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Effect of pressurized CO₂ and N₂ on the rheology of PLA

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Abstract

Melt-polymer processing is conventionally employed for thermoplastic polymeric materials. The rheological behaviour of the polymer is then of critical importance to correctly accomplish the process. The effect of pressurized fluid additives (PFA), such as CO₂ and N₂, has been investigated in this work to determine the extension of their beneficial plasticization effect on PLA. *In-line* measurements performed by a custom-designed slit-die rheometer were conducted at different temperatures and PFA concentrations, and the viscosity values of PLA/PFA mixtures were experimentally determined and compared to those obtained when adding a commercial plasticizer, acetyltributylcitrate (ATBC), to PLA. Our results suggested that a two-fold reduction of PLA viscosity is achievable using addition of 2.65 wt% pressurized CO₂ respect to similar contents of ATBC. Furthermore, a decrease of 10 °C of the processing temperature could be attained when adding 1.70 wt% of CO₂. This work aims at shedding light on the rheological behaviour that PLA experiences during assisted-melt extrusion processing, and on how more favourable energetic processing could be achieved by lowering temperature, if the appropriate type and concentration of PFA is employed during processing.

Keywords: Poly(lactic acid), CO₂, N₂, rheology, melt-extrusion, slit-die.

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1. Introduction

During the last decade, the production of plastics materials has increased steadily from 230 million tonnes in 2005 to 322 million tonnes in 2015 [1], manifesting the impact that polymers have on our life.

5 In general, polymers are processed in the molten state, and during processing physical transformations take place, involving flow, solidification and plastic deformation of materials [2]. As a result, the knowledge of the polymer rheological behaviour becomes of utmost importance to optimize melt-processing. For instance, polymers of high viscosity require processing at high temperatures to
10 enhance polymer flowability. While this alternative could be valid for high viscosity thermally stable polymers, many of them suffer degradation at elevated temperatures, thus a different approach such as the addition of a plasticizer that reduces viscosity might be considered [3]. Depending on the processability and end-use requirements of the polymeric product, there is a wide variety
15 of plasticizers that could be used [4, 5]. However, due to recent health and safety concerns about the migration and toxicity of certain plasticizers, namely phthalates, industries have not only started to develop new bio-based plasticizers, e.g. citrate esters, which assure lower migration and toxicity; but also to modify their conventional processes by the incorporation of physical blowing agents that
20 act as plasticizers and promote better processability and a residue-free product. Within these blowing agents, pressurized fluid additives (PFA) as CO₂ and N₂ have already been employed in assisted-melt extrusion processes [6, 7, 8, 9]. For example, García-Leiner and Lesser [9] proposed the use of CO₂ to improve the processability of intractable and high molecular weight polymers thanks to its
25 plasticization effect and its direct influence on the melting behaviour of the polymeric materials. They investigated polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP) and syndiotactic polystyrene (s-PS), concluding the achievement of continuous processing of these polymers when CO₂ is loaded into the main process flow line. Other authors have, however, focused
30 their attention on the use of blowing agents in melt extrusion for the prepara-

tion of polymeric blends [10, 11], microcellular foaming [12, 13], or to conduct reactive extrusion [14]. In all the cases, the prevailing tendency is to address the melt-processing of bioplastics, whose global production is predicted to grow by 50 % in 2021 (currently, it is 1 wt%) [15].

35 Poly(lactic acid), PLA, is one of the most promising bio-based polymers, truly biodegradable and biocompatible. It is generally recognized as safe (GRAS) by the FDA, and due to its interesting physical properties, it has been widely investigated in the last years for the manufacturing of medical devices [16], and applied for the preparation of daily-based utilities, such as textiles [17, 18], pack-
40 aging materials [19], and diverse consumer goods [20]. Its main drawback with respect to melt-processing falls within its low thermal stability, especially in the presence of moisture and shear, exhibiting a rapid loss of molecular weight while processing. Actually, as suggested by Jamshidian et al. [21], at temperatures lower than its melting point, i.e. 170 °C, PLA undergoes already thermal
45 degradation, which rapidly increases above T_m . It has been postulated that PLA thermal degradation occurs by random chain scissions, where hydrolysis, oxidative degradation, inter- and intramolecular trans-esterification reactions, and depolymerization might as well be involved. To reduce the thermal degradation suffered by PLA during melt-processing, various researchers have proposed
50 to utilize bio-based plasticizers such as acetyltributylcitrate (ATBC) [22, 23], reporting a depression of approximately 25 °C of the glass transition temperature of PLA for 15 wt% plasticizer. Nevertheless, thermally induced migration of ATBC from the processed material occurs even at 100 °C, leading to an increased weight loss of plasticizer at higher temperatures and prolonged exposure
55 times [24]. Therefore, the idea of using PFA's as plasticizers for processing PLA has become popular among researchers who aim to obtain a final product free of additives at the time of improving PLA processability [25, 26, 27, 28], even if foamed products are finally obtained.

In general, it has been shown that CO₂ acts as a molecular lubricant when
60 it is absorbed into a polymer, increasing segmental and chain mobility and also increasing interchain distance [29]. Due to this local increase in mobility, the

glass transition temperature is dramatically reduced and the polymer flows more easily. Similar effects may be possible with other fluids like N₂, but in any case, an understanding of the rheological behaviour of PLA/PFA mixture is of vital importance to determine not only the processing limits, but also the advantage offered by the plasticizer in terms of temperature reduction in extrusion.

To evaluate the viscosity of molten polymers, *In-line*, *On-line* and *Off-line* measurements are available. While both, *In-line* and *On-line* measurements, are implemented directly within the processing line, *Off-line* measurements rely on the post-experimental evaluation of polymer samples collected during processing. Hence, *Off-line* measurements suffer from large elapse of time between the occurrence of process instabilities and their actual detection [30], so they are unable to capture the proper rheological behaviour of polymers when assisted-melt extrusion processing is conducted. On the other hand, *On-line* measurements require to divert the sample from the main process flow line, reducing the risk of interference with the main process, thus implicating delays in measuring response. In contrast, *In-line* measurements lead to faster diagnosis of processing conditions.

Up to now, the data about rheological behaviour of PLA/PFA systems is scarce. So far, some *Off-line* measurements by rotational rheometers have been conducted to determine the effect that CO₂ exerts on the viscosity of amorphous P_{DLLA} [31]. The results of this study suggested the ability of CO₂ to reduce the viscosity of PLA within a range of different temperatures (50 °C - 140 °C) and pressures (5 - 12 MPa), highlighting the advantage of using CO₂ to improve the processability of PLA and to help preventing its thermal degradation. Even so, the selection of *Off-line* measurements similar to the ones conducted by Kelly et al. [31], entail significant differences compared to a continuous assisted-melt extrusion process. Reignier et al. [26] employed *On-line* measurements to perform their experiments, concluding that increasing the content of CO₂ allowed a significant reduction of the shear stress at constant apparent shear rate. This could be interpreted as a reduction of 60 °C of the processing temperature when 10 wt% of CO₂ is dissolved in the system. Despite the supposedly broader appli-

95 capability of their results in real assisted-melt extrusion processes, only amorphous PLA, D-content of ca. 10 wt%, was tested. Any extrapolation to semicrystalline grades of PLA is still lacking.

To further elucidate the effect of PFA on PLA processing, an *In-line* rheological slit-die has been designed and coupled to an assisted-melt extrusion line in this work, and the characterization of the rheological behaviour of semicrystalline PLA/PFA mixtures has been accomplished. Two different PFA's, 100 namely CO₂ and N₂, have been evaluated at different concentrations, temperatures and shear rates, and the obtained viscosity values have been compared with those from PLA/ATBC mixtures at identical processing conditions.

2. Experimental

2.1. Materials

105 Semicrystalline poly(lactic acid), PLA 3001D, with a residual monomer content of less than 0.17 % and a D-content of 1.5 % was purchased from NatureWorks (Resinex, Belgium). Acetyl tributyl citrate (ATBC), commercially known as Citrofol BII, was kindly provided by Jungbunzlauer Inc. (Ladenburg, Germany), and CO₂ and N₂ with a purity of 99.99 % were purchased from Carbagas 110 (Gümligen, Switzerland).

2.2. Experimental equipment

Figure 1 shows the experimental set-up that has been employed to measure the viscosities of PLA, PLA/PFA and PLA/ATBC mixtures during melt-processing. The system was composed of an *In-line* rheological slit-die attached 115 to the exit of a single-screw extruder Rheomex 19/25 OS (ThermoFisher, Germany). Between the extruder and the slit-die, three different elements were mounted to assure proper measuring conditions: 1) a melt gear pump that displaced a nominal volumetric flow of polymer of 1.2 cm³/rpm; 2) an injection port connected to a dosing system that supplied the corresponding amounts of 120 PFA as required; and 3) a static mixing area to improve mixing and to allow

sufficient residence time between PFA and PLA as to assure one-single phase mixture prior to the slit die. The slit-die was conceived based on previous designs of Royer et al. [32], and as such, it incorporated a capillary nozzle at its end to maintain pressure values above phase separation. Table 1 reports the dimensions of the custom made slit-die and of the nozzle utilized in this work, while in Figure 2 a schematic view of the set-up is shown.

2.3. In-line rheological slit-die measurements

A standard experiment to measure the viscosity of PLA or PLA/ATBC mixtures consisted of mainly two steps. In the first step, the temperature of the system was set at the desired value, i.e. 180 °C; 190 °C or 200 °C. Afterwards, PLA pellets, which were previously vacuum-dried at 50 °C for 24 hours, were fed into the system. The loading of the polymeric pellets was performed through a drying-hopper to maintain a water content lower than 100 ppm, reducing the hydrolytic degradation that PLA could suffer while processing. The mass flow of the polymer that was fed into the system was determined by the pressure and the rotating speed selected for the extruder and the gear pump, respectively. The second step was based on recording the steady-state values of pressure (P1-P3) and temperature (T1-T2) displayed by the sensors of the slit-die. This information was used to calculate viscosity as explained in detail in the following section. It is important to mention that these two steps allowed obtaining one single value of viscosity at a specific shear rate and temperature. If the flow curve of the material is required, the procedure should be repeated at different shear rates, i.e. at different rotating speeds of the gear pump, while temperature is kept constant.

When assisted-melt extrusion was conducted, e.g. of PLA/PFA mixtures, the experimental procedure should be slightly modified. Actually, after the first step, PFA was loaded into the static mixing area by means of the dosing system represented in Figure 1. The amount of PFA was controlled by the syringe pump (Teledyne Isco 260D, Louth, Ireland) which was operated at constant flow rate according to the percentage of PFA required in the final PLA/PFA

mixture. Due to its internal construction, the injection port acts as a pressure regulator, allowing the continuous displacement of the corresponding amount of PFA as soon as pressure of the whole system achieves the steady state. After this, the last step accounted for the measuring of the pressure drop and the
155 polymer mass temperature as in a standard experiment. In this case, however, a further consideration of the amount of PFA introduced in the system, and of the mass of polymeric material collected after certain time, was inevitable to correctly perform the viscosity calculations.

In general, an increase of the experimental temperature of 5 °C was observed
160 in the polymer mass temperature. This might be attributed to the viscous dissipation that the polymer experienced during processing. As well, the intrinsic difference of the temperature that sensors located in the electrical heating jackets and those located in the slit-die measure could explain this mismatch. From now on, temperature of *In-line* measurements will be referred to the polymer
165 mass temperature.

2.4. Viscosity calculation

To calculate viscosity values from *In-line* experimental measurements, the standard equations for a slit-die rheometer were employed [32]. A fully developed laminar flow with no-slip on the wall was assumed within the rectangular
170 slit-die. Therefore, the apparent melt viscosity was determined from the experimentally measured pressure drop, $\Delta P = P_1 - P_3$, and the volumetric flow rate of the polymer in the slit-die, Q_v , by applying the following equation [33]:

$$\eta_{app} = \frac{\tau}{\dot{\gamma}_{app}} \quad (1)$$

where τ refers to the wall shear stress, and $\dot{\gamma}_{app}$ to the apparent shear rate in the slit-die. These two values can be obtained as follows [34]:

$$\tau = \frac{h}{2} \frac{\Delta P}{L} \quad (2)$$

$$\dot{\gamma}_{app} = \frac{6Q_v}{Wh^2} = \frac{6Q_m}{W\rho h^2} \quad (3)$$

where L, h and W allude to the length, height and width of the slit-die, respectively (see Figure 2 and Table 1), and Q_v stands for the volumetric flow rate of the melt. This volumetric flow rate was calculated using the experimentally measured mass flow rate, Q_m , and the polymer density, ρ , estimated from an equation of state. In this work, the Sánchez-Lacombe equation of state [35], using the parameters reported in Table 2 for PLA, CO₂ and N₂, was employed for density calculations. As previously mentioned, the employment of equations (2) and (3) for viscosity calculations is strictly valid only for laminar flows of incompressible fluids. To evaluate the effect that PFAs present on the compressibility of the polymer melt, a direct comparison of densities at equivalent pressure conditions and temperatures can be easily performed. Besides, the certainty of a fully developed flow through the slit-die, can be checked by evaluating the linearity of the pressure profile along the length of the slit-die. Both aspects are fulfilled in our experiments.

As the aspect ratio, W/h, of the rectangular channel of the slit-die was bigger than 10, no edge effects were expected to affect the shear stress values [34]. Even so, assuming Newtonian behaviour of the melt as indicated by the proximity of n values to 1, the Rabinowitsch-Weissenberg correction was applied in this work by equation (4). In all our measurements, the difference compared to viscosity values obtained without accounting for edge effects (equation (1)) was always below 1 %, except for the experiments conducted with N₂ as PFA, where the difference was lower than 4 %.

$$\dot{\gamma} = \dot{\gamma}_{app} \left(\frac{2}{3} + \frac{1}{3}n \right) \quad (4)$$

where n refers to the power law index:

$$n = \frac{\delta \log (\dot{\gamma}_{app})}{\delta \log (\tau)} \quad (5)$$

195 In the case of *In-line* rheological measurements, the application of equation
(4) is limited to the knowledge of n , which requires several experiments at
different shear rates and shear stresses in order to obtain enough data whose
representation allow calculating n . In the cases where this approach is not
possible due to technical limitations, Schümmer and co-workers [36] proposed an
200 approximate procedure to determine the viscosity curve without differentiating
the data. In their approach, they estimated the shear rate and viscosity at a
vertical distance, where the apparent shear rate equals the true shear rate. At
that point, the shear rate and shear stress can be calculated multiplying each
of them by x^* , which in the case of a flow in a rectangular slit-die takes the
205 following value [37, 38]:

$$x^* = \left(\frac{3n+1}{4n} \right)^{n/(n-1)} \approx 0.79 \quad (6)$$

Therefore, depending on the accessibility to the power law index, n , the true
viscosity can be obtained from equation (7) if n is known, or from equation (8)
otherwise:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (7)$$

$$\eta = \frac{\tau}{x^* \dot{\gamma}_{app}} \quad (8)$$

In the latter case, the true viscosity obtained is valid for a true shear stress
210 $\tau_t = x^* \tau$ and not for the wall shear stress τ [39].

3. Results and Discussion

Considering the plasticization effect that PFAs have on polymeric materials,
it is expected that the addition of CO₂ or N₂ to the melt-extrusion process
of PLA will lead to a depression of the polymer viscosity that provides a bet-
215 ter processability and a potential temperature reduction. In this study, above
additives were applied to examine the design and limits of operation of a custom-

made *In-line* rheological slit-die. In particular, the effectiveness of the PFAs in comparison to the use of commercial bio-based plasticizers such as ATBC was discussed.

220 3.1. Demonstration of operational limits

Due to the configuration of a melt-extrusion processing line, there are certain considerations that should be taken into account prior to plan the experiments. While *In-line* rheological measurements over a wide range of shear rates are desired, the maximum and minimum shear rate values that are actually attainable
225 depend on the design pressure of the slit-die (P_d). In fact, processing pressures in the slit-die (P_1) below P_d must be assured to guarantee safety concerns.

The processing pressure depends on the volumetric flow rate of the polymeric material, which, in first approximation, is correlated to the rotating speed of the gear pump, and to the processing temperature and specific type of polymer. Actually, to determine the operational limits of the shear rate at different
230 processing temperatures, experiments using different volumetric flow rates of the melt can be conducted to measure the evolution of P_1 . Here, a set of experiments using semicrystalline PLA at three different operating temperatures, namely 185 °C, 195 °C and 205 °C, was carried out to determine the maximum
235 rotating speed of the gear pump, and hence the maximum Q_v of PLA, to assure pressures lower than the P_d of the slit-die, i.e. 34 MPa. Figure 3a shows the evolution of P_1 for different rotating speeds. Pressure followed a linear trend with pump speed independent of temperature. At higher temperatures, however, a divergence of the linear behavior was slightly visible. This might be
240 associated to a shear-thinning behaviour of the polymer, which led to a drop of P_1 in the slit-die, even at high volumetric flows of the melt. According to the design pressure, the dashed area in Figure 3a represents the limit of operation, establishing the maximum rotating speed at each temperature, and thus, the maximum volumetric flow rate of the melt. Figure 3b shows the empirical correlation which associates the rotating speed with the actual shear rate calculated
245 from equation (4): $\dot{\gamma} = 3.33 \times RotatingSpeed$. This correlation provided a sim-

plification for viscosity calculations, but more relevant, it displayed the range of shear rates that were achievable for semicrystalline PLA at each individual temperature. As a result, a proper experimental planning for subsequent rheological measurements of PLA/PFA mixtures could be successfully accomplished as will be discussed in the next section.

3.2. Rheological behaviour of PLA/PFA mixtures

The addition of PFAs into polymer melts usually causes an increase of the free volume of the polymer, resulting therefore in a considerable reduction of its viscosity. Traditionally, CO₂ has been widely employed in extrusion foaming processes, however, the use of other PFAs such as N₂ is not so frequently described in literature.

To determine the plasticization effect of both, CO₂ and N₂, on the processing of semicrystalline PLA, three different set of experiments were conducted. Initially, the viscosity flow curves of pure PLA at three different temperatures and shear rates ranging from 17 s⁻¹ to 150 s⁻¹ were determined from the *In-line* slit-die rheometer measurements, and they served as baseline for comparing the effect of the different PFAs. In the second and third set of experiments, the effect of different amounts of CO₂ or N₂ on the viscosity of PLA was investigated at selected shear rates, and the dependency of viscosity with temperature was determined.

The negative slope of the different curves obtained at each temperature (Figure 4a) manifested the drop of viscosity that PLA experienced in the presence of CO₂. All the data points followed approximately a linear trend in the range of selected concentrations that might be explained by the reduction of the glass transition temperature of PLA with increasing amounts of CO₂. Actually, as theoretically predicted by the Chow model [40], the addition of 1 wt% CO₂ to PLA produces a decrease of almost 10 °C in the glass transition temperature (T_g) of the polymer [41]. However, a small mismatch between the value predicted by the Chow model and the experimental measurements can be encountered. The viscosity flow curve obtained by adding 1.70 wt% CO₂ to PLA

at 185 °C (Figure 4b), was nearly comparable to that of the pure polymer at a processing temperature of 195 °C, i.e. 10 °C higher. Assuming that the viscosity reduction is only related to the depression of T_g , the effect of each percent of CO₂ is in this case equivalent to a decrease of T_g of approx. 6 °C, which is in agreement to previous experimental values reported by Reignier et al. [26]. In fact, considering this depression of T_g per percentage of CO₂, it seems that performing extrusion at higher concentrations of CO₂ would allow to overcome the limitation of processing at temperatures higher than the PLA melting temperature, T_m , i.e. 170 °C, and thus to prevent its thermal degradation. To check the validity of this hypothesis, two experiments at temperatures relatively close and below T_m , respectively 175 °C and 168 °C, were performed and the calculated viscosity values depicted in Figure 4a. In both cases, processing was feasible and PLA was continuously collected from the die. Moreover, when 3.1 wt% of CO₂ was added to the system, a reduction of approx. 19 °C was expected according to the drop of 6 °C/wt% CO₂ previously determined for T_g . This means that an equivalent viscosity to the one of pure PLA at 187 °C should be obtained from experimental measurements. In fact, the obtained viscosity value fulfilled this hypothesis.

To evaluate the relationship between viscosity and temperature, the Arrhenius model was employed as the experimental temperature was always higher than 100 °C + T_g^{PLA} :

$$\eta(T) = A \cdot \exp\left(\frac{E}{RT}\right) \quad (9)$$

where η is the zero shear viscosity (calculated for example with Carreau-Yasuda at each temperature) and E is the flow activation energy. The higher E , the more temperature sensitive is the melt. Accordingly, by calculating the flow activation energy using equation (9), a comparison between the sensitivity of PLA to temperature, with and without CO₂, was derived.

In the range of temperatures from 185 °C to 205 °C, the flow activation energy of pure PLA was calculated as 93.1 kJ/mol, which is rather similar to the one reported by Gu et al. [42], i.e. 113.02 kJ/mol, and whose deviation

might be attributed to the different grade of PLA employed in both studies. Actually, Gendron and Mihai [28] found E values ranging from 70.9 kJ/mol to 84.6 kJ/mol as a function of the different viscosities and D-contents of the PLA investigated in their work, corroborating that different grades of PLA are subjected to close but different flow activation energies.

When using CO₂ as PFA, the flow activation energies of different PLA/CO₂ mixtures showed decreasing values for increasing amounts of PFA, namely 84.3, 83.6 and 77.2 kJ/mol for CO₂ concentrations of 0.85 wt%, 1.70 wt% and 2.65 wt%, respectively, with the correlation coefficient (R^2) being always higher than 0.99. These lower values of E indicated that PLA flowed easier when CO₂ was added to the system, probably due to the increase of the free volume that the addition of the PFA produced in the polymer. Besides, the lower temperature dependency of the viscosities of PLA/CO₂ mixtures allowed selection of a lower processing temperature that could potentially lead to less polymer degradation.

As mentioned before, the effect of N₂ as PFA is scarcely described in literature. Therefore, several experiments on the lines of the ones conducted with CO₂ were performed to evaluate the effect of N₂ on PLA's viscosity. Figure 5 shows the shear viscosity values obtained from equation (4). Similar to the addition of CO₂, adding N₂ to PLA induced a drop in viscosity associated to the plasticization effect of the pressurized fluid, which was theoretically estimated from the Chow model as a drop in T_g of 11 °C per percentage of N₂, i.e. 5 °C more than when using CO₂. Contrary to the quasi linear trend observed for PLA/CO₂ mixtures in Figure 5, increasing amounts of N₂ (filled symbols) did not lead to higher reductions of the shear viscosity, but to a horizontal asymptote, which at high N₂ concentrations exhibited higher viscosities than those obtained for the same amount of CO₂.

This different behaviour of the two pressurized fluids can be explained by their solubility in PLA. Actually, according to the results reported by Li et al. [43] and Mahmood et al. [44], the solubility of CO₂ in the polymer is approx. 10 times higher than that of N₂, at pressures and temperatures investigated in this work. Allocating the position of our experimental runs (cross markers)

in the same figure where the solubility of PFA is reported as a function of
 335 pressure (see Fig. 6), it is clear that whereas the amount of CO₂ added to our
 system was always below the solubility line for PLA/CO₂ mixtures, indicative of
 one single-phase mixture, only 3 experimental runs fall within this single-phase
 region in PLA/N₂ mixtures (open symbols in Figure 5). In fact, those three
 experiments corresponded to the lower N₂ concentrations evaluated, namely 0.37
 340 wt%, 0.44 wt% and 0.59 wt%. Higher amounts of N₂ led to two-phase mixtures,
 explaining the discontinuous and inhomogeneous polymeric flow we experienced
 when collecting the final extrudate at the die exit. This demonstrates that the
 asymptotic value of viscosity observed in Figure 5 is related to the maximum
 solubility of N₂ in PLA and cannot be further compelled to concentrations
 345 higher than those reported by the solubility line.

In summary, when both PFAs allowed the assurance of one single-phase
 mixture, the plasticization effect of N₂ was higher than that of CO₂, as it has
 been theoretically predicted and experimentally corroborated.

3.3. Applicability of PFAs to assist melt-extrusion

350 Conventionally, solid or liquid plasticizers have been used to assist the melt-
 extrusion process of thermoplastics. As such, the bio-based commercial ATBC
 has been widely investigated and employed as a plasticizer for PLA processing.
 Actually, reductions in the range between 1.6 °C and 3.4 °C of the glass tran-
 sition temperature of PLA have been reported for a variety of percentages of
 355 ATBC [22, 23]. Accordingly, to establish the competitiveness of PFAs as plas-
 ticizers, a direct comparison to PLA/ATBC mixtures applied in melt-extrusion
 has been experimentally investigated.

Figure 7a shows the evolution of our experimental viscosity values from
In-line measurements of PLA/ATBC mixtures containing different amounts of
 360 ATBC. Similar to PLA/PFA mixtures, the addition of increasing amounts of the
 bio-based plasticizer led to a drop in viscosity that follows a quasi-linear trend
 in function of temperature, and whose slope is significantly lower than that
 obtained for CO₂ (Figure 4a). Indeed, considering the flow curves obtained

using 1.70 wt% of ATBC (Figure 7b), the reduction in viscosity values was
 365 much lower than that obtained using CO₂, where the effect of the addition
 of the same amount of pressurized fluid was comparable to an increase of the
 processing temperature of pure PLA of 10 °C.

Considering the viscosity reduction, $\eta_{(PLA)} - \eta_{(PLA/plasticizer)}$, derived from
 the addition of PFAs and ATBC at concentrations of 0.80 and 1.70 wt%, Figure 8
 370 shows that the increase in temperature minimized the effect that all plasticizers
 have on viscosity. This observation might be explained by the effect that on
 increasing temperature, not only more energy is supplied to PLA chains, but
 also the thermal expansion of the polymer increases its free volume. As a result,
 the global contribution of the plasticizer to the expansion of the free volume is
 375 downsized, contrary to what happens at low temperatures where it represents
 the main source of viscosity reduction.

Analysing the plasticizing effect of all additives individually, ATBC was the
 one generating the lowest viscosity reduction, manifesting a moderate plasti-
 cization effect compared to pressurized fluid additives and corroborating the
 380 advantage of using PFAs for melt-extrusion processing due to an enhanced pro-
 cessability. Within PFAs, both CO₂ and N₂, seemed to be quite promising
 accounting for the significant reductions of viscosity attained. Whereas lower
 amounts of N₂ were required for the same effects relative to CO₂ at 0.80 wt%,
 what could lower production costs, CO₂ widened the range of operating condi-
 385 tions for melt-extrusion processing (see Fig. 6), as well as the accessibility of
 viscosity reduction (Figure 8b). Even so, the employment of CO₂ or N₂, not only
 reduced viscosity and allowed a better processability, but also led to additive
 free foamed products whose porosity and pore size depended on the operating
 conditions and amount of PFA added to the system. For example, the optical
 390 micrographs of the PLA extrudates obtained from runs at similar conditions
 (approx. 23 MPa and 185 °C) using 0.44 wt% of N₂ and 0.79 wt% of CO₂ can
 be seen in Figure 9. As mentioned before, the solubility of CO₂ in PLA is almost
 10 times higher than that of N₂. Accordingly, much higher supersaturations are
 expected for PLA/N₂ mixtures than for PLA/CO₂, allowing us to theorize that

at similar interfacial tensions in both mixtures, the nucleation rate, as defined by the classical nucleation theory [7], is higher for PLA/N₂ mixtures; hence the addition of N₂ produces more porous extrudates compared to using CO₂, as can be seen in Figure 9.

4. Conclusions

An *In-line rheological* slit-die has been custom-designed and successfully employed in this work to characterize the rheological behaviour of polymer melts during conventional and assisted melt-extrusion processes. Pure PLA, and mixtures of PLA containing CO₂, N₂, or ATBC, have been melt-extruded and measured at different temperatures and concentrations, and their resulting viscosity values have been compared to establish the applicability and extent of the plasticizers considered.

The results showed that pressurized fluids were more effective in terms of viscosity reduction than conventional plasticizers like ATBC. In fact, the addition of only 1.70 wt% of CO₂ to PLA was, in terms of viscosity reduction, equivalent to an increase of the processing temperature of pure PLA of 10 °C, or in other words, it would be feasible to decrease the processing temperature of PLA by 10 °C if 1.70 wt% of CO₂ is incorporated into the polymer. Although the viscosity values obtained by the addition of N₂ could compete against those obtained using CO₂, the processing window at which this improvement in processability occurs was rather small. Actually, the solubility of N₂ in PLA is almost 10 times lower than that of CO₂; accordingly, only at low temperatures and low additive concentrations, N₂ can be considered as an alternative to CO₂ in order to promote further plasticization without ending in inhomogeneous melts. Still, the final extrudate presented higher porosity in case of N₂, as a result of the larger supersaturation taking place while depressurization at the die exit.

The selection of the best additive and its concentration will depend on the expected final properties of the extrudates and the requirements of the process itself. This work has proven the efficacy of pressurized fluid additives, in

particular of CO₂ and N₂, to be used as plasticizers for PLA, which has been
corroborated not only by the lower viscosity values measured *In-line*, but also by
the values of the calculated flow activation energy, *E*. It is important to mention
that when choosing a plasticizer, not only performance has to be accounted for,
but the remaining presence of the additive in the final product should be as well
considered. While CO₂ and N₂ lead to additive-free porous extrudates, where
porosity can be tuned as function of the additive concentration and operating
conditions, ATBC remains in the final product and could drive into migration
problems if special requirements or temperatures above 100 °C are required for
the final polymeric material.

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Table 1. Dimensions of the slit-die and nozzle employed in this work for
520 the rheological measurements.

Table 2. Scaling parameters for Sánchez-Lacombe equation of state (SL-EOS).

Table 1: Dimensions of the slit-die and nozzle employed in this work for the rheological measurements.

Dimension (mm)	Slit-die	Nozzle
Length	65*	38
Width	17	-
Height	1.5	-
Diameter	-	2

*This dimension refers to the length between P1 and P3.

Table 2: Scaling parameters for Sánchez-Lacombe equation of state (SL-EOS).

Compound	P* (MPa)	V* (cm ³ /g)	T* (K)	Reference
PLA	560.2	0.7419	592.2	Mahmood et al.[44]
CO ₂	720.3	0.6329	208.9 + 0.459T - 7.56·10 ⁻⁴ T ²	Mahmood et al.[44]
N ₂	103.6	1.2447	159.0	Li et al.[43]

*As an approximation, the SL interaction parameters k_{12} for the systems PLA/CO₂ and PLA/N₂ are taken from Mahmood et al. and Li et al., respectively.

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525 Schematic overview of the set-up employed in this work for performing *In-line* rheological measurements.

Figure 2:

Schematic diagram of the design of the *In-line* rheological slit-die employed in this work. For further details on dimensions, refer to Table 1.

Figure 3:

530 Establishing operational limits: (a) evolution of processing pressure in the slit-die (P1) in function of the rotating speed of the gear pump; (b) evolution of shear rate (equation (4)) in function of rotating speed. From top to bottom: 185 °C, 195 °C, 205 °C, and overlapping of all experimental curves for obtaining the empirical correlation in the selected range of temperatures.

Figure 4:

540 Evolution of shear viscosity of (a) PLA/CO₂ mixture as a function of CO₂ concentration at different operating temperatures at a constant shear rate of 50 s⁻¹; and (b) of pure PLA and PLA containing 1.70 wt% of CO₂ (◇) as a function of shear rate. Viscosity values were calculated from *In-line* rheological measurements applying equation (4).

Figure 5:

545 Evolution of shear viscosity of PLA/PFA mixtures as a function of PFA concentration at different operating temperatures at a constant shear rate of (a) 16 s⁻¹, and (b) 50 s⁻¹. Open symbols represent one single-phase mixture, while filled symbols account for two-phase mixtures.

Figure 6:

550 Position of our experimental runs (cross markers) within the established solubility curve of (a) CO₂ in PLA 3001D; and (b) N₂ in PLA 3001D, as reported by Li et al.[43] [a] and Mahmood et al.[44] [b]. The dashed area represents the conditions at which one single-phase mixture is achievable.

Figure 7:

Evolution of (a) shear viscosity of PLA/ATBC mixture as a function of ATBC concentration at different operating temperatures at a constant shear rate of 50 s⁻¹; and (b) shear viscosity of pure PLA and PLA/ATBC mixtures (1.70 wt%) as a function of shear rate. Viscosity values were calculated from *In-line* rheological measurements applying equation (4).

Figure 8:

Comparison of the viscosity reduction experienced by PLA/plasticizer mixtures at different processing temperatures using (a) 0.80 wt% of plasticizer in the mixture, and (b) 1.70 wt% of plasticizer in the mixture. Viscosity values were calculated applying equation (4) from *In-line* rheological measurements performed at 50 s⁻¹. * refers to a concentration of 0.44 wt% N₂ and ** to 0.59 wt% N₂.

Figure 9:

Optical micrographs of the extrudates collected from pressurized-assisted melt-extrusion trials using: (a) - (b) 0.79 wt% of CO₂; and (c) - (d) 0.44 wt% of N₂. Notice that (a) and (c) shows the transversal cut of the extrudate, and (b) and (d) the lateral morphology. Scale bars account for 500 μm.

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Highlights

- PLA viscosity during assisted melt-extrusion processing was successfully evaluated.
- PFAs are more effective to plasticize PLA than conventional bio-based ATBC.
- Addition of 1.7 wt% CO₂ allows reducing 10°C the processing temperature.
- N₂ produces the highest plasticization effect, but the processing window is narrow.
- PFAs produce additive-free porous extrudates, while processing at lower temperatures.