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DEVELOPMENTS IN THE SYNTHESIS OF MALEATED POLYOLEFINS BY REACTIVE EXTRUSION

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Abstract: The maleation of conventional and metallocene linear low density polyethylenes by reactive extrusion has been explored with a view to defining the conditions necessary for a robust process that provides both high grafting efficiencies (>80%) and minimal degradation or cross-linking. The dependence of grafting efficiency on various operating parameters (maleic anhydride level, maleic anhydride:initiator ratio, throughput rate, direction of screw rotation, temperature) has been established. Literature methods for characterization of the grafted product based on FTIR or ^{1}H NMR analysis have been critically examined with respect to their ability to distinguish between single unit and oligomeric maleic anhydride grafts and found to yield ambiguous results.

INTRODUCTION

Reactive extrusion is increasingly finding favour as a method of new polymer synthesis. The advantages over alternative processes are many-fold and include (a) no or little use of solvents; (b) simple product isolation; (c) short reaction times; (d) continuous process. Some potential disadvantages or difficulties associated with reactive extrusion relate to: (a) the need to achieve intimate mixing of reactants and substrates; (b) the high reaction temperatures necessary to form the polymer melt; (c) polymer degradation/crosslinking accompanying processing. The potential environmental and economic benefits of the process are such as to justify significant efforts aimed at resolving these problems. Although reactive extrusion has been available as a process for many years, much of the innovative work carried out in this area has been confined to industrial laboratories and little has been published in the open literature. The last few years have seen a partial turnaround in this situation and a drive to achieve greater understanding of the process. This has brought about a significant increase in the number of publications. A recent

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volume edited by Xanthos (Ref. 1) provides a comprehensive survey of reactive extrusion covering both the patent and open literature through 1990.

Our interest is in grafting reactions which yield reactive functionality and are thus useful for generating precursor materials which may subsequently be elaborated into block or graft copolymers. Maleation is one of the most studied polyolefin modification processes yet many aspects of the process remain controversial. As a consequence, the process still attracts much attention both in the open literature (Refs. 2-8) and in patents which disclose refinements to the process (Refs. 9-11).

In the present work, we provide a preliminary report on an investigation into the maleation of linear low density polyethylene (LLDPE) by reactive extrusion. This study is aimed both at improving the reliability and reproducibility of the process, and at furthering our understanding of the nature and distribution of grafts and their dependence on extrusion conditions. In conducting some aspects of this study, we have chosen to use metallocene LLDPEs as substrates. Although, these materials have now been available for some time, very little work has been published on their modification by reactive extrusion. The greater chemical homogeneity and relatively narrow polydispersity of these materials should make them ideal substrates for studies aimed at understanding the chemistry of reactive processing. A further benefit is that, depending on density (comonomer content), they have enhanced solubility in a variety of organic solvents. This permits the use of a range of characterization techniques which have been hitherto impractical or difficult to apply. A complication is that low melt viscosities (a consequence of narrow polydispersity) make the metallocene polyolefins more difficult to process.

MALEATION OF LLDPE

The main side reactions that accompany monomer grafting are radical-induced degradation of the polyolefin substrate by cross-linking or chain scission, and homopolymerization of the monomer. In the literature on melt phase maleation prior to 1990, some degree of cross-linking or degradation is considered to be unavoidable (Ref. 6). The major challenge that has been taken up in this and other laboratories has been to devise conditions which minimize or control these processes.

Polyethylene and ethylene copolymers (HDPE, LDPE, LLDPE, EPR) are prone to branching or crosslinking caused by radical-radical combination. This process is characterized by the formation of gels or a partially insoluble product. A number of interdependent factors need to be optimized to minimize these side reactions, to maximize grafting yields / efficiencies, and to control the nature of the grafted product. These include:

(a) Mixing efficiency - efficient mixing of the monomer(s) and initiator with the polyolefin substrate is of critical importance. The mixing efficiency will determine the local reactant concentrations and is determined by the screw design, temperature, pressure, the rheological properties of the polyolefin, and the solubility of the monomer and the initiator in the polyolefin.

(b) Temperature - higher processing temperatures generally will favor polyolefin degradation and will also influence solubility and rheological parameters.

(c) Pressure - the use of higher pressures can lead to enhanced solubility of the monomer and initiator in the polyolefin substrate.

(d) Initiator - half-life, concentration, solubility and partition coefficient in polyolefin and monomer, reactivity and specificity of initiator derived radicals.

(e) Monomer concentration - solubility in polyolefin. The use of higher monomer concentration may give improved grafting yields. A monomer concentration that is too high can give phase separation and increased homopolymerization.

(f) Coagents - these include comonomers, solvents, transfer agents, inhibitors and other additives.

(g) Venting - removal of unreacted monomer(s) and coagents.

(h) Residence time, residence time distribution - determined by throughput rate, screw design, screw speed and extruder length/diameter ratio (L/D).

Some discussion on the optimization of these parameters is provided in Xanthos' book (Ref. 12). It can also be noted that most recent patents granted in the area of reactive extrusion relate not to the development of new reactions or processes, but to the selection of such operating parameters designed to achieve specific product characteristics (for example, Refs. 9-11).

A problem exists in comparing melt phase processes carried out in different reactors since reaction conditions may vary enormously. Apparently contradictory results may, in some cases, simply reflect differences in mixing efficiency or other operating parameters such as the temperature or pressure. In reactive extrusion, these parameters are often difficult to specify in an entirely satisfactory manner. For example, the effects of shear heating mean that melt temperatures are often substantially different to set barrel temperatures.

EFFECT OF EXTRUSION CONDITIONS ON GRAFTING EFFICIENCY

In developing conditions for maleation of LLDPE, we have taken conditions described by Strait *et al.* (Ref. 9) as a starting point. These authors reported grafting efficiencies of up to 70% (as measured by FTIR analysis) and a product of low odour and coloration. One feature that distinguishes their process from earlier work is that the maleic anhydride (MAH) is introduced by liquid injection as a solution in 2-butanone.

The effect of various experimental variables on grafting efficiency has been explored as follows.

Screw design

It has been pointed out in the literature that efficient mixing of MAH and initiator with the polyolefin is possibly the most critical factor in achieving high grafting efficiencies and in minimizing crosslinking and discoloration. Screw designs required to achieve this end will not be reviewed in this paper due to space limitations. The use of counter rotating (intermeshing partially self wiping) and corotating (intermeshing fully self wiping) screws have been explored as part of the present work. However, no particular merit for one mode of operation over the other can be stated in that similar grafting efficiencies have been obtained using both counter and co-rotating screws. There is some evidence that a shorter mixing zone can be used when operating in counter-rotating mode.

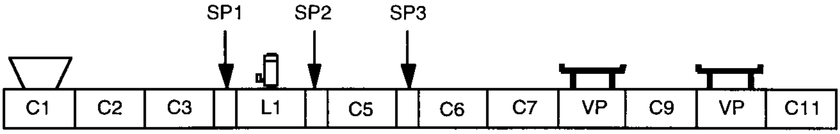


Fig. 1. Schematic diagram illustrating the arrangement of the barrel sections of the JSW extruder. The base polymer is added through the hopper (section C1). MAH/initiator solution is introduced at L1. The mixing/reaction zone comprises sections L1 through C6. The melt temperature quoted is read at SP3. Sections labelled VP are vent ports.

The maleated LLDPEs (conventional or metallocene) formed under the range of conditions defined in this paper were entirely soluble in xylene and there was no evidence of gel-formation. GPC analysis (eluting with 1,3,5-trichlorobenzene at 135°C for polymers based on AT820 or tetrahydrofuran at 30°C for Exact 5008) was performed on selected samples. Molecular weights and polydispersities for maleated products based on the conventional LLDPE AT 820 appeared unchanged from that of the precursor polyolefin.

A significant increase in polydispersity (from 2.1 to > 4.0) was observed when trying to achieve high levels of maleation (5 wt% MAH) of the metallocene LLDPE, Exact 5008. No such problems were experienced in experiments aimed at lower levels of maleation (4 wt% MAH). The greater difficulty in controlling crosslinking/branching during maleation of the of the metallocene LLDPE is attributed to the lower melt viscosity of this polyolefin and the consequent impairment in mixing efficiency.

Effect of temperature

A tendency for a decrease in grafting efficiency with a decrease in the reaction zone melt temperature was observed over the range 200-260°C. The significance of this trend was found to depend strongly on the throughput rate and the initiator level (see Figures 2a-c). The effect of temperature was mitigated by the use of higher initiator levels such that with an initiator/monomer ratio of *ca* 1:10 (w/w) the grafting efficiency becomes independent of temperature. The temperature dependence also appears less for lower throughput rates

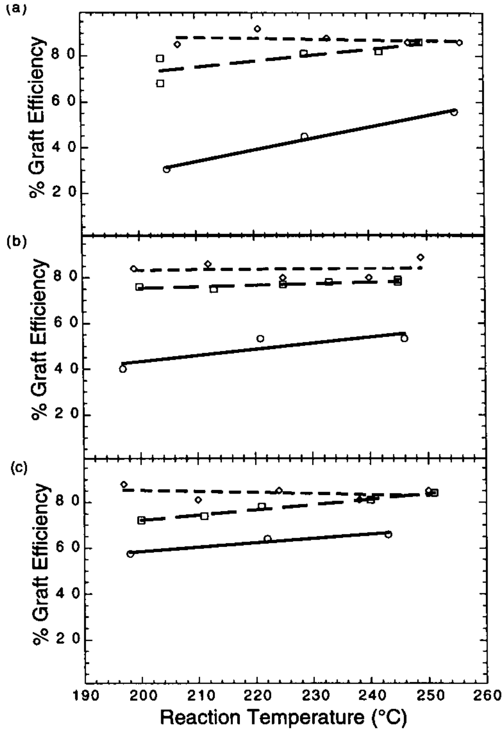


Fig. 2. Grafting efficiency in maleation of LLDPE AT820 as a function of the melt temperature in the reaction zone for throughput rates of (a) 32, (b) 24 and (c) 16 kg h^{-1}. Experimental conditions: corotating screw (408 rpm); MAH (2% based on LLDPE) and DHBP added via liquid pump as a solution in butan-2-one [MAH:butanone ratio 67:33 (w/w)]; DHBP level (wt%) 1.7 (——), 3.5 (– – –), 6.9 (- - -) corresponding to DHBP:MAH ratios (w/w) of 1:39, 1:19, and 1:10 respectively.

Effect of initiator level

For initiator:MAH ratios in the range 1:39 - 1:10 (w/w), a higher initiator level was found to give an increase in overall grafting efficiency (see Figures 2a-c). A greater sensitivity to initiator level was observed both for high throughput rates or lower reaction temperatures.

Effect of throughput rate

The effect of throughput rate on the grafting efficiency can be seen by comparing Figures. 2a-c. There is direct relationship between the throughput rate and the residence time in the reaction zone. A decrease in grafting efficiency with throughput rate is therefore expected. It is noteworthy, that is possible to compensate for the short residence time by using a higher initiator concentration. For a initiator/MAH ratio of 1:10, the dependence of the grafting efficiency on the throughput rate becomes negligible, while for lower initiator levels there is a significant reduction in grafting efficiency with an increase in throughput. The use of higher melt temperatures (faster initiator decomposition) was also found to diminish the dependence of grafting efficiency on throughput rate.

Effect of MAH level and mode of MAH addition

The effect of MAH level on grafting efficiency was explored in a series of experiments where the ratio of initiator:MAH (1:19) and the LLDPE throughput (16 kg h^{-1}) were kept constant while the level of MAH added was varied to give a final graft level of between 1.3 and 4.2 %. There appears to be some tendency for a reduction in grafting efficiency with MAH level under these conditions (see Table 1). However, the effect is small with respect to experimental error (±5%).

Tab. 1. Effect of MAH level on Grafting Efficiency[a]

Experiment	%DHBP (feed)[b]	%MAH (feed)[b]	%MAH (product)[b,c]	%Graft Efficiency
1	0.11	2.0	1.3	67
2	0.10	2.0	1.5	77
3	0.20	3.8	2.6	68
4	0.30	5.8	3.1	53
5	0.36	7.0	4.2	60
6	0.11	2.1 (4.1)[d]	2.3 (3.6)[d]	109 (88)[d]

[a] Experimental parameters: substrate LLDPE AT820; corotating screw (408 rpm); melt temperature in reaction zone: 222-232 °C (barrel set temperature: 200 °C); LLDPE throughput rate 16 kg h^{-1}; MAH and DHBP added as a solution in butan-2-one [MAH:DHBP:butanone ratio 67:33:3.5 (w/w/w)].

[b] Wt% based on LLDPE.

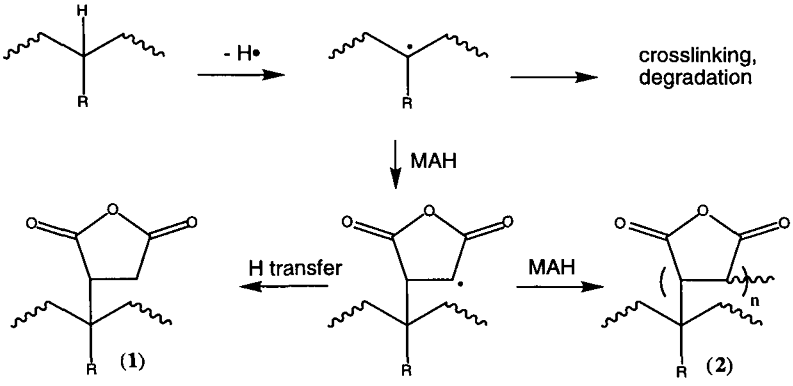
[c] Determined by FTIR analysis on samples extracted to remove any free MAH monomer or oligo(MAH). See Experimental Part.

[d] Grafting carried out in two passes through the extruder. Product from experiment 1 used as substrate. Numbers in parentheses are overall numbers for the two passes.

A strategy for providing increased grafting efficiencies based on multi-point addition of MAH has recently been disclosed by Gross *et al.* (Ref. 11). We have found that substantially higher grafting efficiencies can be achieved by grafting MAH to an already maleated material by means of a second pass through the extruder (experiment 6 in Tab. 1). The precursor material for this experiment was produced exactly as for experiment 1, however, no vacuum venting was applied to remove unreacted MAH. The grafting efficiency achieved in the second pass (109%; value > 100% because of conversion of unreacted MAH left from the first pass) was significantly higher than that achieved in the first pass (67%) suggesting that the first addition of MAH compatibilizes the second addition.

MECHANISM AND STRUCTURE OF MAH GRAFTS

A mechanism for maleation is shown in Scheme 1.



Scheme 1

The structure of MAH grafts may vary in terms of the fraction of grafts appearing as isolated succinic anhydride (SAH) units **1** *vs* oligo(MAH) chains **2**, the length of any oligo(MAH) grafts (**2**), and/or in the distribution of the grafts. These forms of structural variation provide one explanation as to why MAH modified polyolefins obtained from different commercial sources behave differently even though they have the same nominal composition. The possibility of oligo(MAH) grafts (**2**) in LLDPE has been recognized for some time. However, until recently, there has been a general consensus that MAH is grafted to polyolefins as single succinic anhydride units (Ref. 6). If MAH is present as oligo(MAH), then it is possible that high grafting efficiencies reflect the formation of longer chains rather than more grafts. If the ultimate aim is to produce well-defined graft copolymers, it is clearly important to be able to know and control the nature of the grafted units.

Recently De Roover *et al.* (Refs. 3, 4) conducted a systematic study of the infra-red spectra of various commercial and synthesized poly(propylene-*graft*-maleic anhydride) (MAH-PP) and indicated that single unit grafts **1** can be distinguished from oligo(MAH) grafts **2** by infra-red analysis. They pointed out that oligo(MAH) absorbs at 1784 cm^{-1} whereas simple alkyl succinates absorb at 1792 cm^{-1} (MAH monomer and α,β–unsaturated anhydrides also absorb at

1784 cm^{-1}). They concluded that a substantial fraction of MAH units in MAH-PP are invariably present as oligo(MAH) **2**. Applying this rationale to the analysis of a film of poly(ethylene-*graft*-maleic anhydride) (MAH-LLDPE) would suggest that the proportion of such grafts may be even higher, such that most grafts may be oligomeric (see Fig. 3a).

Liu *et al.* (Ref. 13) analyzed MAH-LLDPE by ^{1}H NMR and proposed that oligo(MAH) and single unit SAH grafts may be distinguished by the chemical shift of the anhydride methines [SAH δ (dichlorobenzene-d_4) 2.5-3.5, oligo(MAH) δ (acetone-d_6) 4-5; oligo(MAH) and LLDPE are not both soluble in the same solvent]. They found that signals attributable to oligo(MAH) could not be detected and concluded that MAH-LLDPE contained predominantly single unit grafts **1**. The ^{1}H NMR spectra of our MAH-LLDPE appear qualitatively similar to those reported by Liu *et al.* (Ref. 13). However, this determination is considered unreliable because of the relative broadness of the signal assigned to oligo(MAH).

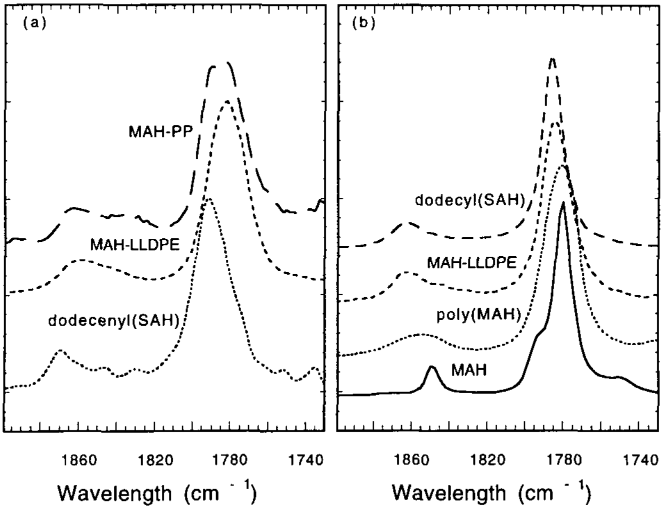


Fig. 3. Segments of the infra-red spectra of (a) films of MAH-PP (Exxelor P1015); MAH-LLDPE derived from Exact 5008; 2-dodecenyl(SAH) (dissolved in Exact 5008) and (b) tertrahydrofuran solutions of poly(MAH); MAH-LLDPE (derived from Exact 5008); *n*-dodecyl(SAH) (in Exact 5008) and MAH.

We have found that for the case of the metallocene MAH LLDPE (Exact 5008), some of the problems [*e.g.* reproducible film thickness, concentration/temperature dependence of absorptions (Ref. 3)] in conducting the FTIR analysis are alleviated by obtaining spectra for solutions in tetrahydrofuran (THF). This solvent was chosen because it dissolves this particular LLDPE as well as all of the model compounds [poly(MAH), MAH, dodecyl(SAH)] and does not itself absorb in the carbonyl region of the infra-red spectrum (note that conventional LLDPE is insoluble in THF). Qualitative analysis of the spectra (Fig. 3b) clearly suggests that MAH is most likely incorporated as a mixture of single unit **1** and oligomeric grafts **2**. This finding is supported by the recent work of Heinen *et al.*(Ref. 2) who conducted a study of the grafting of ^{13}C-labeled MAH onto LLDPE and other polyolefins.

CONCLUSIONS

Conditions have been established for maleation of LLDPE by reactive extrusion which reliably give high grafting efficiencies with minimal complication from side reactions (crosslinking). The grafting efficiencies obtained (up to 85%) are as high or higher than those previously reported. It is clear that various experimental parameters associated with the experiment are highly cross correlated. For example, within the ranges reported, higher reaction temperatures, higher initiator levels and lower throughput rates all provide increased grafting efficiencies. Optimization of any two of these parameters provides a wide operating window for the third parameter. Multi-pass addition of MAH has been found to be advantageous in further raising grafting efficiency.

The effect of processing conditions on the ratio of SAH **1** to oligo(MAH) grafts **2** remains to be established. Existing literature procedures for product analysis have been shown to yield ambiguous results. Analysis of metallocene MAH-LLDPE by solution FTIR suggests a significant proportion of oligo(MAH) grafts **2**. Further work aimed at quantitatively establishing the nature and distribution of MAH grafts is underway in these Laboratories.

EXPERIMENTAL PART

Two polyolefins were used in the present study, a conventional LLDPE (hexene comonomer) designated Alkatuff AT820 manufactured by ICI Australia (melt flow index 20 g/10 min, density 0.925 g/dL) and a metallocene LLDPE (butene comonomer) designated Exact 5008 manufactured by Exxon Chemical (melt flow index 10 g/10 min, density 0.86)

Maleation of LLDPE was carried out with a Japan Steel Works 30 mm diameter twin screw extruder of L/D ratio 42 (JSW TEX 30) and comprising ten temperature controlled barrel sections each with L/D of 3.5, three unheated sampling zones with L/D 1.167, and a cooled feed block with L/D 3.5. The screw design is shown in Figure 1. The polyolefins were fed into the extruder via a JSW TTF20 gravimetric feeder. The initiator (DHBP) and MAH were fed via liquid injection as a solution in butan-2-one using a volumetric liquid addition pump (Fuji Techno Industries model HYM-03-08). The JSW TEX 30 can be operated as either a corotating (intermeshing self wiping) counter-rotating (intermeshing non-self wiping) modes. The melt temperature was monitored at three points along the barrel and in the die. The reaction temperature quoted in the Tables, Fig. 2 and in the text refers to the melt temperature measured in the mixing zone (SP3; refer to Fig. 1).

For FTIR analysis, the maleated LLDPE AT820 was dissolved in xylene and precipitated in acetone to remove any residual MAH monomer or poly(MAH) homopolymer. Grafting efficiencies reported are based on MAH levels determined by FTIR on *ca* 50 μ melt pressed film samples applying the following relationship:

$$\%(\text{MAH}) = 0.032 + 0.411\left(\frac{A^{1784} + A^{1710}}{A^{1365}}\right)$$

Where A^{λ} is the absorbance at λ cm^{-1} measured above a baseline drawn to the valley between the acid (1710 cm^{-1}) and anhydride (1784 cm^{-1}) absorptions. This relationship was validated by titration for MAH levels up to 2%. Experiments which converted the grafted functionality from the diacid to anhydride form (by drying in a vacuum oven) established that the %(MAH) when calculated using this relationship, was independent of the acid:anhydride ratio.

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