A melt flow index-based approach for the viscosity curves determination

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Abstract. To optimize the polymers processing technologies, a rheological characterization of the polymer is essential to predict its behavior at specific temperatures and under varying shear rates. Simulating this process requires providing the simulation software with viscosity curves for the polymer to be processed, ensuring a reliable simulation. However, traditional rheological characterization utilizing a capillary rheometer is known for its high cost, time-intensive nature, and the need for skilled operators. In this study, a more cost-effective approach is proposed, using the Melt Flow Indexer (MFI) to obtain the experimental viscosity curves. These undergo an innovative numerical procedure based on simulating the MFI tests, reducing the numerical-experimental error in terms of pressure applied to the molten polymer. This methodology is applied to characterize three different thermoplastic polymers: polypropylene, 30% glass-reinforced polypropylene and 30% glass-reinforced polyamide. The viscosity curves obtained through this methodology are then compared to those obtained using the capillary rheometer, serving as a reference to assess the accuracy of the proposed approach.

Introduction

Polymeric melts are complex fluids marked by a particular rheological behavior, divided into three zones depending on the temperature and the applied rate of deformation. For a given temperature, the first regime, called the first Newtonian plateau, is obtained with low shear rates and characterized by viscosity that asymptotically approaches a constant value known as zero-shear viscosity. Instead, in the second regime with intermediate shear rates, called pseudoplastic, the viscosity decreases as the shear rate increases, following the shear thinning behavior, described by the power law. Whereas in the third regime, at high shear rates, viscosity asymptotically approaches a constant value known as the limiting viscosity and called the second Newtonian plateau [1].

Since different polymers' processing technologies happen on different shear rates, understanding and characterizing the polymers' rheological behavior is crucial in optimizing processing conditions and evaluating the applicability of a material to a given technology [2]. The flow within the extrusion head during the polymer extrusion process or inside the feed system tubes in an injection molding process can be analyzed using the Hagen-Poiseuille flow model [3].

This model describes laminar flow inside a cylindrical pipe or tube, making certain simplifying assumptions. These assumptions encompass the incompressibility of the fluid, an isothermal, stationary and laminar flow, and the restriction that the flow velocity is only in the direction of the flow, with the other velocity components being negligible. This flow model is also applicable within the die of a capillary rheometer, providing a means to assess the flow behavior of polymer melts under controlled conditions of temperature and velocity. A capillary rheometer consists of a heated barrel with a capillary connected at its bottom, featuring specific length and radius (Fig. 1 (a)). The polymer is loaded into the barrel, and after a period of preheating, a piston controlled at a constant velocity pushes the polymer melt, causing it to be extruded through the capillary die. Hypothesizing the polymer melt to be a Newtonian fluid, the shear rate and the shear stress are therefore approximated using the following equations [4]:

$$\dot{\gamma}_a = \frac{4.Q}{\pi R_n^3}. \tag{1}$$

$$\tau_a = \frac{R_n.P}{2L}. \tag{2}$$

where Q represents the polymer flow rate in $cm^3.s^{-1}$, which is an input data to be configured during the test using the capillary rheometer, Specifically, it is determined by controlling the velocity applied to the piston during the test. R_n and L refer to the radius and length of the capillary die in cm, respectively. P denotes the pressure at the entrance of the capillary die measured using a sensor positioned at the capillary entrance.

The pressure profile inside the capillary die exhibits a curvature due to the so called end effects. Therefore, the calculated shear stress τ_a using eq. 2, has to be corrected to obtain the shear stress at the wall τ_w using the Bagley correction [5]. To carry out this correction, at least two capillaries with the same radius and different length are needed.
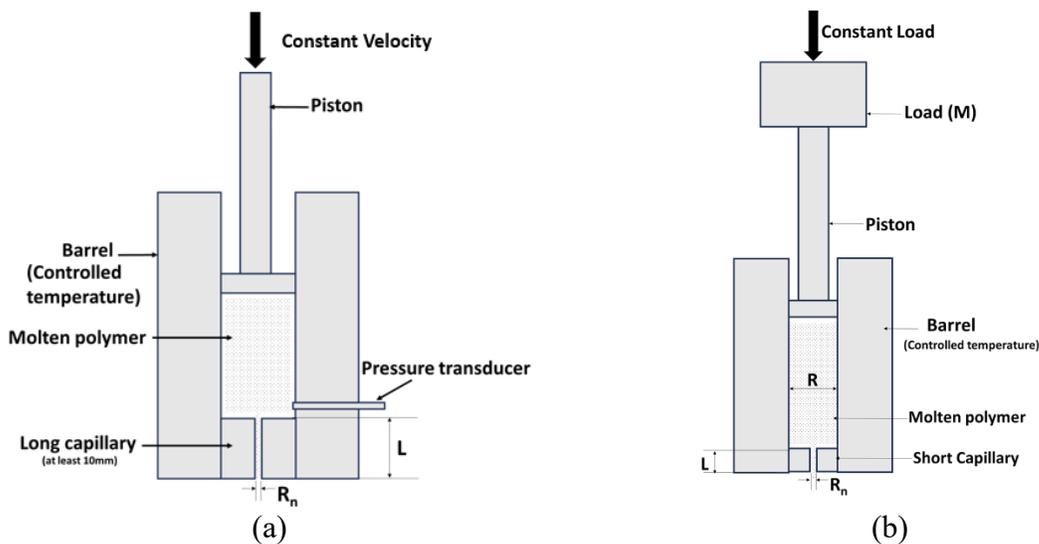
Fig. 1 Typical configuration of (a) the capillary rheometer (b) the Melt Flow Indexer

On the other hand, the apparent shear rate calculated with eq. 1 also requires correction. This equation is only valid for Newtonian fluids. For pseudoplastic fluids, a correction method proposed by Rabinowitch [3] is employed to calculate the shear rate at the wall, γ_w.

Another method employed to assess the characteristics of a polymer melt involves using the Melt Flow Indexer, sometimes referred to as the extrusion plastometer. As seen in Fig. 1 (b), also this instrument consists of a heated barrel with a capillary connected at its bottom, featuring

specific dimensions (2.095 mm diameter and 8 mm length). The polymer, preheated to the targeted temperature, is introduced into the barrel bore and subsequently extruded through the capillary die thanks to the piston actuated by the dead loads positioned at its top. This device is typically employed to determine both the Melt Flow Index (MFI) and the Melt Volume Flow-rate (MVR) of a specific polymer, operating under predefined conditions of temperature and a constant applied load. The MFI along with the MVR serves as an indicator of the polymer's fluidity, precisely quantifying the weight (or the volume, in the case of the MVR) of the extruded polymer in a span of 10 minutes [6].

While in the capillary rheometer the polymer flow rate is controlled (constant velocity applied to the piston during the test) and the pressure applied to the polymer is assessed, in the Melt Flow Indexer, thanks to the dead load applied upon the piston, the pressure applied to the molten polymer is controlled while the polymer flow rate is measured. Another difference lies in the fact that the capillary rheometer comes with at least two capillaries of the same diameter and two different lengths, so that the Bagley correction can be performed, whereas the Melt Flow Indexer comes with only one capillary of standardized dimensions. Notably, the Melt Flow Indexer stands out as an economical machine. Hence, there is a compelling opportunity to utilize it instead of the capillary rheometer for acquiring polymer viscosity curves. This work aims to introduce an innovative and cost-effective experimental-numerical approach for plastic processors to obtain viscosity curves using the Melt Flow Indexer, thereby presenting a viable alternative to the capillary rheometer.

Materials and Methods
In the present work, three diverse polymers were investigated: polypropylene (PP), 30% glass-reinforced polypropylene (PPGF30) and 30% glass-reinforced polyamide (PA6GF30). The standard operating temperature ranges for the examined materials are as follows: 190 °C, 260 °C for PP, 190 °C, 260 °C for PPGF30, and 240 °C, 280 °C for PA6GF30. All the three materials were analyzed at three different temperatures, carefully selected from their respective operating ranges. In particular, the PP and the PPGF30 were analyzed at 200 °C, 230 °C and 250 °C. Whereas the PA6GF30 was analyzed at 245 °C, 260 °C and 275 °C. Since the 30% glass reinforced polyamide is an hygroscopic polymer, it was dried for 6 hours at a temperature of 80 °C before its rheological characterization. Regarding the MFI tests, they were performed using a Melt Flow Indexer called the XNR-400C model. For each temperature setting, four different load conditions were selected: 2.16 Kg, 5 Kg, 10 Kg, and 16.965 Kg for PP; 1.2 Kg, 5 Kg, 16.6 Kg, and 27.432 Kg for PPGF30; and 2.16 Kg, 5 Kg, 10 Kg, and 20.125 Kg for PA6GF30. Consequently, twelve MFI tests were conducted, and each configuration was replicated at least three times to mitigate potential operator-induced errors. As explained in the introduction section, the Melt Flow Indexer could be seen as a simplified capillary rheometer where, instead of controlling the piston velocity, this is actuated through a dead load positioned at its top. At this point, it is possible to use eq. 1 and eq. 2 to calculate the shear rate and shear stress of the polymer in a given MFI test, and in this case L, R_n, P and Q are the MFI capillary length ($L = 8$ mm) and diameter ($R_n = 1.04775$ mm) the pressure applied to the molten polymer during the MFI test and the flow rate measured during the MFI test, respectively. The Melt Flow Indexer is commonly equipped with an encoder that allows for the measurement of the piston displacement during a specified test, enabling the determination of the extruded polymer volume. In each test, the time t necessary for the piston to undergo a 30 mm displacement is recorded. The associated volume for that 30mm length, denoted as *V=2.149 cm³*, along with the measured time, is subsequently utilized to calculate the flow rate by the following equation:

$$Q = \frac{V}{t}. \tag{3}$$

Whereas for the pressure P calculation, knowing the total load positioned upon the piston, together with the mass of the piston, the pressure could be measured using the following equation:

$$P = \frac{Mg}{\pi R_p^2}.$$ (4)

where M is the weight applied during the test, g is the gravity acceleration ($g = 9.80655$ N.kg^{-1}) and R_p is the piston radius ($R_p = 4.7371$ mm). Therefore, for each of the investigated polymers, for each temperature T and for each MFI test, the pressure applied to the molten polymer is fixed (due to the application of a constant load M upon the piston) and the melt volume flow rate is calculated in cm^3/s. The results of all the performed MFI tests are summarized in Table 1.

Table 1 Results of the Melt Flow Index tests for all the three investigated polymers

Polymer	Measured Flow Rate Q [cm^3/s]			
	T [°C] \ M [kg]	2.16	5	10	16.965
PP	200	0.008	0.034	0.154	0.557
	230	0.015	0.064	0.269	1.074
	250	0.023	0.101	0.38	1.978
PPGF30	T [°C] \ M [kg]	1.2	5	16.6	27.432
	200	0.001	0.012	0.126	0.402
	230	0.002	0.022	0.274	0.926
	250	0.004	0.031	0.398	1.287
PA6GF30	T [°C] \ M [kg]	2.16	5	10	20.125
	245	0.031	0.082	0.188	0.526
	260	0.047	0.125	0.264	0.929
	275	0.075	0.183	0.382	1.243

For each MFI test, subsequent to the calculation of the shear rate $\dot{\gamma}_a$ and shear stress τ_a by eq. 1 and eq. 2, respectively, the viscosity η_a can be determined using the following equation:

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a}$$ (5)

Consequently, each MFI test yields a single viscosity versus shear rate point. The viscosity versus shear rate data for each investigated polymer at all three temperatures were fitted using the Cross-WLF rheological model. This model, widely employed in plastic processing simulation software, is characterized by the following equation:

$$\eta = \frac{\eta_0}{1+\left(\frac{\eta_0 \cdot \dot{\gamma}}{\tau^*}\right)^{1-n}}$$ (6)

In this context, n represents the power law index and τ^* denotes the critical shear stress, The zero shear viscosity, denoted as η_0, is defined as follows:

$$\eta_0 = D_1 . e^{\frac{-A_1(T-T^*)}{A_2+(T-T^*)}}$$ (7)

where $T^* = D_2 + D_3.p$, $A_2 = A_3 + D_3.p$, T is the melt temperature, and p is the pressure. Generally, pressure's impact on viscosity is commonly disregarded in many cases. Consequently, in our current investigation, D_3 is assumed to be zero for simplicity. Consequently, the data fitted

coefficients considered in the present work to describe the Cross-WLF rheological model are: A_1, A_2, D_1, D_2, n and τ^*.

Given the simplifying assumptions seen in the introduction section and approximative formulas (equation 1 and equation 2) employed to generate viscosity points through the MFI instrument, it becomes necessary to apply corrections to the resulting experimental viscosity curves. One approach to rectify these curves is through the numerical simulation of the MFI test. On the left of Fig. 2, we have the setup of a typical MFI instrument: during an MFI test, the input is the applied load, i.e., the actual pressure applied during the test, and the output is the measured flow rate, which is used to obtain viscosity curves through the approximative formulations.
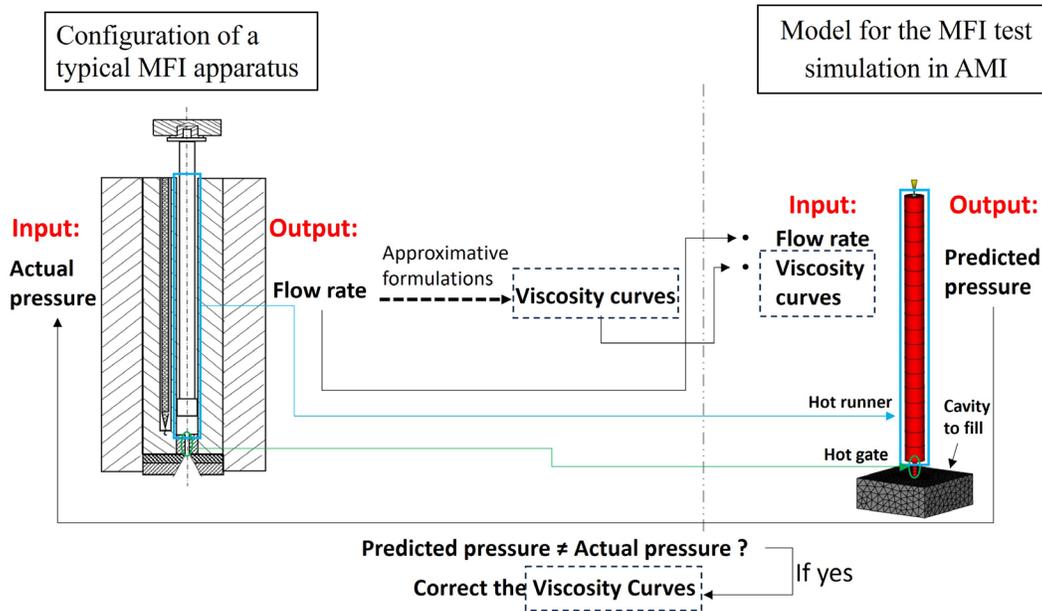
Fig. 2 Experimental-Numerical approach for the viscosity curves determination

On the right of Fig. 2 instead, the proposed model for simulating the MFI test in Autodesk Moldflow Insight (AMI) is presented. In this case, the input includes the flow rate Q measured experimentally during the test and the derived viscosity curves, while the output provides the simulated value of the pressure applied to the polymer during the MFI test. The objective is to compare the simulated pressure to the actual pressure. If these pressures match, then the viscosity curves used in the simulation are deemed accurate; otherwise, corrections to the input viscosity curves need to be applied.

As evident from Fig. 2, in order to simulate the MFI test, which involves extrusion into space, a large rectangle was utilized as the cavity to be filled in the model. Since both the cylinder and the capillary are heated to the temperature of the MFI test, they were modeled as a hot runner and a hot gate, respectively, with the same dimensions. Process parameters included setting the MFI test temperature as both the melt and mold temperatures. Meanwhile, the flow rate Q measured during the actual MFI test serves as a process control parameter in the simulation.

The concept behind calibration is as follows: starting from the experimental viscosity curves obtained with the MFI, the goal is to find the actual viscosity curves that, for each MFI test, minimize the error between the actual pressure applied by the load to the molten polymer and the numerical pressure predicted by AMI. Therefore, we are dealing with an optimization problem where the design variables are the viscosity curves, i.e., the set of parameters of the Cross-WLF model that describe them. The objective functions are the numerical-experimental errors of the pressure applied to the polymer during the MFI tests. Therefore, for three different temperatures

and four different loads, we would have twelve objective functions to minimize. However, to simplify the optimization problem and avoid twelve objective functions, the average of these errors was considered as a single objective function:

$$\frac{1}{12} * \sum_{k=1}^{12} 100 * \frac{\left|P_{actual}^{k} - P_{predicted}^{k}\right|}{P_{actual}^{k}} \tag{8}$$

The iterative procedure for resolving the optimization problem was executed using the modeFRONTIER software. The original Non-dominated Sorting Genetic Algorithm II (NSGA II) was chosen as the optimization algorithm, encompassing 15 generations and an initial Design of Experiments (DOE) with 10 configurations (equivalent to 150 iterations). For each iteration, modeFRONTIER employs that algorithm to propose a new set of Cross-WLF parameters (design variables) and assign them to the input variables. In modeFRONTIER software, a script was written in Visual Basic Scripting language where all the necessary commands were implemented:

- Opening of Moldflow project, containing simulations for the 12 MFI tests.
- Configuring the new set of design variables for all 12 simulations.
- Running all the 12 simulations
- Retrieving the values of injection pressure for all the 12 simulations and assigning them to output variables in modeFRONTIER.

Subsequently, the objective function is computed using eq. 8. At the end of the optimization procedure (150 iterations), the set of parameters yielding the minimum value of the objective function is identified. This specific set of parameters corresponds to the viscosity curves found using the proposed method proposed in the present paper. To validate the accuracy of the proposed method, a comparison was imperative between the acquired viscosity curves and those obtained using the conventional approach: a capillary rheometer. Subsequently, the viscosity curves of the examined polymers were determined utilizing the Ceast Rheologic 2500 capillary rheometer. Each test involved varying the shear rate within the range of $50\ s^{-1}$ to $2000\ s^{-1}$, employing specific values of $50\ s^{-1}$, $100\ s^{-1}$, $200\ s^{-1}$, $500\ s^{-1}$, $1000\ s^{-1}$, $2000\ s^{-1}$. Throughout these tests, the shear rate was imposed on the polymer through the controlled piston velocity. Additionally, a pressure sensor positioned at the capillary entrance providing real-time pressure values of the polymer. Subsequently, eq. 1 and eq. 2 were used to calculate the shear rate and the shear stress, respectively. In order to perform the Bagley correction, the tests were performed using two capillaries with identical diameter (1 mm) but different lengths (10 mm and 20 mm). To enhance precision and minimize potential operator-induced errors, each test was replicated at least three times. After performing the Bagley correction also the Rabinowitch one was applied to obtain accurate results.

Results and discussion

Fig. 3, Fig. 4 and Fig. 5 show the viscosity curves at three different temperatures of the PP, PPGF30 and PA6GF30, respectively. For all the three investigated polymers, the dashed lines represent the curves obtained by fitting the experimental viscosity points directly obtained with the MFI (before applying the optimization procedure). On the other hand, the solid lines represent the viscosity curves obtained at the end of the optimization procedure. Using the proposed procedure, the objective function were reduced from 95% to 6.4% for the PP, from 120% to 10% for the PPGF30 and from 49% to 8% for the PA6GF30. Upon analysis of the figures for all investigated polymers, it is evident that the experimentally obtained viscosity curves using the MFI apparatus initially exhibit high viscosity values. Subsequently, through the application of the numerical optimization procedure, the curves are not only shifted downward but also show an increased inclination of the pseudoplastic segment.
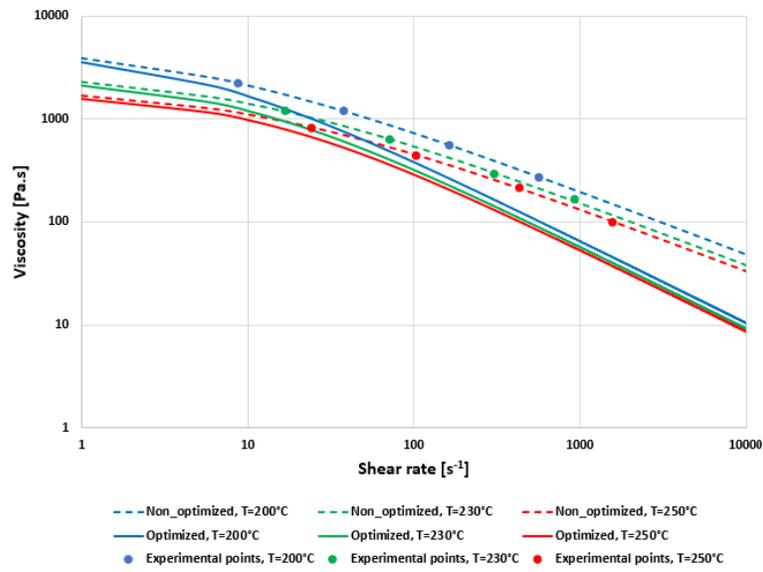
Fig. 3 Viscosity curves obtained at the end of the optimization procedure superimposed to those of the first iteration of the procedure for the Polypropylene (PP)
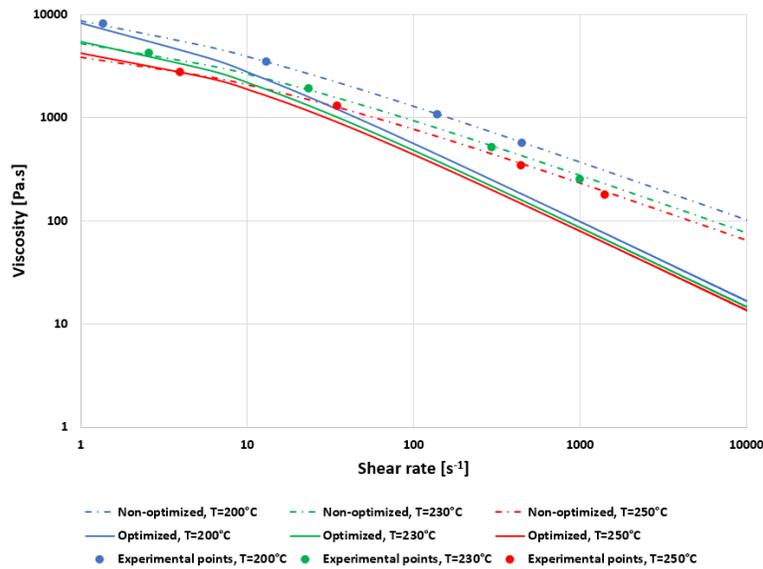
Fig. 4 Viscosity curves obtained at the end of the optimization procedure superimposed to those of the first iteration of the procedure for the 30% glass reinforced polypropylene
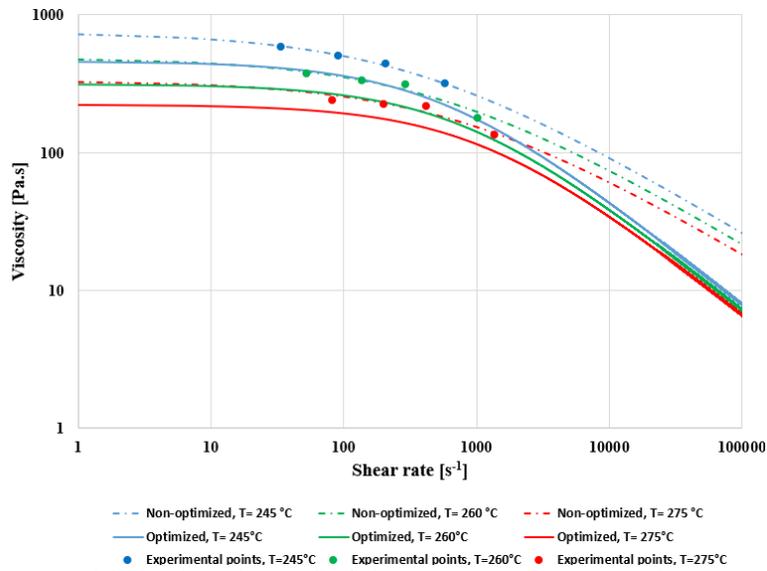
Fig. 5 Viscosity curves obtained at the end of the optimization procedure superimposed to those of the first iteration of the procedure for the 30% glass reinforced polyamide

Fig. 6, Fig. 7 and Fig. 8 depict viscosity curves at three different temperatures for PP, PPGF30, and PA6GF30, respectively. In all three investigated polymers, dashed lines represent curves obtained using the proposed methodology based on MFI, while solid lines represent actual viscosity curves obtained through the conventional capillary rheometer methodology. The figures clearly illustrate a good match between curves obtained by the two methodologies, particularly in the shear rate interval between $50 \ s^{-1}$ and $5000 \ s^{-1}$, characteristic of the capillary rheometer. Notably, excellent matching is observed for PP and PPGF30, while a deviation between curves obtained with the two methodologies is noticeable for PA6GF30 in that interval. This disparity may be attributed to the hygroscopic nature of PA6GF30. It is plausible that this polymer absorbs more humidity, especially before the tests conducted at the capillary rheometer, due to the unavailability of a dryer in proximity to the capillary rheometer. To quantify the deviation and underscore the significance of the proposed numerical optimization procedure, we compared the error between the curves obtained by the capillary rheometer and the non-optimized curves derived experimentally through the MFI with the error between the curves obtained by the capillary rheometer and the optimized curves through the experimental-numerical procedure, for each material. The error was calculated by considering all viscosity points within the shear rate range of $50 \ s^{-1}$ to $5000 \ s^{-1}$, with an increment of $5 \ s^{-1}$. These errors were computed for each temperature, and then their averages were considered to streamline the comparisons. The results of the comparisons revealed that the error after the application of the optimization procedure was reduced by 89%, 97% and 74% for the PP, PPGF30 and PA6GF30, respectively, demonstrating the effectiveness of the proposed methodology in providing accurate viscosity curves.
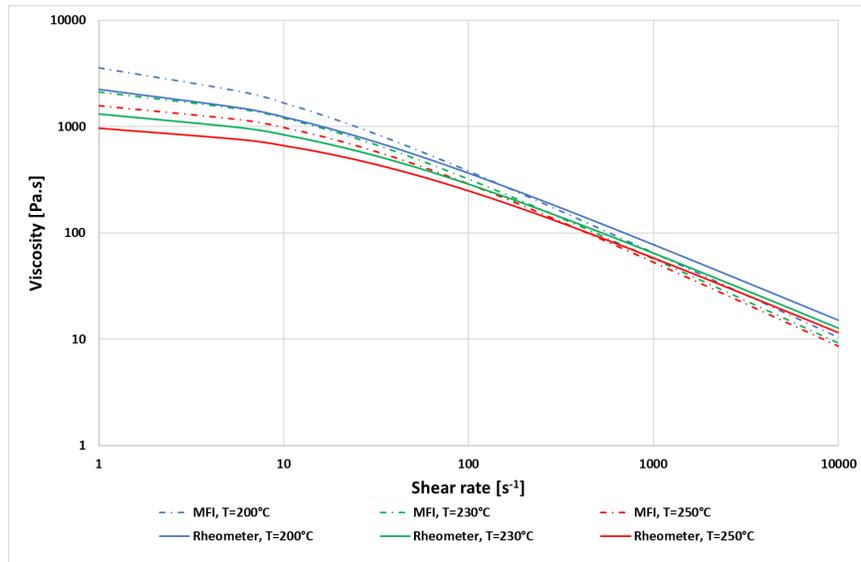
Fig. 6 Viscosity curves obtained at the end of the optimization procedure superimposed to those obtained by the capillary rheometer for the polypropylene
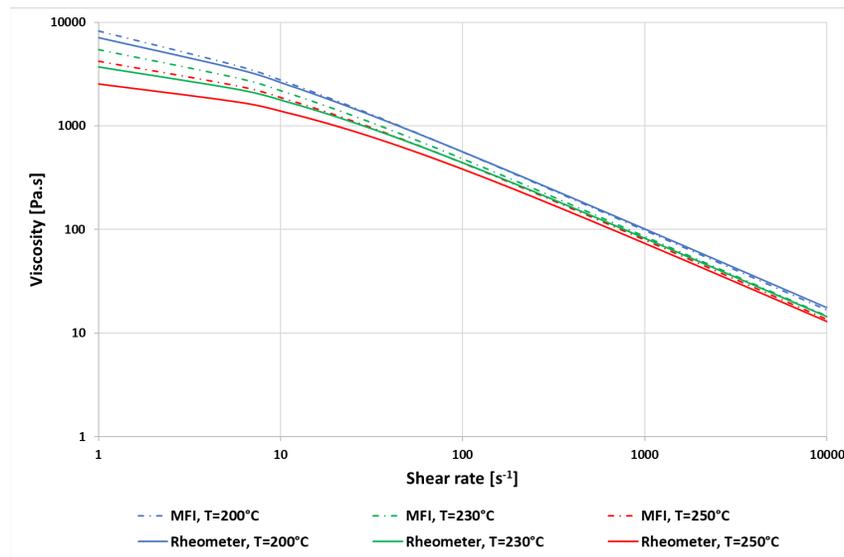
Fig. 7 Viscosity curves obtained at the end of the optimization procedure superimposed to those obtained by the capillary rheometer for the 30% glass reinforced polypropylene
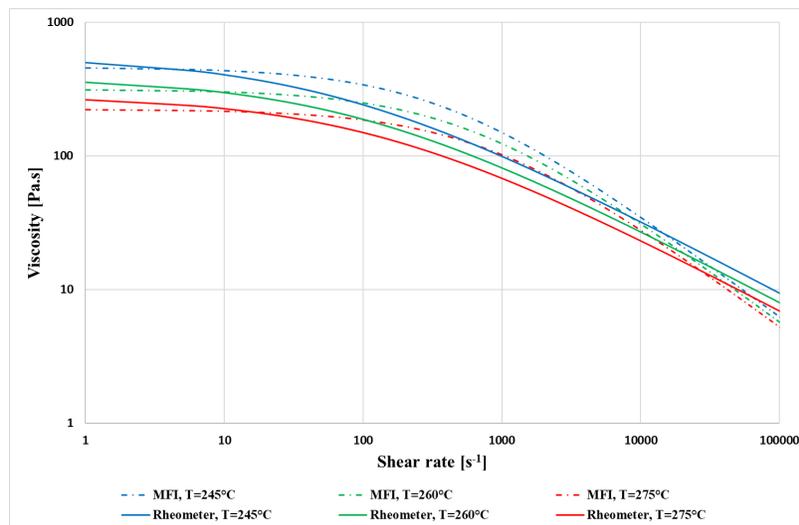
Fig. 8 Viscosity curves obtained at the end of the optimization procedure superimposed to those obtained by the capillary rheometer for the 30% glass reinforced polyamide

Summary

In the present work, an innovative procedure was proposed for performing the rheological characterization of polymers using the MFI apparatus. To correct the experimental rheological curves obtained directly from the MFI, this test was simulated in the injection molding software Moldflow Insight, integrating it with an optimization strategy to identify new rheological curves that minimize numerical-experimental errors in terms of pressure applied to the molten polymer during the MFI test. This identification method was implemented in the optimization platform modeFRONTIER. The proposed procedure permits to identify the Cross-WLF viscosity model parameters implemented in the majority of the plastic processing simulation software. Particularly, this method could be an efficient aid to plastic injection molding processors that can't afford neither a capillary rheometer nor a skilled operators in the rheological characterization field. The only needed instrument is an MFI apparatus which is known to cost ten times lower than a capillary rheometer. The proposed methodology was applied to polypropylene, 30% glass reinforced polypropylene and 30% glass reinforced polyamide. The obtained curves were compared to those acquired conventionally using the capillary rheometer, and favorable matches in viscosity curves were observed, showing errors of less than 18%, 5% and 40% for the PP, PPGF30 and PA6GF30, respectively.

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