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OPTIMIZATION OF REACTION CONDITIONS OF BULK FUNCTIONALIZATION OF EPDM RUBBERS WITH MALEIC ANHYDRIDE

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Abstract—Bulk functionalization of EPDM rubber with maleic anhydride (MAH) using peroxide type initiators led to high grafting efficiency after optimization of reaction conditions. Reaction behavior in the presence of two aromatic peroxides was studied. It was verified that for a fixed initiator concentration the main process control variables were shear rate, mixing temperature, and MAH content in the charge recipe. The formulations containing high MAH levels exhibited anomalous low grafting efficiencies, which could be mechanistically explained by the presence of MAH excited species.

INTRODUCTION

Functionalization of polyolefins with monomers containing carboxylic groups such as maleic anhydride (MAH) has been intensively investigated in order to improve their physical and chemical properties [1–4]. The introduction of succinic groups in ethylene–propylene rubbers is a useful method to improve their adhesion characteristics, and it is a step towards producing new materials specially designed for applications in which unmodified hydrocarbon rubbers exhibit poor performance.

One important application for maleated ethylene–propylene rubbers [EPD(M)-g-SAH] is the production of multipurpose lubricating oil additives [5]. While the elastomeric hydrocarbon macromolecule acts as a compatible viscosity-index improver, the succinic groups are able to post-react with alcohols and amines in order to provide dispersant characteristics to the additive.

Another interesting product derived from these functionalized rubbers are the thermoplastic elastomers [6]. Due to the succinic acid groups incorporated in the rubber, sites for thermally reversible crosslinks are generated. At room temperature the occurrence of hydrogen bonds or of ionic coupling with cationic substances (such as zinc or calcium salts) imparts good final properties to these unconventionally cured elastomers. The flow features of raw EP(D)M are maintained since at processing temperatures charge interaction among chains is drastically decreased.

The more recent development in the field of maleated ethylene–propylene rubbers is the study of impact modification of rigid thermoplastics such as nylons and polyesters [7]. In nylon blends, the flexible hydrocarbon main chain is linked to the polyamide through the formation of imide groups by reaction with the succinic units previously introduced in the rubber, whereas in the polyester mixtures, adhesion is imparted by hydrogen bonding between the modified elastomer and the resin. In the case of synthesis of impact modifiers, products with high gel content are often desirable [8].

The main polymerization routes used for the synthesis of EP(D)M containing succinic groups apply solution [9, 10] or bulk [4, 11–14] production techniques. The solution processes are extremely adequate for the production of lubricating oil additives, due to the ability for direct synthesis of such additives applying base-oil as solvent. Nevertheless, it is known that the solvent type influences the grafting efficiency causing its decrease when the chain transfer constant is high [9]. In the case of bulk processes either continuous (reactive extrusion) [7, 12] or batch (internal mixers) [4, 11, 13, 14] systems have been reported in the literature. Although bulk grafting is often preferred when cost/performance factors are taken into account, the high shear levels present in this technique can lead to intensification of side reactions (mainly oxidation [1] and crosslinking [2]). These reactions are known to occur when maleic anhydride is introduced in polyolefins by free radical initiation, and products with high gel content are often obtained [14, 15].

In this work a batch bulk process was studied in order to verify the influence of process variables in grafting efficiency and also in the extent of side reactions. Two different levels of reaction temperature were used, according to the half-life times of the peroxides tested. Different levels of shear were also tested, and the peroxide as well as the maleic anhydride charge content was varied with the aim of optimizing the reaction conditions to obtain maximum grafting efficiency.

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Table 1. Characteristics of EPDM grades used for grafting with MAH

Feature	EPDM A	EPDM B	EPDM C
Propylene content (%wt)	43.0	27.0	40.0
Termonomer	ENB	ENB	ENB
Iodine number	6.0	15.0	29.0
Molecular weight ($M_n \times 10^{-3}$)	51.0	66.0	58.0
M_w/M_n	2.8	2.9	3.6

ENB = 5-ethylidene-2-norbornene.

Table 2. Grafting of EPDM B with dibenzoyl peroxide

Reaction conditions	SAH content	E	Oxidation index
T, °C/rpm/phr P/phr MAH/t, min	(%wt)	(%)	(A_{1713}/A_{1465})
100/50/2.0/5.0/15	2.40	47.1	1.27
100/50/2.0/5.0/35	2.43	47.6	1.44
120/50/2.0/5.0/15	3.10	60.9	1.69
120/50/2.0/5.0/35	2.57	50.5	1.62
120/100/2.0/5.0/15	2.78	54.5	1.77
120/100/2.0/5.0/35	2.41	47.2	1.71
100/50/2.0/3.0/15	2.73	89.4	1.53
100/50/2.0/3.0/35	2.63	85.9	1.52
120/50/2.0/3.0/15	2.62	85.8	1.52
120/50/2.0/3.0/25	2.48	81.0	1.44
120/50/2.0/3.0/35	2.40	78.4	1.50
120/100/2.0/3.0/15	2.52	82.4	1.51
120/100/2.0/3.0/35	2.41	78.8	1.64

phr P = phr of peroxide initiator in the charge.
phr MAH = phr of MAH in the charge.
SAH content (%wt) = content of bound succinic groups.

$$E = \text{grafting efficiency} = \frac{\text{SAH content (\%wt)} \times \text{PM MAH} \times 100}{\text{phr MAH} \times \text{PM SAH}}.$$

EXPERIMENTAL

50 g of EPDM rubber were mixed with maleic anhydride (MAH) and peroxide initiators in the mixing chamber of a Brabender-like rheometer Rheomix 600 of Haake System 40 (the characteristics of the three grades of EPDM used can be seen in Table 1). The rubbers were supplied by Nitrifex S. A. Indústria e Comércio. Dibenzoyl peroxide of 78% purity (Lucidol 78) and dicumyl peroxide of 99% purity (Luperox 500R) were kindly supplied by Atochem. Maleic anhydride of 99.9% purity was supplied by Riedel. Acetone used for extraction was dried by the standard method and distilled before use.

The charge temperature of MAH was 80°C, and the charge temperature of peroxide varied between 100 and 140° according to the type of initiator tested. Cam rotors were used at fixed velocities of 50 rpm (low shear level) or 100 rpm (high shear level). Torque–temperature diagrams were automatically recorded.

The raw grafting product was extracted with acetone as described elsewhere [16]. The purified rubber was analyzed by FTIR spectroscopy in a Perkin–Elmer 1720 spectrometer equipped with a diffuse reflectance accessory (DRIFT). FTIR runs were carried out with 2 cm^{-1} resolution and 50 scans. Succinic groups' content of the EPDM-g-SAH was determined via the pseudo-absorbance ratio A_{1780}/A_{1465}, and the relative oxidation extent was estimated by the ratio A_{1713}/A_{1465} by the method previously reported [17].

RESULTS AND DISCUSSION

Influence of peroxide type

Bulk functionalization of EPR using aromatic peroxide initiators has been investigated by Gaylord *et al.* [4]. Their results indicate that compared to dicumyl peroxide (DICUP), dibenzoyl peroxide (DIBZ) is less effective both in crosslinking and in grafting ethylene–propylene copolymers. However, in the case of EPDM the presence of termonomer apparently enhances the rubber reactivity towards dibenzoyl peroxide as shown in Table 2. Even at 100°C, a condition of relatively slow initiator decomposition (half-life time of about 27 min [18]), grafting efficiencies are appreciable. A typical spectrum of EPDM-g-SAH obtained with DIBZ initiator, after purification, is shown in Fig. 1.

Comparing these results with those obtained with DICUP in approximately equivalent conditions (Table 3, reaction temperature of 140°), it can be noticed that grafting efficiencies for DIBZ are slightly higher, and oxidation is slightly reduced by applying low temperature levels. DIBZ also caused high gel formation in the product (Table 4). Torque–time curves for DICUP and DIBZ are shown in Figs 2

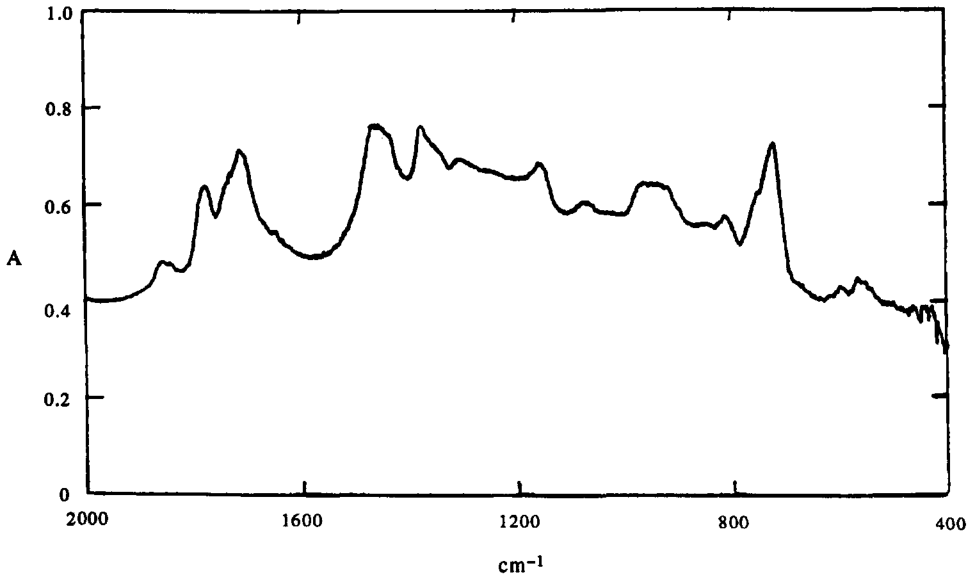

Fig. 1. Typical spectrum of EPDM B-g-MAH (produced with DIBZ initiator).

Table 3. Grafting of EPDM B with dicumyl peroxide

Reaction conditions T, °C/rpm/phr P/phr MAH/t, min	SAH content (%wt)	E (%)	Oxidation index (A_{1713}/A_{1465})
120/50/2.0/5.0/15	2.39	47.0	1.63
120/50/2.0/5.0/35	2.19	42.9	1.21
140/50/2.0/5.0/15	2.43	47.6	1.63
140/50/2.0/5.0/35	2.28	44.8	1.72
120/50/0.5/5.0/15	0.91	17.8	0.60
120/50/0.5/5.0/35	1.83	35.9	0.85
120/100/0.5/5.0/15	2.26	44.3	0.77
140/50/0.5/5.0/15	2.56	50.1	1.84
140/100/0.5/5.0/15	2.20	44.0	1.69
140/100/0.5/5.0/35	2.63	51.5	2.22
120/50/2.0/3.0/15	2.61	85.3	1.61
120/50/2.0/3.0/35	2.31	75.5	1.56
120/100/2.0/3.0/15	2.48	81.0	1.61
140/50/2.0/3.0/15	2.50	81.7	1.61
140/50/2.0/3.0/35	2.25	73.5	1.66
140/100/2.0/3.0/15	2.42	79.1	1.61
120/50/2.0/2.5/15	2.21	86.6	1.33
120/50/2.0/2.5/35	2.03	79.8	1.37
140/50/2.0/2.5/15	2.20	86.6	1.44
120/50/0.5/2.5/15	1.57	61.5	0.76
120/50/0.5/2.5/35	2.34	91.7	1.20
120/100/0.5/2.5/15	2.16	84.7	1.33
140/50/0.5/2.5/15	2.31	90.6	1.47
140/50/0.5/2.5/35	2.51	98.4	1.57
140/100/0.5/2.5/15	2.19	85.8	1.24
140/100/0.5/2.5/35	2.24	87.8	1.29

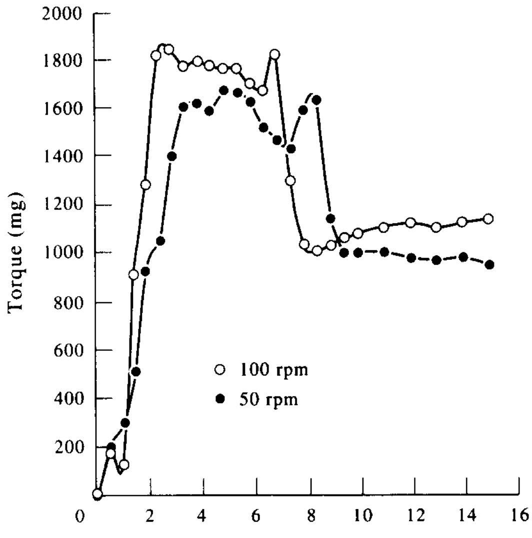

Fig. 2. Torque–time curves for grafting of EPDM B with 2.0 phr of DICUP and 3.0 phr of MAH at 140°.

and 3 respectively. It can be seen that DIBZ initiated reactions exhibit a torque peak near 9 min which is absent for DICUP initiated reactions. That peak can be attributed to a rapid chain scission followed by crosslinking that occurs when low half-life time conditions are employed ($t_{1/2}$ of about 4.5 min at 120°) [18] while for DICUP the process of chain breaking and crosslinking is slower.

Influence of reaction time

In the conditions studied in this work, a general tendency of decreasing efficiency with increasing reaction times was observed when high peroxide level was used (Tables 2, 3, 5 and 6). The expected relationship between grafting efficiency and time would be an initial increase followed by stabilization (as reported for bulk modification of dibutyl maleate [11]). The unusual behavior required a detailed study of the time influence on grafting efficiency (Fig. 4), which confirmed the previous results.

The low molecular weight EPDM rubber, which is formed by chain scission and oxidation processes parallel to grafting in the applied reaction conditions [16], could account for the apparent lowering of efficiency with time if low molecular weight rubber (soluble) was more highly modified than insoluble rubber. The results of acetone extraction revealed a decrease of oxidation indices of purified samples (Fig. 5, EPDMs A and B), while for raw EPDM-g-MAH oxidation indices increased as time increased (Table 7).

The acetone soluble rubber was precipitated with ethanol and analyzed by FTIR. After correction of carboxylic absorption (by applying the maximum value of oxidation index as the reduction factor), the minimum content of succinic group was estimated as 4.0% w/w. This value is higher than those obtained for purified EPDM B-g-MAH, suggesting that soluble extracted rubber is both lower in molecular weight and higher in functionalization degree. The

Table 4. Refluxing toluene insoluble fractions of EPDM B-g-MAH produced with different reaction conditions

Reaction conditions T, °C/rpm/phr P/phr MAH/t, min	Initiator	Toluene insoluble fraction (%wt)
120/50/2.0/5.0/15	DIBZ	>99.0
120/50/2.0/5.0/35	DIBZ	>99.0
120/50/2.0/5.0/15	DICUP	91.0
120/50/2.0/5.0/35	DICUP	94.3
140/50/2.0/5.0/15	DICUP	92.5
140/50/2.0/5.0/35	DICUP	96.3
120/50/2.0/2.5/35	DICUP	94.7
140/50/2.0/2.5/15	DICUP	95.4
150/50/2.0/2.5/35	DICUP	96.3

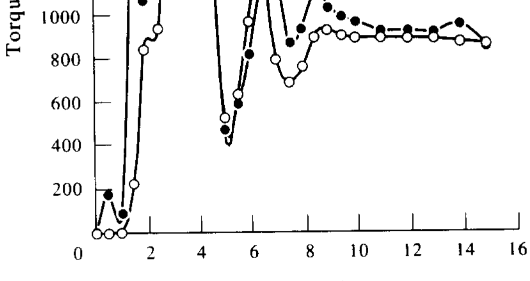

Fig. 3. Torque–time curves for grafting of EPDM B with 2.0 phr of DIBZ and 3.0 phr of MAH at 120°.

Table 5. Grafting of EPDM A with dicumyl peroxide

Reaction conditions	SAH content	E	Oxidation index
T, °C/rpm/phr P/phr MAH/t, min	(%wt)	(%)	(A_{1713}/A_{1465})
120/50/2.0/5.0/15	2.69	52.7	2.08
120/50/2.0/5.0/35	3.16	61.9	2.74
120/100/2.0/5.0/15	1.59	31.2	1.21
140/50/2.0/5.0/15	1.98	38.7	1.71
140/50/2.0/5.0/35	1.75	34.3	1.72
140/100/2.0/5.0/15	1.75	34.3	1.62
140/100/2.0/5.0/35	1.46	28.8	1.48
120/50/0.5/5.0/15	1.20	23.6	1.58
120/100/0.5/5.0/15	2.55	50.0	2.70
140/50/0.5/5.0/15	2.66	62.1	2.10
140/100/0.5/5.0/15	2.92	57.2	2.35
120/50/2.0/2.5/15	1.59	62.3	1.39
120/50/2.0/2.5/35	1.47	57.6	1.37
120/100/2.0/2.5/15	1.78	69.8	1.37
140/50/2.0/2.5/15	1.52	59.6	1.34
140/50/2.0/2.5/35	1.47	57.6	1.32
140/100/2.0/2.5/15	1.57	61.5	1.57
120/50/0.5/2.5/15	1.57	61.5	1.69
120/100/0.5/2.5/15	2.39	93.7	1.70
140/50/0.5/2.5/15	1.80	70.6	1.99
140/100/0.5/2.5/15	1.84	72.1	1.62

purification procedure was necessary to remove unreacted MAH, and therefore could not be by-passed in the evaluation of the content of succinic groups in the samples.

FTIR spectra of acetone soluble fraction after precipitation with ethanol and treatment with NaOH are shown in Fig. 6. The bands attributed to ester (1733 cm^{-1}), acid (1701 cm^{-1}), and carboxilate anion (1588 cm^{-1}) can be due not only to oxidation of elastomeric main chain but also to monoesterification of succinic moieties in the low molecular weight rubber. Olefinic unsaturation bands are also present (1680–1630 and 960–900 cm^{-1}).

The trend of decreasing efficiency with increasing mixing time is not observed when low peroxide level was applied (Table 3). This fact will be discussed together with the influence of formulation.

Influence of shear level

At high rotor speed (100 rpm) the reaction mixture is subjected to shear rates higher than 50 rpm that could promote better homogenization, and thus increase the grafting efficiency. However, high shear levels could also intensify the generation of macroradicals, and consequently promote parallel reactions such as crosslinking or mechanochemical degradation.

It was verified that the main effect of increasing shear levels was decreasing efficiency, without considerable increase in the oxidation index. The analysis of torque–time curves for DICUP initiation (Fig. 2) shows that despite having minimum torque values, the curve of 100 rpm exhibits higher final torque. This indicates that the intensification of macroradical formation in high shear conditions favors not only chain scission but also crosslinking. Having in mind that the amount of acetone extract was not measured and that highly modified low molecular weight rubber is present in the acetone soluble phase, the decrease in

Table 6. Grafting of EPDM C with dicumyl peroxide

Reaction conditions	SAH content	E	Oxidation index
T, °C/rpm/phr P/phr MAH/t, min	(%wt)	(%)	(A_{1713}/A_{1465})
120/50/2.0/5.0/15	1.83	35.9	1.51
120/100/2.0/5.0/15	1.44	28.2	1.52
120/50/0.5/5.0/15	0.93	18.2	0.78
120/100/0.5/5.0/15	1.17	22.9	0.74
140/50/2.0/5.0/15	2.84	55.7	1.70
140/50/0.5/5.0/15	2.97	58.2	1.49
140/100/0.5/5.0/15	2.04	40.0	1.46
120/50/2.0/2.5/15	2.33	91.3	1.40
120/100/2.0/2.5/15	0.91	35.7	1.15
120/50/0.5/2.5/15	1.87	73.3	0.93
120/100/0.5/2.5/15	1.82	71.3	1.27
140/50/2.0/2.5/15	1.97	77.2	1.44
140/100/2.0/2.5/15	2.00	78.4	1.39
140/50/0.5/2.5/15	2.09	81.9	1.23
140/100/0.5/2.5/15	2.39	93.7	1.44

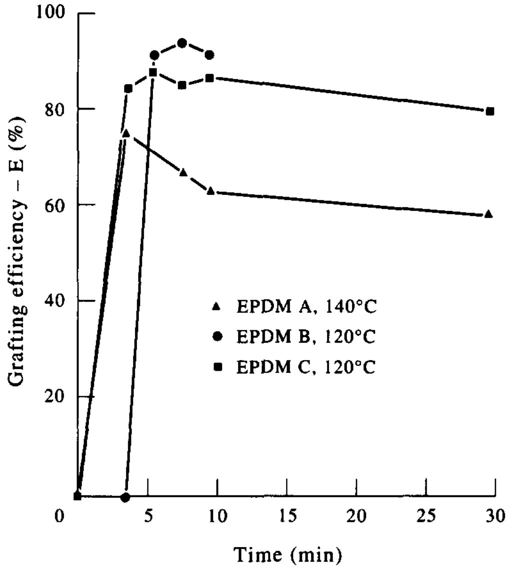

Fig. 4. Influence of reaction time in grafting efficiency for grafting of EPDM with 2.0 phr of DICUP and 2.5 phr of MAH at 50 rpm.

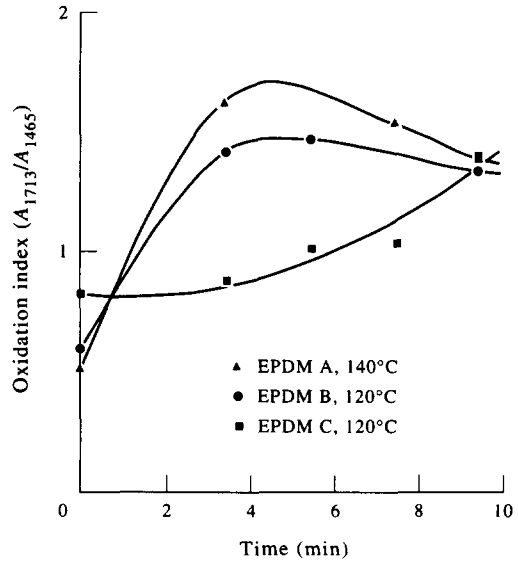

Fig. 5. Influence of reaction time in oxidation index for grafting of EPDM with 2.0 phr of DICUP and 2.5 phr of MAH at 50 rpm.

Table 7. Oxidation index of purified and raw EPDM-g-SAH

EPDM type	Reaction conditions *T*, C/rpm/phr P/phr MAH/*t*, min	Initiator	Purified oxidation index	Raw oxidation index
B	100/50/2.0/5.0/15	DIBZ	1.27	1.74
B	120/50/2.0/5.0/15	DIBZ	1.69	1.85
B	100/50/2.0/3.0/15	DIBZ	1.53	1.65
B	120/50/2.0/3.0/15	DIBZ	1.52	1.72
B	120/100/2.0/3.0/15	DIBZ	1.51	1.57
B	120/50/2.0/5.0/15	DICUP	1.63	1.63
B	140/50/2.0/5.0/15	DICUP	1.63	1.68
B	120/50/2.0/2.5/15	DICUP	1.33	1.47
B	120/50/2.0/2.5/35	DICUP	1.37	1.57
B	140/100/0.5/2.5/35	DICUP	1.39	1.55
A	140/50/2.0/2.5/35	DICUP	1.32	1.48
A	140/100/0.5/2.5/15	DICUP	1.62	2.39
A	120/50/0.5/2.5/15	DICUP	1.69	1.83

efficiency with increasing shear rate can also be apparent (extraction could alter results as discussed for mixing time).

However, when low DICUP level was used at 120° the grafting efficiency increased with increasing shear rate. Furthermore, when DIBZ was used as initiator at the high temperature (Fig. 3), torque–time curves for low and high shear levels were almost similar, suggesting that another parallel reaction which did not affect torque–time curves, but is intensified by increasing radical concentration has occurred.

Influence of reaction temperature

The behavior of grafting efficiency with temperature varied mainly according to the MAH content in the charge. For recipes with high MAH content, a tendency of increasing efficiency with an increase in temperature was observed.

An opposite tendency was verified when low MAH content and high peroxide level were employed. This unusual behavior did not happen when low peroxide, low temperatures, and low shear rate levels were used (as shown in Tables 3, 5 and 6). This temperature increase also caused an increase in oxidation index for EPDMs B and C, and this effect was accentuated for mixtures with high MAH content.

Two different mechanisms have been proposed for grafting of MAH in polyolefinic substrates. The conventional mechanism involves only radical reactions [11, 13] and cannot explain the variation of reaction behavior based on the MAH concentration in the reaction medium. The alternative mechanism considers the presence of excited MAH species that are generated when conditions of fast initiator decomposition are employed [2–4]. The presence of excited MAH dimer would enhance macroradical generation beyond that attributable to normal peroxide dissociation, and could also cause formation of MAH homopolymer (despite the 1,2-disubstituted monomer's low tendency for radical homopolymerization). Excited MAH concentration would depend on [peroxide]/[MAH] ratio: the higher the ratio is, the higher is the MAH excited dimer content in reaction mixture.

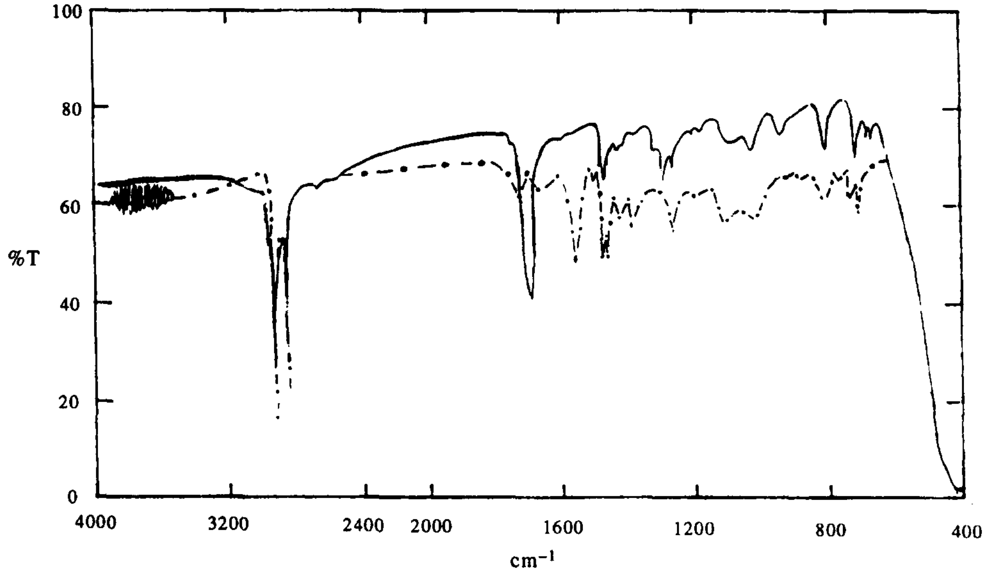

Fig. 6. FTIR spectra of acetone soluble fraction from extraction of raw EPDM-g-MAH. Ethanol insoluble fraction, soluble in *n*-heptane (——); ethanol insoluble fraction, after treatment with NaOH (– · – · –).

When low MAH and high peroxide levels were used in the reaction mixture, the excited MAH concentration would be very high. Any further increase (such as the one caused by the increase of temperature) could intensify MAH homopolymerization, thus causing a decrease in grafting efficiency. In the case of high MAH content formulations, specially with low peroxide levels, the concentration of excited MAH was not high enough, and higher grafting efficiencies were observed when the temperature was increased, despite the higher oxidation indices. This indicates that when excited MAH levels are low, chain scission is intensified by the enhancement of macroradical generation, and predominates over MAH homopolymerization. When the excited MAH concentration was insufficient (low temperature, low peroxide level, and short reaction time) extremely low oxidation indices were obtained. For the same reason these conditions also exhibited low grafting efficiencies.

Influence of formulation

In addition to the effects already discussed, the use of high MAH content in the formulations caused an unexpected decrease in grafting efficiency at fixed peroxide concentrations. Similar results were obtained for continuous bulk modification of EPDM rubber with MAH, applying bis(*t*-butyl peroxy *i*-propyl) benzene as initiator [12]. These results can be explained by phase separation of MAH from rubber [12] or by the alternative mechanism involving MAH excited species [4, 12]. In the latter case the observed decrease in efficiency could be due to the quenching of MAH excimer by an increasing amount of MAH in ground state and also to homopolymerization. Although homopolymer isolation and identification was not possible given that the acetone soluble fraction contained unreacted monomer (main absorption bands in the same frequency as poly-MAH), phase separation of MAH from rubber was not detected.

Furthermore, it was observed that oxidation indices are generally higher when the MAH concentration is high. As homopolymerization proceeds, propagating homopolymer chains can abstract hydrogen from rubber macromolecules, provoking termination in the homopolymerization reaction and inducing chain scission in the elastomeric substrate.This would account, not only for high oxidation indices and intense yellowing of formulations with 5.0 phr of MAH, but also for the decrease in efficiency when high shear level was applied in DIBZ's high temperature excursions.

When low mixing temperatures were employed insufficient peroxide decomposition occurred, and consequently grafting efficiencies were higher with high peroxide levels. However, the effect of initiator concentration on grafting efficiency is better analysed if the radical initiator efficiency (E_i) is considered [13]:

$$E_i = \frac{[\mathrm{MAH}]_g}{2[\mathrm{P}]_0},$$

where:

$[\mathrm{MAH}]_g$ = molar concentration of grafted MAH in the EPDM-g-MAH

$[\mathrm{P}]_0$ = initial concentration of peroxide.

Table 8. Radical initiator efficiencies (E_i) for EPDM-g-SAH

	Reaction conditions		
EPDM type	T, °C/rpm/phr P/phr MAH/t, min	Initiator	E_i
B	100/50/2.0/5.0/15	DIBZ	3.83
B	100/50/2.0/3.0/15	DIBZ	4.38
B	140/50/2.0/5.0/15	DICUP	3.44
B	140/50/0.5/5.0/15	DICUP	14.51
B	140/50/2.0/3.0/15	DICUP	3.54
B	140/50/2.0/2.5/15	DICUP	3.12
B	140/50/0.5/2.5/15	DICUP	13.09
A	140/50/2.0/5.0/15	DICUP	2.80
A	140/50/0.5/5.0/15	DICUP	15.08
A	140/50/2.0/2.5/15	DICUP	2.15
A	140/50/0.5/2.5/15	DICUP	10.20
C	140/50/2.0/5.0/15	DICUP	4.02
C	140/50/0.5/5.0/15	DICUP	16.80
C	140/50/2.0/2.5/15	DICUP	2.79
C	140/50/0.5/2.5/15	DICUP	11.80

As shown in Table 8 the radical initiator efficiencies obtained for both initiators used in this work are much greater than 1.0. Similar results were reported for bulk functionalization of EPR with dibutyl maleate [13]. That behavior can be interpreted as an indication of the generation of macroradicals not only through chain transfer between the propagating graft copolymer and the rubber, but also by addition of monomer units onto propagating copolymer or homopolymer. It is also noticed that radical efficiencies are higher at low peroxide level formulations. The radical mechanism explains this fact through the reduction of secondary reactions as coupling and disproportionation that are more probable to occur when high levels of primary radicals are present. Higher concentrations of macroradicals can also intensify these side reactions, leading to lower radical efficiencies when MAH excimer is in high concentration in the reaction medium.

Contrary to the trend observed in high peroxide level formulations, low peroxide concentration conditions exhibited increasing efficiency with increasing mixing time and shear rate. Those facts also suggest that there is an optimum radical concentration (which in turn is dependent on the [peroxide]/[MAH] ratio) to promote grafting, above which parallel reactions are intensified.

Influence of EPDM type

The main deviations of general tendencies so far discussed were detected when a high propylene content rubber (EPDM A) was used (Table 5). EPDM A exhibited a decrease in grafting efficiency with increasing temperatures at high MAH content formulations, contrary to EPDMs B and C. It also showed very high oxidation indices as well as intense yellowing of raw product in some of the conditions employed. Excessive oxidative degradation can interfere in FTIR spectra, causing difficulty in the base-line drawing, and additional absorptions near 1780 cm^{-1} due to γ-lactones [19] and/or peracids [20]. Succinic groups content determined in such conditions may be overestimated.

In terms of order of reactivity towards the grafting reaction, the rubbers tested exhibited two general behaviors, varying according to the reaction conditions.

(1) EPDM C > EPDM B > EPDM A, for conditions in which high MAH excimer concentration is suspected. EPDM A did not present high oxidation index as expected. The decrease in grafting efficiency in those cases would be predominantly due to homopolymerization. EPDM C, despite exhibiting an induction period for grafting (Fig. 4), exhibited higher reaction rates that resulted in higher grafting efficiency. Induction periods accompanied by rubber crosslinking have been observed for bulk functionalization of EPR with di-butyl maleate, and were explained by diffusion difficulties in the reaction medium [11]. Torque–time curves for the three EPDMs tested are presented in Fig. 7. The slower development of torque for EPDM B can be explained by its initial crumb-like state. However, the torque–time curves for EPDMs A and C are rather similar, showing torque decrease in the first 6 min of mixing. If crosslinking were important in the beginning of reaction cycle, one would expect torque to increase earlier. Therefore in this case diffusion-controlled macroradical generation is probably not the cause of inhibition of grafting in its early stages. EPDM C has the higher termonomer content, and consequently is more susceptible to allylic hydrogen abstraction. On the other hand, the reaction medium would have high MAH excimer concentration, and consequently high probability of homopolymer propagation. Allylic macroradicals preferably couple than suffer β-scission, and after an initial reaction period necessary for their generation would encounter propagating homopolymer chains and terminate, forming graft copolymer at high rates. EPDM C exhibited quite a different oxidation index curve (Fig. 5), with low initial values despite having the highest value at zero time.

(2) On the other hand, EPDM A > EPDM B > EPDM C, for conditions in which low MAH excimer concentration is suspected for EPDM A high oxidation indices were observed despite the higher final torque values obtained (Fig. 8). It is known that propylene sequences are more susceptible to hydrogen abstraction, followed by chain scission and oxidative degradation, than ethylene sequences [13]. The presence of MAH excited species in the reaction medium in low concentrations would enhance chain breaking reactions in the case of high propylene content rubber, but would not be enough to induce homopolymerization, and thus cause great low of grafting efficiency. Chain scission would thus explain the anomalous torque–time curves obtained for EPDM A (absence of the torque peak near 9 min and lower minimum torque values). EPDM A higher final torque values confirm that monomolecular β-scission reactions generated very reactive primary and/or secondary radicals which provoked a higher level of crosslinking by coupling.

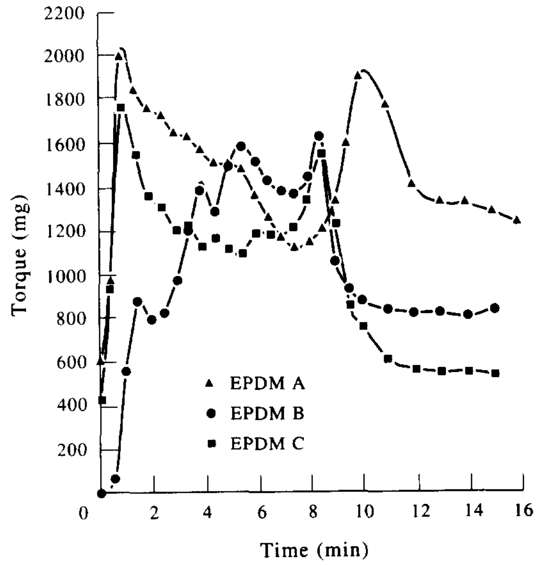

Fig. 7. Torque–time curves for grafting of EPDM with 2.0 phr of DICUP and 2.5 phr of MAH at 120° and 50 rpm.

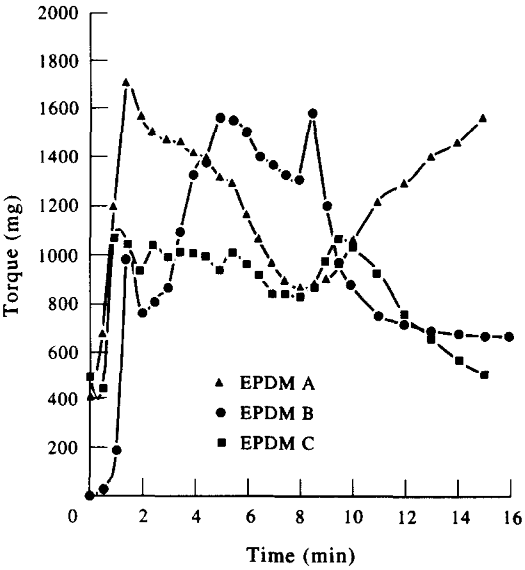

Fig. 8. Torque–time curves for grafting of EPDM with 2.0 phr of DICUP and 5.0 phr of MAH at 120° and 50 rpm.

CONCLUSIONS

The grafting reaction of EPDM in the presence of both aromatic peroxide initiators tested in this work led to appreciable grafting efficiencies when appropriate conditions were chosen. A general tendency of apparent decrease in efficiency with time indicates the intensification of side reactions, mainly degradative oxidation, during the process. Depending on the formulation employed, operations applying high shear levels did not offer advantages to the studied process.

Unusually low grafting efficiencies and high oxidation indices were obtained for high MAH content in the formulation. System behavior also depended on MAH concentration when the effect of temperature on grafting efficiency was analyzed. Furthermore, radical initiator efficiencies far greater than 1.0, specially when low peroxide and MAH levels were used in the charge, indicate the participation of MAH excited species in the reaction.

The grafting behavior of the different EPDMs studied also varied according to the [peroxide]/[MAH] ratio. For low MAH excimer concentrations the influence of propylene content in the rubber was dominant, and its increase caused an increase in grafting efficiency and also in oxidation. For high MAH excimer concentration the influence of diene content became more pronounced, and its increase caused an increase in efficiency without increasing the oxidation index.

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