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Controlled degradation reactions in EPDM bulk modification with maleic anhydride

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Summary

Two kinds of EPDM rubber were bulk functionalized with maleic anhydride, using dicumyl peroxide as radical source, in the presence of stabilizers and electron donor in order to minimize degradative oxidation. Different peroxide type initiators were tested aiming to control oxidation without deleteriously affecting grafting efficiency.

Introduction

Bulk modification of EPDM rubbers with maleic anhydride (MAH) in the presence of peroxide type initiators leads to side reactions such as crosslinking and oxidative degradation [1-3]. The dependence of grafting efficiency on [Primary Radicals]/[MAH] ratio can only be completely explained by an alternative mechanism based on the occurrence of MAH excited species (excimer) in reaction medium [2,4-6]. As the excimer is ionic in nature, electron donors such as N,N-dialkylamides and stearamide have been tested in degradation and/or crosslinking control either in solution or in bulk modification of PP, LDPE, and EPR [2,4-5]. However, no details of their influence on grafting efficiency were found.

The objective of this work was to investigate the effect of stabilizers and electron donors in grafting efficiency and relative oxidation extent of bulk modified EPDM rubber. The influence of peroxide type was also studied aiming to optimize reaction conditions.

Experimental

The modification reaction was carried out in a mixing chamber of a Brabender-like rheometer (Rheomix 600 of Haake System 40). EPDM-A contains 41.3 w % of propylene and 4.0 w % of diene. EPDM-B contains 36.2 % of propylene and 9.6 w % of diene. A phenolic antioxidant (AO-A), a phosphite antioxidant (AO-B), and a polymeric hindered amine (HALS) were tested as thermal stabilizers. Bis-ethylene-stearamide (EBA) was used as amide type electron donor. Tests were performed in the presence of dicumyl peroxide (IN-C). Other initiators tested without the addition of stabilizers were: 1,1'-di(t-butylperoxy)-3,3,5-trimethyl cyclohexane (IN-A), t-butylperoxy acetate (IN-B), 2,5-dimethyl-2,5-di(t-

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butylperoxy) hexane (IN-D), and di-t-butyl peroxide (IN-E). Modified rubber was characterized by FTIR, as previously described [7].

Results and discussion

Influence of stabilizer and electron donor

Overall results obtained are shown in Table 1. Depending on the [Primary Radicals]/[MAH] ratio, the excimer concentration is altered, being higher when the ratio is increased [5]. Thus, at low MAH charge content and high temperatures, one expects high excimer concentration. Under these conditions only the strong radical scavenger stabilizer (AO-A) was efficient in reducing oxidation without affecting significantly the grafting efficiency. However, when the excimer concentration in the medium was probably lower, the addition of phenolic antioxidant strongly depressed grafting, despite of its effectiveness in reducing oxidation.

The significance of the influence of stabilizers and electron donor on the modification was statistically analysed as shown in Table 2, initially applying a set of experiments planned with three-variable factorial design at two levels. The variables chosen were EPDM type, stabilizer or donor in the reaction medium, and MAH content in the charge. The effects of these variables on grafting efficiency (%) and oxidation index (IOX) were calculated according to Yates' Algorithm [8].

The existence of an interaction between MAH content in the charge and presence of stabilizer was observed . In formulations with low MAH content, the positive effect of the addition of AO-B suggested that it would be advantageous for optimization by grafting. However, when the study was broadened to four-variables (taking temperature into consideration) AO-B exerted a negative effect on the grafting reaction. Similar behavior was also shown by EBA. Thus, stabilizer addition caused an overall deleterious effect on grafting efficiency (%), which was intensified in high MAH content formulations. It is worthwile mentioning that despite the slight positive effect of HALS on the grafting efficiency, its use should be avoided even in low MAH content recipes, because of the color of the final product; this is one of the major problems of EPDM-g-MAH synthesis [3,9].

Table 1 - Addition of stabilizers or electron donor in the bulk reaction of EPDM with MAH in the presence of IN-C. Overall results.

Reaction Conditions	% of EPDM A	IOX of EPDM A (A_{1713}/A_{1465})	% of EPDM B	IOX of EPDM B (A_{1713}/A_{1465})
AO-A/T-/M-	19.2	1.20	0.0	1.00
AO-B/T-/M-	62.3	1.39	61.9	0.85
HALS/T-/M-	68.6	1.72	54.9	1.38
EBA /T-/M-	50.2	1.36	61.2	1.20
AO-A/T-/M+	23.7	1.67	0.0	1.28
AO-B/T-/M+	22.8	1.17	27.1	0.76
HALS/T-/M+	31.4	1.45	43.5	1.41
EBA /T-/M+	44.3	1.82	15.5	0.68
AO-A/T+/M-	52.8	0.99	57.0	0.91
AO-B/T+/M-	60.7	1.34	61.1	1.01
HALS/T+/M-	60.1	1.57	61.0	1.35
EBA /T+/M-	57.8	1.31	66.3	0.99
AO-B/T+/M+	37.8	1.12	39.8	1.30
EBA /T+/M+	34.1	1.34	36.1	1.16

Notes: % = grafting efficiency $\left(\frac{\text{grafted MAH} \times 100}{\text{charged MAH}}\right)$
IOX = oxidation index determined by FTIR applying pseudo-absorbance (A) ratio [7].
T- = low mixing temperature (120 °C).
T+ = high mixing temperature (140 °C).
M- = low MAH charge content (2.5 phr).
M+ = high MAH charge content (5.0 phr).

Table 2 - Addition of stabilizers or electron donor in the bulk reaction of EPDM with MAH in the presence of IN-C - Statistical analysis.

Reaction Conditions	Source of Variation	Degree of Freedom	F_c for %	F_c for IOX	$F_{.95}$	Effect on %/IOX
AO-A *	Donor	1	<1.00	8.54	6.61	-16.0/-0.4
AO-A *	Donor/M	1	6.85	2.78	6.61	-41.0/+0.0
AO-B *	Donor	1	4.46	6.00	6.61	+20.3/-0.4
AO-B *	Donor/M	1	11.99	7.60	6.61	-33.0/+0.5
AO-B **	Donor	1	4.72	15.00	4.67	-10.9/-0.5
AO-B **	M	1	35.09	1.61	4.67	-2.9/-0.2
HALS *	Donor	1	5.21	<1.00	6.61	+19.0/-0.1
HALS *	Donor/M	1	10.75	<1.00	6.61	-27.3/-0.2
EBA *	Donor	1	<1.00	5.94	6.61	+5.8/-0.5
EBA *	Donor/M	1	2.03	1.33	6.61	-24.9/-0.3
EBA **	Donor	1	5.74	5.97	4.75	-13.4/-0.3
EBA **	M	1	22.36	2.00	4.75	-26.6/+0.2

Notes: * - three-variable factorial design at two levels.
** - four-variable factorial design at two levels.
M - source of variation is MAH charge content.
Donor - source of variation is donor or stabilizer.
F_c for % / F_c for IOX - calculated F distribution factor of the effect on grafting efficiency (%) or on IOX.
$F_{.95}$ - theoretical F distribution factor for 95 % of confidence interval.
+ - effect of increasing % or IOX.
- - effect of decreasing % or IOX.

Influence of initiator type

Table 3 shows the results obtained when the type of initiator was changed. Decomposition temperatures of the peroxides tested increase in the following order: IN-A< <IN-B <IN-C <IN-D <IN-E [10].

Table 3 - Bulk modification of EPDM with MAH using different types of peroxide initiators. Overall results.

Reaction Conditions	% of EPDM A	IOX of EPDM A (A_{1713}/A_{1465})	% of EPDM B	IOX of EPDM B (A_{1713}/A_{1465})
IN-A/T-/M-	69.5	1.59	83.9	1.50
IN-B/T-/M-	64.6	1.37	73.7	0.75
IN-C/T-/M-	74.8	1.39	91.3	1.40
IN-D/T-/M-	72.3	1.33	83.5	0.63
IN-E/T-/M-	14.9	0.45	0.0	0.32
IN-A/T-/M+	48.0	2.16	33.5	1.82
IN-B/T-/M+	57.8	1.98	41.6	1.64
IN-C/T-/M+	52.7	2.08	35.9	1.51
IN-D/T-/M+	63.1	1.76	28.6	1.27
IN-E/T-/M+	7.4	1.04	6.6	0.80
IN-A/T+/M-	61.3	1.58	74.6	1,57
IN-B/T+/M-	54.8	1.53	81.1	1.51
IN-C/T+/M-	59.6	1.34	79.8	1.44
IN-D/T+/M-	44.7	1.55	85.9	1.66
IN-E/T+/M-	59.9	1.46	77.2	1.46
IN-B/T+/M+	51.1	2.48	39.8	1.81
IN-C/T+/M+	38.7	1.71	55.7	1.70
IN-D/T+/M+	31.6	1.81	57.6	1.66

Note: Abbreviations as in Table 1 and Experimental.

When IN-E was used at low temperatures, an intense decrease in grafting efficiency was observed. This effect was probably due to low radical concentration in the reaction medium, which is similar to the effect of the addition of a strong radical scavenger (AO-A) in IN-C initiated reaction. The use of a fast initiator (IN-A) increased the oxidation index, as well as the color of the final product.

The statistical analysis of the influence of initiator and EPDM type on grafting efficiency and oxidation index is shown in Table 4.

Table 4 - Bulk modification of EPDM with MAH using different types of peroxide initiators. Statistical analysis.

Reaction Conditions	Source of Variation	Degree of Freedom	F_c for %	F_c for IOX	$F_{.95}$	Effect on %/IOX
T+/M-	Initiator	4	0.09	7.40	6.39	NS/HS
T+/M-	EPDM	1	23.60	3.33	7.71	HS/NS
T-/M+	Initiator	4	8.40	40.40	6.39	HS/HS
T-/M+	EPDM	1	9.57	44.98	7.71	HS/HS
T-/M+	Initiator	3	0.62	11.75	9.28	NS/HS
T-/M+	EPDM	1	19.09	57.78	10.13	HS/HS
**	Initiator	1	<1.00	7.97	4.84	+0.4/+0.4
**	M	1	38.41	10.85	4.84	-27.4/+0.5
**	EPDM/M	1	6.93	<1.00	4.84	-11.6/-0.1
**	T/EPDM/Init	1	6.01	1.79	4.84	-10.8/-0.2

Notes: ** - four-variable factorial design at two levels
NS - non-significant effect at 95 % of confidence.
HS - highly significant effect at 95 % of confidence.
Other symbols as previously indicated.

At low excimer concentrations the type of initiator slightly influenced grafting efficiency: $F_c = F_{.95}$ for four degrees of freedom and $F_c < F_{.95}$ for three degrees of freedom (when IN-E was not considered). On the other hand, the effect of initiator on the oxidation index was significant ($F_c > F_{.95}$ for every analysis). At high excimer concentration, the type of initiator only influenced oxidation index, without affecting grafting efficiency; this shows that oxidation control was better achieved by changing the type of initiator than by adding stabilizers.

In experiments at a high temperature and low MAH content, EPDM type had a significant effect only on grafting efficiency (%); this is probably due to high excimer concentration in the reaction medium, which would induce not only polyMAH propagation, but also degradation reactions, and incorporation of MAH small blocks in EPDM. The soluble portion of degradaded rubber was found to be highly functionalized [6], and its extraction during purification procedure [3,6] would account for the apparent decrease in the grafting efficiency observed when EPDM A was applied. At low excimer concentration, EPDM type strongly influenced efficiency (%) or IOX. In these cases the concentration of MAH excited species would be insufficient to form MAH small blocks, but would be enough for inducing chain breaking reactions when the propylene content of the rubber was high. As a consequence higher graftingefficiency and higher IOX were obtained when EPDM A was used.

To quantify the effect of the initiator type, four-variable factorial design at two levels was applied. Rapidly decomposing initiator (IN-A) was used in high level formulations, whereas IN-D was used in low level formulations. Statistical analysis (Table 4) confirmed the lack of influence of initiator type on %, as well as its effect on lowering the oxidation index (when IN-D was used). A negative interaction on % was apparent when high diene content EPDM was used. Thus, according to statistical analysis the choice of the best initiating system depends on the process conditions, mainly on the type of EPDM.

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