On-line rotational rheometry for extrusion and compounding operations

J.A. Covas*, J.M. Maia, A.V. Machado, P. Costa

Institute for Polymers and Composites (IPC), Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

Abstract

The challenges polymer processing and compounding face nowadays are related not only with the design and control of more efficient equipment but also with the intelligent manipulation of the molecular structure of the materials with a view to obtaining better performing products. Of obvious importance in both cases is the possibility of performing in-/on-line measurements of relevant material properties during processing. Current online rheological measurements are mostly performed at the end of the extruder, after diverting a small amount of melt from the main stream. Although useful from a quality control point-of-view, process optimisation would require the availability of data upstream, where a plethora of physico-chemical phenomena (chemical reactions, physical blending, degradation, etc.) determine the final characteristics of the materials.

In this paper, a new on-line rotational rheometer that allows the rheological properties of materials to be monitored as they are being processed in an extruder is presented. The instrument enables such important phenomena as morphology development or reaction kinetics to be followed from changes in the rheological responses measured along the screw axis.

Keywords: On-line rheometry; Materials processing; Blending; Reactive extrusion

Introduction

The objective of on-line rheometry is to characterise a rheological behaviour of a material during its processing in an industrial environment. The data thus obtained can be used to monitor the process with a view either to optimize material recipes, operating conditions or geometrical features or for automatic quality control purposes [1]. For example, in the case of reactive extrusion operations it is crucial to make measurements that are sensitive to morphological evolution (e.g., average size of the dispersed phase in polymer blends), chemical conversion (e.g., during in situ compatibilisation of reactive systems) and

thermal-mechanical history (e.g., degradation of the polymer matrix). During the preparation of composites, nanocomposites or conventional polymer compounds, changes in rheological parameters can provide an insight into (distributive and dispersive) mixing mechanisms.

The majority of on-line systems developed thus far resorts to capillary or slit rheometers that, once inserted between extruder and die, are fed by a secondary flow bypassed from the extruder and by a gear pump, which determines the flow rate into the

metering zone (see, for example [2,3]). One of the exceptions is the "partial Couette" geometry proposed by Dealy, which could be integrated in the die [4]. The main limitations of that type of rheometers include: (i) the time-lag in the measurements, that are only possible after the melt flows in the bypass, (ii) the destructive nature of the test, i.e., the morphology of the material at the detouring point may be changed by the test and (iii) the required location between extruder and die where, under normal conditions, the morphology or chemical reaction will have already achieved steady-state or been completed. As a consequence, the available instruments have revealed to be useful for process quality control, but not for tracking the evolution of properties/characteristics along the extruder.

Recently, a system was developed that adapted a capillary rheometry geometry [5] to sample-collecting devices [6]. This overcame the first and third of the above shortcomings, since the material to be characterised is quickly removed from the extruder and placed in the measuring system, which, in turn, can be fixed at any location along the extruder. The apparatus was used successfully to monitor on-line the peroxide-induced degradation of polypropylene and the preparation of short carbon fibre-reinforced composites [7-9].

The present work refers to an apparatus (designated as O2R) that can be coupled to the motion and measuring head of a commercial rotational rheometer [10], in this case a Paar Physica MCR 150, and allows the non-destructive measurement of rheological properties during extrusion, thus overcoming the second shortcoming above. The rheometer induces the strain and measures the corresponding torque, or vice versa, of samples removed locally from the extruder along its length, in either a parallel-plate or a cone-and-plate geometry. In addition, it is possible to use the software of the instrument, which is capable of calculating automatically the variation of the rheological response as a function of shear strain/stress, to measure other material functions, such as those in small-amplitude oscillatory shear.

Equipment and experimental validation

Equipment description and operation

Fig. 1a illustrates the main parts of the new instrument. The measuring section, fixed in the vicinity of the extruder (a detailed view is depicted in Fig. 1b), is coupled on top to the head of a rotational rheometer via an adapter and on the bottom to an adjusting

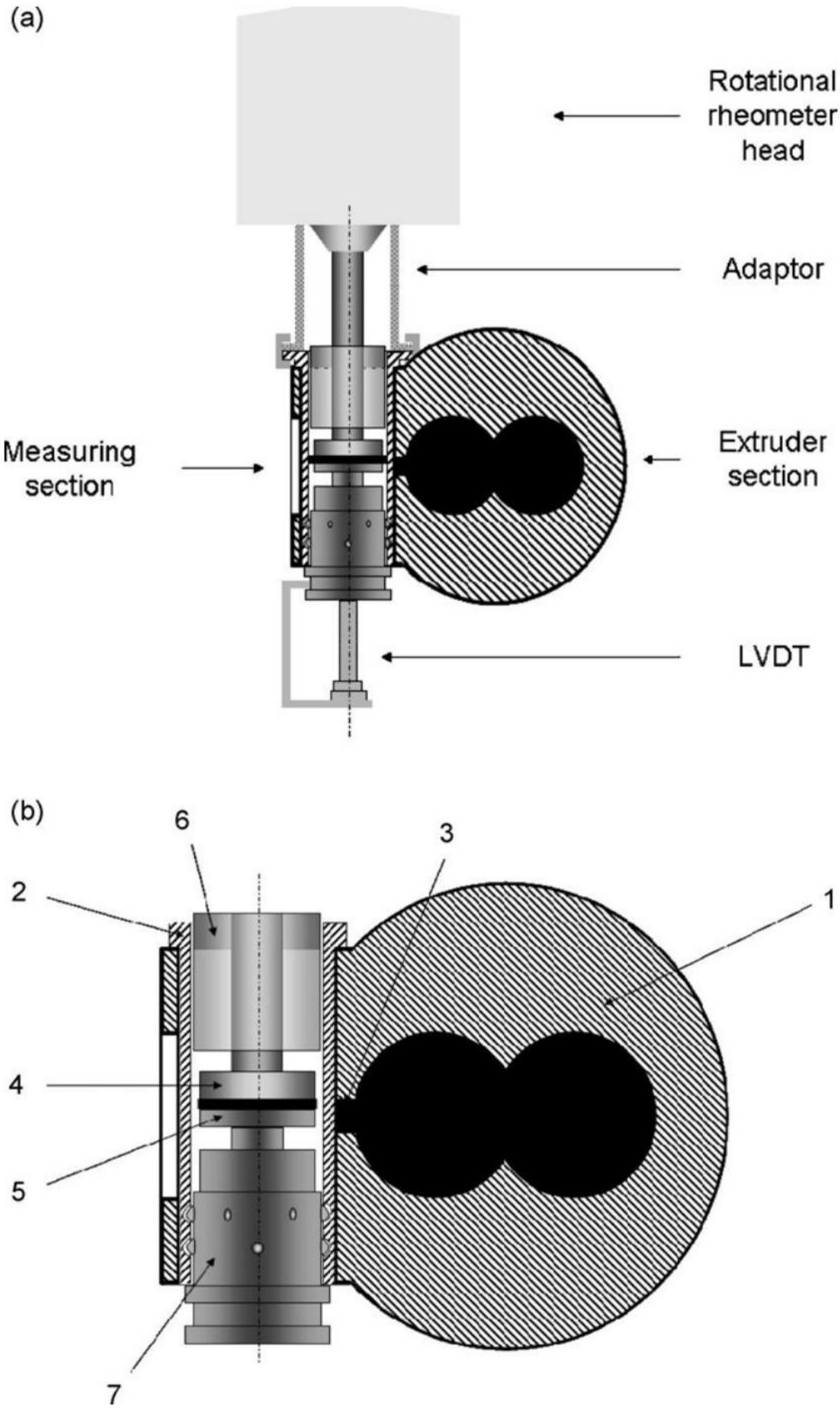
(a)
Rotational rheometer head
Adaptor
Measuring section
Extruder section
LVDT
(b)
6
3
2
1
4
5
7

Fig. 1. General overview of the on-line rotational rheometer, O2R.
system comprising a LVDT (Linear Variable Differential Transformer) displacement transducer. As shown in Fig. 1b, which schematizes the measuring segment of the new apparatus, this is introduced vertically in the corresponding cavity of an insert of the extruder barrel (1), which is an integral part of this invention. Taking advantage of the modular construction of many commercial twin screw extruders, this insert is fixed between any two adjacent extruder barrel segments. Obviously, if several O2R instruments are available, rheological measurements can be performed simultaneously at several locations along the extruder axis.

The short horizontal orifice (3) allows pressure flow of material from the extruder to the rheometer to take place. This is more efficient when the screw channels work fully filled, i.e., when the insert is located next to staggered kneading disks and/or left hand elements of intermeshing co-rotating twin screw extruders, where, in fact, most of the mixing, morphology evolution and chemical conversion take place [11]. Conversely, if the device is to be applied to a single screw extruder, pressure is always positive along the screw (this will not be dealt with in the present work).

The main body (2) of the device has a few important features: (i) its shape guarantees the vertical immobilisation of the whole instrument; (ii) it is hollow, hosting inside it the measuring geometry (4,5) and a cleaning ring (6); (iii) it contains two opposite orifices- when one of them is in line with orifice (3) it allows the intake of material from the extruder, excess material being purged through the opposite hole; (iv) its temperature is controlled by means of an internal coiled heat resistance. Therefore, the body (2) is rotated for material intake and again rotated for interruption of this operation. Measurements or maintenance/cleaning operations can be performed during conventional extruder operation.

The upper plate/cone (4) is coupled directly to the rheometer shaft. The lower plate (5) has two possible movements: (a) pulling part (7) downwards until it immobilizes in a lower position - determined by the action of various stoppers - opens a gap that is adequate for material loading from the extruder, while pushing it again upwards reverts to the initial position where it remains fixed by a similar system; (b) although not represented in Fig. 1b, it is possible to vary the gap by means of an adjustable micrometric screw, which is fixed to one of the ends of the LVDT. The eventual rotation of (4) or (5) due to viscous drag has also been prevented mechanically.

When the gap is fixed and the material is loaded, vertical sliding of ring (6) by means of a lever ensures a smooth material free surface.

The gap that will be used during the measurement(s) must be set before insertion of the measuring section in the extruder barrel. In order to do so, the lower plate is positioned in its upper point and the gap adjusting screw is tightened until the two plates touch each other. Then, the screw is unscrewed slowly until the LVDT sensor indicates the intended gap.

Fig. 2 illustrates the main steps during an operating sequence of the new instrument. First, material must be collected from the extruder. Thus, Fig. 2a shows the two plates pulled apart and the instrument's main body in a position that enables material flow

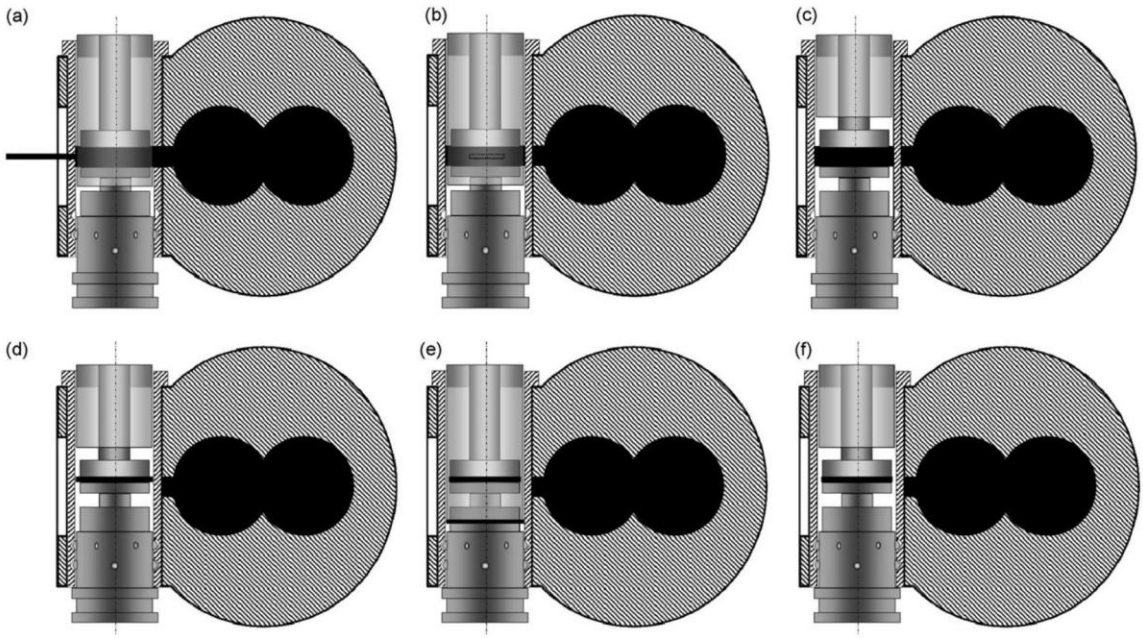

Fig. 2. Operating sequence: (a) initial position; (b) material inflow; (c) gap setting and excess material removal; (d) operation.
from the extruder. Additionally, the cleaning ring is placed at its lower position. When the rheometer is fully filled, overflow is observable through the corresponding hole and the main body must be again rotated to isolate the rheometer from the extruder. This step is shown in Fig. 2b. Obviously, the remaining steps are performed while the extruder is working under conventional conditions.

Fig. 2c-e display the sample preparation stage. The cleaning ring is moved up (Fig. 2c) to generate an open volume and the lower plate is pushed to the upper operating spot, thus defining the pre-set gap (Fig. 2d). Material will obviously emerge from between the plates. Thus, the cleaning ring is moved successively up and down (Fig. 2e) in order to remove the excess material in the free surface of the sample (which will then accumulate below the bottom plate). The material is left to equilibrate thermally (its temperature being monitored by a thermocouple mounted locally). A measurement can then be performed (Fig. 2f) by imposing a rotation/oscillation of the upper plate/cone at different shear rates/stresses and measuring the corresponding shear stresses/rates. Once the experiment is finished, the whole upper geometry is removed from the top and the lower one from the bottom of the main body, which remains in place in order to guarantee the continuation of normal extrusion.

Materials and operating conditions

In order to validate and perform a preliminary exploration of the O2R concept, several materials were used, as summarized in Table 1. The work was then split into several stages:
(a) Determination of sensitivity limits of the O2R. In this case, two low-viscosity silicone oils from Wacker, dubbed Oil

1 and Oil 2 (differing in molecular weight) were tested at 23°C.
(b) Low-temperature off-line validation. Here, a polyisobutylene, dubbed PIB, from BASF was used, also at 23°C.
(c) Temperature stabilisation. Two polymers were used. A polypropylene, PP, was

extruded using a uniform set temperature of 210°C, while a high-density polyethylene, HDPE, was processed at 230°C.
(d) High-temperature validation. Off- and on-line validation were performed using: (i) a material, polystyrene, dubbed PS, with high activation energy, i.e., whose viscosity is very

Table 1
Materials used and their characteristics

Designation	Material	Producer	Grade
Homopolymers			
Oil 1	Silicone oil	Wacker	AK 300000
Oil 2	Silicone oil	Wacker	AK 100000
PIB	Polyisobutylene	BASF	Oppanol B12
PP	Polypropylene	Targor	Novolen 2150 H
HDPE	High-density polyethylene	Borealis	HE 6914
PS	Polystyrene	EniChem	Edistir N 2560
LDPE	Low-density polyethylene	Borealis	FA 7234

Designation	Composition	w/w (%)
Blends		
Blend 1	Polyamide 6/polyethylene-grafted-maleic anhydride (PA6/PE-g-MA)	80/20
Blend-NC	Polyamide 6/low density polyethylene (PA6/LDPE)	70/30
Blend-C	Polyamide 6/low density polyethylene/maleic anhydride-grafted-polyethylene (PA6/PE/PE-g-MA)	70/15/15

sensitive to temperature changes, (ii) a very elastic material, low-density polyethylene, LDPE, and (iii) a multiphase material, a compatibilised polymer blend, dubbed Blend 1. For PS, experiments were performed at 170°C, 190°C (reference temperature) and 210°C and for LDPE at 160°C (reference temperature), 180 and 200°C. In both cases, time-temperature superposition was used to build master curves at the reference temperatures. For Blend 1, the test temperature was 275°C.
(e) Testing of complex multiphase systems. Two different materials were used, a non-compatibilised, immiscible polymer blend, dubbed Blend-NC, and the equivalent compatibilised counterpart, dubbed Blend-C. In both cases the test temperature was 260°C. The experiments consisted in performing small-amplitude oscillatory shear experiments on-line with the O2R at several locations along the extruder barrel and compare the results with those obtained from the same type of tests performed off-line in a Paar Physica MCR 300 rheometer on samples collected on-line at the same locations using specially designed sampling devices [5]. The second set of samples was subjected to

two extra thermal cycles: one upon compression moulding to manufacture the test disks and another in the rheometer as the temperature was again increased.

In general, the region of linear viscoelastic response was determined off-line in the MCR 300 in a parallel-plate configuration ($\phi = 25$ mm) prior to performing the actual off- and on-line frequency sweeps. The results obtained with the O2R were compared to those obtained in the MCR 300 and a Reologica StressTech HR in a parallel-plate configuration with plate radii of 10 mm . In all cases (O2R, MCR 300 and StressTech), the gap used was 0.8 mm .

Off-line validation

The initial off-line validation of the O2R was performed at room temperature, i.e., $23°C$, in two steps: determination of sensitivity limits and comparison with measurements performed with a Paar Physica MCR 300 rheometer.

Fig. 3 shows data for two low-viscosity silicone oils tested in oscillatory shear in both instruments. The results of both rheometers are in good agreement above moduli values of $10 - 20$ Pa, with an average deviation of 9% in G'' and 12% in G' for Oil 1 (with the lowest viscosity) and 4% in G'' and 7% in G' for Oil 2. Below this threshold, the data from the O2R is significantly higher than that of the MCR due to friction effects and, as such, this must be considered the lower operational limit of the O2R.

As would be expected, this discrepancy tends to become smaller as the viscosity of the fluids increases, as can be demonstrated in Fig. 4, where a comparison between the O2R and the MCR data is shown for a high-viscosity PIB. The average deviations are lower than 3% in both G' and G'', which is well within the typical experimental error in these instruments.

On-line validation

Viscous heating during extrusion or compounding of high molecular weight polymers or matrices can yield significant increases of melt temperatures particularly in regions with high flow velocities (e.g., shallow channels, barrier sections), or with intense mechanical action (e.g., kneading blocks). True melt temperatures can reach values up to several tens of degrees higher than the barrel set values [12].

Since the O2R was designed to work on-line during extrusion, it is essential to know the required time to temperature stabilisation, i.e., the time that must elapse between sample col-

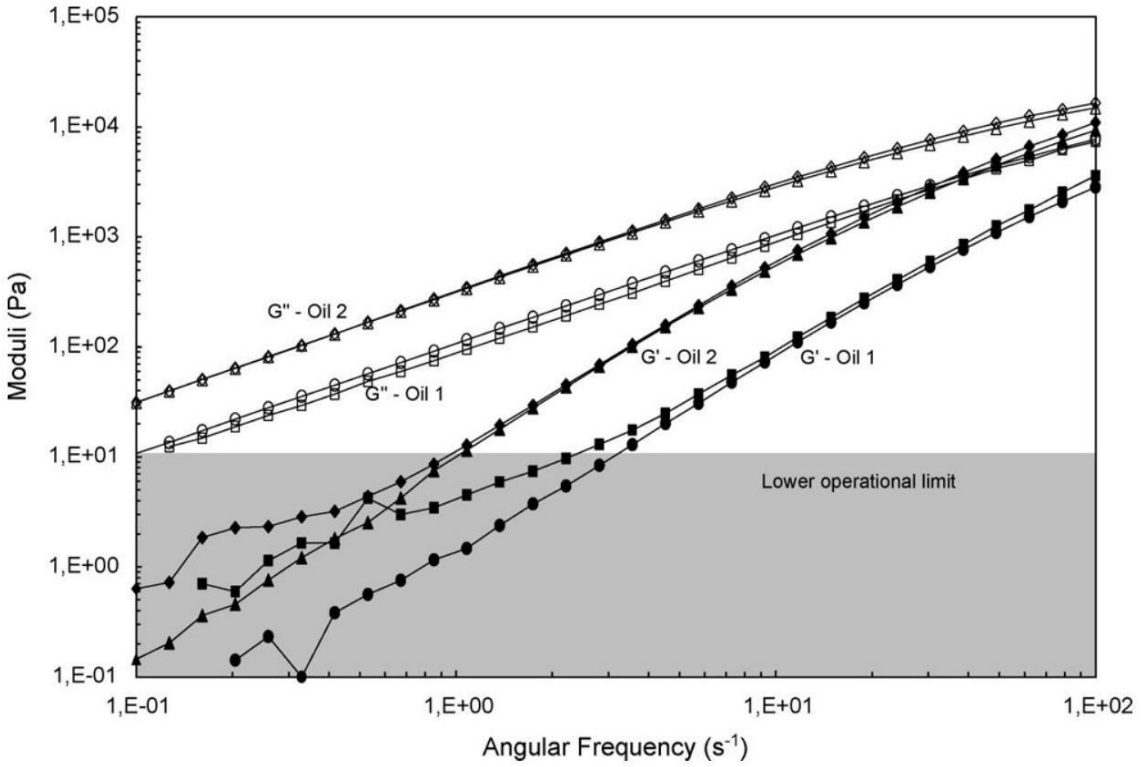

Fig. 3. Linear viscoelasticity results for two silicone oils at 23°C and rheometers (closed symbols-G'; open symbols-G"): (•) Oil 1/Paar Physica MCR 300; (■) Oil 1/O2R; (**Δ**) Oil 1/Paar Physica MCR 300; (( ) Oil 2/O2R.

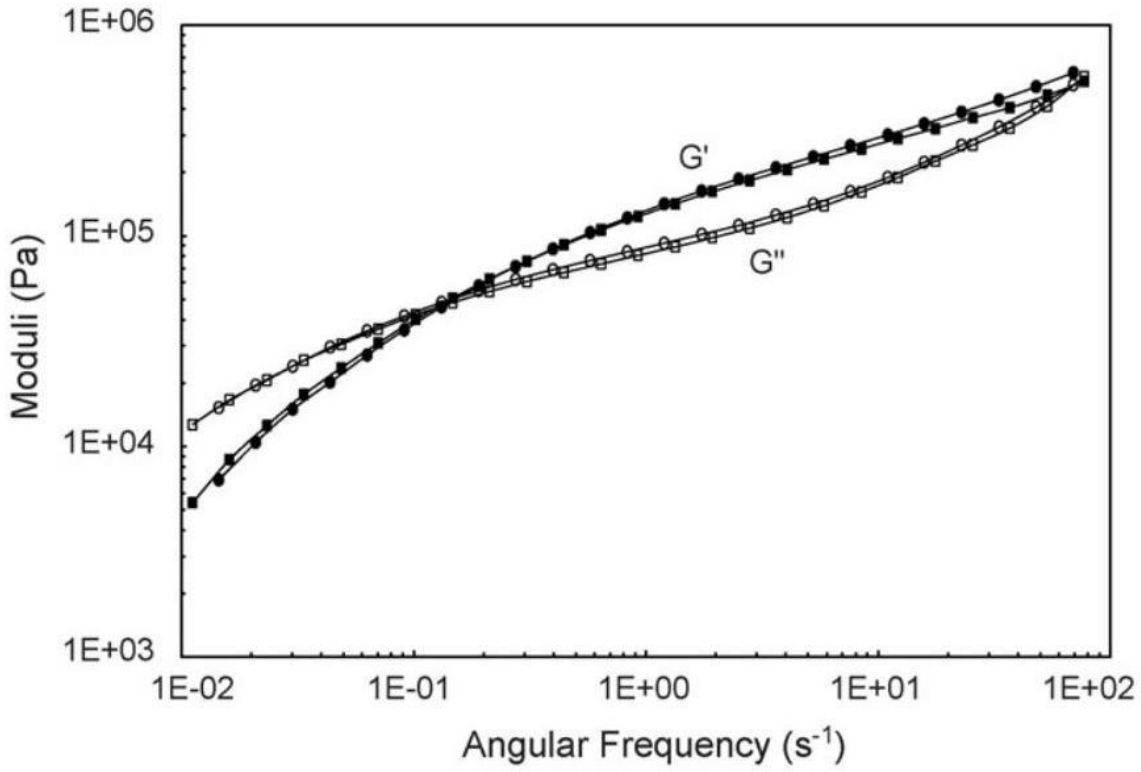

Fig. 4. Linear viscoelasticity results for PIB at 23°C and two different rheometers: (•) Paar Physica MCR 300 and (■) O2R.

lection and stabilisation at the desired test temperature in the rheometer. Thus, experiments were performed on two common high molecular weight linear polymers (see Table 1). Polypropylene was extruded at 210°C, while a high-density polyethylene was extruded at 230°C. In both cases, the O2R was placed at several locations along the barrel, the test temperature was set to 200°C and the true melt temperature evolution in time inside the O2R measured by resorting to a fast response thermocouple in contact with the material sample. The extruder set-up, including the various locations of the O2R and the results are depicted in Fig. 5a-c..

The results for PP (Fig. 5b) evidence that despite the flat barrel temperature profile, the true melt temperature changes significantly as the material moves downstream inside the extruder, its value depending on the geometry of the various restrictive elements that it must cross. Under these conditions, it takes the polymer a maximum of approximately 25 s to reach the set test temperature of 200°C. Fig. 5c shows a more severe situation, in that the maximum true melt temperature is almost 70°C above the test temperature and even in this case stabilisation is achieved in less than 1 min . Values for locations V1 and V2 were not included, since with the output and screw speed conditions chosen, at this place the screws worked partially filled only, hence there was no pressure for efficient material collection. In view of these results, all the subsequent high-temperature on-line experiments were performed with a 1 min stabilisation period in the O2R after sample collection and before running an experiment. In certain systems, such as immiscible polymer blends, it

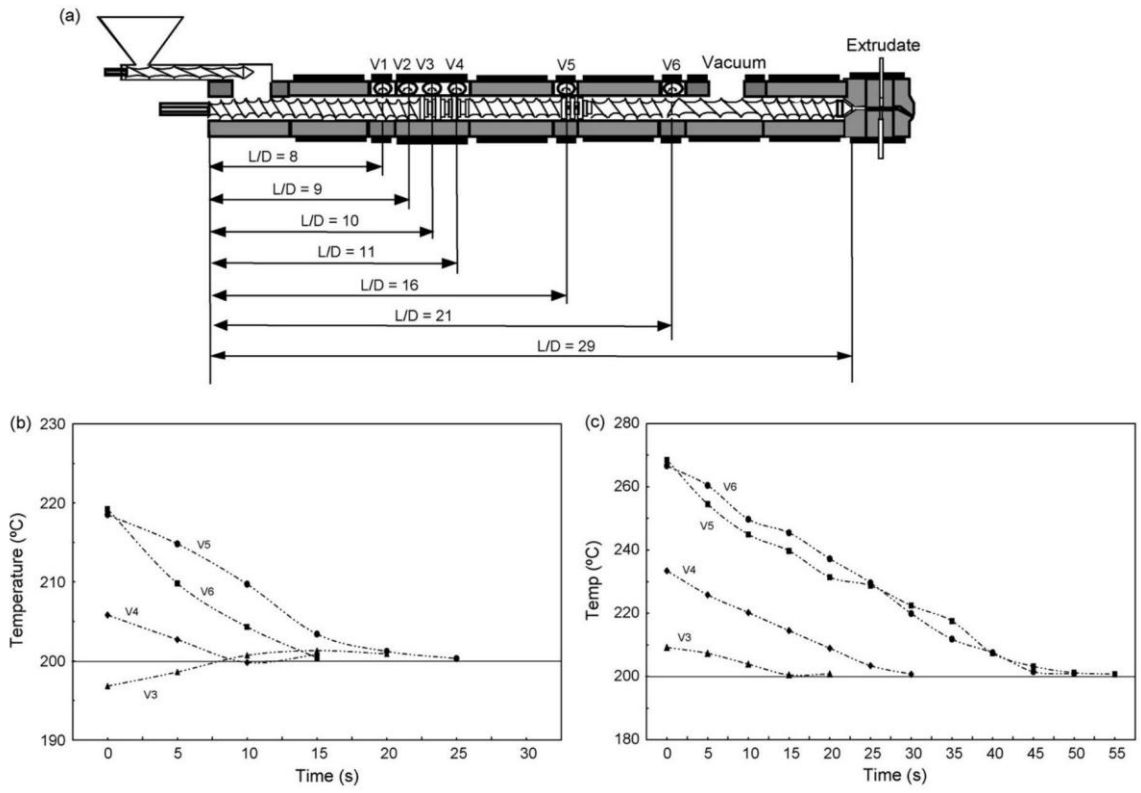

Fig. 5. Stabilisation time to 200°C for two different polymer melts along the extruder: (a) extruder set-up and O2R locations; (b) results for PP (processing temperature of 210°C); (c) results for HDPE (processing temperature of 230°C).

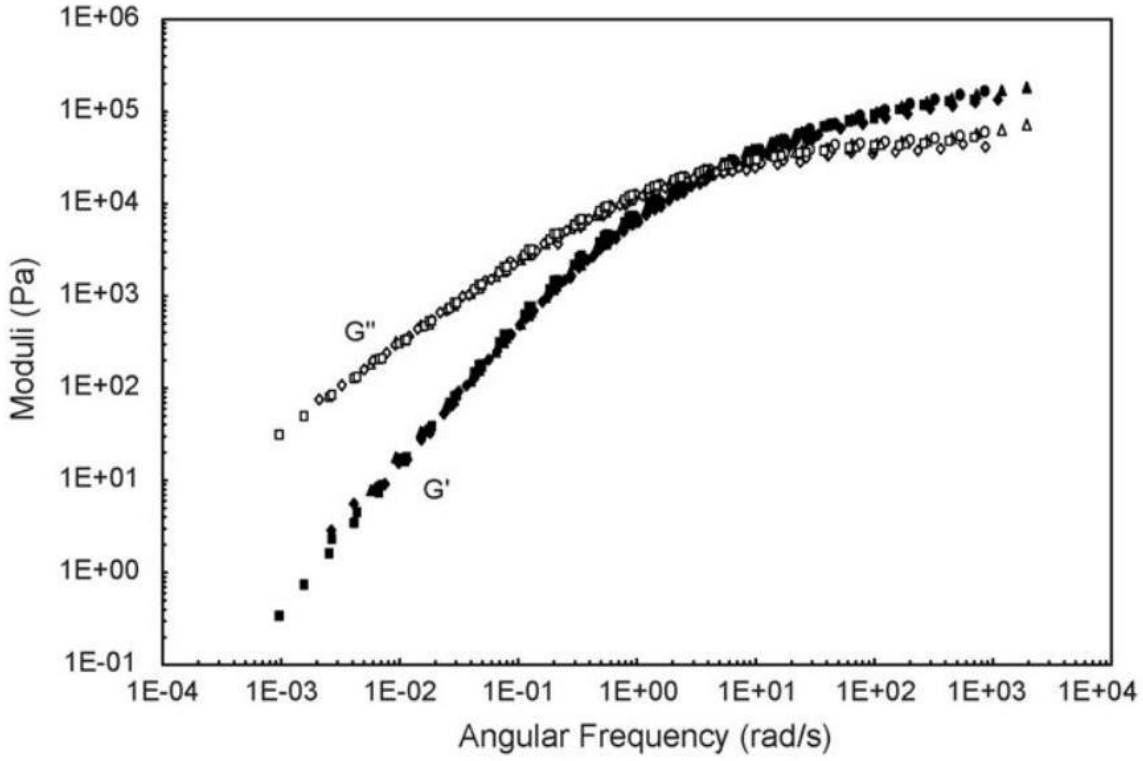

Fig. 6. Linear viscoelasticity results for PS at a reference temperature of 190°C (experiments were performed at 170,190 and 210°C and time-temperature superposition applied) and three different rheometers: (■) Paar Physica MCR 300; (**Δ**) Reologica StressTech HR; (**Δ**) O2R off-line; (·) O2R on-line.
is worth optimizing this stabilisation time if phenomena such as coalescence of the dispersed phase are to be minimised. Conversely, it seems that for various reactive systems the extent of the stabilisation period could be less important, since the absence of flow (and corresponding generation of interfacial area) hinders the progress of undergoing chemical reactions [13].

Figs. 6 and 7 compare data obtained off-line with the MCR, the StressTech HR and the O2R with that obtained on-line with the O2R, for PS and LDPE, respectively. Again, there is excellent agreement between both the off- and on-line results for the O2R and the data from the two commercial rheometers, with the average deviations well within the experimental error (approximately 4-6%, depending on the instrument).

The final step of the on-line validation consisted in testing a multiphase system, specifically a compatibilised polymer blend (Blend 1 in Table 1), against the results from the MCR. As

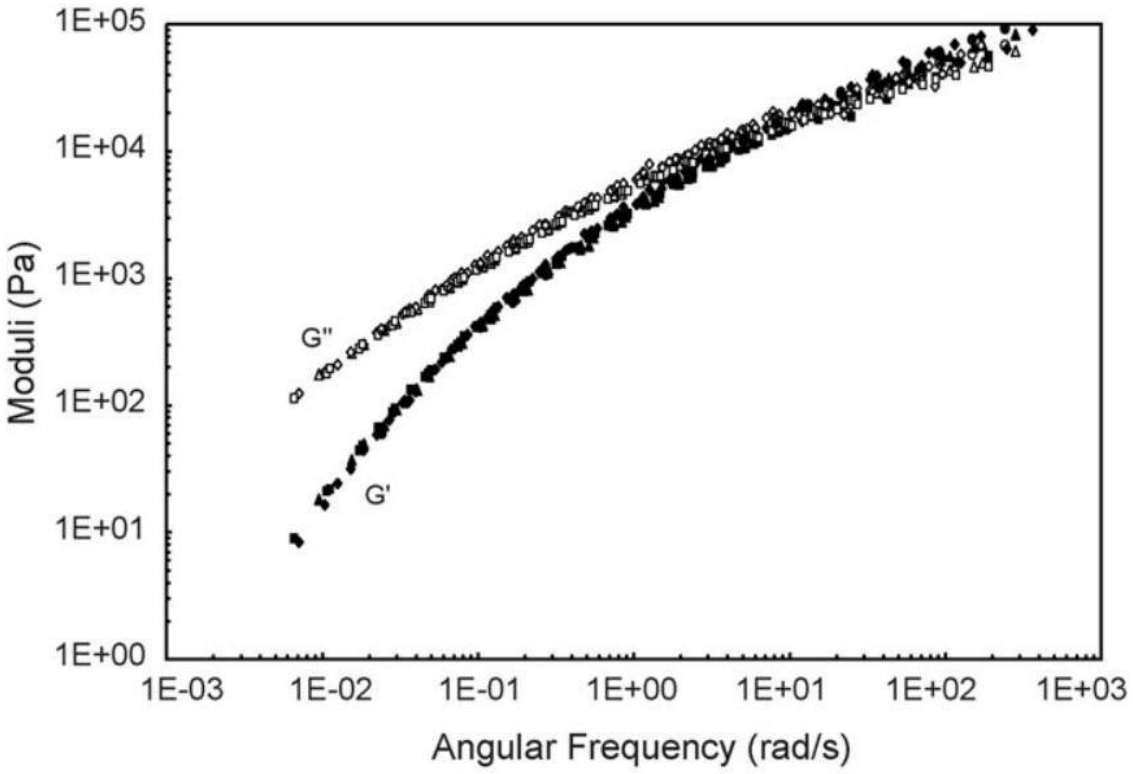

Fig. 7. Linear viscoelasticity results for LDPE at a reference temperature of 160°C (experiments were performed at 140,160 and 180°C and timetemperature superposition applied) and three different rheometers: (■) Paar Physica MCR 300; (**Δ**) Reologica StressTech HR; (**Δ**) O2R off-line; (•) O2R on-line.

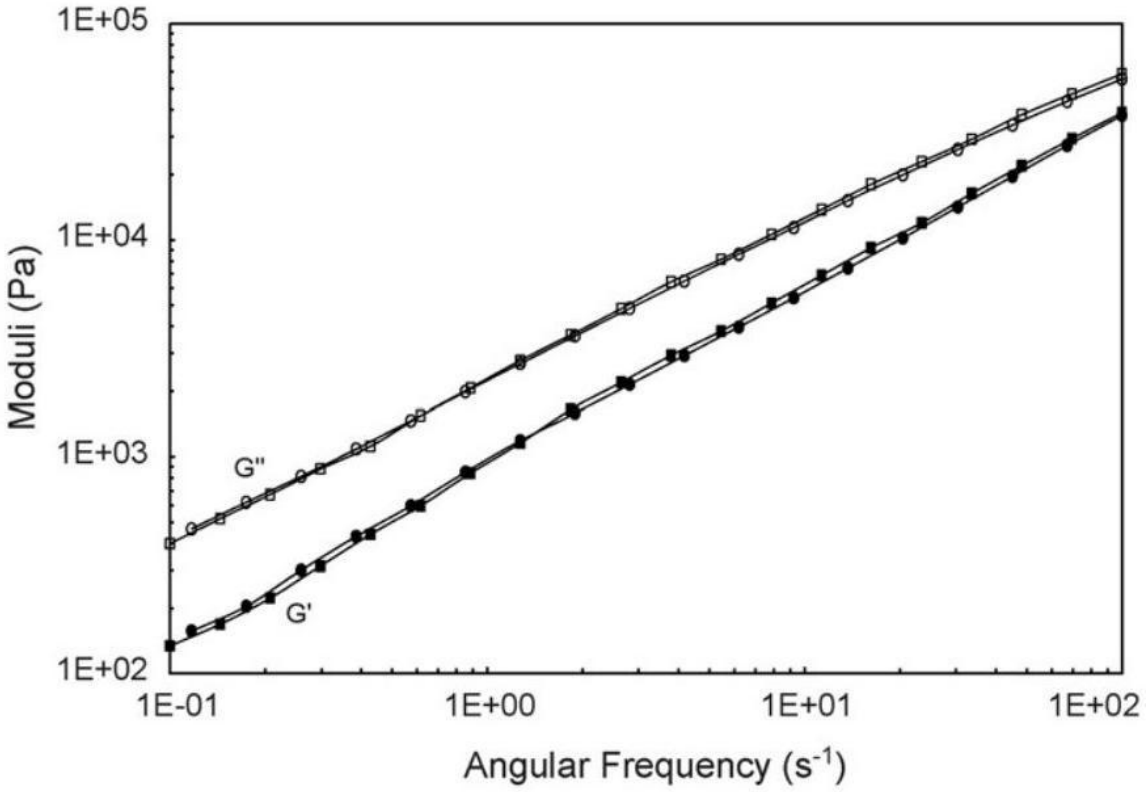

Fig. 8. Linear viscoelasticity results for Blend 1 at 275°C and two different rheometers: (•) Paar Physica MCR 300 and (■) O2R.
shown in Fig. 8, the agreement is again very good, with an average deviation of 3% (and a maximum of 8%) between both instruments.

Generally, these were taken as encouraging results, ones that provided a good degree of confidence on the on-line concept proposed.

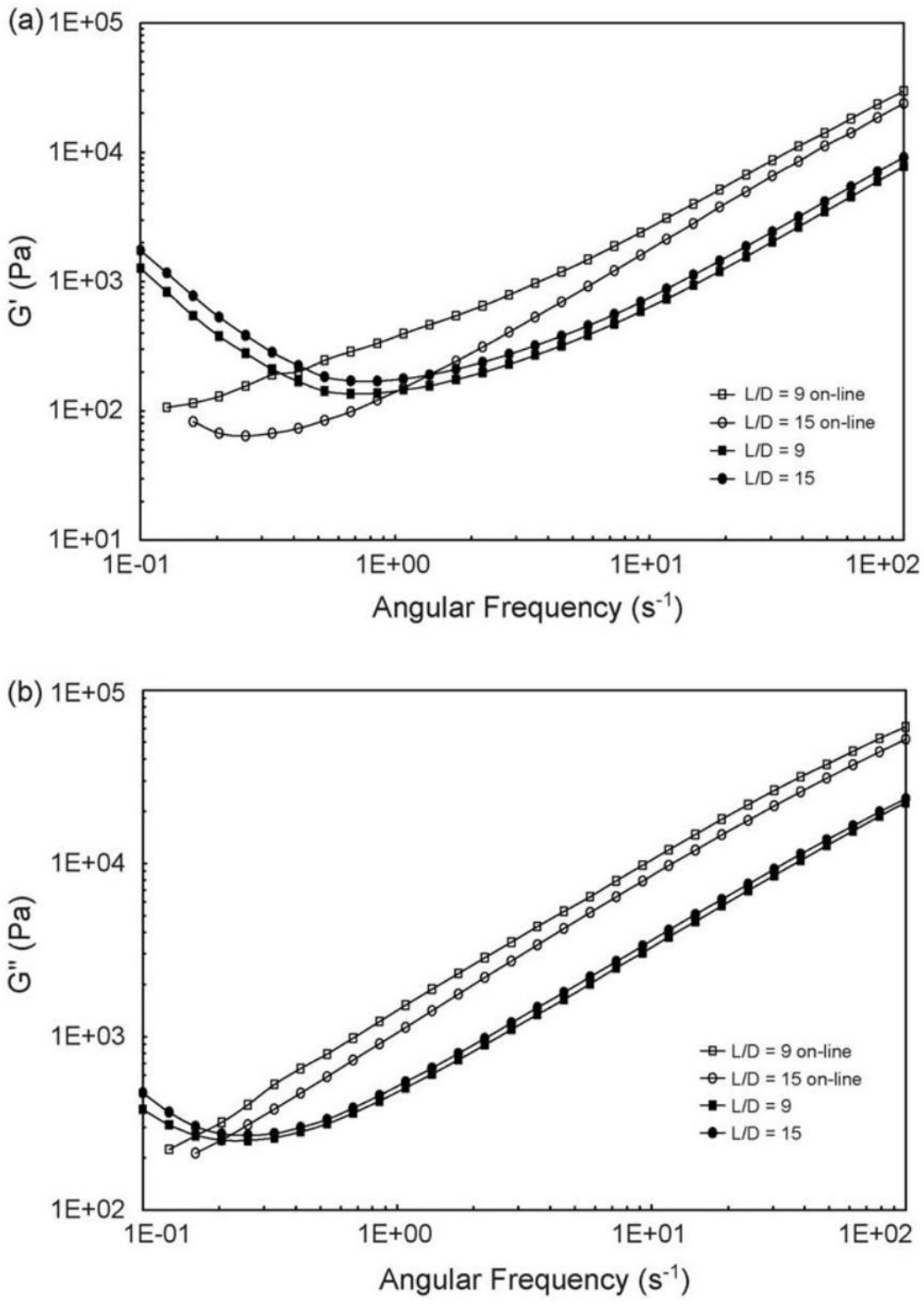

Fig. 9. Linear viscoelasticity results of Blend-NC at 260°C and two different locations in the extruder: (a) storage modulus and (b) loss modulus.

Preparation of multiphase systems

As mentioned above, in addition to the off- and on-line validation of the O2R concept, some exploratory work was also performed to evaluate the effective capacity of this tool to monitor the evolution of the rheological properties along the extruder during the preparation of multiphase complex systems and their relationship with the morphological/chemical development.

A Polyamide 6/low density polyethylene blend was selected for this purpose, due to a combination of reasons: (i) it is a well known, extensively characterised system, that attempts to improve the performance of nylon at low service temperatures; (ii) it is an immiscible blend, hence its morphology is inherently unstable when subjected a thermo-mechanical load, but a compatibilised counterpart can be prepared and has much more practical value; (iii) the polyamide matrix is prone to thermal degradation. Therefore, these material parameters should induce different rheological responses.

As presented in Table 1, the immiscible blend (Blend-NC) results from mixing in the Leistritz extruder under typical operating conditions 70/30 (w/w, %) of a PA6 and a LDPE, while the compatible blend (Blend-C) maintains the same proportion of polyamide, but half of the LDPE homopolymer was replaced by polyethylene grafted with maleic anhydride. The amine groups of the polyamide react with the maleic anhydride groups of the modified PE to form a copolymer at the interface, which acts as a compatibiliser.

Linear viscoelasticity tests in oscillatory shear were conducted at different locations along the extruder barrel ($L/D = 9$, $L/D = 15$ and $L/D = 20$) for both materials and compared to offline ones.

Fig. 9 shows the results for the storage and loss moduli of Blend-NC. It is immediately apparent that the extra thermal cycles imparted on the off-line sample had a dramatic effect on its thermal stability, with degradation setting in at an angular frequency below circa. 2 s^{-1}, or after approximately 10 min . Conversely, the data obtained with the O2R shows a much greater thermal stability. In fact, although G' seems to level off at frequencies below approximately 0.4 s^{-1}, this type of behaviour has often been reported as typical of polymer blends and been attributed to the deformation and recovery of the dispersed phase due to interfacial tension [14,15].

In addition, the evolution of the viscoelastic response is also considerably altered, both quantitative and qualitatively, since while the off-line results seemed to point to an increase in both G' and G'' along the extruder, the on-line ones show the opposite.

This indication of the on-line testing is corroborated by SEM observations (see Fig. 10), which show that:
(a) The morphology is much coarser immediately after sampling than after compression moulding, with a much larger interfacial area in the latter case. This explains the higher values of the moduli in the on-line tests, because in immiscible blends the lack of adhesion between the components (across the interface) often leads to a decrease in mechanical (and rheological) properties of the blend, by comparison with the pure components, this effect increasing with increasing interfacial area.
(b) Despite the above, Fig. 10 clearly shows that at $L/D = 9$ the sample withdrawn from the extruder consists essentially of remains of pellets of PA in a seabed of PE. Obviously,

upon compression moulding both polymers melt and a new

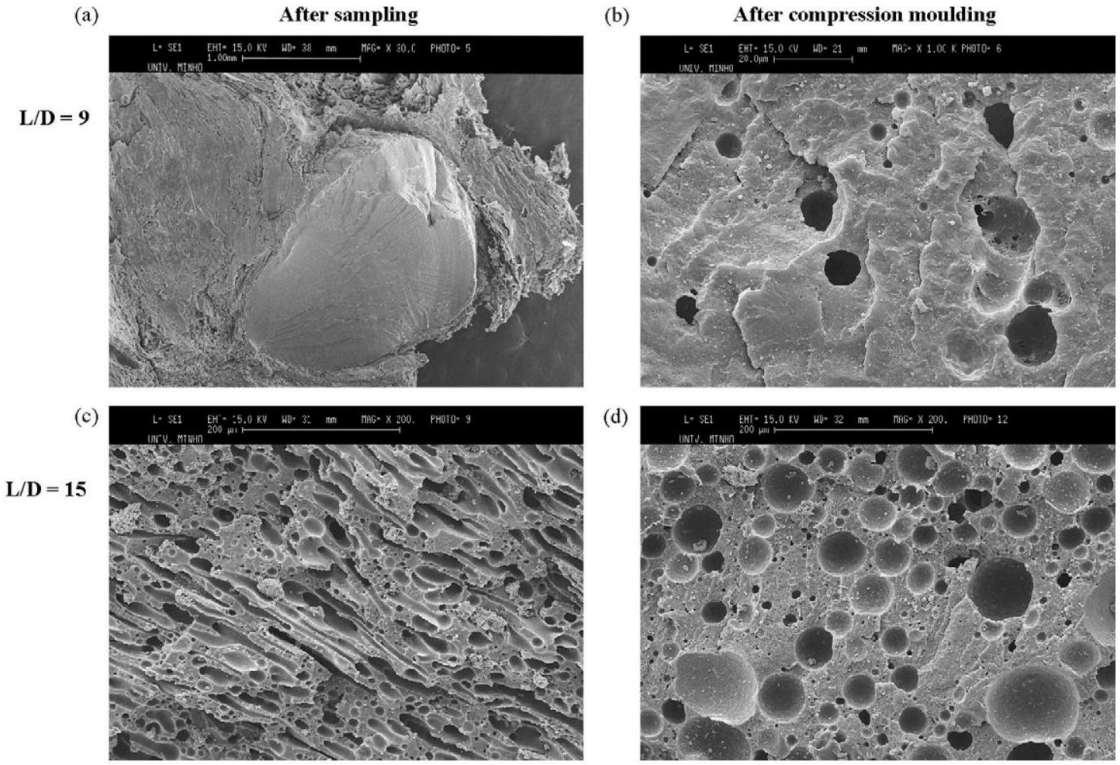

Fig. 10. SEM results of Blend-NC at two different locations in the extruder, after sampling and sampling followed by compression moulding.

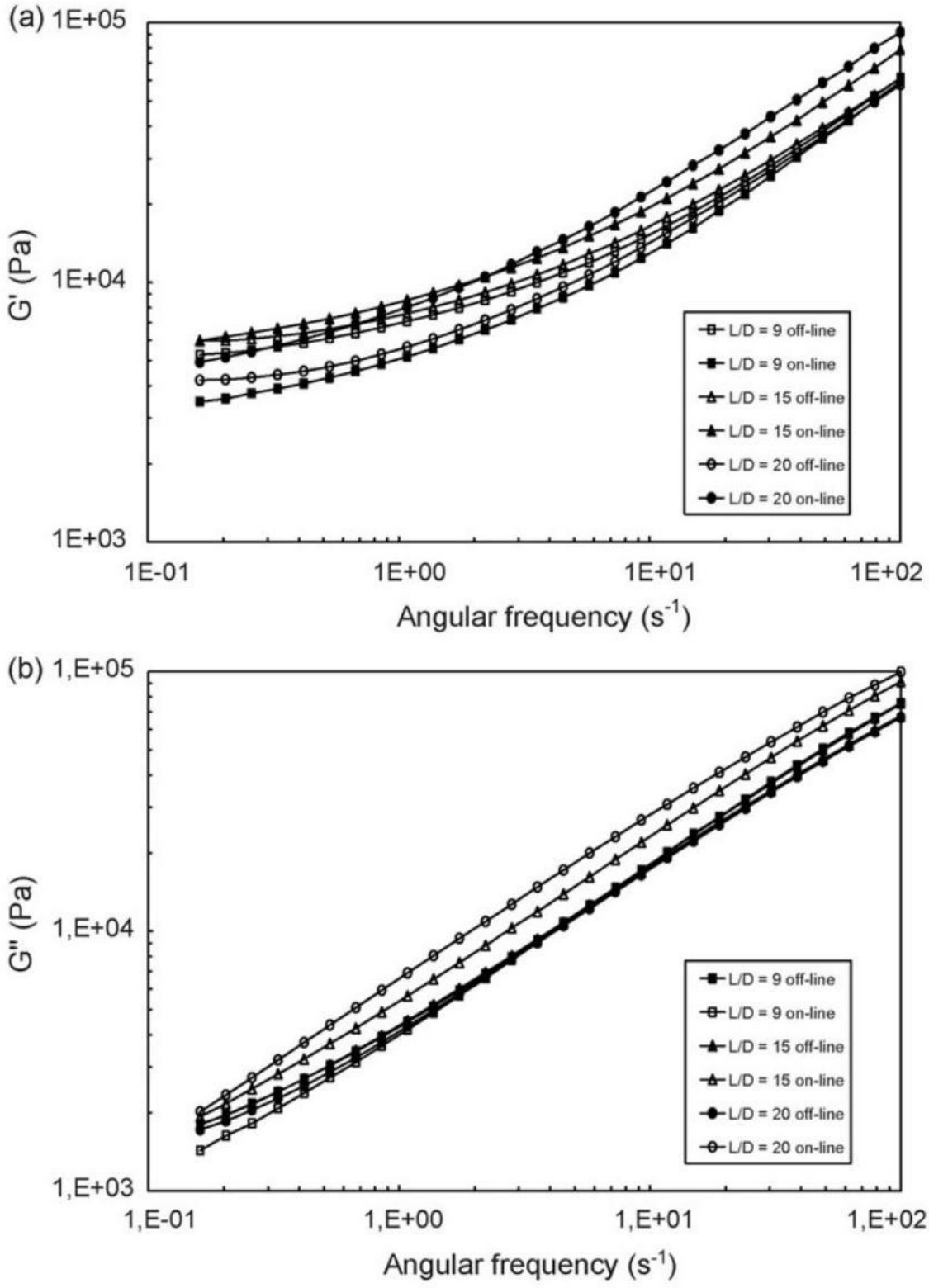

Fig. 11. Linear viscoelasticity results of Blend-C at 260°C and three different locations in the extruder: (a) storage modulus and (b) loss modulus. morphology is formed. Also, at $L/D = 15$, the elongated PE particles/fibrils coalesce upon

compression moulding, and only nearly spherical particles are observed. Therefore, offline and on-line measurements effectively test materials with distinct morphologies. (c) In the off-line tests the morphologies observed at both locations are very similar due to the thermomechanical experience during the manufacture of the disks by compression moulding, which explains the similar values of the moduli in both cases.

These results demonstrate that the morphology of samples to be characterised rheologically on-line in the upstream part of the extruder should be checked for complete melting, otherwise interpretation of their behaviour will be more complex.

The equivalent data for the compatibilised blend (BlendC) is shown in Fig. 11. On-line and off-line behaviours are again diverse, but differences are smaller than for the noncompatibilised case. This is certainly due to the fact that the presence of the copolymer stabilised the morphology and, consequently, compression moulding has now a less important role on this characteristic-see Fig. 12, where the similarity of the morphologies is obvious. However, especially for samples taken at lower screw L/Ds, chemical conversion may have progressed during compression moulding, increasing the availability of copolymer. This explains why off-line moduli for $L/D = 9$ are higher than the equivalent on-line.

The evolution of the viscoelastic moduli along the extruder is re-plotted at a fixed frequency of 1 s^{-1}, in Fig. 13. In terms of the viscous response, it is quite clear that the extra ther-

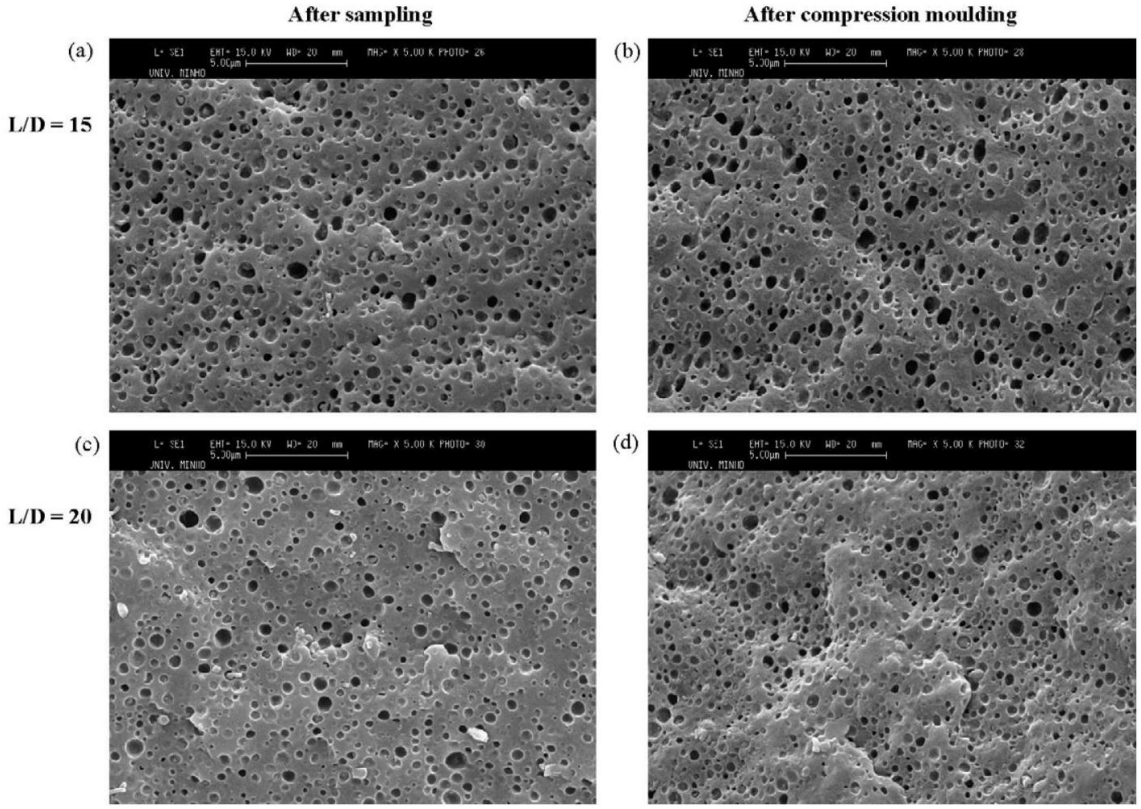

Fig. 12. SEM results of Blend-C at two different locations in the extruder, after sampling and sampling followed by compression moulding.

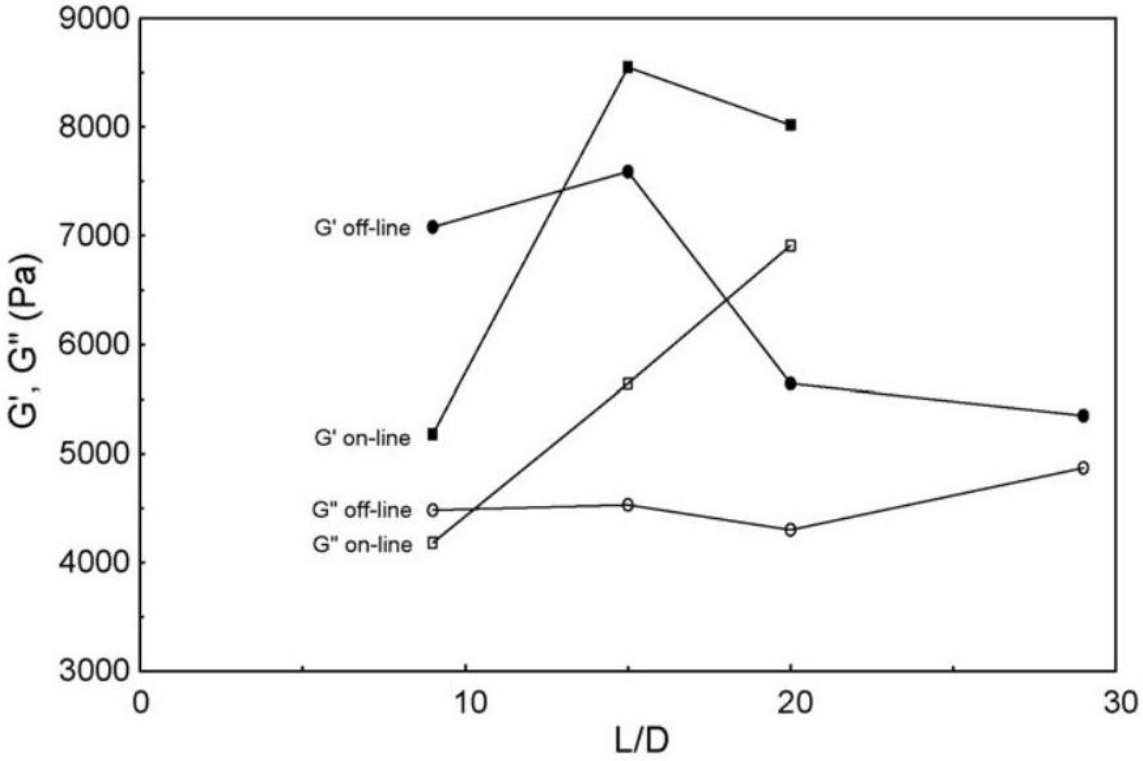

Fig. 13. Linear viscoelasticity results along the extruder of Blend-C at a fixed frequency of $1\ s^{-1}$.

mal cycle created by compression moulding reduces artificially the differences along the extruder-the loss modulus is nearly constant in the off-line tested samples, whereas on-line tests detect an increase larger than 50% between locations L/D = 9 and L/D = 20. In terms of the elastic response, both tests yield an initial increase of the elastic modulus between L/D = 9 and L/D = 15, followed by a decrease thereafter, that is more important for the off-line tests. This decrease could be attributed to degradation of the PA matrix, which is more extensive in the case of the off-line samples, as discussed above.

Conclusions

In this paper, a new on-line rotational rheometer, dubbed O 2 R , that allows the rheological properties of materials to be monitored as they are being processed in an extruder was presented. The instrument enables such important phenomena as morphology development or reaction kinetics to be followed from changes in the rheological responses measured along the screw axis.

The results show that the rheometer is very accurate when compared to commercial laboratorial instruments, the average deviation in results between the O2R working on-line, off-line, a Paar Physica MCR 300 and a Reologica StressTech HR varying between 3 and 8% for various commercial homopolymer melts

and blends. The lower limit to the sensitivity of the instrument is of the order 10 Pa for the linear viscoelastic moduli due to friction effects at low frequencies.

The O2R concept was also tested with complex multiphase systems, namely a compatibilised and an immiscible polymer blend, and the results showed that it was much more accurate in capturing the structural evolutions of the materials along the extruder than analysis performed off-line on samples collected on-line.

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