

# Monitoring Polyolefin Modification along the Axis of a Twin-Screw Extruder. II. Maleic Anhydride Grafting

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## Abstract

The physico-chemical phenomena developing along the screw axis of a twin-screw extruder during the grafting of maleic anhydride (MA) onto polyolefins [polyethylene (PE), ethylene-propylene rubber (EPM), and polypropylene (PP)] were investigated. For this purpose, sampling devices located along the extruder barrel were used to collect polymer samples that were subsequently characterized to follow the degrees of grafting and crosslinking or degradation. A similar evolution of MA grafting was observed regardless of the polyolefin type or MA and peroxide concentration when grafting was performed under identical conditions, that is, the same peroxide type and set temperature. A correlation between the MA grafting and the calculated peroxide decomposition was established. Chemical reactions occurred along the extruder axis until the peroxide was fully converted. More detailed quantitative measurements of the peroxide decomposition and MA grafting would allow the development of accurate process models. The final MA content depended on the polyolefin composition (PE > EPM >> PP). As expected for PE, crosslinking occurred in addition to grafting, but after a certain residence time, the PE network degraded. The PP viscosity reduction after MA grafting was due to the conversion of tertiary PP radicals into primary PP radicals after grafting. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 3919-3932, 2000

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## INTRODUCTION

One of the most common examples of polymer modification, in both academia and industry, is the grafting of maleic anhydride (MA) onto polyolefins. <sup>1-10</sup> Maleated

polyolefins have found widespread application as in situ compatibilizers for blends, adhesives for multilayer systems, and coupling agents for glass fibers. <sup>1-4</sup> Grafting involves the reaction of a polymer with a monomer or a mixture of monomers yielding side groups or

polymer chains attached to the polymer backbone. Free-radical initiators such as peroxides have been used to initiate the reaction. <sup>1-15</sup> The grafting process is usually performed in the melt in an extruder, that is, via reactive extrusion (REX). <sup>1,2</sup> It is carried out at elevated temperatures with highly viscous and probably heterogeneous systems. The extruders used should, therefore, contain intensive mixing zones because efficient mixing of the monomer with the polymer is essential for minimizing the formation of free homopolymer.

Extruders have been used as chemical reactors in academic studies and on a commercial scale for over 30 years. <sup>16</sup> Their use has advantages over alternative processes, including the absence of solvents, which avoids product isolation; short residence times; and a continuous operation. However, important functional characteristics, such as the temperature profile, the screw speed, the degree and type of mixing, and the residence time distribution should be taken into account. <sup>17</sup>

Combining processing and chemical reactions makes REX very complex and, for free-radical grafting in the melt, gives rise to a tremendous challenge in terms of reactivity, selectivity, processing, and product optimization and control. Most studies, both academic and industrial, still treat REX as a black-box process, which is optimized via trial and error. Much effort has been made to establish the kinetics of free-radical grafting and to model the total process. Some authors <sup>18,19</sup> developed a general kinetic model and combined it with generally accepted models for melting in a single-screw extruder. The required input consists of data on the extrudate, such as the molecular weight, grafting content, residence time, and temperature. However, the actual process occurring inside the extruder has remained largely unknown, mainly because of the difficulties in collecting representative samples from the extruder during processing.

Recently, we developed an experimental technique that allowed fast and representative sampling of the melt along the screw axis for subsequent offline characterization. <sup>20</sup> These sampling devices were used to investigate in detail the in situ compatibilization of blends of polyamide-6 with ethylene-propylene rubber (EPM) in the presence of EPM grafted with MA (EPM-g-MA) <sup>21</sup> and the processing of polyolefins in the absence and presence of peroxide. <sup>22</sup> The latter can be considered a starting point for this investigation. In this study, a series of such sampling devices were used to follow the physico-chemical phenomena (the degree of MA grafting and the rheological behavior) developing along the screw axis during the grafting of MA onto polyethylene (PE), EPM, and polypropylene (PP). The melt temperature and average residence time were measured at various locations. Through a combination of all these data, a descriptive model was developed that might serve as the basis for future quantitative approaches with the final goal of mastering REX processes.

Table I. Grafting Recipes

Polyolefin	Experiment	Recipe		Comments
		MA (wt %)	DHBP (wt %)	

PE1	1	4.7	0.94	
	2	4.7	0.47	
	3	4.8	0	Thermal grafting
	4	0.98	0.98	
	5	0.99	0.49	
	6	0	0.99	
	7	4.7	0.94	Separate feed
	8	4.7	-	0.90wt% DBP
	9	4.7	-	1.4 wt % BBP
PE2	10	4.7	0.94	
EPM	11	4.7	0.94	
PP	12	4.7	0.94	
	13	4.7	0.94	Separate feed
	14	0	0.99	

## EXPERIMENTAL

### Materials

Stamylan HD 2H280 (PE1; high-density polyethylene; weight-average molecular weight = 60 kg/ mol), Stamylex 7359 (PE2; high-density polyethylene; weight-average molecular weight = 30 kg/ mol), and Stamylan P 13E10 (PP; weight-average molecular weight = 500 kg/mol) were supplied by DSM; Exxon VA 404 (EPM; 45 wt % ethene) was produced by Exxon. MA was obtained from Aldrich, and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DHBP; Trigonox 101), di-tert-butyl peroxide (DBP; Trigonox B), and 2,2-bis(tert-butylperoxy)butane (BBP; Trigonox D) were supplied by Akzo Nobel. The half-life times of these peroxides at 200 °C were 6.1, 14.4, and 0.8 s, respectively.

### Grafting

The recipes and experimental conditions used in each experiment are given in Table I. For PE1 and PP, the recipe was varied to have different initial amounts of MA and peroxide. Although different peroxides were used, the number of

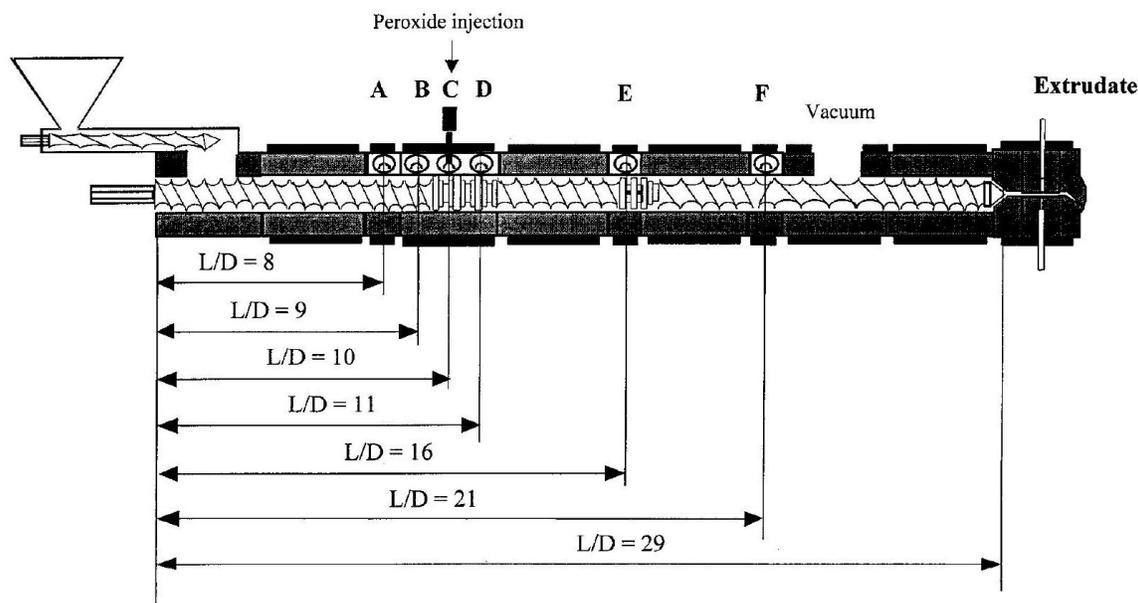


Figure 1. Extruder layout and sampling locations.

moles of peroxide was kept constant in all the experiments (the monofunctionality or bifunctionality and the molecular weight of the various peroxides were taken into account).

The grafting reactions were carried out in a modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder. Most experiments were performed under the same processing conditions, that is, a barrel-set temperature at 200 °C, a screw rotation of 75 rpm, and a throughput of 5 kg/h. Figure 1 shows the extruder layout and the sampling locations (denoted A – F). The screw configuration was identical to that used in the first part of this series<sup>22</sup> and contained a series of transport sections separated by three mixing zones, consisting of staggered kneading disks and a left-hand element. Generally, the polyolefin, monomer, and peroxide were tumble-mixed and fed through the hopper. However, in experiments 7 and 13, a mixture of the polymer and monomer was fed to the hopper, whereas the peroxide, previously dissolved in acetone, was injected at the end of the first kneading zone (location C in Fig. 1) with a high performance liquid chromatography (HPLC) pump.

In all the extrusion experiments, molten polymer samples were collected along the screw axis and from the extrudate and then quenched in liquid nitrogen to avoid further reaction (about 3 g of the sample in 300 mL of liquid nitrogen). The average melt temperature was measured at various locations along the extruder by a preheated needle-type fast-response thermocouple (Coleparmer type K penetration probe; time constant ~ 1 s) being stuck into the freshly collected material.

## Residence Time Distribution

The average residence time at the various sampling locations along the extruder, under the selected operating conditions, was estimated with a tracer impulse technique. After a steady state was reached, a small amount of silicon dioxide (specific surface = 175 m<sup>2</sup>/g)

was added instantaneously to the feed stream at  $t = 0$ . Samples of the modified polymer plus tracer were then collected from one sampling point at various time intervals, the procedure being repeated for all the sampling locations. The relative amount of silica was determined by the ashing of the sample. 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.<sup>23</sup>

## Characterization

Because under the processing conditions selected the melting was not complete at ratio length/diameter of the screw (L/D) = 8 (as observed previously; Fig. 1), the samples at this location were not characterized.

The modified polyolefins were dissolved in toluene (PE and EPM) or xylene (PP) under reflux until a clear solution was obtained. The warm solutions were precipitated in acetone and filtered to obtain purified polymers, which were dried in a vacuum oven for 1 h at 180°C. Thin films were prepared by compression molding, and Fourier transform infrared (FTIR; PerkinElmer 1600) spectra were recorded. For a quantitative determination of the MA content, the 1785  $\text{cm}^{-1}$  peak was used with a consideration of the film thickness. FTIR calibration was carried out by the imidization of some of the MA-grafted polyolefins with  $\text{NH}_3$  and was followed by N-content determination by elemental analysis.

Oscillatory rheological measurements were carried out with a TA Instruments Weissenberg rotational rheometer at 200 °C with a parallelplate geometry. The gap and diameter of the plates was 1.8 mm and 4.0 cm, respectively. A frequency sweep from 0.04 to 40 Hz was performed for each sample, with a strain of 0.01 applied to maintain the response of the material in the linear viscoelastic regime.

Gel content determinations were performed by the samples (ca. 1.5 g) being weighed, placed in 120 – mesh stainless steel cages, and immersed in boiling toluene. The extractions were run under reflux for 24 h. The solvent was renewed once after about 12 h. After removal of the boiling solvent, samples were dried in a vacuum oven for 5 h at 80 °C in a nitrogen atmosphere and weighed again.

## RESULTS AND DISCUSSION

In the first part of this series,<sup>22</sup> the evolution of chemical reactions (branching/crosslinking, degradation, or both) along the extruder for various polyolefins in the absence or presence of peroxide was studied. In the presence of peroxide, branching/crosslinking or degradation occurred along the extruder until the peroxide was fully converted. The degree of branching/crosslinking or degradation depended on the ethene/propene ratio, on the original molecular weight of the polymer, and on the amount of peroxide added. In this work, the evolution of grafting MA onto various polyolefins with different propene contents (0 wt % for PE1 and PE2, 55 wt % for EPM, and 100 wt % for PP) along the extruder, in terms of grafted MA and rheological changes, is discussed. As several variables were investigated, the results obtained in each case are presented and discussed separately.

# Reproducibility

To determine whether unavoidable temperature fluctuations during processing could have an effect on grafting, various samples of modified PE1 (experiment 1 in Table I) were collected at location C of the extruder at random time intervals. The temperature of each sample was measured, and the grafting MA content was determined. During the temperature measurements, a systematic error could be involved because of heat transfer from the metal to the sample and from the sample to the air. The former would result in an increase of the temperature of the sample, whereas the latter would lower the sample temperature. The effect of these errors on the measured temperature would be rather small because the measurements were very fast ( 2 s ). For a barrel-set temperature of 200 °C, the average temperature (at location C) remained at  $187 \pm 2$  °C. The experimental error associated with the determination of the MA-graft content was typically  $\pm 0.1$ wt% MA, as estimated from different measurements carried out on films prepared from the same polymer sample. Figure 2 relates the MA content to the temperature of the various samples. Within the experimental error, the MA content was essentially constant; it was insensitive to temperature fluctuations.

# Grafting along the Extruder

The MA contents along the extruder axis (locations B-F) for the various grafting experiments are presented in Table II. The data for the various polymers after grafting with 4.7wt% MA and 0.94wt%DHBP at 200 °C (barrel-set temperature)-experiments 1,10,11, and 12-are plotted in Figure 3. Regardless of the polyolefin structure, there was a strong increase in the grafting level in the first part of the extruder up to location E , followed by a plateau.

The measured average temperature and residence time (Table III) at each location were combined with an algorithm that numerically integrated the peroxide decomposition for a given

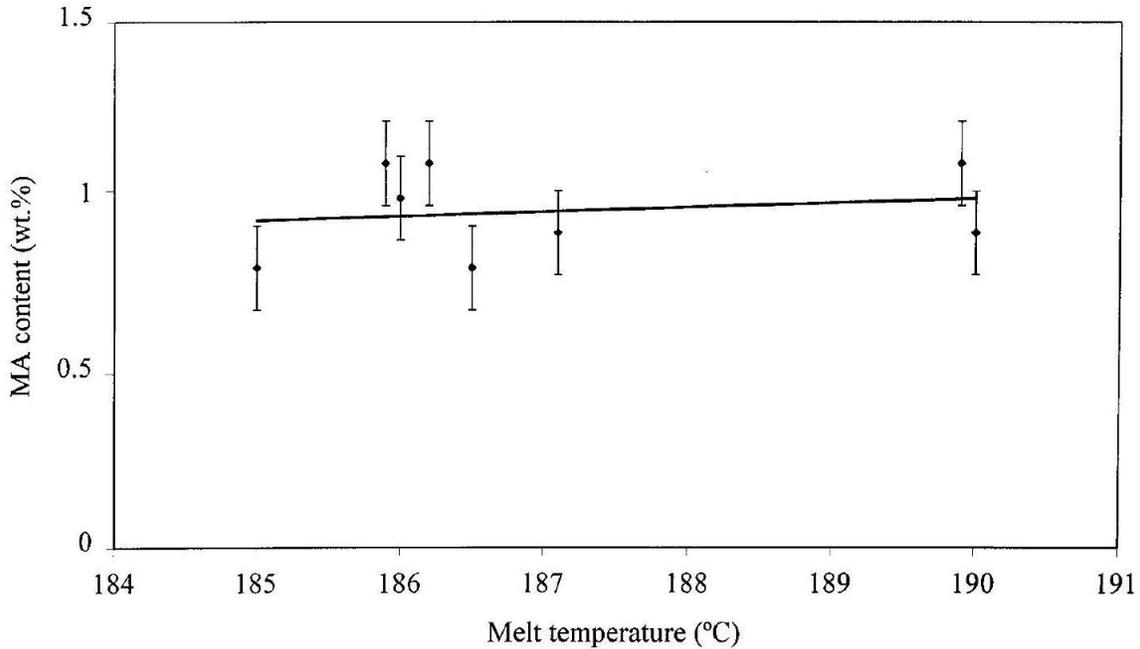


Figure 2. MA content of PE1 versus the melt temperature at location C (4.7 wt % MA, 0.94wt%DHBP, 200°C).

temperature and time. This algorithm used a first-order equation for peroxide decomposition in combination with the Arrhenius equation (data for DHBP, as provided by Akzo-Nobel; dissociation constant,  $k_0 = 1.68 \times 10^{16} \text{ s}^{-1}$ , activation energy,  $E_A = 155.49 \times 10^3 \text{ J/mol}$ ). The use of the average residence time provided a qualitative approach to understanding the MA-grafting profile because a truly quantitative model would require the use of the residence time distribution. Anyway, a small difference of 3 – 4 s in the average residence time resulted in a significant change of the peroxide decomposition profile along the extruder, especially in the first part.

For example, the experimental MA content and the calculated peroxide decomposition for PE1 with 4.7wt%MA and 0.94wt%DHBP at 200°C (experiment 1) are plotted in Figure 4 as a func-

Table II. Grafted MA Content along the Extruder for the Various Grafting Experiments at the Various Sampling Locations

Polyolefin	Experiment	Grafted MA Content (wt %)					
		B	C	D	E	F	Extrudate
PE1	1	0.28	0.71	1.23	1.66	1.75	1.72
	2	0.20	0.36	1.01	1.54	1.55	1.58
	3	0.06	0.11	0.12	0.11	0.12	0.12
	4	0.22	0.28	0.37	0.40	0.40	0.40

	5	0.19	0.23	0.46	0.45	0.46	0.46
	7	0.05	0.05	0.38	0.93	1.94	1.96
	8	0.24	0.29	0.80	1.10	1.34	1.62
	9	0.07	0.07	0.08	0.11	0.11	0.12
PE2	10	0.57	1.44	1.79	1.85	1.93	1.93
EPM	11	0.26	0.64	1.16	1.56	1.57	1.57
PP	12	0.19	0.25	0.41	0.64	0.64	0.64
	13	0.01	0.01	0.11	0.48	0.51	0.53

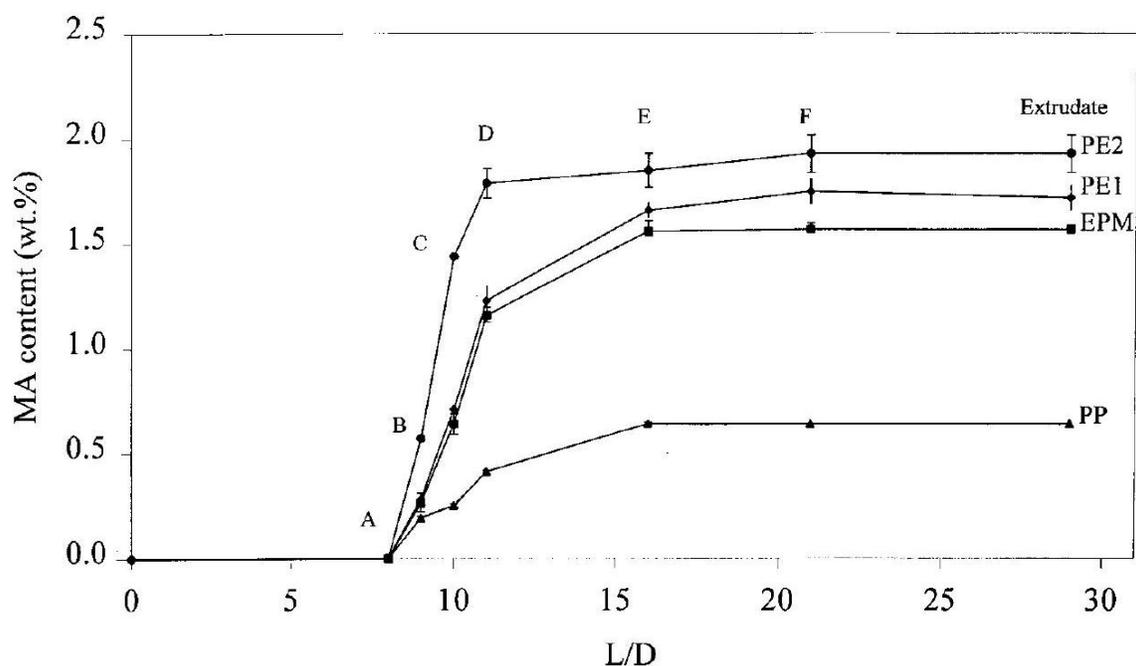


Figure 3. MA content along the extruder for the modification of PE1, PE2, EPM, and PP with 4.7wt%MA and 0.94wt%DBHP at 200°C. tion of the average residence time. The experimental grafting data closely followed the calculated peroxide decomposition. When the peroxide began to decompose (at ca. 160°C at location B, as shown in Table II), the grafting reaction began. Between B and D, the temperature increased sharply from 160 to 204°C, which resulted in the acceleration of the peroxide decomposition and, consequently, the acceleration of the MA grafting. At location E, the peroxide was completely decomposed, and the degree of grafting almost reached a constant level. Thus, the grafting profile along the extruder is explained by the peroxide decomposition.

## Effect of the Polyolefin Structure on Grafting

Even though the MA-graft profiles for EPM and PP were similar to that of PE1, the final amounts

Table III. Measured Mean Residence Time and Temperature Profiles

Sampling Location	Mean Residence Time (s)	Average Temperature along the Axis (°C)			
		PE1	PE2	EPM	PP
B	25	160	179	199	153
C	30	187	194	208	166
D	32	204	206	212	185
E	50	211	207	216	187
F	67	207	203	219	191
Extrudate	110	200	201	207	192

of grafting for PE1, EPM, and PP were different (Fig. 3). The highest amount was obtained for PE1 (1.7 wt %), and the lowest was obtained for PP (0.64 wt %), whereas the MA-graft content of EPM was close to that of PE1. Similar differences have been observed by other authors.<sup>24,25</sup> It has been proposed that the dependence of the MA-graft level on the polyolefin composition is due to competition between grafting and  $\beta$  scission or crosslinking. The latter seems to correlate with the fraction of non-PPP triads.<sup>26</sup>

Tables IV and V show the gel content for PE1, PE2, and EPM and the dynamic viscosity of PP, respectively. For PE1 (with 4.7wt%MA and 0.94 wt % DHBP at 200 °C; experiment 1), the rheological measurements showed (Fig. 5) a very strong increase of viscosity (from 450 to  $1.5 \times 10^5$  Pa · s at  $7 \times 10^{-3}$  Hz ) and elasticity (from 450 to  $1.5 \times 10^5$  Pa at  $7 \times 10^{-3}$  Hz ) at location B, indicating severe crosslinking. Beyond location B, the material response did not change significantly, although elasticity decreased slightly downstream. Therefore, crosslinking occurred initially as a side reaction, followed by some degradation. However, measurements of the gel content showed that crosslinking continued along the screw until location E, as seen in Figure 6. The decrease in gel content observed beyond E was not associated with the peroxide because it had fully decomposed. The decrease in both the storage modulus and gel content indicated network degradation, probably due to the shearing apart

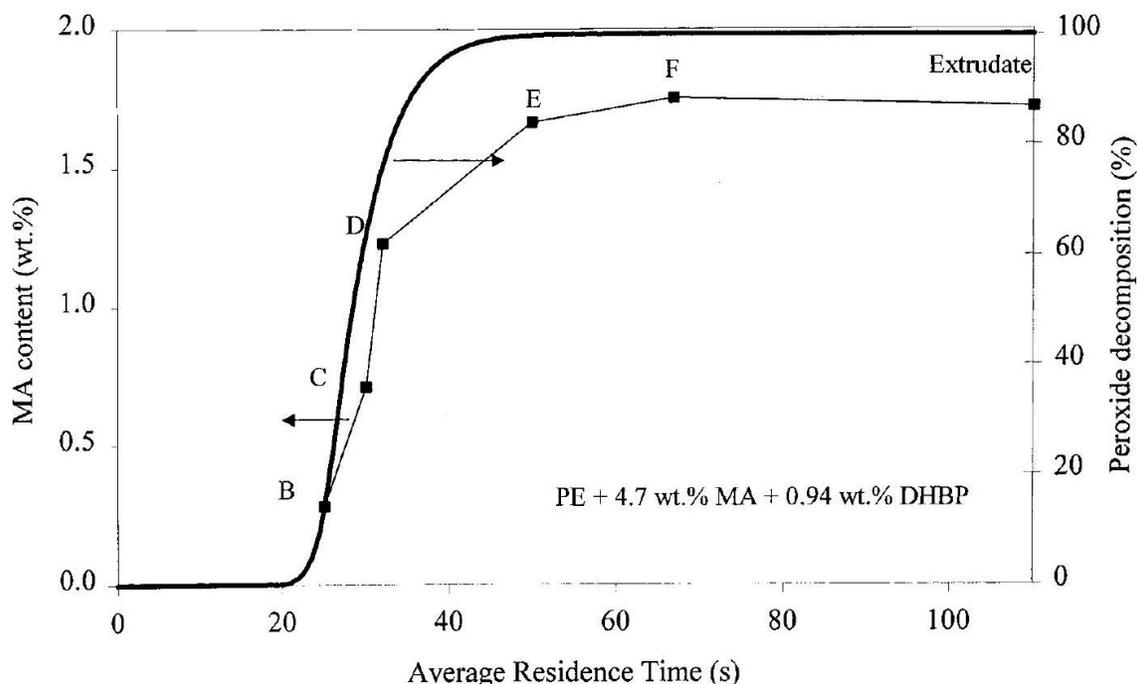


Figure 4. MA-graft content for PE1 and the calculated peroxide decomposition, with 4.7wt%MA and 0.94wt%DHBP at 200°C, as a function of the average residence time.

of the PE1 gels. From the gel content, one could observe that for EPM, crosslinking was significantly smaller.

The final gel content for PE1 grafted with MA was quite different from that obtained when PE1 was processed with peroxide only (for more details, see ref. 22). In the latter case, a higher and constant gel content was obtained. The presence of tertiary carbon atoms in grafted PE, which are weak links in polyolefin chains, may explain the lower gel content for MA-grafted PE1.

When PE2 with a lower molecular weight was grafted, with the same grafting recipe and processing conditions used for PE1, a higher MA-graft content was obtained (1.9 wt %; Fig. 3), and gel formation was not observed (Table IV). Because PE1 and PE2 had the same structure, the significant difference in the grafting content should have been related to the lower molecular weight (lower viscosity) of PE2. In fact, according to Rosales et al.,<sup>14</sup> high-viscosity materials yield lower degrees of functionalization.

Table V demonstrates a dramatic decrease of the dynamic viscosity along the extruder for PP modified with 4.7wt% MA and 0.94wt% perox-

Table IV. Gel Contents for MA-Grafted PE1, PE2, and EPM along the Extruder

Polyolefin	Experiment	Gel Content (%)					
		B	C	D	E	F	Extrudate
PE1	1	5	7	23	29	15	6

	2	1	3	-	5	-	7
	4	1	2	13	52	53	54
	5	1	2	3	15	13	10
	6	1	2	22	49	54	52
	7	-	2	8	20	25	24
PE2	10	0	0	-	-	-	0
EPM	11	3					2

Table V. Dynamic Viscosity ( 200°C,  $7 \times 10^{-3}$  Hz ) along the Extruder for PP Grafted with MA

Polyolefin	Experiment	Dynamic Viscosity ( Pa · s )					
		B	C	D	E	F	Extrudate
PP	12	$3.2 \times 10^3$	$1.1 \times 10^3$	$2.7 \times 10^2$	$2.4 \times 10^2$	$2.5 \times 10^2$	$2.3 \times 10^2$
	13	$1.8 \times 10^4$	$1.7 \times 10^4$	$6.0 \times 10^2$	$5.0 \times 10^1$	$2.7 \times 10^1$	$2.7 \times 10^1$
	14	$2.1 \times 10^1$	$1.9 \times 10^1$	$1.9 \times 10^1$	$1.4 \times 10^1$	$1.3 \times 10^1$	$1.4 \times 10^1$

ide at 200°C. This global behavior has been reported by many authors for samples taken from the extrudate and is attributed to  $\beta$  scission of tertiary PP radicals. However, a close look at Table V shows that the dynamic viscosity continued to decrease beyond sampling position D, although the peroxide was fully decomposed and the MA content had reached a plateau. Thermooxidative PP degradation, known to occur when PP is processed alone,<sup>27,28</sup> may explain this behavior. The decrease of the dynamic viscosity for MA-grafted PP was smaller than that for PP processed with peroxide (experiments 12 and 14 in Tables I and V). This has been previously observed for samples taken from the extrudate and was related to the grafting of MA onto PP.<sup>29</sup> Other studies have shown similar phenomena simply attributed to competition between MA grafting onto PP and  $\beta$  scission. This explanation seems rather superficial because grafting does not result in the loss of free-radical species susceptible to degradation.

A more detailed mechanistic explanation is put forward in Figure 7. Hydrogen abstraction from PP occurred mainly from tertiary carbon atoms, and then  $\beta$  scission occurred or MA added to the tertiary radical. Heinen et al.<sup>30</sup> showed that two PP-g-MA structures with an approximately 50/50 ratio eventually formed. The first one formed via hydrogen transfer of the PP-g-MA radical, resulting in a single succinic anhydride unit attached to the PP chain and a new tertiary PP radical, which might have undergone  $\beta$  scission. Thus, just the occurrence of MA grafting did not suppress  $\beta$  scission. The second graft structure

formed from the first graft structure via hydrogen abstraction by a

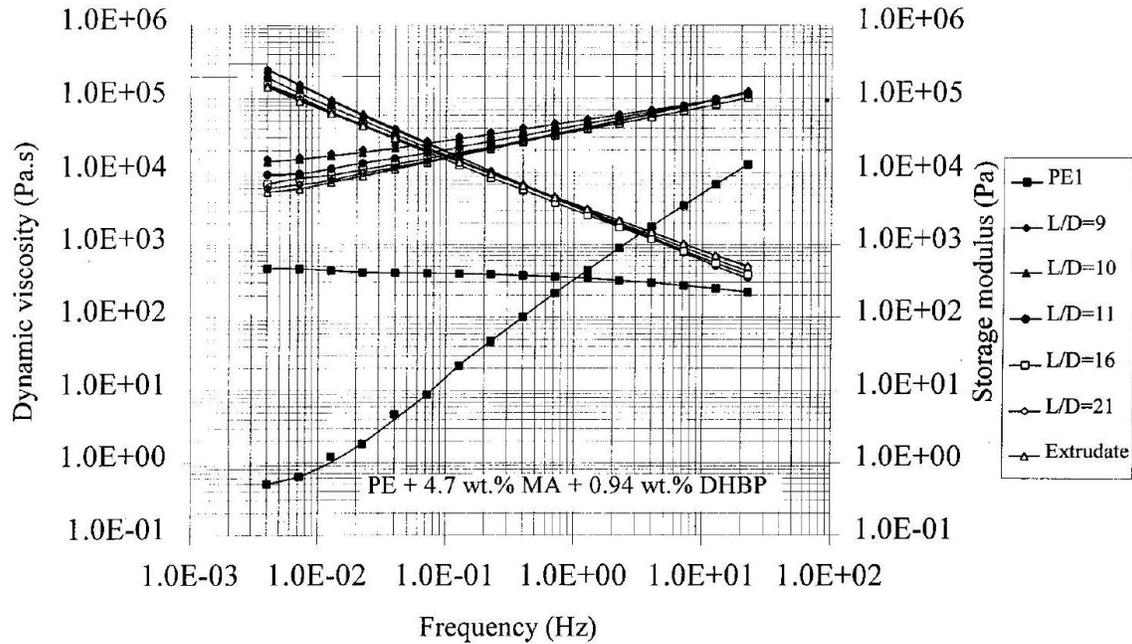


Figure 5. Rheological behavior of graft PE1 along the extruder (dynamic viscosity and storage modulus).

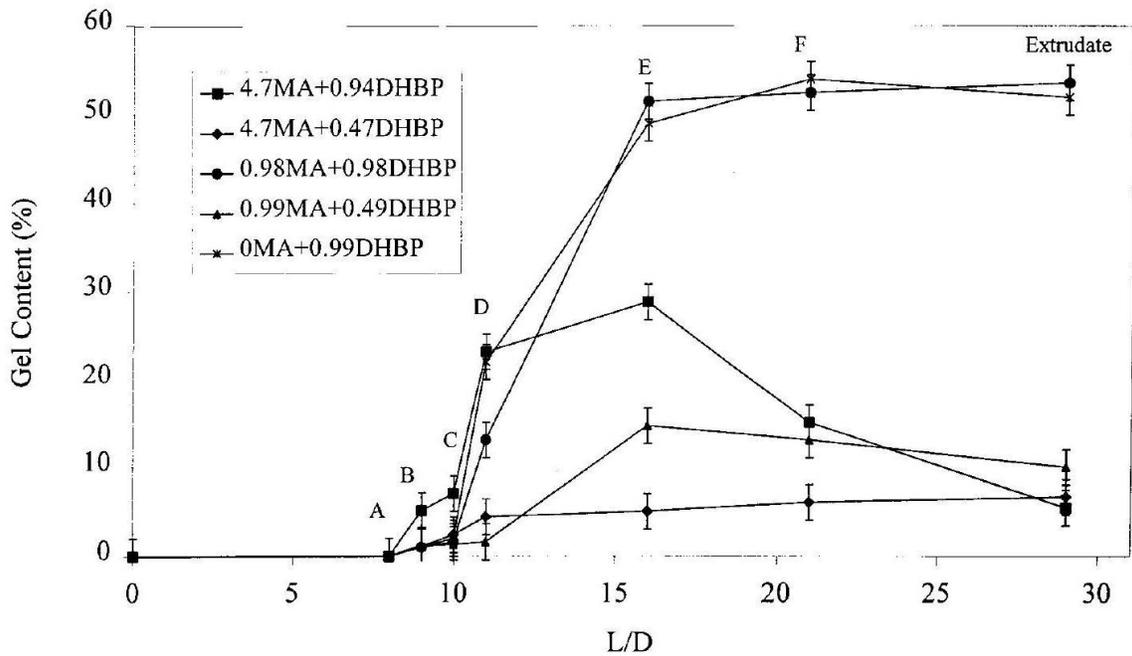


Figure 6. Gel content of MA-grafted PE1 along the extruder with different recipes. tertiary PP radical followed by  $\beta$  scission, yielding a terminal, unsaturated itaconic-anhydride-like structure and a primary PP radical. The latter was not susceptible to  $\beta$  scission and, consequently, terminated, probably via combination. As an overall result of

the formation of the terminal MA-grafted PP, tertiary PP radicals were converted into primary radicals; in this way, degradation was suppressed.

## Effect of the Recipe and Peroxide Type on the Grafting Profile

As shown in Table I, PE1 was processed with various grafting recipes (experiments 1 – 6, 8, and 9). The results are presented in Tables II and IV and Figure 8. As expected, there was a significant decrease of the amount of grafted MA along the extruder axis when the MA feed was reduced from 4.7 to 0.98wt%(DHBP = 0.94wt%). However, within the experimental error the profiles became similar when the peroxide content was decreased from 0.94 to 0.47wt%(MA = 4.7wt%). Some authors<sup>24,31,32</sup> reported a maximum level of grafted MA using 2wt%MA, but the results of these studies are difficult to compare directly with our data because different reactors, set temperatures, mixing conditions, and peroxides were used. The effect of thermal grafting (no peroxide) was also investigated. The level of grafted MA was rather low (~ 0.1wt%; Table II and Fig. 8), and no effect on the dynamic viscosity was detected. In this case, grafting was probably due to the thermo-oxidative formation of free radicals.

The gel content of PE1 (Fig. 6) increased dramatically when 0.98wt% MA and 0.98wt% DHBP were used. The values were much lower when 0.47wt% peroxide was used either with 0.99 or 4.7wt%MA. The latter had even a lower gel content than the former. This was probably related to the higher graft content obtained with 4.7wt%MA, as previously discussed.

The results of MA being grafted onto PE1 with different peroxides (DHBP, BBP, and DBP) are shown in Table II (experiments 1, 8, and 9) and Figure 9. Despite using the same number of moles of peroxide in the three experiments, the grafting profiles were clearly different. Figures 4, 10, and 11 plot the experimental MA-graft content and the calculated peroxide decomposition as a function of the average residence time. Because BBP decomposed quickly, a very small amount of MA was grafted onto PE1 (Fig. 10). Probably, BBP decomposed before it or MA was completely dissolved in PE1. Thus, the amount of grafted MA was strongly reduced. However, DBP decomposed more slowly, the calculated peroxide decomposition was only complete at the end of the extruder, and, as a result, the grafting reaction continued along the whole extruder. This was in accordance

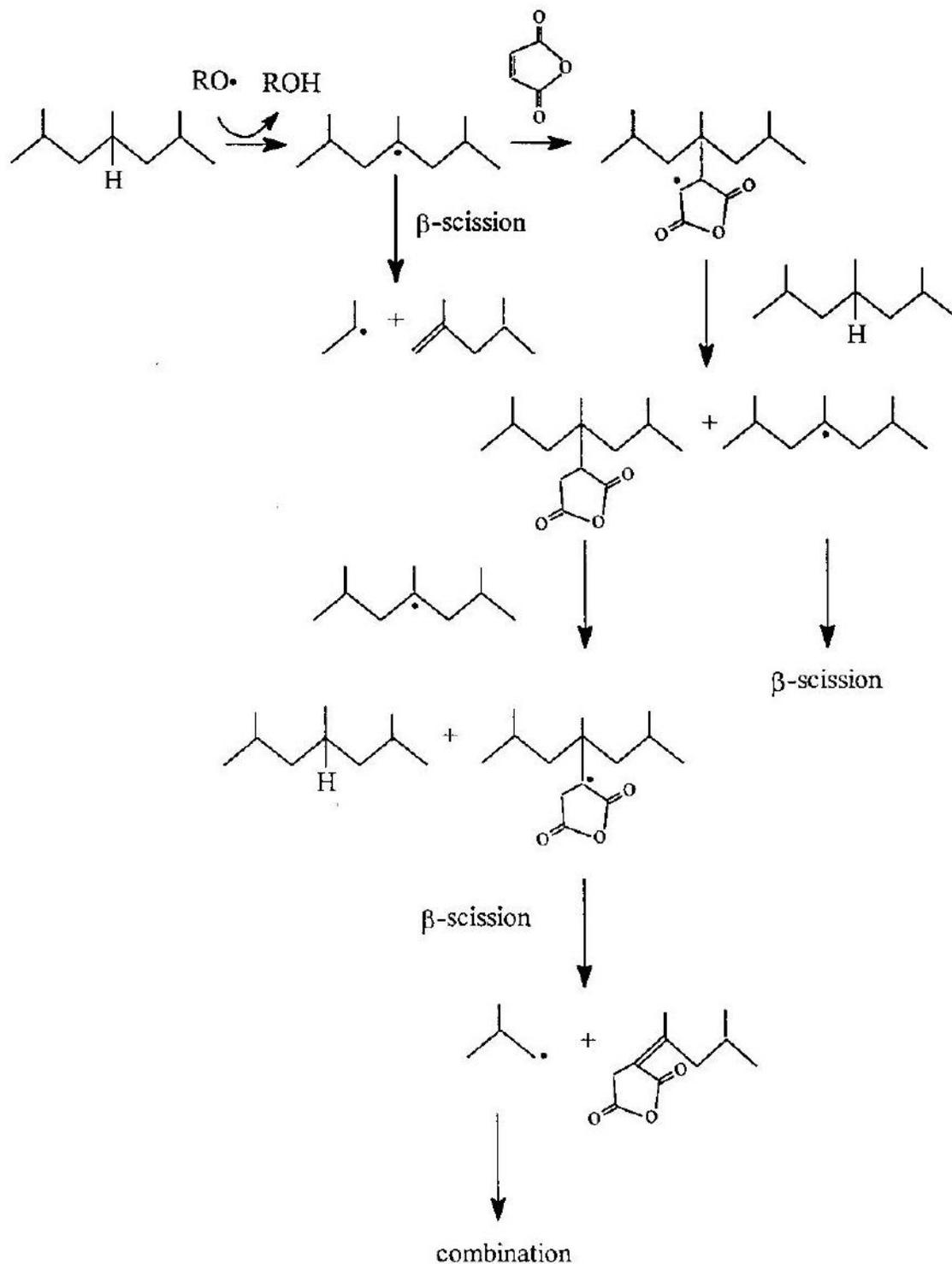


Figure 7. Mechanism of the free-radical grafting of MA onto PP.

with the experimental results, which showed that the MA-grafting level had a lower value in the first part of the screw (location C) but steadily increased along the extruder without reaching a plateau (Fig. 11). The behavior of DHBP was between the behaviors of BBP and

DBP. The calculated decomposition was complete at location E, so grafting continued until the MA-graft content reached a plateau when all peroxide was decomposed.

A correlation between the experimental MA-graft content and the calculated peroxide decomposition is shown in Figure 12. Both for DHBP and DBP, a convex correlation was observed, indicating that grafting efficiency, defined as the degree of grafting normalized to the peroxide decomposition, decreased during the grafting process.

## Separate Feed of Peroxide

The effect of incorporating the peroxide after MA dissolved in the molten polymer was investigated

for PE1 and PP (experiments 7 and 13, respectively). As demonstrated in Figure 9 (for PE1), up to location C, where the peroxide was added, only thermal grafting was possible, so the MA-graft contents were very small. At location D, which was one L/D downstream, an increase of the MA content was observed. The final amount of grafted MA was higher than for a simultaneous MA/peroxide feed. This showed that simultaneous feed dispersion or dissolution of MA into the polymer melt was at least one of the limiting factors of the grafting yield. The gel content of PE1 was similar to the highest gel content obtained when the components were premixed. The difference was that for the simultaneous feed, there seemed to be no time for degradation of the network. For PP, the grafting MA evolution along the extruder was similar to that for PE1, but the final MA content was not significantly different for a simultaneous feed (Table II). However, dynamic viscosity values after location D were lower than the values

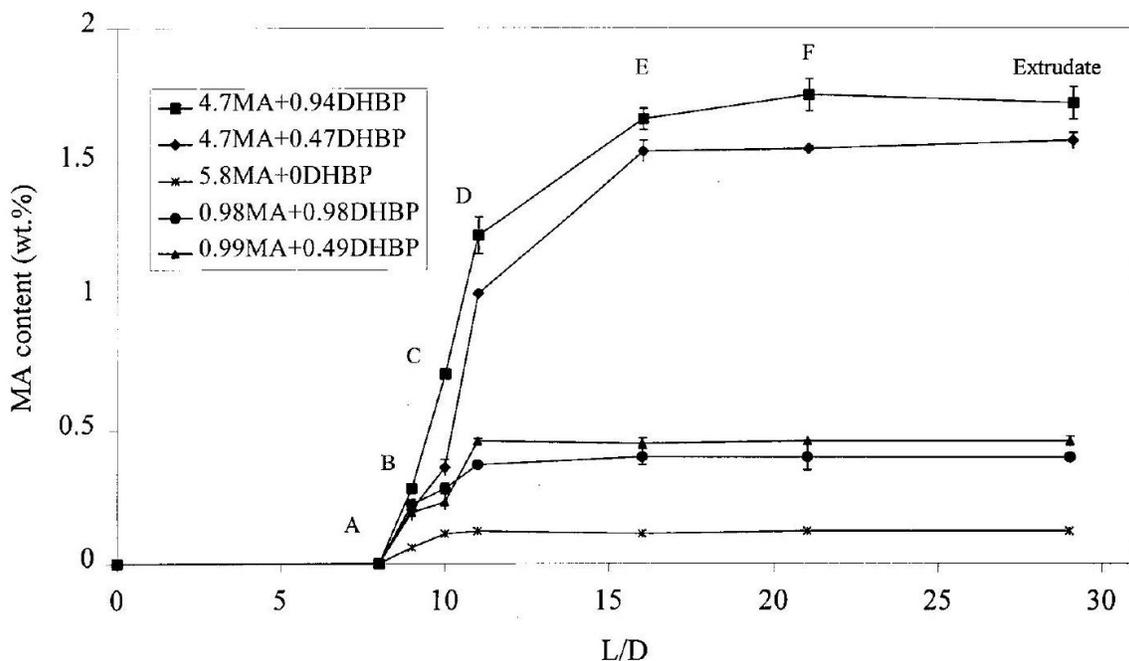


Figure 8. MA-graft content of PE1 along the extruder with different grafting recipes. obtained when the components were premixed (Table V).

# CONCLUSIONS

The grafting of MA onto polyolefins with different ethene/propene ratios was studied along an extruder axis with a series of sampling devices. The MA-graft content followed the same profile along the axis when the same conditions (peroxide type and processing conditions) were used, regardless of the type of polyolefin and the MA and peroxide concentrations. As in the first part of this series,<sup>22</sup> where changes in rheological behavior were related to the peroxide decomposition, a good corre-

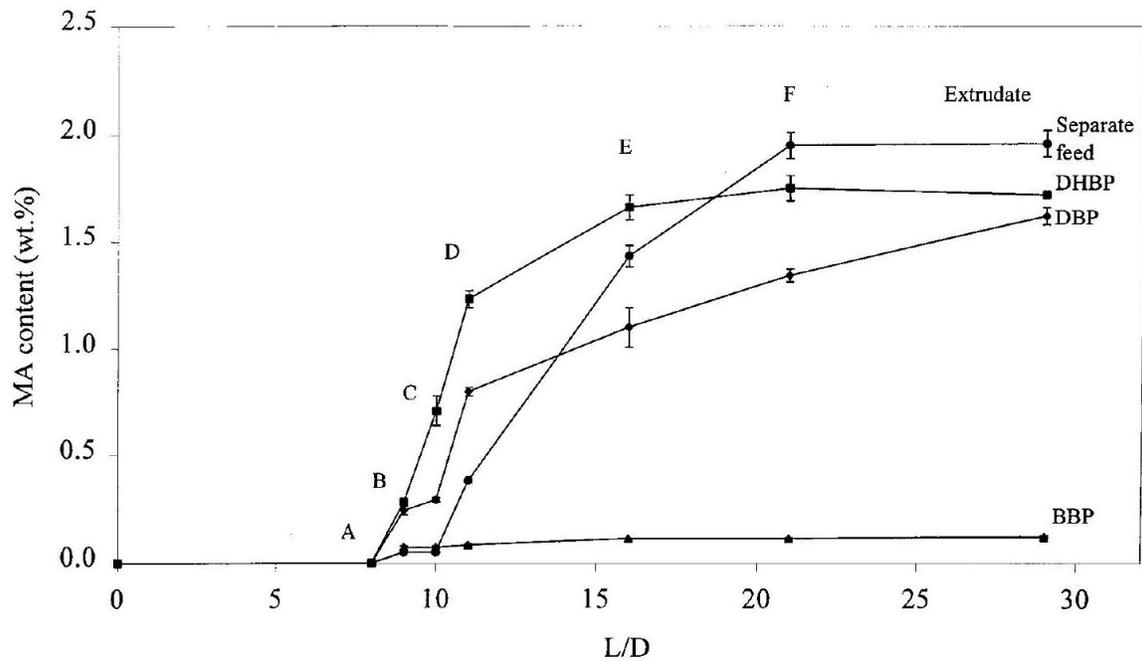


Figure 9. MA-graft content of PE1 along the extruder with different peroxides and a separate feed with 4.7wt% MA and 0.94wt% DHBP at 200°C.

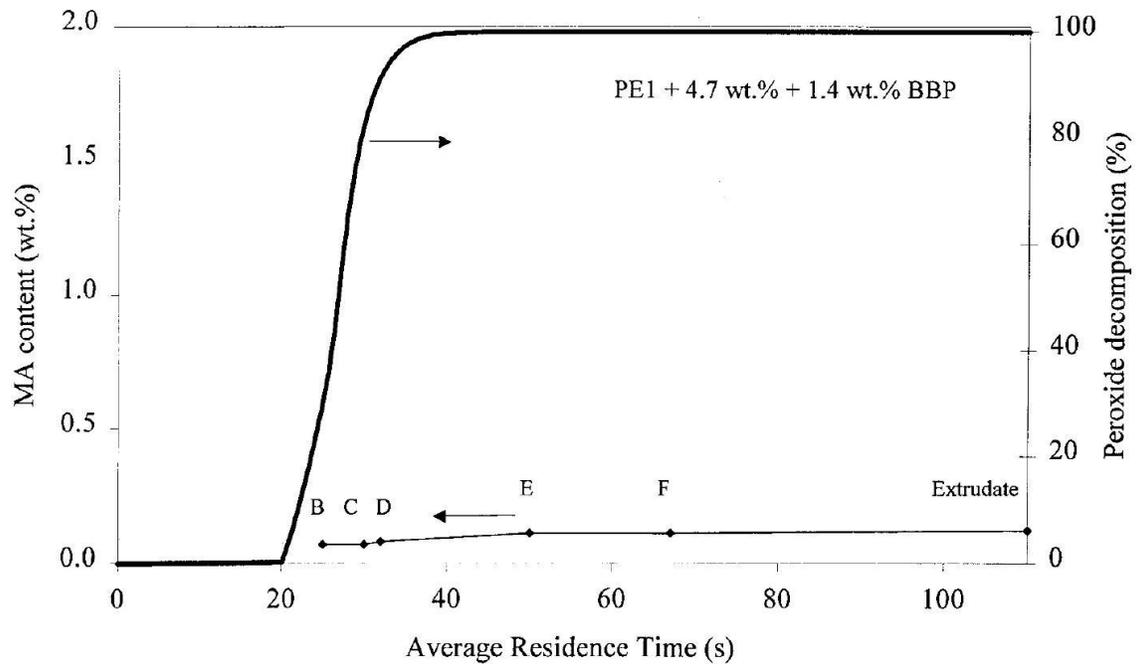


Figure 10. MA-graft content for PE1 and the calculated peroxide decomposition, with 4.7wt%MA and 1.4wt%BBP at 200°C, as a function of the average residence time.

lation was established between the experimental grafting profile and the calculated peroxide decomposition profile. Chemical reactions occurred along the extruder until the peroxide was fully converted. More detailed quantitative measurements of peroxide decomposition and MA grafting would allow the development of accurate process models. As expected, the final MA-graft content

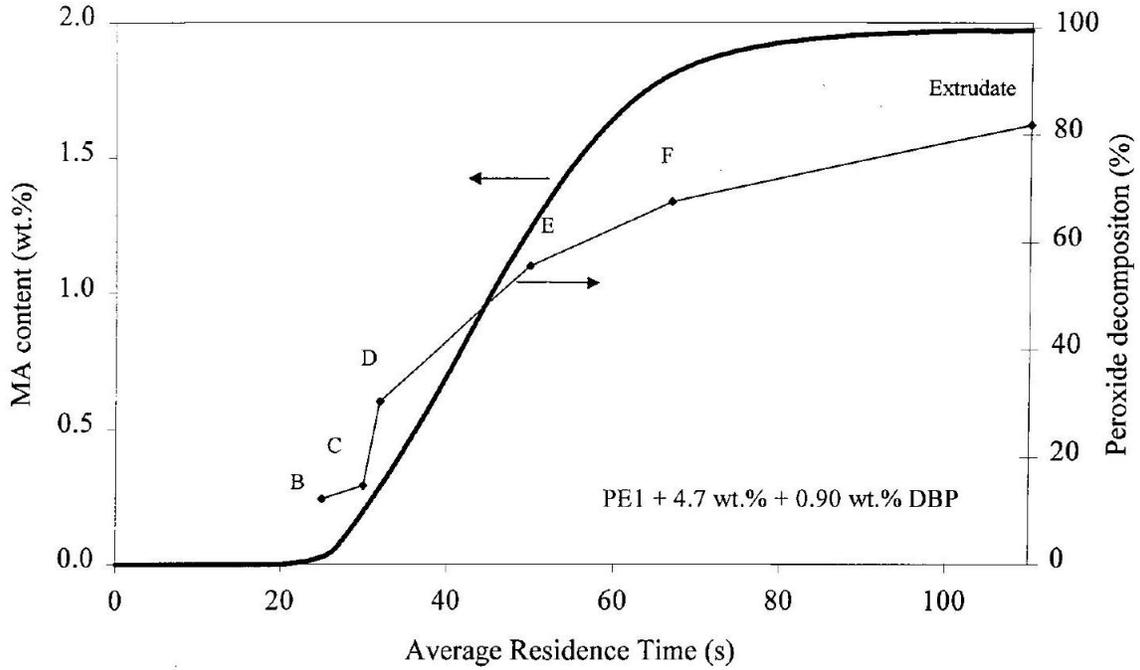


Figure 11. MA-graft content for PE1 and the calculated peroxide decomposition, with 4.7wt%MA and 0.90wt%DBP at 200°C, as a function of the average residence time.

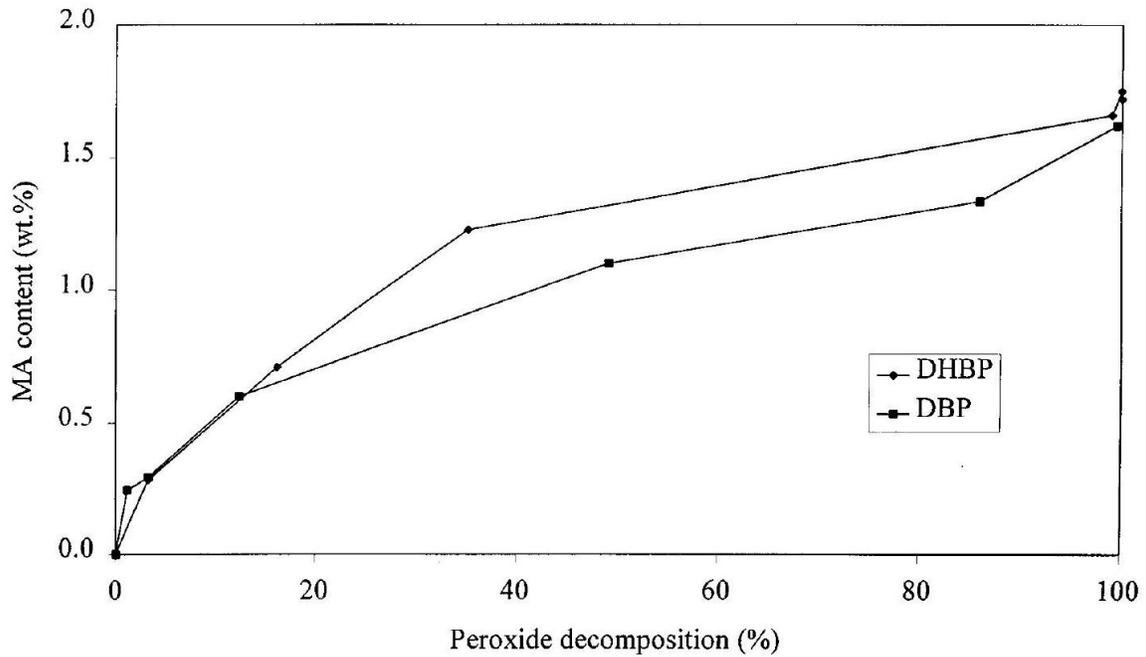


Figure 12. Correlation between the MA-graft content for PE1 and the calculated peroxide decomposition (DHBP and DBP).

depended on the polyolefins composition: PE > EPM >> PP. For PE, crosslinking occurred in addition to grafting, but at a sufficient screw length, the PE network degraded again.

The decrease in PP viscosity after MA grafting was due to the conversion of tertiary PP radicals into primary PP radicals after grafting.

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