Effect of Experimental Conditions on the Grafting of Maleic Anhydride Onto Polyethylene in Extruders

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Abstract

This work investigates the effect of the operating conditions (set temperature and prescribed throughput) on the evolution of the MA grafted content on high density polyethylene along a co-rotating twin screw extruder. Samples were quickly removed from the extruder at relevant axial locations, quenched and subsequently characterized off-line. While grafting was monitored by FTIR, the residual peroxide was determined by gas chromatography. The results show a good correlation between residual peroxide and MA grafted content.

Introduction

One of the most attractive methods for the chemical modification of polymers is via free radical grafting of monomers during processing [1]. This involves the reaction between a polymer and a monomer containing double bonds able to form grafts on the polymer backbone in the presence of an organic peroxide [2]. Maleic anhydride (MA) can be grafted onto polyethylene (PE) to enhance its compatibility with polar polymers or to improve adhesion to metal, glass fibers or to other polymers. Currently, the process is carried out in extruders, hence it is affected by the chemistry involved, by the geometry of the equipment and by the processing conditions. Therefore, in order to maximize the grafting yield and minimize side reactions, parameters such as screw geometry, temperature, pressure, residence time and devolatilization conditions have to be optimized. Although the effect of these variables on free radical grafting is currently well understood, much less is known about the actual evolution of the grafting reaction along the extruder [3]. In order to study this, it is necessary to establish a correlation between MA grafting and residual peroxide content. Therefore, in this work, grafting of MA onto PE was studied under a variety of processing conditions, each experiment providing a series of samples along the extruder with varying residual peroxide and degree of grafted MA. The relationship between the latter and the peroxide decomposition was investigated and correlated with the main process parameters.

Experimental

High density polyethylene (HDPE) Stamylan HD 2H280 (M_w = 60 kg/mol) manufactured by DSM, Maleic anhydride (MA) obtained from Aldrich, and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DHDP) Trigonox 101 supplied by Akzo Nobel, were used. The half-life times of this peroxide at 200°C and at 150°C are 6.1 and 646 s , respectively. The PE was modified with 5 phr of MA in the presence of 1 phr DHBP in a modular Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder fitted with a series of sample collection devices along the barrel length. Figure 1 depicts the extruder layout and the sampling locations, which are able to remove quickly circa 3 g samples from inside the extruder. Two flow rates (6 and 10 kg/h) and two uniform barrel set temperatures (150 and 200°C) were used for a constant screw speed of 150 rpm . All samples were dissolved in toluene until a clear solution was obtained, and subsequently precipitated in metanol, in order to remove the unreacted MA and the residual peroxide. After drying the precipitate at 180°C under vacuum for 1 hour, IR spectra were recorded from compression moulded films on a Perkin Elmer 1620 FT-IR spectrometer. As the intensity of the

1785 cm − 1 peak is proportional to the amount of MA groups present in the sample, the height of this peak (for a known film thickness) can be used to quantify the MA content.

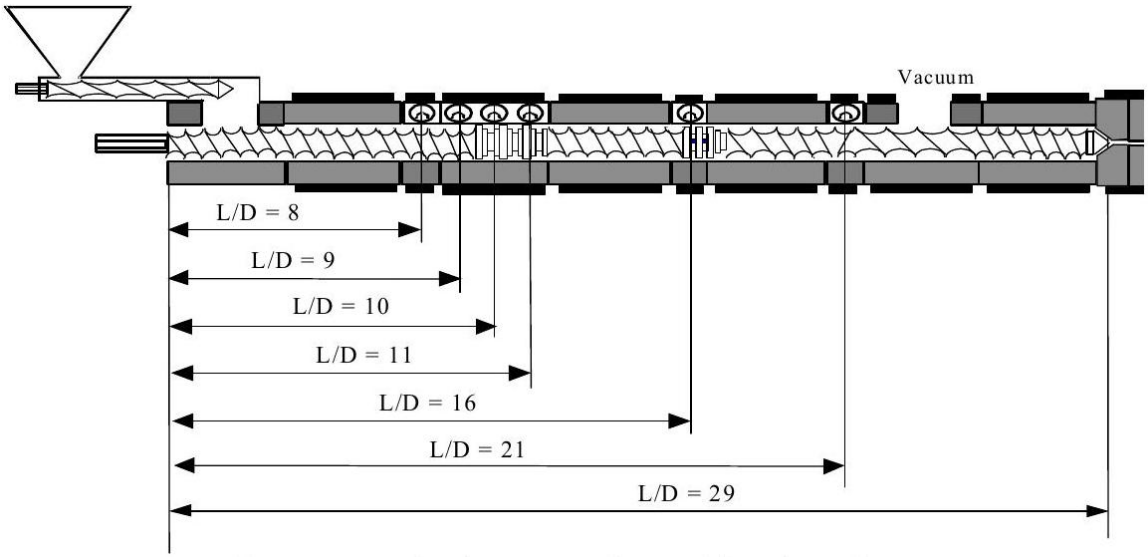

Fig.1. Extruder layout and sampling locations.
FT-IR calibration was carried out by imidization of available MA grafted polyolefins with NH_3, followed by N -content determination by elemental analysis.
The residual peroxide extracted from the samples was quantified on a Chrompack CP9001 gas chromatograph equipped with a FID detector and a 10 m × 0,25 mm i.d. Wcot fused-silica capillary column. The injector and initial column temperature were set at 60°C and 30°C, respectively. The column program is given in Table 1. Toluene solutions containing known amounts of peroxide and the internal standard provided the calibration curve. The analysis was carried out using nitrogen as the carrier gas.

Table 1. GC column-temperature program

Initial temperature/Rate	Step/Final temperature	Hold time
30°C	-	7 min
4°C/min	110°C	2 min
15°C/min	160°C	1 min
30°C/min	270°C	7 min

Results and Discussion

The measured peroxide decomposition and grafted MA content along the extruder for the various operating conditions are presented in Tables 2 and 3, respectively. In all cases, the peroxide decomposition and the grafted MA content increase along the extruder. Generally, the same type of variation is observed, i.e., both reactions (peroxide decomposition and MA grafting) develop mainly in the first part of the extruder, up to L/D = 16. Nevertheless, the operating conditions seem to influence the process. A strong decrease of the peroxide decomposition and a decrease of the grafted MA content are observed when low temperature and high throughput are used. The correlation between these two entities is shown in Figure 2. Shear stress levels, local temperatures and residence times explain the behaviour observed. Since melt temperature and average residence time determine the rate of peroxide decomposition, the latter increases with low throughputs (higher average residence times) and high temperature. In turn, given the correlation with grafted MA content, a higher amount of macroradicals is formed and a higher probability for grafting exists. Therefore, it is not surprising that the grafting of MA along the extruder mirrors the peroxide decomposition (Fig. 3).

Table 2. Measured peroxide decomposition (%).

Temperature (°C) throughput (kg/h)	L/D = 9	L/D = 10	L/D=11	L/D = 16	L/D = 21	L/D = 29
200-6	79	98	100	100	100	100
200-10	68	87	100	100	100	100
150-6	52	70	79	95	99	100
150-10	50	66	72	88	98	100

Table 3. Measured grafted MA content (wt.%).

Temperature (°C) throughput (kg/h)	L/D = 9	L/D = 10	L/D = 11	L/D = 16	L/D=21	L/D=29
200-6	0.58	1.02	1.41	1.42	1.45	1.49
200-10	0.33	0.71	1.01	1.04	1.03	1.04

150-6	0.36	0.54	0.65	1.09	1.35	1.42
150-10	0.21	0.23	0.26	0.36	0.83	0.86

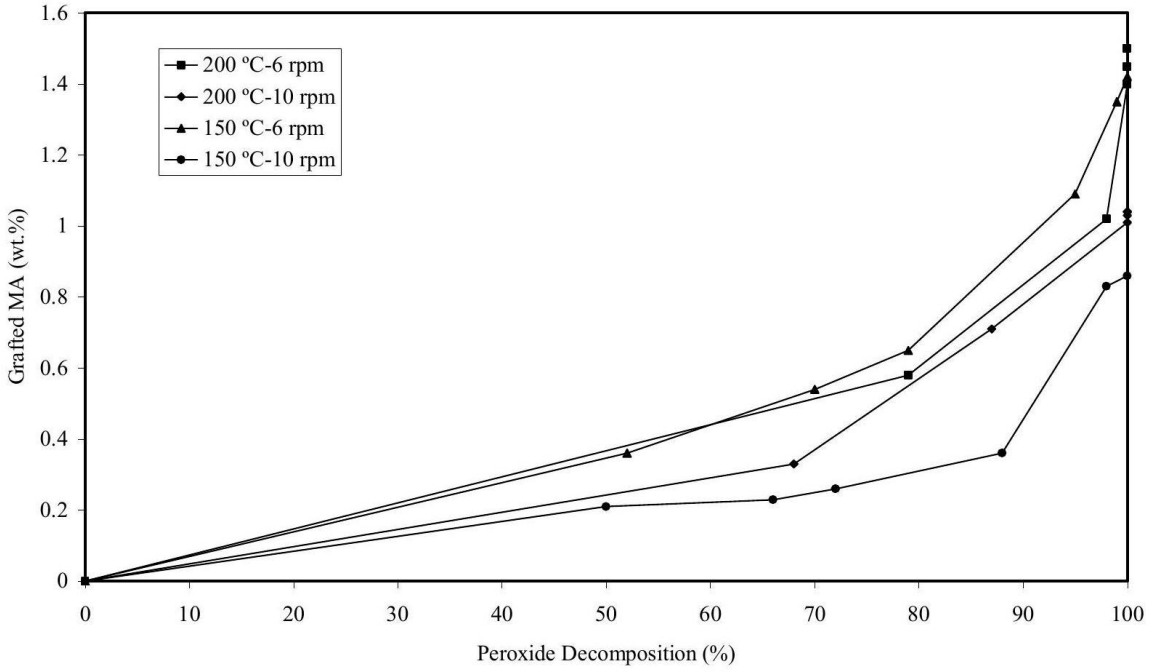

Fig. 2. Correlation between grafted MA content and peroxide decomposition

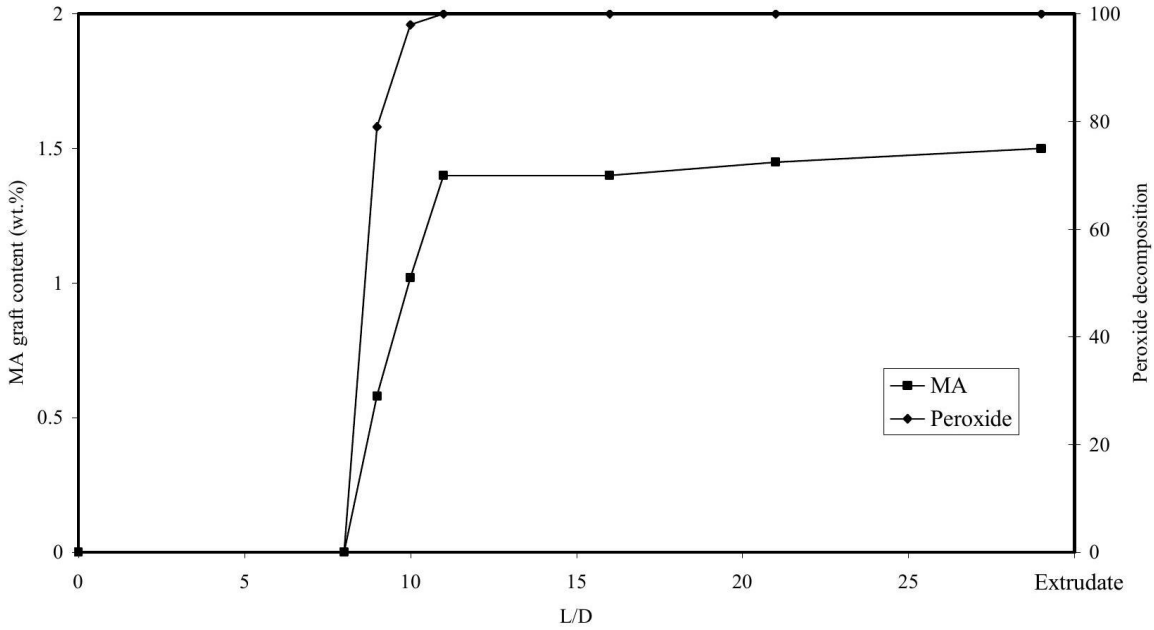

Fig. 3. MA grafting content and residual peroxide along the screw axis.

Conclusions

The variation of the residual peroxide and MA grafted content onto polyethylene along an extruder axis was studied for various operating conditions. The evolution of the MA grafted content mirrors that of the peroxide decomposition, a correlation between both having been identified. The final grafted MA content depends on the combined effect of temperature and throughput.

References

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