

Functionalization of ethylene-propylene saturated rubbers: a study on the grafting of monoethylmaleate and its cyclization reaction

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Summary

A study on the solution grafting of monoethylmaleate onto a saturated ethylene-propylene rubber was conducted. The grafting degree was followed by titration methods as function of the time of reaction and amount of initiator. The insertion of unsaturated molecules always led to some degradation of the polymeric backbone. The subsequent cyclization reaction of grafted monoethylmaleate to maleic anhydride was also studied by Fourier Transform Infrared Spectroscopy either in bulk or in solution. A different behaviour was found in the two cases; furthermore, a different mechanism of reaction led to different amounts of inter- and intra-chain anhydride formation.

INTRODUCTION

Functionalization of polyolefins can be accomplished by grafting suitable unsaturated molecules bearing a functional group of interest through radical reactions initiated by organic peroxides (1-5). Polyolefins modified by insertion of polar groups have been prepared to promote properties as adhesion to metals, dyability, cross-linking, or other physico-chemical characteristics. The polyolefins so modified can be used as starting materials for the preparation of graft copolymers. Such copolymers have been extensively used as interfacial agents in blends of two incompatible polymers (6-10). For example, the presence of EPR-g-Succinic Anhydride (EPR-g-SA) in blends of EPR and polyamide 6 led to a large improvement in the mechanical properties and in the morphological appearance of the blend, mainly attributable to the formation of (EPR-g-SA)-g-PA6 copolymer molecules (9,11). Another method to achieve similar results is to add EPR-g-SA in the course of the hydrolytic polymerization of caprolactam.

The preparation of EPR-g-SA is normally carried on by solution grafting of EPR with maleic anhydride using peroxides as initiators. Such process is not convenient for industrial preparations, where bulk or aqueous suspension processes are preferred. Unfortunately, maleic anhydride is very corrosive in normal extruders, and in aqueous suspensions this molecule leads to the less reactive maleic acid. A convenient monomer which in principle can be grafted in suspension is monoethylmaleate (MEM); it can, upon grafting, be converted to the cyclic form of anhydride by simple heating (12).

In this paper we deal with a preliminary study on the functionalization

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by solution method of the EPR by the insertion of monoethylmaleate, to give an EPR grafted with monoethylsuccinate groups (EPR-g-MES). The functionalized EPRs have been characterized by IR and viscosimetric techniques. Furthermore, the cyclization process of monoethylsuccinate groups grafted onto EPR to anhydride has been investigated either in solution or in bulk at high temperatures by IR spectroscopy.

EXPERIMENTAL

Materials

EPR was a random ethylene-propylene copolymer, kindly supplied by Dutral S.p.A., $M_w = 1.8 \times 10^5$; Melt flow index (100°C) = 40 g/min.

Dibenzoylperoxide was recrystallized from absolute ethanol and stored under vacuum.

Maleic anhydride, a Fluka reagent analytical grade, was used without further purification.

All the solvents were of analytical grade and were purified according to standard procedures when necessary.

Techniques

Titrations were carried out by a Metrohm AG-CH-P100 Herisau potentiometer equipped with a processor for the analysis of the collected data. An Ag/AgCl electrode in a saturated solution of LiCl in isopropanol was used as reference electrode.

The IR spectra were obtained with a Nicolet 5DXB FTIR apparatus, equipped with a control temperature cell which allows scans of temperature from -200 to 250°C (SPECAC 20-100).

The viscosity measurements were performed at 135°C by a Cannon-Ubbelohde viscosimeter. Concentrations of 100 mg/10cc in tetrahydronaphthalene were used.

Monoesterification reaction of maleic anhydride

In a flask equipped with nitrogen inlet 10g of MA were added to 50 mL of absolute ethanol under stirring at room temperature (molar excess EtOH/MA = 10/1). Anhydride reacts completely with alcohol to give monoethylmaleate, which is soluble in ethanol. The excess of ethanol is removed by rotovapor and the product is purified by dissolution in benzene and filtration to remove by-products like dicarboxylic acid. The benzene was finally removed under vacuum at room temperature.

Typical grafting reaction

In a flask equipped with a nitrogen inlet and a condenser 5.0g of EPR were dissolved in 100 mL of chlorobenzene (CB) at room temperature. When the dissolution was complete, the temperature was allowed to rise to 85°C and a solution containing 8.0g (5.5×10^{-2} mol) of monoethylmaleate in 10 mL of solvent was added to the system, together with 0.50g (2.07×10^{-3} mol) of dibenzoylperoxide, previously dissolved in 10 mL of CB. After two hours, the reaction was stopped and the polymeric product was precipitated in methanol, repeatedly washed with acetone and finally dried in a vacuum oven for 24h at 50°C .

Evaluation of grafting degree

The amount of grafted succinate groups in EPR-g-MES has been determined by titration of the carboxylic groups. The titration has been performed by using a 0.10 M potassium hydroxide solution in o-dichlorobenzene/ethanol 90/10 by volume as standard solution.

Cyclization of EPR-g-MES in o-dichlorobenzene solution

2g of EPR-g-MES were dissolved in 40 mL of solvent in a flask equipped with a condenser. After the dissolution was complete, the temperature was risen to 160°C, while N₂ was allowed to bubble inside the solution. Samples were taken off at chosen intervals of time and film for IR analysis were evaporated directly onto a KBr disk.

RESULTS AND DISCUSSION

Solution grafting of monoethylmaleate onto EPR

The grafting reaction has been studied in solution, using dibenzoylperoxide as radical initiator and anhydrous chlorobenzene as solvent. In all experiments, the temperature has been kept at 85°C, because at higher temperatures the free monoethylmaleate is converted to maleic anhydride. Nevertheless, as we can see from the spectrum of fig.1, the final product always contains a little amount of grafted succinic anhydride for the establishment of an equilibrium between monoester and anhydride. The presence of a certain amount of grafted anhydride cannot be avoided, also when the reaction temperature is further decreased (70°C). Actually, it is possible that the cyclization occurs after the grafting onto EPR.

Chlorobenzene is chosen as solvent because it allows higher grafting efficiency if compared with other aromatic solvents (13), while dibenzoylperoxide as initiator has a sufficient high decomposition rate at the reaction temperature.

The reaction has been investigated for two different amounts of peroxide, i.e., 41 and 103 mmol DBPO/100g EPR. Quantitative results in terms of mmol of MES grafted/100g EPR vs. time for both DBPO concentrations are reported in fig. 2, for a total reaction time of three hours. The behaviour is similar to that of other molecules previously investigated. In fact, at the lower concentration of DBPO a plateau is reached in about one hour of reaction. In similar grafting experiments, maleic anhydride gives higher final conversions (13). The higher reactivity of MA can be explained with the enhanced activation of the double bond towards the addition to macroradicals due to a stronger electron-attracting property and higher delocalization ability of the anhydride group respect to the ester group. According to this explanation, the monoethylmaleate reaches the plateau at a value of conversion intermediate between those reached by MA and a diester group, the dibutylmaleate.

The curve relative to the higher DBPO concentration is quite different from the previous one also from a qualitative point of view, because a plateau is not reached in the time scale of experiments. It is believed that, at higher concentrations of peroxide, part of primary radicals R is involved in oligomerization of MEM molecules which can, in turn, graft onto EPR molecules (15). This fact indicates that the grafting of MEM is

very sensitive to the concentration of primary radicals, which influences the mechanism of the grafting reaction.

Furthermore, the grafting of unsaturated molecules onto EPR chains leads to a decrease of the reduced viscosity of the polyolefinic substrate (13). Measures of reduced viscosity at different reaction times confirm this trend, as we can see from the plot of fig. 3. Obviously, a greater concentration of peroxide leads to a greater degradation of EPR chains.

An investigation of grafting degree as function of the amount of starting peroxide has been performed, and the results are reported in the plot of fig. 4. The curve shows a marked increase in the functionalization degree at increasing DBPO concentrations, up to 30 mmol per 100g EPR, while reaches a plateau at higher concentrations. This trend is common to other unsaturated molecules and can be ascribed to three main effects: a) partial saturation of reactive sites onto EPR; b) decreasing efficiency of the initiator, due to recombination reactions between primary radicals, and c) increasing probability of secondary reactions of macroradicals.

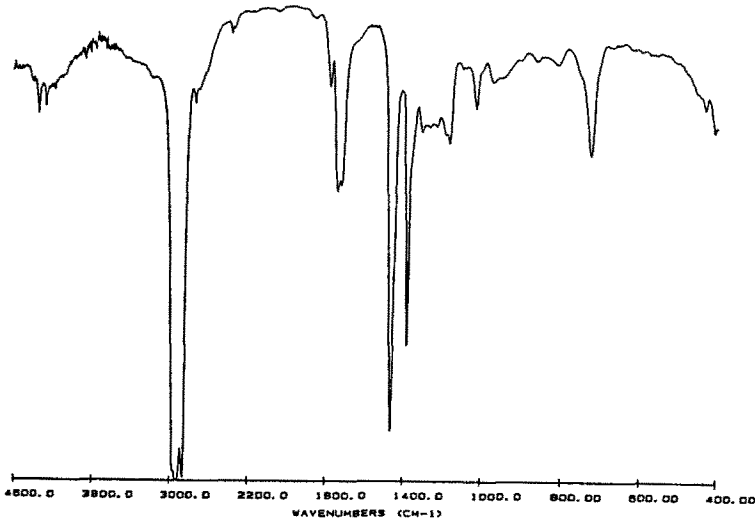


Fig. 1) FTIR spectrum of EPR-g-MES at 6.2% grafting degree.

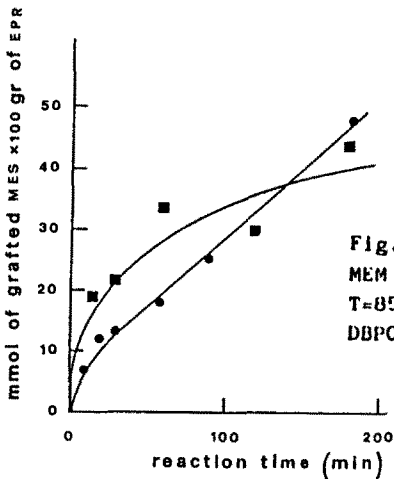


Fig. 2) Dependence of the grafting degree of MEM on the reaction time. Reaction conditions: $T=85^{\circ}\text{C}$; chlorobenzene=100ml; EPR=5.0g; MEM=8.0g; DBPO (■)=0.50g and (●)=1.25g.

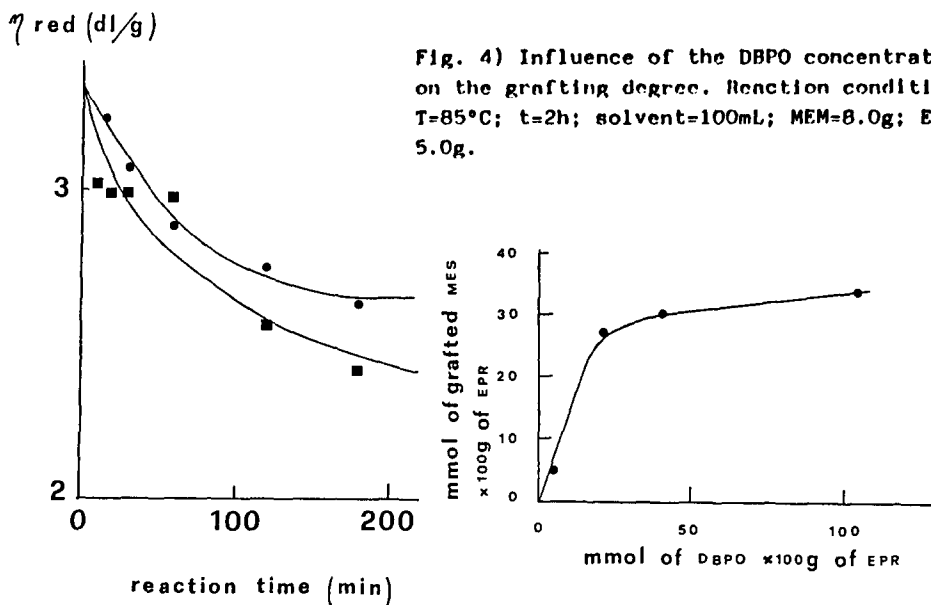
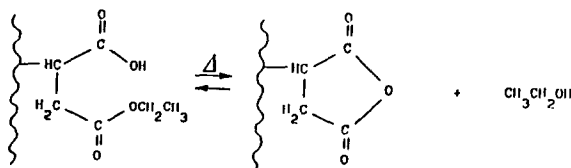


Fig. 3) Dependence of the reduced viscosity of EPR-g-MES on the reaction time. Reaction conditions: $T=85^{\circ}\text{C}$; chlorobenzene=100mL; EPR=5.0g; MEM=8.0g; DBPO (●)=0.50g and (■)=1.25g.

Thermal cyclization of EPR-g-MES to EPR-g-SA

The cyclization of monoethylsuccinate groups grafted onto EPR is an equilibrium reaction (12):

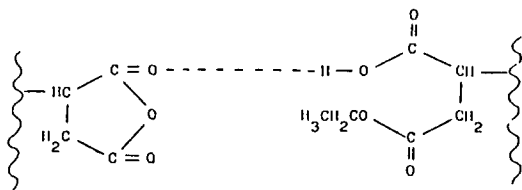


Preliminary investigations on an EPR-g-MES at high grafting degree (>5%) showed that the cyclization occurs at $T > 130^{\circ}\text{C}$, while for $T > 170^{\circ}\text{C}$ the degradation of EPR begins to be evident. Studies on the cyclization in bulk have been performed on films obtained by casting from a xylene solution directly onto a KBr disk at room temperature. The coated KBr disk was put inside the temperature cell which was already at the test temperature, and spectra have been collected at selected times. While collecting spectra, the cell was carefully flushed with a stream of N_2 .

Fig. 5 shows the spectra of a film of a EPR-g-MES, in the spectral range of interest, for a thermal treatment at 150°C . The anhydride band,

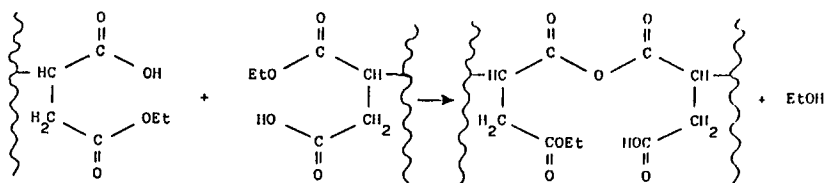
already present in the starting EPR-g-MES, reaches the same intensity of the ester-acid in less than 30 minutes and after 3h the ratio anhydride/ester inverts completely.

Fig. 6 shows the spectra relative to studies performed in solution of o-dichlorobenzene. The behaviour in solution at 160°C is quite different; in fact, after many hours the conversion has not yet reached 50%, and only after several days the anhydride band is more intense than the ester band. From a closer inspection of the spectra, it is seen that the principal peak of anhydride group gradually shifts from 1775 cm⁻¹ (in the EPR-g-MES before heating) to 1783 cm⁻¹ (after heating). This last frequency is more characteristic of free SA groups (14). The initial shift towards lower frequencies can be attributed to polar interactions (hydrogen bonding) between the carbonyl moiety of SA and the acidic part of MES:



Increasing the concentration of SA groups and decreasing that of MES the possibility for such interactions to occur decreases, so the anhydride band shifts to the frequency characteristic of a free five-membered cyclic anhydride.

Anhydride groups could in principle be formed also between a carboxylic and an ester group of two different molecules of MES:



The formation of anhydride linkages between groups grafted onto different EPR chains should lead to crosslinked EPR. To investigate on existence of such crosslinks, studies of solubility in xylene of EPR-g-MES after cyclization have been performed.

A sample which had been heated in bulk at 150°C for 3h (see fig.5) was treated with boiling xylene for long time. A gel fraction was actually found, whose IR spectrum, obtained on a film compression-molded at 150°C, shows a high content of anhydride. On the contrary, the soluble fraction, recovered from xylene, shows an IR spectrum similar to that of the starting material, i.e., before any heat treatment, with a very small anhydride band. We can conclude that the bulk cyclization reaction proceeds via an inter-chain anhydride formation, which is a bi-molecular process. A similar treatment with boiling xylene was made on a sample of EPR-g-MES after solution cyclization. Also in this case the sample shows a small gel fraction which presents at IR analysis no differences from the soluble fraction, indicating thus that both mechanisms of inter- and intra-chain anhydride formation can occur in this case, even if the monomolecular mechanism is preferred, due to the dilution of the system. More work is in progress to characterize prepared rubbers in mechanical and dynamic-mechanical tests and to compare their properties with

analogous EPR-g-SA prepared by solution grafting of maleic anhydride onto EPR. Furthermore, a research was recently started on the suspension grafting of MEM in aqueous medium.

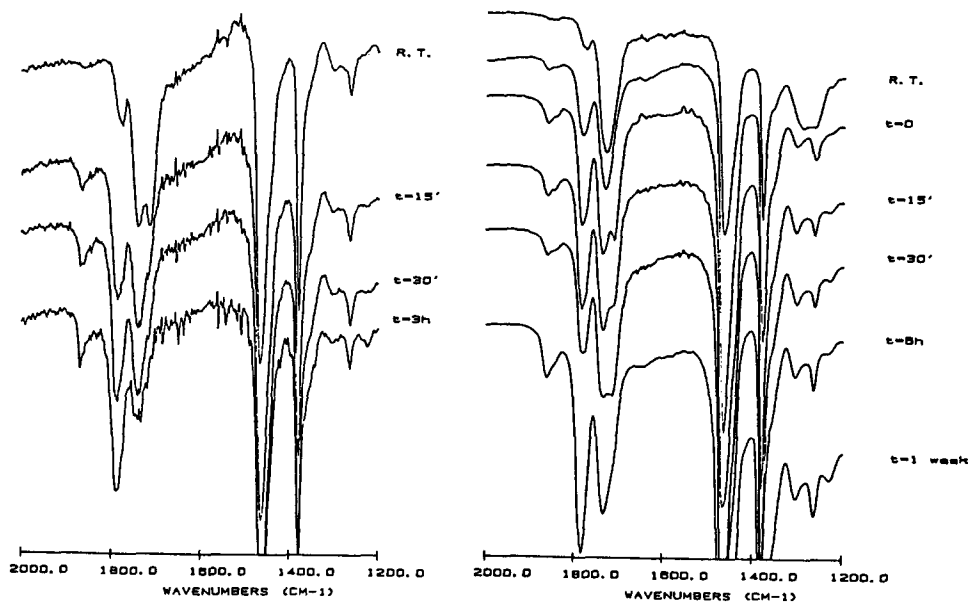


Fig. 5) FTIR spectra of EPR-g-MES at different times during the heating process in bulk at $T=150^{\circ}\text{C}$ (the poor resolution of the baseline is due to the lower resolution obtainable in the presence of the temperature cell accessory). The first spectrum is referred to the starting EPR-g-MES at Room Temperature.

Fig. 6) FTIR spectrum of EPR-g-MES at different times during the heating process in solution at $T=160^{\circ}\text{C}$. The first spectrum is referred to the starting EPR-g-MES at Room Temperature.

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