Online monitoring techniques for studying evolution of physical, rheological and chemical effects along the extruder

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During extrusion and/or compounding, polymeric systems may be subjected to a complex thermo-mechanical-chemical environment, therefore monitoring the evolution of physical, rheological and chemical effects along the extruder is an important tool assisting process understanding and optimisation. Online monitoring concepts that allow sample collection, rheology measurements and RTD characterisation at specific locations along the screw axis of an extruder are presented. Each practical set-up is presented, its operation is described and the results obtained are validated experimentally. Finally, examples of the use of the tools developed for the study of specific polymer systems are presented and discussed.

Keywords: Online monitoring, Extrusion, Online rheometry, Online RTD, Reactive extrusion, Twin screw extrusion

Introduction

Extrusion is not only a major plastics processing technology, yielding mass-consumption products such as pipes, profiles, films and sheet, but is also an important tool for the manufacture of new advanced materials (e.g. modified polymers, polymer blends), compounds and composites. The input of thermal energy and mechanical stresses to the polymer system being processed induces the development of physical, mechanical and chemical effects along the screw, which will determine the final characteristics of the extrudate. [1–3] These effects may be very complex, since they depend not only on the nature of the materials being processed, but also on the geometry of the equipment (which may vary significantly, e.g. from single to twin screws, from conventional helicoidal flow channels to distributive and barrier zones, or staggered kneading blocks) and on the processing conditions (residence time, temperature and stress levels). Thus, practical process optimisation requires the prior study and understanding of the evolution of those phenomena along the extruder, and how they are affected by changes in formulation, equipment geometry and operating conditions.

Therefore, it is not surprising that a significant number of inline and online devices has been developed and used successfully to monitor the processing of a number of polymer systems, using a variety of techniques, such as rheometry, ultrasound, infrared, ultraviolet, Raman and dielectric spectroscopy (see, for example, Refs. 4-12). The aim is obviously to measure important characteristics of the systems being processed quickly,

without perturbing its flow. However, most of the devices developed to date are inserted between the extruder and the die, i.e. downstream of the major morphological and chemical changes that occur in the extruder.

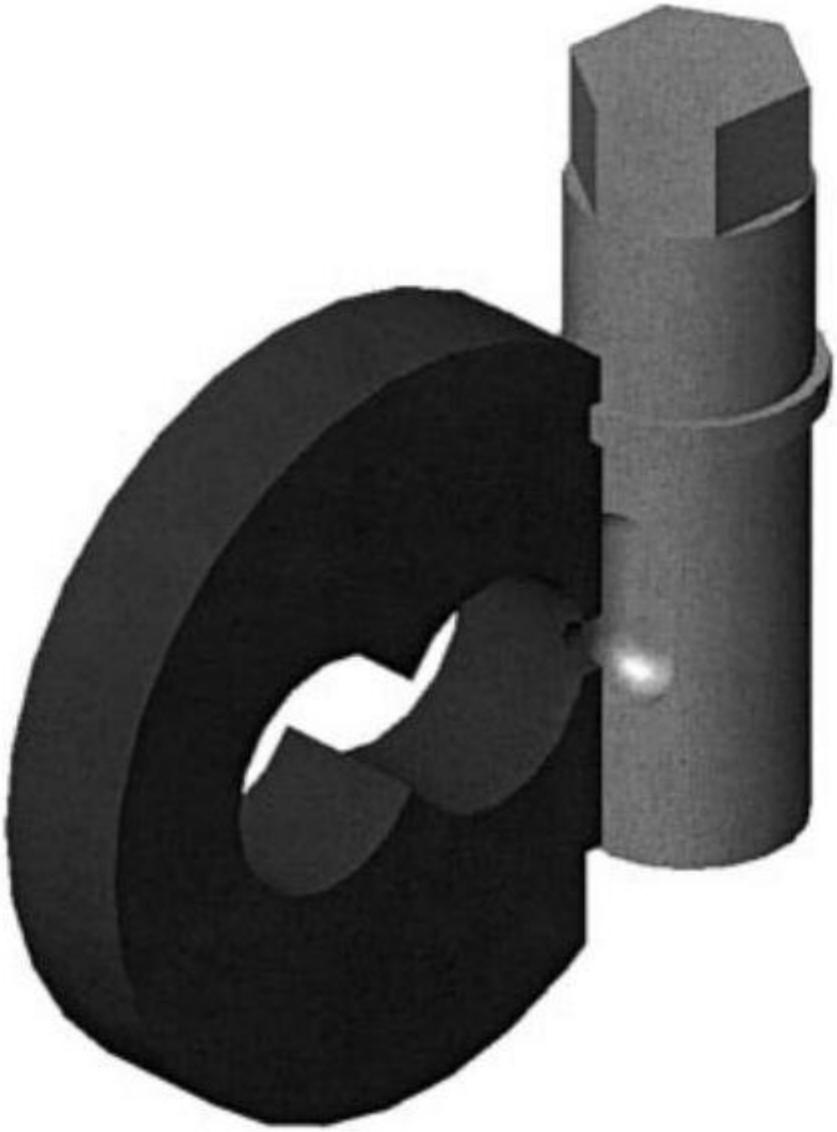
The present work aims to present a new array of equipment for monitoring the evolution of relevant characteristics of polymer systems along the screw axis. The possibility of collecting samples from within the extruder at various locations will be explored, as it provides the opportunity to perform subsequent sophisticated offline analyses. Obviously, if any of these can be performed online, the analysis will be quicker and, most probably, more straightforward. Also, in some cases, the need to manufacture a sample with a prescribed geometry, which could require submitting the material collected from the extruder to a further processing step, is avoided. Since it is well known that rheological data are sensitive to changes in morphology, chemistry, temperature and degree of mixing, online capillary and oscillatory rheometry capabilities were developed. Finally, the determination of local residence times will be discussed, as it is useful to understand, for example, the kinetics of chemical processes, or to estimate the efficiency of axial mixing.

This paper is divided in two main parts. First, the various experimental set-ups are presented, their operation is described and the data obtained are validated by direct confrontation with the corresponding offline results. The potential of the combined use of these techniques for studying the preparation of some materials is then illustrated.

Monitoring concepts and equivalent practical set-ups

Sampling device

As mentioned above, the possibility of collecting material samples from within the extruder at various



Sampling device

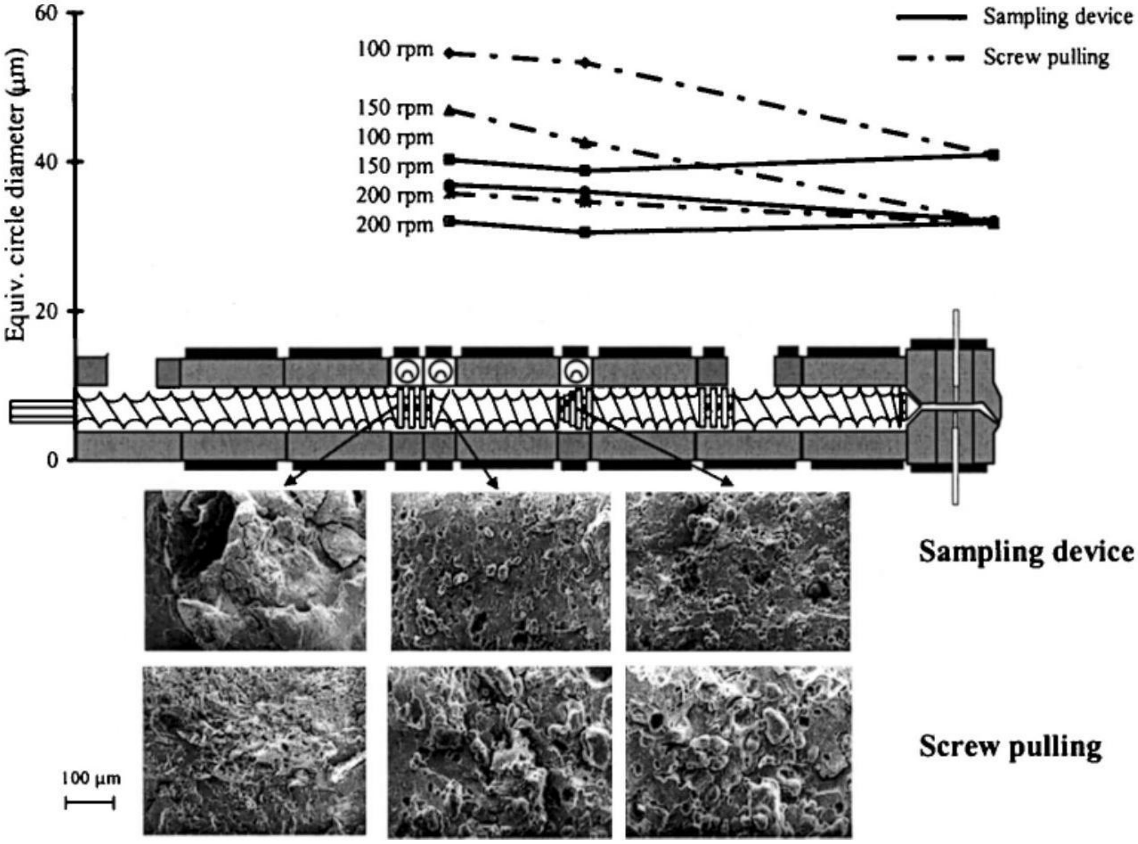
locations yields the opportunity to carry out extensive offline characterisation. In the solution proposed (Fig. 1) material is detoured from the screw channel through a side hole in the barrel, collected in a small cavity, manually removed and quenched immediately. Since the device has been presented and validated elsewhere, [13,14] only a brief description is given here.

A rotating valve exposed to the side hole has two cavities machined in its body. Upon its rotation, each cavity is successively exposed to the incoming material. The first (smaller) cavity collects material that could have been retained in the recess of the side hole, while the second captures a sample of the material that was progressing along the screw in the vicinity of the hole. Each operating sequence takes typically less than 3 s and yields $1 - 2$ g of polymer, this being subjected to low shear rates, which is important to preserve the existing morphology. Also, it allows precise measurement of the melt temperature, by simply inserting a preheated fast response thermocouple into the nut-shaped sample (i.e. a portion of material with low thermal conductivity and low surface/volume ratio). [15] This is important, since differences of 60°C and higher between set and real temperatures have been registered during flow through staggering kneading blocks in co-rotating twin screw extruders.

An assortment of adjacent sampling devices can be used simultaneously (thus making it possible to collect, for example, various samples along a staggering kneading block), or spread along the barrel. Different sizes are available, which may be useful to set the minimum sampling distance between two consecutive devices.

Two examples will be used to evidence the practical usefulness of this tool. Figure 2 compares the evolution of the morphology of a polyamide-6/ethylene propylene rubber (PA-6/EPM) blend ($90:10 w/w$) along a Leistritz 30.34 intermeshing co-rotating twin screw extruder (the screw profile and the location of the sampling devices are shown in Fig. 2), as observed in samples obtained with the sampling devices and with the conventional screw pulling technique (which involves stopping the extrusion operation, quenching the system, removing the die and pulling out the screws). No data are presented for the first part of the extruder, as the material is still solid. At the sampling location upstream, the material obtained with the sampling devices exhibits sheets of PA-6 and rubber, whereas that removed from the carcasses withdrawn from the extruder appear as molten. Also, not only are the EPM particles, observed with conventional sampling, generally bigger, but particle coalescence affects the actual evolution of the average particle size along the screw. [13] Obviously, the conventional screw pulling technique allows significant heat conduction and particle coalescence to take place before sufficient quenching of the material is attained.

The second example concerns the reaction of a styrene-maleic anhydride co-polymer (SMA) with 1-aminonaphtalene (this type of reaction takes place


60
40
20
0
Equiv. circle diameter (µm)
Sampling device
Screw pulling
100 rpm
150 rpm
100 rpm
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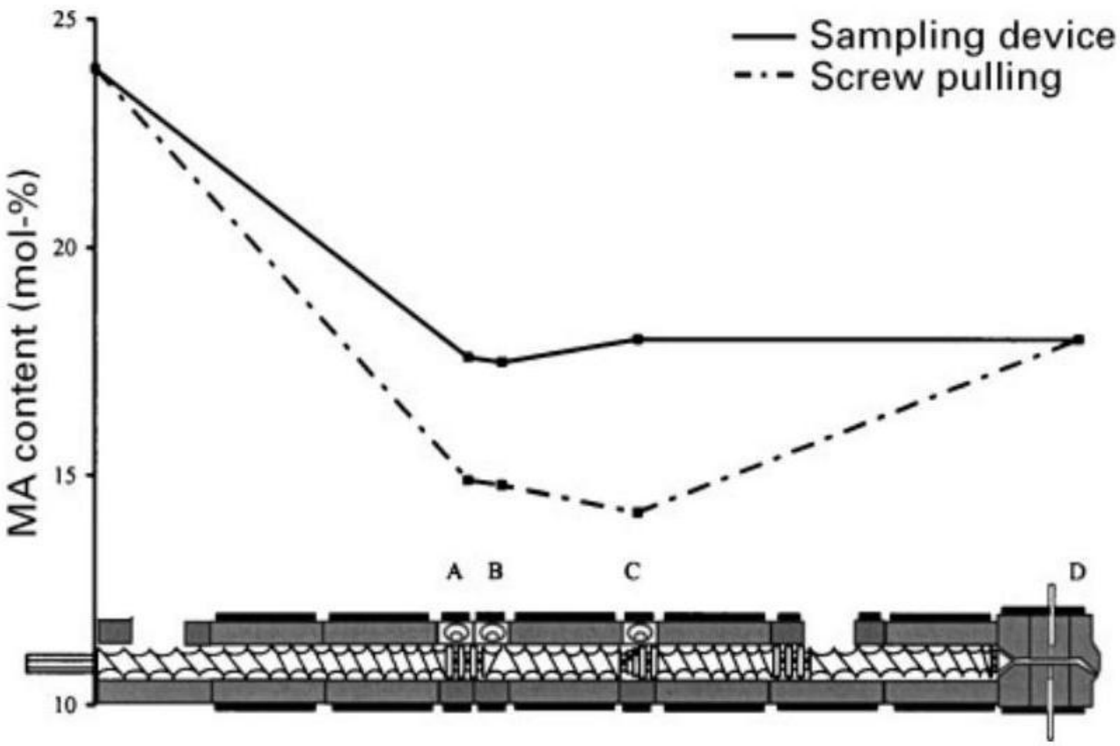
200 rpm
200 rpm
Sampling device
Screw pulling
100 µm



3 Chemical evolution of samples obtained using sampling devices and from screw pulling experiments

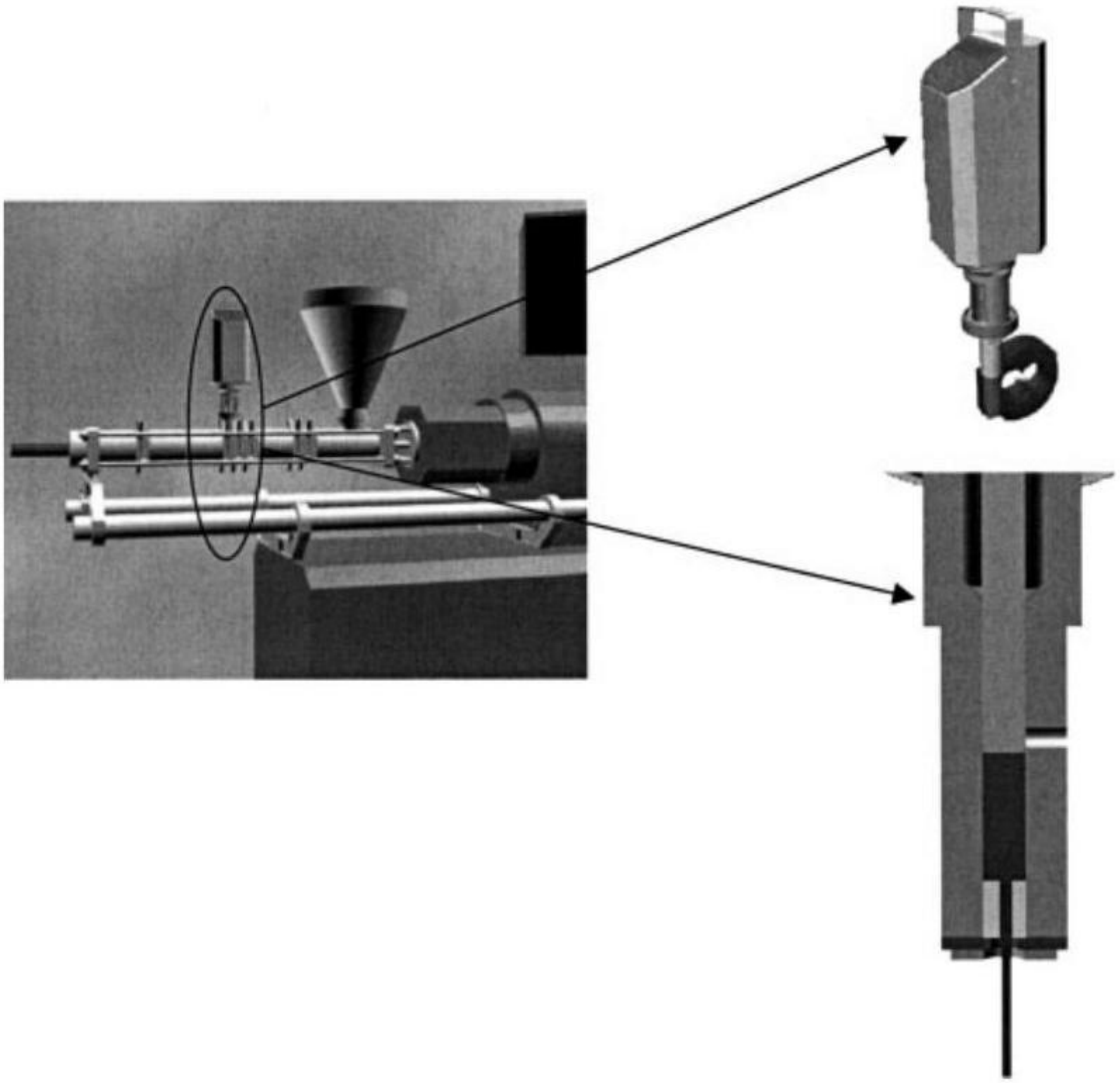
during reactive blending of polyamides and maleic anhydride containing polymers), which results in the formation of cyclic imide, carried out in the same Leistritz extruder. As before, Fig. 3 depicts the evolution of the chemical reaction along the extruder (as well as the geometrical features of the system), in terms of MA content (see experimental protocol in Ref. 13), for the samples obtained using the sampling devices and the screw pulling technique. The solid line shows that the MA content of SMA decreases from 23.9 to 17.6 mol – % at the outlet of the first mixing zone, and that no significant changes occur downstream, i.e. imidation takes place mainly during melting. The long dwell time at high temperature associated to the screw pulling technique induces a decrease of MA content from 23.9 to 14.5 mol – %. Obviously, this value cannot be justified in view of the 18 mol – % measured at the extrudate, which is independent of the sampling technique used.

Online capillary rheometer/MFI

The experimental apparatus illustrated in Fig. 4 (for more details see Refs. 16 and 17) follows three basic concepts:
(i) it contains, as all other conventional capillary rheometers, a heated barrel, a moving piston and a replaceable capillary die
(ii) it uses the sensors and the driver of a portable commercial instrument
(iii) it is geometrically compatible with the sampling devices, i.e. any sampling device inserted on the barrel of the extruder can be replaced by an online capillary rheometer.
The rotational motion of a portable controlled-stress rotational rheometer is converted to

a linear descending/ ascending one. Thus, the piston attached to that rheometer can travel at a set speed determined by the rotating rate of the rotational rheometer head, pushing the material (which was previously pressure driven into the reservoir from the extruder) through the die at a set shear rate. The torque is recorded and used to determine the apparent wall shear stress, after which the usual Bagley and Rabinowitsch corrections to the data are performed to yield true values for the wall shear rate and stress and to obtain a measure of the extensional properties via the entry torque.

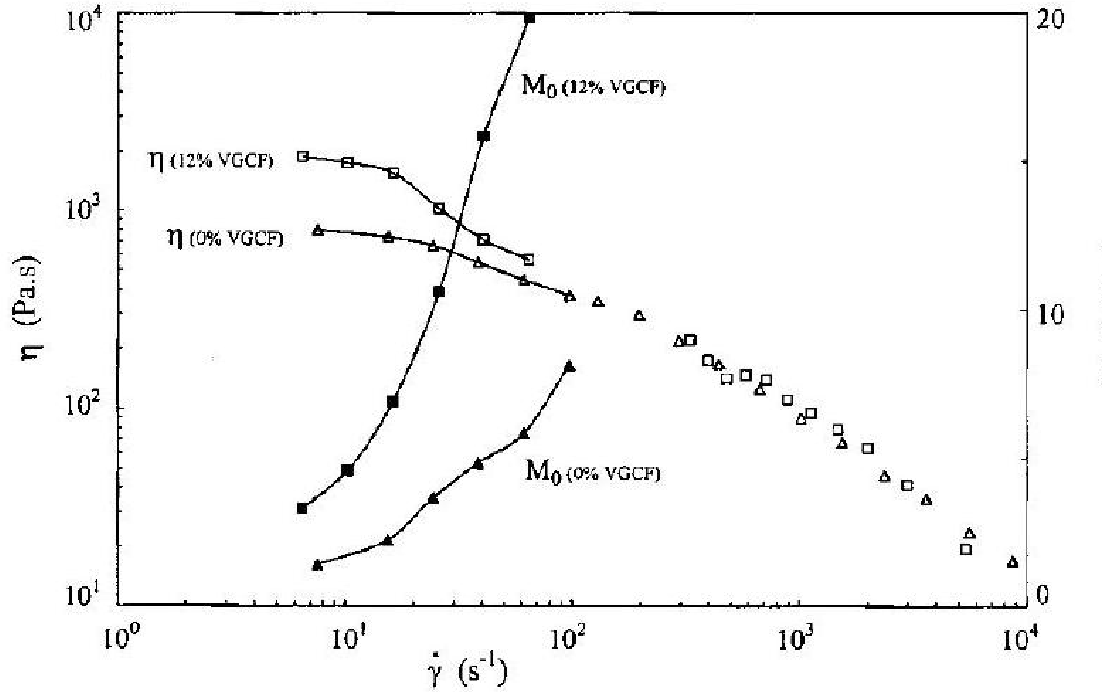
This equipment was used to measure the rheological response of a 12 wt -% polypropylene-based carbon fibre composite after melting in an intermeshing co-rotating twin-screw extruder. [12] Optical microscopy performed on the fibres before feeding the extruder and on samples collected (using the sampling devices) at the point of insertion of



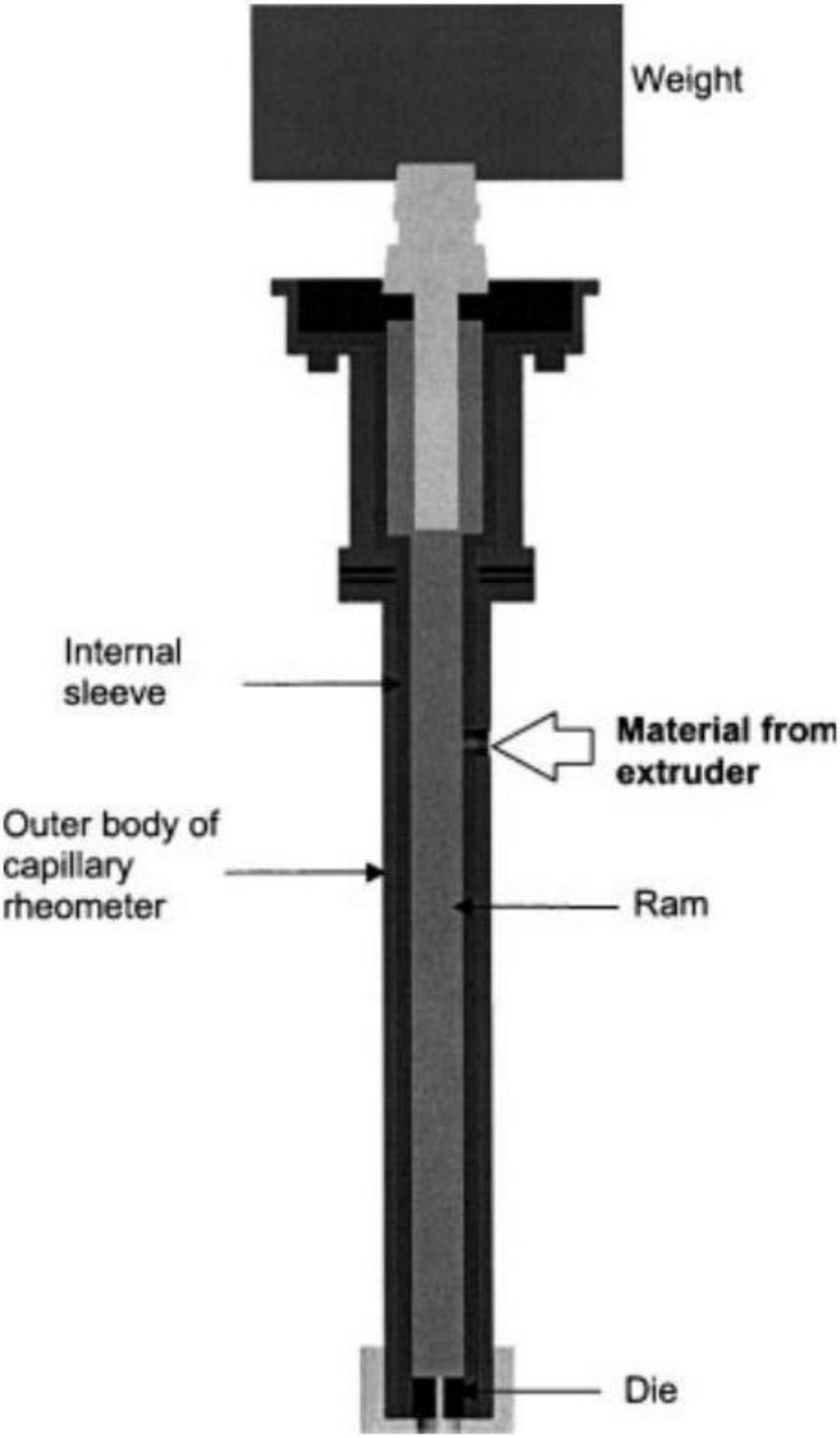
Online capillary rheometer

the online rheometer, i.e. after the mixing section and at the die outlet, revealed that the average fibre size was reduced from 2.83 ± 1.33 to 0.90 ± 0.33 mm, remaining constant thereafter. Figure 5 shows the shear viscosity and the entry torque (which is a measure of the extensional viscosity [16]) for virgin polypropylene (PP) and for the composite. The coherence between the online and offline shear data (the latter determined with a Rosand RH8-2 twin-bore capillary rheometer) is clear.

Both materials are shear-thinning, with very little differences in shear viscosity between them at shear rates above 100 s^{-1}. Below this, i.e. within the shear rate range in which the online capillary rheometer was designed to work, the presence of the fibres causes a significant increase in viscosity (approximately twofold in the viscosities in the Newtonian plateau). As expected, extension dominated (entry) flows are much more sensitive to the presence of the carbon fibres than shear flows (for example, at a wall shear rate of 60 s^{-1}, there is a 26% increase in the shear viscosity between the PP and the composite and a 240% increase in the corresponding



5 Flow curves for PP and PP+12% fibres: data connected with solid line were taken with online capillary rheometer, remainder with offline capillary rheometer



6 Device for online measurement of MFI/MVR

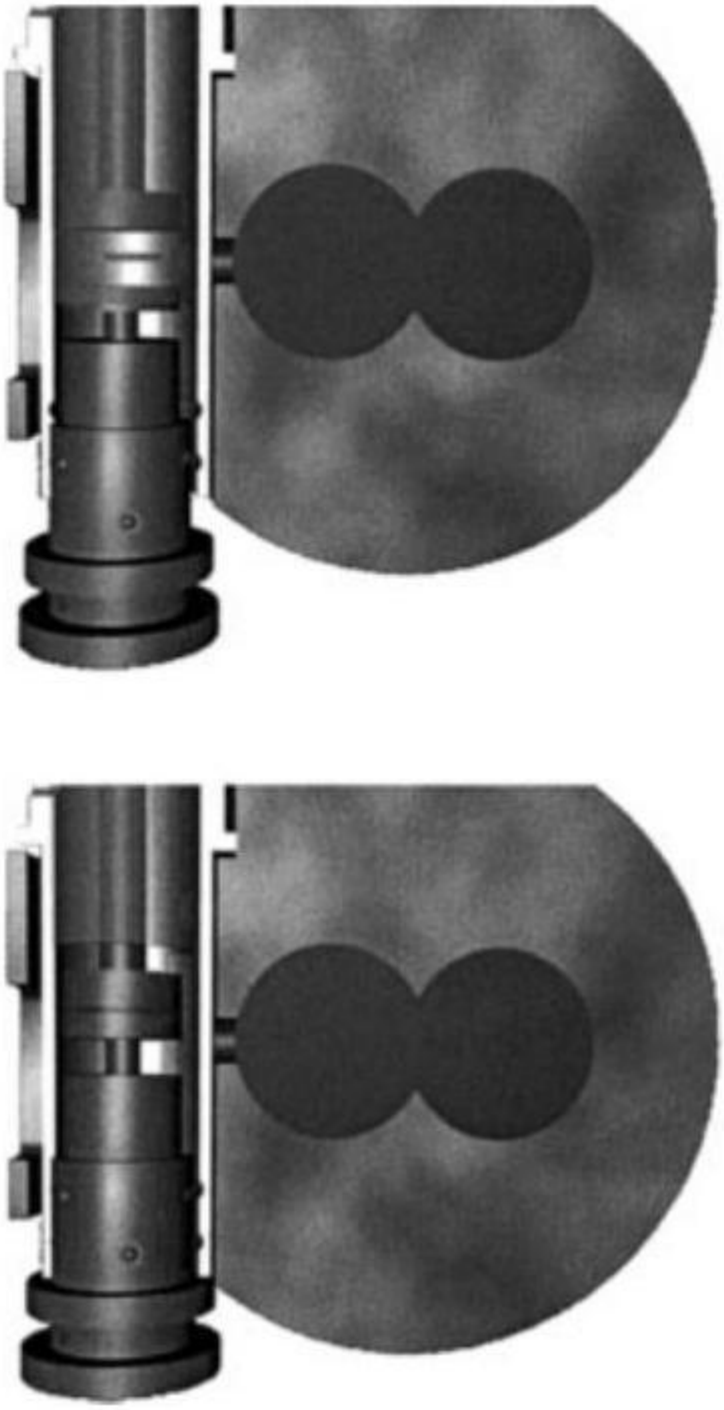
entry torque). Since the fibres are very rigid and, as such, quite difficult to align in the flow direction and pass through the contraction, they lead to a large increase in the observed entry torque.

The device shown in Fig. 4 was modified to allow also for the online measurement of MFI/MVR (melt flow index/melt volume flowrate), which are rheological indices widely used by the polymer industry for process monitoring and control. As illustrated in Fig. 6, this modification consists mainly in: the insertion of a metal sleeve into the barrel of the online rheometer - to create a reservoir with a smaller diameter; the replacement of the initial ram (to be coupled to the rotational rheometer) by a thinner one that will hold the relevant weights; and the use of a specific die. The geometry, dimensions and experimental procedure are compatible with the ASTM D-1238 and ISO 1133 standards.

Online oscillatory rheometer

It is well known that the large deformations and relatively high shear rates associated with the flow in a capillary rheometer may affect the morphology of the material being measured and consequently its rheological response. Alternatively, the linear viscoelastic behaviour [18,19] and, more recently, the non-linear properties (see, for instance, Ref. 20) of materials such as polymer blends are usually studied using oscillatory rheometry and can be correlated with the existing morphology. Thus, online oscillatory rheometry could provide a complementary tool to online capillary rheometry, with a significant potential to be explored in some situations, such as the evolution along the extruder of the morphology of reactive polymer blends or of the chemical conversion in the case of modified polymers.

The set-up illustrated in Fig. 7 preserves some of the solutions adopted for the development of the online capillary rheometer, such as the use of the measuring capabilities and software of a Paar Physica MC150 (specifically modified for this purpose), the



7 Online oscillatory rheometer: collecting material from the extruder (top) and making a measurement (bottom)

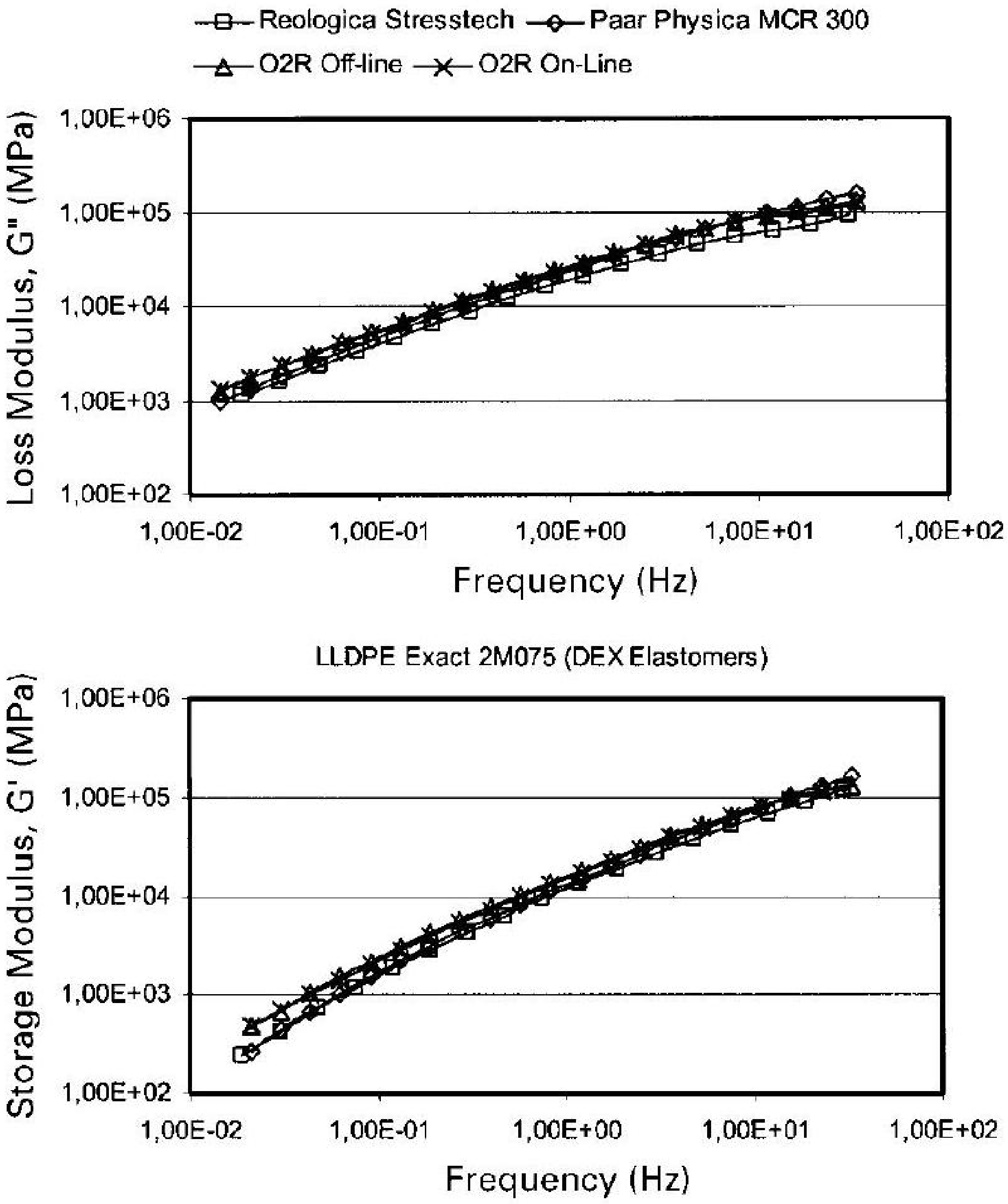
interchangeability with the other available online devices (consequently, making it possible to make measurements at different locations along the extruder) and the possibility of setting different gaps and changing the measuring geometry. It contains three main parts. The hollow body functions as a sampling device, for material collection. The upper part is connected to the measuring head. The lower part sets the gap. The operating sequence includes:

(i) offline gap calibration
(ii) insertion of the device into the extruder
(iii) material inflow (during normal operation of the extruder, by rotation of the hollow body)
(iv) shut material inflow (again, by rotation of the body in the reverse direction)
(v) set gap and wipe excess material (with the help of a sliding ring)
(vi) wait for thermal equilibrium
(vii) perform a measurement.

The experimental validation of the device was carried out for a number of polymer systems. In Fig. 8, the linear viscoelastic response of a LLDPE at 200°C measured offline by two commercial rheometers (Reologica Stresstech and Paar Physica MCR300) is compared with that obtained using the online device inserted in the barrel of the Leistritz twin screw extruder mentioned above (after enough dwell time in the rheometer to reach the set temperature). Within a reasonable experimental error, the results are in good agreement.

Online RTD

Residence time distribution (RTD) characterises the time history of a material inside a specific system. In extrusion, RTD is regularly used to estimate the flow patterns developed, as well as the global mixing performance. [21] As illustrated in Fig. 9, the measurement of RTD involves the incorporation of a tracer pulse (usually at the hopper) to the material stream, and the determination of the variation of its concentration with time (usually at the die outlet). The residence time distribution function $E(t)$, or its cumulative function



8G' and G'' of LLDPE measured online and offline

$F(t)$, are used [21]

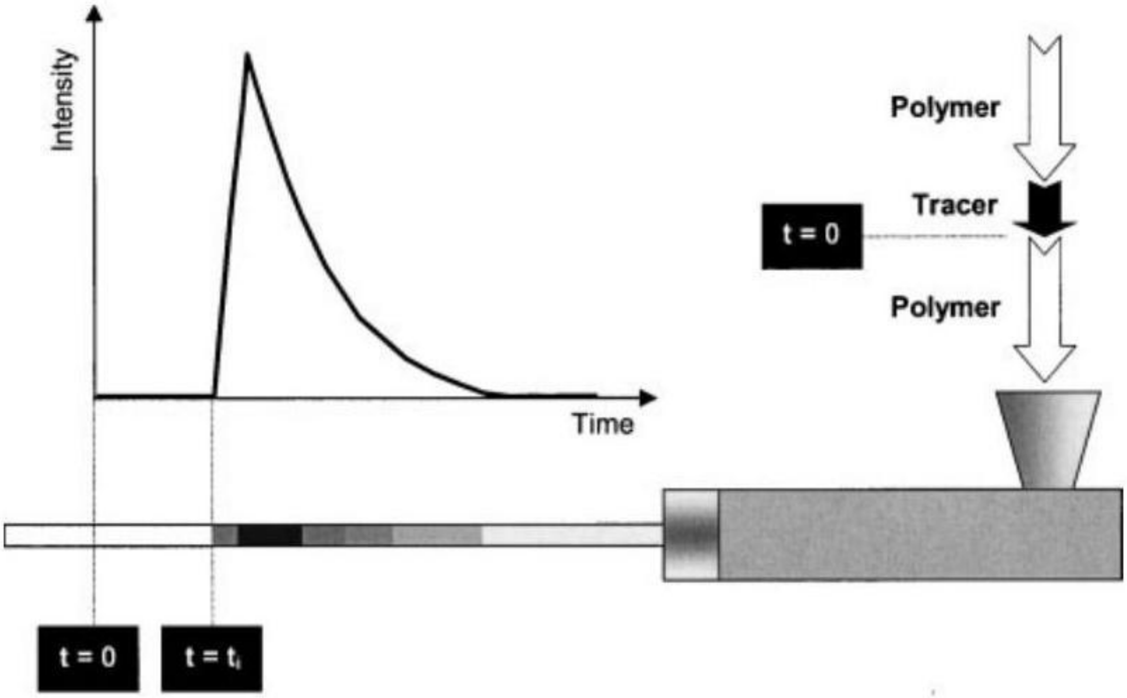
$$E(t) = \frac{c}{\int_0^\infty cdt} = \frac{c}{\sum_0^\infty c\Delta t} \qquad (1)$$

$$F(t) = \int_0^{\mathrm{t}} E(t)dt = \sum_0^{\mathrm{t}} E(t)\Delta t = \frac{\sum_0^{\mathrm{t}} c\Delta t}{\sum_0^\infty c\Delta t} (2)$$

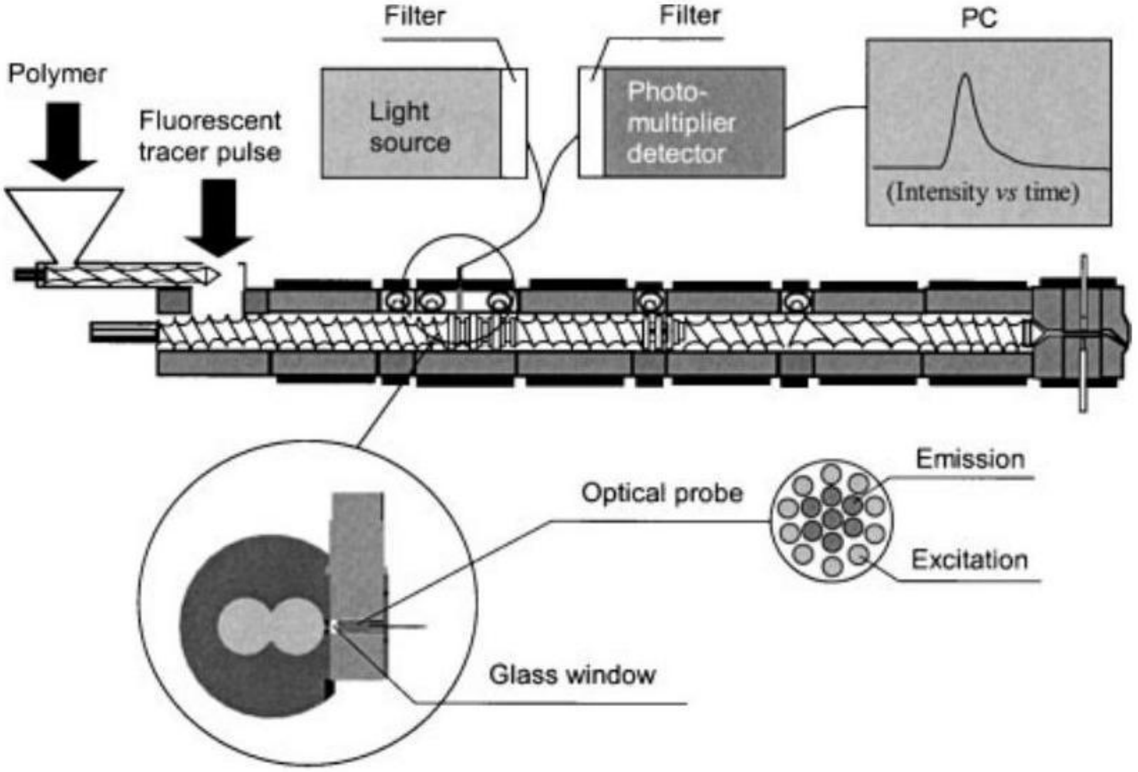
where c is the tracer concentration at time t. The mean residence time $\bar{t}$ is defined as

$$\bar{t} = \int_0^\infty tcdt / \int_0^\infty c\,\mathrm{d}t = \sum_0^\infty tc\,\mathrm{d}t / \sum_0^\infty c\Delta t \tag{3}$$

Usually, the above functions are normalised using a dimensionless time $(\theta = t/\bar{t})$.[21] Knowledge of these parameters along the extruder could provide a better understanding of the local flow patterns, particularly during flow through complex zones, such as staggered



9 RTD measurement principle

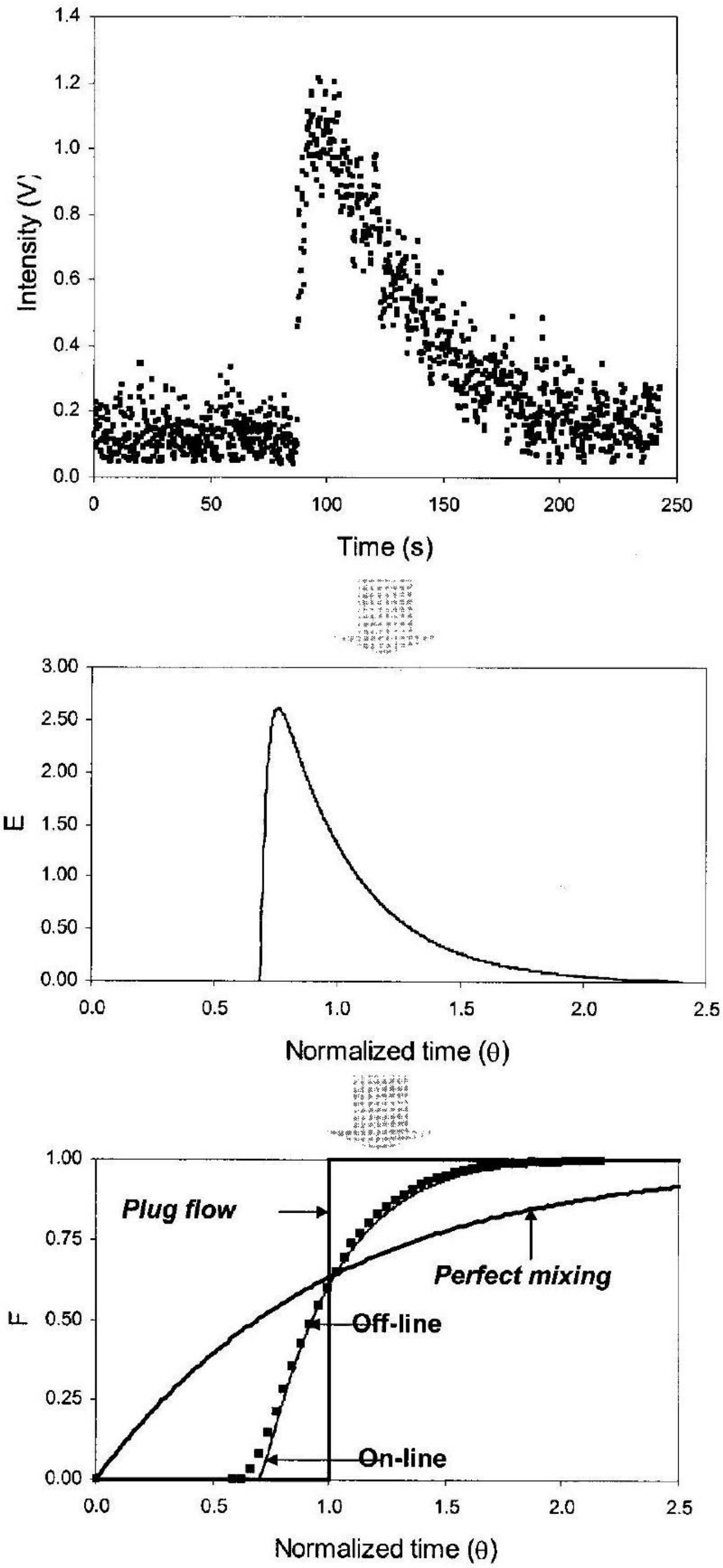


10 Experimental set-up for online RTD measurements

kneading blocks and mixing sections. Also, data on local mean residence times are important for modelling chemical reactions. Several online measurement techniques are currently available (the sensors being usually located between the barrel and the die), namely those based on ultrasound attenuation [22,23] and on light, [24,25] ultraviolet [26,27] or infrared [27,28] absorption. However, the direct determination of partial RTDs, i.e. RTDs corresponding to limited zones of the extruder, requires the capacity for monitoring the tracer concentration at several locations along the extruder, otherwise deconvolution techniques must be applied. [29] Thus, in this work, a technique based on the light emission of a fluorescent tracer (more specifically, a masterbatch of $5 \mathrm{wt}-\%$ perylene dispersed in a polymeric matrix) is used, each sensor being fixed to a piece having a geometry compatible with that of the remaining online devices.

The experimental set-up is schematised in Fig. 10. The light source (excitation) is a mercury lamp, whose emission spectrum matches the perylene excitation wavelength (410 nm). An optical chopper and an interference filter ($404 \cdot 7 \pm 10$ nm) were inserted between the lamp and the excitation optical fibre bundle, to reduce noise and to minimise interference of other light sources. At the emission side, a cutoff filter (>435 nm) reduces the interference of other emission sources by discarding wavelengths (>430 nm) below that of perylene emission. The light emitted by perylene is converted by a photodetector to a voltage signal, which is amplified by a lock-in and transferred, monitored and stored in a PC via a data acquisition system.

The above system was tested on a Periplast singlescrew extruder ($D=25$ mm, $L/D=25$), coupled to a rectangular die, which housed the optical probe near to its exit. A general purpose polystyrene extrusion grade was processed at 190°C, approximately 0.1 g of perylen masterbatch (of the same polymer) being injected through the hopper. Offline experiments were also carried out using a silica tracer, its concentration being inferred from the weight of calcinated extrudates (see Ref. 30 for more details). Figure 11 shows a typical raw data curve (intensity-time) and the corresponding RTD functions. In the case of $F(\theta)$, a comparison is presented between online and offline data and between these and two idealised limit mixing cases (plug flow and perfect mixing). The agreement between the two experimental curves is satisfactory, particularly if one takes in



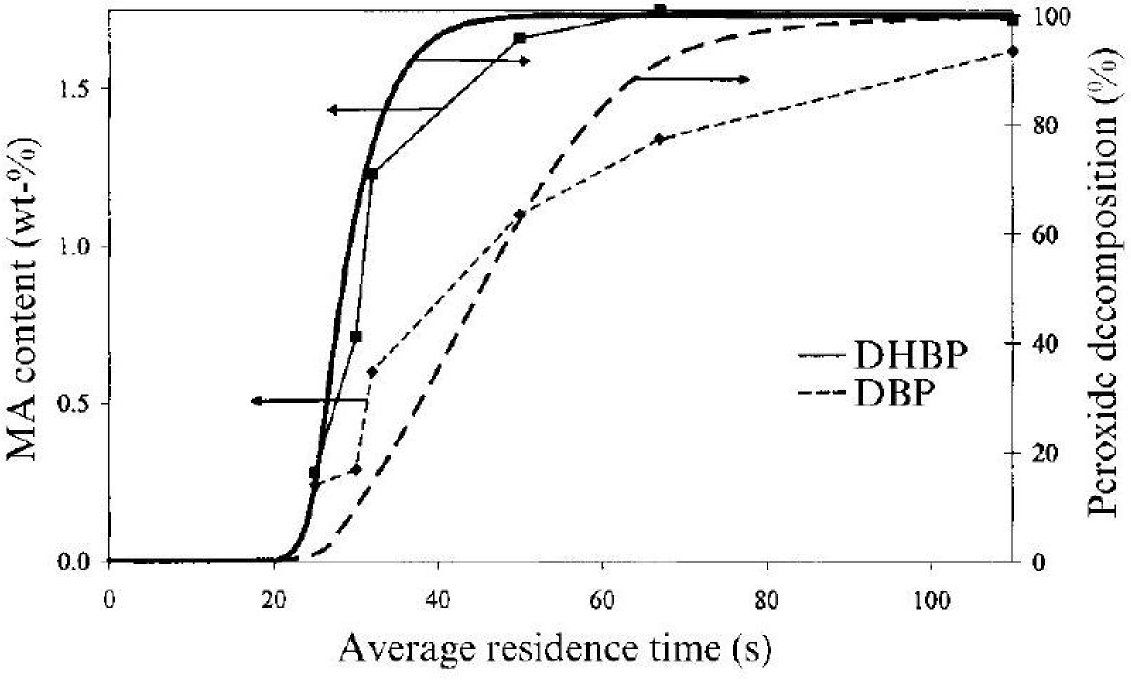
11 Online RTD determination and assessment (top to bottom): typical online raw data, corresponding $E(\theta)$ and online and offline $F(\theta)$ cumulative function

consideration the differences in precision between the techniques used to generate the data.

Monitoring the manufacture of some polymer systems

Grafting of maleic anhydride onto polyolefins

Polymer modification during extrusion has turned into an important technique for the manufacture of new materials. However, since the ingredients (polymer(s), monomers and additives) are subjected to complex thermo-mechanical-chemical effects, significant research has been carried out to establish the kinetics of free radical grafting and to model the total process. A general kinetic model is available, [31,32] but it is based on the availability of experimental data such as molecular weight, grafting content, residence time and extrudate temperature, which is difficult to obtain.



12 Evolution along extruder (converted to cumulative mean residence time) of MA grafted content and of peroxide decomposition using different peroxides

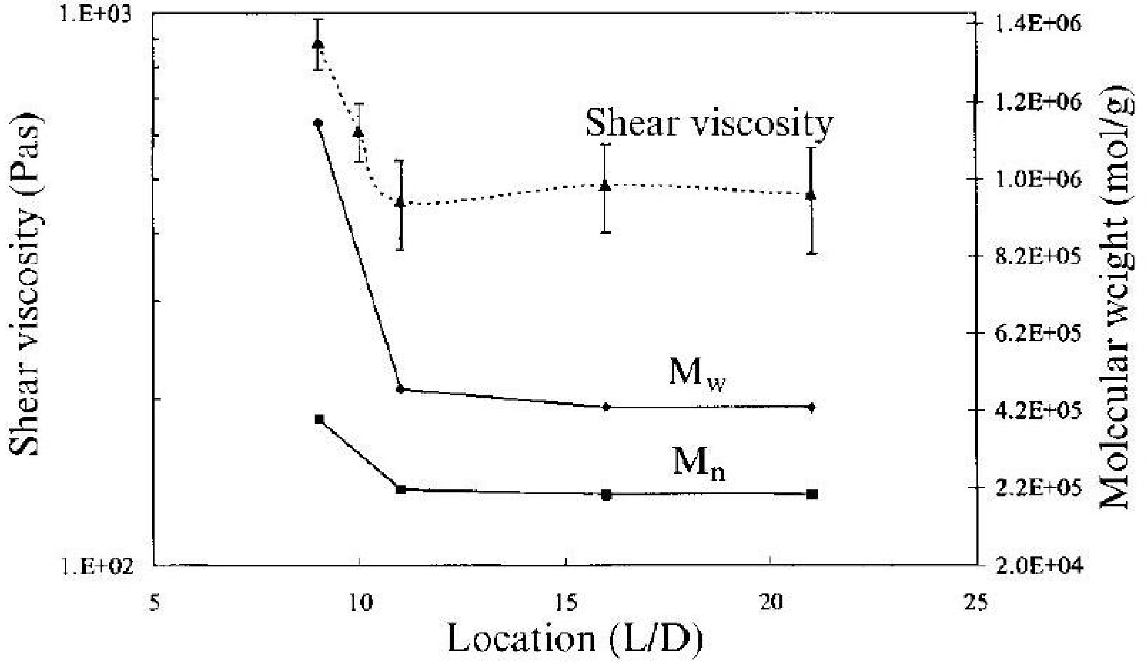
The devices presented in the previous sections were used to follow the physico-chemical phenomena (i.e. the rheological behaviour and the degree of MA grafting) developing along the screw axis of the Leistritz corotating twin screw extruder during grafting of MA onto PE using peroxides with different half-life times (at 200°C, the half-life of 2,5-bis(tertbutylperoxy)-2,5dimethylhexane (DHBP) is 6.1 s and that of di-tertbutyl peroxide (DBP) is 14.4 s). [33] Measurements of melt temperature and of mean residence time at various locations were also performed and combined with an algorithm that integrates numerically the peroxide decomposition for a given temperature and time.

Figure 12 presents the experimental MA grafted content and the calculated peroxide decomposition obtained for experiments with PE with 5 phr MA and either 1 phr DHBP or 1 phr DBP at 200°C, as a function of the mean residence time. Despite using the same number of moles of peroxide in the two experiments, the experimental grafting profiles are clearly different. However, these differences are readily explained by the peroxide decomposition profile, since there is a good qualitative correlation between both curves for each peroxide.

Peroxide-induced PP degradation

This study was performed to provide a greater experimental insight into controlled PP degradation upon processing, in the absence or in the presence of peroxide, under varied processing conditions. Online capillary rheometry and offline molecular weight determination (number and weight molecular weight M_{n} and M_{w}) on samples obtained along the extruder with the sampling devices were carried out.

Figure 13 presents the axial evolution of shear viscosity and molecular weight for PP processed at 200°C and 75$\mathrm{rev\,min}^{-1}$ with 0.1 phr peroxide (DHBP) in a Leistritz co-rotating twin screw extruder fitted with a typical three-zone mixing screw. The shear viscosity suffers a drop in excess of 50% between the beginning and the end of the first mixing block, remaining constant (within experimental error) afterwards. The M_{n} and M_{w} curves also decrease, especially in the first part of the extruder, which is obviously consistent with the viscosity data. Therefore, it seems that the reaction occurs very



13 Evolution along extruder of shear viscosity, M_w and $\boldsymbol{M}_{\mathbf{n}}$ of PP in presence of $\mathbf{0.1}$ **phr** peroxide

quickly and very early in the extruder and seems to be complete at the end of the first mixing block ($L/D = 11$), thus meaning that chain scission takes place mainly upon melting of PP. These results support previous theoretical predictions on similar systems. [34]

Conclusions

Online monitoring along the axis of an extruder can provide a wealth of data that contribute to the understanding of the physico-chemical phenomena occurring inside the machine. The techniques presented and validated experimentally in the present paper represent only a small part of the possible feasible portfolio.

Future work on the topic is likely to follow two parallel trends. The adaptation of other (sophisticated) online and inline techniques for readings along the barrel will certainly confirm in-process analysis as a powerful process analysis tool. Simultaneously, the opportunity for process control should be explored.

Acknowledgements

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