Degradation and Cross-linking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides

NORMAN G. GAYLORD, MAHENDRA MEHTA, and
RAJENDRA MEHTA, *Gaylord Research Institute, New Providence,
New Jersey 07974*

Synopsis

The reaction of EPR with dicumyl peroxide at 180°C or *t*-butyl perbenzoate at 140°C resulted in the formation of a fraction insoluble in cyclohexane at 22°C. The presence of maleic anhydride (MAH) in the EPR-peroxide reaction mixture increased the amount of insoluble polymer, whose concentration decreased as the peroxide concentration increased. The [η] of the cyclohexane-soluble polymer decreased and the MAH content increased as the peroxide concentration increased at constant MAH concentration. The [η] and the MAH content of the soluble polymer increased as the MAH concentration increased at constant peroxide concentration. The EPR-peroxide and EPR-MAH-peroxide reaction products were soluble in refluxing xylene and could be fractionated by precipitation with acetone. The presence of stearamide in the EPR-MAH-peroxide reaction mixture decreased the amount of cyclohexane-insoluble polymer, indicative of decreased cross-linking, but the [η] of the soluble EPR-g-MAH increased, indicative of decreased degradation, analogous to the effect of stearamide in the MAH-peroxide reactions with LDPE and PP, respectively.

INTRODUCTION

Radical catalysts have been used for grafting maleic anhydride (MAH) onto saturated polymers. Peroxide catalysts have generally been utilized at high concentrations and/or at temperatures at which they have a short half-life, that is, conditions that are effective in initiating the bulk homopolymerization of MAH.[1]

The peroxide-catalyzed grafting of MAH is accompanied by cross-linking in the case of molten polyethylene;[2,3] degradation or chain scission is the dominant effect in the case of molten polypropylene.[4] Since saturated ethylene-propylene copolymer elastomers (EPR) contain ethylene and propylene units in the chain, both cross-linking and degradation should occur on reaction with MAH in the presence of peroxides.

The cross-linking of EPR in the presence of organic peroxides has been investigated by Natta and his coworkers[5-10] and others.[11,12] Coagents, such as sulfur[10,11] and unsaturated monomers,[13] including MAH,[10,14] have also been examined in an effort to increase the cross-linking efficiency in the EPR-peroxide system.

The present investigation was undertaken to study the peroxide-promoted grafting of MAH onto EPR and to examine the extent of cross-linking and/or degradation that accompanies the grafting reaction.

CCC 0021-8995/87/072549-10$04.00

Various solvents and procedures have been reported for the determination of the extent of cross-linking in EPR. Natta et al.[14] used benzene at 35°C; Fischer[15] used cyclohexane at 73°F as solvent to determine the amount of insoluble gel. Fischer[15] reported that the gel content obtained in refluxing xylene was 30–50% lower than that obtained in cyclohexane at 73°F. Cyclohexane at room temperature (22°C) and refluxing xylene (133°C) were used in the present investigation.

EXPERIMENTAL

EPR Grafting Reactions

Vistalon 404 EPR, E/P weight ratio 40 : 60, $M_w/M_n = 37$ (Exxon Chemical Co.), was fluxed for 2 min in the mixing chamber of a Brabender Plasticorder at 60 rpm at 140–180°C. A mixture of peroxide (dicumyl peroxide at 180°C, benzoyl peroxide at 160°C, and t-butyl perbenzoate at 140°C), MAH, and stearamide, when present, was added in four portions at 2-min intervals to the 40 g fluxing EPR. After the last addition, mixing was continued for 2 min (total time, 10 min) and then the reaction mixture was quickly removed from the chamber. A nitrogen atmosphere was maintained over the reaction mixture throughout the addition and mixing steps.

Cyclohexane Extraction of Reaction Products

A 5–6 g portion of the EPR-peroxide or EPR-MAH-peroxide reaction product was cut into small pieces and stirred in 250 mL cyclohexane at room temperature for 60 h. The insoluble fraction was separated by filtering the suspension through cheesecloth. The cyclohexane-soluble fraction was recovered by distilling the solvent in vacuo. The polymers were dried in a vacuum oven at 40°C for 24 h.

Xylene Extraction of Reaction Products

A 5–6 g portion of the reaction product was cut into small pieces and heated in 200 mL refluxing xylene for 5 h. The hot suspension was filtered through cheesecloth into 800 mL acetone. The polymer adhering to the sides of the flask and the small amount filtered from the suspension were heated with an additional 150 mL refluxing xylene until complete solution was noted and then precipitated in acetone. The precipitated polymers were combined as fraction I. The combined filtrates were concentrated on a Rotavaporator, and the residual polymer (fraction II), as well as the polymer recovered by precipitation, was dried in vacuo at 140°C for 4 h.

Polymer Characterization

The MAH content of the soluble polymers was determined by heating a 0.5–1.0 g portion in refluxing water-saturated xylene for 1 h and then titrating with 0.05 N ethanolic KOH using 1% thymol blue in DMF as indicator.

The intrinsic viscosity of the soluble polymer was determined in toluene at 30°C.

RESULTS AND DISCUSSION

Reaction of EPR with Dicumyl Peroxide and MAH at 180°C

Mixing EPR in a Brabender Plasticorder at 180°C for 10 min decreased the $[\eta]$ from 1.42 to 1.20 dL/g without any change in the complete solubility of the EPR in cyclohexane at 22°C.

When EPR was mixed in the presence of 0.25 wt% (based on EPR) dicumyl peroxide (DCP) at 180°C for 10 min, extraction of the product in cyclohexane at 22°C resulted in the recovery of 20% cyclohexane-insoluble polymer. The soluble polymer had a higher $[\eta]$ than that of the polymer treated at 180°C in the absence of peroxide, indicative of chain extension. When the EPR was mixed in the presence of 0.5 wt% DCP, the amount of insoluble polymer decreased to 16% and the soluble polymer had a lower $[\eta]$, indicative of chain scission.

The presence of 5 wt% MAH (based on EPR) and 0.25–1.0 wt% DCP increased the amount of cyclohexane-insoluble gel. However, the gel content decreased from 65 to 27% as the DCP concentration increased from 0.25 to 1.0 wt%, respectively. The higher the DCP concentration at constant MAH concentration, the higher was the MAH content of the soluble EPR-g-MAH (Table I).

When the DCP concentration was kept constant at 0.5 wt% while the MAH concentration in the charge increased from 5 to 20 wt%, the amount of cyclohexane-insoluble polymer decreased from 43 to 13%. The $[\eta]$ of the cyclohexane-soluble EPR-g-MAH increased and its MAH content decreased as the MAH concentration in the charge increased at constant DCP concentration (Table II).

When stearamide (SA) was added in admixture with MAH and DCP to EPR at 180°C, the amount of cyclohexane-insoluble EPR-g-MAH decreased, analogous to the effect of stearamide in reducing cross-linking in the LDPE-

TABLE I
Effect of DCP at Constant MAH Concentration in EPR at 180°C

| MAH (wt% on EPR) | DCP (wt%) | | Cyclohexane extraction[a] | | | |
| | | | Soluble[b] | | | |
	On EPR	On MAH	%	$[\eta]^{c}$ (dL/g)	MAH (wt%)	Insoluble (%)
0	0	0	100	1.20[d]	0	0
0	0.25	0	77	1.42	0	20
0	0.5	0	80	1.23	0	16
5	0.25	5	33	1.10	0.9	65
5	0.5	10	56	0.56	1.0	43
5	1.0	20	73	0.89	1.3	27

[a] Extraction with cyclohexane at 22°C for 60 h.
[b] Soluble fraction recovered by solvent removal from filtrate.
[c] Toluene, 30°C.
[d] Untreated EPR $[\eta]$ 1.42 dL/g.

TABLE II
Effect of MAH at Constant DCP Concentration in EPR at 180°C[a]

MAH (wt% on EPR)	DCP (wt%)		Cyclohexane extraction			
				Soluble		
	On EPR	On MAH	%	$[\eta]$ (dL/g)	MAH (wt%)	Insoluble (%)
5	0.5	10	56	0.56	1.6	43
10	0.5	5	66	1.26	0.7	30
20	0.5	2.5	76	1.56	0.6	13

[a]See notes to Table I.

TABLE III
Effect of Stearamide (SA) in EPR-MAH-DCP Reaction at 180°C[a]

MAH (wt% on EPR)	DCP (wt%)		SA[b] (mol% on MAH)	Cyclohexane extraction			
					Soluble		
	On EPR	On MAH		%	$[\eta]$ (dL/g)	MAH (wt%)	Insoluble (%)
5	0.25	5	0	33	1.10	0.9	65
5	0.25	5	20	43	1.18	0.5	55
5	0.5	10	0	56	0.56	1.0	43
5	0.5	10	20	68	1.02	1.6	29

[a]See notes to Table I.
[b]SA-MAH-DCP mixture added in four equal portions to molten EPR at 180°C.

TABLE IV
Fractionation of EPR-MAH-DCP Reaction Product in Xylene[a]

MAH (wt% on EPR)	DCP (wt%)		SA (mol% on MAH)	CH, Insoluble[b] (%)	Xylene fractionation[c]					
					I[d]			II[e]		
	On EPR	On MAH			%	$[\eta]^{f}$ (dL/g)	MAH (wt%)	%	$[\eta]^{f}$ (dL/g)	MAH (wt%)
0	0	0	0	0	82	2.44	0	15	0.60	0
0	0.5	0	0	16	85	1.17	0	15	0.37	0
5	0.5	10	0	43	48	1.38	1.9	46	1.23	2.9
5	0.5	10	20	29	68	1.71	1.2	28	0.94	2.7

[a]EPR reactions carried out at 180°C.
[b]Extraction with cyclohexane at 22°C for 60 h.
[c]Extraction with refluxing xylene for 5 h.
[d]Fraction I recovered by precipitating xylene solution in acetone (acetone-xylene, 4 : 1 v/v).
[e]Fraction II recovered after acetone-xylene removal from filtrate.
[f]Toluene, 30°C.

MAH-peroxide reaction.[16,17] The [η] of the cyclohexane-soluble EPR-g-MAH increased when stearamide was present in the reaction mixture, analogous to the effect of stearamide in reducing degradation in the PP-MAH-peroxide reaction[16] (Table III).

The reaction products formed at 180°C in the reaction of EPR with 0.5 wt% DCP, in the absence or in the presence of 5 wt% MAH, were completely soluble in refluxing xylene, notwithstanding the recovery of a cyclohexane-insoluble fraction upon extraction with cyclohexane at 22°C. When the xylene solution was added to acetone, the precipitated polymer (I) was recovered by filtration. A second fraction (II) of xylene-soluble polymer was recovered by removal of the solvent from the acetone-xylene filtrate.

As shown in Table IV, untreated EPR was separated into a high-molecular-weight fraction (I) ([η]2.4 dL/g), representing 82% of the co-polymer, and a lower molecular weight fraction II ([η] 0.6 dL/g). Treatment of the EPR with 0.5 wt% DCP reduced the molecular weights of both fractions significantly, although their relative amounts were unchanged.

The presence of 5 wt% MAH and 0.5 wt% DCP in the reaction with EPR decreased the amount of the acetone-precipitated fraction (I) from 85 to 48%. Both fractions (I) and (II) had higher [η] than the corresponding fractions obtained in the absence of MAH. The high molecular weight of fraction (II) ([η] 1.23 dL/g) and its MAH content indicate that the separation of the fractions was, in part, influenced by the increased solubility in acetone of EPR-g-MAH with a high MAH content.

The presence of stearamide in the EPR-MAH-DCP reaction mixture increased the amount and molecular weight ([η] 1.71 dL/g) of the acetone-precipitated fraction (I), analogous to its effect in the PP-MAH-peroxide reaction.

The complete solubility in refluxing xylene of the EPR and EPR-g-MAH produced by reaction with DCP at 180°C suggests that, in this case, treatment with cyclohexane at 22°C did not separate the cross-linked polymer from the uncross-linked polymer but rather fractionated the uncross-linked polymer based on molecular weight. Alternatively, the lightly cross-linked polymer was swollen and the cross-links were broken in refluxing xylene.

Reaction of EPR with *t*-Butyl Perbenzoate and MAH at 140°C

The [η] of EPR and its complete solubility in cyclohexane at 22°C were essentially unchanged when the polymer was mixed at 140°C for 10 min. However, when 0.25–1.0 wt% *t*-butyl perbenzoate (tBPB) was present, a cyclohexane-insoluble fraction was formed. The amount of insoluble polymer decreased from 46% at a 0.25 wt% tBPB concentration to 26% at a 1.0 wt% concentration. As the amount of soluble polymer increased with increasing tBPB concentration, the [η] decreased (Table V).

The presence of 5 wt% MAH increased the amount of insoluble gel formed in the presence of 0.5 wt% tBPB from 31 to 63%. The gel content decreased to 34% when the MAH concentration in the charge increased from 5 to 10%. The [η] of the cyclohexane-soluble fraction increased as the MAH concentration increased at constant tBPB concentration. However, the amount of gel

TABLE V
Reaction of EPR with MAH and/or tBPB at 140°C[a]

MAH (wt% on EPR)	tBPB (wt%)		SA (mol% on MAH)	Cyclohexane extraction			Insoluble (%)
				Soluble			
	On EPR	On MAH		%	[η] (dL/g)	MAH (wt%)	
0	0	0	0	100	1.46[d]	0	0
0	0.25	0	0	49	1.02	0	46
0	0.5	0	0	66	0.89	0	31
0	1.0	0	0	62	0.78	0	26
5	0.5	10	0	35	0.81	1.3	63
10	0.5	5	0	59	1.53	0.5	34
10	2.0	20	0	64	1.16	0.9	32
5	0.5	10	20	59	1.54	0.8	37

[a]See notes to Table I.

decreased and the [η] of the soluble polymer decreased as the tBPB concentration increased at constant MAH concentration.

When stearamide was present in admixture with 5 wt% MAH and 0.5 wt% tBPB at 140°C, the amount of cyclohexane-insoluble EPR-g-MAH decreased from 63 to 37%, indicative of decreased cross-linking, and the [η] of the soluble EPR-g-MAH increased from 0.81 to 1.54 dL/g, indicative of decreased degradation.

EPR and EPR-g-MAH prepared with 0.5 wt% tBPB at 140°C in the absence and in the presence of stearamide were extracted in refluxing xylene for 5 h as well as in cyclohexane at 22°C for 60 h. As shown in Table VI, the EPR-tBPB reaction product was 65% soluble in cyclohexane and 100% soluble in xylene. The EPR-g-MAH was 35% soluble in cyclohexane and 86% soluble in xylene when prepared in the absence of stearamide but 59% soluble in cyclohexane and 100% soluble in xylene when prepared in the presence of stearamide. The soluble products recovered from both solvents had a higher [η] and a lower MAH content when prepared in the presence of stearamide. The xylene-soluble EPR-g-MAH had a higher [η] than the cyclohexane-soluble polymer, irrespective of the presence or absence of stearamide during the EPR-g-MAH preparation.

The cyclohexane-insoluble EPR-g-MAH, which becomes part of the xylene-soluble polymer, is either of higher molecular weight than the cyclohexane-soluble polymer and/or has cross-links that are cleaved in refluxing xylene.

Reaction of EPR with Benzoyl Peroxide and MAH at 160°C

In contrast to the behavior of DCP and tBPB, benzoyl peroxide (BP) at 160°C was an ineffective cross-linking agent for EPR. Thus, reaction of 0.5 and 1.0 wt% BP with EPR at 160°C gave 1 and 5%, respectively, of cyclohexane-insoluble polymer. Because of the difficulty in handling such small amounts of gelatinous material, there may actually be no difference in the amount of gel in these experiments. It is noteworthy that BP in the absence of MAH

TABLE VI
Fractionation of EPR-g-MAH in Cyclohexane and Xylene[a]

MAH (wt% on EPR)	tBPB (wt% on EPR)	SA (mol% on MAH)	Cyclohexane extraction[b]				Xylene extraction[c]			
			Soluble[d]			Insoluble (%)	Soluble[d]			Insoluble (%)
			%	$[\eta]$[e] (dL/g)	MAH (wt%)		%	$[\eta]$ (dL/g)	MAH (wt%)	
0	0.5	0	65	0.89	0	31	100	0.67	0	0
5	0.5	0	35	0.81	1.3	63	86	1.10	1.6	13
5	0.5	20	59	1.54	0.8	38	100	1.79	0.6	0

[a] EPR reactions carried out at 140°C.
[b] Extraction with cyclohexane at 22°C for 60 h.
[c] Extraction with refluxing xylene for 5 h.
[d] Soluble fraction recovered by removal of solvent from filtrate.
[e] Toluene, 30°C.

TABLE VII
Reaction of EPR with MAH and/or BP at 160°C[a]

| MAH (wt% on EPR) | BP (wt%) | | Cyclohexane extraction | | | |
| | On EPR | On MAH | Soluble | | | Insoluble (%) |
			%	$[\eta]$ (dL/g)	MAH (wt%)	
0	0	0	100	1.42	0	0
0	0.5	0	98	1.16	0	1
0	1.0	0	92	1.50	0	5
5	1.0	20	70	1.30	0.7	29
5	2.0	40	74	1.29	0.6	25
10	1.0	10	72	1.34	0.5	26
20	1.0	5	75	1.64	0.3	23

[a]See notes to Table I.

does not cross-link polyethylene at 140 or 180°C,[2] despite the ease with which it is cross-linked with DCP.

The presence of 5 wt% MAH increased the amount of insoluble gel formed at 160°C in the presence of 1.0 wt% BP, from 5 to 29%, and the $[\eta]$ of the soluble polymer was slightly lower (Table VII). When the BP concentration was increased to 2.0% while the MAH concentration was maintained constant at 5 wt%, there was a small decrease in the amount of insoluble gel to 25%. When the MAH concentration was increased while the BP concentration was maintained constant at 1.0 wt%, the amount of insoluble gel decreased slightly while the $[\eta]$ of the soluble polymer increased. The MAH content of the EPR-g-MAH was in the range of 0.3–0.7% and decreased as either the BP or the MAH concentration increased.

The apparent changes in gel content and $[\eta]$ were so small as to confirm that the BP-MAH system at 160°C was a far less effective route to either cross-linking or an EPR-g-MAH with a significant MAH content than either DCP-MAH at 180°C or tBPB-MAH at 140°C.

TABLE VIII
Extraction of EPR-g-MAH[a] with Cyclohexane and Benzene

| MAH (wt% on EPR) | BP (wt% on EPR) | Extraction | |
		Cyclohexane, insoluble[b] (%)	Benzene, insoluble[c] (%)
5	1.0	29	39
10	1.0	26	33
20	1.0	23	26
5	2.0	25	35

[a]EPR-MAH-BP reactions carried out at 160°C.
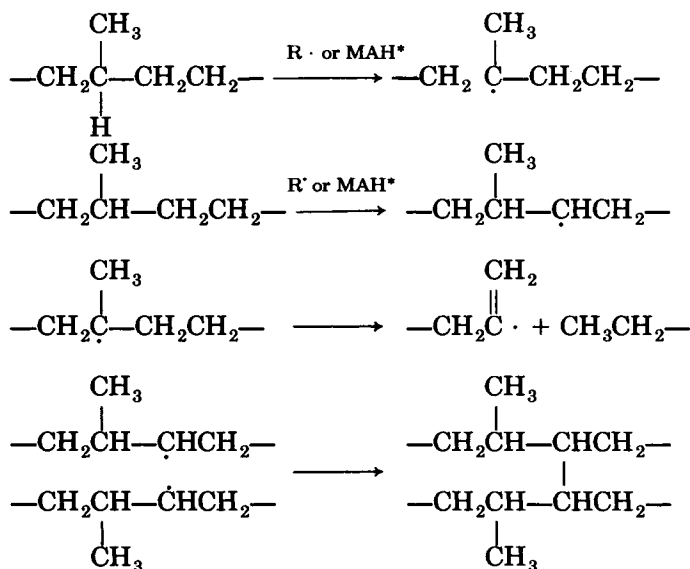[b]Extraction with cyclohexane at 22°C for 60 h.
[c]Extraction with benzene at 35°C for 90 h.

Since Natta et al.[14] utilized benzene at 35°C to determine the amount of cross-linked gel formed in the EPR-BP-MAH reaction at 160°C, EPR-g-MAH prepared under the same conditions was subjected to extraction with both cyclohexane at 22°C for 60 h and benzene at 35°C for 90 h (Table VIII).

Apparently, cyclohexane at 22°C is a better solvent for EPR-g-MAH than benzene at 35°C, and the latter therefore indicates a higher extent of cross-linking. Actually, the differences in gel content found with the two solvents are greater than those found with the same solvent, i.e., cyclohexane, with changes in BP or MAH concentration (Table VII).

Mechanism

The cross-linking of EPR in the presence of radicals from peroxide decomposition is attributable to attack on the secondary CH_2 moieties and the generation of polymer radicals that couple either with similar secondary polymer radicals or tertiary polymer radicals generated by attack on the tertiary CH moieties on the propylene units in the chain. The generation of radicals by the latter route is the dominant reaction. The tertiary radicals preferentially undergo disproportionation, resulting in degradation rather than cross-linking. Increasing the peroxide concentration results in an increase in the amount of soluble polymer and a decrease in its molecular weight due to increased tertiary CH attack followed by disproportionation.

$$
\begin{array}{ccc}
\underset{\substack{|\\ \text{H}}}{\overset{\text{CH}_3}{\underset{|}{}}} & \xrightarrow{\text{R}\cdot\text{ or MAH}^*} & \overset{\text{CH}_3}{\underset{|}{}} \\
-\text{CH}_2\text{C}-\text{CH}_2\text{CH}_2- & & -\text{CH}_2\ \text{C}-\text{CH}_2\text{CH}_2- \\
& & \quad\cdot
\end{array}
$$

$$
\overset{\text{CH}_3}{\underset{|}{-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2-}} \xrightarrow{\text{R}\cdot\text{ or MAH}^*} \overset{\text{CH}_3}{\underset{|}{-\text{CH}_2\text{CH}-\overset{\cdot}{\text{C}}\text{HCH}_2-}}
$$

$$
\overset{\text{CH}_3}{\underset{|\ \cdot}{-\text{CH}_2\text{C}-\text{CH}_2\text{CH}_2-}} \longrightarrow \overset{\text{CH}_2}{\underset{||}{-\text{CH}_2\text{C}\cdot\ +\ \text{CH}_3\text{CH}_2-}}
$$

$$
\begin{array}{ccc}
\overset{\text{CH}_3}{\underset{|}{-\text{CH}_2\text{CH}-\overset{\cdot}{\text{C}}\text{HCH}_2-}} & & \overset{\text{CH}_3}{\underset{|}{-\text{CH}_2\text{CH}-\text{CHCH}_2-}} \\
& \longrightarrow & \qquad\qquad | \\
\underset{\underset{\text{CH}_3}{|}}{-\text{CH}_2\text{CH}-\overset{\cdot}{\text{C}}\text{HCH}_2-} & & \underset{\underset{\text{CH}_3}{|}}{-\text{CH}_2\text{CH}-\text{CHCH}_2-}
\end{array}
$$

The rapid decomposition of a peroxide (DCP $t_{1/2}$ 1 min at 180°C, tBPB $t_{1/2}$ 15 min at 140°C, and BP $t_{1/2}$ 4.5 s at 160°C) in the presence of MAH results in the excitation and homopolymerization of MAH. When the latter is conducted in the presence of polypropylene, the latter undergoes degradation,[4] but polyethylene is cross-linked under the same conditions.[2] This has been attributed to the presence of excited MAH, which increases the radical generation on the polymer beyond that attributable to the radicals from the peroxide.

At a fixed MAH concentration, increasing the peroxide concentration results in a higher concentration of excited MAH and a greater generation of polymer radicals. The latter undergo disproportionation, and the amount of soluble polymer increases and its molecular weight decreases. Notwithstanding, at a given peroxide concentration the presence of MAH increases the amount of cyclohexane-insoluble polymer. At a fixed peroxide concentration, increasing the MAH concentration decreases the concentration of excited MAH and increases the amount of soluble polymer with an increased molecular weight. Further, the MAH content of the polymer decreases with an increase in the MAH concentration in the charge owing to the quenching of excited MAH by increased ground-state MAH.

Although it has been suggested that cross-linking in the presence of MAH involves the coupling of appended MAH radicals with other appended MAH radicals or with polymer radicals,[14] this is improbable because of the tendency for disproportionation rather than coupling between radicals derived from strong electron acceptors, such as MAH. The increased cross-linking may be attributed to the preferential generation of secondary polymer radicals by excited MAH and therefore an increase in the coupling of secondary polymer radicals rather than pendant MAH radicals.

The presence of an electron donor, such as stearamide, in the EPR-MAH-peroxide reaction mixture increases the yield of soluble polymer, that is, decrease in cross-linking, as in the case of polyethylene, which has a higher molecular weight, that is, decrease in degradation, as in the case of polypropylene.

References

1. N. G. Gaylord and S. Maiti, *J. Polym. Sci., Polym. Lett. Ed.*, 11, 253 (1973).
2. N. G. Gaylord and M. Mehta, *J. Polym. Sci., Polym. Lett. Ed.*, 20, 481 (1982).
3. N. G. Gaylord, M. Mehta, and V. Kumar, *Org. Coatings Appl. Polym. Sci. Proc.*, 46, 87 (1982); *Modification of Polymers*, C. E. Carraher, Jr., and J. A. Moore, Eds., Plenum Press, New York, 1983, p. 171.
4. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci., Polym. Lett. Ed.*, 21, 23 (1983).
5. G. Crespi and M. Bruzzone, *Chim. Ind. (Milan)*, 41, 741 (1959).
6. G. Natta and G. Crespi, *Rubber Age*, 87, 459 (1960).
7. G. Natta, G. Crespi, and M. Bruzzone, *Kautschuk Gummi*, 14(3), WT54 (1961).
8. G. Natta, G. Sartori, A. Valvassori, G. Mazzanti, and G. Crespi, *Petrol. Refiner*, 4(8), 103 (1962).
9. G. Crespi and E. di Giulio, *Rev. Gen. Caoutchouc*, 40(1), 99 (1963).
10. G. Natta, G. Crespi, A. Valvassori, and G. Sartori, *Rubber Chem. Technol.*, 36, 1583 (1963).
11. L. D Loan, *J. Polym. Sci.*, A, 2, 3053 (1964).
12. G. A. Harpell and D. H. Walrod, *Rubber Chem. Technol.*, 46, 1007 (1973).
13. L. P. Lenas, *Ind. Eng. Chem., Prod. Res. Dev.*, 2, 202 (1963).
14. G. Natta, G. Crespi, and G. Borsini (to Montecatini Soc. Gen.), U.S. Patent 3,236,917 (1966).
15. W. K. Fischer (to Uniroyal), U.S. Patent 3,806,558 (1974).
16. N. G. Gaylord (to Gaylord Research Institute), U.S. Patent 4,506,056 (1985).
17. N. G. Gaylord and R. Mehta, *Polym. Prepr.*, 26(1), 61 (1985).