Measuring the rheological properties of polymer melts with on-line rotational rheometry

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Abstract

Since the rheological response of a polymer system to an imposed stress is sensitive to composition, morphology, degree of mixing or temperature, on-line rheometry carried out along the length of the processing or compounding equipment - and able to follow the evolution of physical-chemical processes - is of great technical and scientific significance. This work presents and validates a computer controlled on-line rotational rheometer capable of quickly collecting material samples from within an extruder at different axial locations and performing the usual measurements of typical bench top commercial instruments. Validation of the prototype is made by direct comparison of its measurements with those carried out conventionally, including off-line measurements at room and high temperatures and on-line measurements. In order to illustrate its usefulness, the instrument is then used to monitor the evolution of the rheological behavior of three different materials along the axis of a twin screw extruder.

Introduction

The measurement in real time of the rheological properties of polymer systems during their manufacture and processing remains an important scientific and technological target. Since the rheological response of a material to an imposed stress is sensitive to

composition, morphology, degree of mixing, temperature, etc, data measured in real time can be used to assist material formulation, the optimization of operating conditions and/or screw design, as well as for quality control and, ultimately, process control. Usually, during industrial extrusion and compounding only a few process parameters are continuously monitored (typically temperature, pressure and motor amperage), which do not provide a direct assessment of the material attributes, only an estimation of the flow and heat transfer conditions. Therefore, there might be a significant time lag between the detection in the

laboratory of quality non-conformity from measurements of material samples collected from the production line and the correction of the processing conditions, which may lead to significant material waste.

Moreover, if rheological measurements can be carried out along the length of the equipment, the evolution of physical-chemical processes can also be followed. Pertinent examples include the in situ compatibilization of polymer blends (where a major - often complex - morphology evolution takes place within a short screw length) [1], the peroxide-induced degradation of polyolefins (which is dictated by the degradation rate of the peroxide) [2] and the manufacture of nanocomposites containing carbon nanotubes or organoclays [3] (in both cases, certain dispersion levels are necessary for the desired performance levels). It is quite clear that, in these situations, standard off-line measurements performed on samples collected from the equipment (either during or after processing) may provide misleading information, since during the sample preparation step, or during the heating prior to the rheological characterization, the physical-chemical processes that were taking place in the processing equipment might continue to evolve, i.e., the sample measured off-line might not be really representative of the material taken at a specific collection point [4].

During the last two decades, academic groups and rheometer manufacturers have been attempting to develop reliable, precise, simple to operate and economically attractive in-line and on-line rheometers. In-line measurements are of particular interest, as they avoid melt by-passes and the eventual need of purging a certain amount of polymer melt. The "partial Couette" geometry proposed by Dealy [5] is able to measure the shear stress corresponding to a single shear rate (related to the process throughput). The slit in-line rheometer developed by Kalyon and co-workers [6] contains a mechanism for the adjustment of the gap, but the range of workable shear rates is narrow. Another approach for measuring viscosity as a function of shear rate consists in coupling ultrasound flow velocity measurements to pressure difference readings along a certain channel length [7,8]. Preliminary experiments in pipe flow seem encouraging, although the breadth of the shear rate range will depend on the resolution of the ultrasound system. Smith and Glasscock [9] presented an in-line micro-Fourier rheometer using a squeeze flow technique, capable of measuring the linear viscoelastic properties within a reasonable frequency range. However, the correlation between off-line and online data needs to be established for each fluid application, thus reducing the practical utility of the method. The use of semi-hyperbolic dies for measuring the transient extensional viscosity has also been investigated by several authors (see, for example, the recent study by Baird et al. [10]). The majority of these devices consist of - or could be implemented as - instrumented dies. It seems difficult to envisage their application along an extruder axis.

Most commercial solutions use capillary or slit rheometers to provide on-line measurements. Generally, they continuously transfer melt from the main stream, which then feeds the rheometer at constant rate, as set by means of a gear pump. After the

measurement, the by-passed melt merges with the main stream (see, for example in Refs. [11-13]). Design variations and different automation levels exist, but it is normally possible to simultaneously obtain apparent viscosities at different shear rates, as well as transient extensional viscosities from "zero length" dies. Although these devices are usually inserted between the extruder and the die, it is conceptually possible (although apparently not tried) to fix them upstream. In this regard, the Piezo Axial Vibrator is particularly attractive, since its feed port has the geometry of a standard melt pressure transducer (standard 1/2 UNF thread) [14]. This apparatus generates an axial oscillation on the material sample and uses piezo elements to record the rheological moduli. However, it still requires improvements in robustness, handling and signal noise.

On-line solutions seem easier to adapt to different equipment, to calibrate, clean and maintain, provide simpler means of varying the shear rate/frequency and offer good temperature control. However, it is also important to ensure that these devices: i) minimize the time-lag between sample collection and measurement, ii) prevent material morphology changes both during sampling and measurement, iii) enable measurements along the axis of the extruder (under normal conditions, the morphology or chemical reaction of a given polymer system will have achieved steady-state or been completed well upstream of the die) and iv) are capable of performing measurements at temperatures other than the processing temperature (or even carry out temperature sweeps). Covas et al. [15] developed an on-line capillary rheometer capable of collecting quickly, but under adequate conditions, material samples from within an extruder that could be fixed at different axial locations of the machine. The device was successfully used to uncover the viscosity evolution of various polymer systems along the screw, thus contributing to better understand the corresponding mixing and/or chemical mechanisms. Due to the destructive (or potentially destructive) nature of capillary rheometry during the characterization of systems such as polymer blends and nanocomposites, an on-line rotational rheometer, working either in steady shear or oscillatory mode, was later developed [4]. After validating the device, the authors were able to demonstrate its usefulness by measuring the evolution of the rheological moduli (G' and G'') of a non-compatibilized and equivalent compatibilized polymer blend. They also showed how off-line measurements of samples collected from the extruder can produce misleading results, due to the changes in their characteristics that are induced by the several thermal cycles they are subjected to during sample preparation. The number of cycles is obviously minimized in on-line measurements. Despite the encouraging results, the reproducibility of the device was somewhat operator dependent, owing to its mostly manual operation.

This work presents a new version of the original on-line rotational rheometer concept that incorporates design improvements and automated operation. As with most commercial off-line bench top instruments, the new online rheometer is able to operate under different modes, such as steady state, frequency sweep, strain sweep, creep & recovery and stress relaxation, but can be fixed along an extruder barrel. The device is experimentally assessed by comparing its measurements with those carried out using conventional off-line rheometry. The evolution along the extruder axis of the linear viscoelastic response of three different materials is used to illustrate the practical utility of the new tool.

Equipment and operation

The concept of the on-line rotational rheometer is shown in Fig. 1 (see also in Ref. [4] for a detailed description). The idea is to collect melt (1) from within the extruder (2) via

opening the rotating tap (3) and shape it as required - typically into a disk or a tapered disk for parallel plates and cone-and-plate measuring geometries, respectively - by squeezing it between the lower (4) and upper (5) plates. Measurements are undertaken using the motion sensing and controlling capacities of a commercial rotational rheometer (in this case, the head of an Anton Paar DSR301 rheometer) that is coupled to the upper plate (5) and fixed to the device by means of the adapter (6). As in conventional off-line rheometry, the instrument can operate in steady and oscillatory modes, a variety of test types

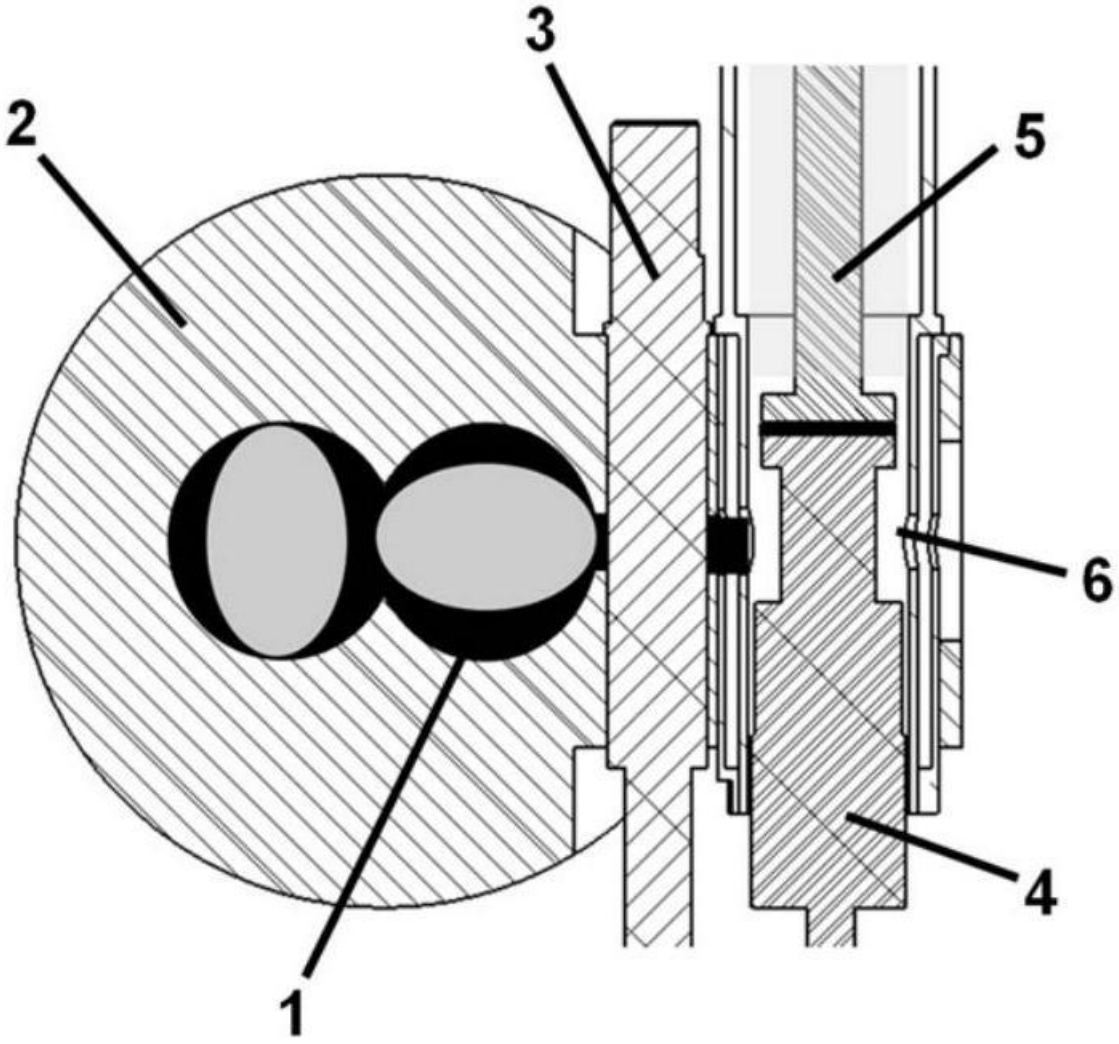


Fig. 1. The on-line rheometer concept. 1 - melt; 2 - extruder; 3 - rotating tap; 4 - lower plate; 5 - upper plate; 6 - adapter for the rheometer.
being possible, namely isothermal steady shear, frequency sweep, amplitude sweep, time sweep and step stress/strain (creep & recovery/stress relaxation). Also, since the device possesses its own temperature control system (it uses a coil heater fixed inside the hollow wall of the testing chamber, not represented in the Fig.), tests at different constant temperatures (namely, distinct from the extruder set temperatures), or temperature sweeps, are also feasible. The compact design, the short thermal history and the negligible shear rate the melt is subjected to upon collection and prior to the rheological

measurement prevent any significant changes in morphology (for example via coalescence) or chemical conversion (including degradation).

The sequence of operations that makes possible a rheological measurement are illustrated in Fig. 2. Fig. 2a shows the extruder operating normally. At this stage, maintenance, cleaning and calibration of the on-line apparatus can be undertaken. Material flow from within the extruder towards the testing chamber will occur due to pressure difference when the rotating tap is opened (Fig. 2b). The tap is closed when enough sample is available, preventing further melt influx (Fig. 2c). This is easy to detect, as melt will start emerging from a hole opposite to the inlet channel and visible to the operator. Typically, this operation takes less than 5 s . In order to manufacture a disk of sample material, the lower plate raises vertically to the pre-defined gap value (Fig. 2d). Then, a cleaning ring slides downwards in order to wipe out any excess material around the edge of the plates (Fig. 2e). A type K thermocouple embedded in the lower plate, with its measuring tip positioned very close to the surface in contact with the melt, makes it possible to monitor the average temperature and decide whether thermal equilibrium at the test temperature has been reached. Obviously, the time necessary to attain this equilibrium depends mainly on the difference between the incoming melt temperature and the required test temperature. It is relevant to recall here that viscous dissipation in co-rotating twin screw extruders can be quite significant, depending on the material and processing conditions, values of $20-60^{\circ}C$ having been measured [16]. Once the rheological test has been performed, the cleaning ring and the lower plate retreat to their initial positions. The whole measuring system can be removed for (manual) cleaning.

As explained above, material inflow from within the extruder towards the testing chamber occurs due to pressure difference, when the rotating tap (3) (Fig. 1) is opened. In the case of a co-rotating twin screw extruder, melt pressure develops only in the fully filled sections of the

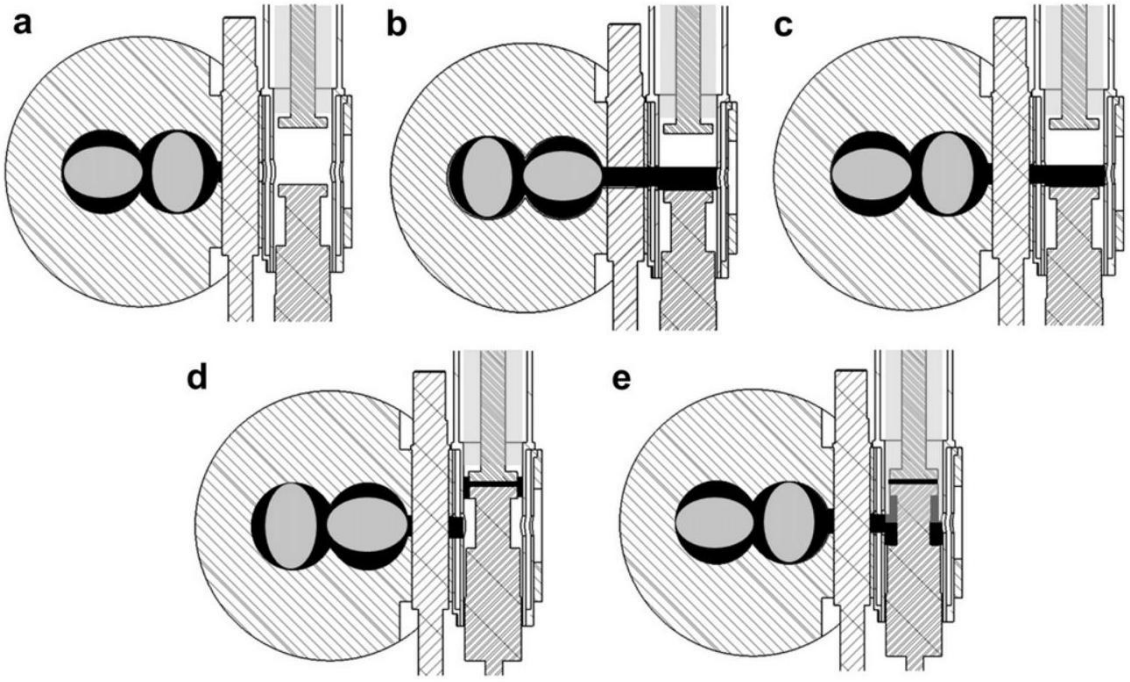


Fig. 2. Operation sequence prior to the rheological test; (a) normal extruder operation; (b) melt flows from the extruder into the rheometer testing chamber; (c) sample collection is interrupted; (d) the lower plate raises to the pre-defined gap value; (e) the cleaning ring removes the excess material surrounding the measuring geometry - the rheological test can start.

screw, i.e., at restrictive zones comprising neutral or negatively staggered kneading disks and/or left handed elements, as well as along a few conveying screw turns upstream [17]. It has been reported that most changes in morphology, mixing levels and chemical conversion occur precisely at these locations [1]. Thus, taking advantage of the modular construction of most twin screw extruders, modified barrel segments containing several rotating taps can be conveniently inserted between original extruder barrel segments, to divert and rheologically characterize material samples at the most relevant screw locations. If enough modified barrel elements are available, rheological measurements at small axial increments (typically 1D, where D is the screw diameter) are possible, i.e., a detailed evolution of the rheological response of a given material can be obtained. It is also worth mentioning that, in practice, these modified barrel elements can also accommodate other available on-line devices, namely an on-line Capillary Rheometer [15] and an on-line optical sensor for the measurement of Residence Time Distribution [18].

Sampling along the axis on an extruder might raise the question of whether the material present in the testing chamber of the on-line rheometer is fully molten, or whether solid polymer particles, even if distorted and smaller in size, are still present. Survival of the latter would obviously influence the rheological behavior and could generate ambiguous results or interpretations. To account for this possibility, the rotating tap (3) of Fig. 1 is in fact a three-way rotating valve. When the valve is in its closed position the extruder operates normally. When it rotates 120°, material is diverted from inside the extruder and can be directly collected by the operator, who can observe its physical appearance and/or save it for subsequent off-line characterization (for example, via electron microscopy and FTIR). This method of quick sampling was previously developed by the authors [19] and has been extensively used to study the evolution of morphology and/or chemical conversion of various polymeric systems [1] and to assess the predictions of processing software [16]. Upon further 120° rotation, melt will flow into the on-line rheometer.

The automatic control of the three-way valve and of all the operations preceding a rheological test (Fig. 2) is made via software written in LabView, specifically developed for that purpose. In turn, the RheoPlus software supplied by Anton Paar controls the experiment. Fig. 3 left displays the sequence of steps that are necessary to perform one test, while Fig. 3 right identifies if each step is controlled by the motion control or by the RheoPlus software, or if it is manually performed. The movements associated with the steps shown in Fig. 3 are created by a rotating step motor that operates the three-way valve, a linear step motor that drives the lower plate and a linear mini actuator that triggers the movement of the cleaning ring (see identification of this hardware in Fig. 4). The motion control software drives the motors and the actuator through a PCI motion controller card from National Instruments inserted on the computer, communication between them being guaranteed by a Universal Motion Interface, also from National Instruments. In addition, the same software guides the user through the various preparation steps of an experiment, including the definition of the various

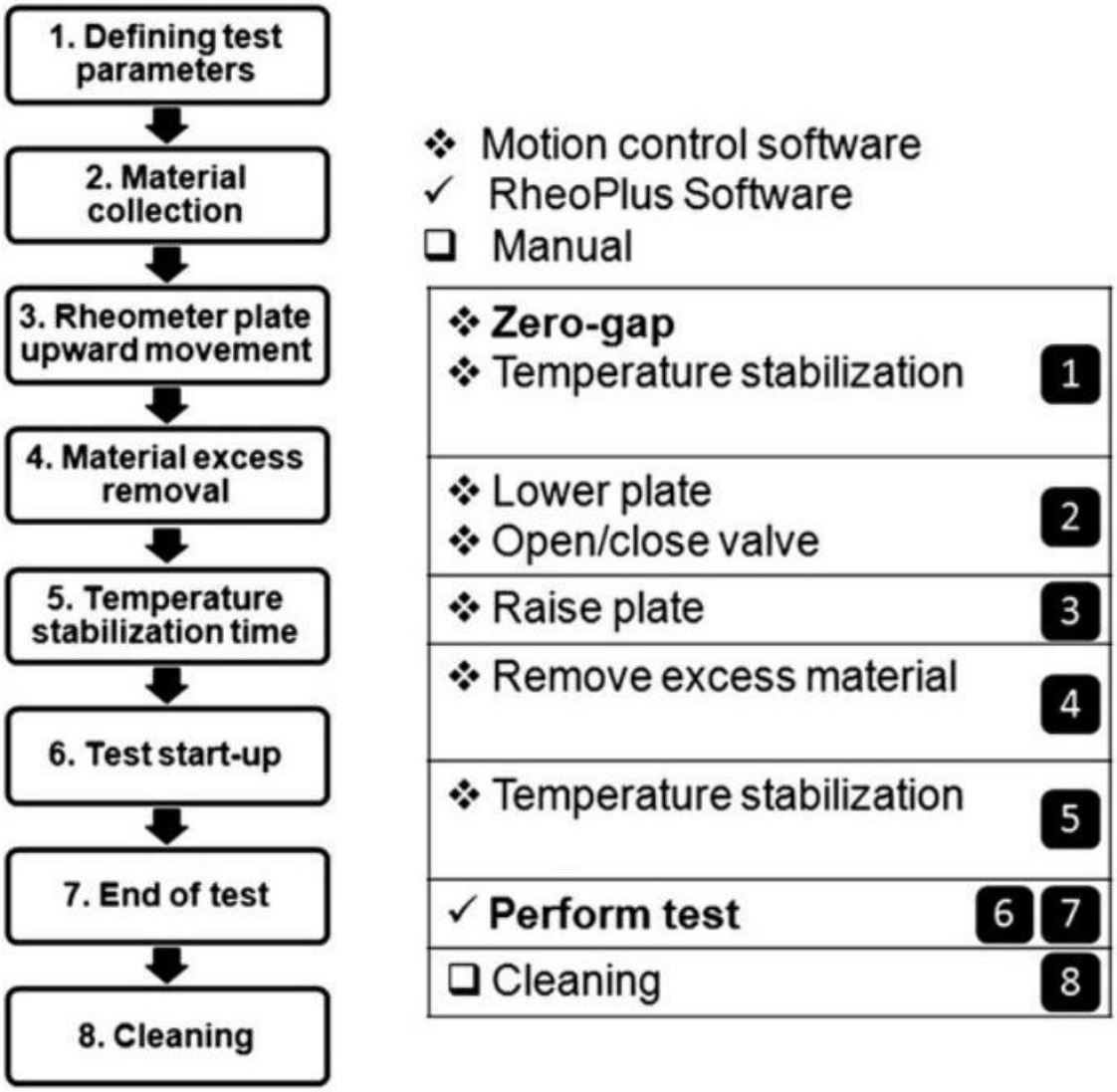


Fig. 3. On-line rheometer control. Left: operation sequence, Right: distribution of steps between both programs.
experimental parameters, material collection, shaping of the sample and thermal stabilization. The former include the gap between plates, the test temperature, the material sampling time and the thermal stabilization time. The device can work either in automatic or manual mode. Emergency stops have been provided. The user is continuously informed about the current step of the sequence, the time elapsed and the temperature of the testing chamber. When the thermal stabilization time is over, the RheoPlus software is used to perform the experiment. Once this is completed, the motion control software is again used to make the on-line rheometer ready for cleaning or maintenance.

Materials

The materials presented in Table 1 were used to experimentally determine the sensitivity limits and assess the on-line rheometer. The two oils from Wacker exhibit a known

constant viscosity along a relatively wide shear rate interval at room temperature. LDPE, PS and PP are polymers extensively used for packaging applications via blow molding, sheet extrusion & thermoforming and injection molding, respectively. Once the on-line

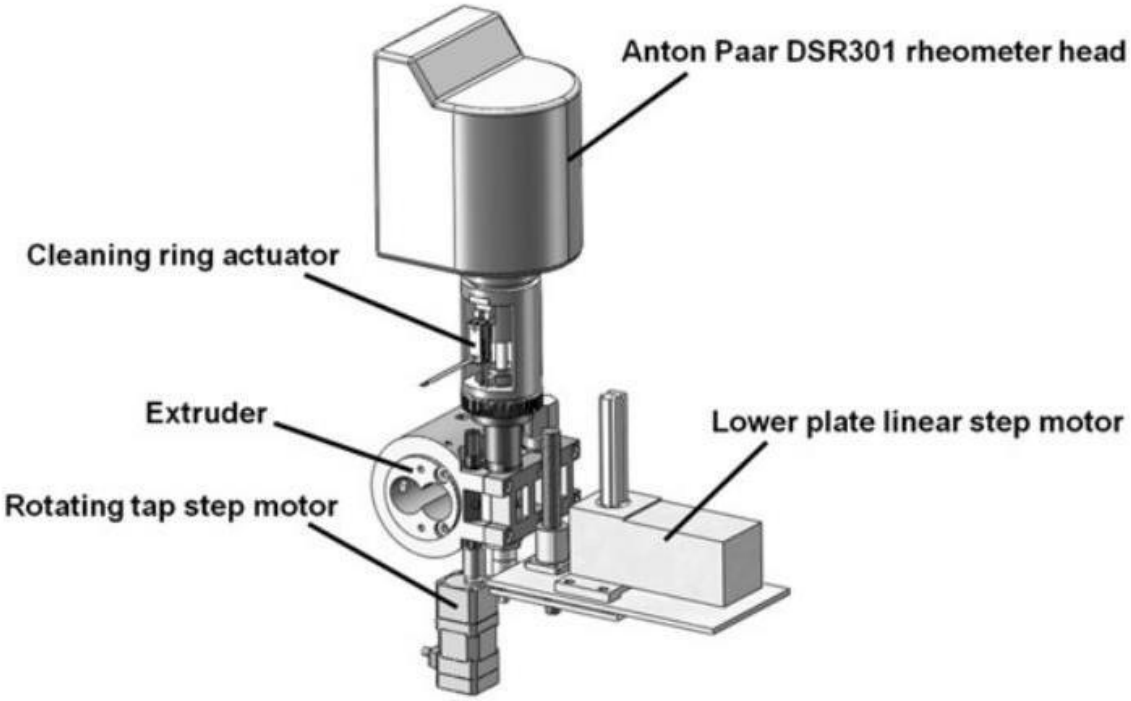


Fig. 4. Motors and actuator used in the on-line rheometer.

Table 1
Materials used for validation.

Material	Producer	Acronym	Grade	Viscosity/MFR
Silicone oil	Wacker	Oil 100	AK 100000	100 Pa s (room temperature)
Silicone oil	Wacker	Oil 1000	AK 1000000	1000 Pa s (room temperature)
Low-density Polyethylene	LyondellBasell	LDPE	Lupolen 1840	0.25 g /10 min(190°C /2.16 kg)
Polystyrene	Polimeri Europa	PS	Edistir N1840	10 g /10min(200°C /5 kg)
Polypropylene	LyondellBasell	PP	Moplen HP500N	12 g /10min(230°C /2.16 kg)

rheometer was validated, the materials shown in Table 2 were compounded in a Leistritz LSM 30.34 laboratory scale, modular intermeshing co-rotating twin screw extruder and the evolution along the barrel of their dynamic rheological response was monitored. Dellite 67G is a naturally occurring montmorillonite modified with a high content of quaternary ammonium salt (dimethyl dihydrogenated tallow ammonium).

Experimental validation

The validation of the measurements made by the new on-line rheometer was divided into three stages, essentially following the strategy adopted to assess the original version [4]:

- room temperature off-line validation and determination of sensitivity limits, using two silicone oils of known viscosity;
- high-temperature off-line validation, using two high consumption polymers (LDPE and PS);
- high temperature on-line validation for another widely used polymer (PP).

The equivalent conventional off-line rheological characterization was performed either in a ARG2 (TA Instruments) or in a MCR 300 (Anton Paar) bench top rheometer, under identical experimental conditions, using a parallel plate configuration with a diameter of 25 mm and a gap of 1 mm (the plate diameter of the on-line rheometer is 20 mm and a gap of 0.8 mm was used). The frequency sweeps were performed from high to low frequencies. The disks for off-line characterization were prepared by compression molding under a pressure of 20 ton and a temperature of $210°C$, $180°C$ and $200°C$ for PS, LDPE and PP , respectively.

Room temperature off-line validation

Fig. 5 compares the dynamic response (in terms of the complex viscosity, η^*, storage and loss moduli, G' and G'', respectively) of the two silicone oils with known viscosities, as measured by the MCR 300 and the on-line rheometer working off-line (i.e., in both cases, the gap between the plates was manually filled with oil). The extent of the linear viscoelastic response was determined off-line in the MCR 300, before performing the frequency sweeps (a 1% strain was applied). The agreement between the two sets of data is satisfactory (average deviation of 5 and 8% in G' and 10% and 14% in G'' for Oil 100 and Oil 1000, respectively), especially for values of moduli beyond $1-10\text{MPa}$ (similar differences were obtained with the original version [4]). The higher differences below this range are probably related to friction effects in the prototype rheometer, but even the data for Oil 100 measured by the MCR 300 seems dubious (the MCR 300 has a torque resolution of $0.1\mu\text{Nm}$, but measurements below $0.6\mu\text{Nm}$ seem unreliable).

High-temperature off-line validation

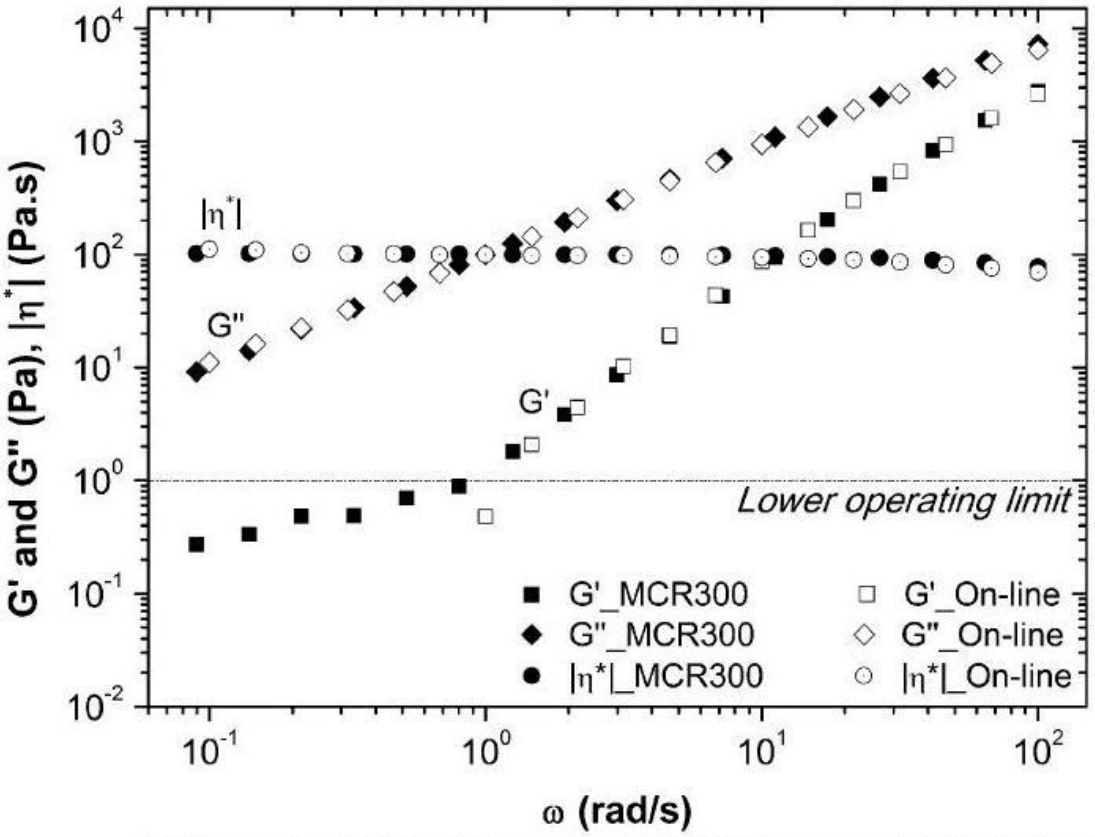
The results with the silicone oils essentially provided a mechanical validation of the set up (in terms of mechanical stiffness, motion transmission and alignment of components). The assessment at high temperatures was carried out for two polymers with good thermal stability, PS and LDPE. Also, PS has a viscosity that is quite sensitive to temperature change, while LDPE is usually a very elastic material (the grade chosen is also known as

IUPAC-X and is extensively used by the academic community for rheology studies [20,21]).

Fig. 6 compares the variation of the dynamic moduli G' of PS with changes in frequency from 0.1 to 100rad/s, at three different temperatures ($200°C, 215°C$ and $230°C$), as measured by the Anton Paar MCR 300 and by the prototype rheometer working off-line. The superposition between the two sets of curves is virtually perfect for frequencies above 1rad/s (differences of 3%). Below this threshold the differences are of the order of 11%. Figs. 7 and 8 concern the rheological behavior of LDPE. Fig. 7 contrasts the linear viscoelastic response at $180°C$ measured by the ARG2 (TA Instruments) rheometer and the prototype rheometer working off-line, while Fig. 8 compares the steady shear viscosity at the same temperature. The agreement between the data is very good throughout the frequency/shear rate. Overall, the deviation between the values measured by the two commercial rheometers and the prototype equipment is lower than 5%, which is well within the experimental error of this type of instrument.

Table 2
Materials used for on-line measurements along an extruder.

Material	Producer	Acronym	Grade	MFR/lamellar distance
Polypropylene	LyondellBasell	PP	Moplen HP500N	12 g /10 min(230°C /2.16 kg)
Polypropylene-graftedMaleic anhydride	Crompton	PP-g-MA	Polybond 3200	115 g /10min(190°C /2.16 kg)
Montmorillonite clay	Laviosa	NC	Dellite 67G	$d_{001} = 3.45$ nm


G' and G'' (Pa), |η*| (Pa.s)
ω (rad/s)
|η*|
G''
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Lower operating limit
G'_MCR300
G''_MCR300
|η*|_MCR300
G'_On-line
G''_On-line
|η*|_On-line

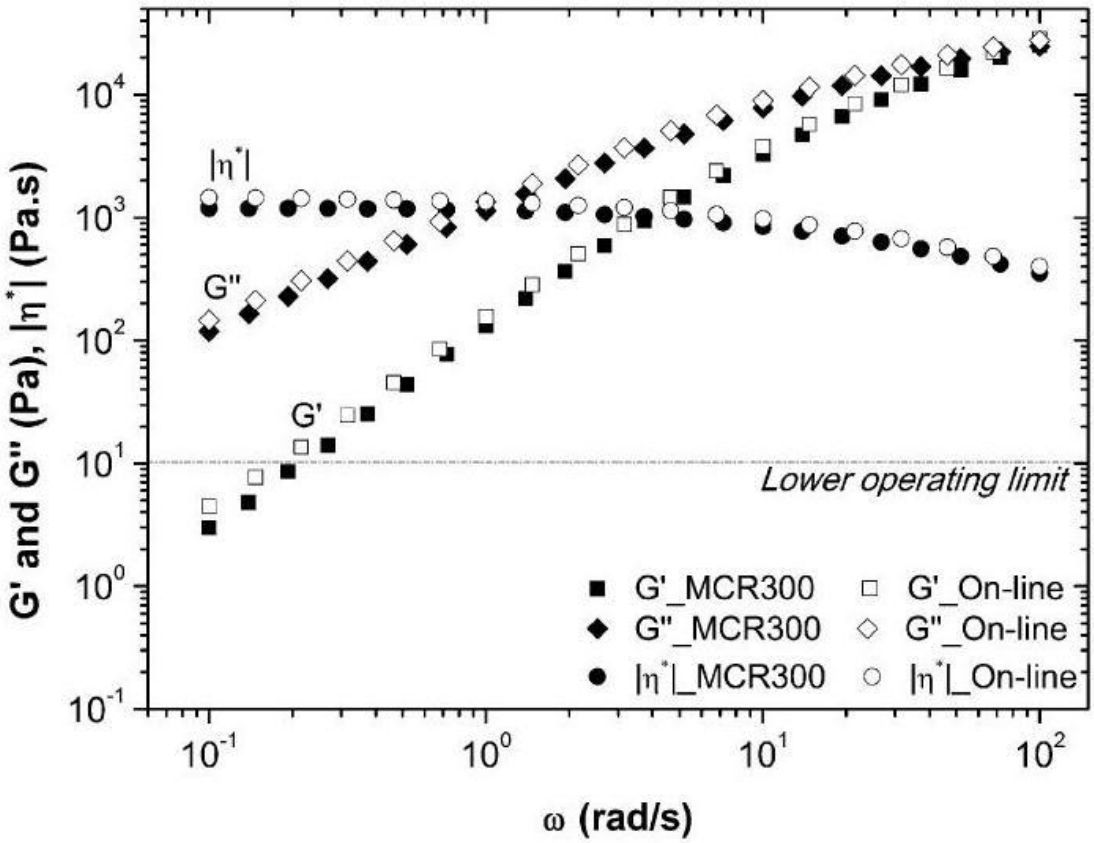

G' and G'' (Pa), |η*| (Pa.s)
ω (rad/s)
|η*|
G''
G'
Lower operating limit
G'_MCR300
G''_MCR300
|η*|_MCR300
G'_On-line
G''_On-line
|η*|_On-line

Fig. 5. Linear viscoelastic behaviour of two silicone oils at 23°C, as measured by the Anton Paar MCR 300 rheometer and prototype rheometer working off-line (top: Oil 100; bottom: Oil 1000).

On-line validation

Before proceeding with the comparison of data measured off-line (with the commercial rheometers) and on-line with the new instrument, it is worth verifying the performance of the latter in terms of its independent temperature control capability. As the equipment will be physically coupled to an extruder, it will be exposed to

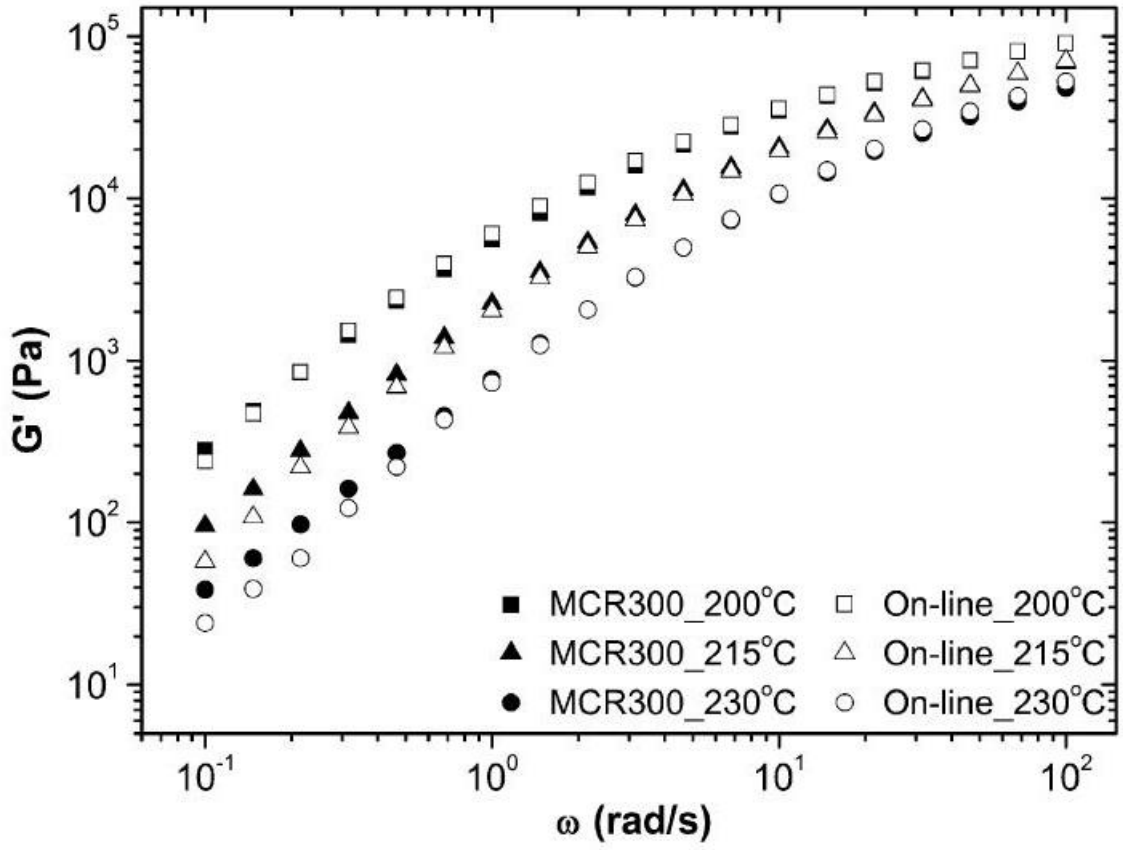


Fig. 6. Storage Modulus of PS at 200°C, 215°C and 230°C, as measure by the Anton Paar MCR 300 rheometer and prototype rheometer working off-line.

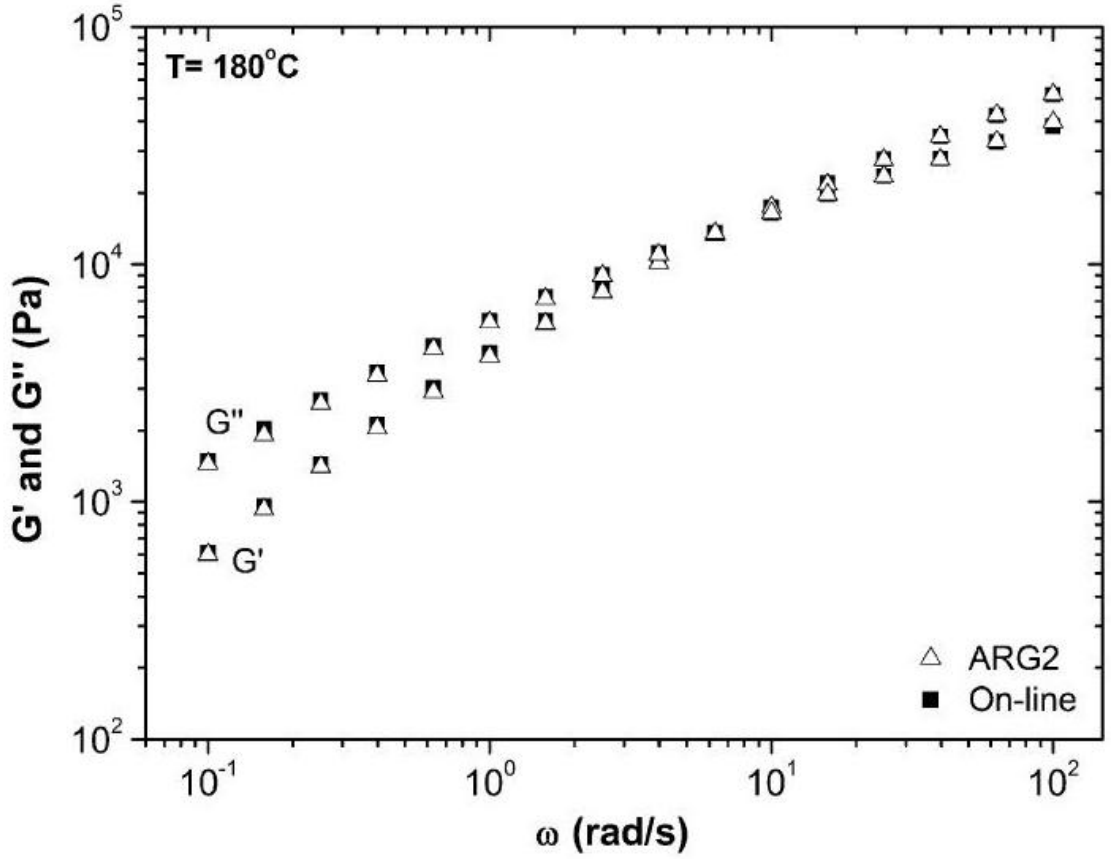


Fig. 7. Linear viscoelastic behaviour of LDPE at 180°C, as measured by the ARG2 (TA Instruments) rheometer and prototype rheometer working offline. conducted and radiated heat from the heater bands of the latter.

Fig. 9 presents the general layout of the modular Leistritz LSM 30.34 twin screw extruder used in this work, which has a L/D (length to screw diameter ratio) of 29 and a screw diameter of 30 mm , together with the screw profile utilized in the experiments, adopting the usual nomenclature to describe it. The screw comprises three mixing zones with different axial lengths, composed of staggered kneading disks and a left handed element, separated by conveying zones that will work partially filled if typical operating conditions are chosen. Melting is expected to occur immediately upstream of the first restrictive zone. Two modified barrel segments, each able to accommodate the on-line rheometer and to collect material from within the extruder from 4 distinct locations, were inserted inbetween original barrel segments, in order to become contiguous with the first two screw mixing zones (in the down channel direction). All extrusion runs reported here were performed with barrel and die set at 200°C, screws rotating at 100 rpm and a feed rate of 3 kg/h.

The response of the temperature control system of the prototype to changes in the set values is depicted in Fig. 10.

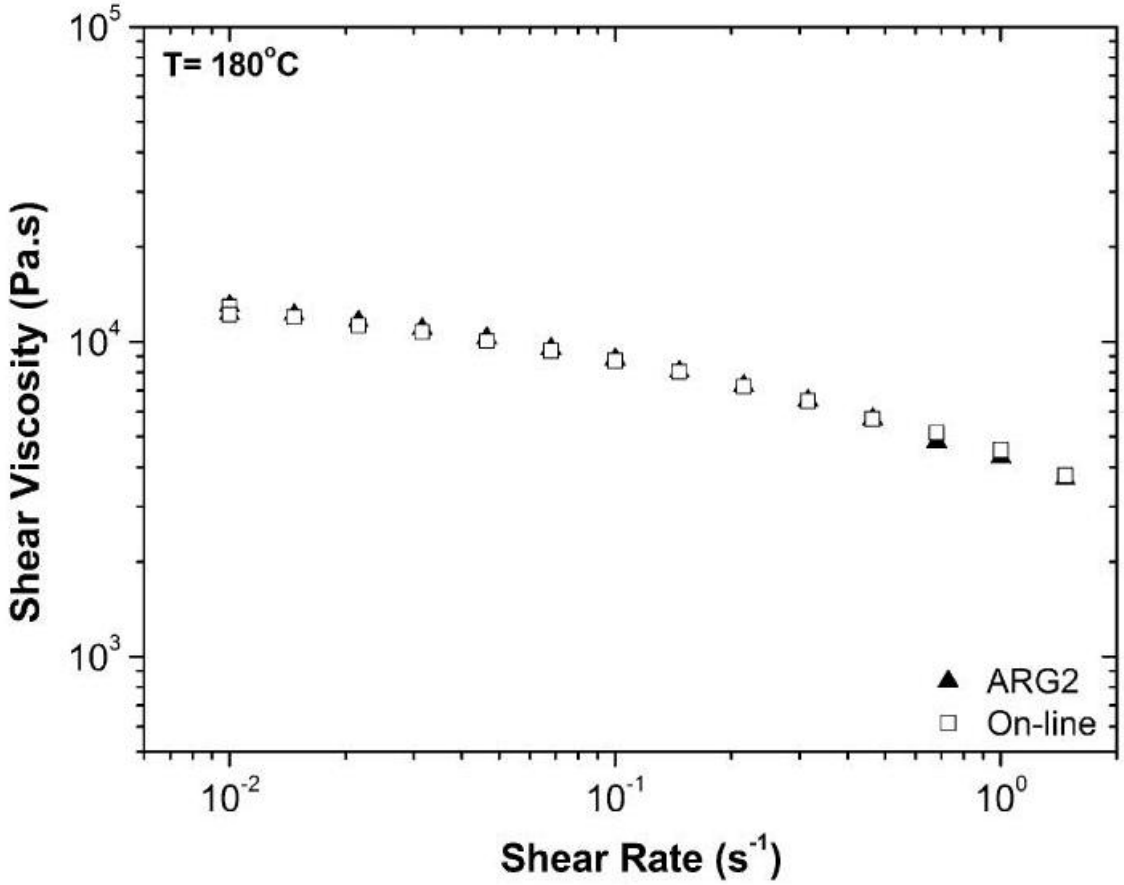
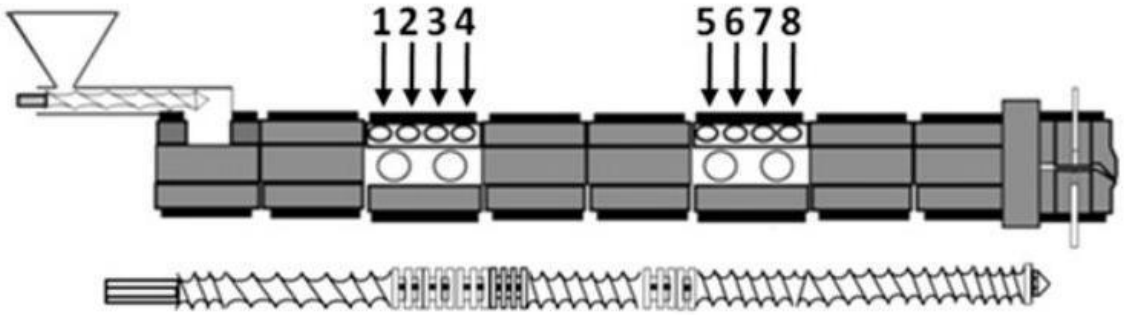


Fig. 8. Shear viscosity of LDPE at 180°C, as measured by the ARG2 (TA Instruments) rheometer and prototype rheometer working off-line.



30R2/60R/60R4/45R2/4KB+60%/5KB90%/4KB-
60%/20R4/30R/5KB90%/30R/20R4L/45R/30R4/30R2/20R2/1KB

Fig. 9. Twin screw extruder fitted with two modified barrel segments (with sampling ports) to accommodate the on-line rheometer and screw profile used in the experiments: xxRy - conveying element, where xx is the pitch (mm) and R(= 120)/y is the length (mm); LH, left handed element; xKByy - kneading block, where *x* is number of discs and yy the staggering angle (in degrees).

Initially, both extruder barrel and rheometer testing chamber were set to 220°C. As seen in the initial part of the graph, there is fine agreement between set and measured temperature. When the former was changed to 250°C, the control system acted immediately and a new stable test chamber temperature, coincident with the set value, was reached after approximately 12 min . When the set temperature was changed back to 220°C, the system took the same time to stabilize at this temperature. It is worth noting that these experiments were made with an empty rheometer, thus facing the thermal resistance of the air. As discussed above, the time required for melt temperature stabilization prior to a rheological measurement depends basically on the difference between the inlet melt temperature and the test temperature. The former can be higher than expected due to the role of viscous dissipation in twin screw extruders. Using a 1 mm gap between plates, experiments with the original version of the on-line rheometer showed that, generally, stabilization time lasts around 20 and 50 s for temperature differences of 20 and 60°C, respectively, when testing PP and HDPE melts [4].

Fig. 13 compares the linear viscoelastic response (G' and G'') of PP at 200°C, as measured both off-line and on-line at sampling ports 3 and 5 (see Fig. 9). The differences between the two measurements are of the order of 21% and 19% at locations 3 and 5 respectively, which is significant. Off-line measurements require the following sequence: i) collect a sample from the same barrel location of the on-line measurement and quench it in liquid nitrogen; ii)

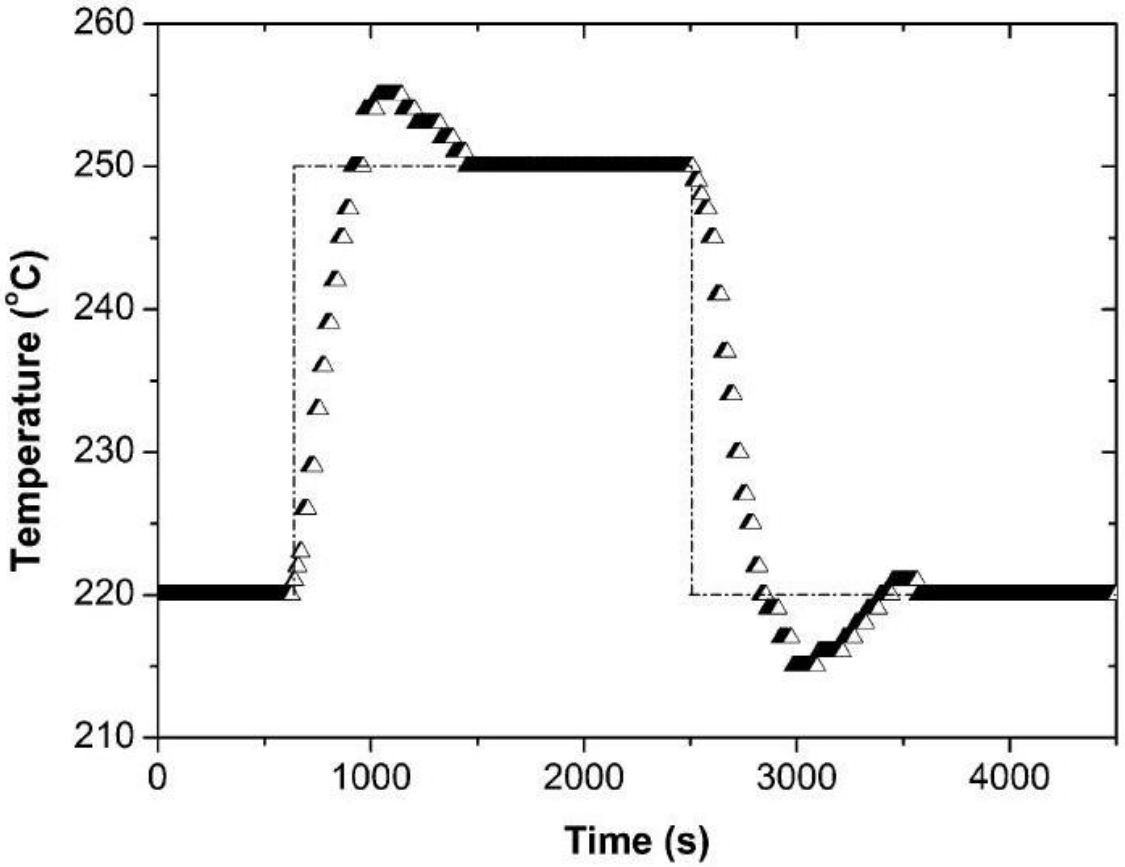


Fig. 10. Response of the temperature control system of the prototype to changes in the set temperature.

manufacture a disk (thickness of 1 mm , diameter of 20 mm) by compression molding; iii) position, re-heat and test the disk in the ARG2. These thermal cycles favor degradation, hence it is probably not a coincidence that the moduli measured on-line are a little higher than those measured off-line. In fact, the absence of a process stabilizer makes PP prone to thermo-oxidative degradation [2,22]. When the contrast between off-line and on-line measurements at the same locations are made for the PP/PP-g-MA system (same PP and 5% in weight of PP-g-MA), better agreement is obtained, as seen in Fig. 12. In fact, the differences reduce now to approximately 6.5% and 13% at sampling ports 3 and 5 respectively, i.e., comparable to those observed for the high-temperature off-line validation. PP/PP-g-MA being more thermally stable than PP, these results provide evidence that the poor mismatch between off-line and online measurements for PP is due to its thermal degradation.

On-line measurements along the axis of an extruder

As a demonstration of the usefulness and aptitude of the new on-line instrument, results of measurements made along the screw axis for three different, although related, polymer systems are presented and discussed.

Fig. 13 depicts the variation of G' and G'' with frequency for PP (same material as in Fig. 11) at axial positions 3, 5 and 7 (Fig. 9). The slight, although progressive, decrease of the moduli along the extruder referred above is now clearer.

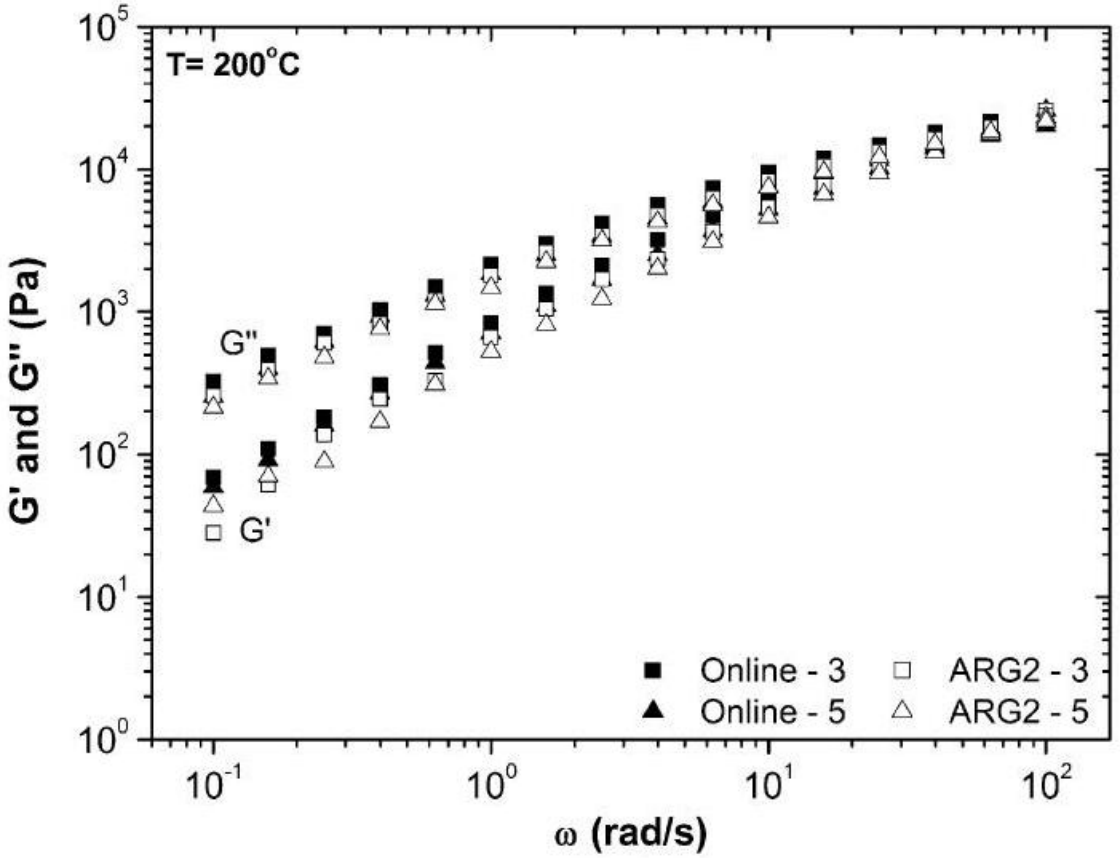


Fig. 11. Linear viscoelastic behaviour of PP at 200°C, as measured by the ARG2 (TA Instruments) and on-line rheometers at sampling ports 3 and 5.

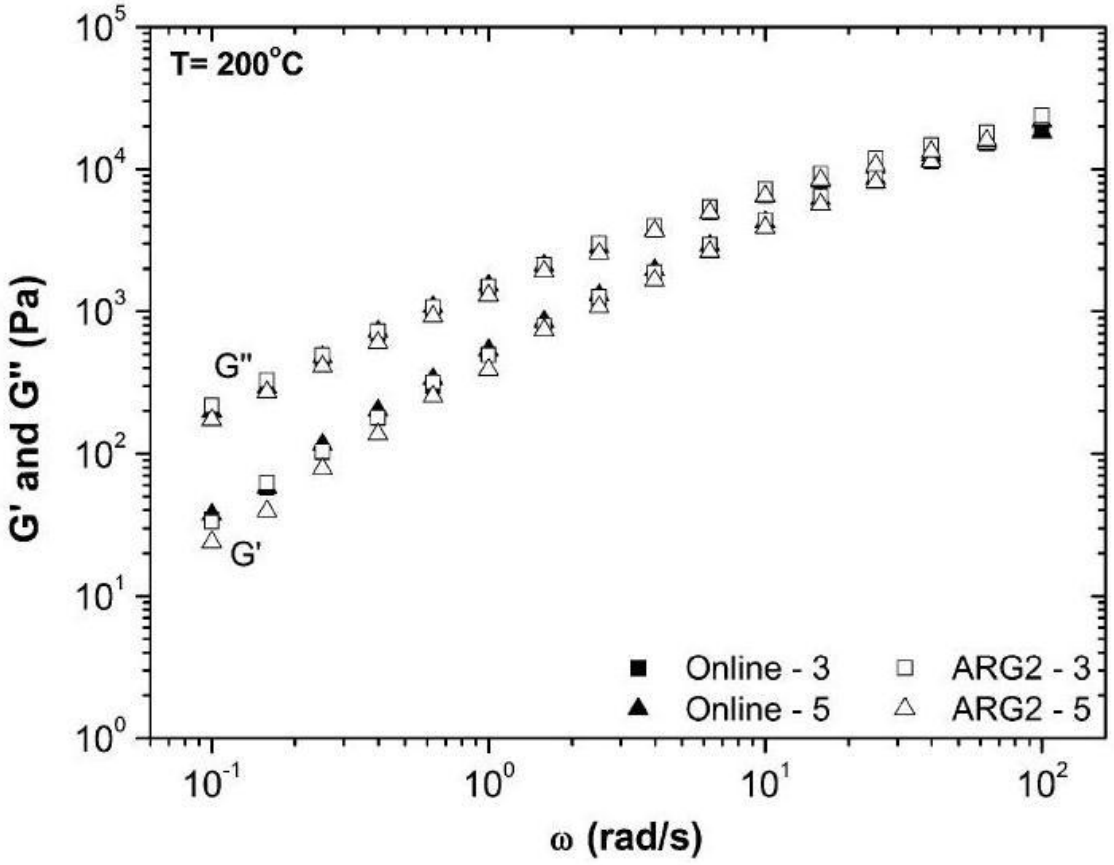


Fig. 12. Linear viscoelastic behaviour of PP/PP − g − MA at 200°C, as measured by the ARG2 (TA Instruments) and on-line rheometers at sampling ports 3 and 5.

This behavior has been observed before [2], thus stressing again the benefit of using process stabilizers with this polymer.

PP grafted with maleic anhydride (PP-g-MA) is often used for in-situ compatibilization of polymer blends, as adhesive for multilayer systems, or as coupling agent for glass fibers and fillers [22,23]. In relation to plain PP, a decrease of the rheological moduli is anticipated, due to chain scission during grafting of MA groups onto the polymer backbone [22,24]. The rheological response of this system is pictured in Fig. 14. Comparison with Fig. 13 confirms the shift of the curves to lower moduli values and the better thermal stability.

In a third extrusion step, the PP/PP-g-MA system was compounded with 8.8%w/w of a montmorillonite organoclay, in order to produce a nanocomposite (a true nanocomposite is obtained when sufficient clay intercalation and clay exfoliation are achieved). The rheological curves of Fig. 15 were obtained for a constant strain of 0.1%, in order to ensure that the response would stay within the linear viscoelastic regime. The results present a number of interesting features:

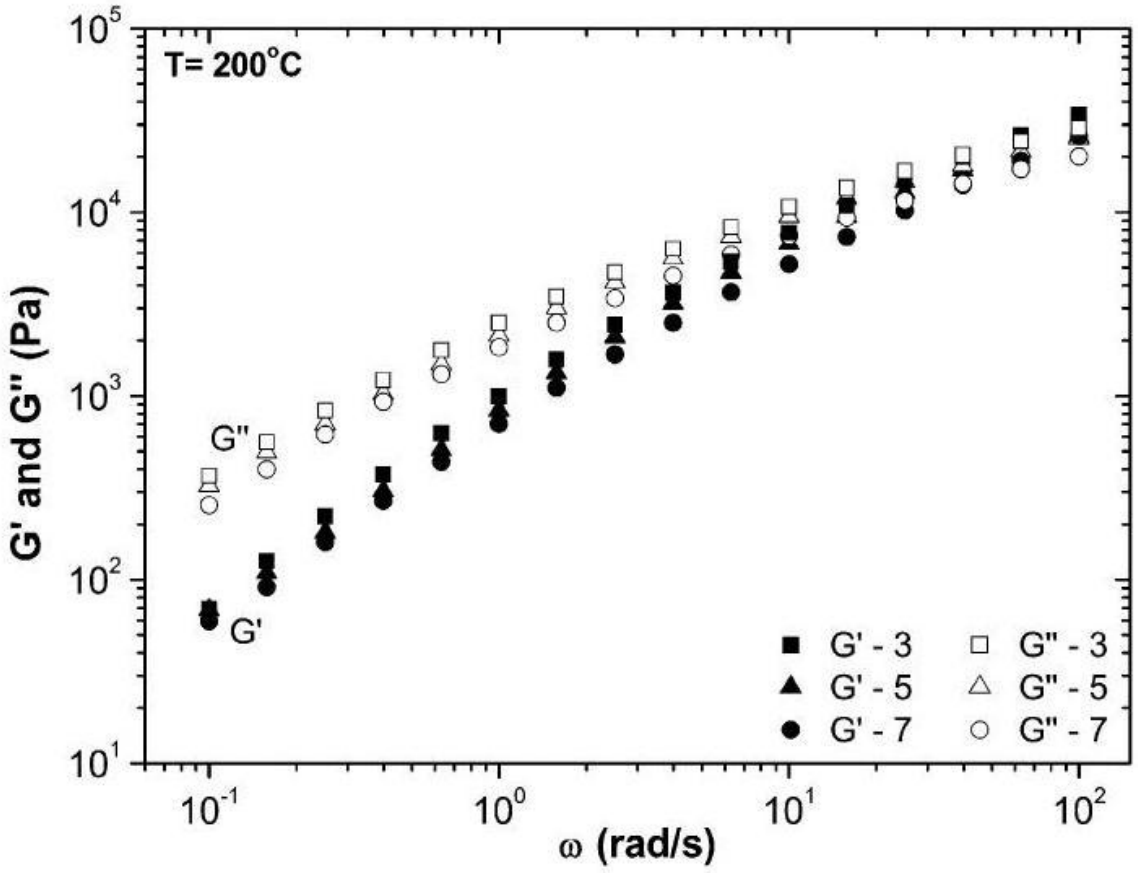


Fig. 13. Linear viscoelastic behaviour of PP at 200°C, as measured on-line.

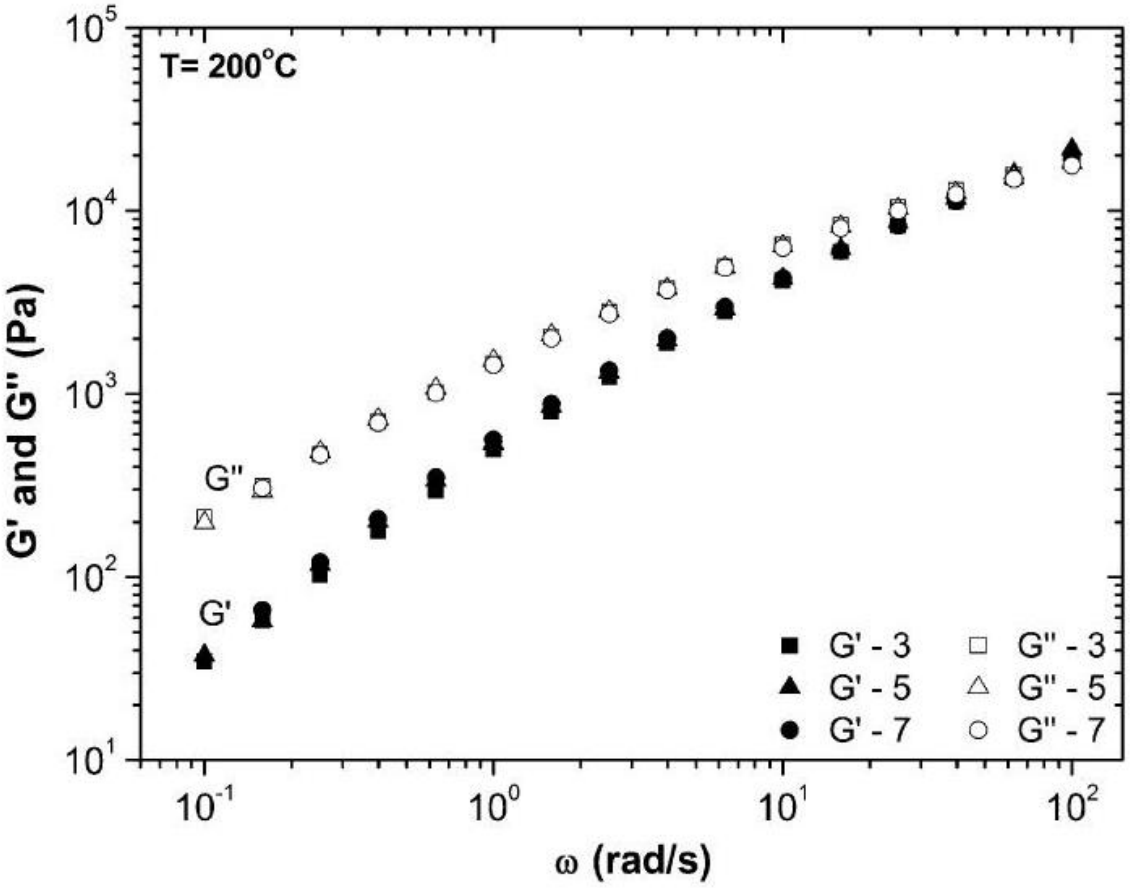


Fig. 14. Linear viscoelastic behaviour of PP/PP – g – MA at 200°C, as measured on-line.

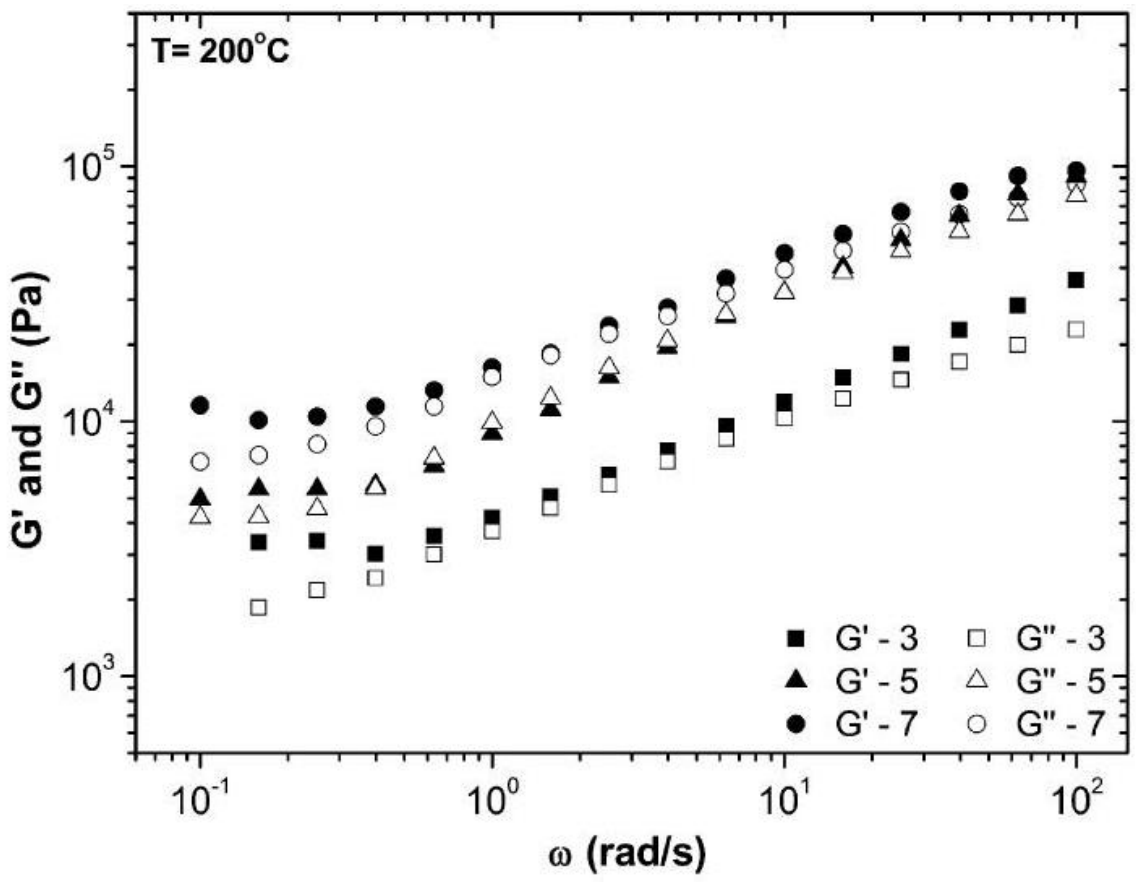


Fig. 15. Linear viscoelastic behaviour of PP/PP – g – MA/NC at 200 °C, as measured on-line.

- as expected, the presence of the clay shifts the curves to higher moduli values (near one order of magnitude relative to plain PP);
- while for molten PP, $G'' > G'$ over most of the frequency range (see Fig. 13), elasticity increases for the composite (both moduli have similar values);
- G′ seems to level-off at frequencies below 0.4 s^{-1}, which is usually attributed to the deformation and recovery of the dispersed filler [25-28];
- evolution along the barrel is clearly observed. Since, in principle, at constant clay content, the finer the dispersion the higher the moduli [3], the gradual increase in the moduli values should be due to progressively higher dispersion levels as the material flows through successive mixing zones.

Conclusions

An on-line rotational rheometer was designed to collect melt samples at specific locations along the barrel of an extruder and characterize them either in steady shear or oscillatory modes. Operation of the instrument is controlled and assisted by motion control software specifically developed for this purpose and by the RheoPlus software from

Anton Paar, which is associated with the DRS 301 measuring head produced by the same manufacturer.

Validation of the measurements performed by this device was made by direct comparison with similar measurements carried out by commercial bench top rheometers, including off-line measurements at room temperature with two silicone oils of known viscosity, offline measurements at high-temperature using two polymers and on-line measurements with one polymer. In all cases, the agreement between the two sets of data was quite good. Thus, the validation step was considered as successful.

The instrument was then used to monitor the evolution of the rheological behavior of three polymer systems along the axis of a twin screw extruder. The results again evidenced the sensitivity and reliability of the apparatus and were in line with observations reported in the literature.

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