Evolution of Morphology and of Chemical Conversion Along the Screw in a Corotating Twin-Screw Extruder

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Abstract

A new sampling device is used to perform near-real-time investigations of physical and chemical processes occurring inside a laboratory twin-screw extruder. Polyamide-6-ethylene propylene rubber (PA-6-EPM) blending and styrene-maleic anhydride (SMA) imidation experiments are reported in terms of morphology development and evolution of the chemical conversion along the extruder, respectively. Comparison of the results obtained using this new technique with those of classical screwpulling experiments evidenced the potential erroneous conclusions than can be drawn from the latter.

Key words: morphology; chemical conversion; polymer blends; reactive extrusion; on-line sampling

INTRODUCTION

Compounding with fillers and/or additives, blending, and chemically modifying existing polymers are attractive methods of developing new materials for specific applications with an improved properties and/or cost balance. Polymer blends and compounds are commonly prepared by mechanical mixing of their components in the molten state. The performance of the materials produced is determined, amongst others, by the final morphology and dispersion, respectively. For blends, the morphology depends on composition, rheological and physical characteristics of the components, relative compatibility, and the nature and intensity of the mixing. In fact, it is well known that by using different mixers, and/or by varying the mixing parameters, it becomes possible to control phase morphology [1–4] and, in this way, to improve the blend performance. Therefore, it is important to monitor the evolution of the morphology of polymer blends during their preparation and relate it to the mixing conditions used in industrial processes.

A variety of reactions has been used for the chemical modification of polymers, [5,6] the most important being grafting, crosslinking, halogenation, condensation, and exchange. In the case of reactive extrusion, it is important to know the effect of the operating conditions on the evolution of chemical conversion. This knowledge is necessary to identify side reactions and to guarantee high conversion.

Intermeshing corotating twin-screw extruders are often used for preparing polymer blends and/or modifying polymers on a commercial scale. However, there is relatively little information available on the morphology development or on the evolution of chemical conversion occurring along the screw in this type of equipment. Actually, an extruder can still be viewed as a black box. Most of the available data has been gathered using screw-pulling experiments, similar to those used in the late 1950s for the understanding of the mechanisms involved in plastication in singlescrew extruders. [7] These experiments are not only complicated but also time-consuming, and several minutes elapse before actually taking the sample. Since freezing the polymer inside the extruder to prevent any subsequent morphological changes is difficult, it is not surprising that coalescence of the minor phase has been reported. [8,9]

The problem of collecting samples from the extruder has been revisited recently by a number of workers. The aim is to produce real-time information that can be used to improve the efficiency of the physical and/or chemical processes, the design of the equipment, and the capacity for on-line control. The approaches proposed encompass using a split barrel, stopping the extruder, and pouring liquid nitrogen into entry ports, [10] removing molten samples at entry ports with tweezers and quenching the material, [8,11] and diverging a small amount of material from inside the extruder through a hole in the barrel and quenching it. [9,12] The use of these techniques decreases the required sampling time from several minutes in the screw-pulling experiment to a few seconds. However, most of the above routines 1) can either work only in pressurized, or conversely, partially filled zones of the screw, 2) require stopping the extruder prior to collecting samples, 3) may affect the melt flow conditions in the extruder, and/or 4) are laborious to manage. An on-line Fourier transform infrared (FTIR) technique has also been developed for studying reactive extrusion, but absolute chemical conversions could not be obtained as a result of polymer melt sticking to the IR probe. [13]

A new device for collecting samples in less than 5 s , using the melt detour concept, was recently developed. [14] The apparatus can be inserted between any two extruder barrel segments, or, alternatively, barrel segments can be replaced by several adjacent collecting units. This provides the possibility of obtaining polymer samples at relatively small increments along the length of the screw. This is particularly relevant when the aim of the work is to study the evolution of the chemical conversion of a reactive system along the extruder. The device can be operated quite simply while running the extruder, both with filled or partially filled screws, although, in the later case, collecting the same amount of material takes more time. This principle has already been used to measure residence time distributions at different locations of the extruder. [15]

This work aims at ascertaining the practical interest offered by this new sampling device in terms of the information on physical and chemical processes occurring inside the extruder. This will

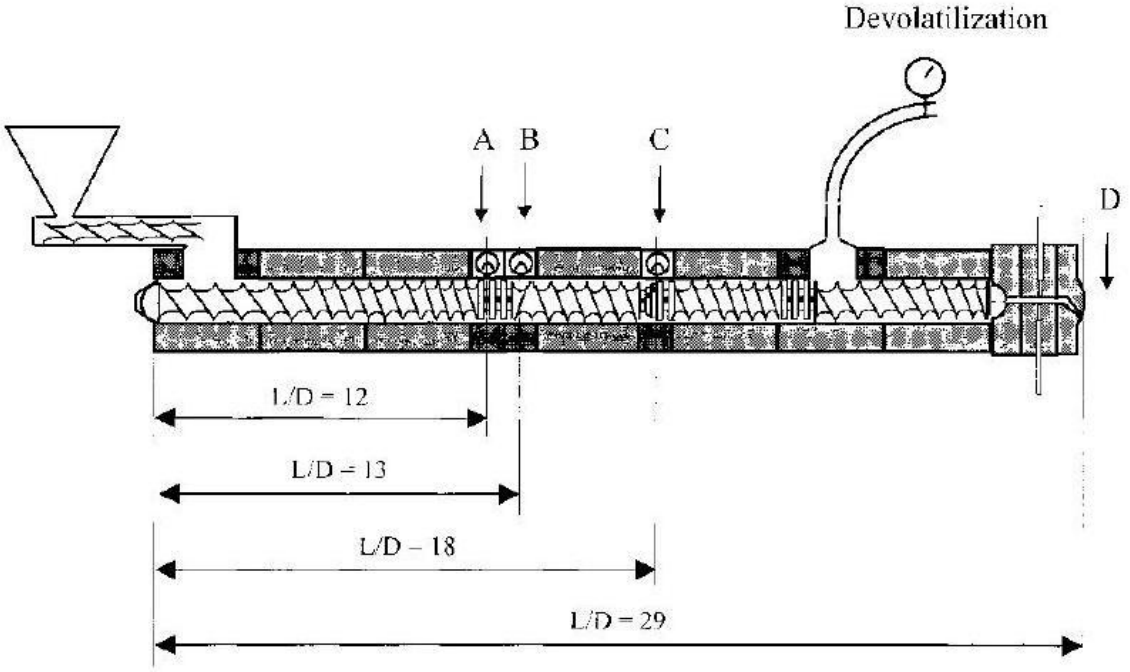

Figure 1 Screw configuration and sampling locations.

be accomplished by studying two different systems. Firstly, the morphology development of a noncompatibilized polyamide-6-ethylene propylene rubber (PA-6-EPM) blend was studied as a function of screw rate. Secondly, the evolution of chemical conversion of imidation of styrene-maleic anhydride (SMA) copolymer with 1 -aminonaphthalene along the extruder was determined. In both cases, characteristics of the samples collected using the sampling device were compared with those obtained using the conventional screwpulling technique.

EXPERIMENTAL PROCEDURE

Materials

Commercial PA-6 (Akulon® K123), EPM (Keltan® 740), and SMA (Stapron® S: 22.8wt%MA) produced by DSM, the Netherlands, were used. The 1 -aminonaphthalene was supplied by Aldrich. In the case of the PA-6-EPM blend, 10 and 20% concentrations of the disperse phase (EPM) were used. The reactive system consisted of a 2.5/ 0.5w/w, SMA-1-aminonaphthalene mixture.

Screw Configuration and Processing Conditions

The 2 systems were prepared in a laboratory modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder coupled to the relevant accessories. The configuration of the screws ($L/D = 29$) and the locations of the sampling devices are depicted in Figure 1.

The blends were prepared using a barrel set temperature of 230°C and feeding the premixed components at a flow rate of 6 kg/h. The intensity of mixing was varied by selecting screw rotation speeds of 100, 150, and 200 rpm. In the case of the

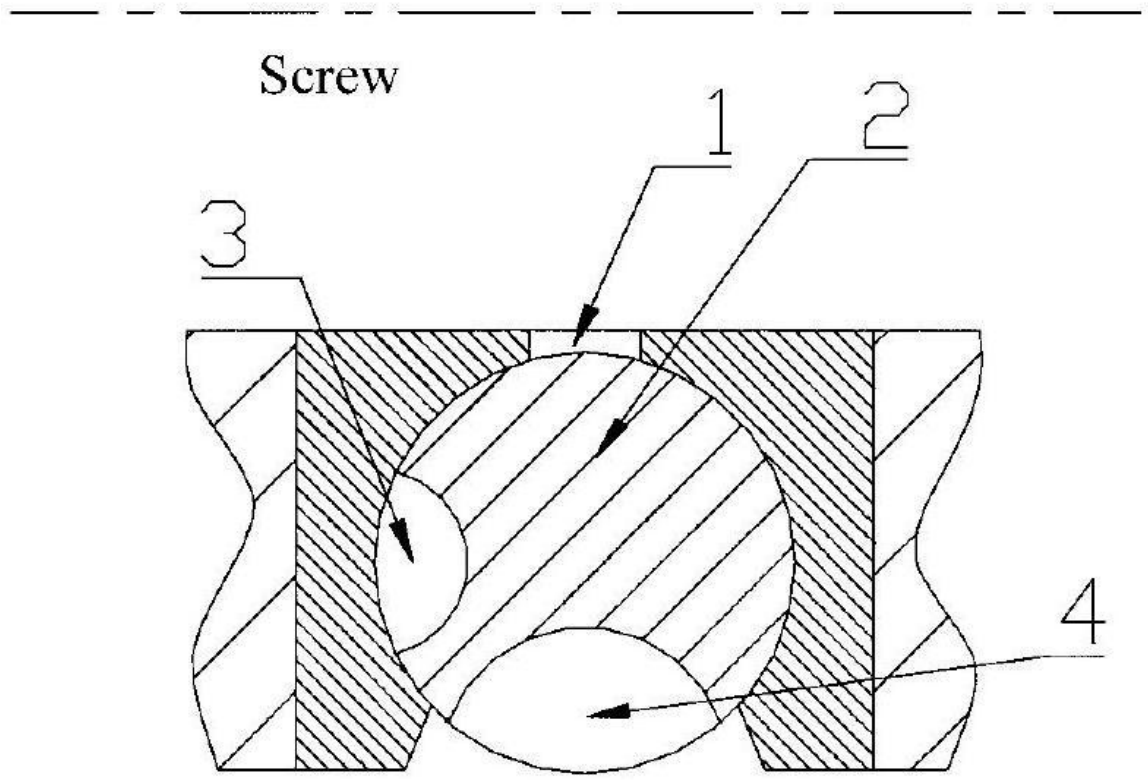

Figure 2 Sampling device.

reactive system, a barrel set temperature of 210°C, screws rotating at 150 rpm , and a flow rate of 6 kg/h of premixed SMA-1-aminonaphthalene were selected.

Sampling for the determination of the morphological evolution, or of the chemical conversion, was carried out at identical locations along the screws, either when using the sampling devices or when pulling the screws with the dedicated tool supplied by Leistritz. Samples of similar sizes were cooled in liquid nitrogen in order to ensure identical thermal histories. This was particularly easy with the new device, as it collects matching nut-shaped specimens.

Sampling Device

The working principle of the sampling device is illustrated in Figure 2. The circular aperture in the barrel wall (1) allows the flow of material out of the extruder. The occurrence of this flow is controlled by the cylindrical valve (2), containing two cavities (3) and (4). When the valve is positioned as shown in Figure 2, there is no flow out of the

extruder. However, accumulation of polymer material in hole (1) will take place. For collecting a portion of material from inside the extruder, the valve is rotated sequentially to expose hole (1) to cavity (3), where the accumulated material can be discarded. Upon further rotation, hole (1) is now exposed to cavity (4), which is rapidly filled with fresh material. The valve is rotated again to the position shown in Figure 2, where the sample is removed and quenched, for subsequent analysis. Collecting circa 2 g of polymer melt takes typically between 3 to 5 s (depending on flow rate and degree of filling).

Residence Time

Upon reaching steady state during an extrusion experiment, a small amount of tracer (silicon dioxide with specific surface of 175 m^2/g) was added instantaneously to the feed stream at $t = 0$. Samples of polymer plus tracer were then collected from each location along the extruder at various time intervals. The relative amount of silica present in each sample determined by ashing the sample is a straightforward measure of concentration with time. From this information, it was possible to compute conventional residence time parameters, such as the cumulative residence time distribution, $F(\theta)$, and the mean residence time, $\bar{t}$. [16]

Materials Characterization

The morphology of the systems under study was determined using a Jeol JSM 6310F scanning electron microscope. The samples were fractured in liquid nitrogen and gold-plated. An automatic method of image analysis (Leica Quantimet 550) was used to quantify the size of the disperse phase. As in other studies, [9,17–21] equivalent circle diameters were computed from individual particle areas. The distribution width was estimated from the variance, that is, the square of the standard deviation of the log-normal function.

The SMA-1-aminonaphthalene samples were dissolved in tetrahydrofuran (THF) and the IR spectra were recorded from the solutions using a liquid cell on a Perkin-Elmer 1720 FTIR spectrometer. The residual maleic anhydride (MA) content of the SMA products was determined using the anhydride carbonyl signal at 1850 cm^{-1}. The FTIR procedure was calibrated via tritation of a set of SMA copolymers with MA contents of 10 to 40wt% MA. Some SMA-1-aminonaphthalene samples were dissolved in acetone and precipitated in *n*-hexane to remove unreacted 1 -aminonaphthalene. Nitrogen contents of the SMA residues were determined after drying at 180°C under vacuum for 1 h using a LECO FP-428 nitrogen analyzer.

RESULTS AND DISCUSSION

PA-6-EPM Blends

Figure 3 shows a direct comparison of the morphologies of the PA-6-EPM blend (80/20 w/w, 150 rpm) at various positions along the screw (locations A, B, and C), as obtained by the two sampling techniques, as well as the morphology of the final extrudate (location D).

Samples collected with the sampling device in location A [Fig. 3(a)]

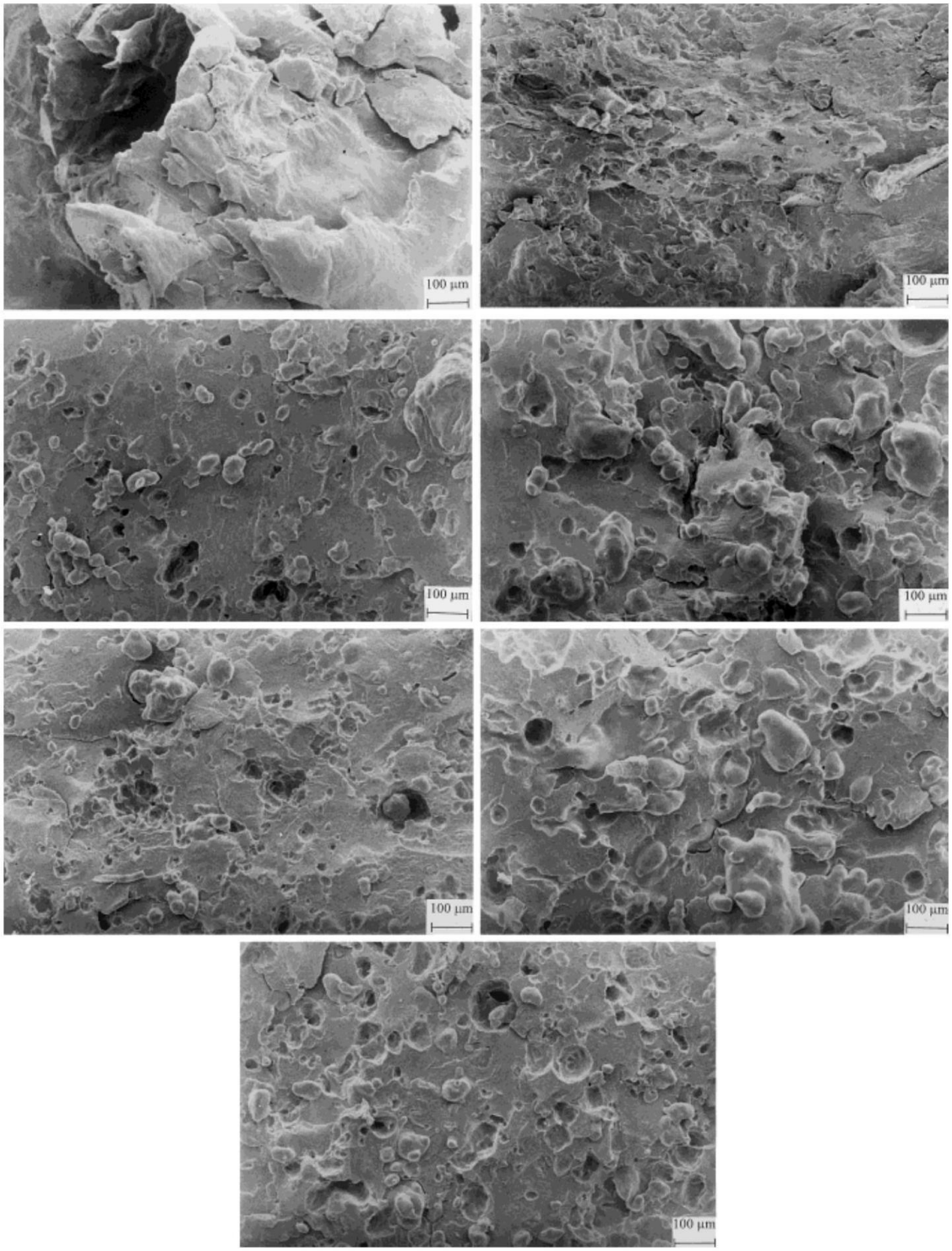

Figure 3 SEM micrographs of PA-6-EPM (80/20w/w, 150rpm) removed from the extruder using the sampling device and collected after screw pulling: (a) location A, sampling device; (b) location A, screw pulling; (c) location B, sampling device; (d) location

B, screw pulling; (e) location C, sampling device; (f) location C, screw pulling; (g) location D.

exhibit sheets of PA-6 and rubber. After the first kneading zone, at location B [Fig. 3(c)], droplets of the dispersed EPM phase distributed in the PA-6 matrix can be observed. This morphological change can be related to the local mixing mechanism, involving a significant dispersive action [17]

Table I Particle Size of the Dispersed EPM Phase in PA-6-EPM (80/20) Blend

Sampling Location [a]	Sampling Method	100 rpm Particle Size			150 rpm Particle Size		
		Average (μm)	Range (μm)	Variance (μm^2)	Average (μm)	Range (μm)	Variance (μm^2)
B	Device	49	26-70	196	40	18-66	169
B	Screw	69	25-106	484	56	23-162	900
C	Device	43	21-109	289	35	20-71	144
C	Screw	53	28-118	576	54	23-80	324
D	Extrudate	38	18-101	324	36	20-60	121

[a] Data for location A is not given since a lamellar morphology is obtained. with rupture and distribution of the minor phase in the matrix. Samples collected in location C present a similar morphology, although the size of the dispersed phase has decreased [Fig. 3(e)], the process continuing up to the die [Fig. 3(g)]. These results show that the most significant evolution of morphology occurred in the initial zone of the extruder. In fact, after the first kneading section, only a moderate decrease in the average particle size of the minor phase can be detected. The final EPM dispersion is still rather coarse, since no compatibilizer was incorporated.

Samples collected using the screw pulling technique show the same type of evolution [Fig. (b), (d), and (f)]. Nevertheless, differences in the morphology of equivalent samples obtained with the 2 methods are evident. The EPM particles shown in Figure 3(a), (c), and (e) are smaller and more regular than those in Figure (b), (d), and (f), respectively. This is attributed to particle coalescence in samples remaining molten for longer periods (circa 5 min), which is the case for those taken using the screw-pulling technique. [5,8,18,19]

The differences in the particle size of the two series of samples (that is, with 10 and 20% concen-

tration of EPM) are also obvious in Tables I and II, in which the evolution of the average particle size in terms of equivalent circle diameter at various screw speeds is presented. The variance values show that the particle size distribution is broad when samples were

collected after screw pulling. Samples collected with the new device show a narrower distribution in locations B and C.

Tables I and II also show the evolution of the average particle size along the extruder, including the effect of the concentration of the dispersed phase and of the screw rotation speed on the particle size. An increase in EPM concentration results in an increase of the particle size since particle interactions become more significant. An increase in screw speed leads to a reduction of the average particle size, which can be attributed to the higher shear stresses, inducing significant droplets break up. These observations are in agreement with other studies. [18,20,22–25]

SMA Imidation

The reaction of SMA with 1-aminonaphthalene at temperatures above 200°C results in the formation of cyclic imide, as follows:

Table II Particle Size of the Dispersed EPM Phase in PA-6-EPM (90/10) Blend

Sampling Location [a]	Sampling Method	100 rpm Particle Size			150 rpm Particle Size			200 rpm Particle Size		
		Average (μm)	Range (μm)	Variance (μm^2)	Average (μm)	Range (μm)	Variance (μm^2)	Average (μm)	Range (μm)	Variance (μm^2)
B	Device	40	20-80	324	37	16-86	225	34	18-72	100
B	Screw	55	17-113	676	47	17-79	289	36	18-77	169
C	Device	39	19-72	169	36	16-68	144	30	18-56	100
C	Screw	53	17-108	529	43	19-90	361	35	18-60	361
D	Extrudate	41	17-76	144	32	16-75	169	32	17-60	121

It was checked that 1-aminonaphthalene does not react with SMA at room temperature in the solid state nor during preparation of the THF solution. Upon processing, the unreacted 1-aminonaphthalene was not devolatized (it has a boiling point of 306°C) but remained in the SMA product.

The residual MA contents of the various SMA samples, as determined with FTIR, are given in Table III. The evaluation of the nitrogen content of some samples allowed the calculation of the imide content and, consequently, of the residual MA content (Table III, between brackets). They are in excellent agreement with the FTIR data.

In the first part of the extruder up to the first kneading zone (location A; $t = 38$ s), the MA content of SMA decreases from 23.9 to 17.6 mol %. Further on the screw (locations B, C, and D, corresponding to $t = 53{,}73$ and 145 s , respectively), the MA content hardly changes (the experimental error is ± 0.5 mol%MA). These results evidence that imidation occurs mainly in the melting zone and that additional reaction proceeds slowly. Since pulling the screws allows for further reaction for 5 min , it is not surprising that the residual MA contents show a small, but significant, decrease to about 14.5 mol%. As shown in Figure 4, the data obtained via the sampling device and screw pulling experiments fit satisfactorily a single curve. According to the recipe (SMA/aminonaphthalene = 2.5/0.5w/w), the lowest residual MA content is 9.5 mol%, which is an indication that the imidation reac-

Table III MA Content (Mol % ± 0.5Mol%) Determined by FTIR for Imidation of SMA [a] with 1-Aminonaphthalene (2.5/0.5w/w) as a Function of the Screw Position

Sampling Location	Sampling Device	Screw Pulling
A	17.6(17.4)[b]	14.9(14.6)[b]
B	17.5	14.8
C	18.0	14.2
D	18.0(17.4)[b]	18.0(17.4)[b]

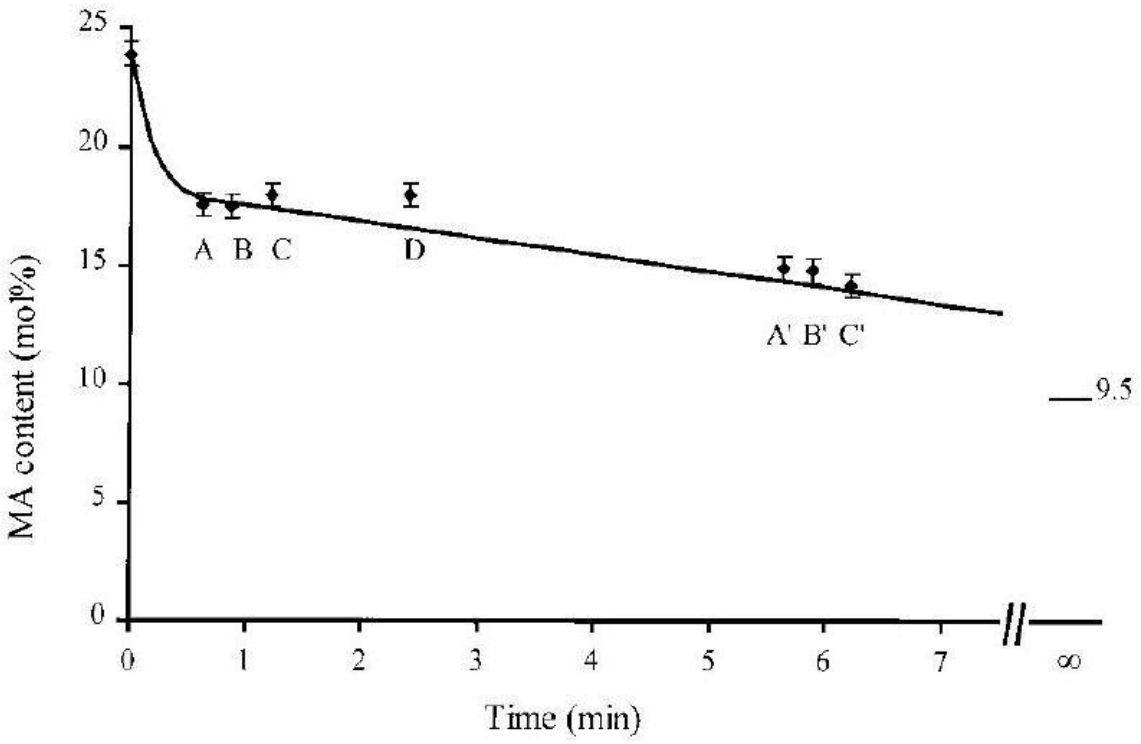

Figure 4 Chemical conversion of SMA-1-aminonaphthalene imidation reaction as a function of the residence time (A, B, C, and D, sampling device; A′, B', and C′, screw pulling).

tion is far from complete. The main conclusion from this part is that pulling the screws allows for further reaction and does not provide the correct chemical data.

CONCLUSIONS

The available sampling device enabled the pursuit of nearly real-time investigations of processes developing inside twin-screw extruders. Both blending and chemical modification of polymers could be studied, as illustrated by the PA-6-EPM blending and SMA imidation experiments reported in this work. It is clearly shown that screw-pulling experiments can result in experimental artifacts and thus induce erroneous conclusions on physical and/or chemical mechanisms. In the near future, we will publish studies on in situ compatibilization of PA-6-EPM-EPM-g-MA blends and grafting of MA using the sampling device described.

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[a] Data for location A is not given since a lamellar morphology is obtained.

[a] MA content of starting material: 22.8wt% ≅ 23.9 mol%.
[b] MA contents as determined via N% between brackets.