On-line rheological measurement of a binary mixture polymer/sc-CO$_2$ in an extruder

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This study is to be seen in the context of the replacement of oil-based polymers by new bio-sourced ones having the same end-user properties. It is also important to use green chemical engineering to process them in a more environmental friendly way. The use of supercritical fluids appears then, to be a promising route. The most interesting fluid is supercritical carbon dioxide (sc-CO$_2$), which is soluble in quite significant quantities in many molten polymers, where it acts as a plasticizer and a swelling agent. It is known to be a green processing agent used, for instance, such as blending of polymers, polymer foaming, particle formation or polymerisation process.

The easiest and most used way of processing polymers in continuous mode is to use an extruder that provides a high shear rate, particularly in the die. Our lab has developed a process coupling single-screw extrusion and sc-CO$_2$. Understanding and improving such process require data, like the solubility of CO$_2$ into the polymer, the diffusion coefficient and the viscosity of the mix. We have then developed an on-line measurement of the viscosity based on capillary rheometry. The method was validated by measurements on a classic capillary rheometer. Both data sets were found in good agreement.

This method was applied to characterize the rheology of a bio-sourced polymer (BsP) itself and of the polymer-CO$_2$ binary system. A pseudoplastic fluid behaviour was observed with a 30 % decrease of the viscosity from 46 to 32 Pa.s at about 5000 s^{-1} and 220°C, upon addition of carbon dioxide. The rheological data were correlated with solubility data and analysed in function of the process parameters. It was observed that the decrease of the viscosity with the amount of CO$_2$ dropped to a plateau before reaching the thermodynamic solubility. It seems that the limitations are due to the kinetics of dissolution and mixing. The higher the shear stress, the higher the amount of CO$_2$ at which the viscosity plateau is reached. This is an indication of a better CO$_2$ dissolution rate when the speed of the screw increases. Therefore, those measurements may quantify the impact of the CO$_2$ on the rheology of the system but also of the efficiency of the mixing process in our experimental setup.

INTRODUCTION

Most of the polymers used in industry nowadays have a petrochemical origin. However, due to the predicted exhaustion of the world petroleum reserves, it is necessary to replace them with biosourced polymers with equivalent properties. It is also important to find new ways of processing them, which comply with the requirements of green chemistry. The use of supercritical fluids in polymer processing has considerably grown up in the last decades. The most used is supercritical carbon dioxide (sc-CO$_2$). It is soluble in large quantities in many molten polymers and can be added in extrusion processes where it acts as a plasticizer and swelling agent [1, 2]. It is known to be a green processing agent of great interest in the

polymer field, such as blending of polymers, polymer foaming, particle formation or polymerization process.

Extrusion is a process converting a raw material into a product of uniform shape and density by forcing it through a die under controlled conditions [3]. It has extensively been applied in the plastic and rubber industries, where it is the most important manufacturing process.
Coupling sc-CO_2 and extrusion modifies the rheological properties of the polymer while flowing through the barrel of the extruder. The reduction of viscosity decreases the mechanical constraints and the operating temperature within the extruder. Thus, this may allow the use of fragile or thermolabile molecules, like pharmaceutical ones. Furthermore, the absence of residues in the final material is also an advantage for a pharmaceutical application.

Using a new sc-CO_2-assisted extrusion process that leads to the manufacturing of microcellular polymeric foams, we have elaborated microcellular foams of a biocompatible amorphous polymer [4, 5]. However, understanding and improving such a process requires the knowledge of physical properties, like the solubility of CO_2 into the polymer, the diffusion coefficient and the viscosity of the mixture. An extruder provides a high shear rate, particularly in the die. However, the viscosity of the binary system under process conditions is very difficult to reach in conventional rheometers. Viscosity under pressure can be measured in different ways [6]. One group of measurements is based on vibrating surface or falling ball rheometers [7]. These techniques require Newtonian or low viscosity polymers. The other main group of measurement techniques is based on capillary rheometry. This technique is widely used for viscous polymers and implementations exist to measure the rheology of mixtures of polymer and sc-CO_2 [8]. We have implemented this on-line technique on a single-screw extruder in order to estimate the viscosity of a bio-sourced polymer and of the binary system under process conditions.

In this work, we have investigated the validity of this method with a biosourced semi-crystalline polymer, called BsP. Firstly, we then compare the obtained results with measurements made on a classic capillary rheometer. Secondly, we apply this technique to the binary system.


THEORY OF CAPILLARY RHEOMETRY

The principle of capillary rheometry is to force melt polymer through a die of length L and diameter D. Knowing flowrate and pressure loss created by the die, the viscosity can be reached (figure 1).
In order to determine this viscosity, several assumptions need to be made. A Poiseuille flow in a tube is assumed with the following hypotheses:
- Incompressible fluid with a laminar, isothermal and established flow,
- No end effects,
- No wall slip.

Figure 1: Principle of a capillary rheometer under pressure
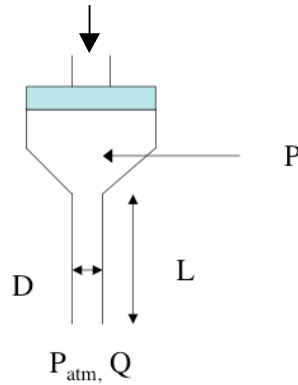
If these hypotheses are confirmed, then the following formulas apply:

$$\tau_p = \frac{D\Delta P}{4L} \tag{1}$$

$$\dot{\gamma}_{app} = \frac{32Q_v}{\pi D^3} \tag{2}$$

$$\eta = \frac{\tau_p}{\dot{\gamma}_{app}} \tag{3}$$

The most arguable hypothesis is the absence of end effects, which may require corrections. One way is to use a long die in order to make the effects negligible. The other method is to implement the Bagley correction. It consists in carrying out measurements with dies of different lengths and to use the slope of P = f(L/D) to calculate τ_p. The problem of this method is the high number of experiments required.

MATERIALS AND METHODS

Melting onset temperature of the BsP polymer is in the range 180-200°C and the glass transition temperature within 40-60°C. The solid density ρ_P, determined by helium pycnometry (Micromeretics, AccuPYC 1330) was 1027±5 kg.m^{-3}. Melt density was found to be 979 kg.m^{-3} at 220°C with a magnetic suspension balance (Rubotherm).
Solubility measurements of CO_2 in the polymer were carried out on the same magnetic suspension balance at 202, 220 and 231°C at different pressures.

Figure 2 shows the experimental set up, which has previously been detailed elsewhere [2, 5]. The single-screw extruder has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 35 (Rheoscam, SCAMEX). A great L/D ratio generally indicates a good capacity of mixing and melting but an important energy consumption. The screw is divided into three parts. The first one has a length to diameter ratio of 20 and the others have a length to diameter ratio of 7.5. Between each part, a restriction ring has been fitted out in order to obtain a dynamic

gastight, which prevents $scCO_2$ from backflowing. The first conical part allows the transport of solid polymers and then, their melting and plasticizing. Then, the screw has a cylindrical geometry from the first gastight ring to the die. The temperature inside the barrel is regulated at five locations: T_a and T_b before the CO_2 injection, T_c and T_d after the injection and T_e in the die. All temperatures were set at 220°C.

Figure 2: Experimental device
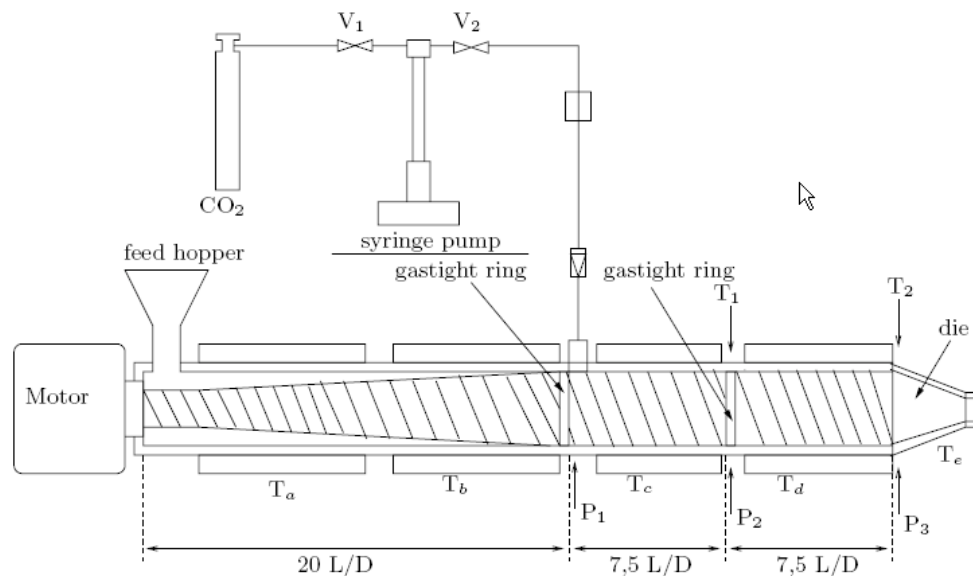
There are three pressure and two temperature sensors: P_1 after the CO_2 injector, P_2 and T_1 before the second gastight ring and P_3 and T_2 by the die. This allows measuring the temperature and the pressure of the polymer inside the extruder. Errors associated to pressure and temperature measurements were about 0.2 MPa and 1°C respectively.

Three dies have been used. They all have a diameter of 1 mm and their lengths are 7, 17 and 22 mm. Those dies will be called here, L7, L17 and L22 respectively.

CO_2 (N45, Air liquide) is pumped from a cylinder by a syringe pump (260D, ISCO) and then introduced at constant volumetric flow rate. The pressure in the CO_2 pump is kept slightly higher than the pressure P_1. The CO_2 injector is positioned at a length to diameter ratio of 20 from the feed hopper. It corresponds to the beginning of the metering zone, that is to say the part where the channel depth is constant and equal to 1.5 mm. The pressure, the temperature and the volumetric CO_2 flow rate are measured within the syringe pump. CO_2 density, obtained on NIST website by Span and Wagner equation of state [9], is used to calculate mass flow rate and thus the CO_2 mass fraction w_{CO_2}. CO_2 flowrate was varied and its influence on the viscosity of the mixture was studied.

Once steady state conditions (tested on P and T measurements) are reached, mass flowrate and pressure (P_3) are measured.

Parallel measurements on a capillary rheometer (CR) (Instron 3211) were made at LMPB (ISTIL-EPUL, Lyon, France) laboratory. This rheometer is equipped with a piston of 0.9525 cm^2 and with a force sensor of 2000 kg with a precision of 0.2 %. One die of L/D=140 (L=70 mm and D=0.5 mm) is used. Measurements were carried out at 220°C.

RESULTS

Comparison of both methods

Measurements on the extruder were carried out with the L22 die because it is the longest. Experiments were compared with results obtained on the capillary rheometer. End effects could be postulated as negligible with those two dies. Nevertheless, Bagley correction [10] was made on the extruder experiments in order to evaluate end effects. Figure 3 shows the comparison of results obtained on the extruder and on the capillary rheometer.

Figure 3: Comparison of different rheological results
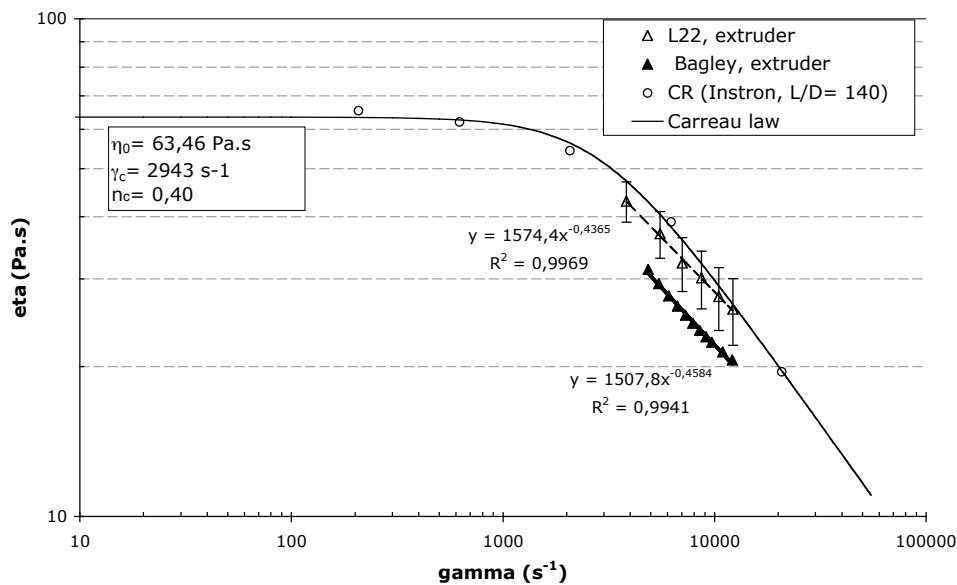
Both series of results are in good agreement. However, results on the extruder treated with the Bagley correction give significantly lower viscosity values. Therefore, the correction is useful for this die. The set of viscosity values obtained with the commercial rheometer are higher. This discrepancy might be ascribed to:

- temperature control during the experiment. Both methods used temperature set at 220°C but the heating takes place through a static polymer in the CR during around 1h whereas there is mixing in the extruder with short residence times (around 3 min).

- pressure level is quite different. Pressure in the CR is in the range 60 to 2000 bars and particularly within 600 to 2000 bars, which corresponds to the range of shear rates encountered in the die of the extruder. This high level of pressure may induce an increase in viscosity. Pressure level in the extruder is between 70 and 250 bars.

- sample storage leading to a possible change in the moisture content. BsP is quite

sensitive to humidity.

In order to further investigate these discrepancies and to use this comparison as a validation of the method, we could use a less sensitive polymer and evaluate pressure corrections to the CR results.
Nevertheless, untreated results still give a good order of magnitude of the viscosity.

Evolution of viscosity of the mixture

Experiments on the binary system were carried out on the extruder only with L22 die, which ensures a good pressure for solubilization of CO_2 in the extruder and minimizes the number of experiments. However, it has to be kept in mind that even though the quantitative value is not exact, due to the lack of correction, the qualitative evolution is correct.
Solubility experimental data were represented by a Sanchez-Lacombe equation of state [11, 12] endowed with one fitted binary parameter. This model was then used to evaluate the solubility (w_{eq}) at each point of the die. Solubility at the die entrance is noted w_{eqi}.

Viscosity of the binary system decreases with the increase in CO_2 content and shear rate (figure 4).

Figure 4: Evolution of the binary system viscosity as a function of CO_2 content and shear rate.
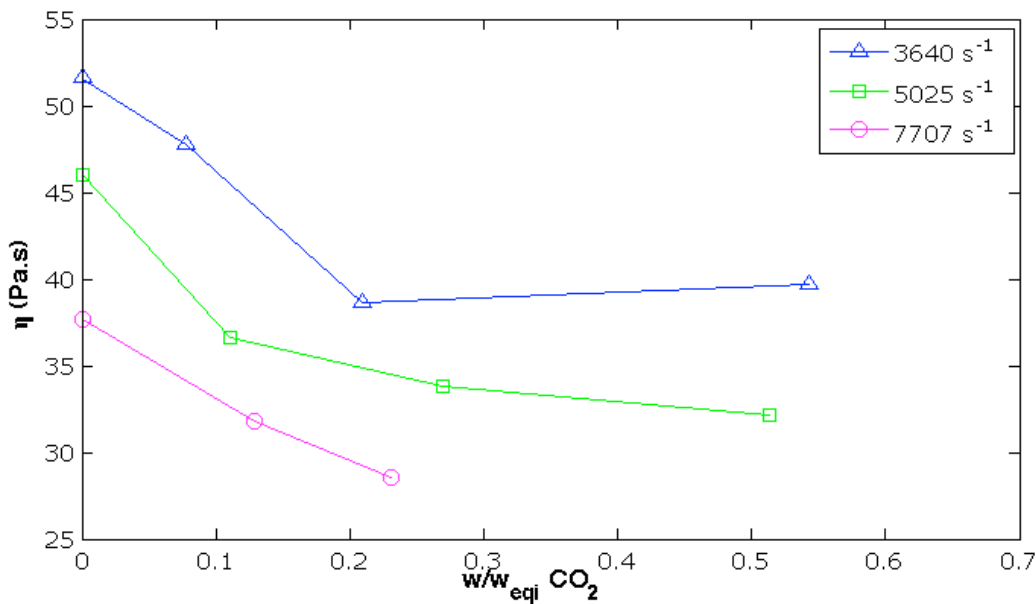
The behaviour in terms of shear rate is not surprising since polymers are often shear thinning. The decrease in viscosity related to CO_2 addition is also consistent with literature observations. This decrease usually follows a power law [13]. However, our measurements suggest a plateau, which is not consistent with such a law. This may be due to the desorption of the CO_2 in the die and the occurrence of a two-phase system that could disturb measurements.

In fact, the main issue with binary mixture is to keep the system in a single-phase. Multiple pressure sensors along the die would be necessary to check this assumption [14]. However,

our system was set with only one sensor at the entrance of the die. Thus, an evaluation of the exact location of desorption in the die was made. A linear depressurisation was assumed from the entrance to the exit [15]. This linear depressurisation was confirmed by modelling the die flow with Comsol Multiphysics®. A Carreau law (figure 3) was used to represent the viscosity of the polymer. An example of the results found by the flow simulation is presented on figure 5. Figures 6, 7 and 8 show the location of the point of desorption for each experimental measurement at the three shear rates studied and for different CO_2 contents. Desorption is assumed to occur when $w=w_{eq}$.
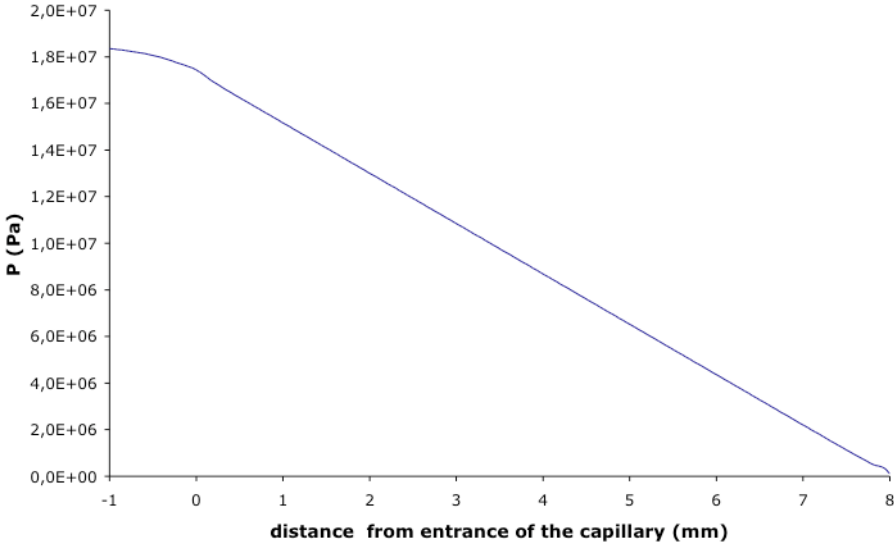
Figure 5: Profile of pressure along the die.

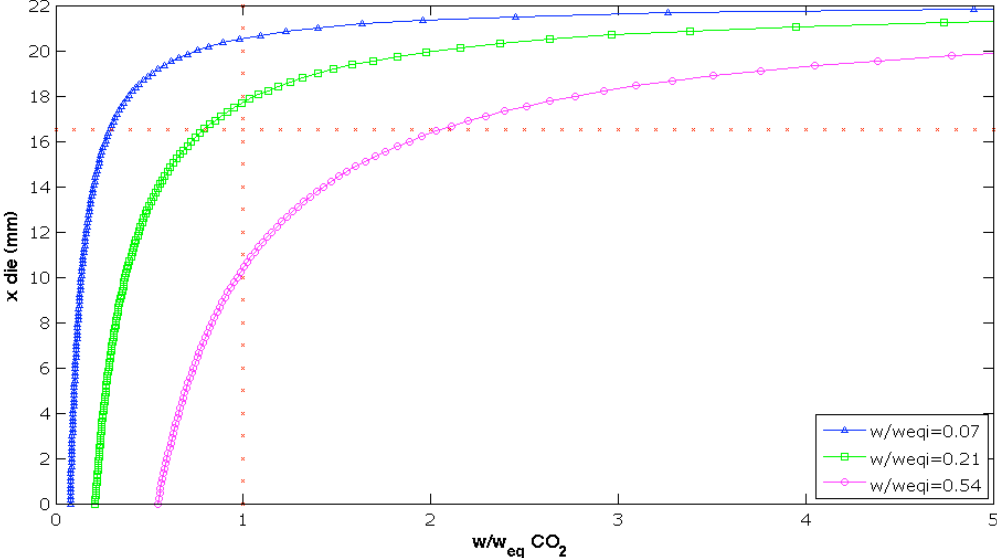**Figure 6: Desorption point at 3640 s^{-1} at 3 different initial ratio**

Figure 7: Desorption point at 5025 s^{-1} at 3 different initial ratio.
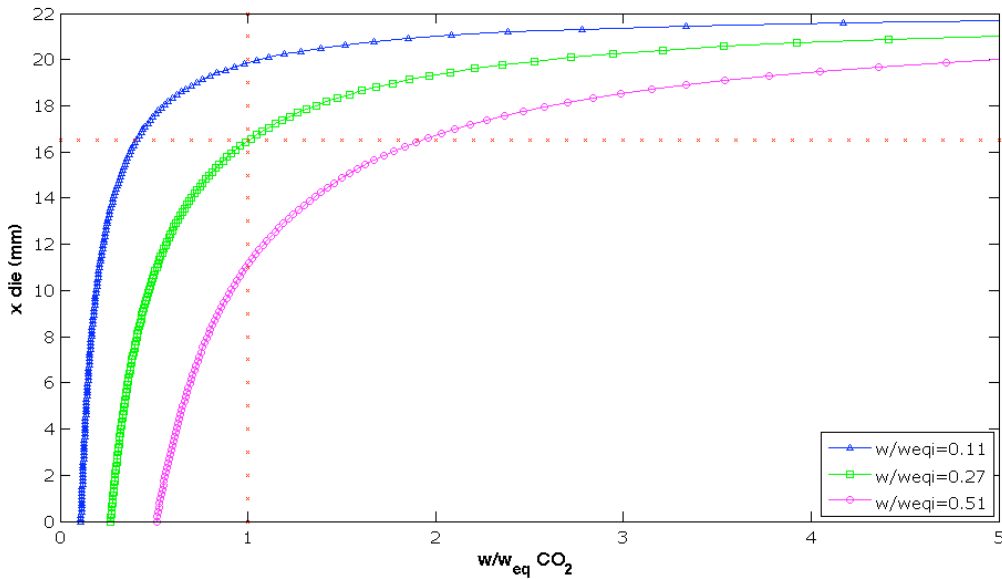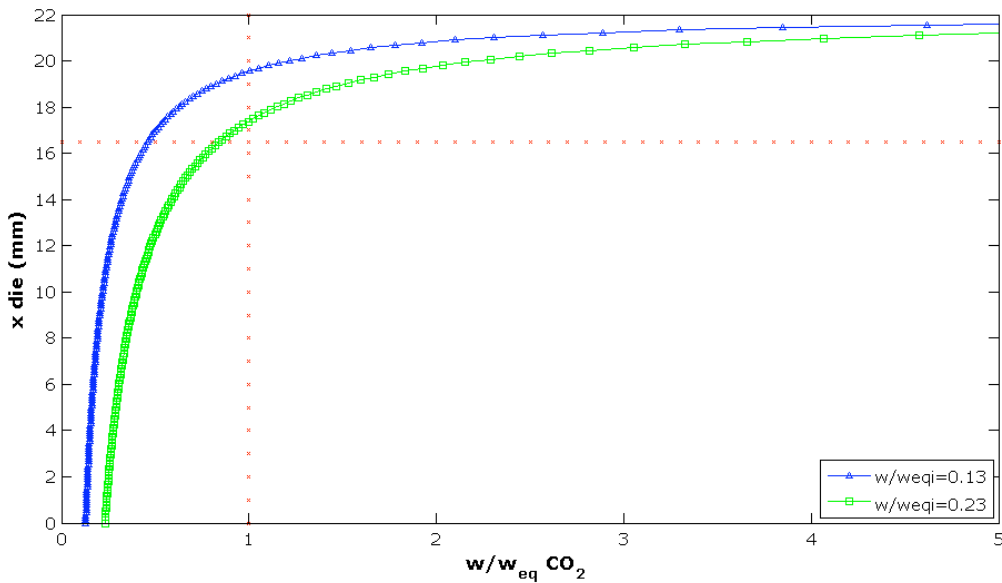

**Figure 8: Desorption point at 7707 s^{-1} at 2 different initial ratios.**

As the CO_2 content increases, desorption occurs earlier in the die. When desorption occurs within the first three quarters of the die length (16.5 mm), viscosity measurements differ from the power law, as shown by the logarithmic chart on figure 9 (n is the index of the power law). Viscosity results can thus be assumed accurate as long as the content of CO_2 is not too high and desorption does not occur too early in the die. In this study, the limit appears to be $w/w_{eqi} < 0.27$.

Finally, a decrease of the viscosity around 25 % is observed in the single-phase criterion region defined above ($w/w_{eqi} < 0.27$, corresponding to a mass percentage up to 2 % of CO_2).

The appearance of the plateau at higher CO_2 content is due to the predominance of the two-phase occurrence along the die. The viscosity measured in this zone can be seen as an apparent viscosity of the mixture in the process. It reflects coupling of flowing with physical phenomena of two-phase occurrence. Then, it can be used to apprehend phenomenological behaviour of the flowing mixture in the process.

Figure 9: Logarithmic chart of the evolution of viscosity of the binary as a function of CO_2 content and shear rate
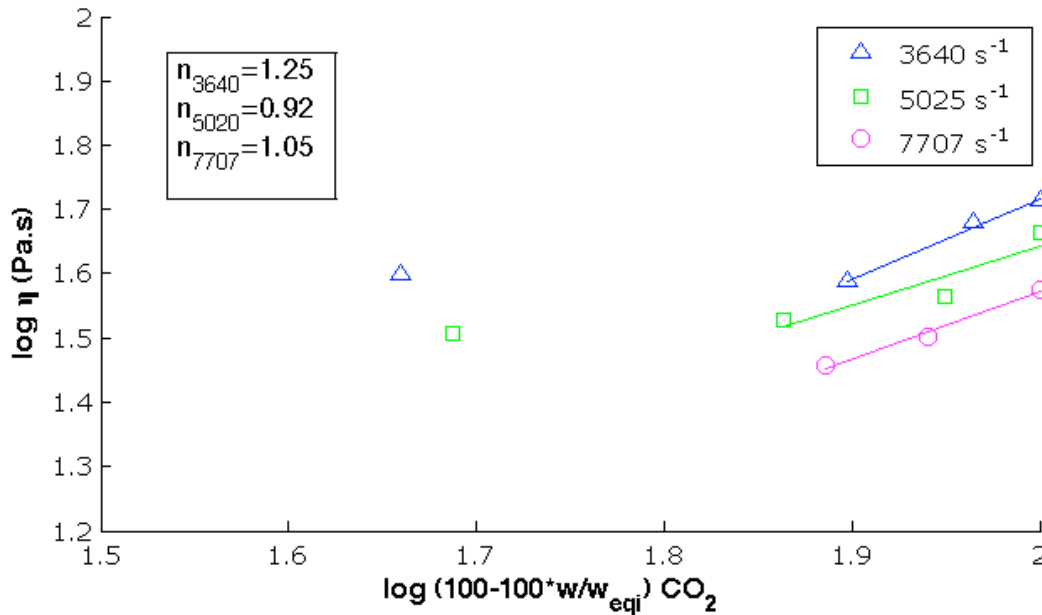
CONCLUSION

Capillary rheometry is an efficient method to measure viscosity of polymer at high shear rate. We implemented this technique on-line on an extruder in order to carry out measurement in processing conditions. Validity of the measurements was checked with a commercial capillary rheometer. Measurements on the binary mixture CO_2/polymer were then carried out. Desorption point along the die was located by means of a solubility model (Sanchez-Lacombe) and correlated with experimental data. A minimal distance before CO_2 desorption must be attained to ensure accuracy of the data. Those experiments and calculation demonstrate the efficiency of capillary rheometry to measure viscosity of polymer and binary system polymer/scCO_2. The set-up with only one pressure sensor at the entrance of the die works at low ratio of CO_2. Above a given CO_2 content, depending on the solubility, pressure and length of the die, depressurisation occurs too early in the die and measurements give access to apparent viscosity in process conditions. To access absolute viscosity of the mixture, a system with multiple pressure sensors would be necessary.

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