A Study of Grafting Reactions During Processing of Polyolefins

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Abstract

The effects of polyolefins composition, that is polyethylene (PE), polypropylene (PP) and a ethylene/propylene copolymer (EPM) of 45/55 monomer ratio, and of operating conditions (screw speed, throughput and screw configuration) on the grafting of maleic anhydride (MA) were investigated. Sampling devices located along the extruder barrel were used to collect samples of modified PE, EPM, and PP that were subsequently characterized in order to monitor the degree of grafting and of crosslinking/degradation. Although a similar trend of MA grafting evolution is observed along the extruder, the final MA graft content depends on the processing parameters, screw configuration, and particularly, throughput have a significant effect on the grafting yield. Taking PE as an example, and by means of a statistical experimental design, an optimal operating window in terms of screw speed, throughput, and geometry was identified, yielding MA graft contents of 2wt% MA.

KEY WORDS: Grafting, Maleic anhydride, Modification, Polyolefins, Processing

Introduction

their adhesion properties and their compatibilizing abilities. [1–4] For example, the production of ethylenepropylene grafted with maleic anhydride (EPM-gMA) yields a reactive product that can be used for the "in-situ" formation of a compatibilizer for the manufacture of useful blends of ethylene/propylene copolymer (EPM) and polyamide (PA). [1,2]

Grafting can be performed in the melt in an extruder, i.e. via reactive extrusion (REX), or in solution. [2] The former is preferable, given the absence of solvents, the short residence

times involved, and the possibility of a continuous operation. Since grafting via REX is carried out at high temperatures with very viscous and, probably, heterogeneous polymer systems, the performance of the grafting process is not only affected by the nature of the constituents and by the chemistry involved, but also by the processing conditions.

A general understanding of the effects of the processing parameters on free radical grafting in extruders has already been achieved. [5–8] Screw geometry and rotation frequency must ensure efficient mixing of the monomer (maleic anhydride), initiator (peroxide), and polymer in order to produce high grafting yields. Melt temperature influences the peroxide decomposition and the solubility of the peroxide and monomer into the polymer. The throughput determines the residence time. Finally, local pressure generation can provide enhanced dispersion and/or solubility of the peroxide and/or monomer into the polymer melt. [9] The majority of previous studies have focused on the characterization of the extrudates in terms of grafting content and degree of crosslinking/degradation, but little information is still available on the evolution of the reactions along the extruder. However, this is important in order to develop process models that maximize the grafting efficiency to optimize the product properties and to enable the correct design of processing equipment.

The authors have followed the processing of polyolefins along the axis of a corotating twin-screw extruder in absence and in presence of peroxide [10] and monitored the physico-chemical phenomena developing during grafting of MA onto polyolefins. [11] A fast sampling technique using devices inserted along the barrel of the extruder was developed for this purpose. [12] In the presence of peroxide, branching/crosslinking or degradation of the polyolefins occurs along the extruder until the peroxide is fully converted. The degree of branching/crosslinking or degradation depends on the ethylene/propylene ratio, the original molecular weight of the polymer, the temperature, and the amount of peroxide added.

The present work was carried out to study the effect of polyolefin composition (polyethylene (PE) and polypropylene (PP) homopolymers). A copolymer of ethylene/propylene (EPM) at 45/55 monomer ratio was also included and the effect of operating conditions (screw speed, throughput, and screw configuration) on the final MA graft content was studied. In all cases, samples were collected at relevant locations along the barrel, in order to monitor the evolution of the MA grafting and of crosslinking/degradation. For one of the materials, a statistical design of experiments was used to define an optimal operating window in terms of screw speed, throughput, and geometry.

Experimental Procedure

MATERIALS

Stamylan HD 2H280 [high density polyethylene (HDPE); $M_w = 60$ kg/mol, MFI = 1.7 g/10 min (190°C and 5 kg/h), and melting temperature of 127°C] and Stamylan P 13E10 [PP; $M_w = 500$ kg/mol, MFI = 1.3 g/10 min(190°C and 5 kg/h), and melting temperature of 152°C] were supplied by DSM. Exxon VA 404 (EPM, $M_w = 280$ kg/mol, with 45wt% ethylene and MFI = 1.1 g/10 min(190°C and 5 kg/h)) was produced by Exxon. Maleic anhydride (MA) was obtained from Aldrich, while 2,5-bis(tert-butylperoxy)-2,5-

dimethylhexane (DHBP; Trigonox 101), in powder form, was supplied by Akzo Nobel. The half-life time of this peroxide at 200°C is 6.1 s .

PROCESSING

The polyolefins were modified with 5 pph of MA in the presence of 1 pph DHBP in a laboratory modular Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder. The polyolefins, MA, and peroxide were tumble-mixed and subsequently incorporated into the extruder by a K-Tron gravimetric feeder set at 5 kg/h. This procedure was adopted due to its simplicity. In fact, using other more sophisticated techniques, such as separate feeding of the components through multi-ports of the extruder, can yield slightly higher levels of grafted MA, but show a low efficiency in the initial stages. [11] The extruder operated with a uniform barrel temperature set at 200°C, and a screw rotation speed of 75 rpm .

For process optimization purposes, the throughput, screw speed, and screw configuration were varied according to Table I, which presents the three levels corresponding to a central composite experimental design with three independent parameters. [13] Figure 1 illustrates the extruder layout and shows the locations where sampling was performed. Generally, these correspond to (i) high screw filling ratios, because melt pressure is required for pumping the material laterally out of the extruder and to (ii) mixing zones inducing higher shear rates and stresses. A (vacuum assisted) devolatilization section was located between the last mixing zone and the die in order to remove the excess maleic anhydride. All the samples collected along the screw axis and from the die, i.e. cut from the extrudate, were immediately quenched in liquid nitrogen in order to avoid further reaction. The screw comprises three mixing zones, two with staggering kneading blocks and a third one with a left hand element. Figure 1 also shows the variations tested in the configuration of the first kneading zone, where the staggered angle of the mixing section upstream was changed from -30 to -60 and to 90°.

The average melt temperature was measured at various locations along the extruder by sticking a preheated fast response penetration probe (time constant ~ 1 s) Cole-Parmer type K thermocouple into the freshly collected material. The efficacy of this simple technique has been demonstrated elsewhere. [11]

The average residence time at the various sampling locations along the extruder, under the selected operating conditions, was measured using an impulse technique involving the monitorization of the change of concentration of a tracer with time. [14] Upon reaching an operating steady state, a small amount of silica powder was incorporated instantaneously to the feed stream of the extruder. Samples of the modified polymer were then collected from one sampling point at various known time intervals. The procedure was repeated for every sampling location. The relative amount of silica, i.e., the concentration of tracer, was determined by ashing the sample and weighing the residue. From these data the conventional residence time parameters, such as the cumulative residence time distribution, $F(\theta)$, and the mean residence time, $\bar{t}$, were computed. [14]

MATERIALS CHARACTERIZATION

The chemical and rheological characterization of the samples obtained was performed following the procedure presented in Fig. 2. The modified polyolefins were dissolved in toluene (PE and EPM) or xylene (PP) at elevated temperature ($\sim 110°C$) and subsequently precipitated in acetone, in order to remove the residual peroxide and unreacted MA. In the case of PE and EPM, any existing gel was removed during precipitation. After drying at $180°C$ under vacuum for 60 min , IR spectra of compression moulded films were recorded on a Perkin Elmer 1620 FT-IR spectrometer. The MA graft content was determined using the ratio of the anhydride carbonyl signal at 1850 cm^{-1} and a reference peak. The FTIR procedure was calibrated using standards with known contents of MA.

Polymer chain branching/crosslinking was estimated from the linear viscoelastic response of compression moulded samples subjected to a frequency sweep (from 4×10^{-3} to 40 Hz) at $200°C$ in a TA Instruments Weissenberg rheometer with parallelplate geometry. The gap and diameter of the plates was 2.00 mm and 2.0 cm , respectively. The strain was kept at 0.01 in order to maintain the material's response within the linear viscoelastic domain. As it has been checked in a previous study, [10] noticeable chemical changes do not take place during sample preparation.

TABLE I
Levels and Variable of the Experimental Design

Level	Throughput (kg/h)	Screw speed (rpm)	Screw Configuration
-1	2	50	1 45R/30R/30R4/20R2/12kb-30 ° /30R/4kb90 °3 kb60° / 45R2/30R2/30R4L/60R/30R2/20R2
0	4	100	2 45R/30R/30R4/20R2/12kb-60 o /30R/4kb90°3kb-60°/ 45R2/30R2/30R4L/60R/30R2/20R2
+1	6	150	3 45R/30R/30R4/20R2/12kb90 /30R/ 4 kb90°3 kb60°/ 45R2/30R2/30R4L/60R/30R2/20R2

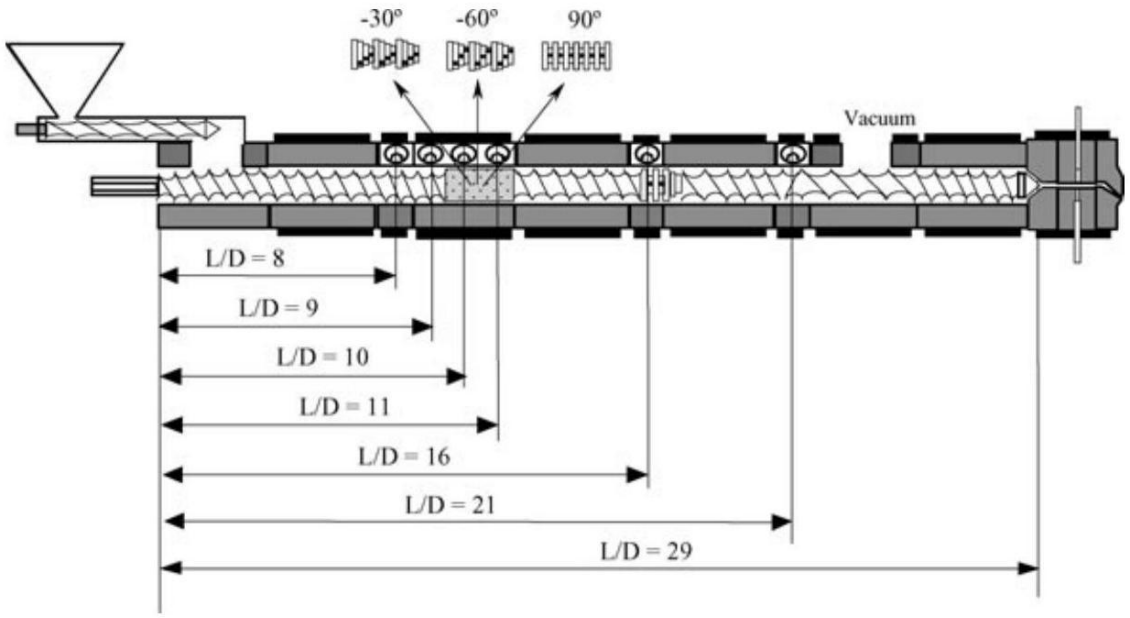


FIGURE 1. Extruder layout and locations of the sampling devices.

Results and Discussion

The evolution of MA grafting onto various polyolefins with different propylene contents (i.e., 0wt% for PE, 55wt% for EPM, and 100wt% for PP), in terms of grafted MA content and rheological changes along the extruder, is discussed first. In order to optimize the grafting efficiency (both along the extruder and for the extrudate), the influence of the processing conditions is analyzed, taking the modification of PE as an example. Finally, the results are analyzed with a view to selecting the most appropriate set of operating conditions that maximize the process efficiency.

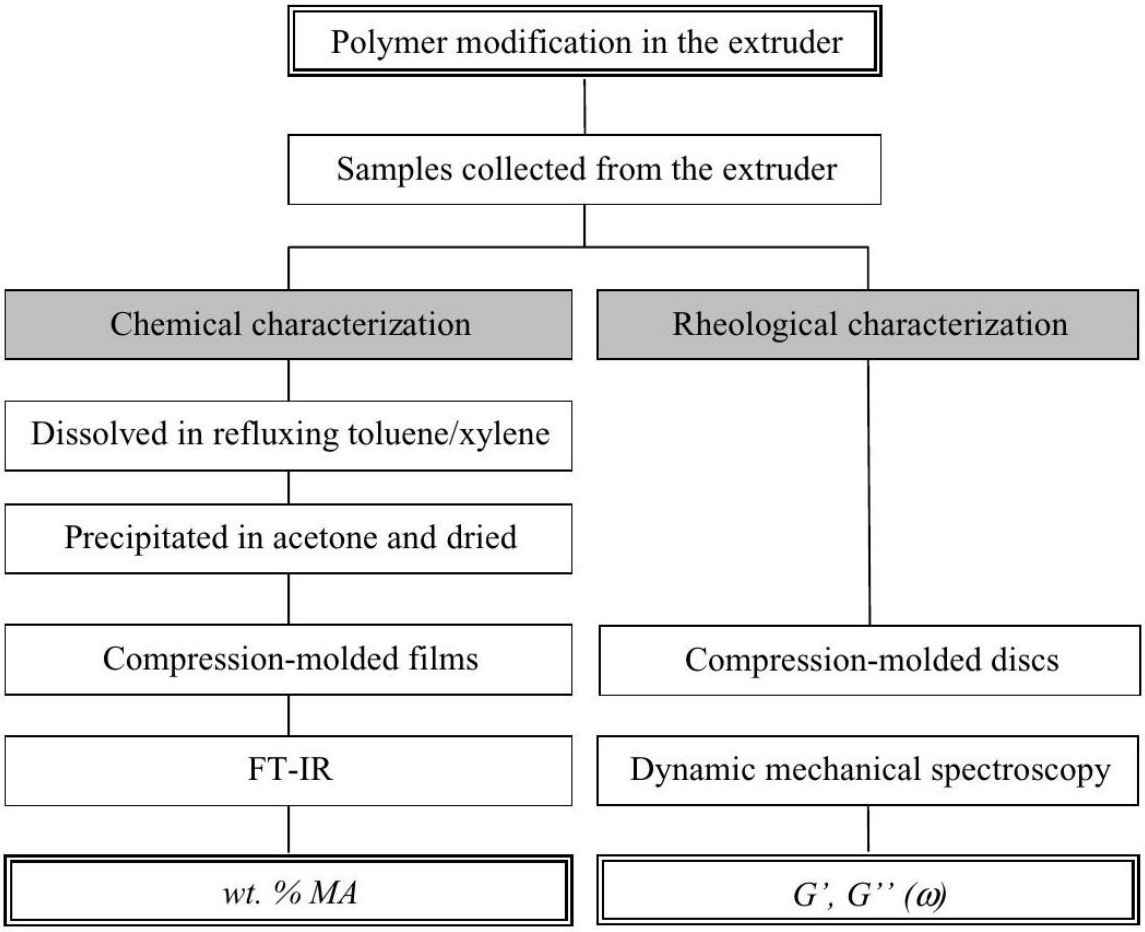


FIGURE 2. Procedure for sample characterization.

GRAFTING OF MA ONTO POLYOLEFINS

The evolution of the MA graft content along the extruder for the three polyolefins was monitored from the point where they are molten (which occurs at $L/D = 9$, and, therefore, at $L/D = 8$ the MA graft content is zero) until they emerge from the die. This is shown in Fig. 3, for grafting with 5 pph MA and 1 pph DHBP at 200°C barrel temperatures. Regardless of the polyolefin structure, there is a strong increase in the grafting level immediately after melting in the first kneading zone (see also Fig. 1). A smaller increase in MA graft content is perceived at the beginning of the second mixing zone, but no significant changes were observed further downstream, despite the presence of a left hand element inducing high shear stresses.

The measured melt temperatures and accumulated average residence times at each sampling location are presented in Fig. 4. While the average melt temperature of EPM remains around 15°C above the set temperature (200°C) throughout most of the extruder, the molten PP behaves the opposite way, and the melt temperature of PE is only slightly above the set value. Melt temperature results from the contribution of heat conduction from the barrel, viscous dissipation, and generated heat from the chemical reaction. Since

the three materials are being processed under the same temperature set values and the grafting recipe is identical, the parameter influencing the observed behavior must be viscosity. In fact, the measured melt temperatures of PE, EPM, and PP correlate well with their rheological behavior after being modified, that is to say that the higher the viscosity of the melt the higher the temperature due to viscous heat dissipation. This is shown in Fig. 5 in terms of variation of loss modulus, G″ (which is proportional to viscosity) of the modified PE, EPM, and PP extrudates. At 7×10^{-3} Hz and 200°C the respective G'' values are 9.2×10^{4}, 4.4×10^{5}, and 89 Pa).

Since temperature and residence time for PE are known at each location, it is possible to integrate numerically the peroxide decomposition for a given temperature and time, by using a first-order equation for peroxide decomposition in combination with the Arrhenius equation (data for DHBP, as provided by Akzo-Nobel are: $k_0 = 1.68 \times 10^{16}$ s^{-1} and $E_A = 155.49 \times 10^3$ J/mole). Taking PE, as an example, Fig. 6 shows the similarity of the evolution along the screw axis of the experimental MA graft content and of the calculated peroxide decomposition. The grafting reaction is initiated when the peroxide starts to decompose at about 160°C at location $L/D = 9$, as shown in Fig. 4. The temperature increases sharply from 160 to 204°C between $L/D = 9$ and $L/D = 11$, which results in a faster peroxide decomposition and, consequently, a higher level of MA grafting. At location $L/D = 16$ the peroxide is completely decomposed and the degree of grafting reaches an almost constant level. Thus, the grafting evolution along the extruder can be explained by the peroxide decomposition profile.

Although the MA graft profiles for EPM and PP are similar to that of PE, the final level of grafting is different for the three polymers (Fig. 3). The highest is obtained for PE (1.7 wt%), the lowest for PP

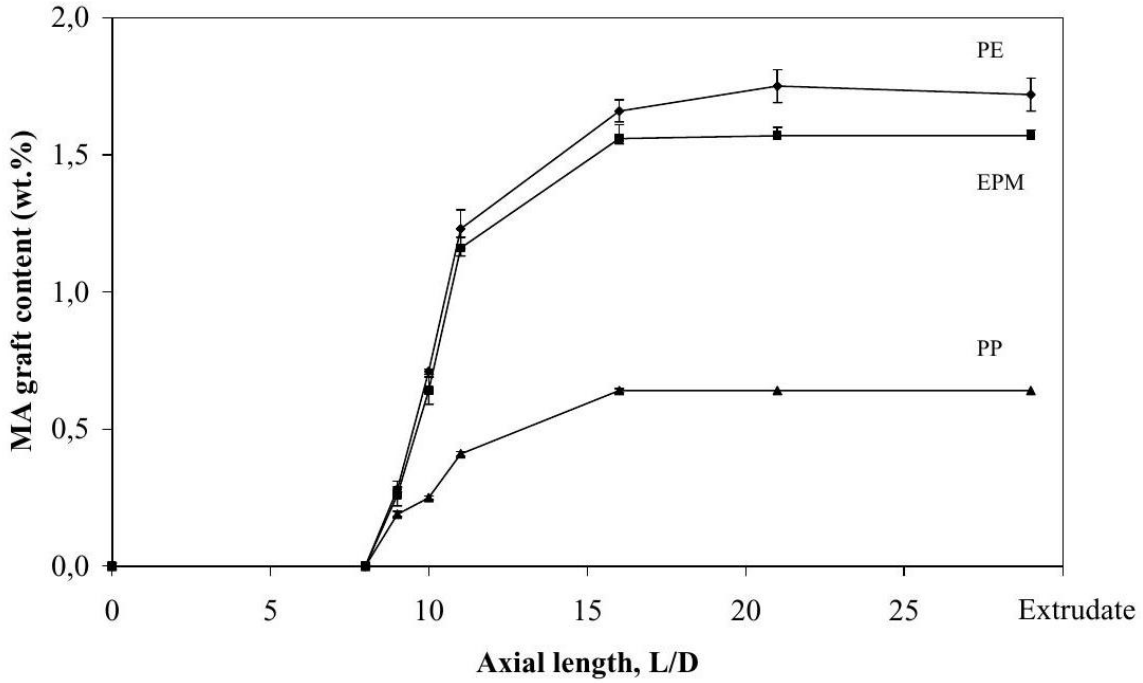


FIGURE 3. MA grafting onto polyolefins along the extruder (200°C, 5pphMA, and 1 pph DHBP).

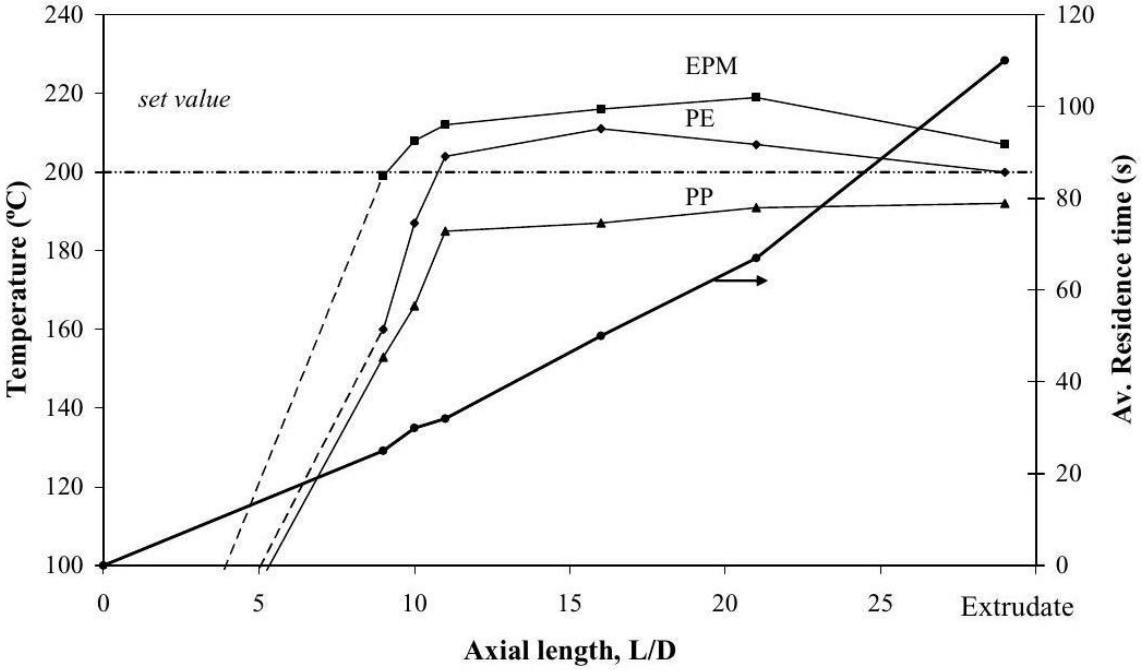
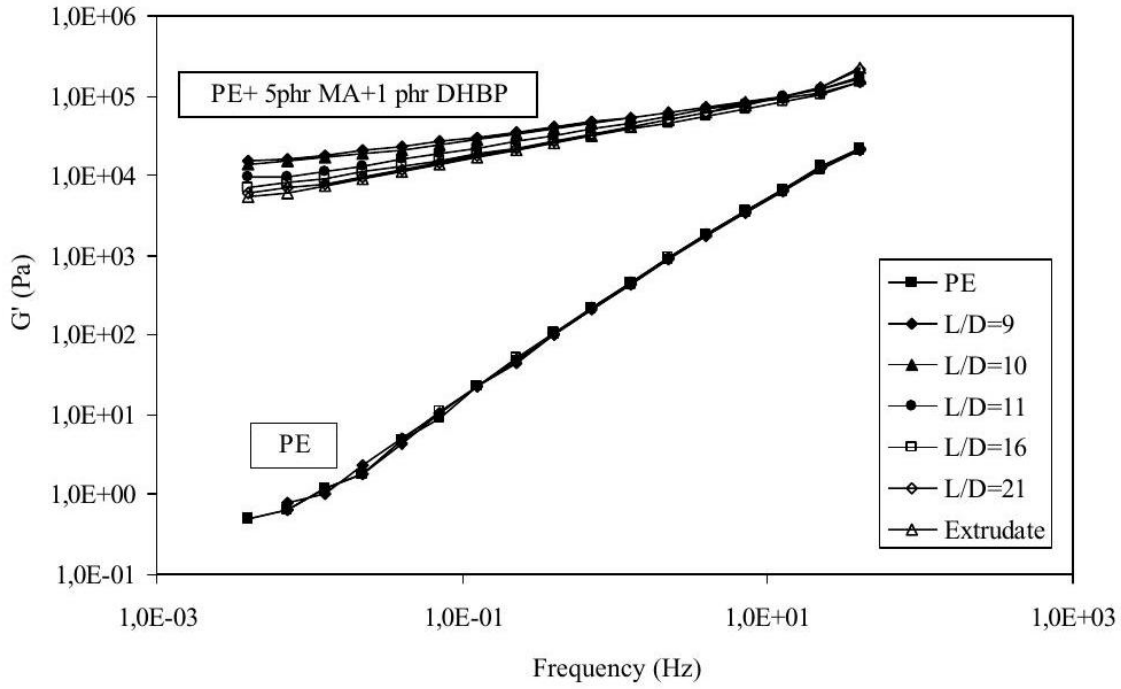
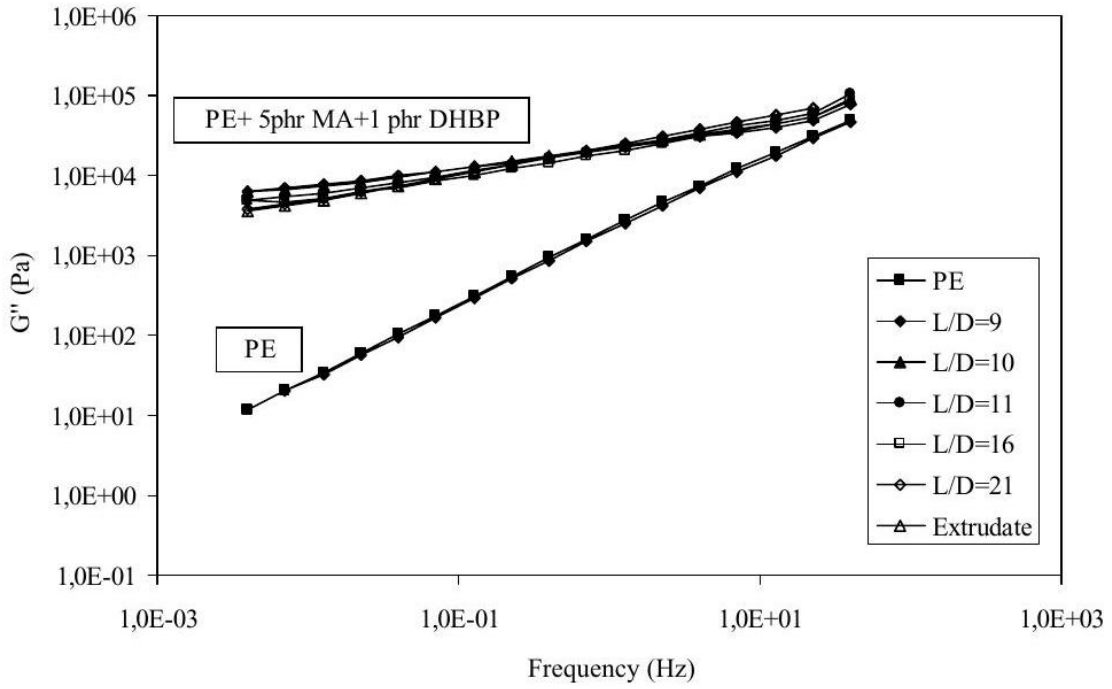


FIGURE 4. Measured temperature and average residence time during MA grafting of various polyolefins (200°C, 5pph MA, and 1 pph DHBP).





(a)

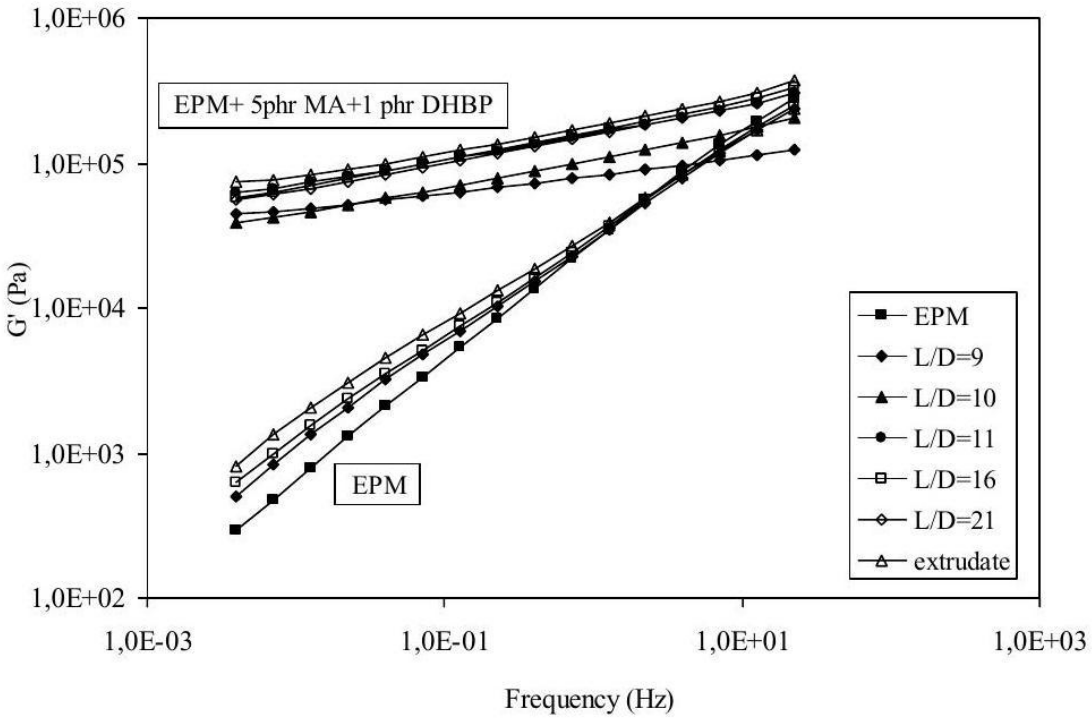
FIGURE 5. Rheological behavior of samples of initial and modified polymers taken from the extruder and extrudate (a) PE, (b) EPM, and (c) PP. (Continued)

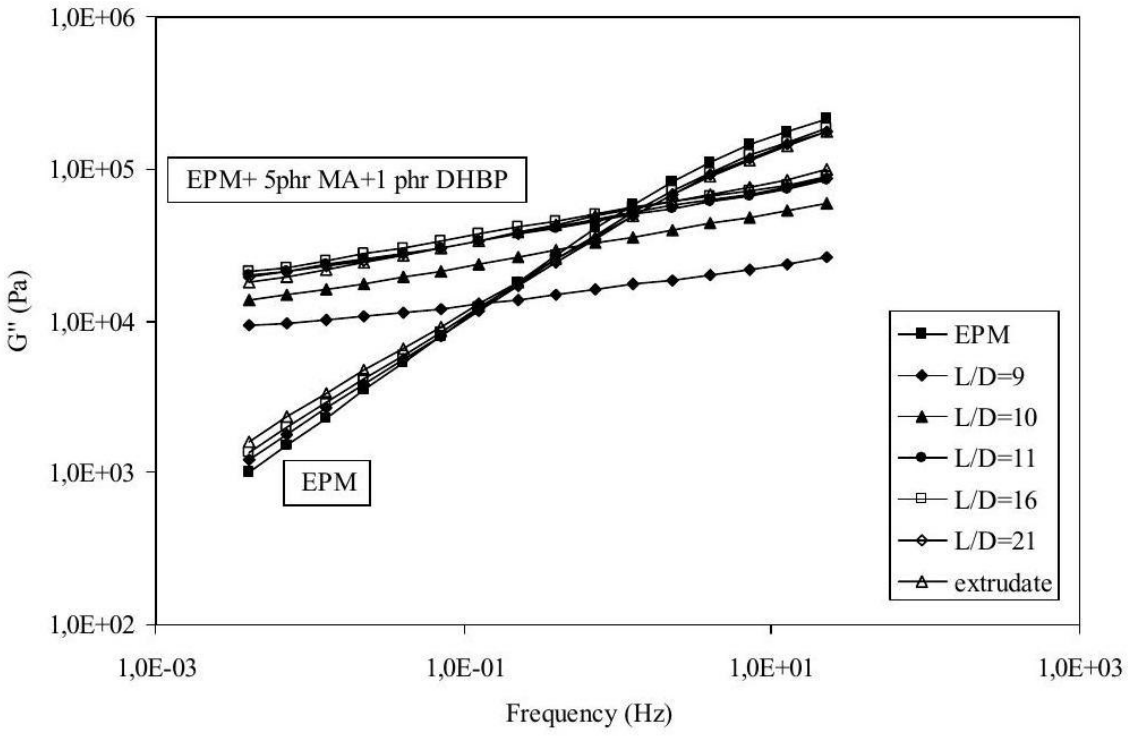
(0.64 wt%), and the MA graft content of EPM is close to that of PE. Similar differences and grafting efficiencies have been observed for similar extrudates by other authors. [15,16]

The dependence of MA graft level on the polyolefin composition is due to a competition between grafting and termination reactions. Depending on the ethylene/propylene content of the polyolefin, different chemical mechanisms develop involving β-scission for polyolefins with high propylene content or crosslinking for polyolefins with high ethylene content. [17]

Figure 5 presents the rheological behavior of samples taken along the extruder of the initial and modified polyolefins processed under similar conditions. When extruded without MA and peroxide, PE shows a good thermal stability (Fig. 5a), but EPM (Fig. 5b) and PP (Fig. 5c) exhibit some tendency for crosslinking and degradation, respectively. These processes become more prominent in the presence of free radicals and initiator. With the exception of PP, where the $G'(\omega)$ and $G''(\omega)$ curves are shifted toward lower moduli values as a result of grafting, in the case of EPM and PE there is also a change in shape, indicating a progressive formation of a more densely cross-linked polymer is taking place. Some degradation of EPM may account for the slight decrease of G'' in the higher frequency range. After grafting, PP changes its behavior from that typical of a viscoelastic fluid to one with a predominantly viscous behavior, as indicated by the slope of $G''(\omega)$ which becomes approximately equal to one.

Both $G'(\omega)$ and $G''(\omega)$ discriminate between samples withdrawn from the various locations along the screw axis. However, the most significant changes


1,0E+06
1,0E+05
1,0E+04
1,0E+03
1,0E+02
G' (Pa)
EPM+ 5phr MA+1 phr DHBP
EPM
EPM
L/D=9
L/D=10
L/D=11
L/D=16
L/D=21
extrudate
1,0E-03
1,0E-01
1,0E+01
1,0E+03
Frequency (Hz)


1,0E+06
1,0E+05
1,0E+04
1,0E+03
1,0E+02
G'' (Pa)
EPM+ 5phr MA+1 phr DHBP
EPM
EPM
L/D=9
L/D=10
L/D=11
L/D=16
L/D=21
extrudate
1,0E-03
1,0E-01
1,0E+01
1,0E+03
Frequency (Hz)

(b)

FIGURE 5.

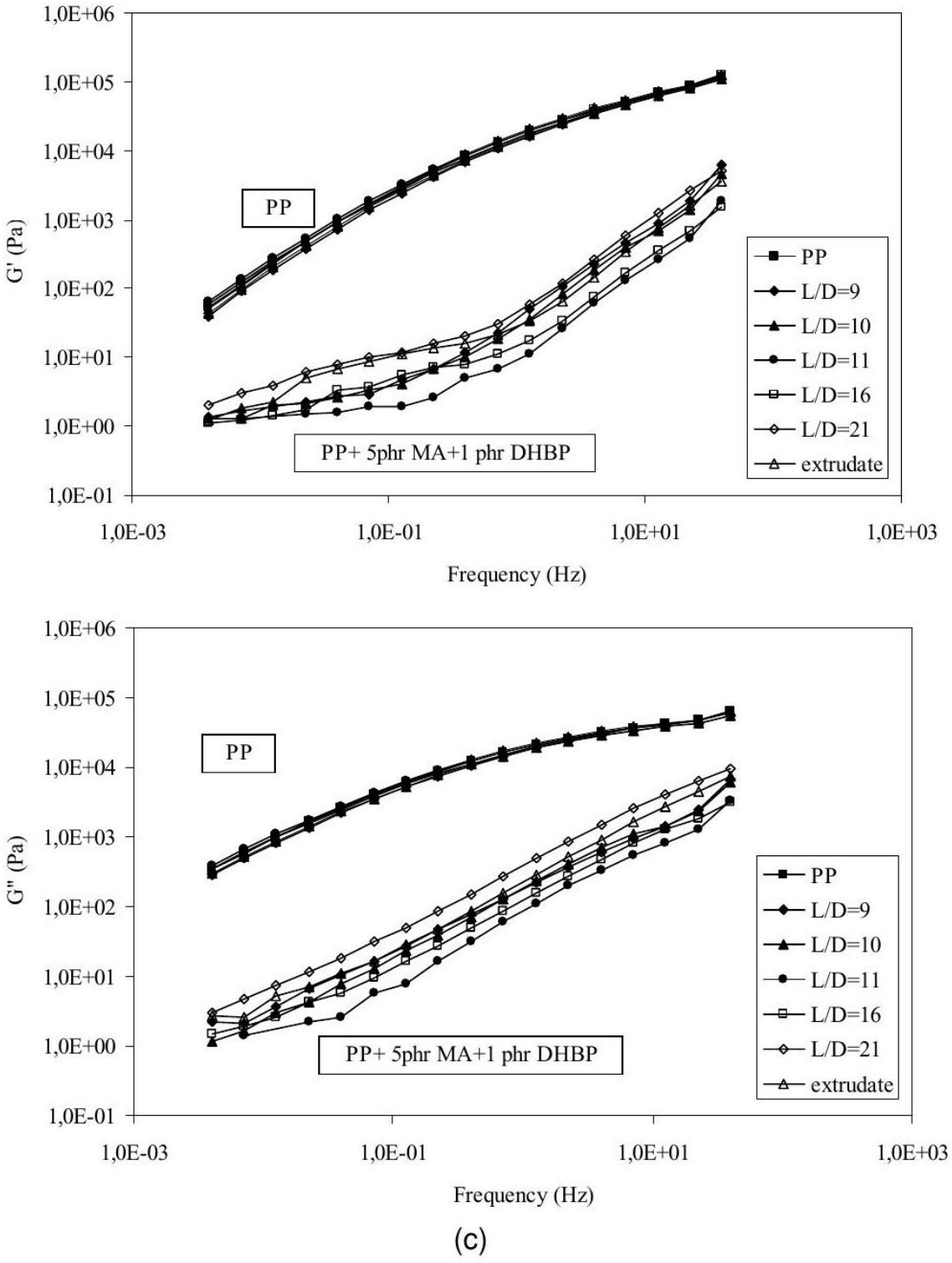


FIGURE 5.

occur up to $L/D = 9$. These differences can be more easily recognized in Fig. 7, which shows the relative variation of G' and G'' (at 7×10^{-3} Hz and 200°C) along the extruder

for the three polyolefins. Taking the unmodified materials as the basis of comparison, the figure shows an evolution of the rheological parameters up to the end of the first kneading block ($L/D = 12$; see Fig. 1), with only small changes being observed downstream. In the case of PE, both G' and G'' increase significantly (from 0.6 and 20.8 Pa to 1.6×10^4 and 7×10^3 Pa, at $L/D = 9$ respectively), indicating severe crosslinking/gel formation. At $L/D = 10$ some degradation starts to occur, since a very slight (but consistent) decrease in G′ can be observed along the screw axis (from 1.5×10^4 at $L/D = 10$ to 6×10^3 Pa at the extrudate). The relative degree of EPM crosslinking is significantly smaller, which is related to its medium ethylene content. Conversely, a strong decrease in G' and G′′ was observed for PP, which is attributed to β-scission of tertiary PP radicals. [10] The differences in behavior between these polyolefins seem to be related to the chemical composition. In fact, if one takes as full scale the ratio between the relative values of the rheological parameters of PE and PP, the value for EPM corresponds approximately to its ethylene content.

THE EFFECT OF PROCESSING CONDITIONS

In order to investigate the effects of throughput, screw speed, and screw configuration on the MA graft content, a central composite experimental

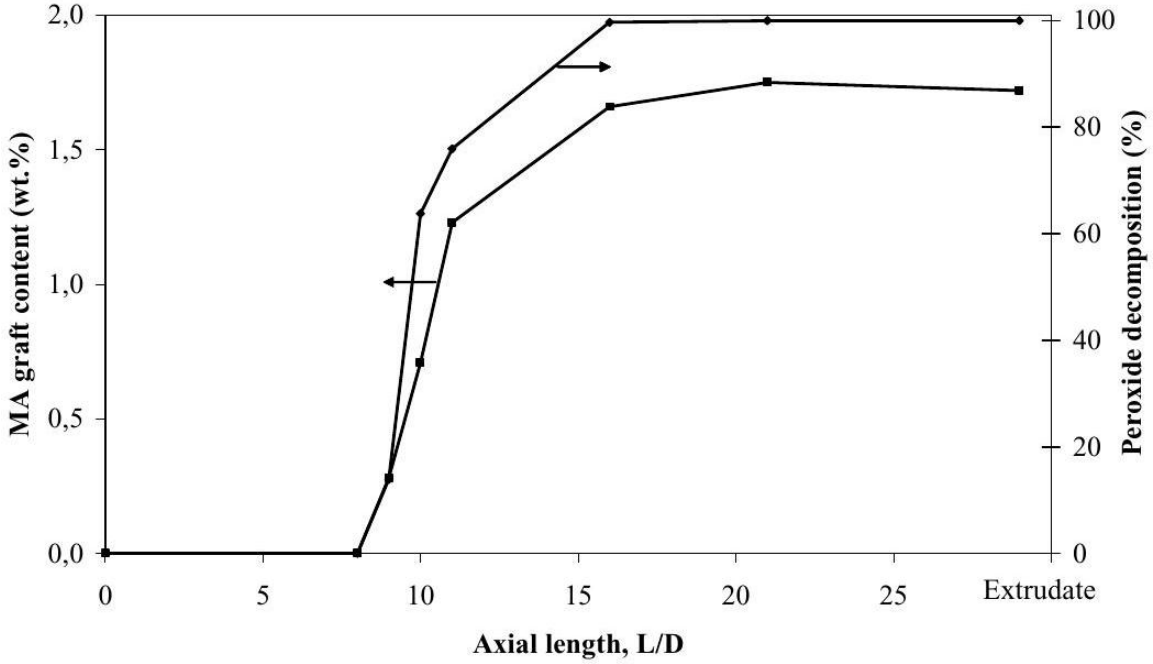


FIGURE 6. MA graft content vs calculated peroxide decomposition for PE (200°C, 5pphMA, and 1 pph DHBP).

design was adopted, the actual values of the variables for the levels −1,0, and +1 being presented in Table I. This study was carried out for PE only, as the highest grafting levels were obtained for this material, therefore, the effect of the above parameters should be

more easily perceived. As shown in Fig. 1, changes in screw geometry consisted in varying the staggering angle of the first kneading block from −30° (configuration 1) to −60° (configuration 2) and to 90° (configuration 3). Since at 200°C the rate of peroxide decomposition is neither too fast nor too slow in comparison with the residence time on the extruder, the set temperature was kept constant and excluded from the group of operating parameters to be studied. However, it should be noted that the actual melt temperature is not constant, i.e., it will vary along the screw axis and will be different for the different experiments. In this sense the melt temperature is a hidden variable that will be included when discussing the results.

Figure 8 presents the evolution of the MA graft content for the three screw configurations. As discussed in the previous section, a strong increase in the grafting level in the first part of the extruder followed by a plateau is observed. A neutral staggering angle of 90° (Fig. 8 bottom) results in a less steep increase in MA graft content and a lower final MA graft content (~ 1.6wt% MA instead of 1.5-2.0

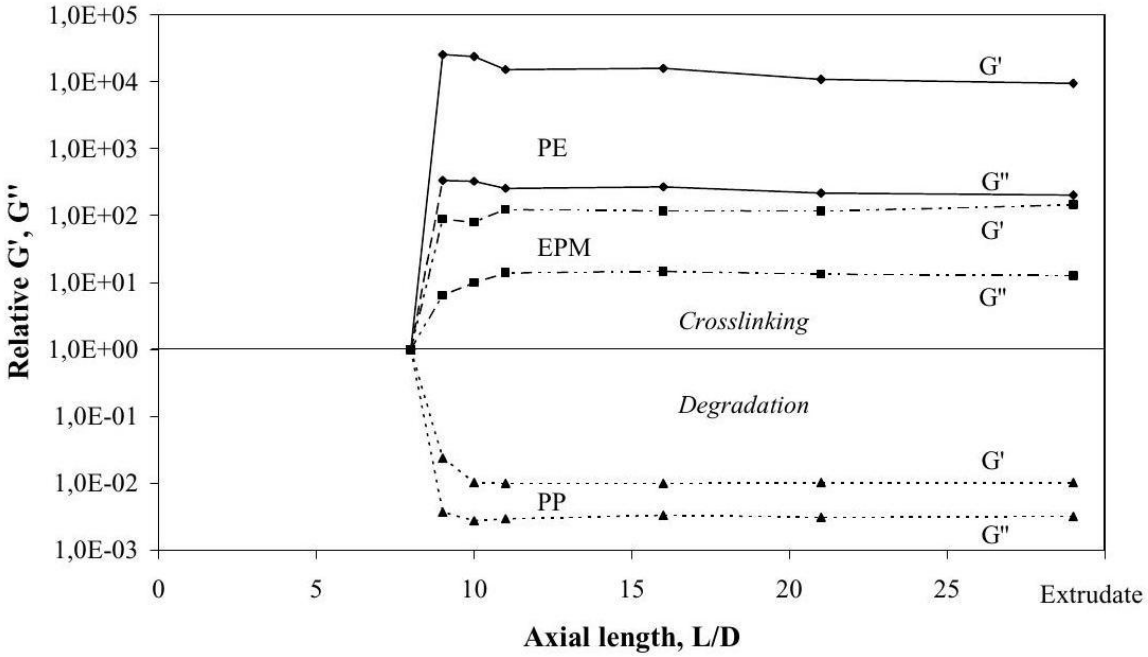
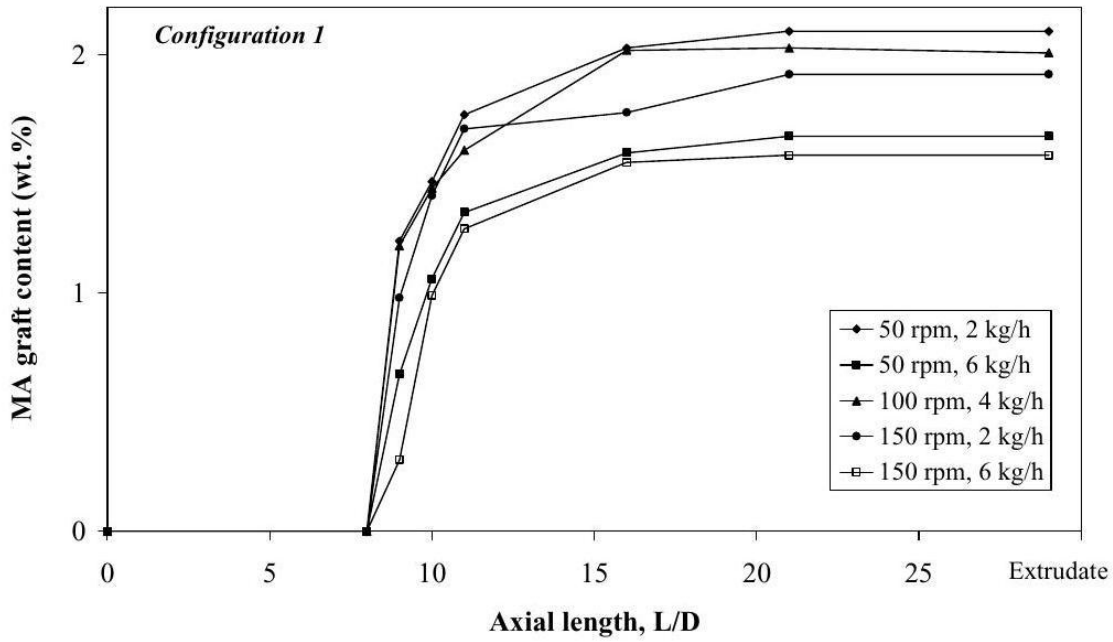
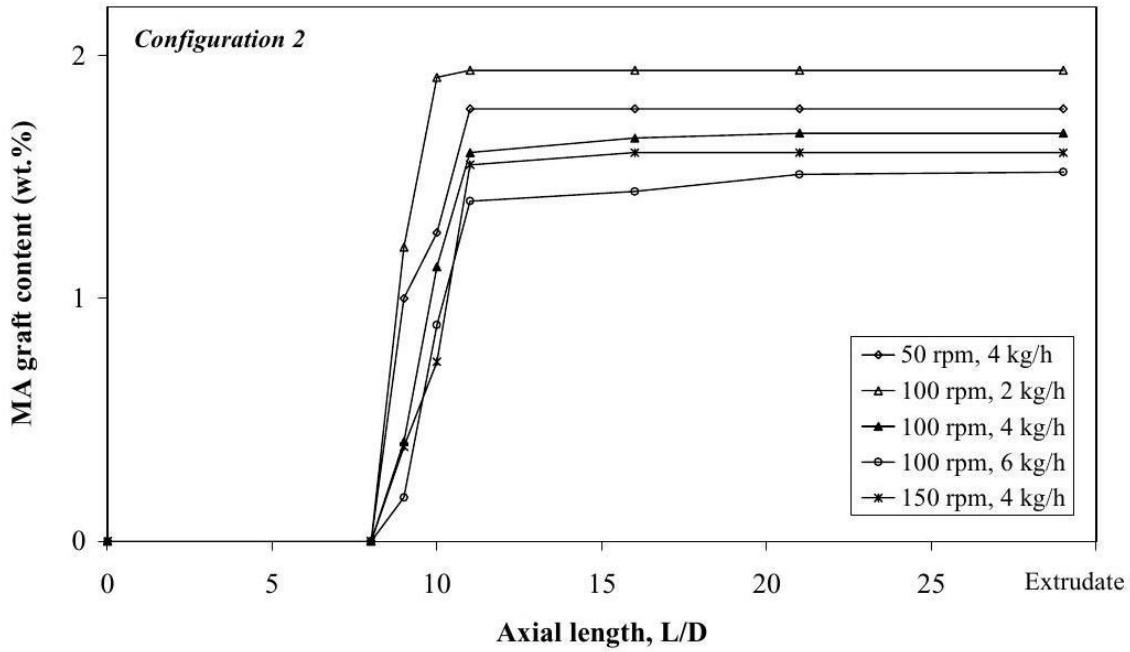


FIGURE 7. Evolution of the rheological parameters (G′ and G′′ are normalized to the values of the starting materials) of the various MA-grafted polyolefins along the screw axis.


Configuration 1
MA graft content (wt.%)
Axial length, L/D
Extrudate
50 rpm, 2 kg/h
50 rpm, 6 kg/h
100 rpm, 4 kg/h
150 rpm, 2 kg/h
150 rpm, 6 kg/h


Configuration 2
MA graft content (wt.%)
Axial length, L/D
Extrudate
50 rpm, 4 kg/h
100 rpm, 2 kg/h
100 rpm, 4 kg/h
100 rpm, 6 kg/h
150 rpm, 4 kg/h

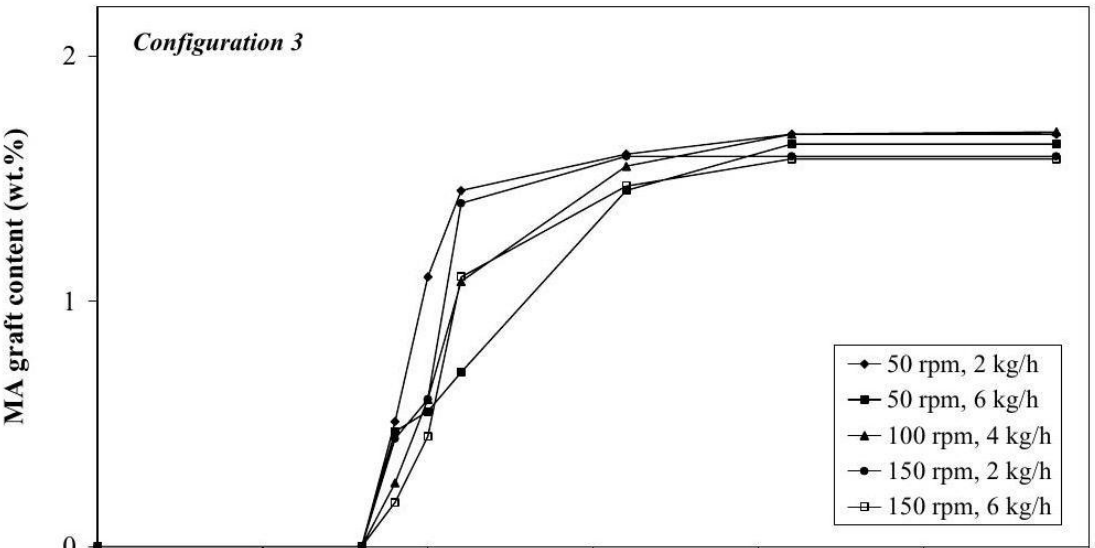
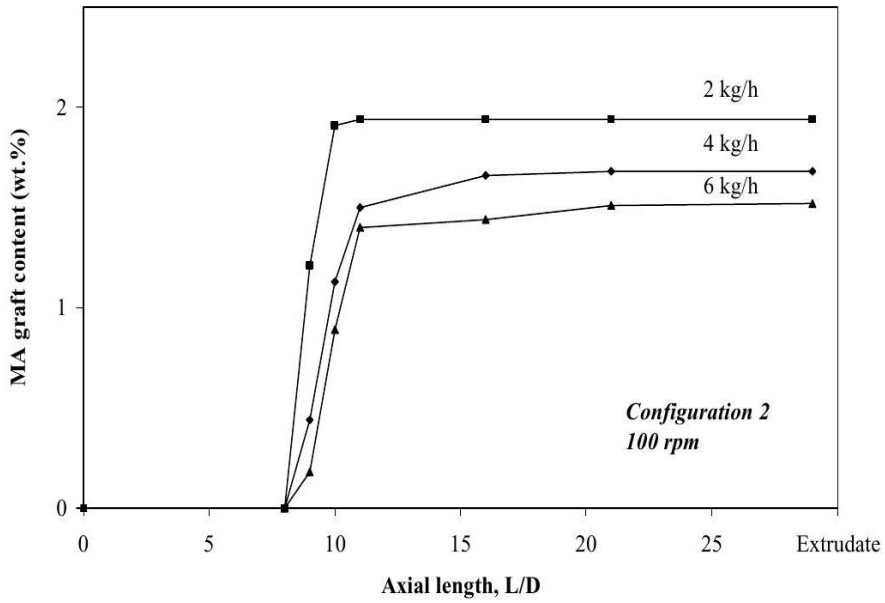
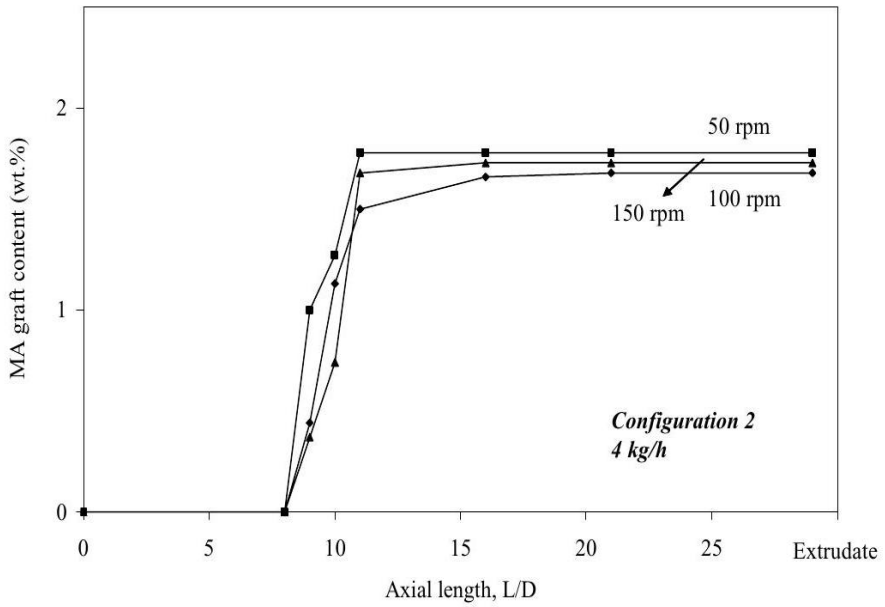

Configuration 3
MA graft content (wt.%)
50 rpm, 2 kg/h
50 rpm, 6 kg/h
100 rpm, 4 kg/h
150 rpm, 2 kg/h
150 rpm, 6 kg/h

FIGURE 8. Influence of the staggering angle on MA grafting onto PE (200°C, 5pphMA, and 1 pph DHBP) (top) −30°; (middle) −60° and (bottom) 90°. wt%MA in the other cases). This is not unexpected, since this geometry is less restrictive than the other two configurations.

The individual effects of screw speed, throughput, and screw configuration on the MA graft content
can be clearly observed in Fig. 9, where the influence of each variable is plotted while keeping the other two constant. A significant decrease of the MA graft content can be observed as the throughput increases [Fig. 9 (top)]. Increasing the throughput decreases


2 kg/h
4 kg/h
6 kg/h
Configuration 2
100 rpm
MA graft content (wt.%)
Axial length, L/D
Extrudate


50 rpm
100 rpm
150 rpm
Configuration 2
4 kg/h
MA graft content (wt.%)
Axial length, L/D
Extrudate

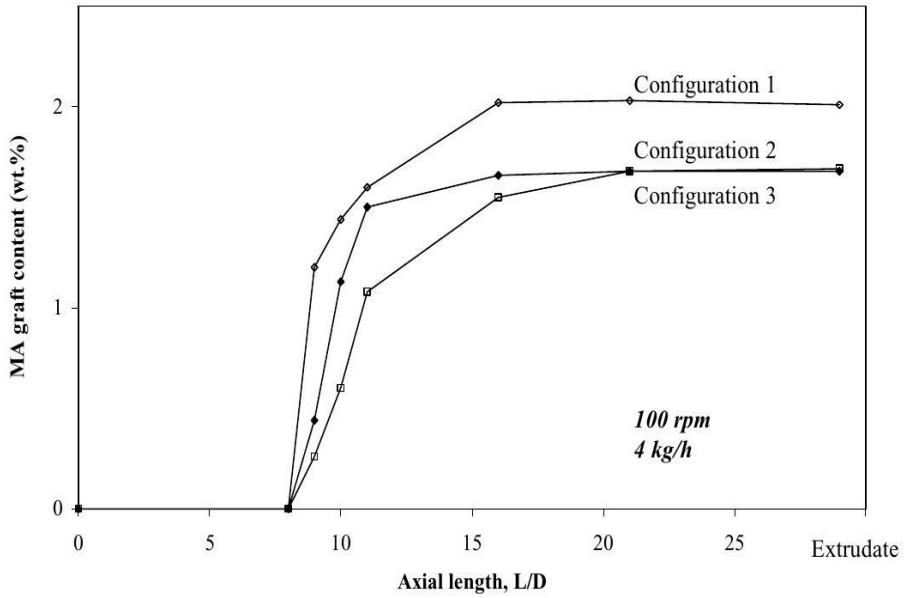

Configuration 1
Configuration 2
Configuration 3
100 rpm
4 kg/h
MA graft content (wt.%)
Axial length, L/D
Extrudate

FIGURE 9. Effect of throughput (top), screw speed (middle), and screw configuration (bottom) on MA graft content of PE along the extruder ($200°C, 5$pph MA, and 1 pph DHBP).

the average and local residence times and the fully filled volume. This results in less time for dispersion and dissolution of the peroxide and MA into the polyolefin melt in the first kneading section. In this section, peroxide that is not fully dissolved is subjected to high temperatures, hence it decomposes without yielding effective grafting.

Changes in screw speed [Fig. 9 (middle)] seem to have a minor effect on the grafted MA content. Increasing the screw speed decreases the local residence times and the filling ratio, with the consequences discussed above. However, local shear rates also increase and, therefore, viscous dissipation (i.e, increasing temperature) could have a positive effect. The overall result will be a compromise between both effects and the level of the viscosity determines their relative importance.

Finally, Fig. 9 (bottom) shows that the staggering angle has an effect on the final MA content. Kneading blocks with negative staggering create backflow, thus inducing better distributive mixing. In principle, the higher the negative angle the more important the backflow. However, recent experimental evidence [18] has shown that the residence time distribution of flow along -30 and $-60°$ staggering angles is very similar. The effect of staggering on filling ratios is not clear, contradictory data having been obtained. [14,18] A 2D calculation performed by Poulesquen [18] predicts that the filling ratios are equivalent for -30 and 90°, and higher for $-60°$, with direct repercussion on the melt pressures (these increase from 90° to $-30°$ and $-60°$). The experimental results shown in Fig. 9 (bottom) confirm that neutral staggering angles are less effective in terms of mixing. Given the discussion above, it is more difficult to account for the differences between $-30°$ and $-60°$.

Table II presents the influence of the screw configuration on the evolution of rheological parameters of modified PE along the extruder axis. The initial strong increase of both G' and G'' due to branching/crosslinking, followed by a steady decrease downstream caused by degradation, which was already observed in Fig. 7, is evident in all cases. As the staggering angle increases from $-30°$ to $-60°$ and to 90°, not only there is a shift downstream of the location where G' and G'' reach their maximum, but the final value of the rheological parameters increases, i.e., the extent of crosslinking decreases. These results support those illustrated in Fig. 9 (bottom), with a better discrimination of the geometrical effects.

PROCESS OPTIMIZATION

As the previous section has demonstrated that the final MA grafted content of the extrudate depends on the screw geometry and on the operating conditions, this raises the question concerning the working combination required to maximize the process performance. However, the results also showed that the final MA content was obtained quite early in the extruder, since a plateau conversion was exhibited throughout a significant length of the screw axis. Therefore, it makes sense to optimize the process not only in terms of the final MA graft content achieved, but also in trying to guarantee that the process is fully developed sufficiently upstream, typically at $L/D = 16$.

TABLE II
Storage, G′ and Loss, G″ Moduli [a] of PE Grafted with MA Under Different Screw Configurations [b]

	Staggering Angle of the First Kneading Block					
	−30°		−60°		90°	
L/D	G′(Pa)	G″(Pa)	G′(Pa)	G″(Pa)	G′(Pa)	G″(Pa)
PE	0.63	20.8	0.63	20.8	0.63	20.8
9	8.91×10^3	4.43×10^3	3.48×10^3	2.31×10^3	6.48×10^3	3.75×10^3
10	6.08×10^3	3.72×10^3	8.84×10^3	4.83×10^3	8.71×10^3	4.17×10^3
11	5.32×10^3	3.58×10^3	5.52×10^3	3.67×10^3	-	-
16	5.01×10^3	3.82×10^3	5.10×10^3	3.54×10^3	1.06×10^4	5.22×10^3
21	4.48×10^3	3.55×10^3	3.17×10^3	2.36×10^3	5.58×10^3	3.54×10^3
Extrudate	2.69×10^3	2.16×10^3	3.57×10^3	2.91×10^3	4.95×10^3	3.63×10^3

[a] G′ and G″ at $200°C, 7 \times 10^{-3}$ Hz.
[b] Compounding at 200°C, 5pphMA, 1pph DHBP, 100 rpm , and 4 kg/h.

The results extracted from a statistical analysis (multiple regression and ANOVA) of a central composite experimental design of three independent variables (output, speed, and geometry) with three levels of variation (see Table I), involving 18 different experiments (15 with distinct combinations of the variables, plus 3 for evaluation of the replication characteristics) are shown in Figs. 10 and 11, in the form of contour plots of the MA graft content of polyethylene (the SAS v6.11 ® software was used). The regression polynomials detect main effects and first-order interactions. The three replication runs show that the experimental error is typically ± 0.1 $wt\%$ MA.

Figure 10 relates to the results for $L/D = 16$, while Fig. 11 presents data for the extrudate. The axes range between the coded star points (levels -1 and +1 in Table I), 0 representing the central point (see also Table I). As already shown in Fig. 3, some grafting is still taking place beyond $L/D = 16$ (in Fig. 3, from 1.66 at $L/D = 16$ to 1.72wt% at the extrudate, in Figs. 10 and 11 from 1.70 to 1.74wt%, for the central point at the same locations).

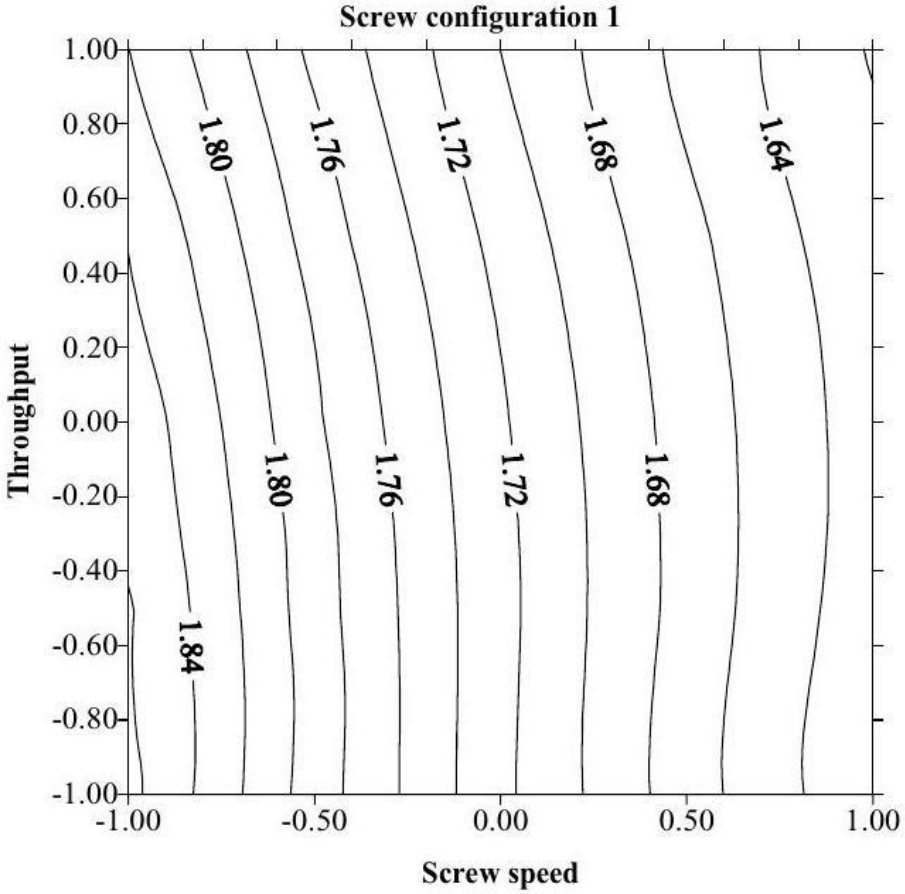
For both locations, the highest MA graft contents are obtained with screw configuration 1 (block of kneading disks staggered $-30°$) and the lowest with screw configuration 3 (neutral angle of $90°$). The screw speed has a deleterious effect on the MA graft content. The effect of throughput is also negative, but is much less important, especially at $L/D =$

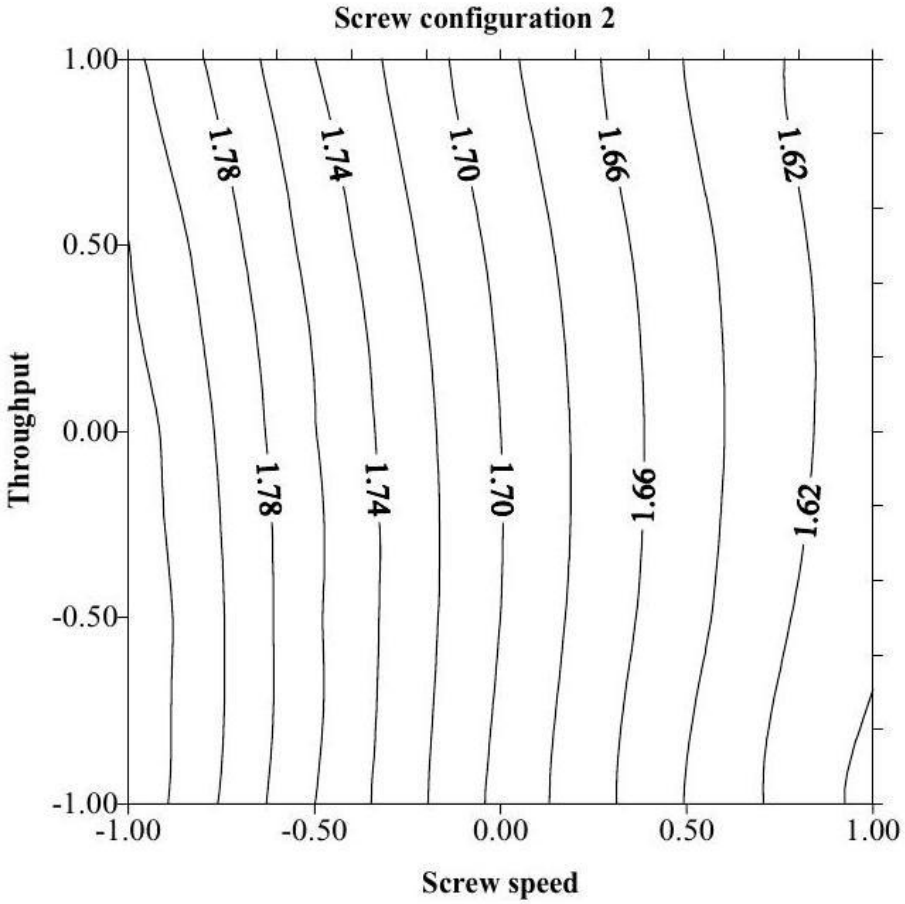
16. In fact, as discussed above, decreasing the screw speed and/or the throughput increases the filled volume, hence favoring the peroxide and MA dispersion into the PE.

Therefore, for a maximum MA grafting the extruder should be operated at low screw speeds using a restrictive first kneading block for inducing polymer melting/mixing and at low throughput. However economical factors should not be ignored, which favor a high throughput. Given the relatively modest effect of throughput on MA graft content, operating at acceptable throughputs will not compromise significantly the efficiency of the polymer modification process.

Conclusions

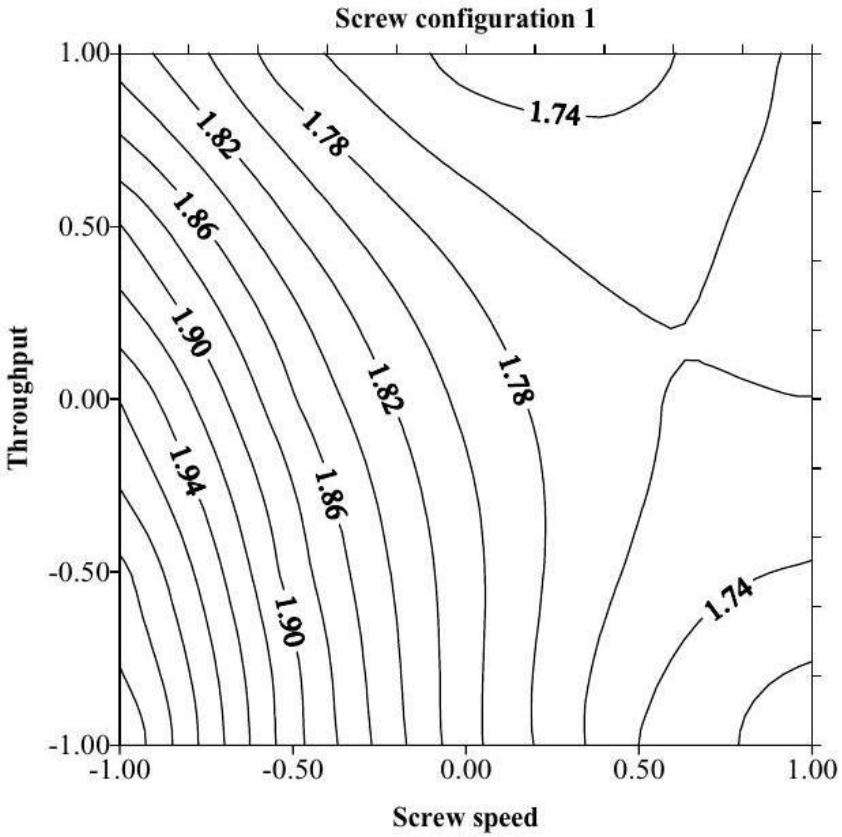
Grafting of MA onto polyolefins (PE, EPM, and PP) was studied along the extruder/die axis, under various operating conditions. Generally, the reaction

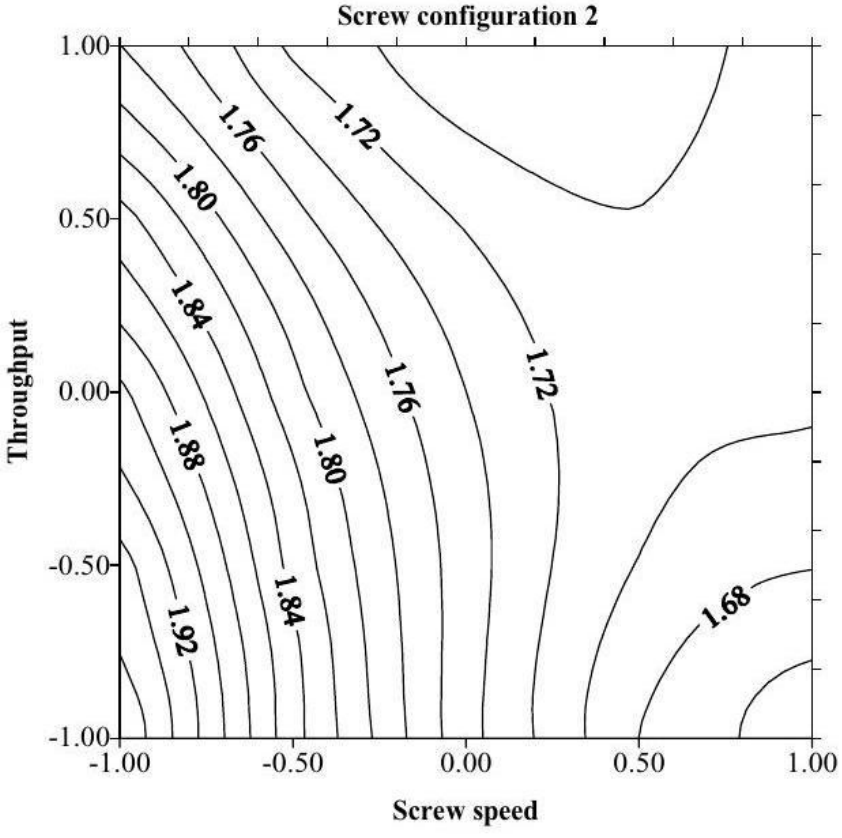

Screw configuration 1
Throughput
Screw speed
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
-1.00
-0.50
0.00
0.50
1.00
1.80
1.76
1.72
1.68
1.64
1.80
1.76
1.72
1.68
1.84


Screw configuration 2
Throughput
Screw speed
1.00
0.50
0.00
-0.50
-1.00
-1.00
-0.50
0.00
0.50
1.00
1.78
1.74
1.70
1.66
1.62
1.78
1.74
1.70
99.1
29.1

L/D=16

FIGURE 10. MA graft content of PE at location $L/D = 16$ as a function of throughput and screw speed for the three screw configurations.


Screw configuration 1
1.00
0.50
0.00
-0.50
-1.00
Throughput
-1.00
-0.50
0.00
0.50
1.00
Screw speed
1.74
1.82
1.78
1.86
1.90
1.82
1.78
1.94
1.86
1.74
1.90


Screw configuration 2
1.00
0.50
0.00
-0.50
-1.00
Throughput
-1.00
-0.50
0.00
0.50
1.00
Screw speed
1.76
1.72
1.80
1.84
1.76
1.72
1.88
1.80
1.68
1.84
1.92

Extrudate

FIGURE 11. MA graft content of the PE extrudate as a function of throughput and screw speed for the three screw configurations.
is very fast and a strong increase in grafting level takes place immediately after melting. This is followed by very little changes downstream.

The grafting evolution is determined by the peroxide decomposition profile. The final grafting yield depends on the polyolefin composition, probably as a result of the competition between grafting and termination reactions. As the ethylene content from PP via EPM to PE increases, the chemical mechanisms change from β-scission to crosslinking. The melt temperature developed along the screw axis correlates well with the rheological behavior.

In the case of PE grafting, the mass throughput and the geometry of the kneading blocks, where melting occurs, have an effect on the final MA graft content. Lower output and decreased staggering angle (90° to -60° and -30°) favor MA grafting. An optimum operating window in terms of screw speed, throughput, and geometry was identified, yielding MA graft contents of 2wt% MA.

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References

1. Xanthos, M. (Ed.). Reactive Extrusion; Hanser Publishers: New York, 1992.
2. Al-Malaika, S. (Ed.). Reactive Modifiers for Polymers; Blackie Academic & Professional: London, 1997.
3. Roberts, D. H.; Constable, R. C.; Thiruvengada, S. Polym Eng Sci 1997, 37, 1421.
4. Gabara, W.; Porejko, S. J Polym Sci, Part A: Polym Chem 1967, 5, 1539.
5. Rosales, C.; Perera, R.; Ichazo, M.; Gonzalez, J.; Rojas, H.; Sánchez, A.; Barrios, A. J Appl Polym Sci 1998, 70, 161.
6. De Roover, B.; Sclavons, M.; Carlier, V.; Devaux, J.; Legras, R.; Momtaz, A. J Polym Sci, Part A: Polym Chem 1995, 33, 829.
7. Sttini, S. P.; Agnelli, J. A. J Appl Polym Sci 1999, 74, 256.
8. Garcia-Martinez, J. M.; Laguna, O.; Colar, E. P. J Appl Polym Sci 1998, 68, 483.
9. Janssen, L. P. B. M. Polym Eng Sci 1998, 38, 2010.
10. Machado, A. V.; Covas, J. A.; Duin, M. J Polym Sci 2001, 81, 58.
11. Machado, A. V.; Duin, M.; Covas, J. A. J Polym Sci, Part A: Polym Chem 2000, 38, 3919.
12. Machado, A. V.; Covas, J. A.; Duin, M. J Polym Sci 1999, 71, 135.

13. Schmidt, S. R.; Launsby, R. G. Understanding Industrial Designed Experiments, 4th ed.; Air Academy Press: Colorado Springs, 1994.

14. Carneiro, O. S.; Caldeira, G.; Covas, J. A. Proc Mat Proc Tech

1999, 92/93, 309.
15. Avela, M.; Lanzetta, N.; Maglio, G. Polymer Blends; Kryszewski, M.; Galeski, A.; Martuscelli, E. (Eds.); Plenum: New York, 1984; Vol. 2.
16. Hogt, A. H. Proc Compalloy'90, New Orleans, 1990.
17. Machado, A. V.; Covas, J. A.; Duin, M. Polym 2000, 42, 3649.
18. Poulesquen, A. PhD thesis, Ecole des Mine de Paris, 2001.