Functionalization of Polyethylenes and Their Use in Reactive Blending

N. C. LIU, W. E. BAKER,* and K. E. RUSSELL, *Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

Synopsis

The grafting of maleic anhydride (MAn) to low density polyethylenes (PEs) dissolved in 1,2-dichlorobenzene (DCB) has been studied. Grafting was successful at temperatures of about 160°C both in air without initiator and under nitrogen with the radical initiator 2,5-di(*t*-butylperoxy)-2,5-dimethyl-3-hexyne (LPO). The presence of succinic anhydride grafts was shown by FTIR spectroscopy of the product; ^{1}H-NMR spectroscopy indicates that the grafts consist of single succinic anhydride units. The graft content was determined by nonaqueous titration, and the extent of crosslinking inferred from the melt flow rates (MFR) of the products. The effects of concentration of initiator, MAn, and PE on the graft content were determined; the influence of PE structure, reaction time, and temperature was also studied. Melt blending of the grafted PE with polystyrene containing oxazoline functional groups (OPS) was investigated using a Rheomix mixer. The interpolymer reaction which occurs during blending was studied by means of FTIR, and the morphology of the blends by scanning electron microscopy (SEM). Information was also gained from the change in torque viscosity during the blending process.

INTRODUCTION

Recent interest in functional polymers has been sparked in part by their potential use in polymer blends. Most polymer pairs are immiscible and their two-phase mixtures have poor mechanical properties. Mixing is aided by the presence in the component polymers of complementary functional groups, either in the backbone or pendent from it; these provide sites for specific interactions, e.g., hydrogen bonding, covalent bonding, or ionic interaction. For example, a coupling reaction during melt blending of OPS and carboxyl-containing PE results in improved compatibility.[1] Similarly, MAn-grafted ethylene–propylene rubber (EPR) is a better toughening agent for nylons because of the presence of covalent bonds at the nylon–EPR interface.[2] It was also proposed that the enhanced compatibility of PE with kaolin and bentonite clays in the presence of MAn resulted from *in situ* grafting of the PE, followed by the condensation reactions with the clays.[3] In general, however, there have been few detailed studies of the chemistry and kinetics of melt blending reactions, due primarily to the low concentrations of functional groups available for reaction.

Grafting of preformed polymers is an important method for the preparation of polymers with functional groups. MAn is a reactive monomer and it has

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* To whom correspondence should be addressed.

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been grafted to PE by mechanical, free radical, ionic, and radiation techniques.[4,5] The grafting process may be carried out in solution, in molten PE, or on suspended films. The pendent anhydride group provides functionality for crosslinking and other chemical reactions, and it aids compatibility of PE with other polymers.

Gabara and Porejko[6,7] proposed that the heterogeneous grafting of a PE film suspended in an acetic anhydride solution at 80–110°C proceeds through the coupling of PE· macroradicals with poly(MAn)· macroradicals; they noted that oxygen has a significant effect on grafting under these conditions. Porejko et al.[8,9] concluded that the reaction of MAn with PE in xylene at 110°C, initiated by benzoyl peroxide or azobisisobutyronitrile, proceeds through a different mechanism, i.e., formation of PE· radicals by the attack of initiator radicals on PE followed by polymerization of MAn at these radical sites. They found little difference between grafting in air and nitrogen under homogeneous conditions at 110°C. In both cases the grafts were thought to consist of poly(MAn) side chains.

Braun and Eisenlohr[10] concluded that the reaction of MAn with PE in xylene at 139°C in the presence of benzoyl peroxide does not yield poly(MAn) side chains or homopolymer. They proposed that radicals are generated on PE chains and add only one MAn unit to form PE–MAn· radicals. These react with PE· or PE–MAn· radicals by coupling or disproportionation, with initiator radicals by coupling, or with PE by hydrogen abstraction.

Gaylord et al.[11] reported that the heterogeneous reaction of MAn with molten PE in the presence of benzoyl peroxide at 140 and at 180°C resulted in the grafting of both poly(MAn) chains and single MAn units to the PE. Some crosslinking occurred but this was reduced by the presence of dimethylformamide. Gaylord proposed that two separate reactions occur: (1) the homopolymerization of MAn with the participation of MAn excimers and cationic intermediates, accompanied by the graft copolymerization of MAn on to PE, (2) the grafting of individual MAn units on to PE by the addition of PE· radicals to MAn or MAn excimers. Gaylord and Mehta[12] showed that the presence of MAn in PE–cumyl peroxide mixtures at 180°C also leads to increased crosslinking but that this can be reduced or eliminated by the addition of various nitrogen-, phosphorus-, and sulfur-containing organic electron donors. The absence of crosslinking was indicated by the formation of soluble product instead of insoluble gel which results when reactions are performed without organic electron donors.

The detailed structure of MAn grafted PE remains difficult to determine and in particular there is little known concerning graft size. More information is required on the influence of oxygen on the grafting process and on the factors influencing crosslinking. In this investigation, MAn was grafted on to PE under nitrogen at high temperatures in a homogeneous medium; the initiator was LPO and the solvent DCB. The grafted product was characterized by means of FTIR and ^{1}H-NMR. The effects of initiator and MAn concentration on graft content and on crosslinking were investigated. The effect of air on the extent of grafting in the absence of initiator was also investigated. The results are discussed in terms of a simple reaction scheme. The reaction of grafted PE with OPS during melt blending was also studied.

EXPERIMENTAL

Materials

The starting material was a low molecular weight PE in pellet form supplied by Eastman Chemical Products. This PE has a density of 0.906 g/mol, a melt index of 2,250 g/10 min, and a molecular weight of 8000. The FT-IR spectrum indicated that a small amount of branching was present.

The OPS used was a copolymer of 1.7% vinyl oxazoline and styrene produced by Dow Chemical Co. (XUS −40056.00). It has a molecular weight (M_w) of about 200,000 g/mol and an MFR at 190°C of 0.8 g/10 min (ASTM D1238, condition E).

The MAn (99%) was used as received. The solvent, DCB, was laboratory reagent grade.

The initiator, Lupersol 130 (LPO), a 90% solution of 2,5-di(*t*-butylperoxy)-2,5-dimethyl-3-hexyne with a half-life of about 12 min at 165°C was used as received from the Lucidol Division, Pennwalt Corp.

Grafting Procedure

The grafting reaction was carried out in a three-neck flask equipped with a stirrer and thermometer. The temperature in the flask, which was heated in a heating mantle with voltage controls, was maintained with a precision of ±1°C. PE was dissolved in DCB at about 120°C, the temperature was raised to the desired value, and MAn was added. Initiator solution in DCB (5 mL) was added in five equal portions. The reaction time was measured from the first addition of initiator. After a determined time, the reaction was stopped and the reaction product was poured into 5–10 volumes of acetone with constant stirring. The precipitated product was filtered, washed twice with acetone, and subsequently dried overnight at 60°C in vacuum.

Blending Procedure

The grafted PE was melt blended with OPS in a Haake-Buchler Rheomix mixer Model 600, with roller blades. A 40 g charge of OPS and grafted PE (70 : 30 by wt) was dry blended and then fed into the mixer, which already had been adjusted to required conditions; the mixing was continued for 15 min unless otherwise specified. The reaction temperature and mixing speed were maintained at 190°C and 100 rpm, respectively, for all runs. The torque and melt temperature were continuously monitored as a function of time.

Analysis

Films for infrared analysis were compression-molded at 165°C and 2000 psi. The films of both grafted PE and their blends were about 75 μm thick. FTIR spectra were obtained by means of a Bruker IFS-85 spectrometer.

Proton NMR spectra of samples in deuterated 1,2-dichlorobenzene solution were obtained on a Bruker AM-400 spectrometer at 120°C.

The MFRs of the reaction products were measured at 190°C using a Tinius-Olsen extrusion plastometer with a load of 2160 g (ASTM D1238, condition E).

The weight percentage of grafting was determined by direct titration. About 0.5 g of the grafted product was dissolved in 40 mL hot DCB, cooled to about 80°C, and titrated with ethanolic NaOH using thymol blue as indicator. The ethanolic NaOH was standardized with analytical grade benzoic acid. Corrections were made based on results with nongrafted product and with a standard acid.

Scanning electron micrographs of the blends were taken on a JEOL model JSM 840 microscope. Samples were prepared by fracturing a blend under liquid nitrogen and gold-coating before electron microscopy.

RESULTS AND DISCUSSION

Characterization of Grafted PE

The grafted PE is a yellow powder, and the intensity of color increases with increasing percentage of grafting. It is soluble in boiling toluene when its MFR is not zero; even products of zero MFR value dissolve to some extent. Since the grafted product is an anhydride, it undergoes the typical hydrolysis reaction of anhydrides. After having been exposed to the atmosphere for a few weeks, it becomes mostly hydrolyzed.

Figure 1 shows the infrared spectra of the pure PE and a grafted product made under nitrogen. The spectrum of the grafted product shows a very strong band at 1783 cm^{-1} and a weaker band at 1862 cm^{-1}, which are characteristic

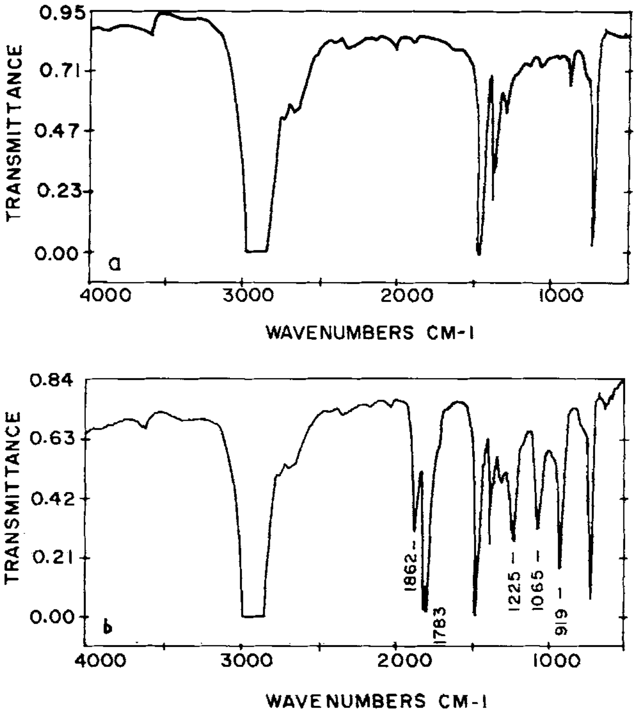


Fig. 1. FT-IR spectra of (a) pure PE and (b) grafted PE.

of a saturated ring anhydride. In order to confirm the grafting, a grafted PE sample was redissolved in DCB, then precipitated into five volumes acetone, filtered, washed, and dried. The FTIR spectrum remained unchanged after this reprecipitation. Since MAn and its homopolymer dissolve easily in acetone, there is very little probability that after reprecipitation the monomer is still present in the sample, i.e., the grafted PE is free of monomer. Moreover, a grafted PE sample was dissolved in DCB, precipitated in acetone, and filtered. The wet product was then shaken in refluxing water for 20 h. The FTIR spectrum showed a strong band at 1710 cm^{-1} which arises from the hydrolysis of the anhydride. This further confirmed that the FTIR absorbance of grafted PE was not due to residual monomer but to grafting.

The proton NMR spectrum of grafted PE is shown in Figure 2(a). Supporting evidence for the conclusion that succinic anhydride rings are individually attached to the PE chains comes from a comparison of the above spectrum with that of poly(MAn) [Fig. 2(b)].[13,14] The broad group of resonances of poly(MAn) is centered at 4.5 ppm, and little signal was detected below 3.5 ppm. On the other hand, the spectrum of the grafted material shows resonances only in the 2.5–3.7 ppm region and this is typical of a substituted succinic anhydride. Thus, grafts containing more than one succinic anhydride unit must be absent or present in a small amount. Resonances close to 2 ppm are associated with acetone residues from the precipitant. This is consistent with results previously reported[15] for grafted products of MAn on to a model compound, *n*-eicosane ($C_{20}H_{42}$).

Elemental analysis gave an estimate of graft content which is fairly consistent with those obtained from NMR, FT-IR, and titrations.

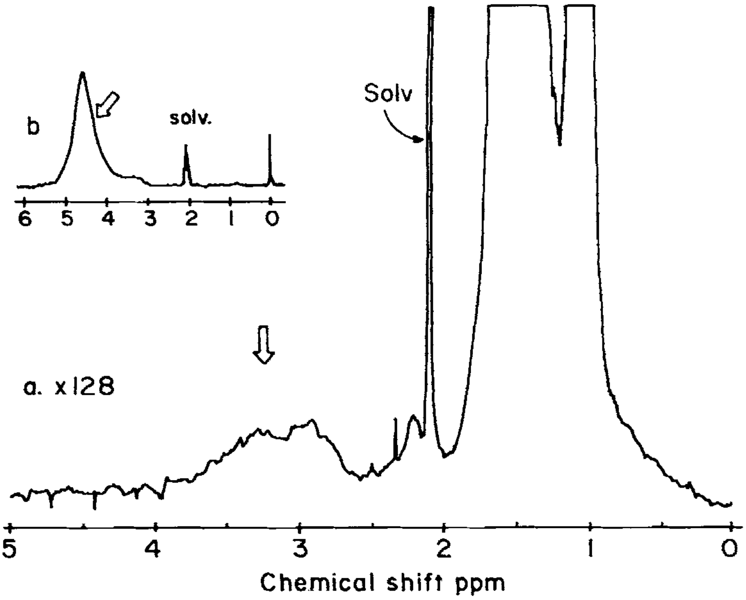


Fig. 2. Proton NMR spectrum of (a) grafted PE and (b) poly(MAn).[13-14]

Mechanism of Grafting

The scheme is eqs. (1)-(9) describes some of the reactions taking place that may be considered responsible for grafting and/or crosslinking:

$$\mathrm{LPO} \rightarrow 4\,\mathrm{RO}\cdot \tag{1}$$

The primary RO· radical produced by thermal decomposition of LPO abstracts a hydrogen atom from PE chains:

$$\mathrm{RO}\cdot + \mathrm{PE} \rightarrow \mathrm{ROH} + \mathrm{PE}\cdot \tag{2}$$

The resulting PE· macroradical reacts with a MAn molecule yielding a PE–MAn· macroradical which undergoes chain transfer generating again a PE· macroradical:

$$\mathrm{PE}\cdot + \mathrm{MAn} \rightarrow \mathrm{PE{-}MAn}\cdot \tag{3}$$

$$\mathrm{PE{-}MAn}\cdot + \mathrm{PE} \rightarrow \mathrm{PE}\text{-}g\text{-}\mathrm{MAn} + \mathrm{PE}\cdot \tag{4}$$

Since experimental results showed no homopolymer side chains on the grafted PE backbone, homopolymerization of MAn to PE–MAn· must be absent or occur to a small extent. This can be explained by the low ceiling temperature for hompolymerization of MAn.[15]

The free radicals may be terminated by several reactions:

$$2\,\mathrm{RO}\cdot \rightarrow \text{products} \tag{5}$$

$$\mathrm{PE}\cdot + \mathrm{RO}\cdot \rightarrow \text{products} \tag{6}$$

$$\mathrm{PE}\cdot + \mathrm{PE}\cdot \rightarrow \mathrm{PE{-}PE} \tag{7}$$

$$\mathrm{PE}\cdot + \mathrm{PE{-}MAn}\cdot \rightarrow \mathrm{PE{-}MAn{-}PE} \tag{8}$$

$$\mathrm{PE{-}MAn}\cdot + \mathrm{PE{-}MAn}\cdot \rightarrow \mathrm{PE{-}MAn{-}MAn{-}PE} \tag{9}$$

FTIR analysis of grafted PE did not provide any evidence for the presence of double bonds. Therefore, termination by disproportionation of PE· and PE–MAn· macroradicals is absent or does not occur to a significant extent.

Figure 3 shows the influence of initiator concentration on the percentage of grafting and on reaction efficiency, defined as the molar ratio of the grafted MAn to four times the employed LPO. Grafting reaction did not take place under nitrogen without the presence of initiator; then a rapid increase was observed at low initiator concentrations. The percentage of grafting increased slowly with LPO concentration after the initial rapid increase. Meanwhile, the reaction efficiency dropped significantly from 11 at 0.33 mL LPO/100 g PE to 2.7 at 2 mL/100 g PE. This is due to the faster termination rate of free radicals at higher free radical concentrations, i.e., radical consuming reactions such as (5)-(9) are favored at high free radical concentrations.

The influence of MAn concentration on the percentage of grafting and reaction efficiency is shown in Figure 4. Increasing amount of MAn leads to an increase in the percentage of grafting. The percentage of grafting approaches

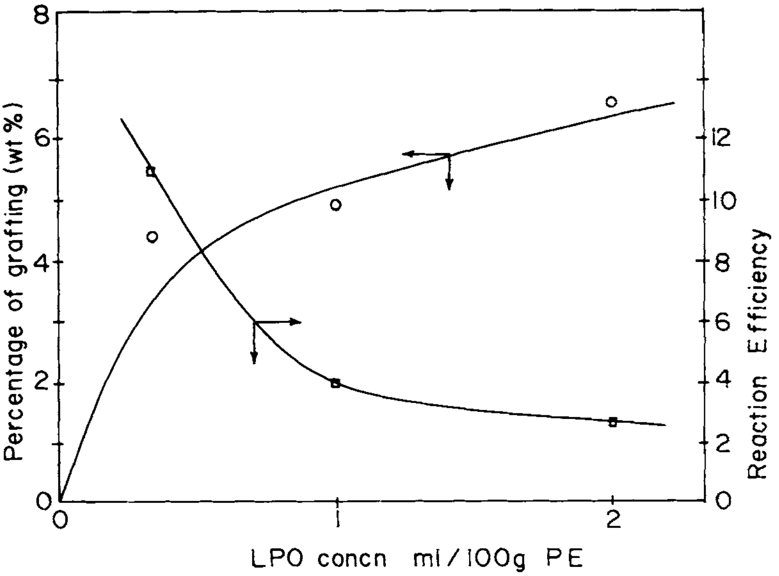


Fig. 3. The influence of initiator concentration on the percentage of grafting and reaction efficiency PE concentration, 10 g/100 g DCB; MAn concentration, 10 g/100 g PE; reaction temperature, 165°C; time, 2 h.

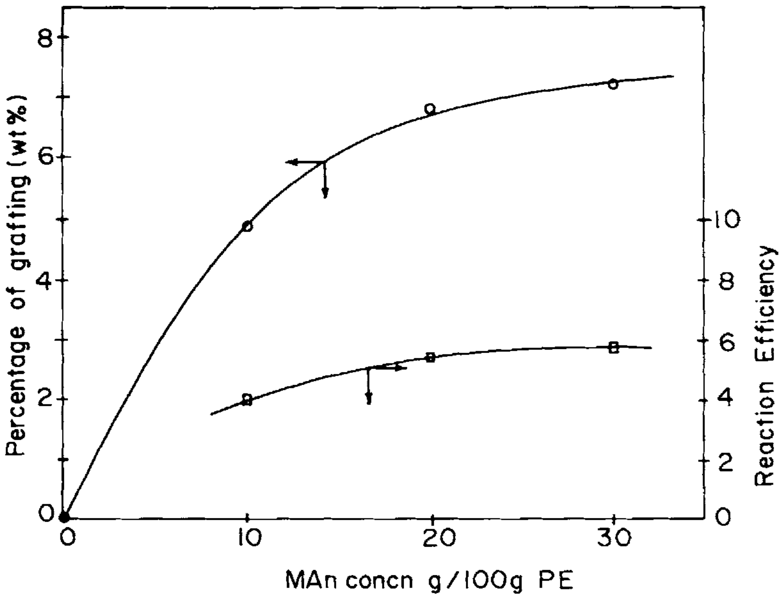


Fig. 4. Influence of MAn concentration on the percentage of grafting and reaction efficiency PE concentration, 10 g/100 g DCB; LPO concentration, 1 mL/100 g PE; reaction temperature, 165°C; time, 2 h.

a constant value at initial MAn concentrations above 20% by weight on PE. On the other hand, the MAn concentration has much less influence on reaction efficiency than LPO concentration. This is because high MAn concentration may only improve the reaction efficiency by decreasing the probability of free radical termination before the grafting of MAn, whereas initiator concentration directly affects the total concentration of free radicals [eq. (1)], which in turn affects the termination rate.

As shown in Figures 3 and 4, the reaction efficiency is always significantly higher than one. Since homopolymeric side chains are absent, this high reaction efficiency must result from the chain transfer reaction [eq. (4)].

The influences of reaction time, PE concentration, and structure on the percentage of grafting and reaction efficiency are included in Table I. Both higher PE concentration (columns 2 vs. 1) and lower molecular weight (columns 3 vs. 1) result in higher reaction efficiency. Shortening the reaction time leads to a lower percentage of grafting and reaction efficiency (columns 5 vs. 4).

Crosslinking of PE during Grafting under Nitrogen

Crosslinking of PE occurs in all cases studied as indicated by the dramatic decrease of the MFR of grafted product. Figure 5 shows the influence of MAn concentration on the MFR, where the initial concentration of initiator is kept constant at 0.1 mL/100 mL DCB. In the absence of MAn, the MFR of PE after reaction dropped significantly from 2000 g/10 min to several hundred grams per 10 min. The high MFR was difficult to determine but it was estimated to be between 200 and 400 g/10 min. This reduction in MFR is due to the coupling of PE• macroradicals. When 10% MAn on PE by weight was present in the initial reaction mixture, the MFR of grafted PE further dropped to about 10 g/10 min; it dropped rapidly with increasing MAn concentration. This dramatic effect of MAn on the MFR is most probably the result of the coupling reactions involving PE–MAn• [eqs. (8) and (9)]. In addition, the interpolymer polar interaction between anhydride groups in the grafted PE may play some

TABLE I
The Influence of Reaction Conditions on the Percentage of Grafting and Reaction Efficiency (under Nitrogen at 165°C)

	1	2	3	4	5
PE concentration (g/100 g DCB)	10	25	10[a]	10	10
MAn concentration (g/100 g DCB)	1	1	1	1	1
LPO concentration (mL/100 g DCB)	0.1	0.1	0.1	0.033	0.033
Reaction time (h)	2	2	2	2	1
Percentage of grafting (wt %)	4.9	2.6	6.2	4.4	2.4
Reaction efficiency	4.0	5.2	5.0	11	5.8
MFR (g/10 min)	30	81	240	30	66

[a] PE used in this case has a lower molecular weight of 2000 g/mol.

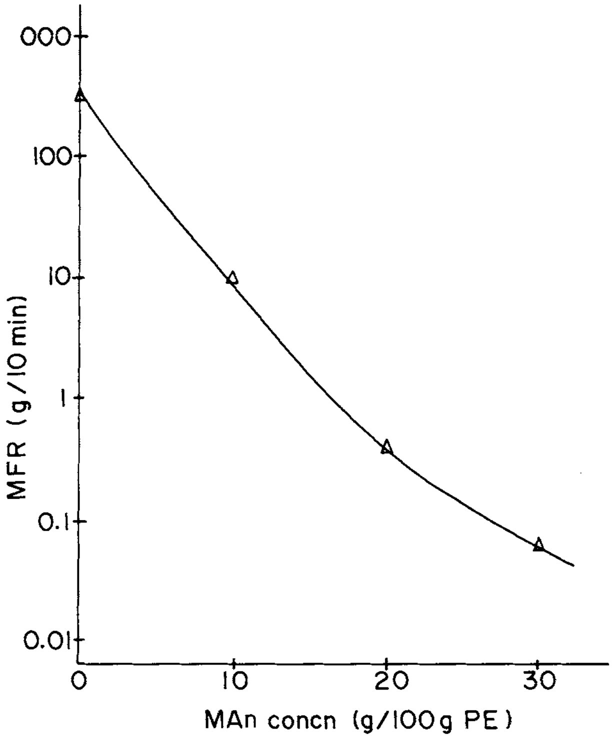


Fig. 5. MFR vs. MAn concentration. Conditions same as in Figure 4.

part in the decrease of MFR. The much lower MFR of the hydrolyzed product compared with that of the unhydrolyzed material can be ascribed to the additional interaction due to hydrogen bonding.

The influence of LPO concentration on the MFR is shown in Figure 6. The MFR of grafted PE decreases with increasing LPO concentration at low LPO concentrations; then it becomes relatively constant. On the one hand, increasing initiator concentration results in increased chances of crosslinking and grafting; on the other hand, high initiator concentration leads to low reaction efficiency and high probability of termination involving primary radicals [eqs. (5) and (6)] which will not yield crosslinking. The balance of these influences results in the slower decrease of MFR at higher initiator concentrations.

In order to find out if there is any relationship between the MFR and the percentage of grafting, the MFRs of grafted samples made under nitrogen with various reaction times and temperatures, and LPO, MAn, PE concentrations are plotted vs. their percentages of grafting in Figure 7. The MFRs are more scattered at higher percentages of grafting due to the greater influence of grafting conditions such as MAn concentration, LPO concentration, etc. There is however a clear indication that, at low percentage of grafting, the crosslinking of PE due to the presence of MAn is not serious and may be controlled by adjusting grafting conditions, e.g., by sequentially adding MAn in small amounts, keeping its concentration low.

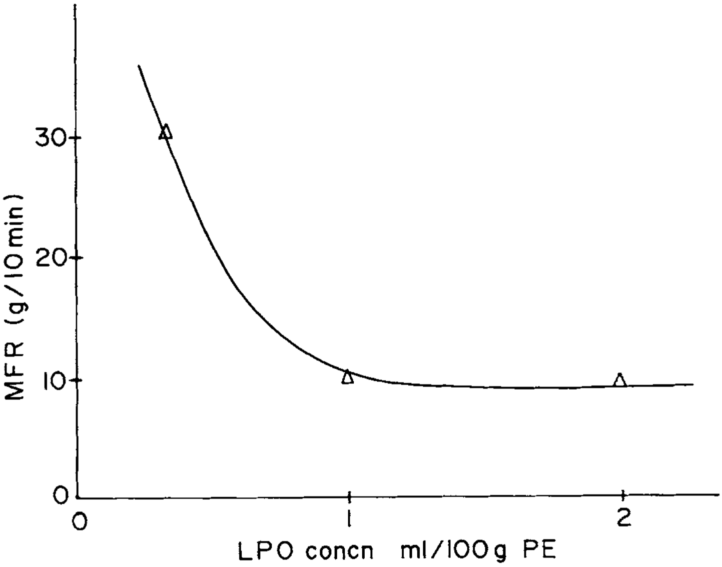


Fig. 6. MFR vs. LPO concentration. Conditions same as in Figure 3.

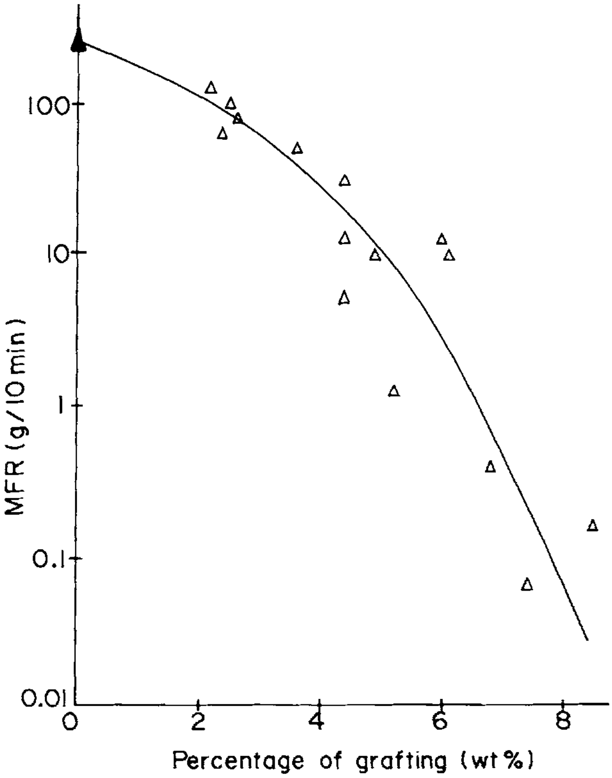


Fig. 7. MFR vs. the percentage of grafting for samples made under nitrogen.

Effect of Air on Grafting

MAn was successfully grafted to PE in air without addition of a free radical initiator. The reaction was carried out in DCB for 5 h at a MAn concentration of 1% and a PE concentration of 10% based on DCB by weight. The influence of temperature on grafting was studied (Fig. 8). Little grafting was obtained below 135°C, but when the reaction temperature was raised to 155°C, grafting took place to an extent comparable to that obtained in the presence of initiator. The percentage of grafting increased only slightly with temperature above 155°C. Initiation probably involves the formation of free radicals, and since MAn cannot be grafted on to PE at 165°C under nitrogen if no radical initiator is present, oxygen in the air must take a part in the initiation reaction.

The influences of reaction time and MAn and PE concentration on grafting were also studied (Table II). Reactions were conducted at 155°C. The percentage of grafting is proportional to the reaction time (columns 1 and 2), indicating that the grafting rate, and in turn the free radical supply rate, is almost constant during the period of reaction. Although MAn concentration does not affect the percentage of grafting much (columns 1 and 3), higher PE concentration (columns 1 and 4) improves MAn conversion significantly.

Nature of the Interpolymer Reaction in Melt Blending

The following experiments were performed to confirm that interpolymer reaction occurs during the melt blending of grafted PE and OPS. The melt coupling reaction between two reactive polymers causes an increase in molecular weight and viscosity, and this in turn is expected to be manifested by an increase in torque during mixing. Figure 9 shows the torque–time relationships for both reactive and nonreactive blends from the Haake mixer. An increase in torque

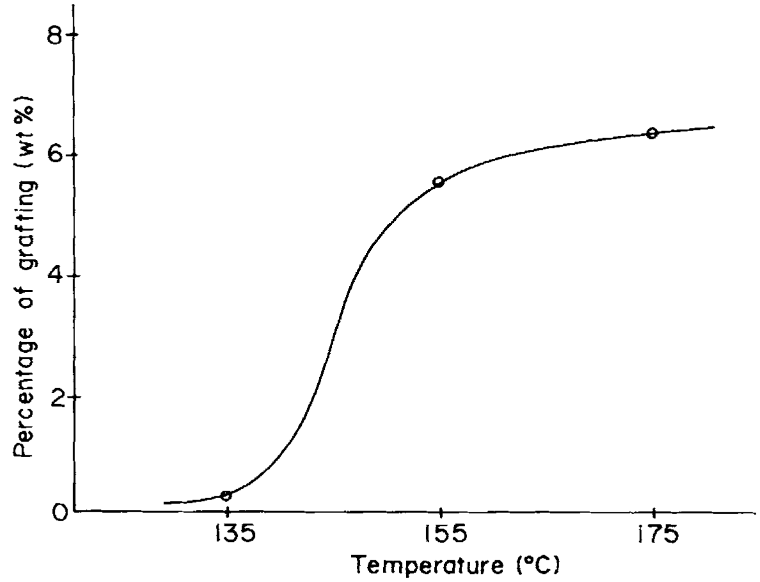


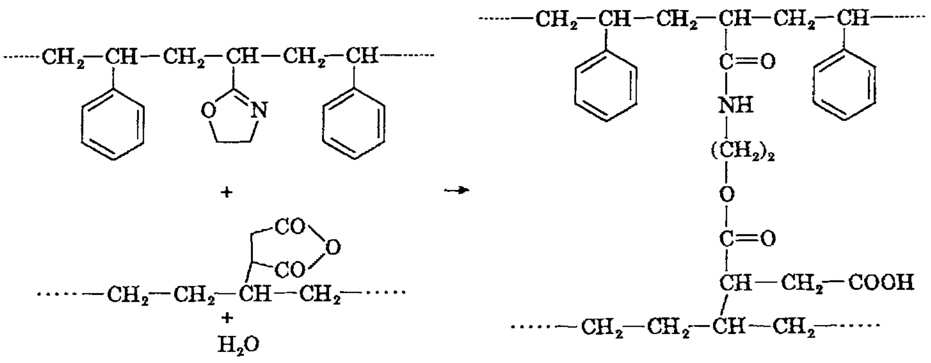
Fig. 8. The influence of temperature on the percentage of grafting in air.

TABLE II
The Influence of Reaction Conditions on the Percentage of Grafting and MAn Conversion (in Air at 155°C)

	1	2	3	4
PE concentration (g/100 g DCB)	10	10	10	25
MAn concentration (g/100 g DCB)	1	1	3	1
Reaction time (min)	300	100	300	300
Percentage of grafting (wt %)	5.5	1.4	6.5	2.9
MAn percent conversion	55	—	—	73

was observed in the reactive blends when both component polymers have functional groups but not in the corresponding nonreactive blends without functional groups in both components. This indicates the occurrence of an interpolymer coupling reaction.

The chemical structures of both nonreactive and reactive blends were investigated by FTIR spectroscopy. Figures 10 and 11 show the spectra of nonreactive blends and reactive blends respectively. The absorbance at about 3440 cm^{-1} appearing in the spectrum of reactive blends but not in that of nonreactive ones is characteristic of the N-H stretching vibration of a secondary amide. This confirms the formation of amide groups resulting from the following reaction occurring during melt blending:



The new strong peak at 1734 cm^{-1} is ascribed to the ester part of the interpolymer linkage, whereas the adjacent peak at 1713 cm^{-1} characteristic of carboxylic acid groups is the result of the opening of succinic anhydride rings of the grafted PE. On the other hand, the intensity of the oxazoline peak at 1659 cm^{-1} (shifted to 1663 cm^{-1} due to overlap with carbonyl peak) is somewhat reduced compared with that in nonreactive blends. The small absorbance at 1782 cm^{-1} arises from unreacted succinic anhydride groups.

The morphological structures of the blends were investigated by scanning electron microscopy. The micrograph of a nonreactive blend of OPS with PE [Fig. 12(a)] reveals morphology typical of an incompatible blend. The PE

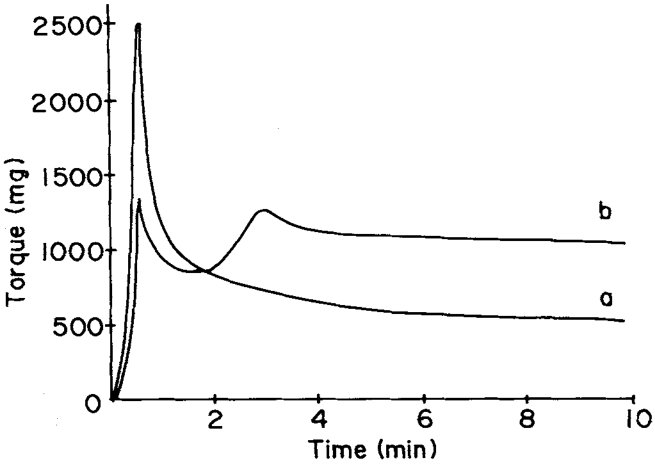


Fig. 9. Torque–time relationships for (a) nonreactive blend of OPS with PE and (b) reactive blend of OPS with grafted PE.

dispersed domain has a well-defined shape. On the other hand, the micrograph of the reactive blend of OPS with grafted PE [Fig. 12(b)] shows a very different morphology. There is a fine and uniform dispersion with no precise shape and size of domains. All this suggests that there is very good adhesion between the two phases, and it is the result of interpolymer reaction. This reinforces the FTIR and torque evidence for the reaction.

The reaction is fast and may be over in 3 min as indicated on the torque–time curves during blending. This was proved by studying the SEM micrographs

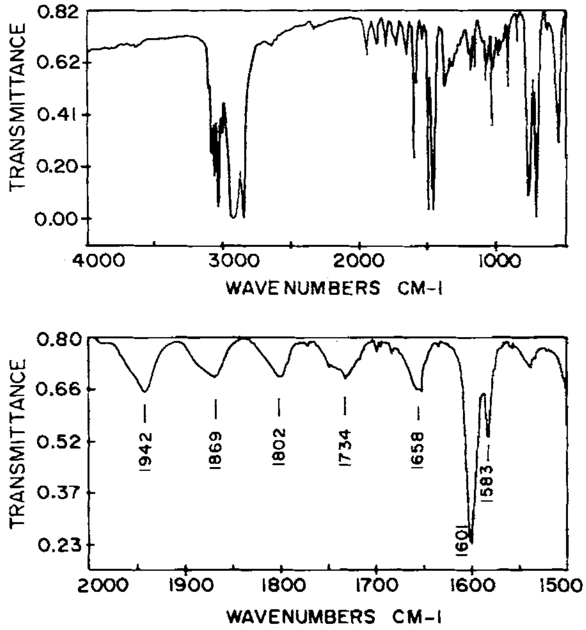


Fig. 10. FT-IR spectra of nonreactive blends of OPS with PE.

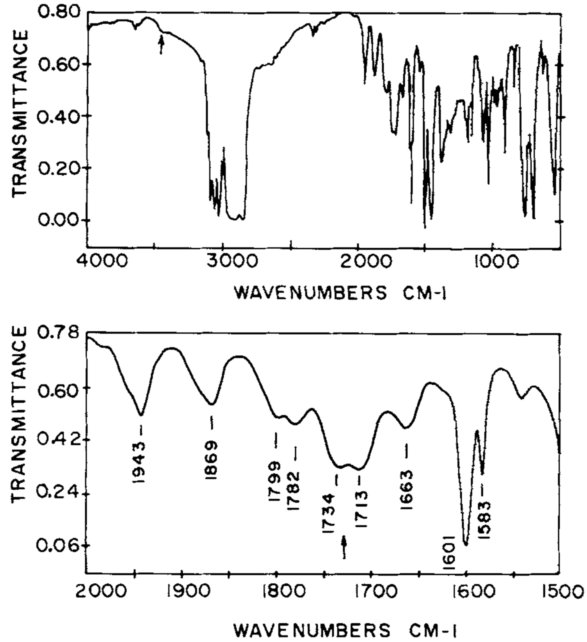


Fig. 11. FT-IR spectra of reactive blends of OPS with grafted PE.

of the blends mixed for only 3 min; no significant difference was observed between them and those obtained for the blends mixed for 15 min. This is in contrast to earlier studies[1] in which the polyethylene had reactive carboxylic acid groups in place of the succinic anhydride and the reaction rates were slower.

CONCLUSIONS

1. Maleic anhydride can be grafted onto polyethylenes at high temperatures in homogeneous media. The grafting takes place both in air without free radical initiator at temperatures above 155°C and under nitrogen in the presence of initiators.
2. Succinic anhydride rings are individually attached to the polyethylene backbone.
3. Crosslinking of polyethylene occurs in all cases studied. However, it is dramatically increased by the presence of maleic anhydride. The maleic anhydride concentration is the most important parameter affecting crosslinking. When the percentage of grafting does not exceed 2% by weight, the crosslinking is not serious and can be controlled.
4. Interpolymer reaction takes place during the melt blending of polystyrene having oxazoline groups and polyethylene containing succinic anhydride functionality. The reaction is fast and it results in greatly improved compatibility of polystyrene with polyethylene.

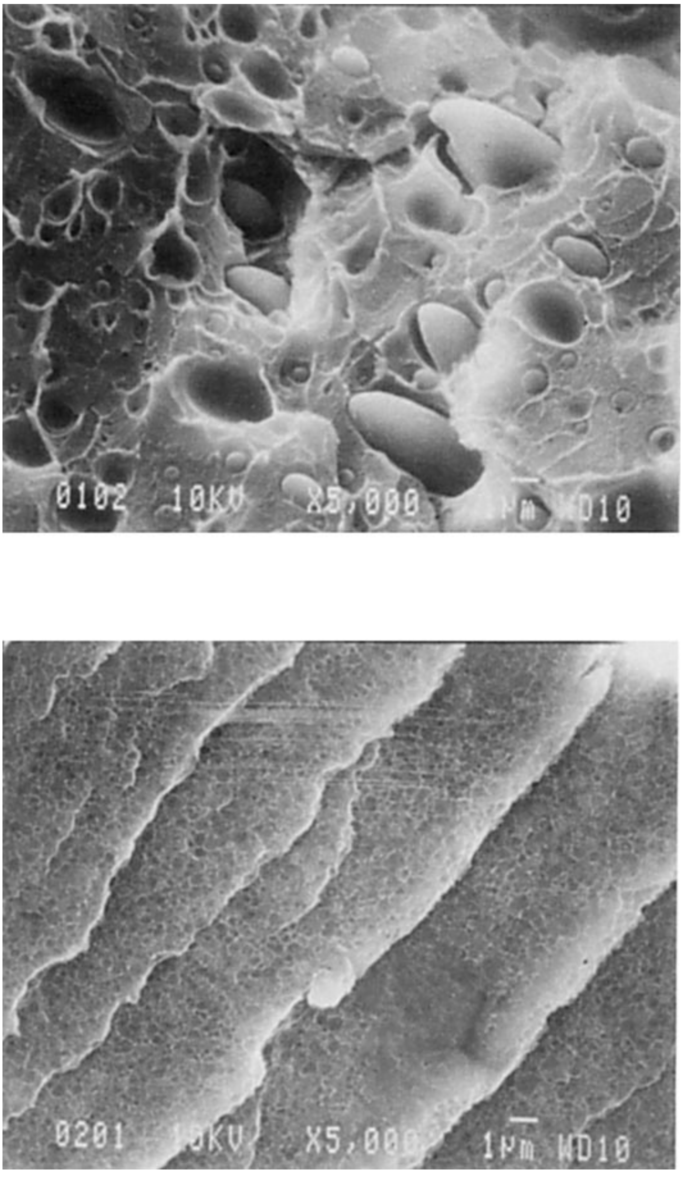


Fig. 12. Scanning electron micrographs of (a) nonreactive blend of OPS with PE and (b) reactive blend of OPS with grafted PE.

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