in the close-packed mixture the same as the sum of the pair interactions of the components in their pure close-packed states, *i.e.*, $\sum_i r_i^o N_i = rN$ where N_i is the number of i molecules and N is the total number of molecules in the lattice.

The combined result of these material balances is to introduce a surface area effect so that a component in a binary mixture with a larger mer volume can have more interactions in the mixture than in its pure state. The average close-packed mer volume in the mixture is defined by:

$$v^* = \sum_i \phi_i^o v_i^* \quad (7)$$

where $\phi_i^o = r_i^o N_i / \sum_i (r_i^o N_i)$ is the close-packed volume fraction of component i in the mixture. The average number of lattice sites occupied by the mixture, r , is weighted by mole fractions:

$$r = \sum_i x_i r_i \quad (8)$$

The characteristic pressure P^* of the mixture is taken as pairwise additive:

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* ; P_{ij}^* = (P_i^* P_j^*)^{1/2} (1 - \delta_{ij}) \quad (9)$$

where ϕ_i is the volume fraction of component i in the mixture, given by $\phi_i = r_i N_i / \sum_i (r_i N_i)$. The binary interaction parameter δ_{ij} , the only mixture parameter, corrects the deviation of the mixture's P_{ij}^* from the geometric mean of components' characteristic pressures, P_i^* and P_j^* . In the application of the EOS to a binary or pseudobinary mixture, v^* , r and P^* for the mixture are calculated from Eqs. 7-9 and then the other three parameters ε^* , T^* and ρ^* are determined from the relationships given in Eq. 6.

The phase equilibrium is defined by equating the chemical potentials of gas in the two phases: $\mu_1^G(T, P) = \mu_1^P(T, P, \phi_1)$ where the superscripts G and P represent the gas and polymer phases, respectively; the subscript 1 represents the lighter component (gas). The upper phase is assumed to be pure. The difference of the chemical potentials of component 1 in the two phases, which must vanish at equilibrium, is given by:

$$\frac{\Delta\mu_1}{RT} = 0 = \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + r_1\tilde{\rho}X_1\phi_2^2 + \tilde{v}\tilde{\rho}\ln\tilde{\rho} - \tilde{v}_1\tilde{\rho}_1\ln\tilde{\rho}_1 + r_1^0 \left[-\frac{\tilde{\rho}-\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{P}_1(\tilde{v}-\tilde{v}_1)}{\tilde{T}_1} + \tilde{v}(1-\tilde{\rho})\ln(1-\tilde{\rho}) - \tilde{v}_1(1-\tilde{\rho}_1)\ln(1-\tilde{\rho}_1) \right] \quad (10)$$

where $X_1 = (P_1^* + P_2^* + 2P_{12}^*)v_1^*/RT$ is the only parameter containing δ_j .

3. Experimental

3.1. Materials

The polymer used in this study was polypropylene (HP602N, Polymirae) whose density was 0.9 g/cm³ and MFR was 12.5 g/10 min. The average molecular weight, \bar{M}_w , was 222,400 and the polydispersity ratio, $\bar{M}_w/\bar{M}_n = 5.23$. Carbon dioxide (99.99% purity) was used as a supercritical fluid in the experiments.

3.2. Experimental procedure

The experimental apparatus used is based on the extrusion rheometer developed first by Han and Ma (1983), and later used by Lee *et al.* (1999) and Park *et al.* (1998) and Royer *et al.* (2000). The viscosities of the neat PP and PP/CO₂ solutions were measured using an extrusion rheometer equipped in co-rotating twin screw extruder. The inter-meshing co-rotating twin screw extruder (model TEK 25 from SM Platek Co.) was specially designed for the polymeric compounding, where CO₂ was injected into a metering zone of its barrel and pressure transducer was attached to barrel as shown in Fig. 1. The barrel pressure at the injection point is monitored for a stable injection of CO₂.

The extruder has 10 barrel sections and the temperature of each section is controlled separately. Its screw diameter is 25 mm and L/D is 41. To inject the CO₂ into the extruder under precisely controlled condition, the injection system is required. The injection system consists of a CO₂ gas cylinder connected in series to a syringe pump (model 260D from ISCO) and a back pressure regulator. With the pump supplying CO₂ set to run at a constant flow rate, the back pressure regulator acts maintaining constant pressure. When the system reaches steady state, the injection of CO₂ occurs at both constant pressure and constant flow rate. In order to inject supercritical CO₂ into the barrel, pressure transducer port on the barrel was used and a special injection device was designed.

The preparation of polymer/CO₂ solutions can be achieved only at pressure above the solubility pressure. Even though the operating pressure is maintained over the solubility limit, the actual soluble amount of CO₂ might be less due to the limited residence time during the extrusion. The prepared solutions must be maintained over the solubility pressure through the extrusion process in order to prevent the precipitation of CO₂. Mostly, the conventional operating pressure of twin-screw extruders, however, is relatively low when it is compared to that of single-screw extruders. Therefore, special screw configurations are required not only for the pressure generation but also the stable injection of CO₂. Fig. 2 shows a schematic of screw configuration used in this work. This configuration was designed for preparing polymer/CO₂ and polymer blend/CO₂ solutions in a twin-screw extruder. It should be noted that a slit die and a nozzle are always attached to this configuration. Three main design concepts were applied to the configuration. First, the injected CO₂ should be prevented

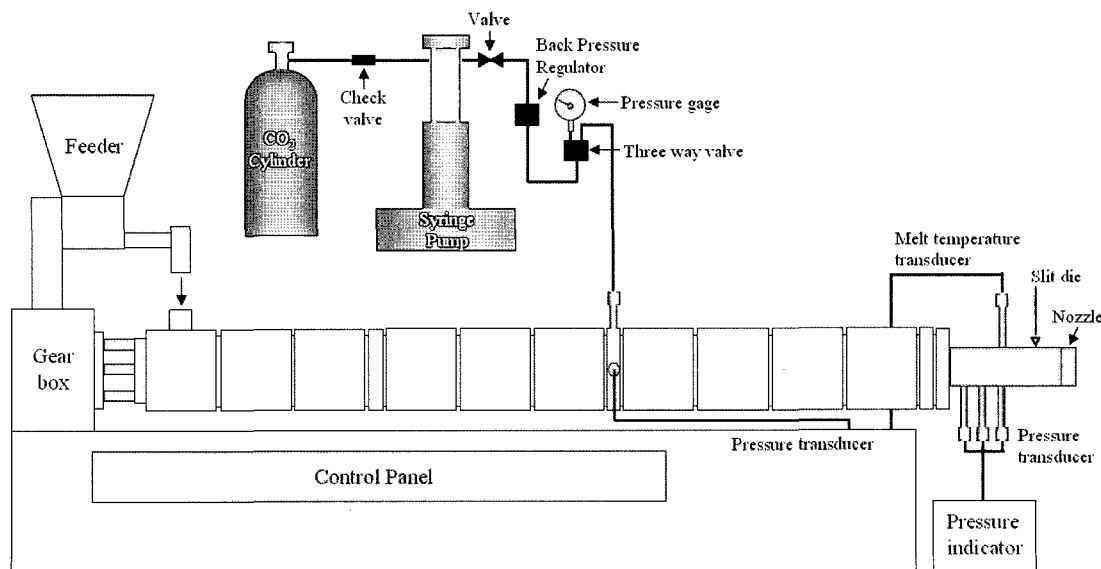


Fig. 1. Co-rotating twin screw extruder with high pressure slit die extrusion rheometer and metered CO₂ injection system.

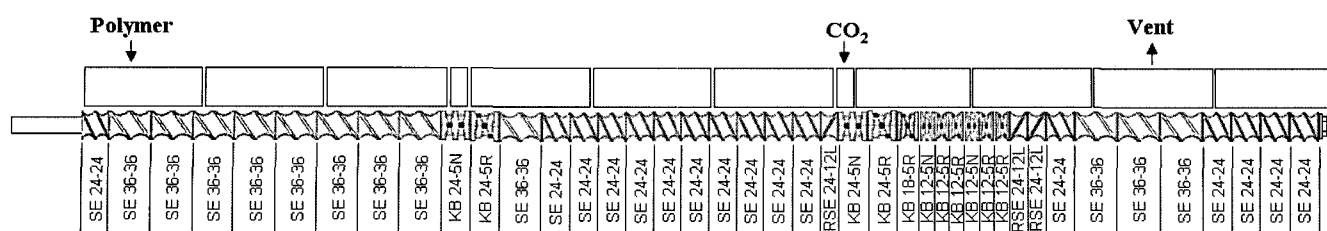


Fig. 2. Schematic of screw configuration of a co-rotating twin screw extruder.

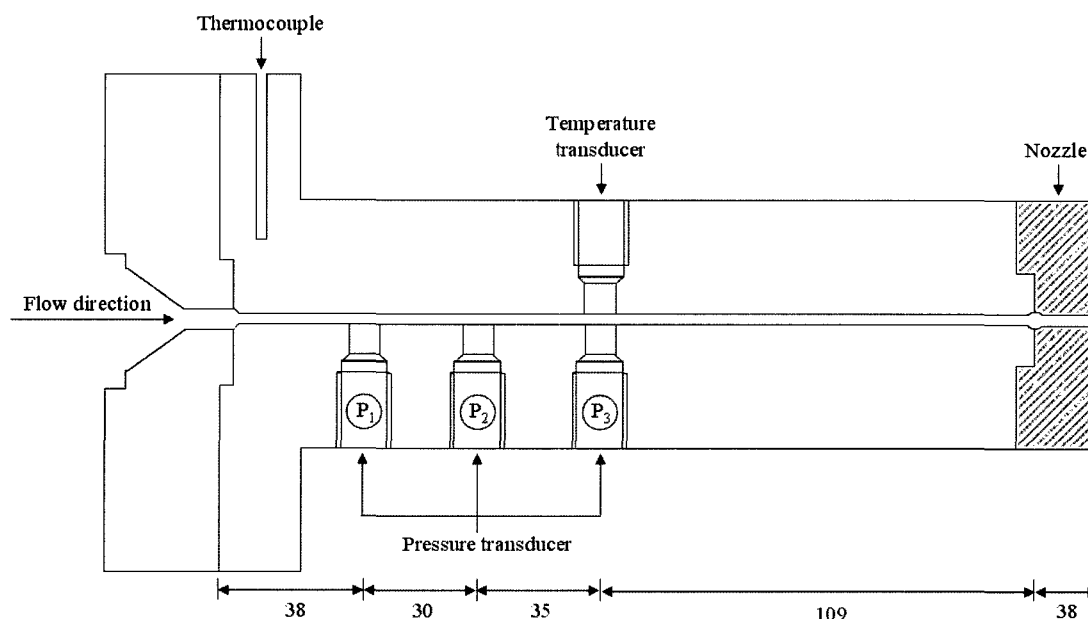


Fig. 3. A schematic of the slit die and nozzle.

from leaking backward along the barrel. A reverse conveying element was positioned right before the CO_2 injection to generate a melt seal and prevent CO_2 back-flow. Second, the barrel pressure after the CO_2 injection should be maintained over the solubility pressure. The high pressure was generated by controlling the flow resistance at the nozzle attached to the slit die. The generated pressure level depends on the die opening area and the melt viscosity. Finally, an extensive mixing of the polymer and CO_2 is essential for the complete dissolution of supercritical CO_2 under a limited residence time. The extensive mixing was achieved using dedicated mixing elements.

A schematic of the slit die and nozzle used in this work is shown in Fig. 3. The nozzle is required to elevate the pressure within the slit die above the bubble pressure ensuring that a one-phase mixture is maintained during measurement with CO_2 . The dimensions of the slit die and two nozzles are displayed in Table 1. The pressure drop and melt temperature across the slit die are measured via three pressure transducers (PT462E from Dynisco) and one temperature transducer.

Table 1. The dimensions of the slit die and two nozzles

Dimension	Slit die	Nozzle 1	Nozzle 2
Length	65 mm($P_1 - P_3$)	38 mm	38 mm
Width	15 mm	-	-
Height	2.5 mm	-	-
Diameter	-	1.5 mm	2.5 mm

4. Results and discussion

4.1. Experimental verification of rheometer design

In order to determine the viscosity measuring conditions when CO_2 was injected, the available processing variables such as the resin feed rate and the screw speed, were tested. The barrel temperature was set to 145/170/175/180/180/180/180/180/180 with the die at melts temperature of 180°C. Pressures at the barrel and the slit die were monitored at various screw speeds and feed rates. The effects of each variable are described in this section.

4.1.1. Screw speed

Maintaining the high pressure during the extrusion with

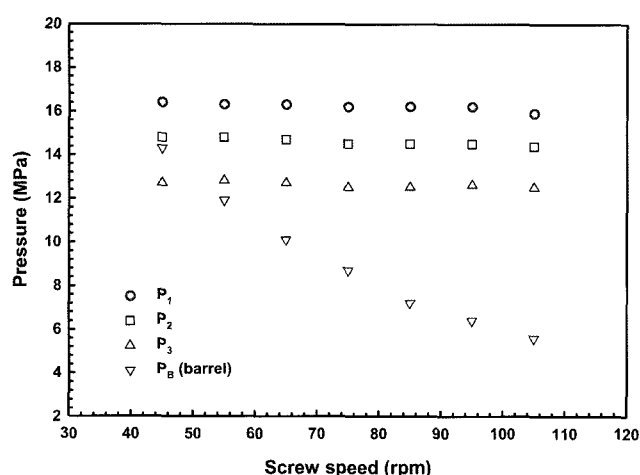


Fig. 4. Relationship between pressures and screw speed during extrusion.

CO₂ is critical because the injected CO₂ should be dissolved into the polymer within a given residence time. Therefore, the effect of the screw speed on the pressure was investigated for polypropylene/CO₂ system, and the behavior at various screw speeds is shown in Fig. 4. When the polymer feed rate was fixed at 5.1 kg/h, the barrel pressure consistently decreased with increasing the screw speed, while the pressures at the slit die remained relatively constant. This indicates that, as expected, higher screw speeds decrease the degree of fill due to the increased conveying capability.

4.1.2. Feed rate

The pressure behavior with the polymer feed rate was also investigated at 55 rpm. As expected, all pressures at the barrel and the slit die increased as the polymer feed rate increased, as shown in Fig. 5. It should be noted that the barrel pressure increases faster than the slit die pressure. As a result, low screw speeds and high polymer flow rates are recommended to maintain high pressures during the extru-

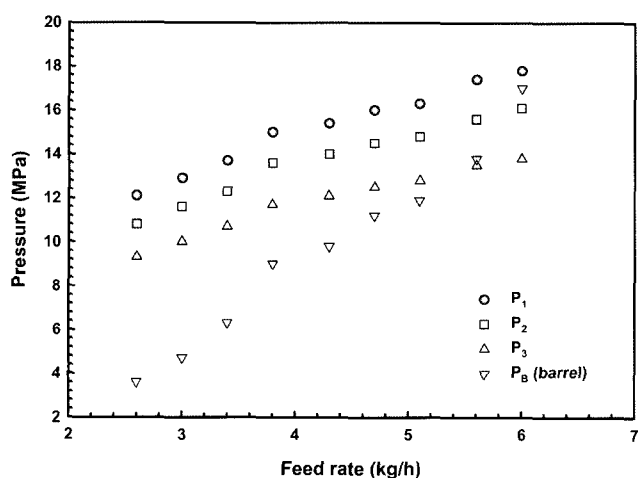


Fig. 5. Relationship between pressures and feed rate during extrusion.

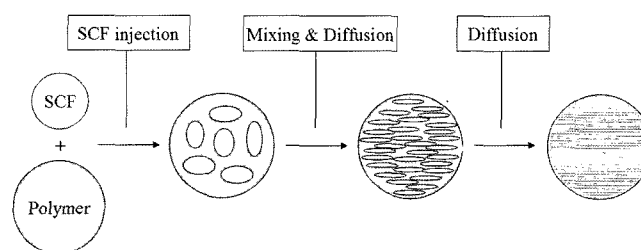


Fig. 6. Mechanism for morphology change of polymer/SCF system in the extrusion process.

sion. Therefore, in this work, viscosity measurement as a function of shear rate was carried out by the change of feed rate at constant screw speed.

4.1.3. Pressure profile at slit die under conditions with and without CO₂

The viscosity of polymer/CO₂ mixture must be measured at one-phase state. Mechanism for morphology change of polymer/supercritical fluid (SCF) system in the extrusion process shows in Fig. 6. After CO₂ injected into barrel, it is mixed with polymer and diffused into polymer. Lastly, polymer and scCO₂ will be maintained one phase by diffusion. Additionally, a homogenous one-phase mixture must be present under fully developed flow conditions. In several publications on polymer melt rheology it is suggested that a length greater than 12 times the height (H) is required before fully developed flow is achieved (Laun, 1983; Leblanc, 1976). However, some experimental results have shown that an entrance length of upwards of $15H$ is required (Rauwendaal *et al.*, 1985). An entrance length of $15H$ has been used in this study (*see* Fig. 3). The condition of fully developed flow was examined by measuring the pressures at three positions along the length of the slit die. First of all, pressure drop along slit die length of the neat PP was measured for various feed rate at constant screw speed as shown in Fig. 7. The experimental data points for all conditions show a linear pressure drop across the length of the slit die, respectively. Fig. 8 shows pressure drop along slit die length of PP containing CO₂ 2 wt% as a function of feed rate. Their pressure drops shows linear behavior as well as the results of neat PP. This means that one phase system was maintained during the measurements. In the viscosity measurement of PP/CO₂ system, CO₂ was injected into the barrel up to 4 wt%. The pressure drop of PP containing CO₂ 4 wt% also shows linear behavior, and all viscosity measurements were performed at operating conditions over supercritical pressure of CO₂ (73.8 bar).

4.2. Determination of density for pure PP and PP/CO₂ mixture

In order to obtain viscosity measurements at constant CO₂ concentrations, the estimation of the mass flow rate is required. To accomplish this estimation, polypropylene is

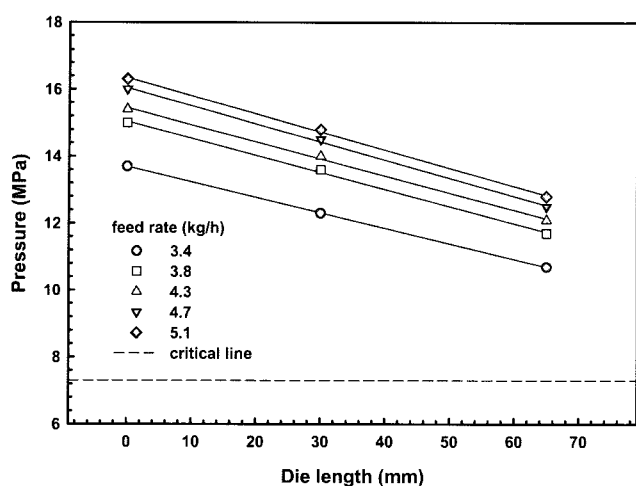


Fig. 7. Pressure drop along slit die length during viscosity measurement at screw speed of 55 rpm.

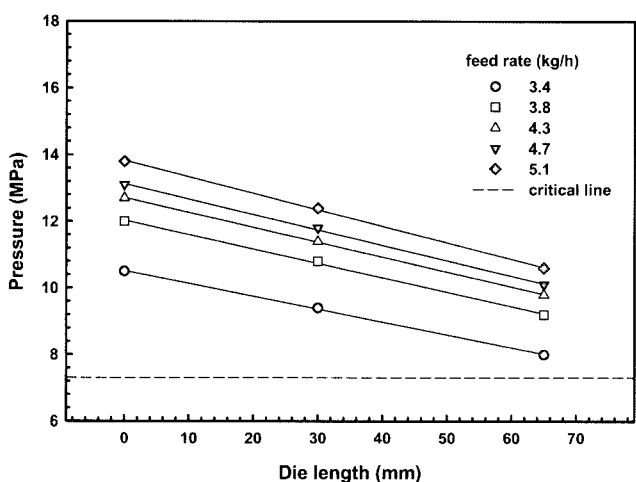


Fig. 8. Pressure drop along slit die length during viscosity measurement at screw speed of 55 rpm.

fed to the extruder via the hopper and the feed rate is used to generate pressure, forcing the melt into the slit die. The pressure drop is recorded and samples of the melt are taken at the exit of the die to measure the mass flow rate. The volumetric flow rate, which is required to determine the viscosity of the melt, is calculated using the measured mass flow rate and the density estimated from an equation of state. For the purpose of this analysis, the *S-L EOS* is used with the mixing rules described previously (see Section 2.2). To derive the *S-L EOS* for the polymer/ CO_2 mixtures, the characteristic parameters of the equation for both the neat polymer and CO_2 were required. Fig. 9 shows *PVT* data of the neat polypropylene in the range of 50 to 250°C and 0.1 to 80 MPa at cooling rate of 5°C/min. The characteristic parameters of the *S-L EOS* were obtained by fitting Eqs. 5–6 to the experimental data in the range from 0.1 to 50 MPa and from 120 to 250°C as shown in Fig. 10. The resulting char-

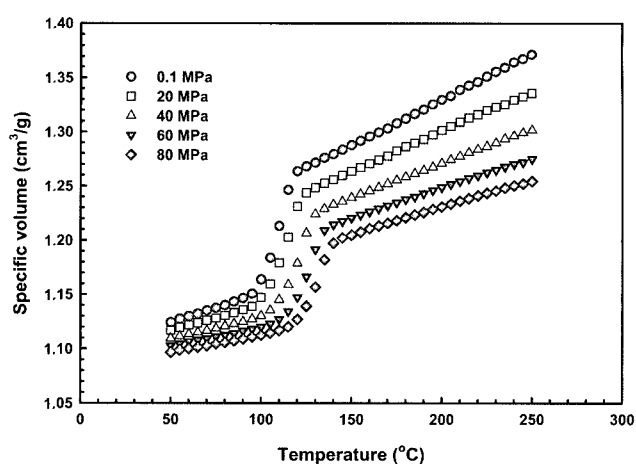


Fig. 9. PVT data of polypropylene at cooling rate of 5°C/min.

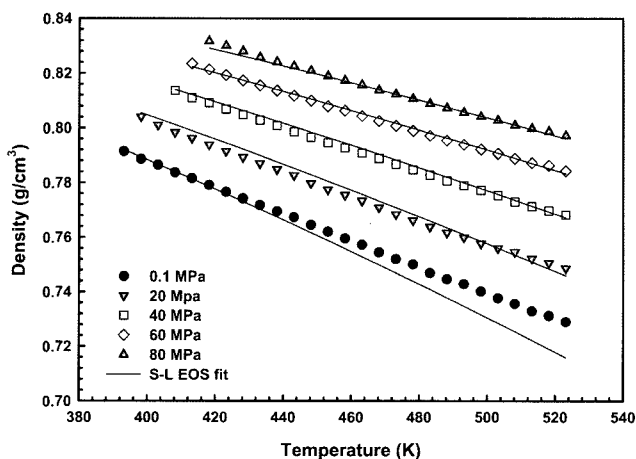


Fig. 10. The best fit of *S-L EOS* for PVT data over melt condition of polypropylene.

Table 2. Characteristic parameters of pure components

Substance	P^* (MPa)	ρ^* (g/cm^3)	T^* (K)	Reference
Carbon dioxide	369.1	1.253	341.2	(15)
Polypropylene	270.5	0.8772	688.8	-

acteristic parameters of PP are listed in Table 2. The characteristic parameters of CO_2 could be found in the literature (Sato *et al.*, 1999) and listed in Table 2 together with those for the neat PP. The interaction parameter between the polymer and CO_2 was calculated from the solubility of CO_2 into PP. The CO_2 -solubility data for PP was found in literature (Sato *et al.*, 1999). The solubility data in Fig. 11 was measured by a magnetic suspension balance (MSB) from Rubotherm Inc. The interaction parameter, δ_{12} , of PP/ CO_2 system was experimentally obtained by correlating the solubility data with *S-L EOS*. The calculated interaction parameters were listed in Table 3. The density for PP/ CO_2 mixture at

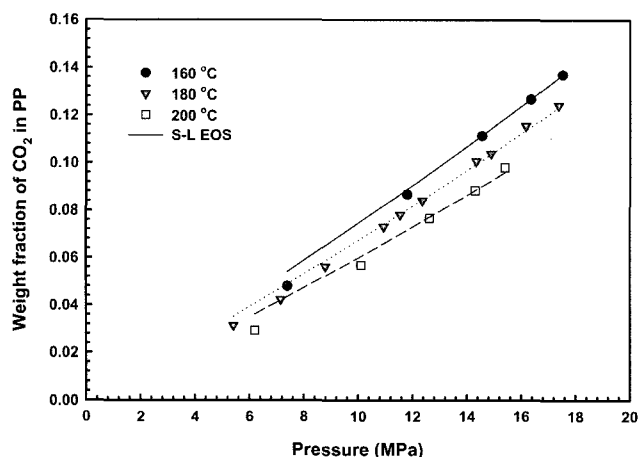


Fig. 11. Solubility of CO₂ in the molten polypropylene.

Table 3. Binary interaction parameter

T (°C)	Binary interaction parameter, δ_{12}
160	-0.214
180	-0.243
200	-0.271

various pressures and temperatures was estimated from *S-L EOS* and known interaction parameter.

4.3. The viscosity measurement of the neat PP and PP/CO₂ mixture

The viscosity of the neat PP and PP/CO₂ mixture were measured at various shear rates and different temperature for two nozzles. All viscosity measurements were performed at the condition with linear pressure drop profile as a function of die length. They were carried out as a function of feed rate at fixed screw speed of 55 rpm. The desired amount of CO₂, based on the mass flow rate calibration, is injected by varying the tension on the back pressure regulator and the flow rate of the syringe pump. The viscosity of polypropylene is shown in Fig. 12 with CO₂ concentrations of 0, 1, 2, 3 and 4 wt% at 180°C and nozzle 1. The viscosity is found to decrease with increased incorporation of CO₂. The viscosity shear rate curve appears to preserve its shape and shift to lower values. This trend of viscosity reduction has been observed not only for CO₂ addition (Han *et al.*, 1983; Elkovitch *et al.*, 1999), but for other plasticizers as well (Gould, 1965; Ritchie, 1972). Experimental measurement of viscosity reduction of PP for nozzle 2 at 180°C with the addition of pressurized CO₂ is displayed in Fig. 13. The viscosity was found to decrease with increased CO₂ concentration at various shear rates and two nozzles. Viscosity data of PP and PP/CO₂ mixtures at nozzle 1 showed generally higher values compared to nozzle 2. This result is due to pressure effect. However, slopes of viscosity vs. shear rate were almost the same. Fig. 14

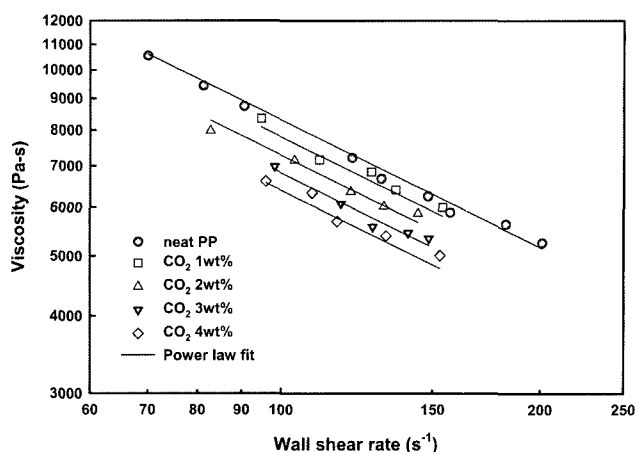


Fig. 12. Viscosity vs. wall shear rate at nozzle diameter of 1.5 mm and 180°C.

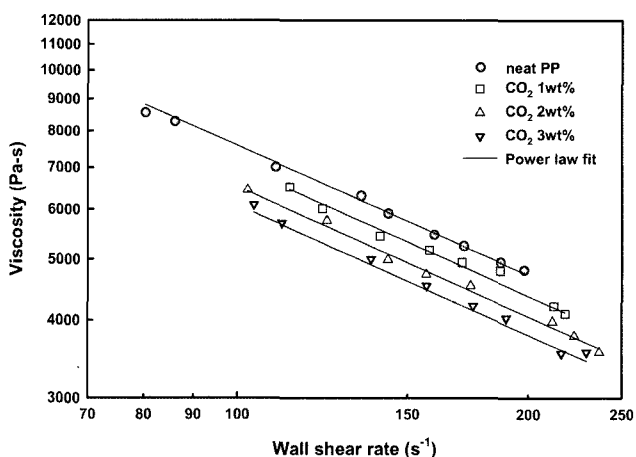


Fig. 13. Viscosity vs. wall shear rate at nozzle diameter of 2.5 mm and 180°C.

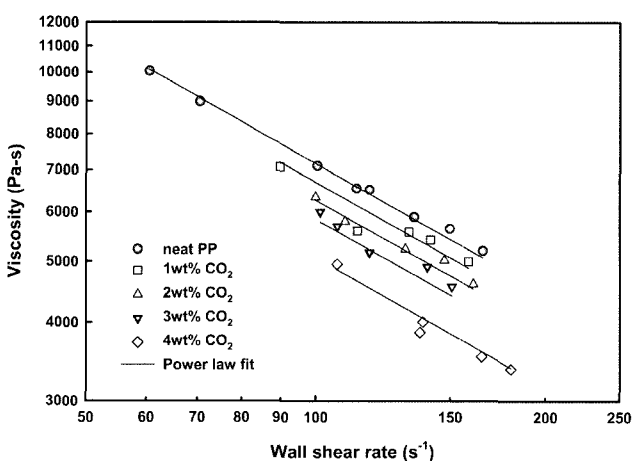


Fig. 14. Viscosity vs. wall shear rate at nozzle diameter of 1.5 mm and 200°C.

shows the viscosity curves of PP as a function of CO₂ concentration at 200°C and nozzle 1. In comparison with result

in Fig. 12, for temperature effects, CO₂ acts as an effective plasticizer, decreasing the viscosity with increasing CO₂ concentration. However, as temperature is increased the observed reduction in viscosity decreases slightly. The data in Figs. 12~14 confirm that CO₂ is an efficient plasticizer for polypropylene, lowering the viscosity of the polymer melt by 10-70% depending on operating conditions.

5. Conclusions

A high-pressure extrusion slit die rheometer was constructed to measure a wide range of viscosities for polymer melts plasticized with dissolved carbon dioxide. Nozzles added to the slit die rheometer were required to elevate the system pressure above the bubble pressure of the polymer/CO₂ mixture and thus maintain a one-phase solution. Measurements of pressure drop confirmed the presence of a one-phase mixture and a fully developed flow in the system. Experimental measurements of viscosity as a function of shear rate, pressure, temperature and CO₂ concentration were conducted for commercial polypropylene. The CO₂ was shown to be an effective plasticizer for polypropylene, lowering the viscosity of the polymer melt by as much as 70%, depending of the process conditions and CO₂ concentration. This is due to the reduction of chain-chain interactions and increasing the inter-chain distance.

Acknowledgements

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Nomenclatures

H	: The slit height
M	: Molecular weight
N	: The total number of molecules in the lattice
N_i	: The number of i molecules
ΔP	: The measured pressure drops
\tilde{P}	: The reduced pressure
P^*	: The characteristic pressure
Q	: Volumetric flow rate
R	: The number of lattice sites occupied by a molecule of molecular weight
R	: Gas constant
\tilde{T}	: The reduced temperature
T^*	: The characteristic temperature
v^*	: The characteristic volume of a lattice site
W	: The slit die width

Greek Letters

$\dot{\gamma}_{ap}$: Apparent viscosity
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$\dot{\gamma}_w$: Wall shear rate
δ_{ij}	: The binary interaction parameter
ε	: The interaction energy
η	: Viscosity
$\tilde{\rho}$: The reduced density
ρ^*	: The characteristic density
τ_w	: Wall shear stress
ϕ_i	: The volume fraction of component i in the mixture
ϕ_i^o	: The close-packed volume fraction of component i in the mixture

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