

Grafting Maleic Anhydride and Comonomers onto Polyethylene

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SYNOPSIS

Grafting dicarboxylic anhydrides onto polyolefins has great practical importance. The process of grafting maleic anhydride onto high-density polyethylene in the presence of various comonomers in an intermeshing corotating twin-screw extruders was studied. Three types of comonomers were investigated: (i) vinyl monomers, including styrene and methacrylic acid; (ii) esters of dicarboxylic acids forming succinic groups after grafting, such as fumaric acid; and (iii) esters of fumaric and maleic acid and ethylenically unsaturated cyclic dicarboxylic anhydrides, such as Diels–Alder adducts of maleic anhydride; and (iv) dienes and dodeceny succinic anhydride. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

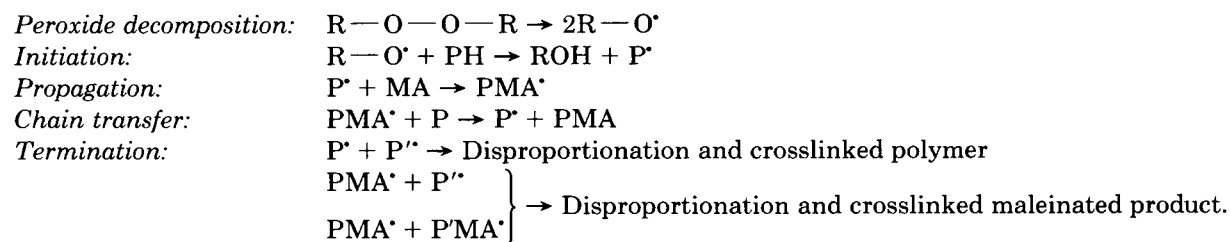
Efforts to modify polyolefins with peroxides and combinations of peroxides with a second monomer have been in progress since the 1960s.^{1–5} Most attention has been given to peroxide grafting of maleic anhydride, which has been found to be a successful compatibilizing agent in blends of polyolefins and polyamides.^{6,7}

In the present article, we turn our attention to grafting mixtures of maleic anhydride and second monomers onto polyolefins. The reasons for grafting a second monomer with maleic anhydride onto polymer backbones are that maleic anhydride has a low reactivity with itself and its graft onto polymer

backbones generally has only one maleic anhydride unit and the maleation reaction brings about termination, leading to crosslinking and/or gel forming in the grafted material. Studies of this type seem to have initially been made by Gaylord,^{8,9} but there has been little subsequent study. This type of process was considered more recently by Wong¹⁰ and by Lambla.¹¹

BACKGROUND OF GRAFT POLYMERIZATION MECHANISM

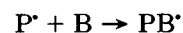
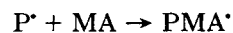
The grafting mechanism of maleic anhydride (MA) onto a polymer backbone with peroxide initiation would involve a mechanism:



With polyethylene, crosslinking is dominant. With

polypropylene, disproportionation and degradation of P^{\bullet} occurs.

If a second monomer, B, is introduced, the propagation step is modified to



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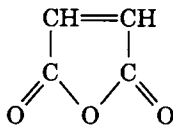
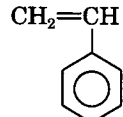
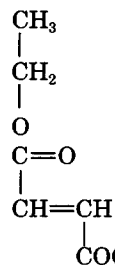
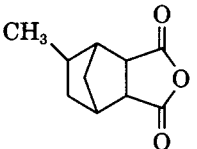
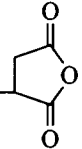
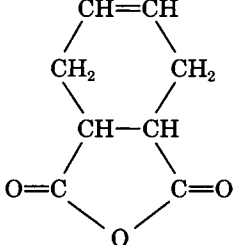
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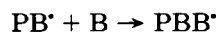
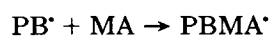
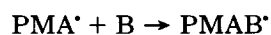
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Table I Monomers Used in This Study

Name	Abbreviation	Structure
Maleic anhydride	MA	
Styrene	S	
Acrylic acid	AA	$\text{CH}_2=\text{CH}-\text{COOH}$
Fumaric acid	FA	$\text{COOH}-\text{CH}=\text{CH}-\text{COOH}$
Monoethyl fumarate	MF	
Dimethyl maleinate	DMM	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$
Methyl nadic anhydride	MNA	
Dodecyl succinic anhydride	DSA	$\text{CH}_3-(\text{CH}_2)_9-\text{CH}=\text{CH}-$ 
Tetrahydrophthalic anhydride	THPA	



Long PB_n and $\text{P}(\text{MA})_m \text{B}_{m-n}$ grafted chains may form sites for chain transfer and chain termination

as they involve PB^* - and PMAB^* -type radicals. In termination reactions, P^* , PMA^* , PBMA^* , and PMAB^* radicals are present. These radicals determine the characteristics of the final, stable molecules. If recombination is dominant, crosslinked products can be expected. If disproportionation or some other type of deactivation is the main reaction,



Figure 1 Screw configuration of modular corotating twin-screw extruder.

the original structure of the initial linear polyethylene (PE) chains is restored. If the propagation results in long growths of the side chain, the resulting molecules will have relatively long polar side chains. If this growth is hindered by steric and chain-transfer effects, many small side groups will be formed on the main PE chain.

From the above, one may see that the type and the quantity of comonomers used together with MA in grafting reactions have a determining role in the architecture of the resulting product. It was the purpose of this article to investigate this effect.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) experimental powder was supplied by Tosoh has a density of 0.963 g/cm³ and an MFI of 20 was used in our experiments. The peroxides were 2,5-dimethyl, 2,5-di(*t*-butylperoxy)hexane (Trigonox 101, AKZO Chemicals) and Lupersol 101 AtoChem).

The following monomers were investigated:

Maleic anhydride (Nippon Oil and Fat Co.)
Styrene (99%) (Aldrich)

Fumaric acid (Aldrich)
Monoethyl fumarate (Aldrich)
Dimethyl maleate (Aldrich)
Tetrahydrophthalic anhydride (Anhydrides and Chemicals Inc.)
Methyl nadic anhydride (Buffalo Color Corp.)
Dodecyl succinic anhydride (Buffalo Color Corp.).

These monomers are summarized in Table I. The solvents were *m*-xylene, acetone (reagent grade), and hexane from Aldrich and anhydrous ethanol from Quantum Chemical Co.

Apparatus

Model experiments were carried out in a Haake Rheocord laboratory batch internal mixer. The experimental procedures are as in our earlier experiments. The temperature was 180°C, and the rotor speed, 50 rpm.

A Labotex 30 twin-screw extruder (Japan Steel Works) was used in some experiments. This was used in an corotating intermeshing mode with the screw configuration shown in Figure 1. The modular screw contains three sets of kneading disc blocks. The feed rate of the polymer powder mixture was 5 kg/h and a screw rpm of 50 was used. The residence time under these conditions was approximately 200

THE FT-IR CALIBRATION CURVE OF MALEATED POLYETHYLENE

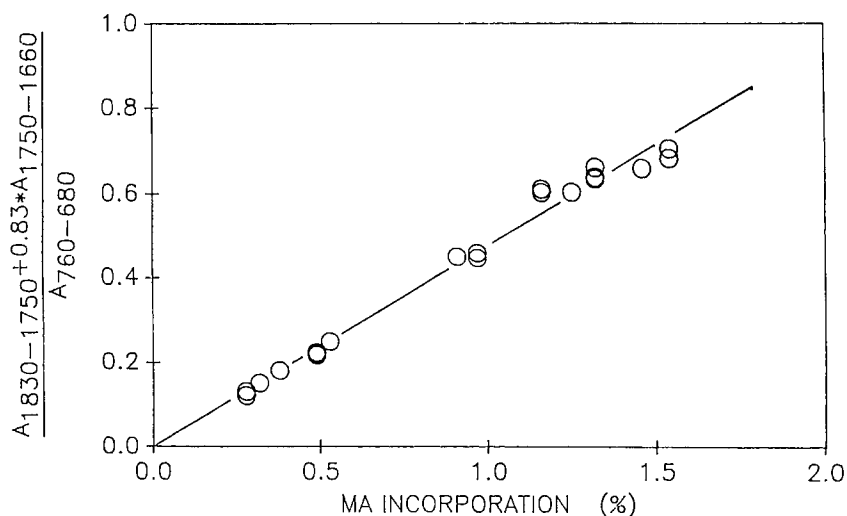


Figure 2 Calibration curve for determining the incorporated MA content from the FTIR spectrum.

The FT-IR spectrum of sample grafted by pure DMM

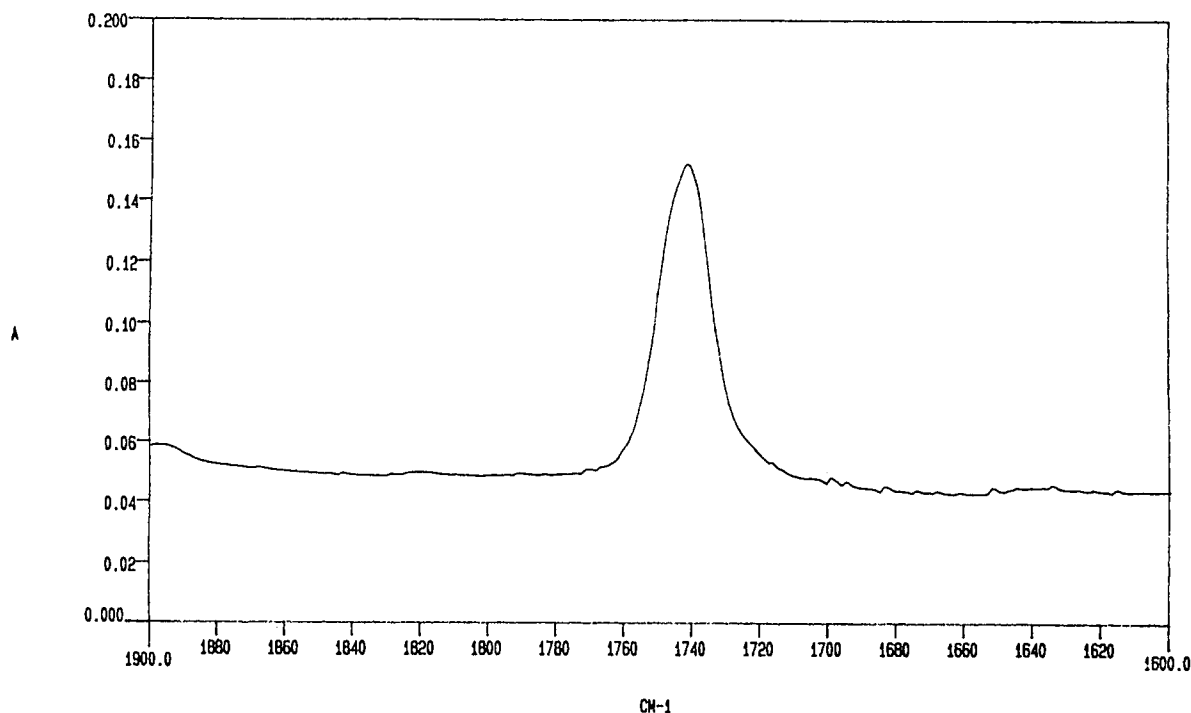


Figure 3 FTIR spectrum of DMM-grafted PE.

s. The temperatures set along the extruder barrel were 140 (port) and 140, 140, 180, 200, 200, 200, and 200°C (die). The polymer and the other ingredients were premixed for 1 h in a tumbler and fed by an AccuRate volumetric feeder.

Characterization

MA contents and shear viscosities were measured on the grafted PE. The shear viscosity of the initial and grafted PEs were measured using an Instron capillary rheometer, using a capillary of 0.6 mm diameter and L/D of 30. Melt flow indices were estimated from shear viscosities.

The MA content was determined by Fourier transform infrared (FTIR) spectroscopy. The samples were prepared using a Carver laboratory press at 180°C with 10 tons force between alumina sheets to form films of 80–10 μm . The spectrum was recorded in the region of 2000–440 μm^{-1} . The peaks between 1830–1750 and 1750–1660 μm^{-1} were analyzed, while the peak in the region of 160–680 was used as the internal standard. The incorporated MA content was then calculated from the integrated absorbances as follows:

$$\% \text{ MA} = 211 \frac{A_{1830} + 0.83A_{1750-1660}}{A_{760-680}} \quad (1)$$

The calibration curve for the determination is shown in Figure 2.

RESULTS

Dimethyl Maleate (DMM)

We made experiments with DMM both in an internal mixer and in the twin-screw extruder. In the internal mixer, 0.07% Trigonox 101 and 2% DMM was used with HDPE at 180°C for 14 min at 50 rpm in preliminary experiments. The FTIR spectrum indicated a considerable amount of DMM incorporated.

Experiments were carried out with DMM in a twin-screw extruder using 0.15% Lupersol 101 and 2.9% DMM. DMM, 0.8%, was incorporated. The FTIR spectrum is seen in Figure 3.

DMM and MA in a 1 : 2 molar ratio were used for grafting in the twin-screw extruder with 0.15% Lupersol 101. Studying the FTIR spectrum, it was

The FT-IR spectrum of sample grafted by MA:DMM = 2:1 molar ratio mixture

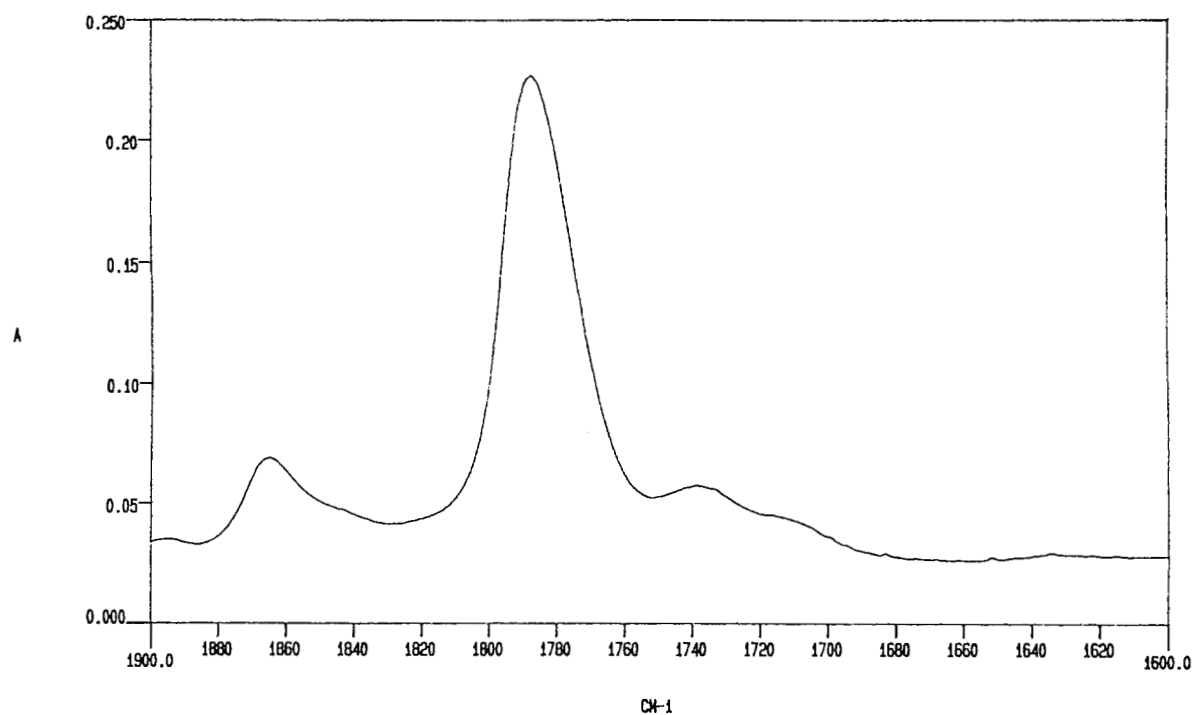


Figure 4 FTIR spectrum of DMM/MA-grafted PE.

The FT-IR spectrum of sample grafted by fumaric acid

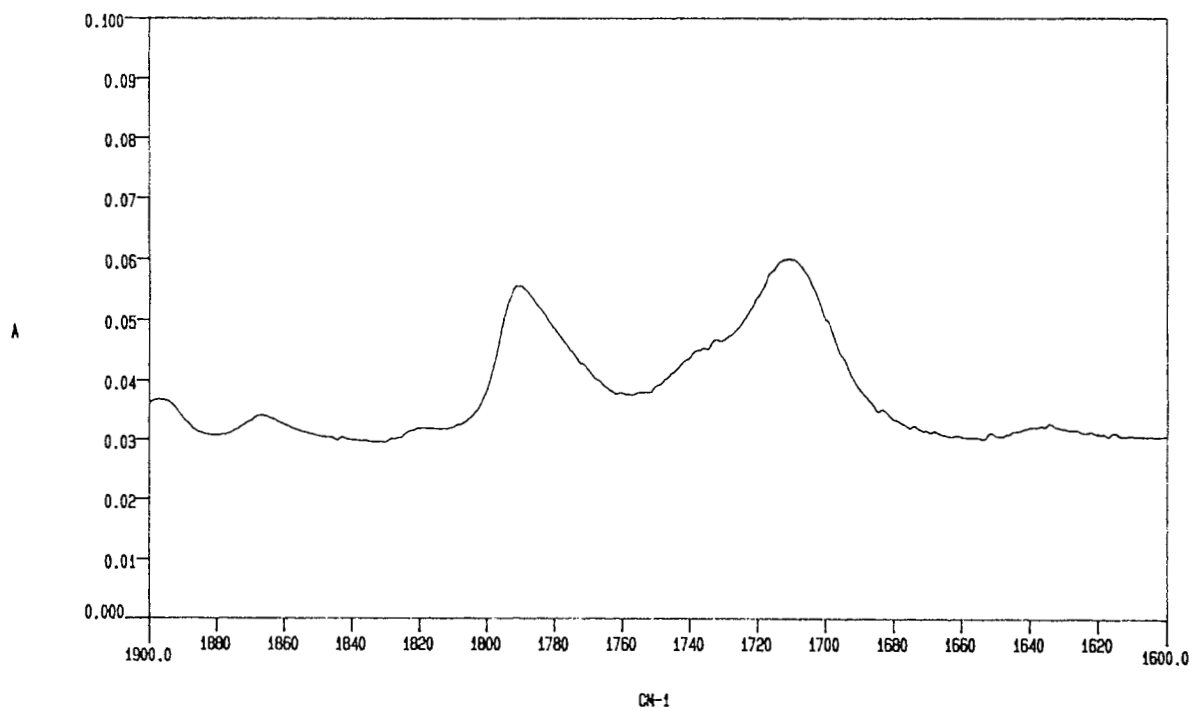


Figure 5 FTIR spectrum of FA-grafted PE.

The FT-IR spectrum of sample grafted by MA:FA = 2:1 molar ratio mixture

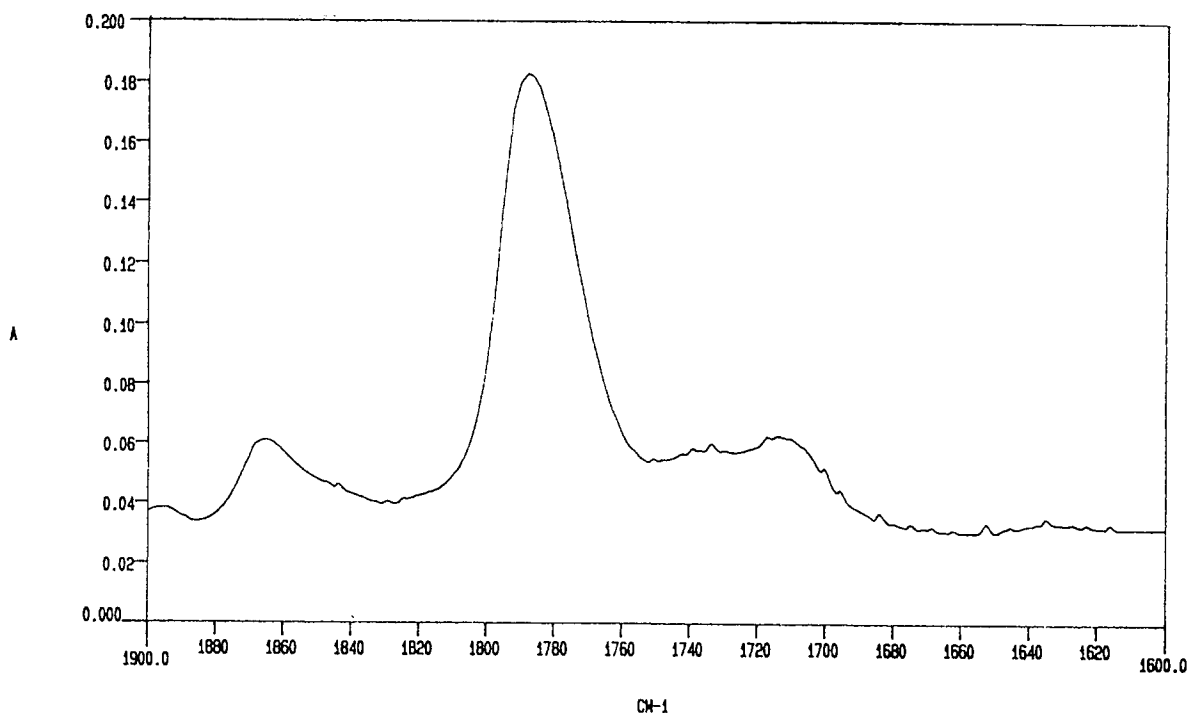


Figure 6 FTIR spectrum of FA/MA-grafted PE.

found that only MA was incorporated at high levels. DMM seems to have little effect. MA, 1.55%, was incorporated. The shear viscosity rose from 400 to 1560 Pa-s. The FTIR spectrum is seen in Figure 4.

Fumaric Acid (FA) and Monoethyl Fumarate (MEF)

Experiments were made on the twin-screw extruder to graft FA on HDPE using 2.3% FA and 0.15% Lupersol 101. FA, 0.6%, was incorporated as determined from FTIR. The spectrum is shown in Figure 5. FA and MA, in a 1 : 2 molar ratio, were reacted with HDPE using 0.15% Lupersol 101; 1.18% MA equivalent carboxyl groups were incorporated. The shear viscosity was 1542 Pa-s. The FTIR spectrum is shown in Figure 6.

MEF in a concentration of 2.9% was grafted using Lupersol 101 (0.15%) onto HDPE in the twin-screw extruder; 1.38 wt % was incorporated. (See the FTIR spectrum in Fig. 7.) MEF and MA, in a 1 : 2 molar ratio, were reacted with HDPE using the same amount of peroxide. An MA equivalent dicarboxylic group, 0.96%, was incorporated. The shear viscosity increased from 400 to 1602 Pa-s. The FTIR spectrum is shown in Figure 8.

Ethylenically Unsaturated Cyclic Dicarboxylic Anhydrides

We made grafting experiments with dodecyl succinic anhydride (DSA), tetrahydrophthalic acid (THDA), and methyl nadic anhydride (MNA).

Tetrahydrophthalic Anhydride

Table II summarizes the experimental results in grafting THPA and THPA/MA mixtures. Lupersol 101, 0.15%, was used in each case.

Methyl Nadic Anhydride

Table III summarizes the experiments and results made with MNA and MNA-MA mixtures. Lupersol 101, 0.15%, was used in each case.

Dodecyl Succinic Anhydride

Grafting experiments were made both with pure DSA and MA/DSA mixtures using 0.15% peroxide. The results are summarized in Table III.

The FT-IR spectrum of sample grafted by monoethyl fumarate

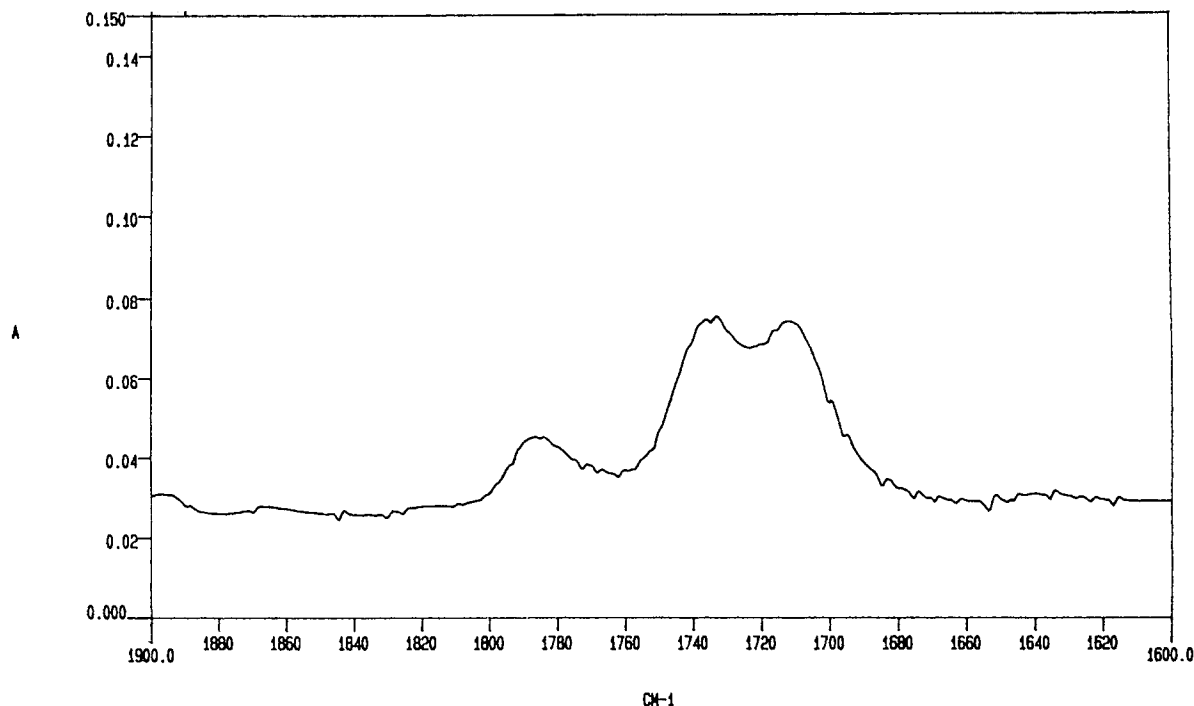


Figure 7 FTIR spectrum of MEF-grafted PE.

Vinyl Monomers

The kinetic chain length of the polymerization can be increased by using comonomers alternately copolymerizing with MA. The most common monomers of this type are vinyl monomers, such as styrene and acrylic and methacrylic acids. Using these comonomers, not only the kinetic chain length, but also the length of the side chain, can be increased. In Figure 9, the results for grafting MA and styrene, MA and methacrylic acid, and MA and acrylic acid in equimolar quantities on PE are represented. It can be seen that the maximal torque in the Haake mixer, which reflects on the crosslinking reactions, is much less than in the case of grafting pure MA. In Figure 10, the MA incorporation is seen as a function of % peroxide using equimolar MA/comonomer mixes in grafting in the twin-screw extruder. It is seen that the same amount of peroxide results in much higher MA incorporation if a comonomer is used.

DISCUSSION: COMPARISON OF DIFFERENT MONOMERS

It is well known that MA itself grafts on PE with significant levels of conversion,^{2-5,8} but the termi-

nation brings about a highly crosslinked product and increase of melt viscosity. Steric hinderance might affect both propagation and termination reactions. Fumaric acid, monoethyl fumarate, and dimethylmaleate were supposed to exhibit steric hinderance because of the molecular configuration and pendant esterified groups. Among the materials examined, only monoethyl fumarate was incorporated in an amount of greater than 1%, meaning a conversion of 47%. Even this level of conversion is much less than the usual grafting conversion of MA (~ 70%). If mixtures of fumaric and maleic acid with MA are compared, the following conclusions can be drawn: Comparing the IR spectra of the materials obtained with pure comonomer and equimolar mixtures, it is seen that the main component of the incorporated material is MA (see Figs. 3-8). The only case when the incorporated MA and comonomer quantities are comparable is monoethyl fumarate. The increase of incorporated monomers was accompanied in each case with increasing viscosity, reflecting on the effect of the comonomer on crosslink formation. Now, let us turn our attention to the ethylenically unsaturated cyclic dicarboxylic anhydrides.

In Figure 11, the conversion (incorporated/initial anhydride content) is plotted as a function

The FT-IR spectrum of sample grafted by MA:MEF = 2:1 molar ratio mixture

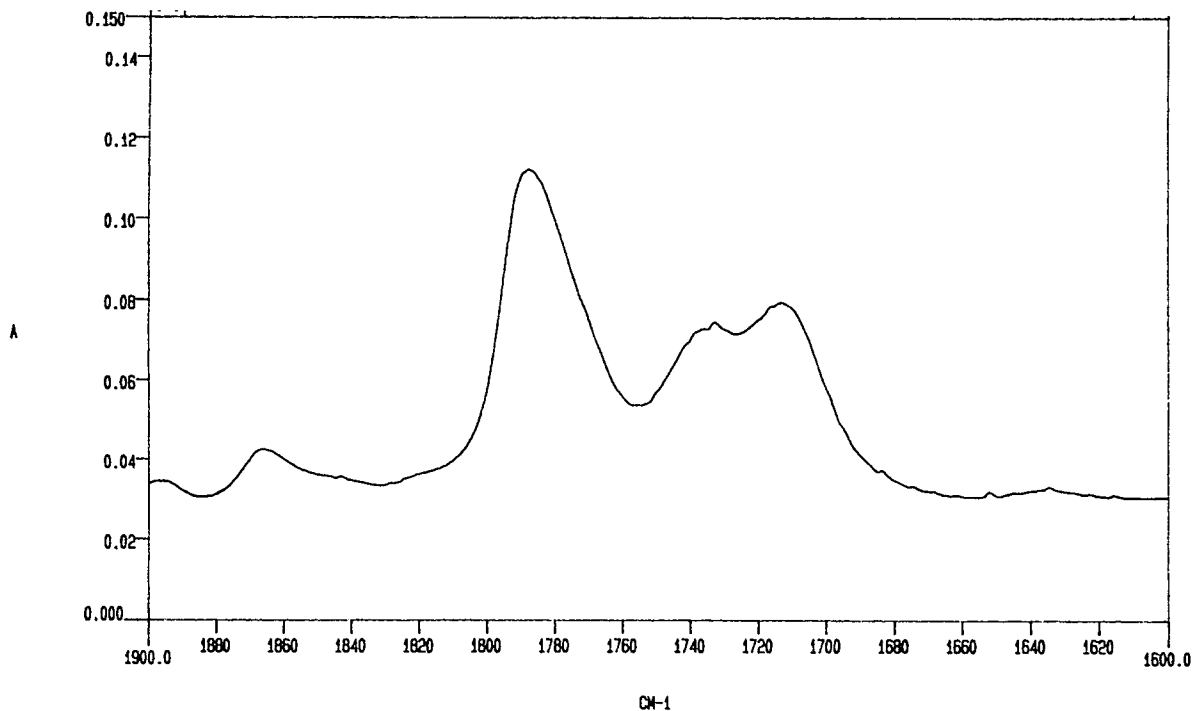


Figure 8 FTIR spectrum of MEF/MA-grafted PE.

of the MA/THPA molar ratio in the initial mix. According to this plot, THPA has little tendency to graft onto HDPE and inhibits the incorporation of MA. Even a small amount of THPA in the system (0.13 MA equivalent %) causes a drop in MA incorporation. Usually, MA incorporation using this peroxide content and temperature the MA incorporation is higher than 1.5%,¹² but the viscosity increase is considerable. (The viscosity of the initial HDPE was 430 Pa-s.)

It can be supposed that THPA reacts with MA and thus peroxide has little effectiveness in grafting. The efficiency is unchanged in crosslinking reactions.

Our results are in accordance with the data of Wu et al.¹² In his experiments, 10 phr THPA and 3 phr peroxide were used at a higher temperature, with 0.5% THPA incorporation (~ 5% of the initial amount), and a 30-fold decrease of MFI was found.

Table II Grafting Tetrahydronaphthalic Anhydride (THPA) onto PE

THPA (%)	MA Equivalent THPA (%)	MA (%)	MA Equivalent Anhydride (%)	Viscosity (Pa-s)
0.2	0.13	2	1.11	1782
0.5	0.32	2	0.8	1702
1.0	0.65	2	1.05	1602
1.5	0.96	2	1.26	1762
2.0	1.29	2	0.77	1242
3.12	2.01	0	0.07	741

Table III Grafting Methyl Nadic Anhydride (MNA) onto PE

MNA (%)	MA Equivalent MNA (%)	MA (%)	MA Equivalent Anhydride (%)	Viscosity (Pa-s)
0.25	0.14	2	1.48	1462
0.64	0.35	2	1.78	1842
1.27	0.70	2	1.52	1682
1.91	1.05	2	1.18	1402
4.06	2.23	2	1.39	1402
4.06	2.23	0	0.38	781

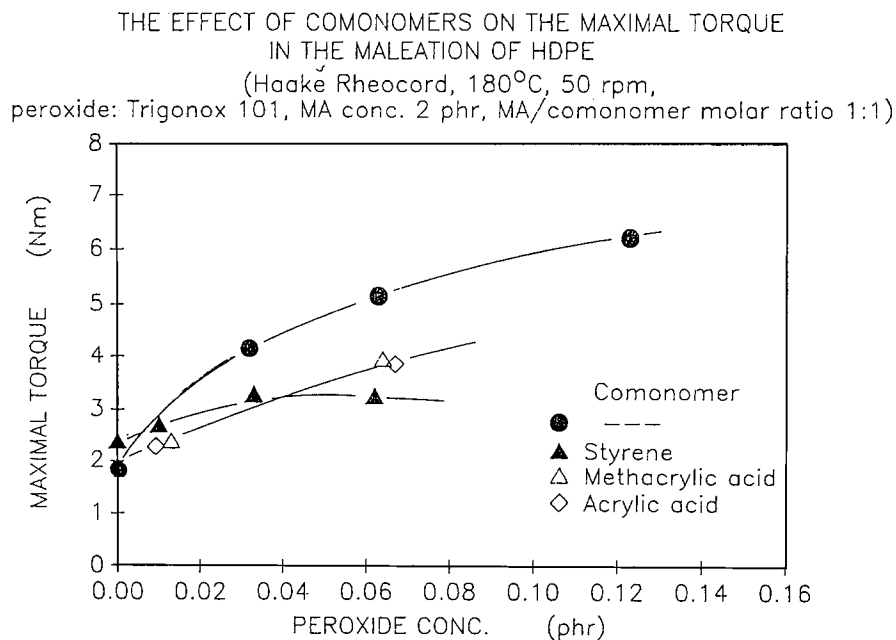


Figure 9 Maximal torque in Haake mixer as a function of peroxide concentration in grafting MA with vinyl comonomers.

In Figure 12, the conversion of the initial anhydride is shown as a function of the molar ratio, MA/MNA. It is seen that MNA is grafted in a relatively high proportion alone, but as the MA content was increased in the initial mix, the conversion also increased. We now consider the next viscosity. It can be seen that a fair amount of anhydride incorporation did not cause total loss of processability. It had

only a weak tendency for inhibiting crosslinking reactions.

If the grafting efficiency of MNA and THPA is compared, it can be seen that the anhydride incorporation from the pure anhydride is four times higher in the case of MNA than of THPA. Seventeen percent conversion of pure MNA was found, and this value is comparable to that published by Wu et

COMPARISON OF MALEIC ANHYDRIDE GRAFTING ONTO POLYETHYLENE
WITH AND WITHOUT COMONOMER

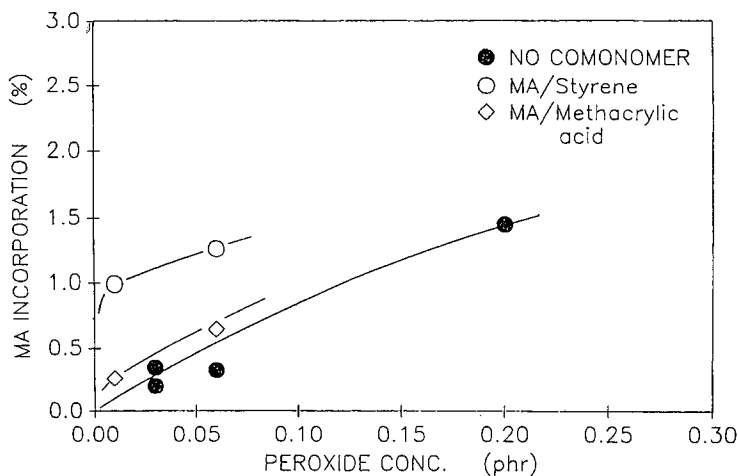


Figure 10 MA incorporation as a function of peroxide concentration in grafting MA with vinyl comonomers.

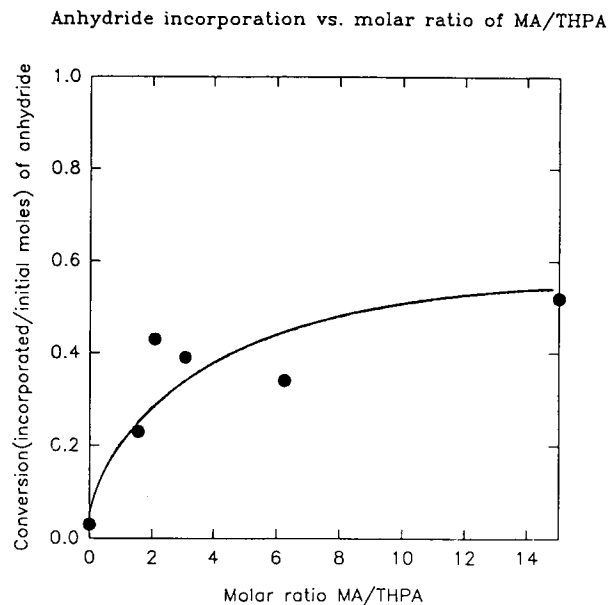


Figure 11 Conversion of anhydride as a function of MA/THPA molar ratio.

al.¹² However, while in the patent of Wu et al. a 20-fold decrease of MFI was reported, in our case, the estimated viscosity value was about 2.5 times less than that of the initial polymer.

When MA and MNA were used together, the crosslinking was moderate in comparison with the relevant values for THPA. If DSA is grafted alone, the incorporation is very low, and there is no increase, but rather a decrease of viscosity. The reason is probably that DSA has a very little tendency to

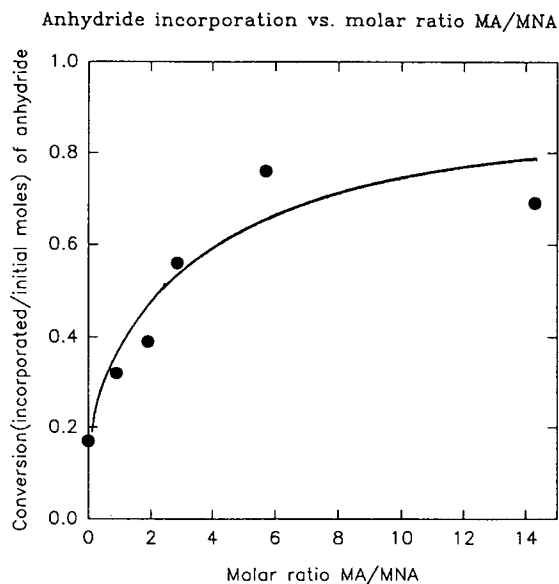


Figure 12 Conversion of anhydride as a function of MA/MNA molar ratio.

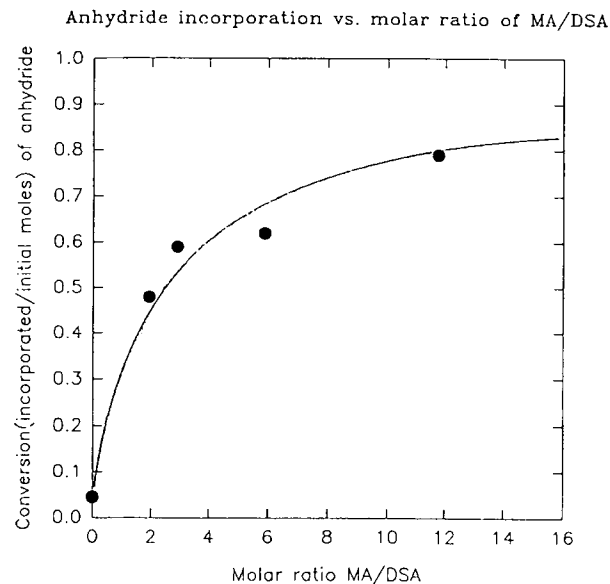


Figure 13 Conversion of anhydride as a function of MA/DSA molar ratio.

graft onto PE, but might react with peroxide. The DSA molecules undergo scission or react with another DSA molecule and the resulting molecules behave as an internal softener, decreasing the viscosity.

The dependence of MFI of carboxyl group incorporation when comonomers are used in maleation of HDPE

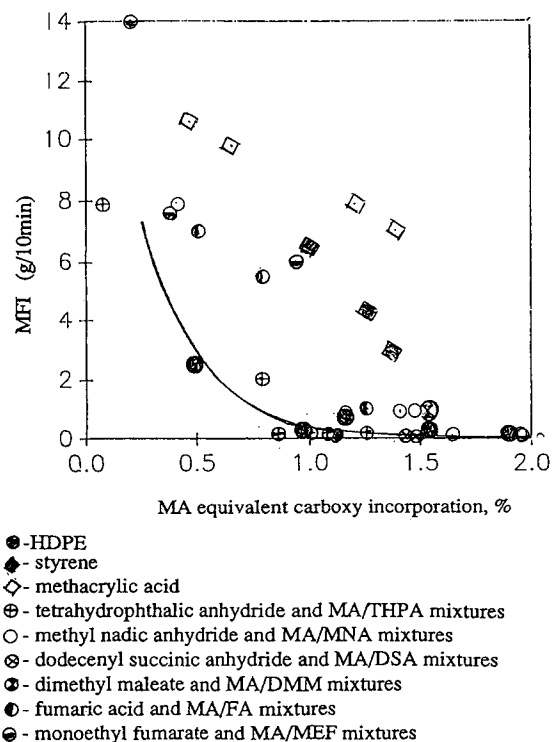


Figure 14 MFI as function of MA incorporation.

If DSA and MA are used together, the MA incorporation shows only a small dependence on DSA content, and the crosslinking reactions are considerable. In Figure 13, the conversion of the initial anhydride is plotted as a function of the MA/DSA molar ratio in the initial mixture. It can be seen that a conversion of about 0.6 is reached already if the MA/DSA ratio is < 2 and reaches a value of 0.7 when almost pure MA is in the system. The incorporated anhydride values in Table IV are similar to those that can be obtained in grafting pure MA under similar circumstances, if the MA/DSA ratio is greater than 2.

Vinyl comonomers in an equimolar ratio form long alternating side groups on a PE chain, which is understandable on the basis of the reactivity ratios.¹³ Thus, these comonomers can be well grafted together with MA without extensive increases of viscosity.

Figure 14 is given to summarize the results on grafting MA onto PE together with comonomers. The figure shows the relation of the MFI values and the incorporated carboxylic groups. From the figure it can be seen that vinyl comonomers are the most effective in increasing the molecular mass of the grafted HDPE. In this case, the kinetic chain length is high; a considerable amount of MA can polymerize onto the PE chain without a great probability of recombination.

The esters of maleic and fumaric acid should show steric hinderance characteristics in recombination reactions. Monoethyl fumarate grafts onto PE with nearly the same probability as does MA, but it cannot prevent crosslinking reactions.

Ethylenically unsaturated cyclic dicarboxylic anhydrides show much less tendency to graft onto PE,

than does MA, especially if the unsaturation takes place on a long aliphatic chain. Somewhat greater is the affinity for grafting of Diels–Alder adducts of MA with conjugated dienes, but much less than that of MA. Extensive crosslinking was found to be somewhat less only in case of methyl nadic anhydride.

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