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MOLECULAR AND MECHANISTIC ASPECTS OF THE FUNCTIONALIZATION OF POLYOLEFINS WITH ESTER GROUPS

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Abstract : In the present paper the functionalization reaction of polyolefins in the melt with diethylmaleate (DEM) in the presence of peroxide is revisited. The process was analyzed on the basis of several experiments carried out in the Brabender mixer with 30 min residence time and at constant temperature, 190° C for EPR and 200° C for LLDPE samples, while varying the number of branching in the starting polyolefin, the amount of DEM and of dicumyl peroxide (DCP). For reference purposes similar experiments were also examined as performed with EPDM and isotactic polypropylene (PP).

At the end of the reaction, the polymeric product was treated with boiling acetone to remove low molecular weight products. In general, the acetone insoluble polymer was soluble in heptane and the functionalization degree (FD) referred to this fraction was in the range 0.2-2.0% mol of DES groups per 100 moles of monomeric units.

The contemporary occurrence of the degradation and chain extension, including crosslinking reactions, provides a reasonable explanation of the results obtained. The analysis of the process performed in the present work helps to select proper conditions for controlling the characteristics and FD of the polyolefin and keep undesired secondary reactions under control.

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INTRODUCTION

The mixing of polyolefins with more or less polar polymeric materials to give at least partially miscible blends is made possible by the use of macromolecular compatibilizers [Ref. 1] produced in situ during the melt mixing of the blend components through reactive processing of the polar polymer macromolecules with functionalized polyolefin macromolecules

[Refs. 2-4]. These last are generally obtained by attaching to the polyolefin backbone a limited amount (generally around 1% mol), of functional groups. The preparation of the polyolefin compatibilizer precursor is carried out in the melt [Refs. 5, 6] or in solution [Refs. 7, 8] by means of organic peroxides as free radical initiators. The most commonly used functional molecule has been maleic anhydride [Refs. 9, 10] owing to the high reactivity of the anhydride group in successive reaction [Refs. 11, 12].

In previous papers we have reported that polymers of monoalkenes (HDPE [Ref. 13], EPR [Ref. 14], isotactic and atactic polypropylene [Ref. 15] can be functionalized in the melt with unsaturated dicarboxylic acid esters such as diethylmaleate (DEM): in the presence of a peroxide initiator. The structure of the grafted groups was shown [Ref. 16] to be that of 2-(diethyl succinate) (DES).

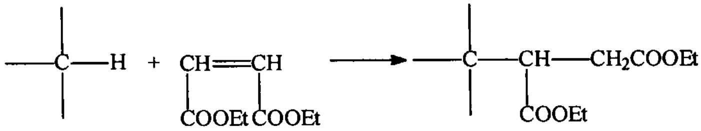
Ester groups were also grafted on polyolefin chains through reaction with diazoesters [Ref. 17] and the structure of the grafted group was confirmed by NMR [Ref. 18].

From the application point of view the former process seems to be more convenient, but looks more complex and more difficult to control.

Indeed several side reactions can occur due to the reaction conditions (high temperature and free radical mechanism) and the quantitative aspects are not well understood. Therefore a detailed study under well defined conditions was considered very useful in order to grant a better reproducibility of the functionalization degree (FD) and put some light on the whole mechanism.

The experimental data reviewed in this paper derive from experiments performed in our laboratory. Diethylmaleate (DEM) was used as functionalizing agent and dicumylperoxide (DCP) as free radical generator. The polyolefin structure was varried regularly from LLDPE to EPR and PP. Experiments carried out with EPDM are also examined as providing information about the role of insaturation during the functionalization reaction.

Standing the clear evidence that the functionalization reaction at least for saturated polyolefins follow a simple route with formation of 2-(diethylsuccinate) groups (DES) attached to the backbone (scheme 1), the main reaction was examined by collecting accurate information about the functionalization degree (FD= number of DES groups in 100 monomeric units) obtained in different cases.



P DEM P-DES

P= polyolefin macromolecule

Scheme 1. Scheme of the functionalization reaction

An analogous direct evaluation of the side reactions, such as formation of DEM oligomers, degradation and chain extension (including crosslinking) is not possible. However combination of solvent extraction, GPC, FT-IR and NMR analysis provided useful data allowing to offer a general picture of the whole reaction system and the role of both molecular and process parameters.

RESULTS AND DISCUSSION

Evaluation of the Reaction Products

The degree of functionalization FD (number of DES groups in 100 monomeric units) was determined with good accuracy on the basis of the comparison of FT-IR spectra of the functionalized polyolefin with standard mixtures of the same polyolefin and polydiethylfumarate of known composition. In many cases an independent control was carried out by NMR.

The general route followed is summarized below.

The IR spectra of the standard mixtures show bands typical of both polymers, the most useful for their high optical density being those at 1738 cm^{-1} (stretching C=O; A1) and at 1460 cm^{-1} (bending $-CH_2$; A2). By plotting the peak areas ratio (A1/A2) *vs.* the composition of the mixture, in the range of composition going from 14% wt to 1% wt of poly(diethylfumarate) (corresponding to an FD from 2.8 to 0.3 molar), a good correlation was obtained. This suggests that the A1/A2 band area ratio can be safely used for detecting FD of EPR and LLDPE2 (containing 9% of 1-butene) samples functionalized by DEM grafting. Before using directly the A1/A2 ratio for evaluating FD of EPR and LLDPE samples, a further control was made by reporting A1/A2 values of different functionalized samples vs. the FD values as detected by ^{13}C-NMR; a good linear correlation between the ratio A1/A2 of the peak areas and FD, as determined by ^{13}C-NMR (at 12-14 ppm, $-O-CH_2-CH_3$, and at 9-10 ppm, $-CH_3$ of 1-butene), was obtained in the case of functionalized samples derived from LLDPE1 containing 8.7 mol% of propene and 5.2 mol % of 1-butene.

Thus, FD depends linearly on the ratio A1/A2 of the peak areas in the functionalization range 0.2-2.8 mol % of 2-(diethylsuccinate) groups grafted on the polyolefin backbone of both LLDPE and EPR. The correlation [eq.1] can then be used for ethylene polymers with different structure; clearly different values of the coefficient *a* and *b* of eq. 1 are observed for the various samples [Ref. 19]

$$\mathrm{FD} = a + b\,(\mathrm{A1/A2}) \qquad \text{[eq.1]}$$

The same method has been now used also for EPDM and iPP even if, particularly in the former case, the values of FD are less accurate due the more complex structure and the possible interference with double bonds absorptions. This can be also evinced from the data of eq. 1 (Table 1) showing that the value of *a* is further from zero for PP and EPDM, and the corresponding linear correlation factor (R) is appreciably lower than unity.

Table 1. Values of coefficients of eq.1 and linear correlation factor (R) for different polyolefins

Polymer	a	b	R
LLDPE1	0	1.98	0,995
LLDPE2	-0.11	2.00	0,990
EPR	-0.01	2.07	0,998
EPDM	-0.30	2.31	0,984
PP	0.12	2.22	0,978

The negative values of *a* derive from the fitting of the experimental data, and do not have any physical meaning.

Influence of the Reaction Parameters on FD

The functionalization reaction was carried out in a 30 ml Brabender mixer with 30 min residence time at varied temperatures (190 and 200°C) for the different samples; DEM and DCP were used as functionalizing molecules and initiator, respectively. In order to get information allowing a reliable picture of the whole reaction mechanism and identify parameters for a controlled modulation of the process, the DEM/DCP and DEM/polyolefin ratios were varied independently for the different polyolefins.

The mere thermal treatment in the Brabender provides little changes in the solubility of LLDPE, EPR and EPDM, whereas produces a large increase of the toluene soluble fraction of iPP according to an extensive thermal degradation (Table 2). Under the same conditions the presence of peroxide determines an appreciable crosslinking of the three first polymers whose extent seems to decrease in the order

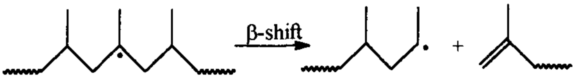
EPDM > LLDPE > EPR

as shown by the decreasing amount of residue to the toluene extraction. Again iPP behaves notabily, the presence of DCP rendering even more efficient the main thermal degradation process with about 90% of polymer extractable with boiling toluene (Table 2).

Table 2. Solubility of the used polyolefins before and after reference treatments in the Brabender

Polyolefin	Run	Treatment	Extracted with (%)			Residue
			acetone	heptane	toluene	%
EPDM	00	Brabender	1.8	98.2	0	0
	0a	0.11 mol % DCP	0.7	0	0	99.3
EPR	00	Brabender	1.0	99	0	0
	0a	0.11 mol % DCP	0.9	84.1	3.5	11.5
LLDPE1	01	Brabender	0.5	99.5	0	0
	02	0.11 mol % DCP	0.5	48.6	8.3	42.6
LLDPE2	01	Brabender	0.3	99.7	0	0
	02	0.11 mol % DCP	0.4	60.2	0	39.4
iPP	00	none	0.2	-	24.8	75
	01	Brabender	0.8	-	87.2	12
	03	0.08 mol % DCP	0.3	-	99.7	0

These data provide a clear evidence that the thermal treatment for 30 min. in the Brabender at 200°C gives a modest amount of free radicals or at least of products deriving from their possible formation in case of LLDPE, EPR and EPDM, that is all polymers containing more than 70 mol % of ethylene units. Accordingly no functionalization is observed even by addition of 1.8% mol of DEM. Under the same conditions iPP gives extensive degradation, suggesting the formation of free radicals on the backbone which are preferentially involved in intramolecular degradation (scheme 2) rather than in recombination (crosslinking) [Ref. 20 and 21] or functionalization when DEM is present.

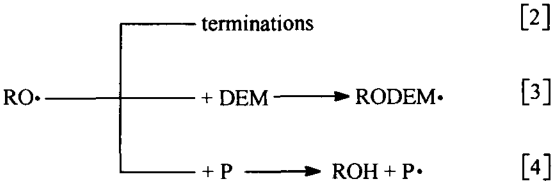


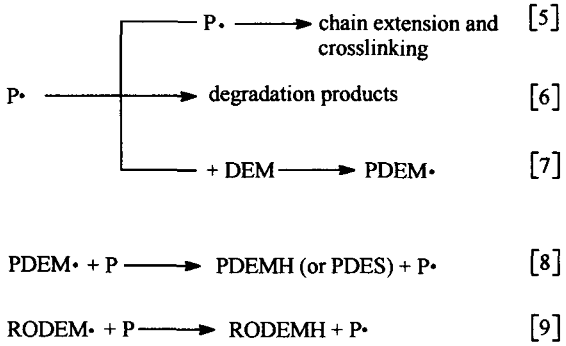
Scheme 2. Bond cleavage through β-H shift

According to what is known [Refs. 22, 23] about free radical reactions involving long chain saturated hydrocarbons, the functionalization reaction with DEM in the presence of DCP can be described on the basis of the series of successive and parallel reactions reported in the scheme 3. In this scheme P indicates any polyolefin macromolecule and P• all possible types of macromolecular free radicals with different length and formed through either secondary or tertiary or allylic hydrogen abstraction or chain thermal breaking. Actually these different macromolecular free radicals have probably distinct attitude for the reactions indicated and this should be considered for a more detailed quantitative analysis.

$$P \xrightarrow{\Delta} \text{degradation products} \qquad [0]$$

$$DCP \xrightarrow{\Delta} 2RO\bullet \qquad [1]$$





Scheme 3. Simplified reaction mechanism of the polyolefin (P) functionalization with diethylmaleate (DEM) and dicumylperoxide (ROOR) as initiator.

As at the end of the reaction only 1-2% of the polyolefin units $[U]$ = [P]/(MW of the average monomeric unit) are functionalized, the concentration $[U]$ can be considered equal to the initial concentration $[U\circ]$ at any time. Thus FD is given by:

$$FD = k_8[U\circ]\int_0^t [UDEM\bullet]dt \qquad \text{[eq. 2]}$$

The instantaneous rate of formation of $U\bullet$ and $UDEM\bullet$ radicals results from equations 3 and 4:

$$\frac{d[U\bullet]}{dt} = [U\circ]\{k_4[RO\bullet]+k_8[UDEM\bullet]+k_9[RODEM\bullet]\}-[U\bullet]\{k_5[U\bullet]+k_6+k_7[DEM]\} \qquad \text{[eq. 3]}$$

$$\frac{d[UDEM\cdot]}{dt} = k_7[U\bullet][DEM] - k_8[UDEM\bullet][U^\circ] \qquad \text{[eq. 4]}$$

By assuming a stationary state at which the concentration [UDEM-] is constant, [eq. 2] can be rewritten as

$$FD = k_7[DEM]\int_0^t [U\bullet]dt \qquad \text{[eq. 5]}$$

This equation predicts a linear proportionality between DEM concentration and FD.

The experimental data at a fixed reaction time suggest that this is indeed the case for all the ethylene polymers investigated (fig. 1) in the range of DEM and DCP concentration reported which was selected to prevent crosslinking (formation of toluene insoluble material) [Ref. 18].

The dependence on the concentration of macromolecular free radicals $U\bullet$ remains complex. Indeed $[U\bullet]$ is affected by the occurrence of various formation and consumption reactions ([eq. 3]).

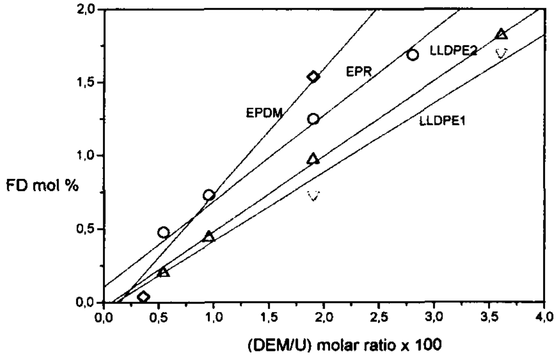


Fig 1. Dependence of functionalization degree (FD) on the DEM/U (polyolefin) molar ratio with a fixed DCP/DEM molar ratio =0.06.

On the other side an increase of $[DCP]$ favors an increase of $[U\bullet]$, but does not necessarily imply an increase of FD as also the rate of degradation and particularly crosslinking are increased. Therefore an optimal concentration of DCP can be expected. The trend of FD with the $[DEM]/[U]$ ratio indicates a maximum value reached at a defined value of the ratio itself which is characteristic of each ethylene copolymer (Fig. 2). When the $[DEM]/[DCP]$ ratio is too low, the macroradicals formed do not immediately react with DEM and can undergo degradation and even more chain extension which is proportional to $[U\bullet]^2$. This limits the growth of FD as only a fraction of the formed $U\bullet$ evolves to $UDEM\bullet$.

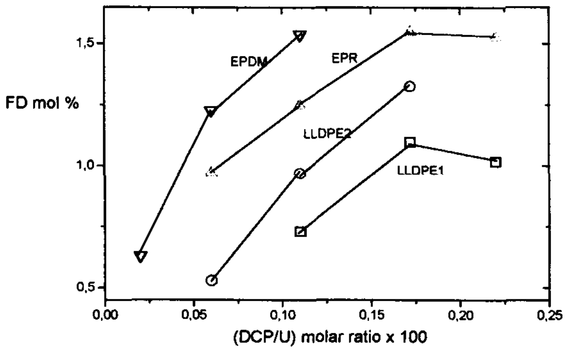


Fig 2. Dependence of functionalization degree (FD) on the DCP/U molar ratio with a fixed 1.8 mol % DEM concentration.

Semiquantitative information about crosslinking and degradation can be obtained from the solubility data before and after functionalization. As observed in the reference experiments (Table 2), DCP alone produces crosslinking while the thermal treatment is responsible for a certain degradation. The presence of DEM can hinder the crosslinking by rapidly converting P• into PDEM• through the reaction [7]. This is also valid for EPDM even if the allylic H favors crosslinking. The higher FDs values for EPDM with respect to the FDs of the other ethylene copolymers are probably due to a contribution of the 'ene' reaction between the double bonds present on the polymer and DEM [Ref. 24]. These considerations do not apply for polypropyene which gives mainly degradation through reaction [0] and [6], favored by the formation of tertiary C radical which undergo bond cleavage through β-H shift (scheme 2) [Ref. 20]. The cleavage reaction is clearly less effective for ethylene copolymers where tertiary carbon atoms are spaced by methylene groups.

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