One-Step Functionalization of an Ethylene/Propylene Random Copolymer with Two Different Reactive Groups

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ABSTRACT: The efficiency of a macromolecular compatibilizer for reactive blending is strongly dependent on its potentiality of producing a grafted or block copolymer during processing. For the preparation of such a compatibilizer, the grafting of two different reactive groups onto the backbones of ethylene/propylene copolymer macromolecules was performed. The ethylene/propylene (70/30) copolymer was then processed in a Brabender mixer at 190°C in the presence of a mixture of maleic anhydride and diethylmaleate with either dicumyl peroxide or di-*tert*-butyl peroxide as an initiator. The experiments clearly showed that the two functionalities, 2-diethyl succinate and 2-succinic anhydride, could be grafted in one step. The effect of the feed composition demonstrated that the two monomers influenced the reciprocal reactivity and the resulting product. A detailed Fourier transform infrared analysis of the grafted macromolecules was performed, and the respective amounts of ester and anhydride derived groups were detected by deconvolution of the vibrational bands in the carbonyl spectral region. The validity of the process on an industrial scale was tested by the successful performance of the reaction in a twin-screw extruder. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 14–23, 2003

Key words: functionalization of polymers; polyolefins; FT-IR; extrusion

INTRODUCTION

Different monoalkene polymers (polyolefins) bearing either 2-succinic anhydride (SA)[1,2] or 2-dialkyl succinate[3] grafted groups were successfully used to compatibilize polyolefins with polyamides through reactive processing.

These studies indicated that the performances of the compatibilizers could be affected significantly by the structure of the polyolefin and the nature and concentration of the grafted functionalities.[4–8] Moreover, the properties of functionalized polyolefins depend on the distributions of functional groups on the backbones of the polymers and on the occurrence of secondary reactions such as crosslinking and degradation. Free-radical-induced grafting has been used to obtain maleic anhydride (MAH)-modified polyolefins in many laboratories.[9,10] In our laboratory, diethylmaleate (DEM) was used as a grafting monomer because of its better stability, the well-defined structure of its grafted groups, and its easy handling as a liquid.[11] A detailed study of grafting under different conditions and with various structures of the functionalized macromolecules was performed.[12,13] Also, a kinetic investigation allowed a mechanistic description of the complex system of occurring reactions and a proposal for a mathematical model consistent with the experimental data.[14]

On this basis, we report the preparation of a more flexible and efficient compatibilizer with two different functional groups grafted onto polyolefin macromolecules. A simplified preparative route is described that is based on the one-step reaction of ethylene/propylene rubber (EPR) in bulk with mixtures of MAH and DEM in a Brabender mixer to graft in one step both 2-diethyl succinate (DES) and succinic anhydride (SAH) groups (Scheme 1). The effects of different peroxides and feed compositions were evaluated, and the structures and concentrations of various functional groups grafted onto the polymer were detected with a Fourier transform infrared (FTIR) analysis.

EXPERIMENTAL

Materials

EPR-CO-038 (28 wt % propylene), supplied by Enichem Elastomeri (Milan, Italy), had a melt-flow index (MFI) of 0.5, a weight of 5 kg (ASTM D 1238), a
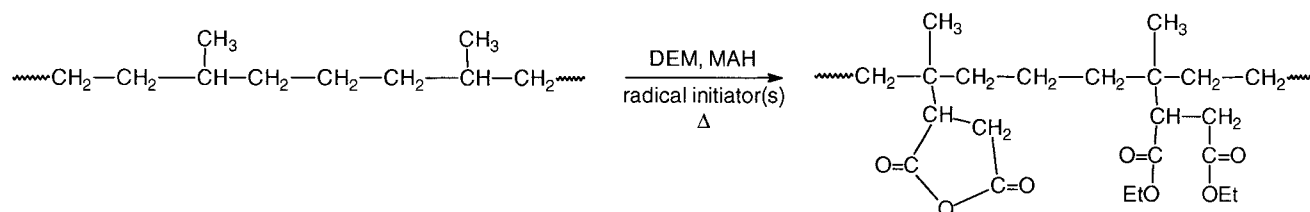
Scheme 1

weight-average molecular weight (M_w) of 205,000, a number-average molecular weight (M_n) of 67,800, and less than 1 wt % material that was extractable with acetone (see run 1 in Table I); it was used without purification. Powdered high-density polyethylene (HDPE) was supplied by Enichem Elastomeri and used without purification. DEM (Aldrich, Milwaukee, WI) was distilled under reduced pressure (45°C at 0.2 mmHg). MAH (Aldrich) was purified by recrystallization from benzene (Carlo Erba, Milan, Italy), which was purified by distillation over Na and K. Dicumyl peroxide (DCP; Aldrich), di-*tert*-butyl peroxide (TBP; Aldrich), acetone (Carlo Erba), and toluene (Carlo Erba) were used without further purification. Poly(di-

ethyl fumarate) (PDEF) was prepared by free-radical polymerization (azobisisobutyronitrile) as reported in the literature.[15]

Functionalization

The functionalization reactions were performed in a Brabender Plastigraph mixer equipped with a 30-mL mixing room and in an ICMA 110 twin-screw extruder (length/diameter = 40, diameter = 110 mm).

In the former case, the polymer (20 g) was introduced to the mixer under a nitrogen atmosphere at 190°C; after 3 min, a mixture of the monomers and radical initiators was added. The reaction was carried

TABLE I
FD and Solvent Fractionation of EPR Reacted with DEM and MAH and Peroxides in the Brabender Mixer

|	Feed composition		Functionalized polymer				
Run[a]	DEM/MAH (mol/mol)	DCP/TBP (mol/mol)	Acetone-soluble (wt %)	Toluene-soluble (wt %)	Residue (wt %)	FD(DEM) (mol %)	FD(MAH) (mol %)
1EPR	—/—	—/—	1.0	99.0	—	—	—
2EPRC	—/—	0.12/—	0.9	89.1	10.0	—	—
3EPRT	—/—	—/0.12	0.6	80.4	19.0	—	—
4M(1.2)C	—/1.2	0.12/—	0.4	50.2	49.4	—	0.41
5M(2.4)C	—/2.4	0.12/—	0.4	44.8	54.8	—	0.67
6M(8.0)C	—/8.0	0.12/—	7.4	39.8	52.8	—	0.77
7M(1.2)T	—/1.2	—/0.12	0.7	43.4	55.9	—	0.43
8M(2.4)T	—/2.4	—/0.12	0.3	34.5	65.8	—	0.72
9M(8.0)T	—/8.0	—/0.12	8.1	23.5	68.4	—	0.78
10D(1.2)C	1.2/—	0.12/—	1.1	98.9	0	0.51	—
11D(2.4)C	2.4/—	0.12/—	2.6	97.4	0	0.84	—
12D(8.0)C	8.0/—	0.12/—	2.8	97.2	0	1.29	—
13D(1.2)T	1.2/—	—/0.12	1.3	98.7	0	0.54	—
14D(2.4)T	2.4/—	—/0.12	1.9	98.8	0	0.93	—
15D(8.0)T	8.0/—	—/0.12	2.1	97.9	0	1.30	—
16MD(0.6)C	0.6/0.6	0.12/—	0.6	93.1	6.3	0.33	0.35
17MD(1.2)C	1.2/1.2	0.12/—	1.7	75.8	22.5	0.43	0.47
18MD(4.0)C	4.0/4.0	0.12/—	7.2	64.8	28.0	0.51	0.58
19MD(0.6)T	0.6/0.6	—/0.12	0.4	49.9	40.7	0.27	0.20
20MD(1.2)T	1.2/1.2	—/0.12	1.0	48.8	50.2	0.39	0.29
21MD(4.0)T	4.0/4.0	—/0.12	9.3	43.0	47.7	0.40	0.55
22MD(0.6)CT	0.6/0.6	0.06/0.06	0.8	60.6	38.6	0.30	0.22
23MD(1.2)CT	1.2/1.2	0.06/0.06	1.4	54.4	44.2	0.42	0.36
24MD(4.0)CT	4.0/4.0	0.06/0.06	6.1	47.8	46.1	0.45	0.57
25MD(1.9)1/4C	0.5/1.9	0.12/—	1.1	90.5	8.4	0.57	0.28
26MD(1.9)1/4CT	0.5/1.9	0.06/0.06	0.8	86.9	12.3	0.59	0.26
27MD(0.5)4C	1.9/0.5	0.12/—	1.0	69.1	29.9	0.28	0.43
28MD(0.5)4CT	1.9/0.5	0.06/0.06	1.0	62.59	37.5	0.24	0.39

[a] M = MAH; D = DEM; C = DCP; T = TBP.
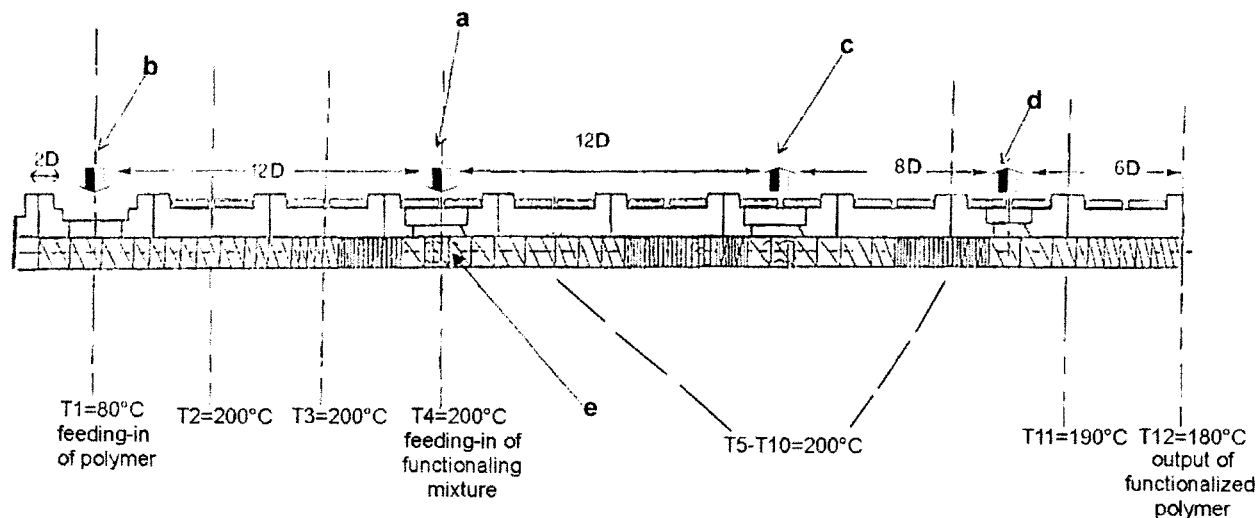
Figure 1 Scheme and temperature profile of the twin-screw extruder used (ICMA 110).

out for 30 min and then stopped. The recovered polymer was sequentially extracted with boiling acetone and toluene. The toluene-soluble fraction and the residue (when present) were characterized with FTIR and NMR.

In the latter case, the polymer (127–175 kg/h) was fed into a hopper in area b, and the functionalizing mixture (1.5–5 kg/h) was fed into a hopper in area a (Fig. 1). The functionalizing mixture, prepared by the mixing of 0.6 kg of DEM (11.6 wt %), 2 kg of MAH (39 wt %), and 0.18 kg of DCP (3.4 wt %), was adsorbed onto 0.35 kg of silica (7 wt %; average size of particles = 5μm, bulk density = 0.185 g/cm^3, —OH = 0.8 mequiv/g of silica) and then diluted with 2 kg (39 wt %) of powdered HDPE with the aim of increasing the precision of dosing through the screw feeder.

The corotating twin-screw extruder (Fig. 1) had a length of 40 diameters and contained two degassing valves, one of which was set 24 diameters from the point of the influx of the polyolefin, with the other set 8 diameters from the first. The influx of the polyolefin to be functionalized was carried out in the area marked b. In area a, set 12 diameters from area b, the functionalizing mixture was fed into the device with a twin-screw batcher (labeled e). The two degassing valves (c and d were set 24 and 32 diameters from area a, respectively, and could be made to operate simultaneously or independently. The extruder was equipped with an end-cutting device with a water bell for the pelletization of the copolymers after the functionalization reaction. The temperature profile is reported in Figure 1.

Measurements

The functionalization degrees (FDs) were determined with FTIR (PerkinElmer model 1330). When DEM was

the only functionalizing monomer, the calibration curve obtained from EPR/PDEF mixtures was used.[11] The spectra were recorded on films obtained by the deposition of a toluene solution onto a KBr disk or by hot-press molding. The FD was also determined by ^{1}H-NMR (Varian Gemini 200) analysis on a 1,2,4-trichlorobenzene solution of functionalized polymers with 1,1,2,2, tetrachloroethane-d_2 as an internal standard. For samples functionalized with MAH, the determination of FD was performed by the titration of carboxylic groups after hydrolysis with 100/56/10 (v/v/v) toluene/n-butyl alcohol/water at 75°C for 1.5 h.[16] When both the ester and anhydride groups were present, the determination of FD was performed by FTIR, and the broad system of absorption in the >C—O region was analyzed by deconvolution (see the appendix).

RESULTS AND DISCUSSION

Functionalization in the brabender mixer

The ethylene/propylene (72/28 w/w) copolymer was selected as the starting macromolecular material. Previous results have shown that EPR can be functionalized with DEM to an appreciable extent (1.88 mol % grafted DES groups) with limited degradation and without crosslinking.[11] The very modest occurrence of these two last undesired reactions was attributed to the substantial isolation of propylene units and the prompt reactivity of macromolecular free radicals with DEM.[17] The former situation makes improbable the β-hydrogen shift, whereas the grafting removes the free radical from the chain backbone with the formation of a new radical species, which very promptly undergoes the transfer[17] (Scheme 2). Therefore, even if the concentration of free radicals on the
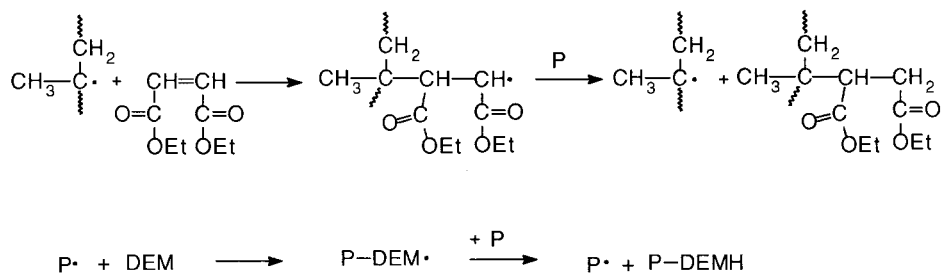
Scheme 2

chain remains constant during the stationary state, the permanence time on a backbone carbon atom is reduced because of the very rapid grafting of DEM.

Both MAH and DEM were used as functionalizing monomers, either individually or as a mixture in an amount ranging from 1.2 to 8.0 mol % with respect to EPR monomeric units. DCP or TBP, as single components or as a mixture, were used as free-radical initiators with a fixed total amount of 0.12 mol % with respect to EPR monomeric units. The reactions were carried out for 30 min at 190°C in the Brabender mixer by the addition of the monomer/initiator mixture to the polymer preheated at the reaction temperature (Table I).

The reaction products were first extracted with boiling acetone for the removal of low molecular weight compounds, such as unreacted monomers, initiator fragments, and oligomers derived from the monomer/initiator interactive reactions and macromolecular degradation. The acetone extraction was followed by a second extraction with toluene for the detection of the possible presence of insoluble crosslinked chains.

The FD (molar percentage of grafted groups with respect to the EPR monomeric units) of the acetone-insoluble material was determined by FTIR, NMR, and acid titration for MAH units. The different techniques were used according to the polymer solubility and the types and amounts of functional groups. For samples functionalized with DEM, FD was determined as A_{1736}/A_{1400} by FTIR, according to the standard procedure previously described for linear low-density polyethylene.[10] The same procedure could not be used when MAH was present in the functionalizing mixture. Indeed, the absorption in the $>C-O$ stretching region is rather complex (Fig. 2), confirming the presence of different functional groups. In fact, it was possible to observe at least three absorption bands: at 1860 cm^{-1}, symmetric stretching of the anhydride carbonyl group; at 1780 cm^{-1}, asymmetric stretching of the anhydride carbonyl group; and at 1736 cm^{-1}, the stretching of the ester carbonyl group. Sometimes it
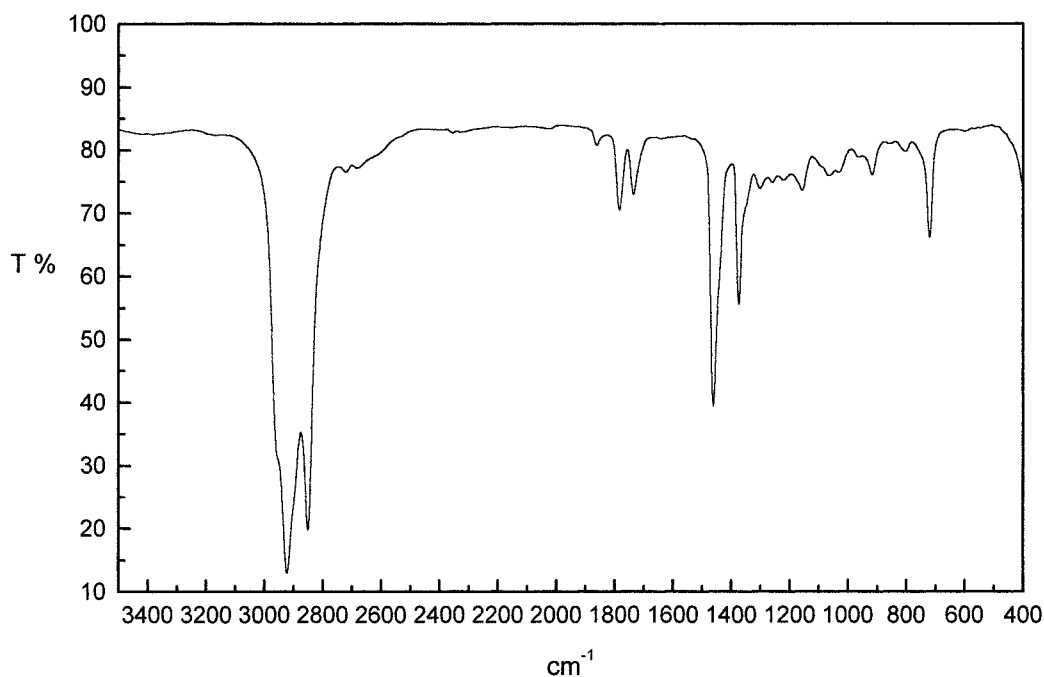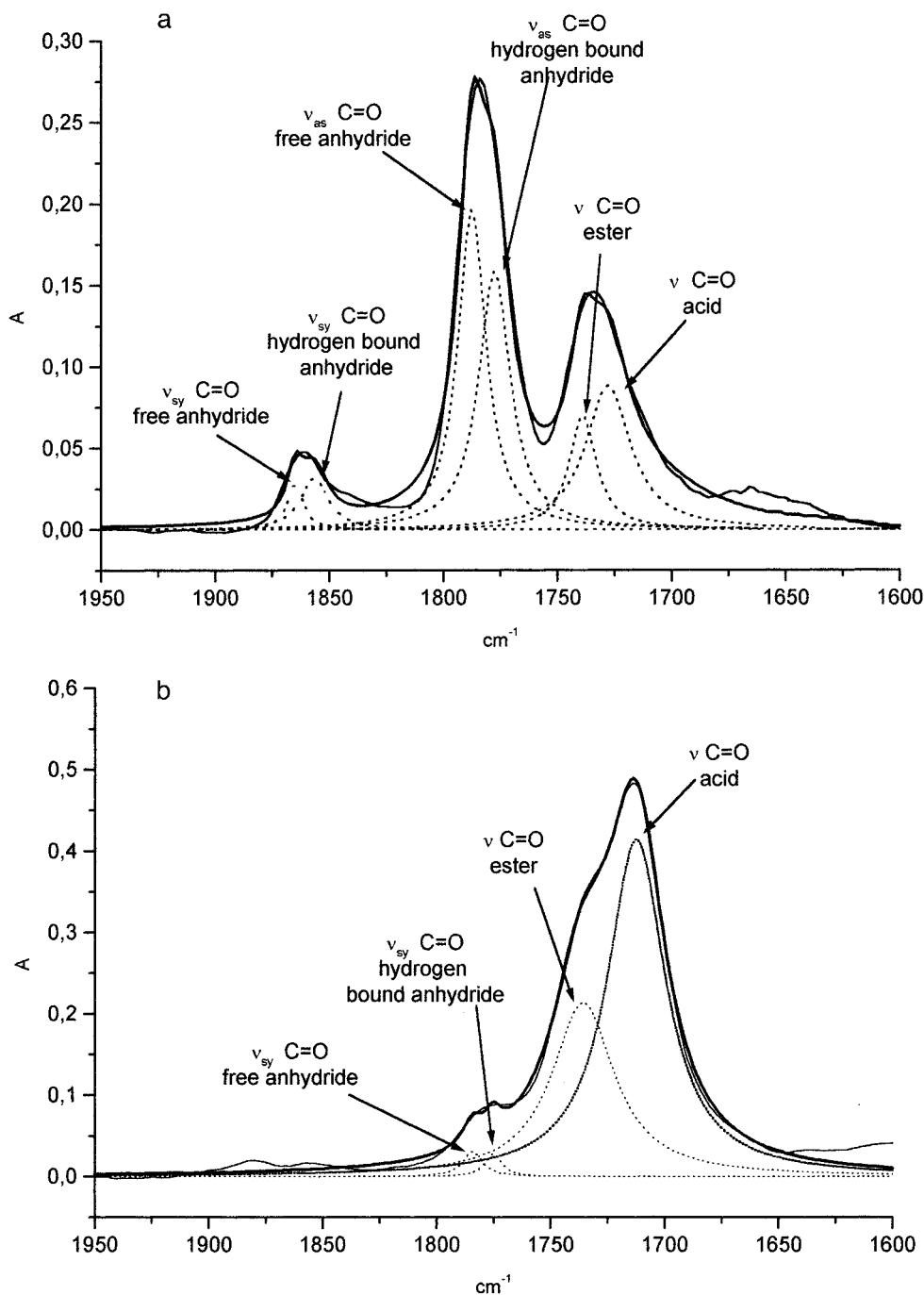

Figure 2 IR spectrum of the acetone-insoluble polymer from run 16(MD)0.6C.

Figure 3 Deconvolution of the vibrational bands in the range of the C=O absorption of EPR functionalized with DEM and MAH: (a) run 17MD(1.2)C and (b) run 17MD(1.2)C after a storage time of 7 months.

was possible to observe an additional peak at 1720 cm^{-1} due to the stretching of the acid carbonyl group, which was formed by hydrolysis of the anhydride. This last absorption band could be less or more evident because of the hydrolysis degree, which depended on the storage time and conditions. Therefore, with MAH as the sole grafting monomer, the polymer was treated with a 10/5.6/1 toluene/butanol/water mixture to hydrolyze completely the anhydride groups into free carboxylic groups, and these last were deter-

mined by titration.[16] An evaluation of the grafted functional groups was also performed by deconvolution (see the appendix) of the FTIR absorption in the region of the >C=O group vibrations [Fig. 3(a)]. Vibrational bands of C=O in the ester group (1736 cm^{-1}), carboxylic group (1720 cm^{-1}), and hydrogen-bound (symmetric at 1855 cm^{-1} and asymmetric at 1775 cm^{-1}) and free anhydride (symmetric at 1860 cm^{-1} and asymmetric at 1780 cm^{-1}) can be observed (dotted lines). The best fitting obtained by means of deconvolution (dashed

TABLE II
Functionalization of EPR[a] in the Double Twin-Screw Extruder

	Feed (wt %)			Functionalized polymer				
Run	MAH	DEM	DCP	FD(MAH) (wt %)	FD(DEM) (wt %)	$M_n \times 10^{-3}$	M_w/M_n	MFI
A4(0.60)C	0.46	0.14	0.04	0.40	~0.1	55	3.1	0.60
A5(1.20)C	0.92	0.28	0.08	0.70	0.1 ÷ 0.2	59	2.9	0.70
A6(1.43)C	1.10	0.33	0.10	0.90	0.1 ÷ 0.2	57	3.0	0.65

C = DCP.
[a] EPR: $M_n = 67.8 \times 10^3$, $M_w/M_n = 3$, MFI = 0.50.

line) perfectly agrees with the experimental curve (solid line) obtained by FTIR. Interestingly, these spectra change with time because of the slow hydrolysis of the anhydride, indicating a possible storage problem for MAH-functionalized compatibilizers [Fig. 3(b)].

With this methodology, it was possible to obtain a complete characterization of the functionalized samples, as reported in Table I.

Functionalization in the twin-screw extruder

On the basis of the results of the batch experiments carried out in the Brabender mixer, the scale-up of the process for preparing EPR with two types of grafted reactive groups was performed in the twin-screw extruder with a rotation rate of 100 rpm and a working temperature of 200°C. EPR was introduced at 80°C and heated up to 200°C, and then the functionalization mixture was added at 200°C. The experiments were carried out, starting with feed mixtures of the following composition ranges: 0.46–1.10 wt % MAH, 0.14–

0.34 wt % DEM, and 0.04–0.10 wt % DCP (with respect to EPR monomeric units; Table II). The IR spectra of the products collected from the extruder show the presence of >C—O stretching at 1860 cm^{-1} (SA) and at 1740 cm^{-1} (DES), showing that both functionalities were grafted to EPR macromolecules (Fig. 4). The quantitative evaluation performed by FTIR analysis (Fig. 5; performed within the error limits), as for experiments carried out in the Brabender mixer, shows that the conversion of initial monomers into grafted groups was much higher than that in the latter case. However, one should consider that the feed compositions in the two sets of experiments were different, the MAH–DEM/EPR ratio being smaller for the extruder experiments. Moreover, in the latter mixer, the monomer/peroxide mixtures were absorbed onto silica and diluted with powdered HDPE. The change of the mixing machine could have, moreover, a certain role in determining the increased yield of grafting because of the better dispersion of the reagents in fluid EPR with the twin-screw extruder. The accessibility of
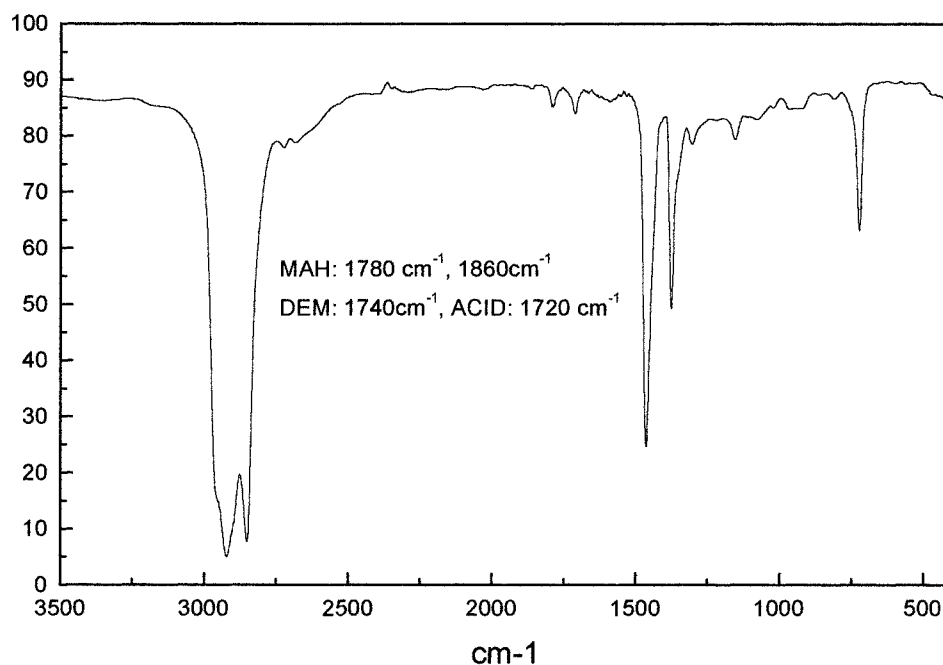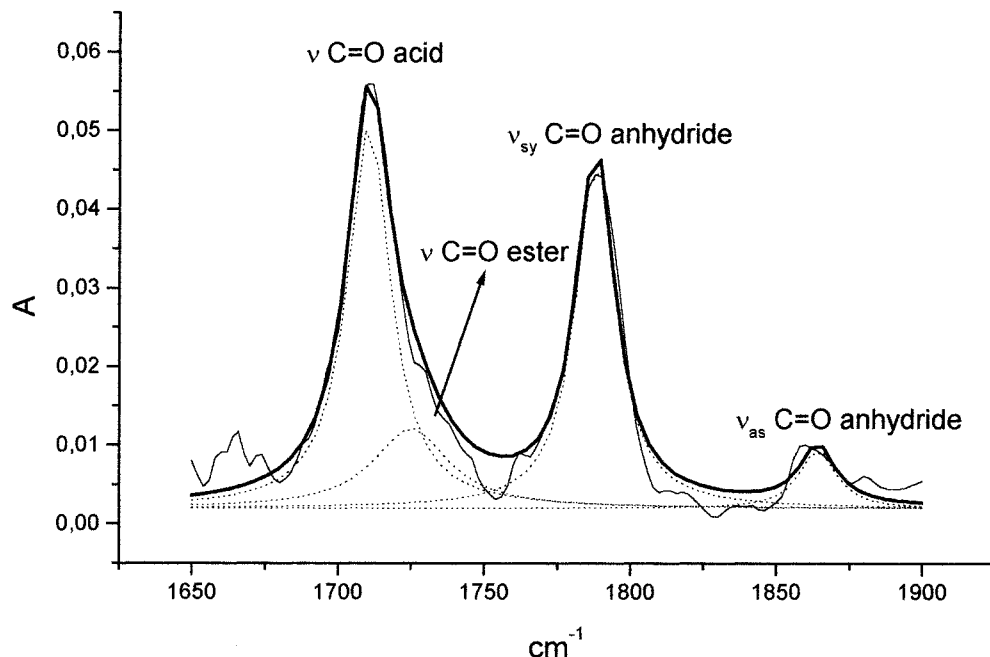

Figure 4 IR spectrum of EPR functionalized with DEM and MAH in the twin-screw extruder (run A4).

Figure 5 Deconvolution of the vibrational bands in the range of the C=O absorption of EPR functionalized with DEM and MAH in the extruder (run A4).

the macromolecules to the primary radicals could then be improved, thereby producing a greater amount of macromolecular radicals, which reacted preferentially because of the more efficient dispersion in the fluid polymer.

Influence of the feed nature and composition on functionalization

The collected FD data in the Brabender experiments, with the feed composition and nature changing, show first of all that the replacement of DCP with TBP did not effect the functionalization reaction appreciably. The half-life time at the reaction temperature (190°C) was higher for TBP (45 s) than for DCP (28 s), but the difference was clearly rather small with respect to the residence time (30 min). From the perspective of the mechanism, the similar FDs for the two peroxides indicated that the respective primary radicals displayed an analogous capacity to produce macromolecular radicals through H abstraction from the polyolefin chains. Even the use of a mixture of the two peroxides (runs 22–24, 26, and 28 in Table I) did not change the FD, despite a probably longer stationary state. The larger amount of the crosslinked polymer in the presence of TBP (cf. runs 25 and 27 with runs 26 and 28 and runs 16–18 with runs 19–21) can be related to a larger instantaneous concentration of macromolecular radicals. However, as the amount of free radicals involved in the crosslinking was rather modest, this interpretation is not straightforward and must be considered to be purely indicative.

In the experiments with a sole monomer, either DEM or MAH, and a sole initiator, either DCP or TBP (runs 4–15), FD increased with the monomer starting concentration. DEM provided a larger FD than MAH under any conditions tested, with a consistent amount of crosslinked material formed when MAH was used as the monomer, either alone or in combination with DEM. Indeed, in the presence of this latter monomer, no crosslinking was observed even at a DEM/DCP (or TBP) molar ratio as low as 10, whereas a product more than 50% crosslinked was formed even at an MAH/DCP (or TBP) molar ratio as high as 60–70, and the formation of insoluble material increased with the increasing MAH concentration in the feed.

As mentioned previously, crosslinking and degradation could be reduced by a decrease in the average residence time of a free radical on the chain backbone because of the grafting reaction (Scheme 3). Therefore, the aforementioned results apparently imply a lower grafting rate constant for MAH than for DEM. Also, the higher homopropagation rate constant of MAH
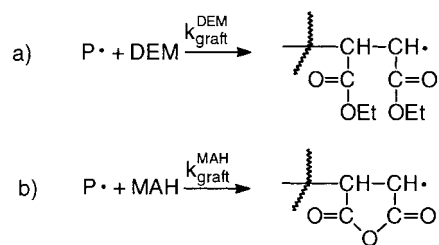
Scheme 3
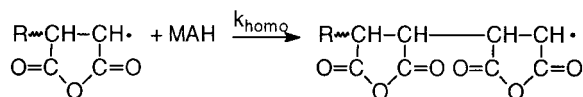
Scheme 4

with respect to DEM could play a certain role because it reduced the fraction of macroradicals reacting with the monomer.

A remarkable crosslinking was also observed with MAH/DEM mixtures, even though the presence of DEM had an appreciable depressing effect. In fact, if we compare runs with the same contents of monomers and DCP, but one (run 5) with MAH alone (2.4 mol %) and the second (run 17) with both MAH and DEM (2.4 mol % total content, MAH/DEM = 1/1 mol/mol), the amount of crosslinked product decreases and the FD (derived from either MAH or DEM) increases.

The formation of a material not extractable with toluene was also connected in a not simple way with the number of grafted SAH units (derived from MAH grafting) because of the interactions between functionalized side chains, such as hydrogen bonding between >C—O and carboxylic acid groups formed by the hydrolysis of SAH units. Indeed, the apparent amount of crosslinked material was higher with an MAH/peroxide mixture than with peroxide alone (runs 4 and 2 In Table I).

Some indications, moreover, suggest that MAH also reacted with its own radical rather than with the macroradical, thereby giving some propagation (Scheme 4) and less grafting [Scheme 3(b)].[18] This hypothesis is borne out by the fact that the polymerization of MAH showed a high but certainly finite value of k_t/k_p ($k_t^{1/2}/k_p = 109$, where k_t is the rate of termination and k_p is the rate of propagation), indicating that k_p is not zero and is comparable to the rates of many other sluggish monomers such as isoprene and methyl isopropenyl ketone.[19] For the same reason, MAH, after reacting with the primary radicals derived from the

initiator, could induce homopropagation (thereby generating not-grafted oligomers from MAH), thereby reducing the amount of monomer available for the reaction with the macroradicals of the polyolefins, reducing FD, and increasing the probability of crosslinking. This is probably not valid for DEM; indeed, the reactivity ratios determined for the copolymerizations of the DEM/methylmethacrylate[20] and DEM/styrene[21] systems showed that DEM participated only to a very small extent in the propagation step.

Interesting indications were obtained by an evaluation of the grafting efficiency (E) observed in the various experiments. E was calculated as the ratio between the FD (molar percentage of grafted units) and the molar percentage of the initiator divided by 2. In this way, E corresponded to the number of grafted units per primary radical produced by decomposition of the peroxide. The value of E in the Brabender experiments depended on the monomer concentration, and it was slightly higher for DEM than for MAH (Table III); in the extruder (Table IV), the values of E were much higher than those in the Brabender mixer (Table V). E divided by the monomer concentration was proportional to the rate of grafting when the number of macroradicals on the polyolefin was proportional to that of the primary radicals. The slightly higher value of E/[M] (where [M] is the monomer concentration) observed for TBP could be attributed to its better efficiency at producing polyolefin macroradicals. However, the higher value of E/[M] for MAH in the presence of DEM was not easy to rationalize and could derive from improved monomer diffusion due to the liquid DEM acting as a solvent. The roles of diffusion and interfacial interaction were further emphasized by the better E/[M] values observed in the extruder, which provided more efficient mixing of the reagents.

CONCLUSIONS

The contemporary use of two different unsaturated monomers (DEM and MAH) in the free-radical bulk

TABLE III
Relative Efficiency of Primary Radicals During Functionalization Reactions Carried out in the Brabender Mixer

Run	Initiator (I)	Grafting monomer (M)	M/I (mol)	Efficiency[a]
4M(1.2)C	DCP	MAH	10	1.7
7M(1.2)T	TBP	MAH	10	1.8
10D(1.2)C	DCP	DEM	10	2.1
13D(1.2)T	TBP	DEM	10	2.1
5M(2.4)C	DCP	MAH	20	2.8
8M(2.4)T	TBP	MAH	20	3.0
11D(2.4)C	DCP	DEM	20	3.5
14D(2.4)T	TBP	DEM	20	3.8
17MD(1.2)C	DCP	MAH + DEM	20	3.7 (1.8 DEM; 1.9 MAH)
20MD(1.2)T	TBP	MAH + DEM	20	2.7 (1.6 DEM; 1.2 MAH)
23MD(1.2)CT	DCP/TBP	MAH + DEM	20	3.2 (1.7 DEM; 1.5 MAH)

M = MAH; D = DEM; C = DCP; T = TBP.
[a] Number of functional groups per primary radical.

TABLE IV
Relative Efficiency in the Twin-Screw Extruder

Run	Initiator (I)	Grafting monomer (M)	M/I molar ratio	Efficiency[a]
A4(0.60)C	DCP	MAH + DEM	37	14.9 [13 (MAH) + 1.9 (DEM)]
A5(1.20)C	DCP	MAH + DEM	37	14 ÷ 15 [13 (MAH) + 1 ÷ 2 (DEM)]
A6(1.43)C	DCP	MAH + DEM	37	13.2 ÷ 13.9 [12.5 (MAH) + 0.7 ÷ 1.4 (DEM)]

C = DCP.
[a] Number of functional groups per primary radical.

functionalization of polyolefins allows the one-step grafting of two different reactive functionalities into EPR macromolecules. The types and concentrations of the inserted functional groups can be detected by spectrometry (FTIR and NMR), IR spectral deconvolution, and titration with good accuracy.

The overall extent of the grafting and the ratio between the two different functional groups can be modulated by the feed composition, reaction parameters, and mixing machine. The grafted groups composition does not correspond to the starting one, suggesting possible interactions between the unsaturated monomers during the reaction affecting the respective reactivity. This last conclusion is supported by the dependence of the crosslinking reaction on the DEM/MAH ratio.

The overall FD does not appear to be very much affected by the peroxide types having different decomposition times ($\tau_{1/2}$). A much higher conversion of the monomer into grafted groups is instead reached when we go from the Brabender batch mixer to the continuous and more efficient twin-screw extruder, even if the residence time is lower in the latter case.

The use of the liquid comonomer DEM facilitates the addition of the solid reagents (MAH and peroxide) to the melt polymer, providing important support for the technical development of the process.

APPENDIX

The deconvolution of the vibrational bands in the carbonyl stretching range is based on the following hypotheses:

TABLE V
Effect of Monomer and Initiator on the Specific Grafting Efficiency (EFF/[M]) to EPR Macromolecules

Initiator (run)	Reactor	Monomer	EFF/[M]
DCP (6, 5, 4)	Brabender	MAH	0.4, 1.1, 1.4
TBP (9, 8, 7)	Brabender	MAH	0.4, 1.2, 1.5
DCP (12, 11, 10)	Brabender	DEM	0.7, 1.5, 1.8
TBP (15, 14, 13)	Brabender	DEM	0.7, 1.6, 1.9
DCP (18, 17, 16)	Brabender	MAH (in DEM)	0.6, 1.6, 2.4
TBP (21, 20, 19)	Brabender	MAH (in DEM)	0.6, 1,0, 1.4
DCP (18, 17, 16)	Brabender	DEM (in MAH)	0.5, 1.5, 2.3
TBP (21, 20, 19)	Brabender	DEM (in MAH)	0.4, 1.3, 1.9
DCP (A4, A6)	Extruder	MAH (in DEM)	93, 37
DCP (A4, A4)	Extruder	DEM (in MAH)	73, 3

- C=O stretching is considered approachable by a Lorentzian curve. However, in addition to instrumental band-widening effects, even molecular effects, such as the rotational fine structure, hydrogen bonding, and possible existence of multiple conformations, affect the shape of the absorption band.[22] When a complex system of absorption bands is present (as in our experiments) and the components swerve from the Lorentzian shape, the system can be worked out as a Lorentzian band system,[23] as well as the number of component bands.[24]

- Between 2000 and 1600 cm^{-1}, six different components[25] are considered present: ν C=O symmetric of free anhydride, ν C=O symmetric of hydrogen-bonded anhydride, ν C=O asymmetric of free anhydride, ν C=O asymmetric of hydrogen-bonded anhydride, ν C=O of ester, and ν C=O of the carboxylic acid.

- The procedure followed to determine the half-width of bands is based on the optimization of the values during deconvolution, the starting baseline, and the shape of the peak. All the absorption bands are described with the Lorentz equation:

$$y = y_0 + \frac{2A}{\pi} \cdot \frac{w}{4(x - x_c)^2 + w^2} \qquad (A.1)$$

where y_0 is the value of the baseline (zero), A is the area of the peak, w is the half-width of the bands, and x_c is the maximum of the peak. A, w, and x_c are determined from the starting values variable within a predetermined range.

The chosen software used[26] the nonlinear least-squares fitter (NLSF) method, which minimizes the discrepancy (DIS of Morrow e Cody). For all cases, the values of DIS < 0,01 indicate a good fitting.[24]

It is possible to limit the range of the allowed values of the parameters during the fitting by the establishment of linear constraints. For this purpose, knowing the linear dependence between the FD and $A_{C=O}/A_{1460}$ ratio, we write:

$$FD(DES) = \frac{[DES]}{[EPR]} = \frac{\dfrac{\bar{A}_{DES}}{l \cdot \bar{\varepsilon}_{DES}}}{\dfrac{\bar{A}_{1460}}{l \cdot \bar{\varepsilon}_{1460}}} = \frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{DES}} \cdot \frac{\bar{A}_{DES}}{\bar{A}_{1460}}$$

$$FD(SAH) = \frac{[SAH]}{[EPR]} = \frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{SAH}} \cdot \frac{\bar{A}_{SAH}}{\bar{A}_{1460}}$$

$$FD(SA) = \frac{[SA]}{[EPR]} = \frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{SA}} \cdot \frac{\bar{A}_{SA}}{\bar{A}_{1460}}$$

where FD(DES), FD(SAH), and FD(SA) are the FDs related to ester, anhydride, and acid groups, respectively; [DES], [SAH], [SA], and [EPR] are the molar concentrations of the species in the polymer. The values of ε are derived from literature data,[27] except the ε value for the band at 1460 cm^{-1}, which is inferred from our calibration curve.[12] Then, the linear constraints are

$$\frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{SA}} \cdot \bar{A}_{SA} + 2 \cdot \frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{SAH}} \cdot \sum_I \bar{A}_{SAH,I} \leq 2 \cdot FD_{SAH}^T \cdot (\bar{A}_{CH_2} + \overline{A_{CH_3}})$$

$$\frac{\bar{\varepsilon}_{1460}}{\bar{\varepsilon}_{DES}} \cdot \bar{A}_{DES} \leq 2 \cdot FD_{DES}^T \cdot (\bar{A}_{CH_2} + \overline{A_{CH_3}})$$

where $\overline{A_{CH_3}} + \overline{A_{CH_2}}$ is the area of the band centered at 1460 cm^{-1} and FD_{SAH}^T and FD_{DES}^T are the theoretical FDs derived from the feed composition. The experimental FD values are considered to twice as large as the corresponding theoretical FD [(FD)^T] because of the two C=O groups in the molecules. By deconvolution with NLSF, we can obtain the values of the areas (see the FDs of the grafted DEM and MAH reported in Table I). Two examples of deconvolution results are reported in Figures 4 and 5 for samples containing ester, anhydride, and acid grafted before and after the hydrolysis of SA into the acid groups.

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