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MONITORING OF POLYMER EXTRUSION AND COMPOUNDING PROCESSES

Abstract: This work focuses on monitoring of polymer extrusion and melt compounding using single or twin-screw extruders. Standard extruder instrumentation aims at detecting eventual instabilities in flow and heat transfer in the extruder. Strategies for in-process monitoring considering the actual characteristics of the material being processed are presented and discussed. On-line and in-line approaches are defined. The advantages of sampling along the extruder barrel are demonstrated. Examples of the development and application of in-process optical spectroscopy and rheometry techniques are presented and discussed.

Keywords: extrusion, process monitoring, sampling, in-line, on-line

1. Standard extruder instrumentation

The process control parameters of screw extruders include screw speed, feed rate (in the case of starve feeding, which is usually adopted in intermeshing twin screw extruders (TSE)), barrel and die temperatures, and vacuum level if the equipment is configured for a devolatilization stage. During operation, these parameters are kept within pre-defined intervals by programmable logic controllers (PLCs). Their values impact directly on the level of the thermomechanical stresses generated and on the residence time in the extruder.

Shear stress τ is the product of shear rate γ by melt viscosity η . If the latter follows a power law, τ is given by:

$$\tau = k \gamma^n H(T) \quad (1)$$

where k and n are the melt consistency and power law index, respectively, and $H(T)$ is the temperature dependence, which can follow an Arrhenius-type law. Due to the complex flow patterns in the screw channels of an extruder, the shear rate varies locally but an average value γ_{av} can be estimated from:

$$\gamma_{av} = (\pi D N)/(60 h) \quad (2)$$

where D is the screw diameter, N is the screw speed and h is the channel depth. The maximum shear rate occurs in the gap between the crest of the screw flight (or the tip of the kneading disks, for co-rotating twin-screw extruders (co-TSE)) and the inner barrel wall. In the case of co-TSEs, the maximum shear rate is approximately 30

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times higher than the average value [1].

The average residence time in the extruder is the ratio between the volume occupied by the material (assuming that the screw channel(s) work fully filled) and the volumetric output. Thus, this time is strongly influenced by the flow patterns developing along the various process stages along the screw(s) (typically, solids conveying, melting, melt conveying, mixing). For example, due to the helical flow pattern in the metering zone of a single screw extruder, the residence time in the center region of the channel is the lowest and increases towards the screw and barrel surfaces [2]. The total residence time distribution (RTD) has been used as a measure of the distributive mixing of the extruder [3], and is also important to estimate the necessary material thermal stability. Determining the average residence time and RTD in starve fed machines is even more complicated, as these characteristics are also influenced by the degree of fill. Either numerical modelling of the global plasticating process or experimental measurements using tracers can provide precise data on this topic.

Shear rate and melt viscosity will also affect viscous dissipation, i.e., the increase in melt temperature resulting from intermolecular friction. Rauwendaal [2] showed analytically that in the metering zone of a single screw extruder the temperature rise increases with viscosity, channel length, screw diameter and screw speed, and decreases with melt density, specific heat, channel depth and helix angle. Figure 1 shows the effect of screw speed on the development of melt temperature along the length of a co-TSE during compounding of Polylactic Acid (PLA) with a chain extender. The barrel was fitted with a series of specially designed sample collecting devices [4] and kept at 210°C. The melt temperature was measured by sticking a fast response thermocouple into the freshly collected melt (it takes less than 2 seconds to obtain a sample). Melting starts at screw turn number 9, as the material flows through a kneading block extending up to screw turn 11. Varying the screw speed between 100 and 300 rpm generated melt temperature differences of up to 60°C, and melt temperatures as high as 276°C, i.e., almost 70°C higher than the set value.

Given the complexity of flow and heat transfer in screw extruders illustrated above, it is obviously important to monitor the process, i.e., to obtain information in real time that helps to understand the phenomena developing in the extruder. This provides a better understanding of the process and opens the possibility to detect changes or anomalies that require action by the operator. Conventional extruder monitoring is usually limited to readings of motor amperage or torque, melt pressure and melt temperature, often measured at the die entrance. Motor torque can be used to calculate the specific mechanical energy (SME) (also known as specific energy consumption (SEC)), which represents the mechanical power consumed per unit mass of extrudate produced. Up to 70-80% of the total SME is consumed to raise the temperature of the solid polymer and melt it. SME can be computed by the following

equation, where the gearbox efficiency usually varies between 0.93 and 0.97:

$$\text{SME [kWh/kg]} = \frac{(\text{nominal motor power}) (\text{applied torque}/\text{maximum torque}) (\text{screw speed}/\text{maximum screw speed}) (\text{gearbox efficiency})}{\text{mass throughput}} \quad (3)$$

SEM can be used for quality control, to compare different manufacturing operations, or for scale up purposes. It correlates with screw speed, feed rate and barrel temperature. As wear increases, so does SME. Different materials exhibit distinct typical values of SME, from values lower than 0.25 kWh/kg for reactive polymer blending, to approximately 0.25 kWh/kg for polyolefins and up to 0.4kWh/kg for TPVs [2,5,6].

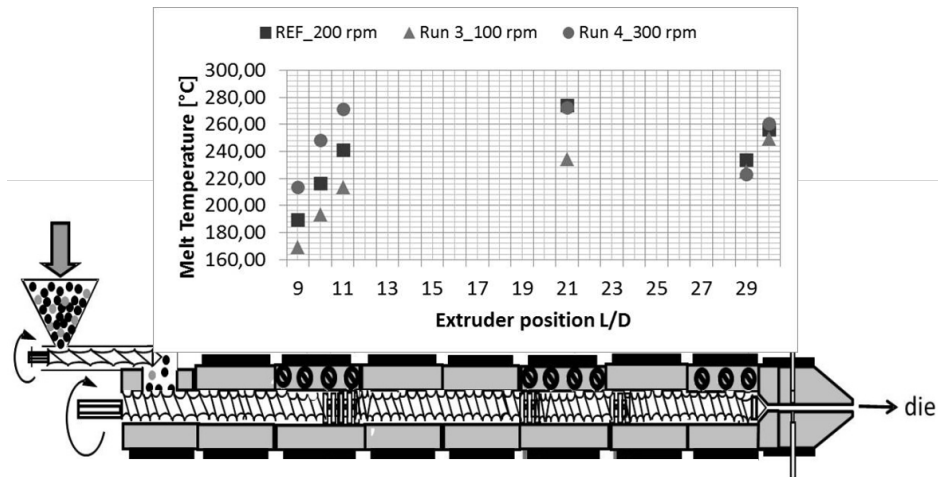


Fig. 1. Effect of screw speed on the development of melt temperature along the screw axis and die of a co-rotating twin screw extruder during compounding of Polylactic Acid with a chain extender (set temperature: 210°C)

While readings of melt pressure are reliable and useful for process monitoring, the temperatures obtained from flush-mounted or even protruding temperature transducers can differ significantly from the true values, because these devices are usually not insulated from the barrel wall and thus are largely influenced by its temperature [7]. Figure 2 compares the temperatures measured using flush-mounted transducers and a manual thermocouple stuck into the melt collected from sample collecting devices, for co-rotating twin-screw extrusion under different processing

conditions. Significant differences of up to 80°C were observed, as the readings of the transducers were largely influenced by the barrel temperature [7].

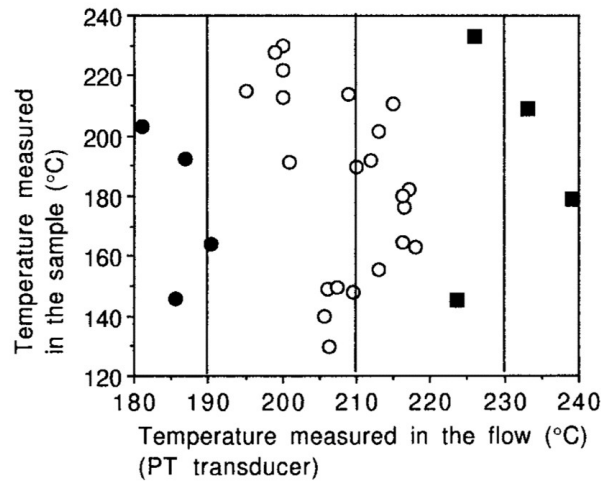


Fig. 2 Comparison between temperatures measured in the flow by PT transducers and in material samples collected from the extruder at the same locations: (full circles) $T_b=190^\circ\text{C}$; (open circles) $T_b=210^\circ\text{C}$; (squares) $T_b=230^\circ\text{C}$ [7]

2. Strategies for monitoring extrusion

Standard extrusion instrumentation aims at sensing attributes that relate to flow and heat transfer in the extruder. It is suited to assess process stability and to trigger corrective actions during operation whenever necessary. However, this type of instrumentation does not offer information on the actual characteristics of the material being processed. Consequently, practical material characterization often consists of collecting extrudate samples at regular intervals and perform tests in the laboratory. This off-line procedure is time consuming and entails important delays between sample collection and the eventually necessary adjustments to the extrusion operation (meanwhile, non-conform extrudate is being produced). These delays decline when the testing equipment is operated next to the processing equipment (known as at-line). A significant further reduction is achieved by coupling the testing device to the extruder and perform in-process measurements. When the data is obtained directly from the main melt stream (typically between extruder and die, or at die), measurements are named as in-line. On-line measurements are normally performed on a melt stream or material sample that was detoured from the main flow. After testing, the material is either wasted or returned to the main channel.

Figure 3 illustrates these concepts, using rheological measurements as example. In off-line testing, a sample is collected from the extrusion/compounding line and taken to the laboratory, where it is first subjected to compression moulding in order to obtain a disk that will be charged in the rotational rheometer and re-heated prior to the measurement. Thus, during sample preparation, the material is subjected to two extra thermal cycles, which may trigger degradation or changes in morphology and/or in chemical conversion. On-line monitoring implies detouring a melt sample from the main flow channel, which is then tested under specific conditions (rate of deformation, temperature) and wasted or returned to the melt stream. During in-line monitoring, measurements are made in the main flow channel, usually at the die, or between the extruder and the die, under the local processing conditions.

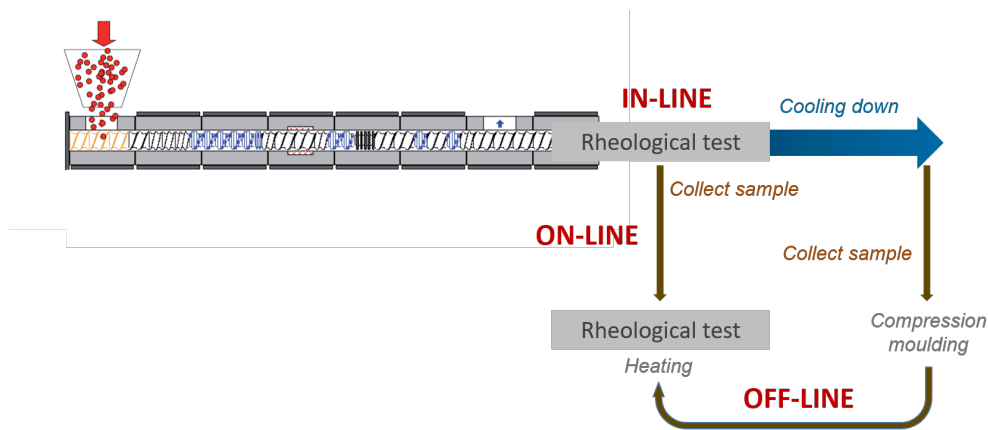


Fig.3 Off-line, on-line and in-line monitoring concepts in extrusion, using rheological measurements as example

In-process measurements are useful to assess both process stability and product quality, are essential for smart process control, and may contribute to swifter material and/or process development (e.g., fine tuning of a formulation, or determining the best operating window). A detailed discussion of in-process measurements advantages and requirements can be found elsewhere [8]. In extrusion, compounding and reactive extrusion, in-process monitoring can be performed using a variety of techniques, either alone or together, such as optical spectroscopy (Ultraviolet–Visible (UV–VIS), Infrared (IR), Fourier transform infrared (FTIR), Near-Infrared (NIR) and Raman), which deliver molecular or chemical composition information, rheometry, which is sensitive to the structure and morphological features at various dimensional scales, as well as other spectroscopy methods (e.g., fluorescence), small-angle light scattering (SALS), polarimetry, turbidity, ultrasonic attenuation and dielectric spectroscopy. Fluorescence

spectroscopy is often used to determine residence times and RTD by inserting fluorescent tracers in the flow stream [9-11]. SALS can estimate the size and shape of the droplets of the minor phase in a polymer blend or of the fillers in a polymer nanocomposite down to the sub-micron scale, but only for very low volume fractions [12,13]. Turbidity was utilized to estimate the particle size and shape of the dispersed phase in immiscible polymer blends [14], but again limitations in particle size and concentration apply. Polarimetry measures in real time polymer flow birefringence, which correlates with molecular weight, MW [15]. Ultrasound (vibrations with a frequency typically above 20 kHz) techniques have been frequently employed to monitor chemical conversion, MW, density, viscosity, melt temperature, orientation and relaxation, blend composition, blend morphology, RTD, melting evolution, etc. However, current commercial sensors can only sustain temperatures up to 150 °C and 30 bar. Consequently, the testing set-up is relatively complicated, with measurements being made through-the-wall via a buffer and needing correction calculations [16]. Also, it may be difficult to discriminate the various effects in the signal captured. Dielectric spectroscopy was applied to detect variations in the composition of polymer/co-monomer [17] and liquid crystalline polymer (LCP)/PP blends [18].

Figure 4 depicts the in-process monitoring techniques developed at the University of Minho and presented in detail elsewhere [19-22]. Most of them can be applied at specific locations along the barrel of modified single and twin-screw extruders. Material sampling during operation enables subsequent off-line characterization, whilst shaping immediately after sampling yields specimens or disks for tensile testing or rotational rheometry, respectively (thus saving the material from being subjected to further thermal cycles). Capillary, rheo-optical slit, rotational and extensional rheometries are available on-line. RTD, electrical conductivity and NIR spectra can be measured directly on the flow in the screw channel, i.e., in-line.

The selection of the in-process technique(s) and experimental /procedure for a given extrusion or compounding operation depends on the type of data necessary, on the required rate of sensing, on the coupling possibilities to the extruder, among others [8]. Monitoring between extruder and die or at die are the most common, while obtaining data along the barrel of the extruder is rarely reported. The spectra produced by optical spectroscopy can be correlated with composition, and structural and morphological features. On-line capillary rheometry yields a viscosity flow curve (or the popular melt flow index (MFI)), which correlates with degree of polymerization, chain extension and degradation (either premature or controlled via reactive extrusion). Small amplitude oscillatory shear (SAOS) tests are commonly applied to analyze the in-situ compatibilization of polymer blends or the degree of filler dispersion in nanocomposites. Extensional viscosity is sensitive to changes in interfacial tension and thus is also relevant for polymer blends. Quality control requires good sensitivity to changes in the variable being monitored and reasonable

delay between sampling and obtaining data, while process control demands repetitive quick measurements. Various aspects of in-process monitoring techniques and applications have been discussed in the literature [8, 23-26].

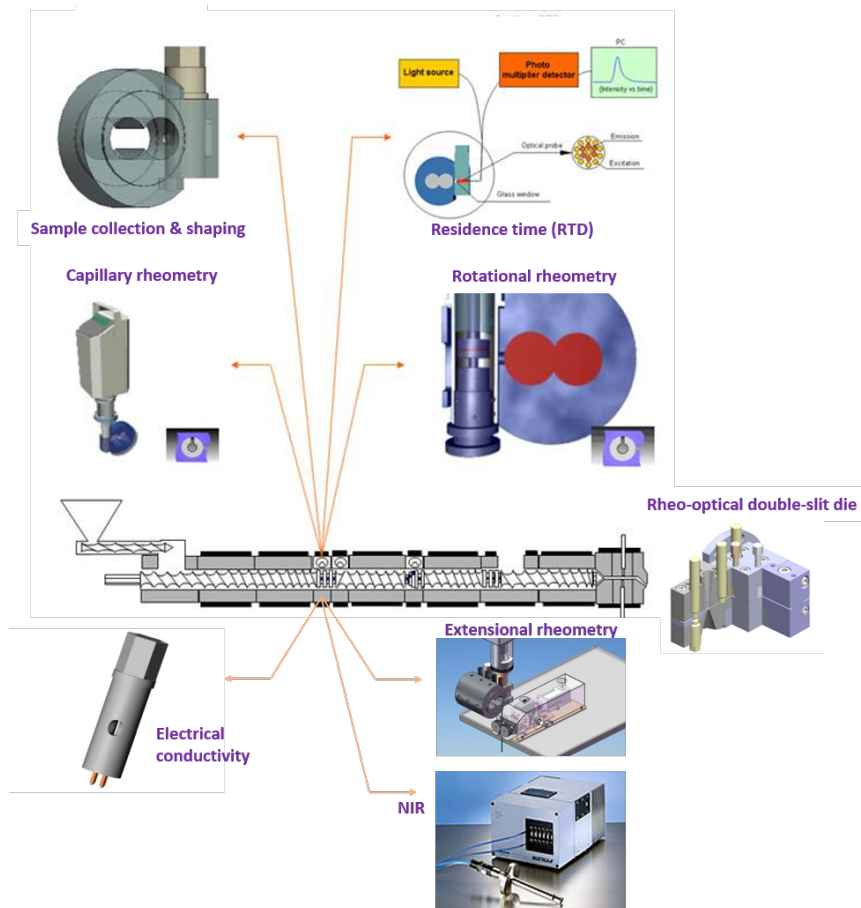


Fig. 4 In-process monitoring techniques for polymer extrusion and compounding implemented at the University of Minho

Figure 5 presents a mini-extrusion and compounding line (single and co-rotating twin-screw extruders can be interchanged) that was instrumented with the objective of characterizing multiphase polymer systems, such as polymer blends and nanocomposites, using small amounts of material. The extruder is fitted with a series of sample collecting devices and is coupled to a rheo-optical slit die. The extrudates can be used to obtain test specimens for the measurement of engineering properties.

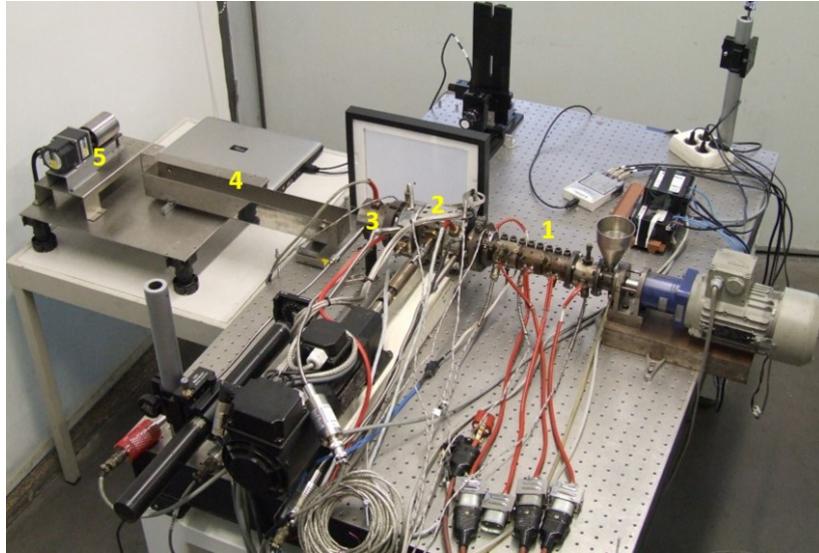


Fig. 5 – Mini-(single/twin) screw extrusion line with in-process monitoring capabilities; 1 - extruder with sample collecting devices; 2 - gear pump; 3 - rheo-optical slit die; 4 - water bath; 5 - winding

3. Sampling along the barrel

Monitoring along the axis of an extruder the development of melting, mixing, morphology, rheological response, chemical conversion and properties of a given polymer system may be important to uncover the underlying physico-chemical mechanisms and correlate them with the processing parameters, as well as to define the most adequate material recipe, screw geometry and/or operating conditions. In practice this is difficult to achieve, since the barrel of extruders is a black box. Therefore, a significant percentage of the experimental data obtained along the screw(s) was collected from screw-pulling experiments (known as Maddock-type, honouring the pionner of this method) that involve interrupting extrusion, cooling down the barrel, removing the die and pulling out the screw(s) to expose the material. Not only this procedure is laborious and time-consuming, but since it is very difficult to freeze rapidly the material in the extruder, melting, coalescence or reagglomeration in the case of polymer belnds or nanocomposites, respectively, and chemical conversion if a reaction is taking place, may develop or continue during the process [27]. This situation is clearly demonstrated in Figure 6, which compares the evolution of the average particle size (computed here as equivalent circle diameter) of ethylene/propylene copolymer (EPM) droplets suspended in a polyamide 6 (PA6) matrix, measured on samples collected from the same axial locations, but obtained with the sampling devices mentioned above and with the classic screw pulling

experiments. Samples collected during operation of the machine showed that melting occurred upstream of the location inferred from conventional experiments. Moreover, particle sizes were generally smaller in the first case, thus indicating that during cooling of the extruder and extraction of the screws coalescence developed, which is not surprising since PA6/ and EPM form immiscible blends [28].

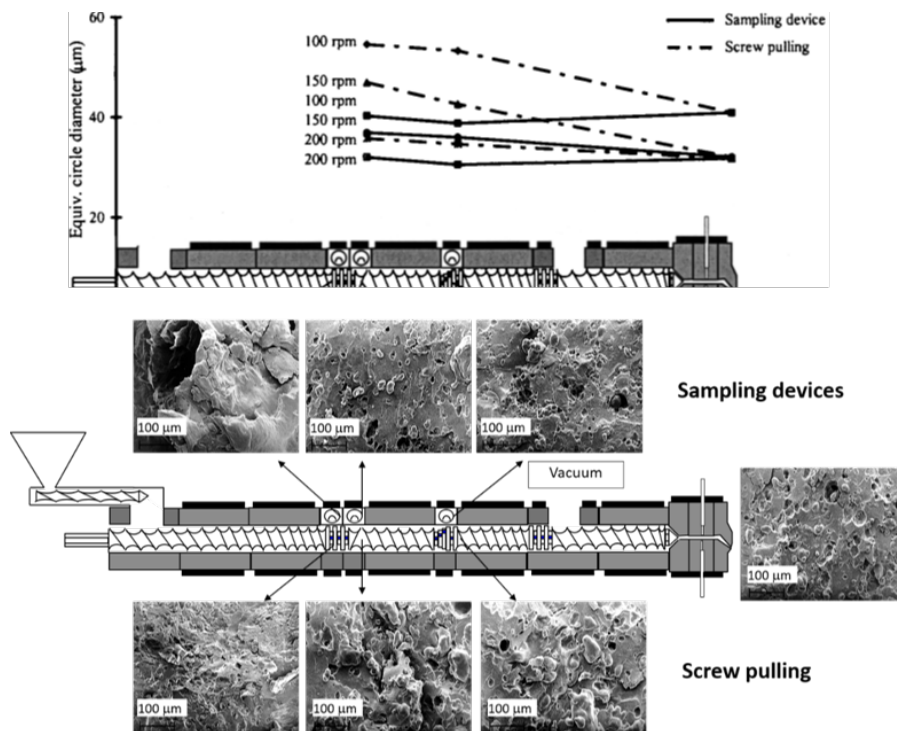


Fig. 6 Evolution of the morphology of a PA6/EPM immiscible blend along the axis of a co-rotating twin extruder, as measured on samples obtained at the same axial locations by sampling devices and screw pulling experiments [28]

Various experimental sampling methodologies have been developed, such as using a split barrel (known commercially as a clamshell extruder), a sliding-barrel, stopping the extruder and pour liquid nitrogen into entry ports, removing molten samples at entry ports with tweezers, or diverging a small amount of material from inside the extruder [4]. The ideal technique should be simple and allow quick access to representative material samples during operation of the extruder, without affecting

the local flow conditions.

Figures 7 and 8 demonstrate the relevance (and sometimes uniqueness) of the information that can be accessed by sampling along the extruder and perform a subsequent characterization in the laboratory. Figure 7 concerns the preparation of a PA-6/EPM-g-MA (80/20) wt% blend (EPM-g-MA denotes EPM with grafted maleic anhydride (MA)) in a twin screw extruder. Because of the screw design and operating conditions, at $L/D = 12$ the PA-6 pellets are embedded in a continuous rubber phase. One screw turn later ($L/D=13$), the blend is already fully molten, exhibiting the usual matrix/suspended droplets morphology [4, 28]. Interestingly, at $L/D=12$, using higher magnification unveils a morphology at the PA-6/EPM-g-MA interface consisting of stretched, wavelike rubber domains perpendicular to the PA-6 surface, and thin spider-web-like filaments. These features confirm the validity of the dispersion mechanism of liquid-liquid systems proposed by Scott and Macosko [29], which was proposed based mostly on experiments performed in internal batch mixers.

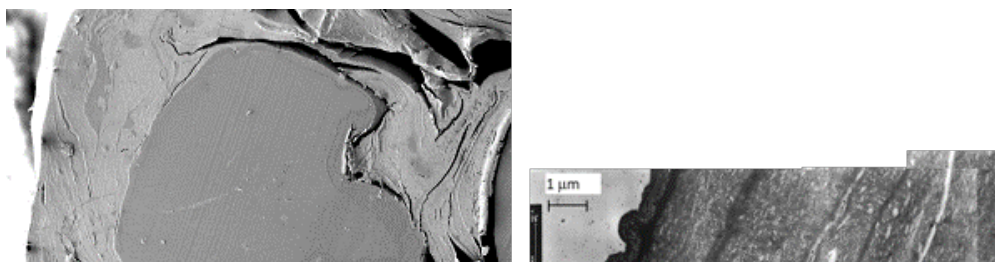


Fig.8 Evolution of the morphology of PA-6/EPM-g-MA (80/20) w/w blends at two consecutive screw turns of a twin-screw extruder (adapted from [4, 28])

Figure 8 refers to the grafting of MA onto polyolefins (polyethylene (PE), EPM and polypropylene (PP) [30]. The graph displays the relative variation of the rheological moduli (G' and G'') along the extruder for the three materials. The reaction is very fast, as can be confirmed by the sharp variation in the rheological responses, with very little change further downstream. The final grafting yield depends on the polyolefin, as a result of the competition between grafting and termination reactions. Specifically, as the ethylene content increases, the chemical mechanisms change from β -scission of tertiary PP radicals, to small crosslinking in EPM and to severe crosslinking/gel formation, together with some degradation, in the case of PE.

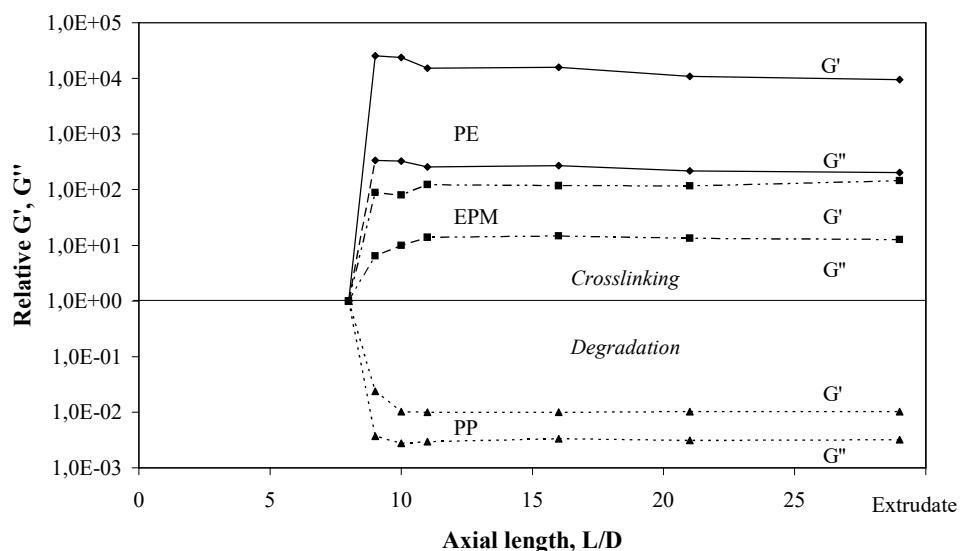


Fig. 9 Evolution of chemical conversion along the axis of a co-rotating twin-screw extruder during reactive grafting of polyolefins with MA. The rheological moduli G' and G'' (at 7×10^{-3} Hz) were normalized to the values of the starting materials [30]

4. In-process optical spectroscopy

Radiation at different wavelengths induces a range of molecular motions that can be used to obtain useful information on the polymers analyzed. UV-VIS (0 - 1000 nm) causes electronic transitions that enable assessing the concentration of a particular species. For example, the technique was applied to monitor the process-induced degradation of poly-lactic acid (PLLA) [31]. Within the IR region ($12000 - 400 \text{ cm}^{-1}$), the MIR range ($4000 \text{ to } 400 \text{ cm}^{-1}$) is related to molecular vibrations, while NIR ($12,000 - 4000 \text{ cm}^{-1}$) includes bands that result from harmonic overtones of fundamental and combination bands linked to hydrogen atoms (which are relevant for compounds containing CH, OH and NH bonds). A change in the absorbance band intensity can be associated to a variation in concentration. MIR was employed to monitor the reaction of styrene-maleic anhydride copolymer with a long chain alkyl amine [32]. Commercial NIR probes work either in transmission or in diffusive reflectance mode (thus enabling on-line and in-line measurements, respectively) (see [33] for a comparison of performance). For example, the technique was adopted to monitor the composition of PP/ethylene vinyl acetate (EVA) copolymer blends [34], to determine the MW of partly glycolised polyethylene terephthalate [35], to follow the graft copolymerisation of MA onto PP [36], to analyze the conversion of a

styrene/maleic anhydride co-polymer [32], to monitor the transesterification of EVA [36], and to investigate the esterification of an ethylene-vinyl-alcohol (EVOH) co-polymer [37]. In order to extract from NIR spectra as much information as possible, calibration models relating the spectral data to reference characterization parameters are developed – this is known as chemometrics. In principle, a single calibration model could yield information on chemical, physical and morphological characteristics, so that NIR could replace several other characterization techniques. However, a change in the material recipe or in the geometry of the extruder usually requires a new calibration of the chemometric model. Figure 10 demonstrates how in-line NIR can be used to monitor the evolution along the axis of the extruder of the level of dispersion of polymer/organoclay nanocomposites. The analysis by X-ray diffraction (a well established technique used to assess the degree of intercalation of this type of systems) of samples collected at various positions along the screws by sampling devices shows that intercalation increases along the screws (perhaps together with exfoliation), but during flow through the die part of the intercalation is apparently reverted (Figure 10a). These results were confirmed by NIR data (Figure 10b). Figure 10b also shows that, as expected, the rate of dispersion increases with increasing screw speed, but reversion of dispersion at the die was always observed. This phenomenon was attributed to the degradation of the clay surfactant that, in combination with lower melt viscosity due to viscous dissipation, facilitated the flow of the polymer out of the clay galleries [38].

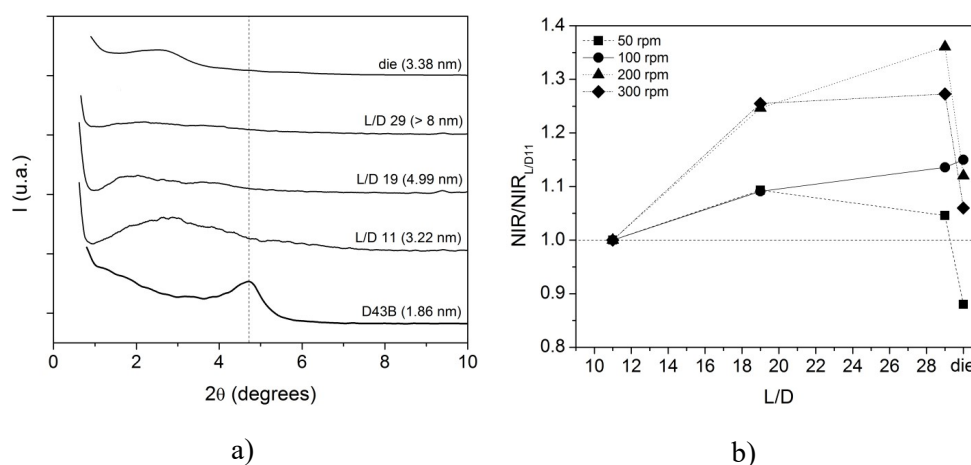


Fig 10 Evolution of the dispersion along the screws of a PA6/organoclay (95/5 wt.%) nanocomposite (100 rpm, 3kg/h). a) X-ray diffraction spectra (100 rpm, 3kg/h); b) effect of screw speed on the degree of dispersion as measured by NIR (values along the screw were normalized to the value at $L/D=112$, where melting

was completed

The absorbance bands of ATR-FTIR spectra can be linked to chemical composition. However, since the technique involves a path length that is much shorter than the depth of the screw or die flow channels, on-line testing is required to obtain data representative of the bulk. The technique was applied to follow PE grafting with organosilanes [39], to follow the thermal degradation of polyoxymethylene (POM) [40] and to evaluate the monomer/polymer ratio during polymerization of ϵ -caprolactam [41]. Raman spectroscopy detects vibrations modifying the polarizability of a molecule, which enables analyzing the polymer backbone structure and conformation, usually by studying the intensity of the spectral band of interest. The technique was employed to monitor the grafting of glycidyl methacrylate (GMA) onto low density polyethylene (LDPE) [42]. Coates et al [43] used simultaneously on-line MIR, in-line transmission NIR and in-line Raman to monitor the single screw extrusion of HDPE/PP blends and concluded that NIR exhibited the best resolution, although it was challenging to quantify in real time changes in specific bond vibrations.

5. In-process rheometry

The rheological response of a polymer is sensitive to changes of MW, MWD and degree of branching, and to composition, interfacial stress and morphology of polymer blends. An increase in MW causes an increase in viscosity. In small amplitude oscillatory shear (SAOS), the curves of G' and G'' vs. frequency shift horizontally to lower frequencies with increasing MW. The maximum in G' , G'' and the cross-over frequency assess the broadness of the MWD. Long-branching increases the shear rate dependence of linear polymers, and can be estimated from measurements of G' , of the first normal stress difference N_1 , or by measuring the strain hardening effect on the extensional viscosity. Compatibilized blends are usually less shear-thinning than the equivalent immiscible ones. The size of the dispersed droplets in a blend can be estimated from G' and N_1 [44]. The viscosity curves of compatibilized blends generally show two plateau regions, at low and moderate frequencies, the first stemming from interfacial effects. Similarly, an additional slow relaxation process in SAOS on both physical and chemically compatibilized blends was attributed to interfacial elasticity [44]. It becomes therefore evident that using the rheological toolbox by means of in-process monitoring is of great value.

In-line slit rheometry can be used straightforwardly by coupling a rheological die to an extruder. The die contains at least two flush mounted melt pressure transducers along the slit. Melt viscosity can be determined from measurements of throughput and of the lengthwise pressure difference. N_1 can be estimated from the hole-

pressure or exit pressure methods, but these require highly accurate experiments that may be difficult to perform in an industrial production environment [45]. The slit geometry can also easily accommodate flush mounted optical windows, for example to use SALS or polarized optical microscopy to obtain structural and morphology information or UV-fluorescence transducers to measure RTD. Figure 11 exhibits the shear viscosity, N_1 and SALS patterns as a function of shear rate for a PS/PMMA 98/2 wt.% blend [22]. SALS patterns exhibit an ellipsoid superimposed on a streak, both oriented normal to the flow direction, that are typically associated to the presence of a morphology consisting of elongated (ellipsoidal) droplets and filaments or strings (streaks). The pattern becomes more ellipsoidal with increasing shear rate, indicating more droplet elongation along the flow and the streak becomes more intense and thinner.

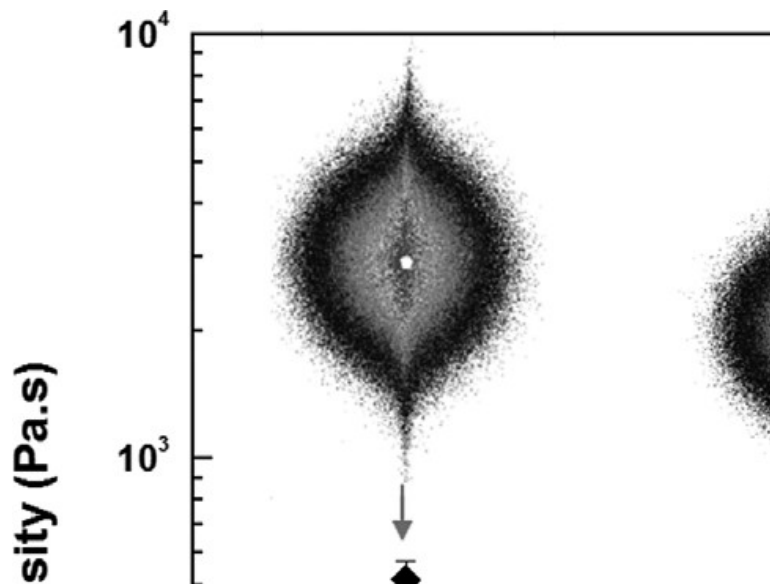


Fig. 11 Shear viscosity, N_1 and SALS patterns as a function of shear rate for a PS/PMMA 98/2 wt.% blend processed at 230 °C (flow develops in the horizontal direction) (adapted from [22])

In-line slit rheometry also has some significant drawbacks. Coupling a slit die to an extruder eliminates the possibility of extruding products with other cross-sections, making this set-up mostly adequate for R&D work. Also, the real melt temperature along the die is unknown, not only because of the inherent viscous dissipation, but

also due to the fact that the thermomechanical history of the material in the extruder cannot be instantly relaxed up to the die entry. More importantly, measuring both the extrusion throughput and pressure drop will yield a single point of the viscosity vs. shear rate curve. To generate a range of shear rates, the output of the extruder must be changed, which will modify the thermomechanical history of the material inside the machine. In turn, this may lead to changes in chemical conversion, homogeneity, thermal stability and/or morphology, i.e., at each shear rate a different material would be characterized. To evade this problem, several variant slit die designs allowing to acquire various points of the flow curve in a single extrusion experiment have been suggested (for a review see [46]). For example, in the twin-slit design adopted by Teixeira *et al* [46] (Figure 12) the inlet flow channel contains a melt pressure transducer and is divided into two parallel slits, one being used for the measurements (and containing at least two melt pressure transducers along its length). Two vertically moving valves are located at the entrance of each channel. It is possible to change the shear rate at the measuring channel while keeping constant the total pressure drop in the die by moving its valve in one direction, and simultaneously adjust as necessary the other valve in the opposite direction.

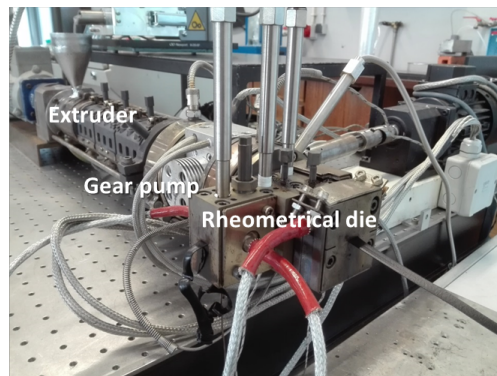
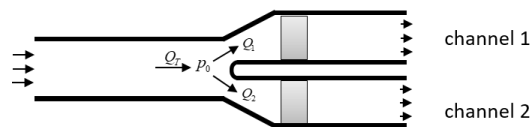


Fig. 12 Twin-slit rheometrical die: concept (top) and practical construction (bottom). The two channels are set at 90°. A gear pump is used to stabilize the flow from the extruder

On-line capillary rheometers analyze a material stream that was detoured from the

main flow channel, usually between extruder and die. In this way, the melt can be conditioned to the required testing temperature prior to the measurement and the shear rate can be changed independently. Various commercial solutions are available and used in production environment (see example in Figure 13). They vary in design, working ranges of shear stress and shear rate, time delay between sample collection and measurement, single vs. multiple measurements in parallel or in series (e.g. to perform the Bagley correction for end effects), amount of sample needed, and whether the material is wasted or returned to the main flow. Usually, a gear pump controls accurately the flow rate in the testing chamber, where the pressure drop is measured. A few instruments have interchangeable measuring geometries, allowing to switch between slits and capillaries. The latter are more popular, as they are easier to clean, provide a wider measuring range under moderate pressures and are more suitable to determine the MFI.

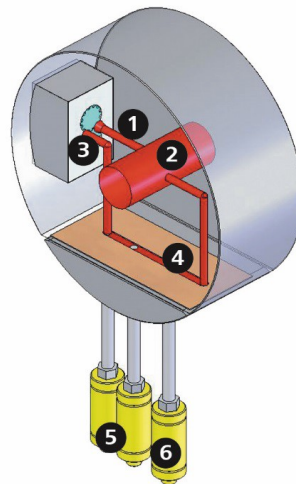


Fig. 13 Gneuss VIS on-line capillary rheometer: 1 – bypass; 2- main melt flow; 3 – gear pump; 4 – measuring geometries; 5 – temperature sensor; 6 - pressure transducers [47].

On-line capillary rheometry along the extruder is also possible. The device shown in Figure 14a is secured to a modified extruder barrel containing a channel linking the inner barrel wall to the reservoir of the rheometer. The instrument comprises the measuring head of a commercial rotational rheometer, a heated body, a replaceable die and a moving ram. The rotational movement of the rheometer shaft is converted into a linear vertical ram movement, while the torque is recorded and used to determine the apparent wall shear stress [48]. This prototype was used to monitor effect of peroxide content on the shear viscosity of PP along the extruder axis

(Figure 14b) [49]. The reaction is extremely rapid, and the higher the peroxide content, the lower the shear viscosity due to chain scission.

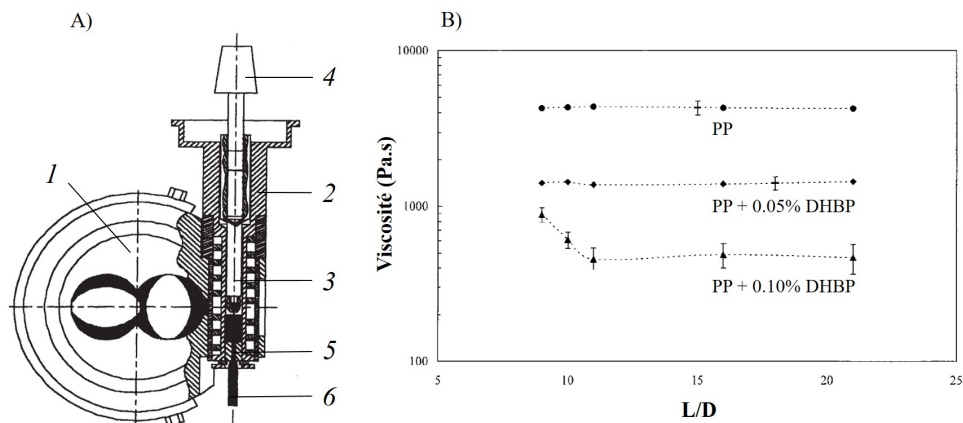


Fig. 14 On-line capillary rheometer. A) The instrument coupled to the modified barrel of an extruder (1 – extruder barrel; 2 – rheometer body; 3 – ram; 4 – rheometer shaft; 5 – capillary die; 6 – extrudate); B) influence of peroxide (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DHBP)) content on the axial evolution along the extruder of the shear viscosity of PP [48,49]

Oscillatory rheometry is a convenient technique to characterize multiphase systems as it preserves the material morphology due to the small deformations involved, unlike capillary or slit rheometries. Commercial equipment is available, but the operational window is usually unsuitable to the practical temperatures/viscosity values required for polymer melts. Figure 15a presents the concept of an on-line rotational rheometer that can be coupled to a modified extruder barrel with the sensing capacities and testing modes of a conventional laboratory instrument [50,51]. The device controls the position of the lower plate, admits the material sampled and moves vertically a ring cleaning the outer surface of the test disk. A commercial rotational rheometer head executes the experiments. Figure 15b plots data obtained with this apparatus concerning the evolution of G' and G'' along the extruder for PLA and the same PLA with a chain extender (CE). As expected, the rheological moduli for PLA+CE are larger than those for neat PLA. The reaction took place upstream very quickly, upon melting. Further downstream, a slight reduction in the moduli is consistently observed and probably caused by thermal degradation.

In-process rheometers can also generate extensional flows. Superimposed shear and extensional flows develop in "zero length" or short convergences. Hyperbolically

converging dies induce uniform elongation rates [52]. The extensional viscosity can be extracted when applying the well-known Cogwell [53] or Binding [54] analyses. Convergences can be created simply by joining two consecutive slits with different heights [55-58]. Kracalik et al [59] used a Rheotens (a device that pulls filaments by means of four rotating wheels connected to a displacement sensor [60]) to stretch extrudates. Figure 16 reports an on-line variant of this method, which can be applied along the axis of the extruder [61].

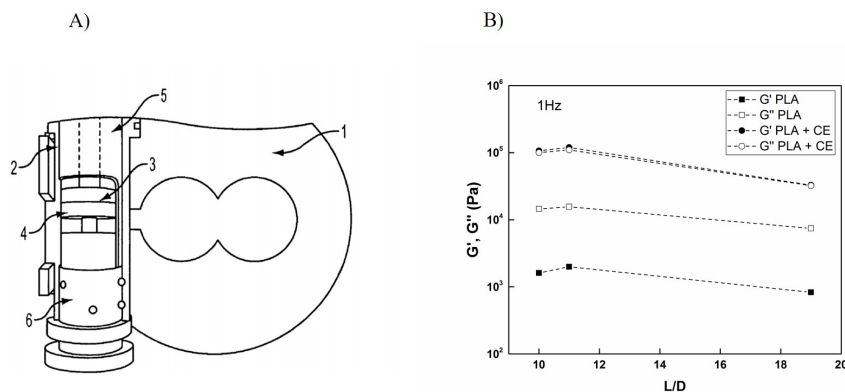


Fig. 15 On-line rotational/oscillatory rheometry. A) Rheometer coupled to the modified barrel of an extruder (1), consisting of a body (2), a cleaning ring (5), a lower support (6) and top (3) and bottom (4) parallel plates; rotation of (2) admits material from the extruder; the top plate (3) rotates/oscillates via coupling to the head of a commercial rheometer; B) progress of G' and G'' along the extruder for PLA and PLA with chain extender (CE)

6. Conclusions

In-process measurements in extrusion and compounding aim at obtaining information in real time about the characteristics of the materials that are being processed, rather than monitoring process variables that relate to flow and heat transfer conditions in the extruder, which is the approach of conventional instrumentation. Therefore, they must necessarily encompass a wide range of techniques. This chapter summarized approximately 30 years of efforts of many teams in academia and industry to develop in-line and on-line instruments and measuring techniques capable of extracting quickly relevant, representative, precise and reliable material data. A few application examples were discussed. Emphasis is given on the work carried out at the University of Minho, Portugal.

In-process monitoring techniques have gradually convincingly demonstrated their

usefulness both for R&D and production, particularly for material development and quality control. The future will certainly involve the implementation of smart process control on the basis of material attributes and, for this purpose, in-processing measurements are indispensable. Therefore, the utilization of in-process monitoring in extrusion and compounding processes is expected to grow substantially in the next coming years.

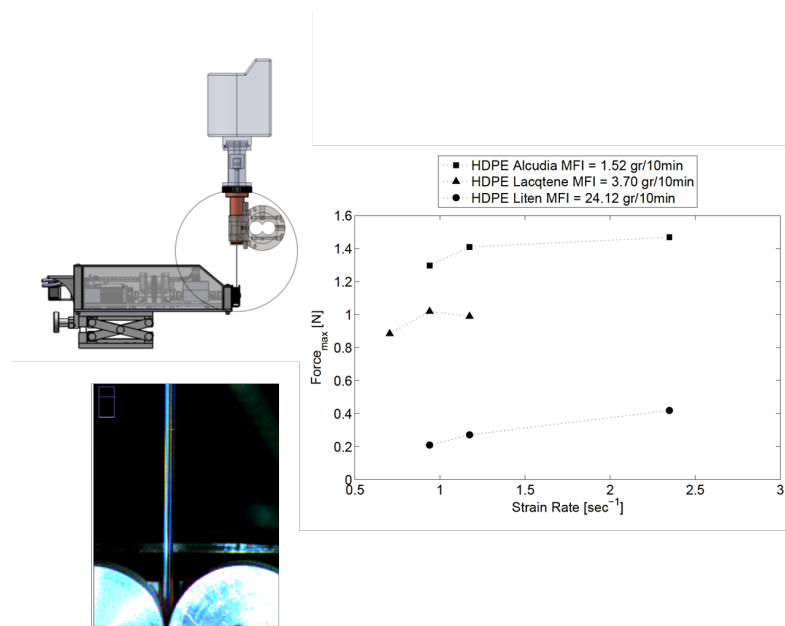


Fig. 16 On-line extensional rheometry. Schematic view of the device and image processing of a filament being stretched (left), and maximum stretching force at different strain rates for HDPE with various MFI (right) [61]

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