Bulk Functionalization of Ethylene-Propylene Copolymers I. Influence of Temperature and Processing on the Reaction Kinetics

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Synopsis

The dicumylperoxide (DCPO) promoted functionalization of an ethylene-propylene copolymer (EPR) by means of dibutyl maleate (DBM) has been studied in bulk at constant reactant composition (100 : 10 : 1 by wt EPR-DBM-DCPO) in the range of temperature from 140 to 200°C. The reactants have been premixed in a Brabender-like apparatus at 90°C in which no decomposition of the radical initiator could occur. This was done in the frame of a general discussion of polyolefin functionalization, to assure the homogeneity of the reactant mixture before the reaction occurred.

The kinetics of the reaction followed by an infrared (IR) technique was carried out according to two different procedures: a static one in a thermostatic bath and a dynamic one in the same mixer used for the premixing step. The kinetics in the two cases are very comparable, and a common activation energy of 40 kcal/mol has been measured. Some minor differences exist, however, which are very interesting from a scientific point of view.

The kinetics of EPR degradation during the reaction has been indirectly monitored by means of solution viscosimetry. The results have been compared with the reaction kinetics.

A thorough discussion of the proposed mechanism for grafting and degradation reactions has been also provided.

Further work is in progress to analyze the effect of the EPR copolymer and of reactant composition on the functionalization and degradation reactions.

INTRODUCTION

Polyolefin modification by attaching unsaturated polar groups onto their chain backbones has received considerable attention in recent years[1-6] to improve such properties as adhesion and dyeability or to utilize these materials for further reactions, such as cross-linking or grafting. Functionalization has been generally carried out in solvent media and initiated by means of organic peroxides.[3-8]

The more commonly used functional molecule has been the maleic anhydride (MAH) owing to the high reactivity of the anhydride group in successive reactions. In fact, a modified ethylene-propylene copolymer (EPR-g-MAH) has been used in binary polyamide PA6/EPR-g-MAH or in ternary PA6/EPR/EPR-g-MAH blends prepared either by melt mixing of the compo-

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nents or during the hydrolytic polymerization of ϵ-caprolactam.[9-14] In both cases an EPR-g-PA6 graft copolymer was formed that acted as an interfacial agent between the rubber and the PA6 phases, reducing the EPR particle size and increasing their adhesion to the PA6 matrix. These blends therefore succeeded in greatly improving the impact resistance of PA6 at low temperatures, especially those obtained by melt mixing.

Maleic and fumaric esters have also been grafted by solution reactions on EPR copolymers,[7] and in this case the best end-use results were obtained in the hydrolytic polymerization of the ϵ-caprolactam.[13] In fact, in the melt-mixing process the short residence times did not allow the less reactive ester groups to sufficiently react with the amino end groups of PA6. In spite of the interesting results obtained, particularly with EPR-g-SA, the solution grafting process did not seem to be suitable for large-scale industrial application. Therefore some attempts were made to functionalize polyolefins directly in bulk.[14-19] The maleic anhydride, however, although more reactive than the esters, is very volatile, toxic, scarcely compatible with EPR, and strongly corrosive with respect to the metallic surfaces of the equipment used. For these reasons it was discarded, and dibutylmaleate (DBM) was chosen as the unsaturated molecule for a study undertaken in our institute on the basis of its low volatility and of its compatibility with EPR.

The reactants EPR and DBM and dicumylperoxide (DCPO) as radical initiator were introduced at one time in the reactor (one-step process), and the results showed that the grafting of DBM onto the EPR backbone occurred easily in the temperature range from 140 to 160°C.[16] The number of grafted groups was a function of the reaction time, temperature, and reactant composition. Some preliminary data were also presented for the reaction obtained in a two-step process. This consisted of premixing the reactants at 90°C, a temperature at which almost no DCPO decomposes, and the successive reaction. The conceptual importance of separating the two main steps of the process was recognized, provided that the components are mixable. This would assure that the reaction can occur in a homogeneous mixture, thus yielding a very regular modified EPR.

In the present study the double-step process was used throughout, and furthermore, two different procedures for the reaction were adopted. This was done to perform a more fundamental analysis of the effect of temperature and processing on functionalization kinetics. This is the first of three papers; the others will deal with the influence of reactant composition and EPR composition on the reaction kinetics. The main purpose is to elucidate the reaction mechanisms involved, as well as to optimize the reaction process itself, in view of further interesting applications of these functionalized copolymers in polyvinyl chloride (PVC) or polybutylene terephtalate (PBT) based blends.

EXPERIMENTAL

Materials

The EPR copolymer used was Dutral CO/054, kindly supplied by Dutral S.P.A., an ethylene-propylene amorphous copolymer 62.8% by mol in C_2, having a M_w of 1.8×10^5 and an intrinsic viscosity of 1.98 dL/g (in tetrahy-

dronaphthalene at 135°C). The dibutylmaleate was reagent grade. The dicumylperoxide was crystallized from absolute ethanol and stored on P_2O_5 under vacuum. The acetone was reagent grade and used without further purification.

Premixing of Reactants

EPR (45.0 g) as introduced in the mixing chamber of a Brabender-like apparatus (Rheocord EC of Haake, Inc.) with sigma-shaped kneader blades at a temperature of 90 ± 2°C. The chamber was closed by a 10-kg ram. After stabilization of the temperature a solution consisting of 4.50 g DBM and 0.450 g DCPO was added and the mixture was further mixed for 5 min at a roller speed of 32 rpm.

Determination of Composition After Mixing

The real composition of the reaction mixture after the premixing step was performed in two different ways:

Gravimetric Method

Finely grounded reaction mixture (11.51 g) was extracted for 2 days by 150 mL boiling acetone. The extraction residue (EPR) was dried overnight in a vacuum oven at 40°C.

Evaluation of the amount of extracted DBM and DCPO was performed from both the weight of the insoluble fraction (10.61 g) and the weight of the residue of the acetone solution after solvent removal (0.91 g). By this method it was found that the amount DBM + DCPO is 7.81% by weight.

Spectroscopic Method

The mixture (0.100 g) was dissolved in 10 mL carbon tetrachloride. The 1738 cm^{-1} C=O stretching absorption of the DBM was used as the analytic band. From a calibration curve obtained from a series of solutions of known concentration of DBM in CCl_4, the amount of free DBM in the mixture was estimated (7.43%).

The weight ratio DCPO-DBM in the reaction mixture (1:10) was determined by analysis of the [1H]NMR (nuclear magnetic resonance) spectrum of the residue of the acetone-soluble fraction, comparing the areas of the aromatic protons of DCPO at 7.76δ with those of —CH= and of —O—CH$_2$— protons of DBM at 6.75δ and 4.61δ, respectively.

Reaction Procedures

Two different methods were used to perform the grafting reaction.

Dynamic Method

After the premixing step, the temperature of the Brabender apparatus was rapidly raised from 90°C to the selected value (140° or 160°C) in a transient period lasting 3–5 min. The mixture was then mixed at constant temperature
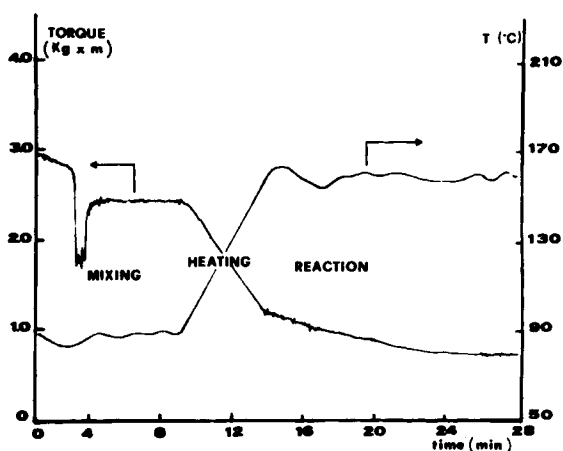
Fig. 1. Torque-temperature diagram obtained in a typical reaction carried out in the Brabender apparatus.

and at 32 rpm. Samples of the reaction mixture (0.5 g) were withdrawn at increasing times to follow the progress of the reaction.

The mixing apparatus can monitor the torque, related to the viscosity of the material, the temperature, and the time. A typical plot for a reaction carried out in the dynamic mode is reported in Figure 1. Three zones are clearly defined:

1. Premixing step. After addition of the DBM-DCPO solution to the rubber at 90°C, the torque of the two-phase system decreases sharply until it reaches a new steady-state condition. This indicates that all the absorbable liquid DBM has been absorbed by the rubber.

2. Heating step. After complete homogeneization of the system, the temperature is linearly increased up to the prefixed value (160°C in this case). In this step, which takes about 5 min, the torque decreases linearly.

3. Reaction step. Most of the reaction is carried out at this temperature, but it starts earlier in the preceding transient period. The torque decreases with time as the reaction proceeds, indicating a change in the molecular characteristics of the system as a consequence of chemical reactions.

Static Method

After the premixing step, 0.5 g of the reaction mixture was introduced in a glass tube immersed in a thermostatic bath kept at the desired temperature. The reaction was stopped by quenching the sample with cold acetone.

Product Analysis

At the end of the reaction, the product (in form of films of 0.15-mm thickness) was freed from unreacted DBM and other secondary products, in acetone at room temperature. It was verified that after 12 h the purification procedure is complete. Evaluation of the grafting degree of the EPR-g-DBM samples was performed using the same procedure previously described for the determination of free DBM in the reaction mixture. In this case, a calibration

curve obtained with DBS in CCl_4 was employed. The $[\eta]$ values were measured with a Cannon-Ubbelhode viscometer at 135°C using concentrations from 0.200 to 1.00 dL^{-1} of product in freshly distilled tetrahydronaphthalene.

RESULTS AND DISCUSSION

General Considerations in the Reactive Processing of Polymers

One of the specific problems in a bulk reactive processing involving polymeric species is that the reactants must come in close contact to ensure an acceptable efficiency of the reaction. For polyolefin functionalizations, the reactants are a preformed polymer, a functional molecule (ester or anhydride), and a radical initiator (organic peroxide). Since the third component is generally soluble in the second, the problem substantially consists of the mixability of the latter in the polymeric substrate. Two cases are possible:

1. The functional molecule is highly compatible with the polymer at the reaction temperature, and the absorbable amount is greater than that needed for the desired conversion.

2. The compatibility between the two substances is so low that the condition 1 cannot be verified.

In case 1 it is necessary, however, that the kinetics of mixing is faster than the kinetics of the reaction to allow a regular progress of the reaction. In other words, if t_M is the time needed to achieve a satisfactory mixing of the reactants in a given mixer and t_R is the time to get a certain conversion of the reaction, the condition that must hold is

$$\frac{t_R}{t_M} \gg 1$$

If this is not the case ($t_R/t_M \leq 1$), it is indispensable to perform the entire process in two well-separated steps. In general, however, it is not easy in practice to know t_R and t_M and therefore is advisable in any case to adopt the following procedure (as we have done for our system):

Mixing at conditions under which no reaction can take place

Reaction at the desidered temperature T_R

With regard to the reaction step, simple exposure of the reactant mixture at T_R should be sufficient to make it to react properly (static method). This is based on the idea that, for a compatible system, the reaction occurs in a homogeneous medium, once the mixing step has been accomplished. Some authors, recognizing the problem, have chosen a functional modifier compatible with the polymeric substrate.[15]

Case 2 is more complicated. In fact, the reaction can take place satisfactorily only in a dynamic way since the two components tend to separate, at least partially, under static conditions. As a matter of fact, the reaction may occur to a limited extent in the homogeneous phase and most of the functionalizing reactant will be inactive, unless the interphase is continuously renewed by the action of shearing forces (dynamic method). If the two components are very incompatible the reaction can occur only at the interphase, which therefore, even more so in this case, must be renewed continuously and fast. The

reactive process must therefore be designed case by case, knowing the exact limits of compatibility of the reactants and the mixing efficiency of the equipment used.

In the literature, a system that can be considered to fall in the step 2 category is that of maleic anhydride and molten polyolefins (polystyrene, polyethylene, and polypropylene) because of the highly polar nature of the functional molecule.

One of the techniques used to overcome this problem has been that of adding stepwise reduced amounts of MAH to the molten polymer.[17,18] Our system (EPR, DBM, and DCPO) falls into case 1, as experimentally evidenced. The amount of DBM absorbed in the mixing step is, in fact, 7.4% by weight using an EPR-DBM feeding ratio of 10:1, whereas the maximum amount of grafted DBM is only one-half this value, as will be shown later. Demixing the reactants prior to the reaction step cannot occur as the equilibrium concentration of DBM in EPR is higher than 15% by weight at room temperature.

Proposed Mechanism

The functionalization reactions were accomplished in a two-step process using DBM as a molecule to be grafted onto the EPR and DCPO as radical initiator. The encompassed temperature range was 130–200°C. The DCPO was chosen as radical initiator because of its rate of decomposition in the explored temperature range and on the basis of previous results obtained on the solution and on the bulk grafting of EPR.[7,16] The occurrence of the grafting reaction had been previously demonstrated by means of infrared spectroscopy[16] and was confirmed by the presence in the 200 MHz [^{1}H]NMR of the purified reaction product of a resonance (triplet) at 4.06δ attributable to the —CH$_2$—O protons of the grafted ester.

The following mechanism has been proposed in the literature for the EPR grafting process[7,16]:

$$PH + R \cdot \rightarrow P \cdot + RH \qquad (1a)$$
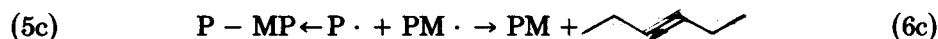
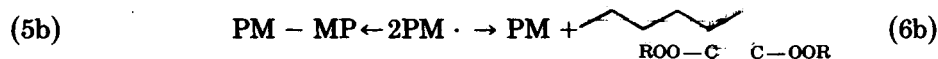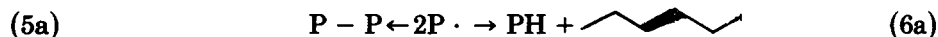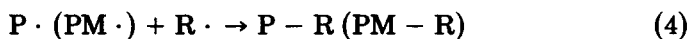$$P \cdot + M \rightarrow PM \cdot \qquad (1b)$$

The primary radicals R · generated by the thermal decomposition of DCPO abstract hydrogen atoms from EPR chains (PH), forming polymeric macroradicals (P ·). These highly reactive species may add to the activate double bond of the DBM(M), forming PM · macroradicals. According to this reaction scheme, a single DBM molecule is grafted for each R · produced by the decomposition of the peroxide. The grafting reaction may, however, also derive from PM · macroradicals by addition of other DBM molecules and/or by intermolecular or intramolecular chain transfer reactions:

$$PM \cdot + M \rightarrow PMM \cdot \qquad (2)$$

$$PM \cdot + PH \rightarrow PMH + P \cdot \qquad (3)$$
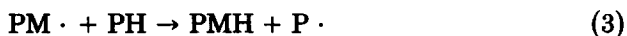
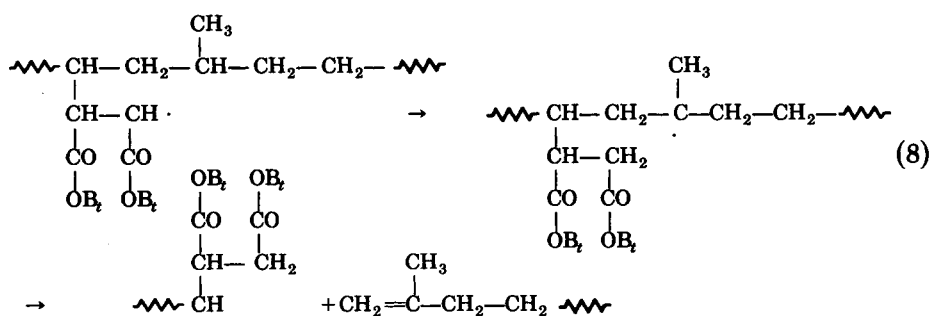Both reactions (2) and (3) increase the number of DBM molecules that can be

grafted for each primary radical R · . However, as M is a 1,2-disubstituted olefin, we do not expect reaction (2) to give a large contribution to the grafting and we may therefore assume, as a rough approximation, that most of the M molecules are grafted to the EPR chains as single units.

The active species thus generated may terminate according to the following reactions:

$$P \cdot (PM \cdot) + R \cdot \rightarrow P - R \, (PM - R) \tag{4}$$

(5a) $P - P \leftarrow 2P \cdot \rightarrow PH + $ (6a)

(5b) $PM - MP \leftarrow 2PM \cdot \rightarrow PM + $ (6b)

          ROO—C   C—OOR

(5c) $P - MP \leftarrow P \cdot + PM \cdot \rightarrow PM + $ (6c)

Note that the coupling reactions (5) increase the molecular weight of the EPR, but bimolecular disproportionation reactions (6) do not affect it.

On the other hand, the molecular weight of the polymeric substrate can be reduced by some chain breaking of P · and PM · , which may occur through a monomolecular β-scission mechanism[1]:

$$\underset{\substack{|}}{\sim\!\!\sim\!\!\sim CH_2 - \underset{\substack{| \\ CH_3}}{C} - CH_2 - CH_2 \sim\!\!\sim\!\!\sim} \rightarrow \sim\!\!\sim\!\!\sim CH_2 - \underset{\substack{| \\ CH_3}}{C} = CH_2 + \cdot CH_2 \sim\!\!\sim\!\!\sim \tag{7}$$

$$
\begin{array}{c}
\sim\!\!\sim CH - CH_2 - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - CH_2 - \sim\!\!\sim \\
\underset{\substack{| \\ CH - CH \cdot \\ | \quad | \\ CO \quad CO \\ | \quad | \\ OB_t \quad OB_t}}{}
\end{array}
\rightarrow
\begin{array}{c}
\sim\!\!\sim CH - CH_2 - \underset{\substack{| \\ CH_3}}{C} - CH_2 - CH_2 - \sim\!\!\sim \\
\underset{\substack{| \\ CH - CH_2 \\ | \quad | \\ CO \quad CO \\ | \quad | \\ OB_t \quad OB_t}}{}
\end{array}
\tag{8}
$$

$$\rightarrow \quad \sim\!\!\sim \underset{\substack{\cdot}}{CH} \quad + CH_2 = \underset{\substack{| \\ CH_3}}{C} - CH_2 - CH_2 \sim\!\!\sim$$

These latter reactions occur without loss of radical activity. The decay of a macroradical according to the β-scission mechanism is accompanied in fact by the formation of a primary or secondary alkyl radical, leading through transfer reactions to another tertiary macroradical with the possibility of replicating the fragmentation process.

Dynamic Method

In Figure 2 the results of the reaction carried out in the dynamic mode are reported. Figure 2a refers to the grafting degree (expressed as millimoles of grafted DBM per 100 g product) as a function of the reaction time. Two different reaction temperatures have been investigated (140 and 160°C). Both curves, after an initial linear trend (with a slope increasing with enhancing the temperature), level off to plateau regions. The observed gradual decrease in
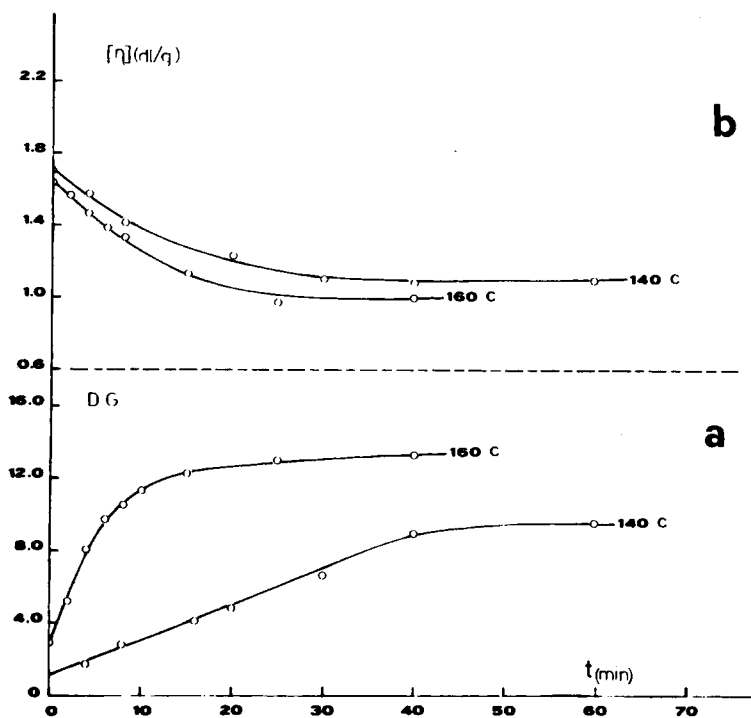
Fig. 2.   Influence of the reaction time on the grafting degree (a) and on the intrinsic viscosity of the products (b) for the reaction carried out with the dynamic method at temperatures as indicated.

the overall reaction rate can be attributed to DBM diminution and to DCPO consumption in the reaction mixture. The values of grafting degree relative to the plateau region are higher at 160 than at 140°C. This effect will be discussed in more detail when the influence of the reaction temperature on the grafting degree is analyzed.

Note that the time origin in this plot has been chosen as the instant when the selected reaction temperature is reached. However, during the transient period needed to reach this temperature, the reaction has already started; and at zero time, a finite value of grafting degree is observed at both 160 and 140°C. This effect makes an accurate kinetic analysis of the process using this reaction procedure difficult, as the initial grafting does not occur under isothermal conditions.

In Figure 2b, the values of the intrinsic viscosity $[\eta]$ of the products have been reported as a function of the reaction time. Because of the relatively low functionalization degrees of all the products tested, it can be reasonably assumed that their intrinsic viscosities are not strongly affected by the functionalization degree and may therefore be considered representative of their viscosity-average molecular weights, at least for a qualitative discussion. For both temperatures a lowering of the intrinsic viscosities is observed during the process. This indicates that, in our case, chain scission reactions of the type in reactions (7) and (8) strongly prevail over coupling reactions (5).
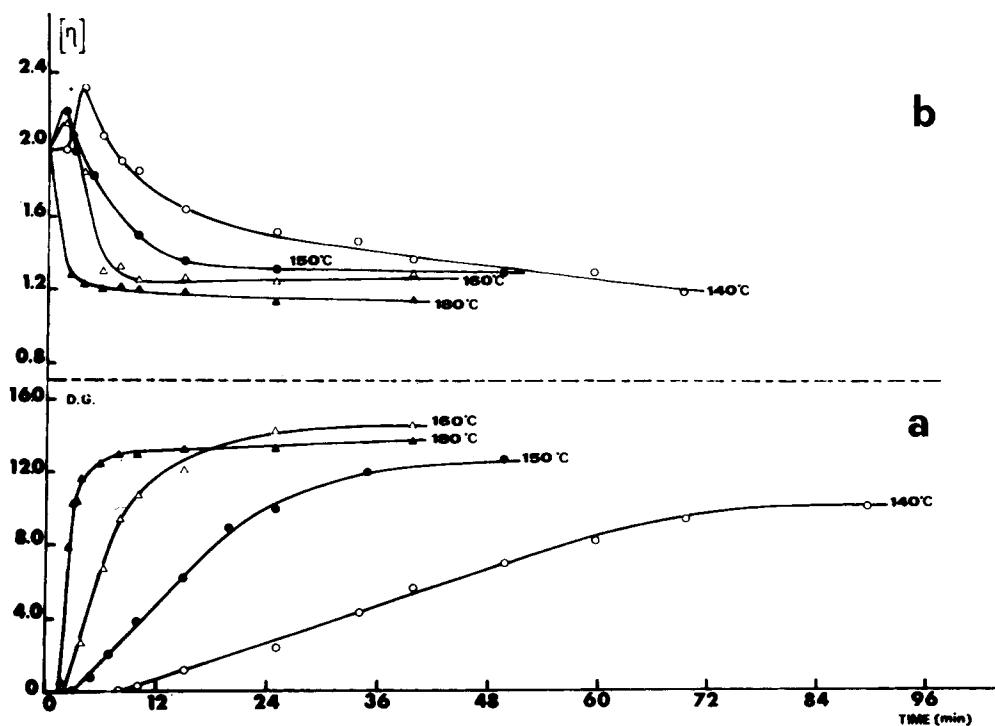
Fig. 3. Influence of the reaction time on the grafting degree (a) and on the intrinsic viscosity of the products (b) for the reaction carried out with the static method at temperatures as indicated.

The degradation effect is more pronounced at 160°C than at 140°C. Moreover, for both temperatures, the intrinsic viscosity of the products at zero time is lower than that of the starting EPR, confirming once again the initiation of the process during the transient period. To avoid the shortcoming of having a ill-defined time origin and to verify the possible role of the shear forces a different second step has been used, which may also have some technological advantages as discussed later. (This was done in the hypothesis that the static and the dynamic mode should give analogous results since the reactions occurs in a homogeneous reactant mixture.)

Static Method

In Figure 3a, the values of grafting degree versus the reaction time have been reported for the process carried out with the static method. A more detailed analysis has been carried out in this case, and four different temperatures have been investigated (140, 150, 160, and 180°C). The shape of the curves is similar to that found in the dynamic mode, but here an induction period is observed in which no grafting is detectable. This point will be discussed later, together with the variations of M_w of EPR. The induction time (9 min at 140°C) decreases by increasing the temperature. After this period, a linear increase in grafting degree with time is observed, followed by a gradual reduction of the reaction rate. The slope of the curves increases with
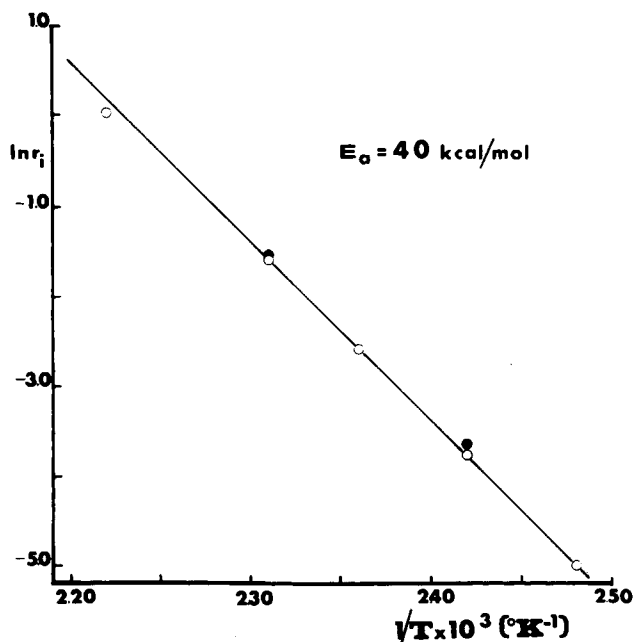
Fig. 4. Arrhenius plot of the initial reaction rate for the static (open circles) and for the dynamic method (solid circles).

increasing the temperature, and the values of the grafting degree relative to the plateau region are very similar at 150, 160 and 180°C and lower at 140°C.

From the slopes of these curves the initial rate of the grafting reaction at the various temperatures has been estimated. Its values correlate well in an Arrhenius plot (empty circles in Figure 4) with an activation energy of 40 kcal/mol (in the same figure the solid circles refer to the dynamic mode). Comparing this value with that of the activation energy of the DCPO thermal decomposition (37 kcal/mol), it can be suggested that the main contribution to the overall activation energy of the process is due to the thermal decomposition of the radical initiator, which could be the rate-determining step of the reaction.

In Figure 5, the grafting degree versus the temperature has been reported for three different reaction times (3, 10, and 40 min). For the upper curve (40 min), a maximum of the grafting degree at 160°C is observed. At temperatures below and above this value, parasitic processes that consume macroradicals, such as cross-linking reactions (4) and (5) or, more probably, bimolecular disproportionation, reaction (6), or even R · coupling, are favored. All these reactions contribute to lowering the functionalization degree of the EPR. For the 10-min curve the trend is very similar to that previously discussed. The lower curve (3-min) indicates that, by choosing an appropriate temperature, a sufficient degree of grafting can be achieved even in a very short time. This is of certain technological interest since twin- or single-screw extruders with limited residence times could be directly used for such a process.

A complex rearrangement of the molecular characteristics of the EPR chains occurs during the grafting process under static conditions. It leads to
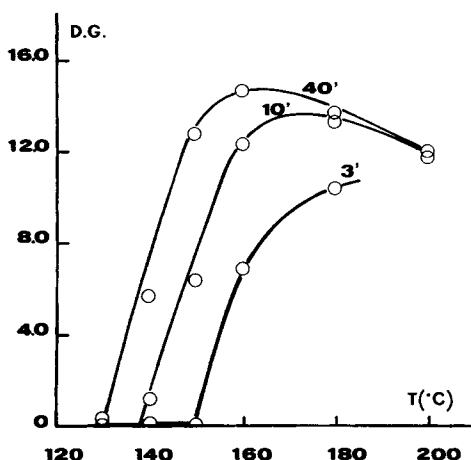
Fig. 5. Dependence of the grafting degree on the temperature for the reaction carried out with the static method at different reaction times.

chain degradation of grafted EPR, as previously found in the case of dynamic experiments.

This phenomenon has been qualitatively monitored by determining the intrinsic viscosity of the functionalized EPR. The $[\eta]$ values of the products versus the reaction time have been plotted in Figure 3b for all the temperatures investigated. The most interesting feature of these curves is the presence of a maximum in the $[\eta]$ values at 140, 150, and 160°C. The increase in molecular weight of the rubber occurs in the early stages of the process when the grafting is not detectable, that is, during the induction period. Such behavior was not observable in dynamic experiments (see Fig. 2). The initial increase in molecular weight can be accounted for on the basis of the following considerations.

The decomposition of a molecule of radical initiator generates a pair of highly reactive primary radicals R · , which produce, by hydrogen abstraction from neighboring EPR chains, a pair of P · macroradicals. Owing to the lack of molecular mobility in static conditions, the radical sites are very close to each other, and therefore there is a high probability of cross-linking reaction (5a). The net result is an increase in the molecular weight as well as radical consumption. On the other hand, the cross-linking reaction (5a) may actually compete with a chain transfer of the type

$$\text{P· ·P PH} \longrightarrow \text{P · PH P·} \tag{9}$$
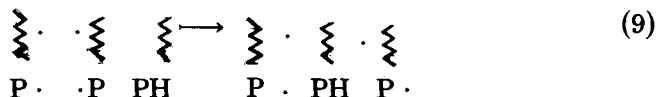
by which radical sites can migrate through the polymeric bulk. This reaction occurs easily. In the case of polyethylene an activation energy of only 4 kcal/mol has been determined.[20]

Therefore in a certain period of time a definite number of radical sites could escape from the coupling trap. For each of these events, several chain scissions can occur because of the chain character of the fragmentation reaction. Thus,

although in the early stages of the static process coupling reactions (5a) are more favored, as soon as a critical concentration of escaped macroradicals has been built up in the system, β-scission reactions as well as grafting of DBM prevail. This mechanism may explain both the steep decrease in molecular weight following the maximum in Figure 3b and the induction period of Figure 3a.

The data of Figure 4 also suggest that grafting degree and extent of degradation are somewhat related to each other. This point is more clearly shown in Figure 4, where the $[\eta]$ values of the reaction products have been plotted against their grafting degree. In fact, the data fall on a unique curve independent of their temperature and reaction time dependence. It is worth remarking that when the reaction was carried out in the absence of DBM, cross-linking occurred, as evidenced by the finding of a considerable amount of gel fraction in the reaction product (gel content 49.4% by weight, at 150°C for 30 min and 100 : 1 EPR-DCPO by weight). The coupling prevails over β-scission in the absence of grafting, but an opposite trend is found in the presence of DBM. The simplest explanation of this behavior is that both secondary and tertiary macroradicals are expected from hydrogen abstraction on the polymeric substrate promoted by primary R $\cdot$ radicals. Their relative amount depends on their stability (tertiary > secondary) and population (secondary > tertiary). In the absence of DBM, secondary macroradicals preferentially yield coupling reactions and tertiary macroradicals lead to β-scission processes.[21,22] As a matter of fact, the cross-linking efficiency of organic peroxides is much higher in polyethylene than in polypropylene.[23] In the presence of DBM the grafting occurs together with the above reactions. If it involves the secondary macroradicals more easily than the tertiary, the balance between coupling and β-scission is clearly shifted toward the latter. This assumption seems to be quite reasonable because of the steric hindrance exerted by the methyl group on the approaching DBM molecule. Moreover, previous results obtained from the solution grafting of PE, PP, and EPR[9] indirectly confirm this. It was found, in fact, that under the same experimental conditions the grafting degree of the different polymers follows the order

$$PE \simeq EPR \gg PP$$

An additional contribution to chain degradation may be related to the fate of PM $\cdot$ macroradicals. In fact, when a PM $\cdot$ macroradical is formed by reaction (1b), it could react by an intramolecular chain transfer by which an hydrogen is abstracted from a neighboring carbon atom, transferring the active site onto the same EPR chain [see reaction (8)]. For this latter species PM $\cdot$, the coupling reactions are less probable with respect to a P $\cdot$ macroradical because of the steric hindrance of the bulky succinic ester group attached onto the chain, but β scission is still likely to occur. We may therefore conclude that grafting successfully competes with coupling, favoring the β-scission reactions.

In Figure 6, at high degrees of grafting the curves level off, showing no further decrease of $[\eta]$ with respect to the DG. This seems to be in contrast with the claimed influence of grafting on the degradation mechanism. However, note that $[\eta]$ is an indirect measure of the degradation rate and the leveling off of the curve may be fallacious. In fact, $[\eta]$ is a very sensitive
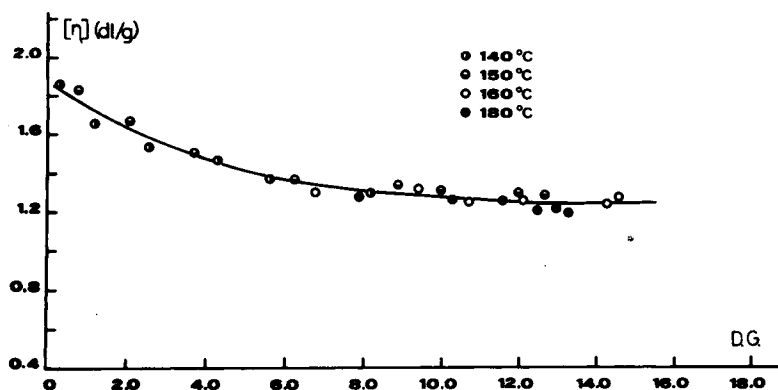
Fig. 6. Dependence of the intrinsic viscosity on the grafting degree for the reaction carried out with the static method.

parameter at high-molecular-weight values but becomes more and more insensitive as the molecular weight decreases. On the basis of our data it is not possible to give a further and more accurate description of the degradation process such as that proposed by other authors in the literature for some different systems.[24]

Comparison of the Dynamic and Static Reaction Modes

The curves of DG versus time reported in Figures 2 and 3 exhibit comparable plateau values at the same temperature, indicating a similar efficiency of the grafting reaction in the two modes. A better comparison is shown in Figure 7, where the grafting degree relative to the plateau region is reported for the static (open triangles) and the dynamic method (solid triangles) as a function of the reaction temperature. In both cases a maximum occurs at about 160°C. In the temperature range below 160°C, the increase in DG with
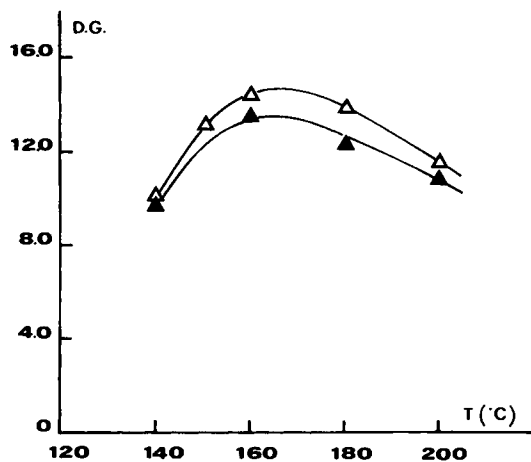

Fig. 7. Influence of reaction temperature on the maximum grafting degree obtained with the static (open triangles) and with the dynamic method (solid triangles).

temperature could be ascribed to a higher temperature dependence of the rate constants of the grafting active reactions (1b) and (2) compared with those that decrease the grafting efficiency, such as reactions (4), (5), and (6).

On the other hand, at temperatures higher than 160°C, the decomposition rate of the initiator becomes very high. Hence secondary reactions among primary radicals and/or macroradicals can be more easily induced by the large concentration of these species. Also, the overall kinetics are very similar, as shown in Figure 4, where the data relative to the static (empty circles) and to the dynamic mode (full circles) fall on the same straight line. The induction period is present in the former case because of the absence of acting shear forces. The different molecular mobility in the two cases also has a certain influence on the degradation kinetics. In fact, for the dynamic mode the maximum of the $[\eta]$ versus time curves observed for the static mode is not detectable.

Finally, comparing Figures 2 and 3, it is possible to observe that the $[\eta]$ values relative to the dynamic mode are lower than the corresponding values of the static method. This effect could be attributed to the fact that in the static method the degradation starts after an initial increase in molecular weight.

CONCLUSIONS

In this paper a contribution to a better rationalization of the problems involved in the bulk polyolefin functionalization promoted by organic peroxides has been provided according to the preliminary consideration that separation of the mixing and reaction process is generally convenient, if not necessary, for compatible systems. In the case of EPR functionalization by DBM, similar kinetic behavior in the static and dynamic processes have been found, as expected for compatible reactant mixtures. Minor but meaningful differences between these processes occur at the beginning of the reaction and can be interpreted in terms of chain mobility and radical trapping. Free-radical cross-linking is suppressed in the presence of DBM, and comprehensive molecular mechanisms for the grafting and the degradation have been proposed. At high temperatures, the functionalization is fast enough to suggest the possibility of using a technological processing apparatus (i.e., extruders) as the reactor. The results refer, however, to a constant composition of the reaction mixture. Work is in progress to analyze the influence of this parameter as well as that of the EPR composition on the reaction kinetics and to check the reliability of the proposed molecular mechanisms under different reaction conditions.

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