Recent Developments on On-line Rheometry to Monitor the Extrusion Process

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Abstract. On-line rheometers are generally inserted between extruder and die and generate data that is typically utilized for quality control purposes. However, on-line rheometers have also the potential to detect changes in structure, morphology, or composition of a given material system, thus assisting materials research and processing optimization, if they can be used along the axis of the extruder or compounder. The authors have previously developed on-line capillary and rotational/oscillatory rheometers that can be inserted and used at specific locations along the extruder. Since these devices are operated manually, their manipulation may be cumbersome and data may lack reliability. This work presents new versions of these rheometers, with improved functionalities and motorized operation. Details on the validation of one of them is also given.

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INTRODUCTION

Measuring the rheological response of a system is a sensitive probe to detect changes in structure, morphology, or composition. Therefore, the in-line rheological characterization of a material system along the axis of a processing machine (typically an extruder) not only provides the means to understand the evolution of important physico-chemical phenomena (such as compatibilization reactions, degradation and/or cross-linking, or dispersion levels), but can be also utilized for process optimization and quality control.

In-line rheological measurements involve the use of sensors that are located directly in the process without perturbing the main flow stream. This is quite difficult to implement, particularly along the axis of a processing machine. Thus, the few devices of this type developed so far are usually located at the die [1, 2]. Most efforts have focused on the development of on-line techniques, which involve the diversion of a small stream of material towards a special channel containing the sensors, the melt eventually merging later with the main melt stream. The majority of the designs use the capillary rheometry concept [3-5], but a few employ rotational/oscillatory plate geometries [6, 7]. Generally, the apparatuses are fixed between the extruder and the die. Blanch et. al. [3] used a bypass to divert the melt from the extruder by means of a

gear pump and determined the viscosity by controlling the melt flow rate required to maintain a constant pressure drop between two specific locations along the capillary. In the case of the design patented by Mode et al. [4], there is a stream parallel to the capillary channel where a rotary valve has been inserted, to enable a reduction of the residence time of the polymer melt. Various on-line rheometers using these concepts are commercially available.

Taking advantage of the fact that the barrel of many modern twin screw extruders has modular construction (one barrel consisting of various modules fixed together), Covas et al. developed a modified barrel module concept [8], an on-line capillary rheometer [5] and an on-line rotational/oscillatory rheometer [6, 7]. The first provides ports for either sample collection or insertion of an on-line probe. The remaining two are compatible with the first and, consequently, can perform measurements at various locations along the barrel. Even though these on-line rheometers have been adequately validated and shown to be able to generate valuable data [5, 6], they rely on manual operation and their manipulation is relatively complex. This may limit the reliability of the results and increase the amount of time required for making measurements. Thus, this work reports improvements in the design of these devices, aiming at increasing the precision of the measurements and enabling automatic operation.

ON-LINE RHEOMETRIC COMPONENTS

Extruder Barrel Module

As explained in the Introduction section, the on-line rheometers are inserted in ports machined in purpose-built barrel segments. In the previous design, each port could accommodate either a sampling device, or an on-line sensor. In the case of rheology measurements, it is important to check for the homogeneity of the sample, e.g., whether all the material is melted, or solid particles are still present. Therefore, the new version of a barrel module combines independent sample collection and measurements. As shown in Figure 1, samples can be collected from four different locations using rotating valves that are powered by a stepper motor (not represented in the figure). These valves also control the incoming flow from the extruder into the rheometer chamber. The extruder barrel segment has two series of four lateral orifices – see Figure 2. The series in the inner barrel wall is used for sample collection. The series at the outer wall accommodates sensors, such as melt pressure transducers.

On-Line Oscillatory Rheometer

As illustrated in Figure 3, the new prototype on-line rotational rheometer consists of a cylindrical module (*rheometer module*) that is inserted into one of the orifices of the extruder barrel segment described above. This module has an independent temperature control system. The position of the lower plate is controlled automatically by a stepper motor, in order to define a pre-specified gap (for plate-plate or cone-and-plate geometries). A material sample is collected from the extruder by opening one of the automatic sample collection valves, melt flowing due to pressure

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difference into the rheometer chamber. Sample collection takes a few seconds only. A motorized ring removes the excess material between the parallel plates, creating a good quality free surface. After temperature stabilization (monitored via a thermocouple imbedded in the lower plate), the test begins. A commercial rheometer head (Anton Paar DSR301) is employed to impose a rotating velocity / oscillation frequency to the upper plate, and to measure the resulting torque. The variation of G' and G'' during isothermal frequency sweeps, or shear flow curves at a range of shear rates, can be readily obtained.
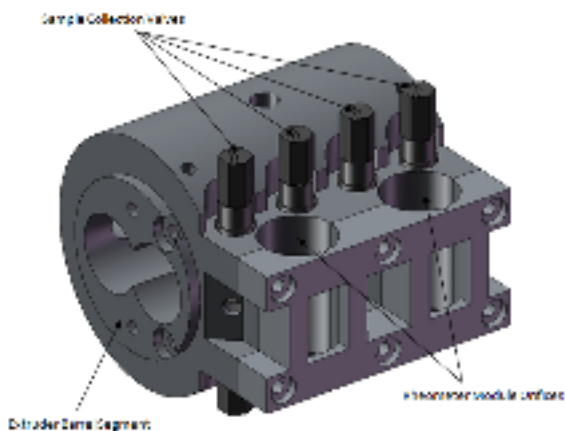
FIGURE 1. Extruder barrel module, with sample collection valves and orifices for on-line sensors.
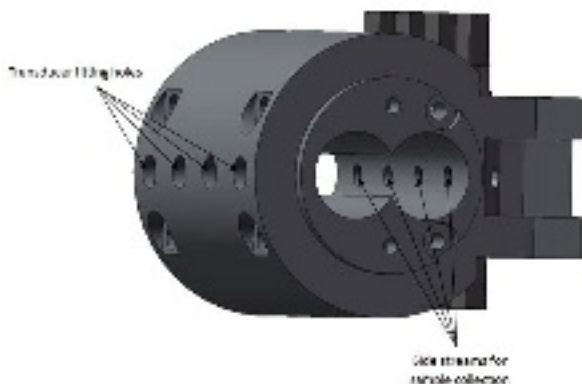
FIGURE 2. Back view of the extruder barrel module showing lateral series of holes.
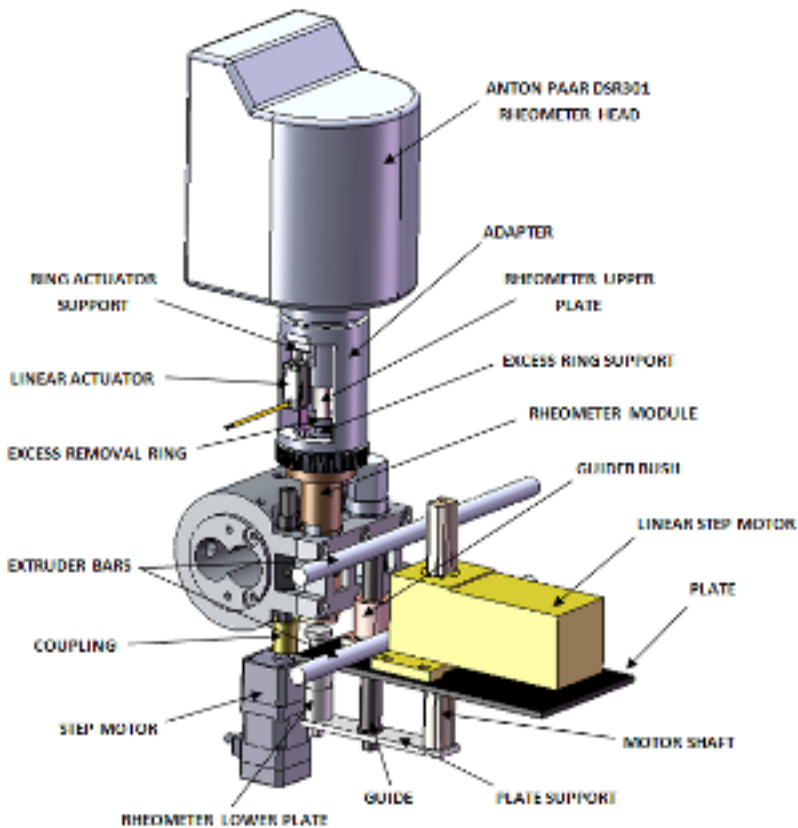
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FIGURE 3. Global layout of the on-line rotational/oscillatory rheometer.

On-line Capillary Rheometer

The on-line capillary rheometer contains the same general constructional and operating principles of the rotational rheometer, as illustrated in Figure 4, i.e., it consists of a cylindrical module that is also fitted in the extruder barrel module, and it uses the same commercial rheometer head described above.

The rheometer module comprises a temperature-controlled hollow barrel, a piston coupled to the rheometer head and a (replaceable) capillary die fixed at the bottom. Upon sample collection by the usual manner, melt from the extruder fills in the reservoir of the rheometer. By converting the rotational movement of the rheometer shaft into a linear descending movement of the piston, the latter forces the melt out of the capillary die at a certain rate. Isothermal shear flow curves are obtained after running several tests at different piston velocities, the values of torque for each case being measured by the rheometer head sensor. During a sample collection / measuring

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cycle all the required rotational movements are powered and controlled by means of stepper motors (not shown in the figure).
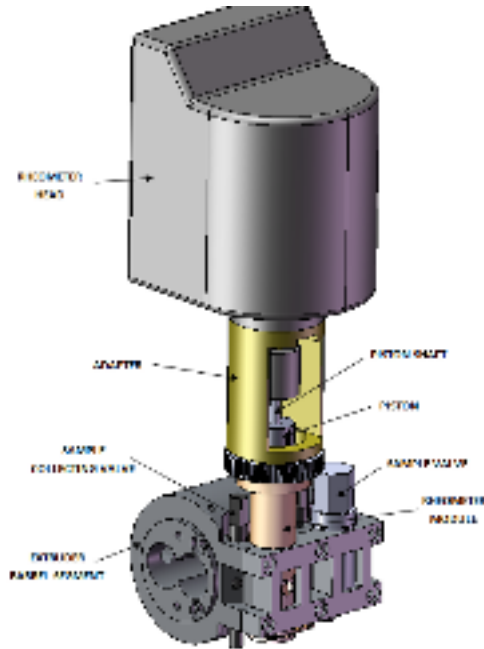

FIGURE 4. Global view of the on-line capillary rheometer system.

VALIDATION AND TESTING

Validation and testing of the oscillatory rheometer is presented here as an example. Three important validation steps were undertaken. First, the adequacy of the rheometer construction and design were verified by performing measurements made at room temperature with a fluid of known viscosity. A silicon oil (AK 1000000, from Wacker) with a viscosity of 1000 Pa.s at 25ºC was selected for this purpose. Measurements were also made with a conventional Paar Physica MCR301 rheometer. Figure 5 shows the results. A newtonian plateau exists at low frequencies/shear rates, the values of the viscosity measured with the two instruments overlapping. When observing the behavior of *G'* and *G''*, unstable data is obtained for moduli below 1 Pa. It has been shown that this is correlated with the minimum measuring capabilities of the rheometers [6].

Second, the temperature control capabilities of the on-line rheometer were evaluated. This is also very relevant, since the temperature at which the rheological characterization is performed must be well controlled, but may be quite different from the extruder barrel set temperature. Figure 6 presents the variation of the elastic

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modulus with frequency (isothermal frequency sweep) measured at 180 and 220ºC for a polypropylene (PP HP500N from Basell) collected from a Leistritz co-rotating laboratorial twin screw extruder operating with barrel set temperatures of 180 and 220ºC, a feed rate of 8 kg/hr and a screw speed of 230 rpm. Again, overlapping of the two pairs of curves is quite satisfactory.
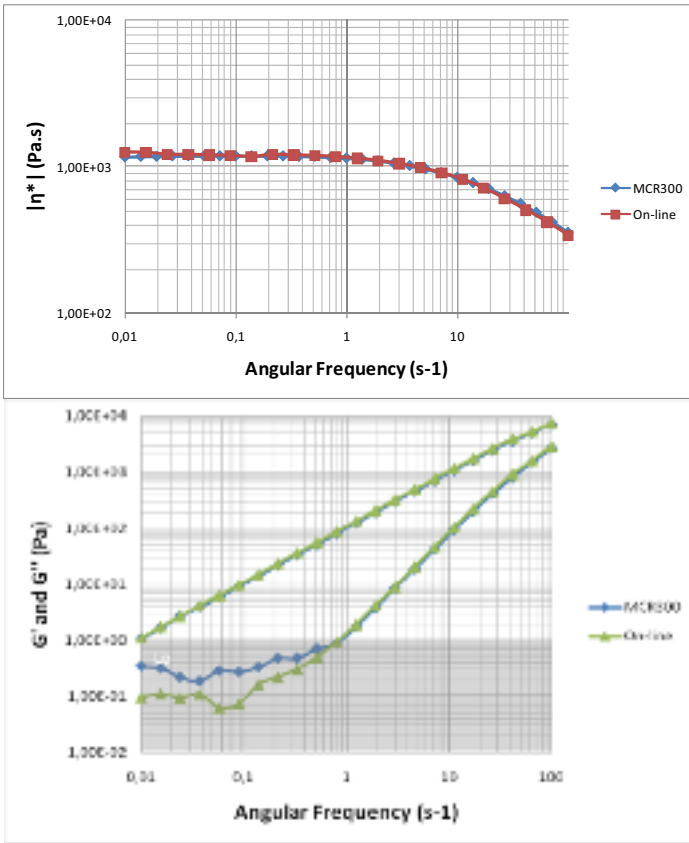

FIGURE 5. On-line and off-line frequency sweeps at 25ºC of a silicon oil with a viscosity of 1000 Pa.s.

Finally, it is important to confront directly off-line and on-line equivalent data. For this purpose, the same PP was processed in the same extruder and same processing conditions (the barrel temperature was kept at 220ºC). The on-line rheological tests were performed in oscillatory shear, at 200ºC, and with a strain amplitude of 5 %. At the same location where the tests were performed, material samples were collected, converted into disks by compression moulding and later characterized using an TA Ares rheometer under the same test conditions.
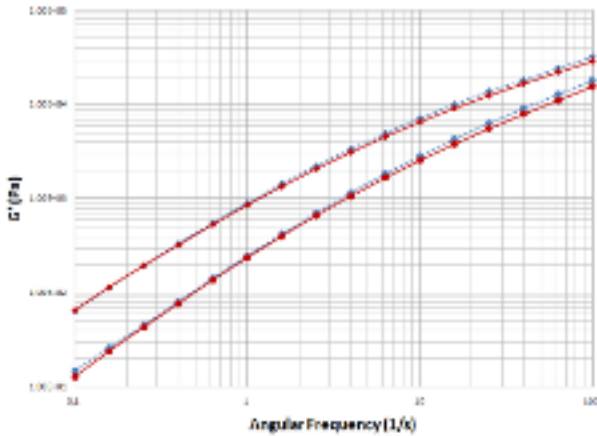
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FIGURE 6. Storage Modulus measured on-line at 180ºC (✛) and 220ºC (✹), using two different set extruder barrel temperatures: 180ºC (----) and 220ºC (——);
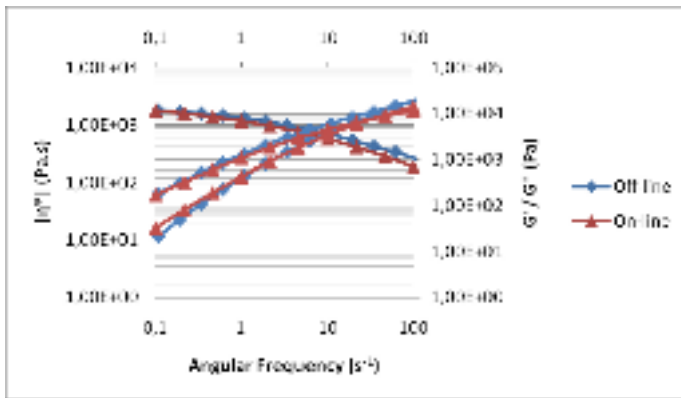

FIGURE 7. On-line and off-line measurements of a polypropylene at 200ºC.

Figure 7 depicts the two sets of data. An encouraging good agreement between off-line and on-line data is obtained, although not perfect. One must keep in mind that a comparison is being made between samples with quite distinct thermo-mechanical experiences. The on-line sample was removed from the extruder and spent a few minutes in the rheometer to ensure thermal equilibrium, being immediately characterized. The off-line sample was removed from the extruder and cooled; reheated, compression moulded and cooled; reheated and tested.

Once confidence in the new on-line rheometer is gained, it is interesting to explore its potentialities. An example is given in Figure 8, which is related to PP degradation during processing. As shown in the figure, the viscosity of PP drops along the extruder, due to chain scission and consequent decrease in average molecular weight [9].
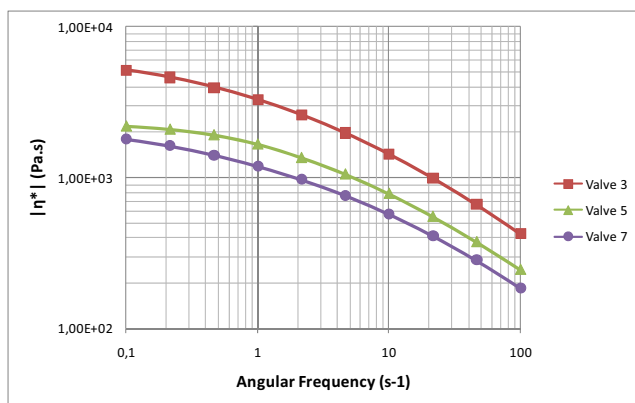
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FIGURE 8. PP degradation along the extruder.

CONCLUSIONS

This work presents new motorized versions of two on-line rheometers developed previously by the authors, based on capillary and oscillatory rheometries, and capable of making measurements along the axis of an extruder. The improvements achieved are significant both in terms of functional capabilities, reliability and ease of use, although further validation of the data generated is still required.

ACKNOWLEDGMENTS

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