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Recycling of thermoplastic materials: Development of a self-adaptive process to the recycled materials

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Abstract. Over the last few decades, thermoplastic polymers have become increasingly popular and widely used materials in our lives. However, these mass consumptions remain difficult to reuse. Although mechanical recycling is being seriously proposed as an alternative solution [1], until now many obstacles prevent its application to polymers. Undetermined initial properties and aging conditions of post-consumer waste, which are, in fact, extremely variable, result in an ignorance of the aged material rheological properties before their reprocessing. As a consequence, the adjustment of extrusion parameters becomes very difficult and can vary over time and between supply batches. In this context, the project RECYPLAST-DEMO was proposed aiming at developing a prototype able to characterize, in real-time [2], the rheological properties of extruded waste materials and self-adjust the operating parameters of the machine, with the help of artificial intelligence, to maintain products of required quality. Our work concerns inline rheological characterization of materials using an instrumented die numerically tested with the software POLYFLOW® for the viscosity range of a PP, designed and experimentally validated in a later step of the project. The goal is to obtain the rheological behavior of the material from pressure difference measurements along the length of the developed die and assess data compared to rheological characterization measurements performed in laboratory on virgin material and aged ones. This paper highlights the effect of the processing temperature and the residence time on the aging of the polymer. Moreover, the numerical work of the developed extrusion die is presented and explained.

Introduction

The global plastics market has experienced exponential growth over the past 70 years, due to the use of polymers across almost all sectors. Aware of its responsibilities toward solving climate and environmental-related problems, the European Union has been putting forward agreements [3] aiming to control end-of-life plastic products by means of imposing taxes, promoting eco-design and developing collection and recycling of plastic waste [4]. The purpose is to transform the linear "produce, consume, throw away" economy into a circular one, consisting of a "production, use, recycling" loop [5]. On the other side, plastic industry is undergoing major changes mainly in waste management to overcome economic challenges. It started with the reintegration of controlled amounts of post-industrial waste, also known as "clean" waste, into the process after demonstrating similar technical properties to virgin materials [6]. Although incineration maintains its originality as a solution for solid waste in general, mechanical recycling is a serious alternative solution to revalidate plastic waste following the rise in raw material prices. However, recycling of post-consumer products [1] remains difficult to put into action due to many obstacles preventing, until now, the processing of waste polymers, such as polypropylene (PP), which is the second most-widely produced plastic after polyethylene.

Extrusion is one of the best processes for continuous plastics production. When working with a raw material, a characterization step precedes the production phase to determine the processing parameters, for instance processing temperature and screw speed. Once known, they are set for long runs. However, in many cases, adjustments to process parameters have to be made for each batch of material, especially in plastics waste recycling as we encounter a major material heterogeneity problem. First of all, the presence of several polymers, in most cases immiscible with each other, results in incompatible phase mixtures in the molten state [7]. Moreover, additives are added to polymer blends without clearly specifying the composition [8], which could complicate the recycling process and result in products with poor properties. Second, the properties of the product, before consumption and after aging, can't be determined and are, in fact, extremely variable. This results in an ignorance of the waste material rheological properties before its reprocessing. At this level, recycling is viable but the adjustment of extrusion parameters becomes very difficult and can vary over time and between supply batches requiring well-trained operators in control of the process. This could explain why industrials do not favor the shift towards reincorporating large amounts of recycled materials into their processes. Further, the effect of processing temperature and residence time on the aged material should be studied as it becomes more significant for reprocessed material. In their article on the effect of multiple extrusion, Hermanova et al. [9] confirmed the drop of material molecular weight due to PP chains scission. Thus, in terms of melt viscosities, the deterioration of the non-stabilized polymer was reflected by an increase in the melt flow index (MFI). Another study showed a reduction in the particle size and particle size distribution of the dispersed rubbery phase during reprocessing [10]. The processing stability is primarily dependent on variables such as additive concentration, mainly stabilizers, temperature and the origin and composition of polymer. It can be quantitatively assessed by a processing degradation index (PDI) defined as the plot of MFI vs the number of extrusions [11], [12].

Given the complexity of the plastic production process and its effect on the quality of the final product, it is obviously important to monitor it in order to understand and analyze the material's behavior in real time. The instrumentation of the extrusion process could be designed to detect flow instabilities and heat transfer of the material in its molten state using ultrasonic techniques, spectroscopy, pressure sensors, etc. There are several methods for characterizing extruded material, from on-line characterization, where the measurement is carried out on a bypass channel deviation, to the inline measurement known for real-time characterization on the main flow channel. This latter is more reliable as it operates under real conditions. One of the key properties of molten polymers is viscosity as it provides information about the molecular structure of the polymer, the processability and the final product properties. Previous studies show successful pressure drop measurements along the extrusion die converted into viscosity. In their research, M. Padmanabhan et al. [13] developed a flat die of constant geometry that worked as an inline rheometer, measuring viscosity at different shear rates by varying the screw speed of the extruder. Later on, P.X. Li et al. [14] developed the previous model as they found that varying the screw speed did not maintain a constant flow and therefore influenced the pressure measurements. In their model, they proposed a system of valves to control the flow rate. Given the limitations of pressure range, researchers began to look for innovative die designs. In 2010, F. Robin et al. [15] introduced the concept of adjustable twin slit die consisting of two independently controlled parallel rectangular channels modified during the process to vary the shear rate in the measuring channel. With a lower level of complexity, a single-channel rheometer was introduced, a few years later, by M. Horvat et al. [16] based on the concept of a fixed outer geometry with insertion modules of different rectangular cross sections which allowed the measuring of the material

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rheological behavior. Moreover, the interest in conducting measurements on a deviated channel still exists. In 2020, J.A. Covas proposed a twin-slit die design [2] that divided the initial flow of material between 2 parallel channels. By controlling the flow rate in the measuring channel and using two pressure sensors, measures of melt viscosity were taken.

Inspired from previous works, and in response to the crucial situation regarding the environment, the project RECYPLAST-DEMO is funded by the Pays de La Loire region and aims to set up, by 2025, a device able to self-adapt a production line according to the variability of the input plastic waste materials. Therefore, our work concerns developing an instrumented die with the objective of measuring the complete rheological behavior curve of the material during production. In parallel, the polymer aging phenomenon is studied to develop an understanding of the waste's behavior under multiple reprocessing. In the following parts, we will present the material used in the first phase of the project and the methods applied during the rheological characterization. Then, we will briefly introduce the numerical model of the instrumented die that will be machined and validated experimentally in a later step of the project. The last part shows results regarding material aging and the numerical simulation of the developed die.

Materials and Methods

Materials

In this study, three grades of extrusion PP are used (supplied by Gazechim Plastics, France). During the first phase of the project, the purpose is to experimentally test the device with a diversity of virgin PP materials. Later on, mixtures of two or more components will eventually take place, to imitate an example of real case recycling scenario. Table 1 summarizes the main properties of the three different PP grades.

Table 1. PP properties of 3 commercial grades.

Material	Density (g/cm^3)	Tg (°C)	Tm (°C)	MFI (g/10 min)
PP089Y1E	0.85	-8.4	165.8	30.70
PP-040G1E	0.89	-9.6	164.7	3.26
PP-030G1E	0.86	-10.3	165.8	1.55

Sample Preparation

Prior to characterization, PP samples were prepared under similar extrusion conditions. The three grades were extruded separately with a plate die to form plastic films of which circular cuts were taken.

Rheological Characterization

Specimens are submitted to rheological characterization by a HAAKE Mars III rheology instrument using a parallel plate geometry with a diameter of 25mm and a fixed gap thickness of 1mm. Frequency sweep tests were carried out at temperatures ranging from 175°C to 210°C with an amplitude of γ_0=1% for frequencies in the range of 0.1 Hz to 100 Hz. By applying the Cox-Merz rule [17], we obtain the shear-rate-dependent viscosity $\eta(\dot{\gamma})$, converted from the oscillatory shear measurements $\eta^*(\omega)$ as follows in Eq. 1:

$$\eta^*(\omega) = \eta(\dot{\gamma}) \quad (1)$$

The PP melt results are then fitted by the nonlinear viscoelastic Cross law, given by Eq. 2:

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{1 + (\lambda\dot{\gamma})^n} \quad (2)$$

Where η_0 is the zero-shear rate viscosity, λ is a time constant, and n is the power law index.

Aging Test

To develop an understanding of the material's aging conditions, samples of the three PP grades were tested at different temperatures, ranging from 180°C to 210°C, using the same previous rheometer. Three protocols were followed:

- Mode 1: rotational test at shear rate equal to 0.01 s^{-1} for 15 minutes, repeated for 12 cycles with break gaps of 3 minutes.
- Mode 2: a periodic oscillating strain with an amplitude of γ_0=1% at a constant frequency w = 0.0628 rad/s, over 2.5 hours, conducted in air.
- Mode 3: a periodic oscillating strain with an amplitude of γ_0=1% at a constant frequency w = 0.0628 rad/s, over 3 hours tested under nitrogen gas.

Numerical Simulation

Extrusion Die Model

Numerical simulations of the flow in the extrusion die were performed using the commercial CFD package POLYFLOW®, by ANSYS. The 2D-axisymmetric geometry was modeled and solved as a steady-state problem using finite-element method (FEM). The fluid package was set as a Generalized Newtonian isothermal flow problem, considering the experimental extrusion conditions for the PP089Y1E grade at 190°C. As for meshing, a simple configuration of quadratic elements was constructed. The boundary sets for the problem are shown in Fig. 1 and the conditions at the boundaries of the domain are:

- BS 1: flow inlet, for a diameter = 45 mm
- BS 2: outer wall, with a maximum shear = 165 s^{-1}
- BS 3: flow exit, for a diameter = 6 mm
- BS 4: symmetry axis

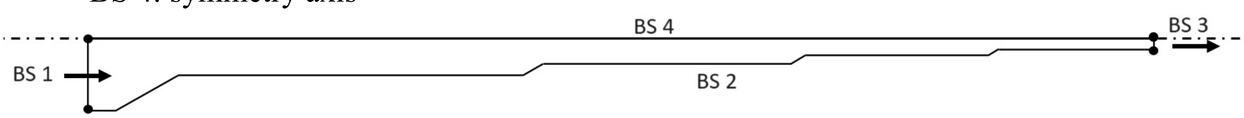

Fig. 1. Boundary sets on 2D-axisymmetric extrusion die schematic.

No-slipping was considered and the model was tested for the PP089Y1E grade material, at a flow value of Q =10 kg/h, using the Cross law obtained from the succeeding rheological characterization step.

Mathematical Model

Pressure loss measurements along the length of different sections will be converted to shear stress data [18] at the boundary, given by Eq. 3:

$$\tau_w = \frac{\Delta P - \Delta P_e}{4L/D} \tag{3}$$

Where, τ_w is the shear stress, ΔP is the measured pressure loss, L is the distance between 2 measuring points, D is the diameter of the section and ΔP_e is the Bagley correction, it is used to correct a pressure reading measured before the die inlet.

From the Newtonian fluid formula, the apparent shear velocity, $\dot{\gamma}_{aw}$, is defined according to Eq. 4. To convert it into the real shear velocity, $\dot{\gamma}_w$, a correction is proposed by Rabinowitsch applied as follows in Eq. 5 and Eq. 6:

$$\dot{\gamma}_{aw} = \frac{32\ \mathrm{Q}}{\pi D^3} \tag{4}$$

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'}\right) \dot{\gamma}_{aw} \tag{5}$$

With,

$$n' = \frac{dlog\tau_w}{dlog\dot{\gamma}_{aw}} \quad (6)$$

Once correction is applied, viscosity can be determined as follows using Eq. 7:

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

Results

Rheological Characterization

Figures 2 and 3 present master curve plots of the complex modulus, G*, versus angular frequency, ω, for grades PP-030G1E and PP-040G1E, respectively. Further, the experimental viscosity-to-shear data at 190°C of the different grades of PP (Fig. 4) were fitted by the Cross model (Eq.2), with the parameters listed in Table 2. Clearly, results show that the Cross model fits the measured values and successfully describes the measurements. Therefore, these parameters will be used as entry data for the numerical model and later on, to validate the experimental extrusion measurements of the instrumented die.

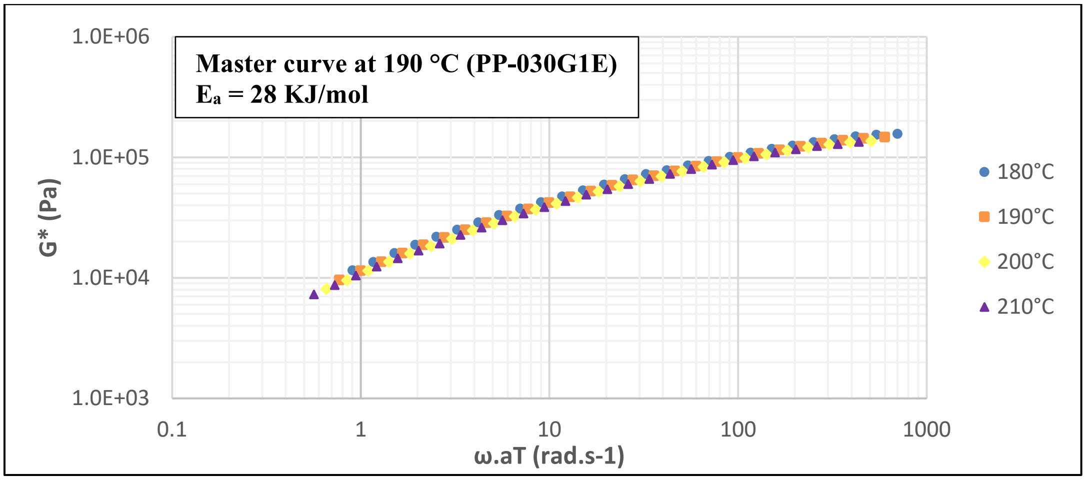

Fig. 2. Master curve of complex modulus for PP-030G1E grade at 190°C.

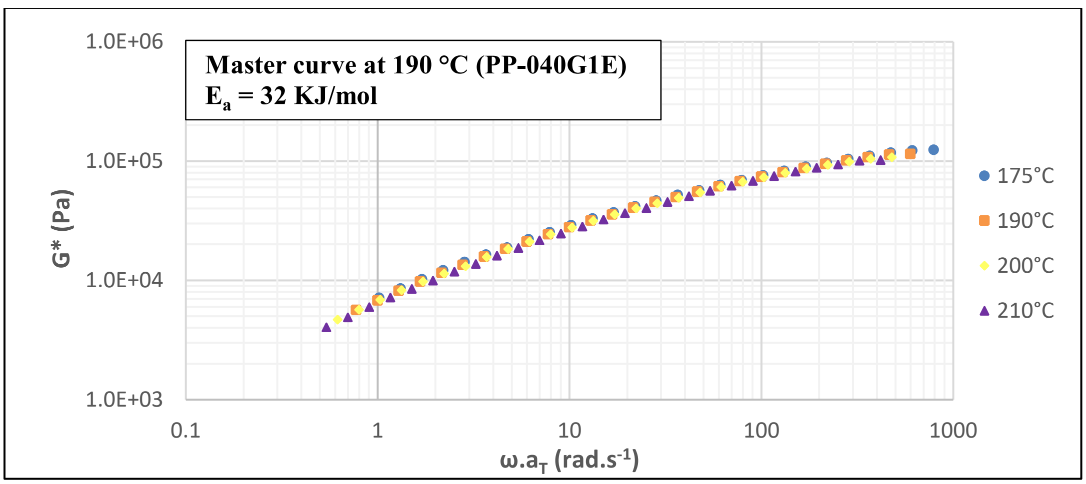

Fig. 3. Master curve of complex modulus for PP-040G1E grade at 190°C.

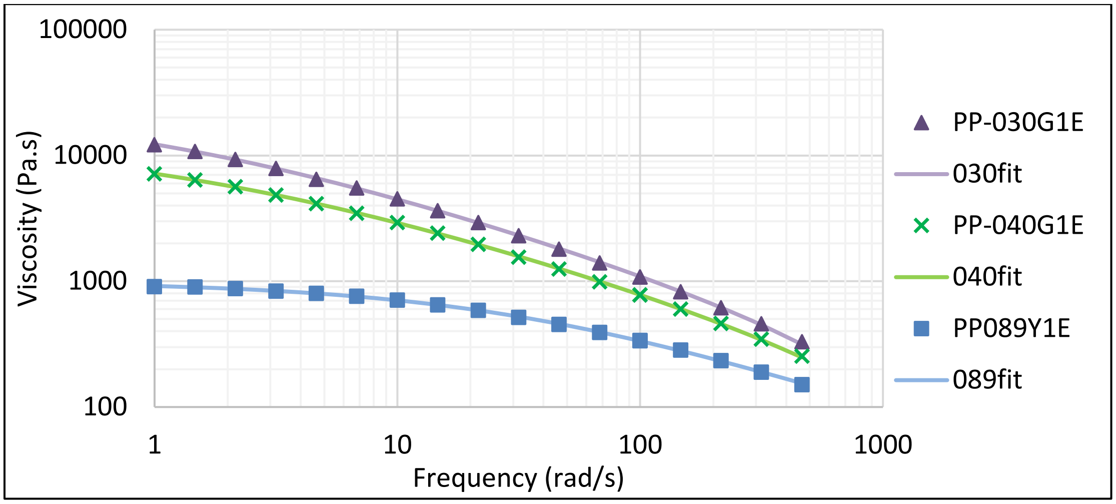

Fig. 4. Frequency sweep characterization test for the three grades of PP at 190°C, fitted by the Cross model.

Table 2. Parameters for the PP melt at 190°C obeying the Cross model.

	Value			
Material	η_0	η_∞ [1]	λ	n
	(Pa.s)	(Pa.s)	(s)	(-)
PP089Y1E	993.1	12.06	0.0281	0.691
PP-040G1E	1.34e4	-121.8	0.768	0.607
PP-030G1E	2.56e4	-191.2	1.118	0.626

[1] The minus sign of η_∞ is due to the fit of the measured points and has no physical meaning. It also means that the model can not be extrapolated out of the measuring range.

Material Aging

As the waste material will be subjected to multiple reprocessing under heat and mechanical deformation, we were interested in examining the viscosity variation along this process. Therefore, we submitted a sample of PP-030G1E grade to four consecutive characterization tests at 200°C. All curves present the Newtonian plateau at low shear rates and a pseudoplastic behavior at higher shear rates. However, after each test, the viscosity value dropped as shown in Fig. 5, reaching an initial viscosity loss of nearly 90% between the first and the last test.

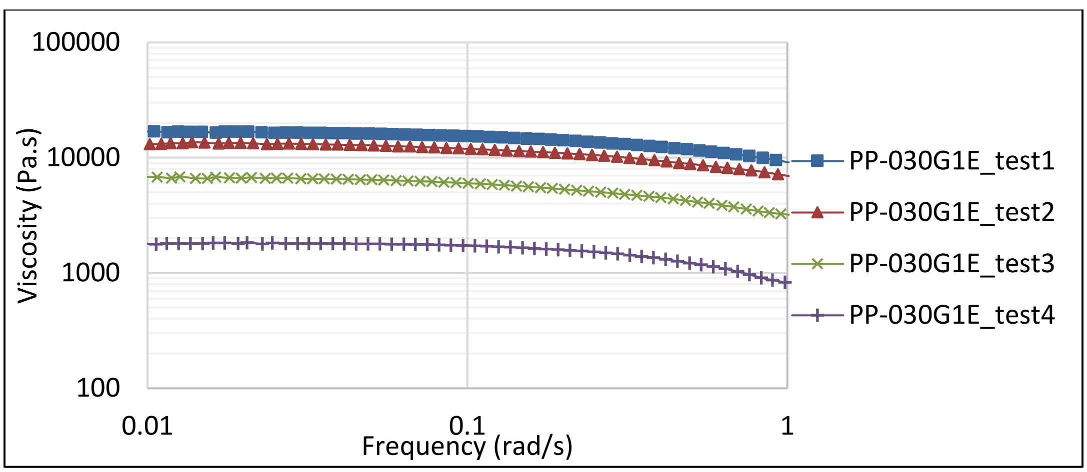

Fig. 5. Frequency sweep test for a PP-030G1E grade sample at 200°C, repeated consecutively 4 times.

To further investigate this property loss, we conducted tests at constant rotational speed relative to a low shear rate for the grade of PP-040G1E at two different temperatures. As expected, the viscosity values dropped with time, showing a faster decrease at higher temperatures (Fig. 6). Until now, this phenomenon can only be explained by the degradation of material and possibly the reorientation of the polymer chains at the micro-structural level as the specimen was exposed to a constant rotational deformation under heat. Moreover, we noticed that after a certain time of test, each curve reached a threshold and showed a nearly constant viscosity, which could be related further to the material's total residence time in the extruder under reprocessing.

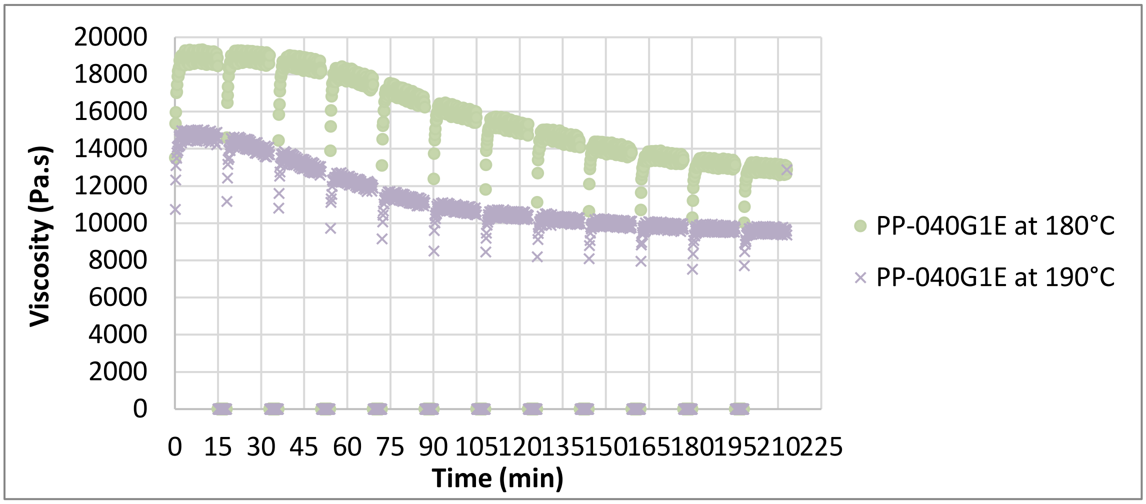

Fig. 6. Rotational time sweep test of PP-040G1E grade at different temperatures following mode 1 (section 2.4).

To eliminate the effect of micro-structural modifications, oscillatory tests of low deformation were applied on the same grade of PP at different temperatures. A lower decrease in viscosity is observed in Fig. 7, putting ahead thermally activated chemical degradation, likely oxidation, over the mechanical one. Similarly, the threshold was observed. This information could be significant to the number of cycles a waste material could undergo while maintaining its properties.

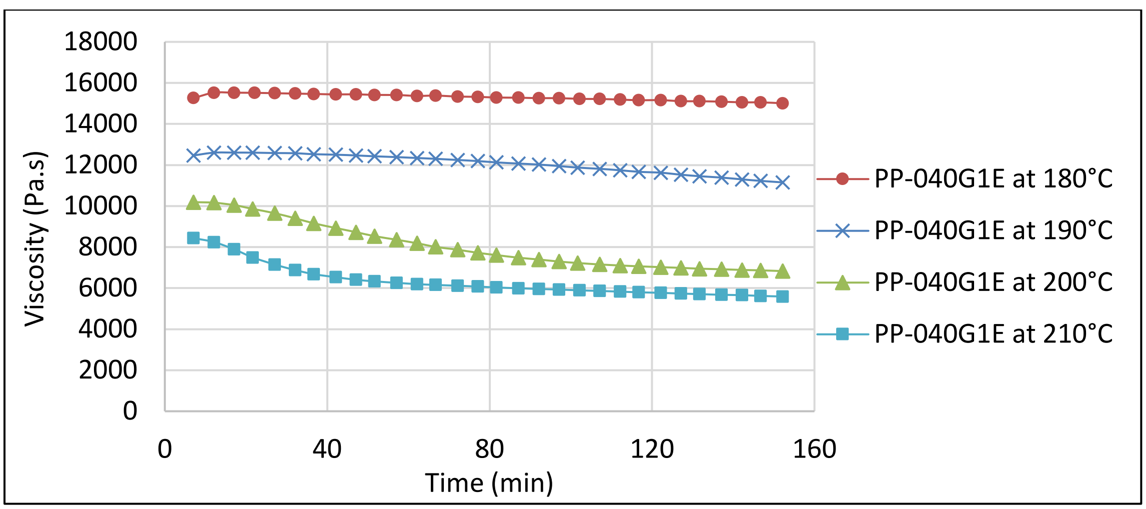

Fig. 7. Oscillatory time sweep test of PP-040G1E grade at different temperatures following mode 2 (section 2.4).

Finally, to examine the effect of air on the oxidation of PP-040G1E, we tested samples under the inert nitrogen gas. Results (Fig. 8) show a decrease in the aging of the specimen under nitrogen compared to the ones in air, which promotes the use of inert gases during the recycling process to reduce the thermal degradation and maintain the viscosity of material as long as possible.

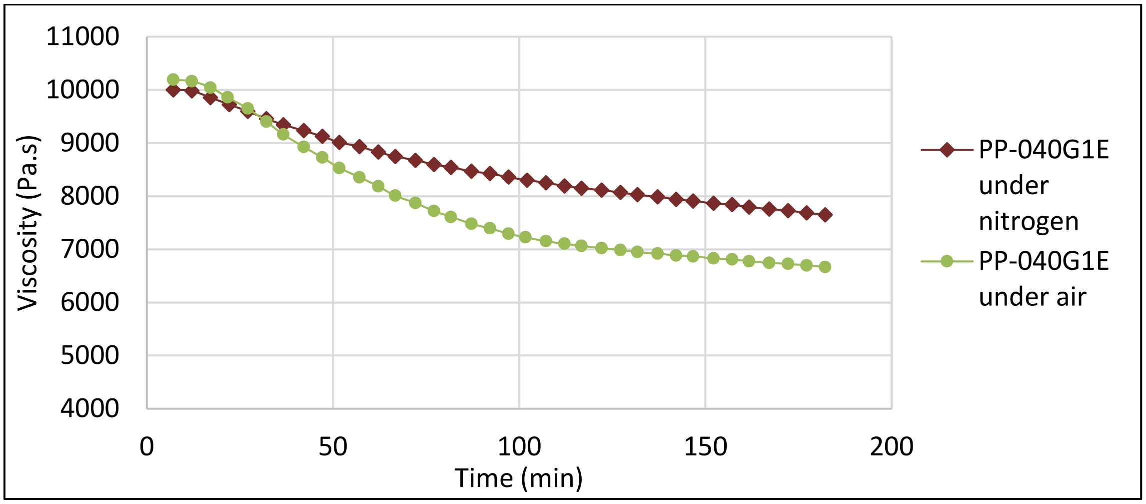

Fig. 8. Oscillatory time sweep test of PP-040G1E grade at 200°C following mode 3 (section 2.4).

Numerical calculation

The RECYPLAST-DEMO die was designed and machined as shown in Fig.9 based on numerical calculations. It is composed of 4 sections of independent heating zones. The extrusion die will be tested experimentally, in a later step, for validation of the numerical model.

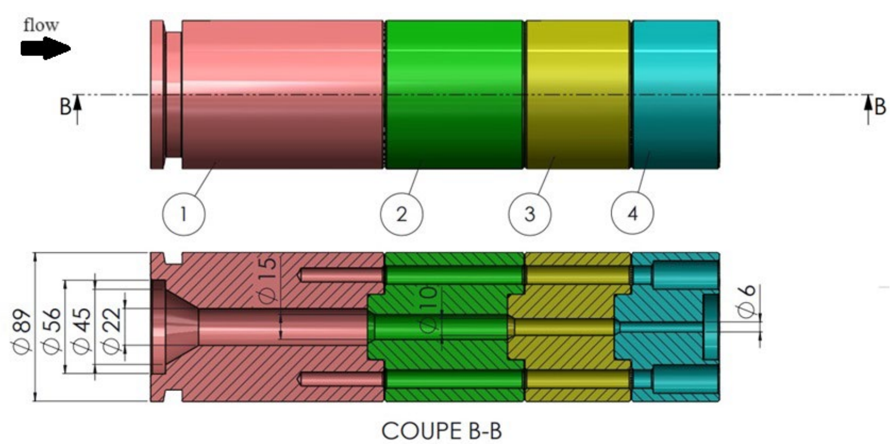

Fig. 9. RECYPLAST-DEMO extrusion die.

As mentioned earlier, an isothermal simulation was calculated using the viscous Cross model of the PP089Y1E grade, at 190°C. The software shows 3D view (Fig. 10) and graphical representations (Fig. 11) of the flow stress distribution in the geometry, which helps us mount pressure sensors in the die.

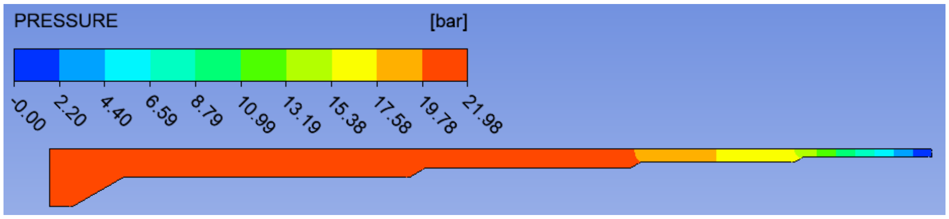

Fig. 10. Pressure distribution in the extrusion die simulated by POLYFLOW®.

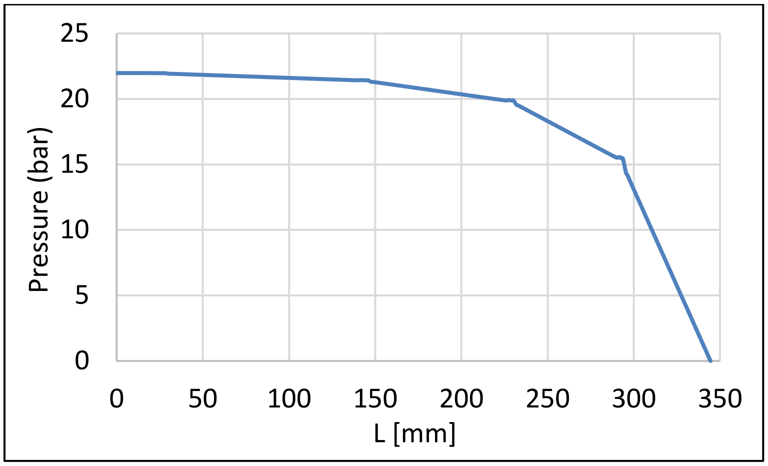

Fig. 11. Pressure along the length L of the die.

Conclusion

The global plastic production has been growing rapidly since the 1950s, and correspondingly the plastic waste accumulation causing serious environmental damage. Moreover, as we are draining non-renewable resources, prices have been rising at an increasing rate. Hence, it became necessary to work for a circular economy and recover the value of the waste material by reprocessing it. However, this solution results in further degradation of the material. Therefore, our project proposed to create a device able to characterize the material in real time, to be able to monitor different properties of the material, namely viscosity, during the reprocessing. At first, we characterized three grades of virgin PP that will be used in this project and data was fitted by the Cross model to be applied in the numerical model. Then, we developed an instrumented extrusion die using the software POLYFLOW® to calculate the flow stress distribution. Moreover, we investigated the aging phenomenon of PP samples under heat and mechanical deformation. Results from the rotational mode tests showed that the material viscosity dropped drastically when subjected to mechanical deformation. Furthermore, to reduce the effect of thermal degradation, oscillatory tests of low deformation were conducted showing favorable results under nitrogen gas compared to tests under air.

Further investigation and testing are needed to validate, theoretically and experimentally, the device's suitability for mechanical recycling of PP while maintaining, for a maximum number of reprocessing cycles, the quality of material waste.

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