Monitoring Reactive Processes along the Extruder

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This paper reports data obtained from monitoring the evolution of chemical conversion and morphology during the production of a compatibilized polymer blend of PA 6/EPM/EPM-g-MA and of modified polyolefins (grafted with MA) in a co-rotating twin screw extruder. In the first case, the MA content of the modified rubber decreases strongly to almost zero-level and the particle size reduces dramatically from mm to sub- μ m level already in the melting zone. The process seems to be mainly influenced by the local flow characteristics, as they assure efficient generation and renewal of interfacial area. In the second case of MA grafting, a similar evolution is observed regardless of the polyolefin type but, for this kind of reactions, temperature and residence time play an important role.

A brief presentation of the on-line monitoring tools used in the above studies is also included.

Introduction

Reactive extrusion has been widely adopted by the polymer industry for the continuous manufacturing of commercial materials, via polymerization of monomers, chemical modification of existing polymers (e. g., inducing controlled degradation, chain extension, branching, grafting and/or modification of functional groups) and blending of immiscible polymers [1,2]. Despite its economical, environmental and logistical advantages, reactive extrusion is a complex technology involving interactions between chemistry, rheology and morphology, which must be compatible with the thermo-mechanical history developing inside the extruder where it is applied.

Therefore, it is not surprising that this technology has engaged intense research both by academic and industrial teams. For practical reasons, most studies focussed on the development of (eventually new) specific polymer systems in co-rotating twin screw extruders, by correlating formulation, processing conditions and characteristics and performance of the extrudates [3, 4]. However, despite of these efforts, the nature and rate of the physico-chemical processes (reactivity, solubility, temperature and flow) developing inside the extruder have remained largely unknown. The understanding of the reaction kinetics in the melt and the morphology development under real processing conditions would also be valuable for product development and process optimization. This challenge of producing real time information requires the availability of

sophisticated in-line monitoring capabilities able to measure directly, or indirectly, the evolution of chemistry, morphology and rheology or, alternatively, the possibility of collecting relevant material samples from the extruder at different barrel locations.

A few authors have pursued the last approach by developing specific experimental techniques/devices (e. g. [5 to 9]). These include quenching the material and extracting the screw, stopping the extruder and pouring liquid nitrogen into entry ports, using a split barrel, removing molten samples at entry ports with tweezers and diverging a small amount of material from inside the extruder through a hole in the barrel. These techniques require sampling times ranging from several minutes (e. g., in screw pulling) to a few seconds and, in some cases, oblige stopping the extruder prior to collecting the samples. Also, most sampling techniques work only either in pressurised, or conversely in partially filled zones of the screw. Moreover, they may affect the melt flow conditions in the extruder and consequently the morphology of the sample being removed, and they can be laborious to manage.

The authors try to combine on-line monitoring and sample removal approaches. A technique to enable fast and representative sampling along the screw axis, for subsequent off-line characterization, was first designed (and allows the measurement of average local melt temperatures) [10]. Subsequently, this was combined with on-line rheology and residence time distribution (RTD) measurements at the same barrel locations [11, 12] (other researchers developed sometimes quite sophisticated on-line techniques but, in most cases, applied them only downstream of the extruder - see, for example [13 to 15]). Since temperature and RTD data are important to determine the kinetics of chemical processes, and because rheology is a powerful tool to assess morphology [16], these two on-line measurements could complement the off-line characterization of the samples collected (e. g., by spectroscopy, electron microscopy).

This paper discusses the development of chemical reactions and morphology along the extruder during reactive extrusion. As examples, we selected the in-situ compatibilization of polyamide 6 (PA 6)/ethylene-propylene rubber (EPM) blends in the presence of EPM grafted with maleic anhydride (EPM-g-MA) [17, 18] and the grafting of MA onto polyolefins [19, 20].

On-line Monitoring Techniques

This section provides a short overview of the devices that were gradually developed for monitoring the evolution of relevant material characteristics along the extruder axis (for a more
comprehensive explanation of the constructional and operational features, see [12, 21]). The overall concept uses the following principles (see also Fig. 1):

- Specifically designed barrel sections are inserted, where required, between the conventional barrel segments of a modular twin-screw extruder. Each contains one or several side holes (aligned axially) in the barrel, through which material is detoured from the screw channel into an outer chamber and kept under a controlled temperature. This chamber accommodates one of the various available collecting/measuring devices, i. e., diverse on-line experiments can be performed at each axial location, simply by inserting the relevant device.
- The side hole in the barrel is as short as possible to diminish the flow time, and its aperture is a compromise between minimizing the detoured flow/screw channel flow ratio and reducing the average shear rate and pressure drop in the hole, which could induce modifications in the chemical conversion and morphology of the material being sampled.

- All the devices use the rotating valve principle, i. e., by sequentially rotating their bodies, their inlet opening can be shut-off and the extruder operates conventionally, or the inlet channel can be opened for material sampling. Measurements and sampling can be performed while the extruder continues to run.

Sampling Device

In this device the cylinder contains two cavities of different size. Upon rotation, each cavity is exposed to material flowing out from inside the extruder. While the smaller cavity receives essentially the material that had been retained in the side hole, the main larger cavity collects fresh material. Upon further rotation, the latter cavity is presented to the operator, who typically removes the material and quenches it in liquid nitrogen. The above sequence takes only a few seconds and yields 0.5 to 2 g of sample, depending on the size of the device (this dictates the axial distance between adjacent sampling ports). Instead of quenching, the operator can choose to insert a preheated fast-response thermocouple in the sample, to obtain a realistic measurement of the local mass temperature (differences of more than 60°C between set and real temperatures have been registered).

On-line RTD

The technique consists in monitoring the variation in tracer concentration with time at a specific barrel/die location, after having incorporated it step wise in the material stream. A fluorescent tracer was used (more precisely, a masterbatch of 5%

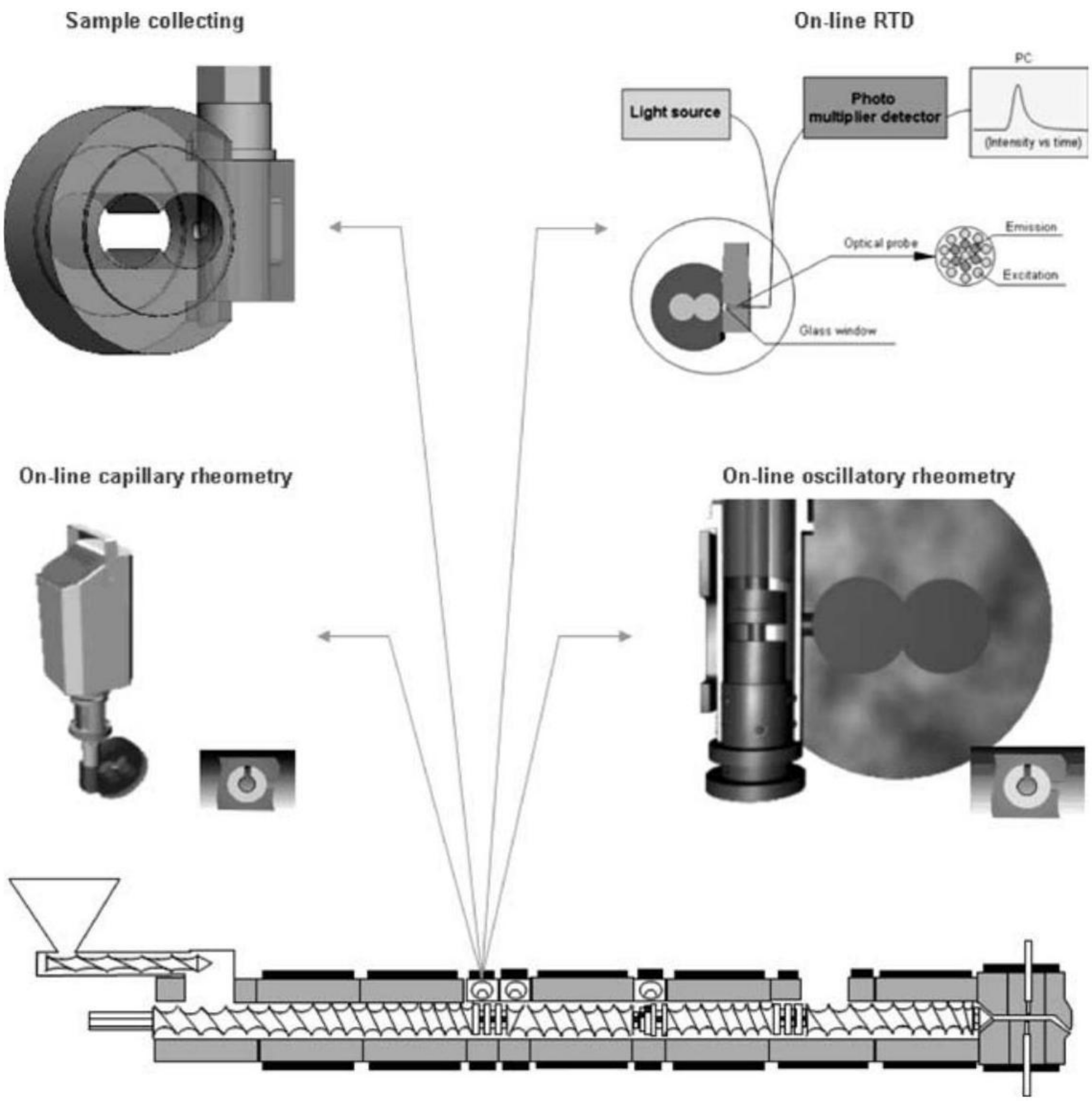


Fig. 1. On-line monitoring/sample collecting techniques
perylene dispersed in the polymeric matrix), since small amounts can be used (approximately 0.1 g of masterbatch is sufficient for an extrusion throughput of circa 5 kg/h) and, consequently, the flow pattern along the extruder is little affected by its presence. The experimental set-up comprises (i) a Y-shaped optical fibre bundle, whose ends are exposed to the flowing material (via a probe placed in the barrel's outer chamber), (ii) the excitation light source (mercury lamp) and (iii) the emission detection (photodetector and lock-in amplifier, plus filters to reduce noise and interference with other light sources).

On-line Capillary Rheometer

As in conventional rheometers, the apparatus contains a heated hollow cylinder (inserted in the barrel's outer chamber), a moving piston and a (replaceable) capillary die. Upon rotation, a lateral hole in the cylinder becomes in line with the lateral hole of the extruder barrel, thus enabling the inflow of the melt to be tested. In turn, the rotational motion of the shaft of a portable constant stress rotational rheometer sitting on top of the cylinder is converted into the linear ascending/descending piston displacement. Thus, the commercial rheometer is used to set and control the piston speed, wish pushes the melt through the die at a given shear rate. The corresponding torque is employed to determine the apparent wall shear stress. The usual procedures for performing the Bagley and Rabinowitsch corrections are performed.

On-line Oscillatory Rheometer

This contraption maintains some of the features of the capillary rheometer by also using a (modified) commercial rheometer for inducing the sample deformation and measuring its response. The hollow body works as a sampling device. Its upper part accommodates the moving cone/plate (which is directly coupled to the rheometer shaft), while the lower section contains the lower plate (with adjustable height in order to set the gap). The operating sequence consists in: i) the off-line gap calibration, ii) inserting the device into the extruder in the off position, iii) opening the inlet lateral orifice and subsequently shut it off, iv) fixing the gap and wiping the excess material using the sliding ring, v) waiting for thermal equilibrium, vi) performing a measurement, vii) cleaning the device.

Materials and Experimental Procedure

The materials used in both studies were PA 6 (Akulon [(8)] K123), EPM (Keltan ® [8] 740), high density polyethelene, PE (Stamylan HD 2H280) and polypropylene, PP (Stamylan P 13E10), all produced by DSM, The Netherlands. The EPM rubber (VA 404, with 45wt.% ethane content) and its modified counterpart, EPM-g-MA (Exxelor VA 1801, 1803, 1820 and 1810, containing 0.49, 0.47, 0.31 and 0.22wt.%MA, respectively, as determined by FT-IR) were provided by Exxon, Spain. Maleic anhydride (MA) was obtained from Aldrich, while the peroxide (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, DHBP, Trigonox 101) was supplied by Akzo Nobel.

Blending and chemical modification of the polyolefins was carried out in a modular Leistritz LSM 30.34. intermeshing co-rotating twin-screw extruder. Generally, the materials were pre-mixed in a tumbler mixer and fed through the hopper via a K-Tron gravimetric feeder.

Fig. 2 shows the extruder layout and sampling locations used for each system. In both cases each screw contains three mixing sections, made of staggered kneading disks and/or a left hand element. The section upstream induces melting, the second contributes for further dispersive/distributive mixing, while the third complements the previous mixing action and provides a seal for devolatilization. Sampling/monitoring was carried out in these zones, not only because the positive pressure facilitates the detour of material towards the barrel's outer chamber, but also because the most important variations in morphology, chemical conversion, rheological response and mass temperature are expected to take place where the ther-mo-mechanical stresses are most intense.

The chemical evolution along the extruder was monitored by recording the FTIR spectra (Perkin-Elmer 1600) of thin films prepared by compression-moulding. For quantification purposes, the height of the characteristic peak of the original, or modified, polymer sample, with known thickness was used.

The morphology of the blends was analyzed using a Philips CM200 Transmission Electron Microscope (TEM). Coupes of 70 nm were prepared at $-100°C$ from samples previously stained with a 50/50 osmium tetroxide/formaldehyde mixture. Some samples were characterized after extraction of the rubber with boiling xylene using a Jeol JSM 6310F Scanning Electron Microscope (SEM). The average size and size distribution of the dispersed phase were determined from TEM and SEM micrographs, assuming an equivalent circle diameter for each particle (Leica Quantimet 550 image analysis system). Circa 200 particles were typically considered for each case.

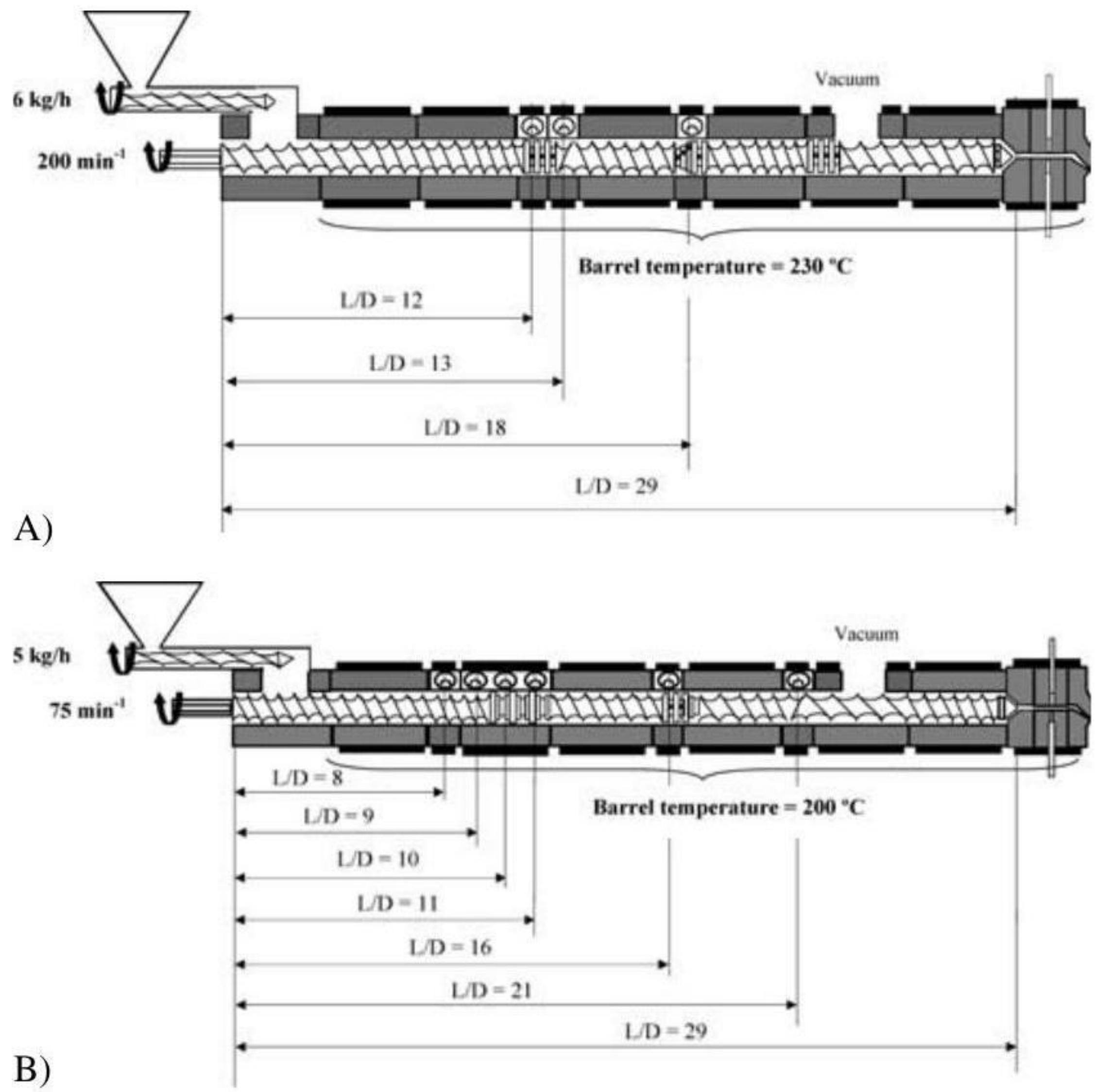


Fig. 2. Extruder layout and sampling locations for A: compatibilization of PA 6/rubber blends and B: grafting of MA onto polyolefins

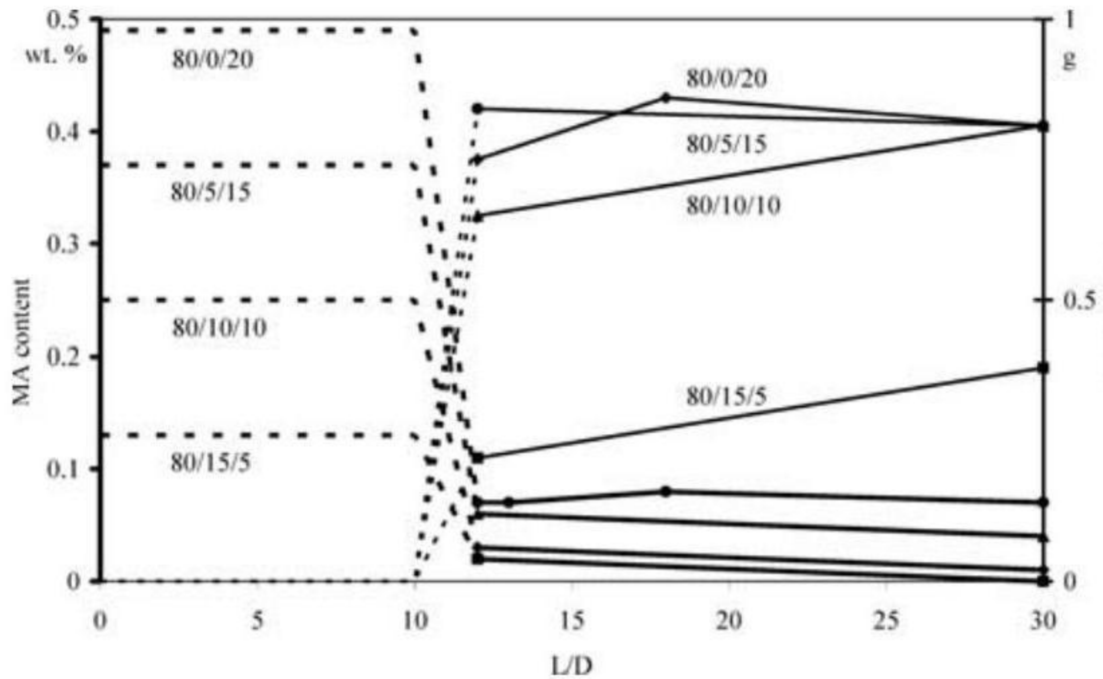


Fig. 3. Evolution along the screw of MA conversion (decreasing lines) and amount of grafted PA 6 at the interface of PA 6/rubber blends (increasing lines) with various compositions

The oscillatory rheological data was obtained from frequency sweeps from 0.04 to 40 Hz carried out with a TA Instruments Weissenberg rotational rheometer, using a parallel-plate geometry (the gap and diameter of the plates was 1.8 mm and 40 mm , respectively). A strain of 0.01 was induced in order to maintain the material's response in the linear viscoelastic regime.

Results

Polymer Blends

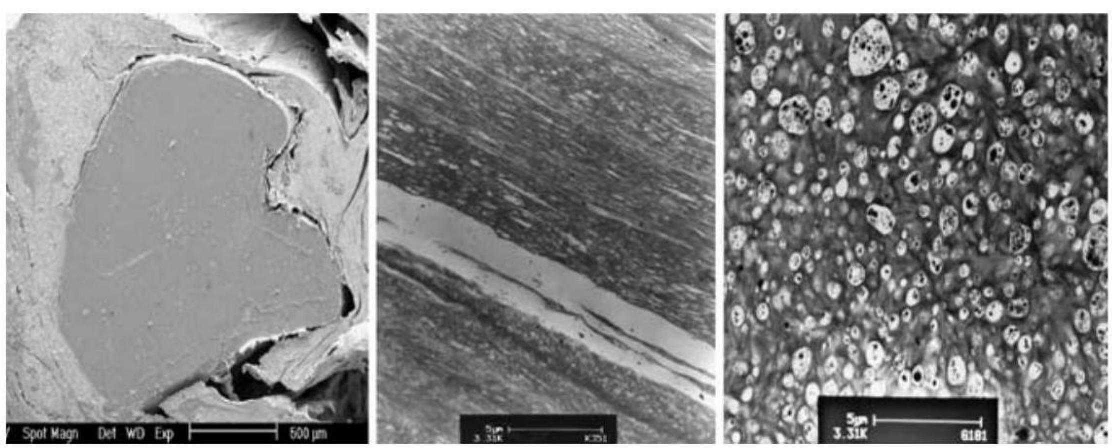
The effect of blend composition on the chemical, rheological and morphological evolution along the extruder of blends of PA 6 and MA-containing polymers was investigated. For this purpose, 80% PA 6/20 % rubber (EPM/EPM-g-MA) w/w blends were prepared with the relative proportion of EPM-gMA varying from 0 to 20%.

Hydrochloric treatment of the material collected with the sampling devices enabled the identification of the cyclic imide and, consequently, the quantification of the MA conversion. As shown in Fig. 3, in all cases the MA content decreases drastically in the beginning of the first kneading zone (L/D = 12), i. e., upon material melting. In fact, at this location PA 6 pellets were still clearly visible. Since almost all MA has reacted so quickly, an additional steady decrease further downstream is no longer possible. In fact, the residual MA content evolution along the extruder seems to be independent of the original MA content of the blend, as no noteworthy reaction occurred even for the blends with higher EPM-g-MA.

Selective extraction of the non-reactive PA 6 with formic acid at room temperature, followed by elemental analysis to determine the nitrogen content of the residue, allows the quantification of the PA 6 graft content in the PA 6/EPM/EPM-gMA blends [17]. The evolution of the former should be the reverse of the MA conversion. As seen in Fig. 3, the amount of grafted PA 6 at the interface increases in the first part of the extruder and then reaches a plateau. The final value depends on the blend composition, i.e., it increases with increasing modified rubber content up to 10 to 15wt.%.

With the exception of the non-reactive blend, the evolution of morphology is also very fast, a stable and well distributed disperse phase forming very quickly. As an example, Fig. 4 illustrates the morphology of the PA 6/EPM-g-MA (80/20, w/w) blend at $L/D = 12$ and 13. As referred above, at the first sampling point PA 6 pellets were present and surrounded by molten rubber. At the higher magnifications made possible by TEM, it became apparent that the molten part of the system presents a very heterogeneous morphology, with thin PA 6 regions drawn from the unmolten PA 6 pellets, EPM-gMA sheets, thin elongated EPM-g-MA and PA 6 domains, EPM threads in the process of breaking up, etc. being also noticed. The actual dispersion process seems to be rather chaotic, similarly to that reported by Scott and Macosko for morphology development in a batch kneader [22]. However, a few centimeters downstream a continuous molten PA 6 matrix was formed, dispersed rubber domains a few micrometers in size, exhibiting occlusions of PA 6, being now observed. Beyond the first kneading zone the average rubber particle size remained constant, which indicates that the copolymer formed at the interface stabilizes the morphology and prevents coalescence.

Given the above results, the residual MA groups probably dwell inside the rubber particles and not at the interface and, for that reason, despite the intense generation of interfacial area provided by the kneading disks, are not available to react with the amine of PA 6. An alternative explanation has been put forward by Yin et al. [23] and Hu et al. [24], who argued that when the interface is covered by the copolymer formed, the reactive groups cannot diffuse through the copolymer. Hu referred to this phenomenon as interfacial screen effect [24].



A) B) C)

Fig. 4. SEM and TEM micrographs of PA 6/ EPM/EPM-g-MA (80/0/20; w/w) a) SEM at $L/D = 12$, b) TEM at $L/D = 12$ and c) TEM at $L/D = 13$

Polymer Modification

The evolution of grafting MA onto various polyolefins having different propene contents (0wt. % for PE, 55wt. % for EPM and 100wt. % for PP) was monitored along the screw axis. The recipe included DHBP, which was used as initiator. Fig. 5 presents some of the data gathered when grafting each of the polymers with 5 phr MA and 1 phr DHBP, at 200°C. Regardless of the polyolefin structure, there is a strong increase of the grafting level in the first part of the extruder (the first kneading block extends from L/D = 8.5 to 11.5), followed by a plateau, despite further flow through two mixing blocks. A similar evolution was reported by Hu et al. [24] for grafting of glycidyl methacrylate (GMA) onto PP.

Even though the grafting profiles are similar, the final grafted MA content varies with the material, the lowest being obtained for PP (0.64 wt.%), while the highest was measured for PE (1.7wt. %), EPM behaving similarly to PE. This can be related to the presence of different types of hydrogen atoms having different reactivity and, as a consequence, the corresponding macroradicals are not equally reactive to the monomer to be grafted. PE contains almost exclusively methylene carbons, whereas in PP each repetitive unit has three different carbons, methyl, methylene and methane.

The evolution of the rheological behaviour along the extruder is also shown in Fig. 5, in terms of the ratio viscosity of the modified materials/viscosity of the initial polymer. Polyethylene evidences a strong increase in viscosity (two orders of magnitude) at the beginning of the first kneading zone, which indicates severe crosslinking, followed by a small, but consistent viscosity decrease. Therefore, crosslinking occurs initially as a side reaction, followed by limited degradation. Conversely, the viscosity of PP decreases drastically in the first part of the extruder (also around two orders of magnitude), which is a clear and expected sign of degradation, and this continues much more subtly in the remaining of the extruder. The viscosity of modified EPM is much more stable along the extruder, a slight degradation in the second part of the extruder being perceived. Probably, this behaviour results from a balance between degradation and crosslinking of the ethylene/propylene sequences.

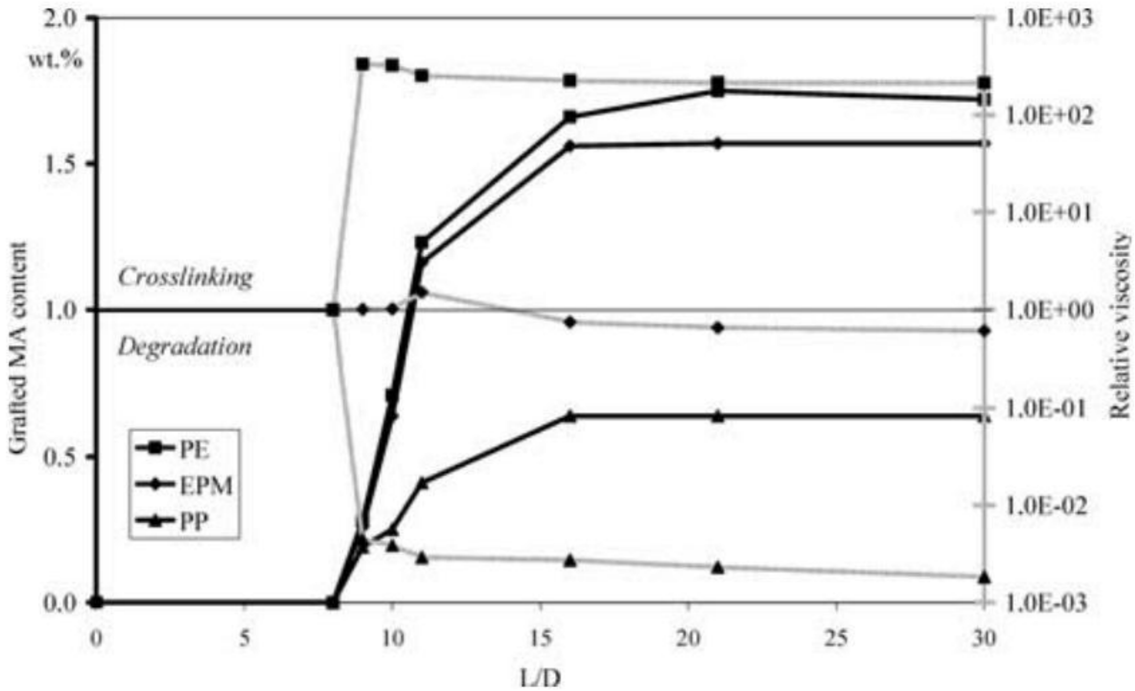


Fig. 5. Evolution along the screw of MA grafted content and relative viscosity of modified PE, EPM and PP (with 5 phr MA, 1 phr DBHP at 200°C)

Discussion

The selected results presented above for the two systems, as well as the data gathered during other reactive extrusion studies [21,25], showed unequivocally that chemistry and morphology are interrelated and develop quite rapidly in the extruder, even upon melting of the composing polymers. Therefore, it is interesting to identify and determine the role of the major process parameters in reactive processing. In fact, despite some recent discussions [26], the influence of flow, temperature, reactivity and solubility during processing on the development of chemistry and morphology is far from being fully established.

It is generally accepted that major changes in morphology development are associated with high chemical conversion rates [17, 18]. The data shown above for the polyamide/rubber blend demonstrates that this occurs quite early in the extruder. Since the underlying chemical reaction (aliphatic amine/anhydride) is fast (30 s in solution [27]), the copolymer formed at the interface reduces the interfacial tension and a fine and stable morphology is produced. However, Macosko [26] showed that this reaction takes hours at the interface of static thin-films of these components that are put in contact at elevated temperatures, which contradicts the practical observation that it is almost impossible to follow the gradual development of the process in the extruder.

Thus, flow is a very important parameter for reactivity in high viscous media, high reactivities being related to the efficient generation and renewal of interfacial area. The former induces the reaction of the available reactive groups, while the latter prevents the formation of a static copolymer layer at the interface area. Operating conditions and screw geometry should therefore play a role in chemical conversion and morphology development.

The data presented in Fig. 6 was obtained during reactive extrusion of the PA 6/EPM/EPM-g-MA 80/0/20 % w/w blend in the Leistritz extruder now fitted with smaller sampling devices, which made possible to collect material at half L/D intervals, i. e., the evolution of the reaction could be monitored in greater detail. The curve for the barrel set at 230°C and the screws operating at 6 kg/h corresponds to that for 80/0/20 in Fig. 3, but now more data points are available. That curve can be directly

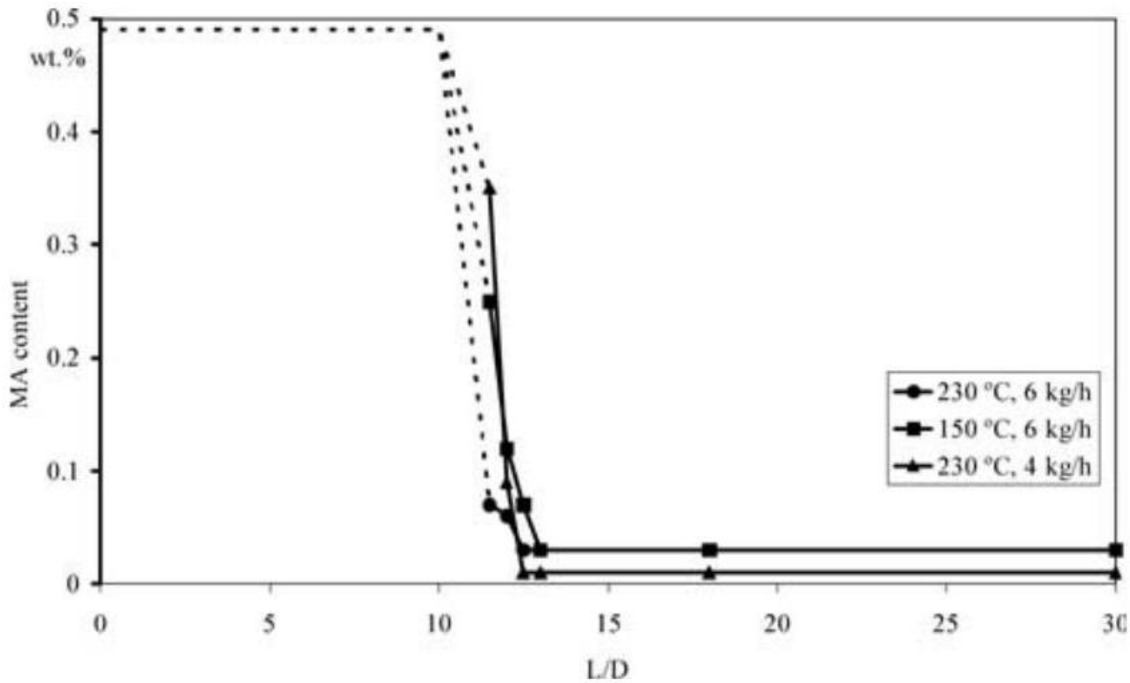


Fig. 6. Evolution along the screw of MA conversion for the PA 6/EPM/ EPM-g-MA (80/0/20; w/w) blend produced under different processing conditions

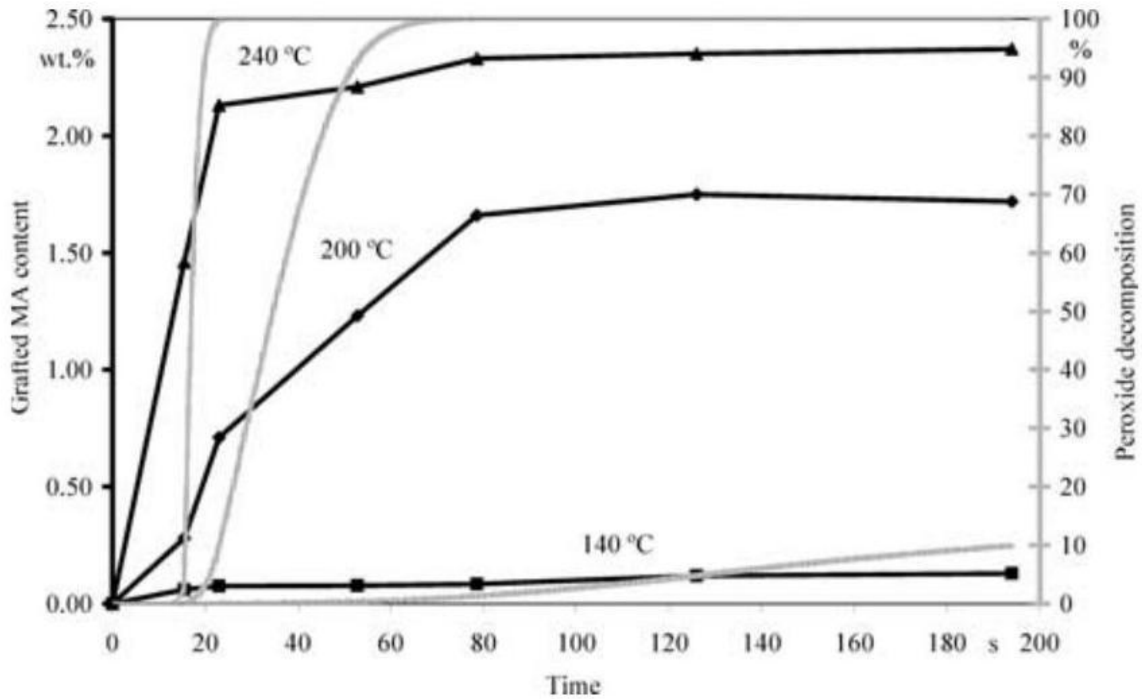


Fig. 7. MA grafted content and calculated peroxide decomposition for PE at 140, 200 and 240°C (5 phr MA, 1 phr DBHP) compared to the curve for 150°C and 6 kg/h, to reveal the effect of temperature. As expected, lower temperatures decrease the reactivity, the residual MA plateau being attained further downstream. However, these differences are not very significant. Decreasing the feeding rate does not seem to affect the reaction rate, but can yield slightly lower MA contents, given the higher local residence times.

In fact, along fully filled kneading blocks the average residence time is simply given by V/Q, where V and Q are the local volume and volumetric feed rate, respectively, i. e., residence time is independent of screw speed. Therefore, a decrease in Q produces a linear increase in the local time for reaction. On the other hand, screw speed should not play a role in reactivity. In the case of grafting MA onto polyolefins, the radical formed in the polymer backbone by hydrogen abstraction after the peroxide decomposition can react either with the monomer, or follow crosslinking/degradation reactions. Therefore, the grafting efficiency will improve if the solubility and reactivity of the monomer increases.

Fig. 7 presents the evolution of the experimental MA content and the calculated peroxide decomposition along the screw for PE with 5 phr MA and 1 phr DHBP at 140,200 and 240°C. For this purpose, the average mass temperature and residence time at each location (measured on-line) were combined in an algorithm that computes the peroxide decomposition for a given temperature and time [19]. The two sets of curves are qualitatively similar, i.e., when DHBP starts to decompose the grafting reaction begins, when the rate of peroxide decomposition increases so does the MA grafting, when the peroxide is fully decomposed the degree of grafting remains constant.

The final amounts of grafting increase with increasing temperature and can be related to the peroxide half lifetime, which is 1883 s, 6.1 s and 0.28 s at 140,200 and 240°C, respectively.

Thus, at 140°C the peroxide decomposition is slow and only a few radicals are available for grafting, which results in low amounts of grafting. Conversely, at 240°C the half lifetime is small, and so not only the peroxide decomposition is fast, but the reactivity of the monomer with the macroradical is also higher. Similar conclusions could be obtained for the effect of throughput, i. e., increasing the throughput, the rate of peroxide decomposition diminishes due to a reduction of the average residence time, this bringing about a decrease in grafting.

Conclusion

Monitoring the evolution of chemistry and morphology along the extruder can contribute to a better understanding of the underlying chemical and physical phenomena involved in the preparation of innovative polymer systems. The availability of online monitoring techniques, relatively simple to operate, combined with fast sampling of the material along the screw for subsequent thorough off-line characterization are important tools to achieve that goal. The potential of these tools was illustrated for two reactive systems.

In the preparation of compatibilized polymer blends, it was shown that chemistry and morphology are interrelated and develop fast, upon melting of its components. Flow pattern seems to be a major factor, since it contributes to the efficient generation and renewal of interfacial area. Although the operating characteristics may have an effect, it seems that the flow pattern developed along staggered kneading blocks of co-rotating twin screw extruders is generally quite favourable for these reactions.

Grafting reactions are also fast in this type of machines (the final grafting level depending on the polymer structure). Grafting efficiency depends not only on the availability of radicals formed in the polymer backbone by hydrogen abstraction after the peroxide decomposition, but also on the reactivity of the monomer with the latter. It was shown that the grafting yield follows generally the peroxide decomposition profile. Therefore, temperature and residence time play a major role in this type of systems.

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