A Look Inside the Extruder: Evolution of Chemistry, Morphology and Rheology Along the Extruder Axis During Reactive Processing and Blending

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Summary: A simple device was recently developed for fast sampling (within a few seconds) of representative melt samples (about 2 g) on a running extruder. An array of such devices has been mounted on a twin-screw extruder. The goal of this study was to de-black-box reactive processing of polymers by studying some typical examples.

- Processing of polyolefins in the presence of peroxides: when the polymer is molten and the melt temperature is sufficiently high branching/cross-linking of PE and degradation of PP occurs; the conversion follows a convex profile along the screw axis, which profile is similar to the exponential profile calculated for peroxide decomposition.
- Free-radical grafting of maleic anhydride (MA) onto polyolefins: MA grafting onto PE and PP also follows a convex profile with branching/cross-linking as parallel side reaction for PE and degradation for PP; for PE degradation of the formed grafted/cross-linked gel is observed at the end of the extruder.
- Reactive blending of PA-6 with EPM-g-MA: within a few seconds the in-situ compatibilization reaction, resulting in PA-6/EPM graft copolymers, is completed and the degree of rubber dispersion has changed from the mm to the sub-µm range, regardless of the MA content of EPM-g-MA and the EPM-g-MA content of the blend; PA degradation occurs along the whole extruder.

Introduction

Over the past three decades the growing demand for specialty plastics has led to increasing scientific and industrial interest in chemical modification and melt blending of polymers. Reactive extrusion (REX), i.e. the use of extruders as a chemical reactor, has proven to be a key technology in the polymer industry[1,2] . At the present time, REX is seen as an efficient means for the continuous polymerization of monomers and for the chemical modification of existing polymers (controlled degradation, chain extension, branching, grafting and modification of functional groups). The use of an extruder as a chemical reactor allows

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high-viscosity polymers to be handled in the absence of solvents. It also affords a large operational flexibility, as a result of the broad range of processing conditions (0 - 500 atm. and 70 - 500 °C), the possibility of multiple injection and the controlled residence time (distribution) and degree of mixing. Co-rotating intermeshing twin-screw extruders have been found to be suitable for many REX processes, because of the wider control of the residence time distribution, the good mixing intensity, the superior heat transfer and the self-wiping operation[3]. Blending of two polymers usually requires some sort of compatibilization if a finely dispersed blend morphology and improved properties are to be obtained[4,5]. For commercial applications the compatibilizer is usually produced in-situ, i.e. a copolymer is formed via interfacial reaction of polymers having suitable chemical functionalities[6]. It has been shown that morphology development in (reactive) blends is a relatively fast process, occurring mainly during the early stages of mixing, i.e. during the melting and softening of the blend components[7-9].

Reactive processing of polymers is a complex technology, involving different steps, such as feeding, transporting, melting, mixing, reaction and devolatilization, in a single process with a continuous and mutual interaction between chemistry, rheology and morphology. Although reactive processing has been studied for many years and is used for commercial purposes, the phenomena occurring inside the extruder are still not fully understood. As a result, the extruder may still be seen as a black box. A variety of experimental approaches has been followed in an attempt to obtain more insight in reactive processing, namely screw-pulling, using a split barrel and then stopping the extruder and pouring liquid nitrogen into the entry ports[10], removing molten samples at entry ports with tweezers[10-12], on-line FT-IR[13], experimental set-ups with simplified flows or using batch mixing devices. All these attempts suffered from one or more practical and/or fundamental problems.

The aim of this study is to investigate the evolution of physicochemical phenomena along a co-rotating twin-screw extruder so as to gain a better understanding of reactive processing. It is hoped that eventually guidelines can be established for optimizing reactive processes and improving the properties of the corresponding products. A device has been developed that can be inserted between barrel segments or, alternatively, barrel segments can be replaced by a set of these devices, to collect molten polymer samples in less than five seconds for off-line characterization[14]. This paper provides an overview of more detailed studies (see references 15-21) that show the benefits of using sampling devices for studying both polymer modification and blending.

Sampling device

An intermeshing co-rotating twin-screw extruder was equipped with 3 up to 7 sampling devices located at the kneading zones (Figure 1). The sampling device (Figure 2) consists of a circular aperture in the barrel wall (1), allowing material to flow out of the barrel. A cylindrical valve (2), containing two cavities (3) and (4), controls the occurrence of this flow. When the valve is positioned as shown in Figure 2, there is no flow out of the extruder. However, aperture (1) will be filled with polymer melt. For collecting a portion of material from inside the extruder, the valve is rotated so that aperture (1) communicates with cavity (3). The melt that has accumulated here is discarded. Upon further rotation, aperture (1) communicates with cavity (4), which is rapidly filled with fresh material.

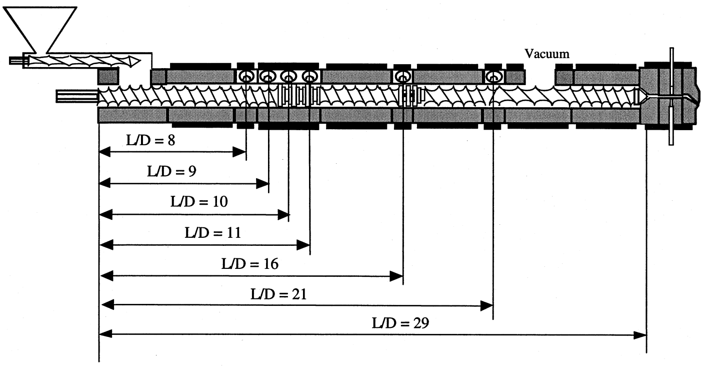

Figure 1: Typical extruder lay-out and sampling positions.

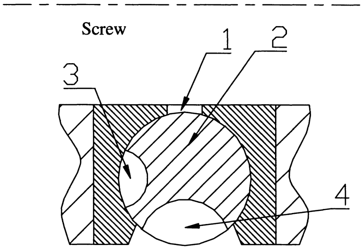

Figure 2: Schematic drawing of sampling device.

The valve is rotated on to the position shown in Figure 2, from where the sample is removed and quenched for subsequent analysis. Collecting some 2 g of polymer melt typically takes between 3 to 5 sec.

Before detailed studies were performed some preliminary experiments were carried out to evaluate the performance of the sampling devices and to make a comparison with traditional screw-pulling experiments, which require typically 5 min. for collecting samples. We showed that screw-pulling experiments result in serious artifacts when studying the morphology development in uncompatibilized blends of PA-6 and EPM and the chemical conversion of the imidization of poly(styrene-co-maleic anhydride) with 1-aminonaphtalene[21]. We concluded that the sampling devices enable nearly real-time investigation of processes developing inside the twin-screw extruder.

Materials

The materials used in these studies are given in Table 1.

Table 1: Materials

Material	Supplier	Trade name	Characteristics
EPM1	Exxon	PE 805	22. wt.% propene, M_w ~ 120 kg/mol
EPM2	Exxon	EPM X1-703F2	27 wt.% propene, M_w ~ 80 kg/mol
EPM3	Exxon	VA 404	55 wt.% propene
EPM-g-MA1	Exxon	Exxelor VA 1801	0.49 wt.% MA
EPM-g-MA2	Exxon	Exxelor VA 1803	0.47 wt.% MA
EPM-g-MA3	Exxon	Exxelor VA 1820	0.31 wt.% MA
EPM-g-MA4	Exxon	Exxelor VA 1810	0.22 wt.% MA
HDPE1	DSM	Stamylan HD 2H280	high density, M_w ~ 60 kg/mol
HDPE2	DSM	Stamylex 7359	high density, M_w ~ 30 kg/mol
LDPE	DSM	Stamylan LD 2100TN00	low density, M_w ~ 360 kg/mol
PA-6	DSM	Akulon K123	M_n ~ 13 kg/mol
PE-g-MA	DSM	R&D product	high density, 0.93 wt.% MA
PP	DSM	Stamylan P 13E10	isotactic, M_w ~ 500 kg/mol
PP-g-MA	Exxon	Epolene E-43	isotactic, 2.5 wt.% MA
SMI	DSM	R&D product	4 wt.% MA

Processing of polyolefins and the effect of peroxide

The first detailed study related to the processing of PE, PP and EPM as such and in the presence of peroxides[15]. When PEs (HDPE1, HDPE2 and LDPE) were processed in the absence of peroxide we found no evidence of mechanochemical effects on the viscoelastic behavior, i.e. the PEs were relatively stable under the conditions selected. When 0.1 phr 2,5-bis(tert-butylperoxy)-2,5-di-methylhexane (BPDH) was added to the two HDPEs, both the viscosity and the storage modulus increased significantly upon melting as a result of branching/cross-linking. After melting only minor changes were observed down-stream. With 1.0 phr BPDH the increase in viscosity and elasticity was even larger. These increases were significant up to L/D = 11 and the values decreased slightly further along the extruder. The variation in gel content confirmed the rheological results regarding the evolution of branching/cross-linking reactions along the extruder. When 0.1 phr BPDH was added the gel content leveled off at about 5 wt.%, whereas for 1 phr BPDH it reached a constant level at 55 wt.%.

When processing PP in the absence of peroxide, the viscosity and storage modulus decreased slightly under these conditions, indicating PP degradation. This decrease was much more important, particularly in the melting zone, when 0.1 or 1.0 phr BPDH were added. This indicates the occurrence of free-radical induced β-scission of PP. Processing of EPM copolymers took an intermediate position in between PE and PP. Branching was observed for the EPM with a low propene content (EPM1) and degradation was observed for the EPM with a high propene content (EPM3). For the EPM with an intermediate propene content (EPM2) only small rheological changes were observed. However, this should not be interpreted as evidence of the absence of any reactions. Probably, branching and degradation more or less compensate each other at these intermediate propene levels.

Finally, experimental residence times and melt temperatures were used to calculate the peroxide decomposition along the extruder axis using the Arrhenius equation. BPDH starts to decompose at L/D = 9 and not any sooner, simply because the temperature is too low (Figure 3). Decomposition proceeds very rapidly because the melt temperature jumps to 190 - 200 °C. Complete BPDH decomposition is achieved at the end of the extruder. The calculated peroxide decomposition and the experimental gel content for HDPE processed in the presence of 1.0 phr BPDH show similar curves. This indicates that there is a close correlation between peroxide decomposition and branching/cross-linking.

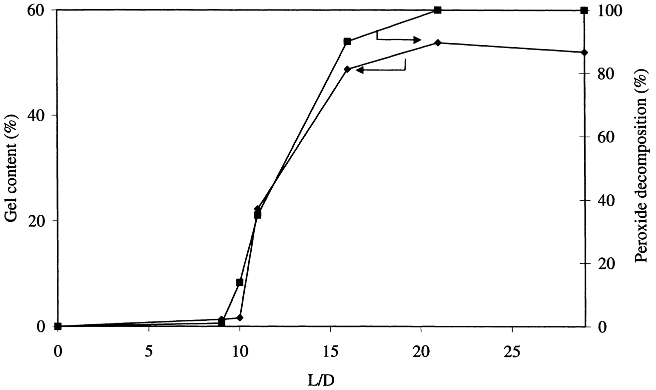

Figure 3: Evolution of gel content (HDPE1 with 1.0 phr BPDH) and calculated peroxide decomposition along the extruder.

Free-radical grafting of maleic anhydride onto polyolefins

In a second series of studies the free-radical grafting of MA onto PE, PP and EPM was studied along the screw axis[16,17]. Figure 4 shows the evolution of the graft content. Regardless of the polyolefin structure there is a strong increase in the grafting level in the first part of the extruder up to location E followed by a leveling off. We found that the curve for the experimental MA graft content is similar to that of the calculated peroxide decomposition. The latter starts at 160 °C at location B, sharply increases when the temperature increases to 200 °C at location D and is complete at location E. A plot of the MA content versus the peroxide decomposition gives a convex correlation, indicating that the grafting efficiency, defined as the degree of grafting normalized to the peroxide decomposition, decreases during grafting.

When grafting the two HDPEs with 5 phr MA and 1 phr BPDH, a very strong increase in viscosity and elasticity occurred at location B, indicating severe cross-linking. Beyond location B the material's rheological properties did not change significantly, although the elasticity seemed to decrease slightly downstream. However, measurements of the gel content showed that cross-linking continues to occur along the screw up to location E. The decrease in gel content observed past location E is not related to the peroxide, since it is fully decomposed. Both the decrease in storage modulus and gel content are indicative of network degradation, probably as a result of PE gels being sheared apart. The final gel content for the HDPEs grafted with MA was quite different from that obtained when the HDPEs were processed with peroxide only. In the latter case a higher and constant gel level was obtained. The presence of tertiary C-atoms in grafted PE, which are weak links in polyolefin chains, may explain the lower degrees of cross-linking for MA grafted HDPEs.

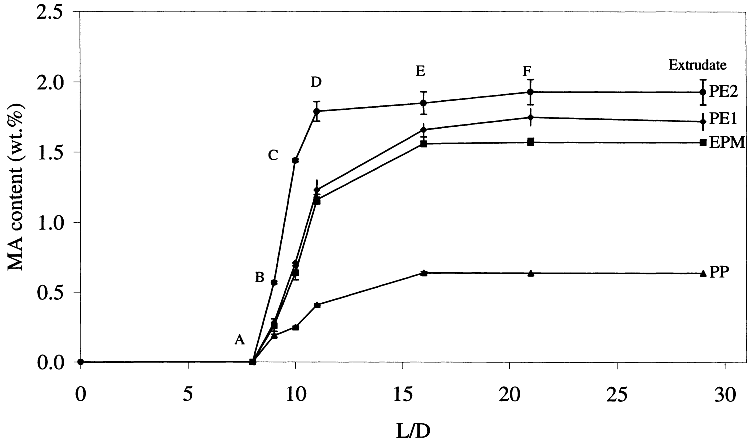

Figure 4: MA content along the extruder for modification of HDPE1, HDPE2, EPM3 and PP with 5 phr MA and 1 phr BPDH at 200 °C.

As expected, there was a significant decrease in the amount of grafted MA along the extruder axis when the MA feed was reduced from 5 to 1 phr. However, the profiles became similar when the peroxide content was decreased from 1.0 to 0.5 phr. The effect of thermal grafting (no peroxide) was also investigated, but the level of grafted MA was rather low (~0.1 wt.%) and we observed no effect on the dynamic viscosity. When using 2,2-bis(tert-butylperoxy)-butane (BBP) as peroxide hardly any grafting was observed along the extruder. Through calculation we established that BBP is completely decomposed at location B as a result of the small half-life time of BBP in combination with the high melt temperature. Probably, BBP decomposes before it and/or MA is completely dissolved in HDPE. On the other hand when di-tert-butyl peroxide (DBP) was used as peroxide, the experimental grafting reaction proceeded along the whole extruder. This agrees with the calculated peroxide decomposition, reaching full conversion only at the end of the extruder. A plot of the MA graft content versus the calculated DBP decomposition gives a convex curve, similar to the one observed for BPDH.

Even though the grafting profiles for EPM3 and PP were similar to those of the two HDPEs, the final degree of grafting was different. The highest degree was obtained for PE (1.7 wt.%) and the lowest for PP (0.6 wt.%), whereas the MA content of EPM3 was somewhat below that of the HDPEs. Similar differences have been observed in other studies[22,23]. It has been suggested that the dependency of the MA content on the polyolefin structure results from competition between grafting and β-scission or cross-linking. This competition seems to correlate with the fraction of non-PPP triads[17]. MA grafting of PP is accompanied by severe degradation as witnessed by the strong decrease in viscosity and the storage modulus along the screw axis. Obviously, β-scission of PP occurs during MA grafting. The dynamic viscosity continued to decrease beyond sampling point D, although it was calculated that the peroxide is fully decomposed and the MA content had reached a constant level. Thermo-oxidative PP degradation, known to occur when processing PP as such, may explain this behavior. The decrease in dynamic viscosity for MA grafted PP was smaller than that of PP processed with peroxide only. This has also been observed previously[24]. It is explained by the formation of terminal MA grafted PP[25], which results in the conversion of labile tertiary PP radicals into relatively stable primary PP radicals, which probably will terminate[16].

Reactive blending of PA-6 with polymers containing maleic anhydride

In a final series of studies, we determined the effects of the blend composition and the processing conditions on the chemical, rheological and morphological evolution of blends of PA-6 and MA-containing polymers along a twin-screw extruder[18-20]. First, we studied the effect of the amount and composition of the rubber phase of PA-6/(EPM+EPM-g-MA) blends. Although we varied the total rubber content between 10 and 80 wt.%, the EPM-g-MA content of the rubber phase between 0 and 100% and the MA-content of EPM-g-MA between 0.22 and 0.49 wt.% (EPM-g-MA1–4), similar observations for all blends were made. PA-6/EPM-g-MA graft copolymer formation occurred mostly in the melting zone.

At the first sampling location the residual MA-content had decreased to almost zero (Figure 5) and the amount of grafted PA-6 had already reached its highest value. Regardless of the amount and composition of the rubber phase the residual MA-content did not decrease any further beyond this point and the PA-graft content had reached a constant level. This is in line with data obtained by Scott, who monitored a similar reactive blending system in a batch kneader and reported a very fast reaction[26].

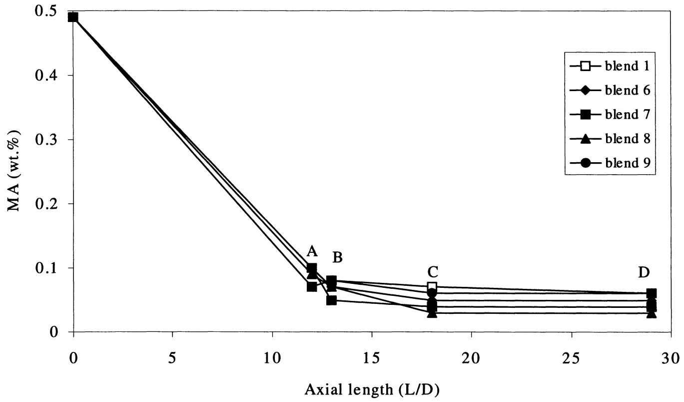

Figure 5: MA conversion of PA-6/EPM-g-MA1 blends with 20 up to 90 wt.% EPM-g-MA1.

SEM and TEM showed that at the first sampling point the PA-6 pellets were not completely molten and that they were surrounded by a thin EPM-g-MA film/particles. However, at the second sampling point 4 cm downstream solid pellets were no longer present. Only rubber domains a few micrometers in domain size and dispersed in a continuous PA-6 matrix were observed. Beyond the first kneading zone the average rubber particle size showed a small but significant decrease due to dispersion of the larger rubber domains, resulting in a narrower particle size distribution. The rubber particles contained PA-6 occlusions. The number of occlusions did not change along the extruder, indicating that the formation of occlusions occurs in the melting zone and is related to the initial blend dispersion process. Probably, the occlusions are formed from grafted PA-6 upon complete melting of the PA-6 pellets.

The use of PE-g-MA (T_m 132 °C), but especially of PP-g-MA (T_m 165 °C) and imidized SMA (SMI) (T_g 190 °C) resulted in a delayed decrease in the residual MA-content in the first kneading zone and constant levels were reached only further downstream. Similar observations were made when the rubber was side fed, the extruder set temperature was lowered and/or the screw rotation speed was decreased. For the latter blends we tried to obtain a more detailed picture of blend dispersion by equipping the first kneading zone of the extruder with 6 sampling devices. All sorts of morphologies with intermediate dimensions were observed: un-molten PA-6 particles, thin PA-6 regions drawn from the particles, EPM-g-MA sheets, thin elongated EPM-g-MA and PA-6 domains and EPM threads in the process of breaking up. Although most of these morphological features have been observed in the past for blends prepared in a batch kneader[7,8], our results were obtained in a commercial twin-screw extruder under industrially relevant processing conditions. For none of the blends studied did we observe actual phase inversion, i.e. the transition of a PA-6 phase dispersed in the amorphous EPM phase into a rubber dispersion in a PA matrix.

Finally, we found that PA-6 degraded during reactive blending. Firstly, the number averaged molecular weight of the PA grafts of the PA-6/EPM-g-MA compatibilizer at the first sampling location was only 1 – 2 kg/mol - which is much smaller than that of the original PA-6 (~20 kg/mol) - and this molecular weight did not change further down the screw. Earlier studies have shown that PA-6 degrades when it is blended with MA-containing polymers if the molar ratio MA/(PA-6 amine end groups) is close to or larger than unity[27]. This degradation reaction involves the water liberated upon reaction of anhydride and amide towards imide. Secondly, we observed a continuous decrease in the dynamic viscosity and the storage modulus (measured at low frequencies) along the screw axis, regardless of the composition of the rubber phase. Up to sampling point B these changes can be explained by the formation of an interphase consisting of PA-6/EPM-g-MA graft copolymers and a decrease in the average rubber particle size. However, this continuing decrease further down the screw can not be accounted for by the same morphological and chemical effects. When PA-6 as such was processed under the same conditions, we observed again a decrease in dynamic viscosity and storage modulus, indicating that thermal degradation and/or hydrolysis of PA-6 occurs. Clearly, the PA matrix of the PA-6/EPM blends also degrades.

Conclusions

The overall conclusions of these studies are that:

- these novel sampling devices are essential for obtaining a qualitative description and for future quantitative modeling of reactive processing in extruders,
- the crucial part of an extruder for reactive processing is the very first kneading zone and
- the sampling devices probably are not suitable for studying processes, which are extremely fast (less than a few seconds), which mainly occur in incompletely filled zones, which are very heterogeneous by nature and/or in which the orientation of dispersed particles is of importance.

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