Suppression of side reactions during melt functionalization of ethylene–propylene rubber

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Grafting of maleic anhydride (MAH) onto ethylene–propylene rubber (EPR) was performed by melt mixing in a laboratory-scale internal mixer with the addition of an initiator (dicumyl peroxide, DCP) and an ingredient (stearamide, SA) for the suppression of side reactions of cross-linking and chain scission. Effective suppression of side reactions was realized for systems of moderate or low DCP contents upon addition of SA, but no apparent changes could be identified at high DCP loadings. Within the confidence level of Fourier-transform infrared spectroscopic measurements, the extent of grafting appeared to be little affected by the addition of SA. Possible reaction paths in the present system are discussed. In particular, SA is considered as a chain transfer agent which tends to suppress the more populated reaction path, whether it be cross-linking or chain scission.

(Keywords: melt functionalization; ethylene–propylene rubber; maleic anhydride; stearamide; cross-linking; chain scission)

INTRODUCTION

Copolymers have been widely used for rendering immiscible polymer blends compatible as well as improving interfacial adhesion in polymeric composites[1,2]. In comparison with traditional copolymerization processes, the modification of existing polymers by reactive melt processing offers not only flexibility in tailoring polymer properties for specific applications but also reductions in equipment investments[3]. Consequently, reactive polymer processing has received increasing attention among polymer scientists and engineers[4–12]. For example, the graft reaction of maleic anhydride (MAH) on to polyethylene (PE), polypropylene (PP), or ethylene–propylene rubber (EPR) in the melt state has been extensively studied by Gaylord *et al.*[7–9]. More recently, the graft reaction of dibutyl maleate on to EPR by means of a melt process using dicumyl peroxide (DCP) as the initiator has been reported by Greco *et al.*[10–14].

In the peroxide-initiated functionalization of polyolefins in the melt state, it is typically observed that cross-linking and/or chain scission may occur simultaneously with the graft reaction. For PE, the dominant side reaction is cross-linking; for PP, the dominant side reaction is chain scission. In the case of EPR, both cross-linking and chain scission may be important. In a separate article[15], the present authors have reported results of a study of the grafting of MAH on to molten EPR (using DCP as the initiator) in a laboratory-scale internal mixer. It is observed that the presence of MAH strongly enhances cross-linking reactions, although the scission of EPR chains remains important. As a result, the functionalized EPR may possess a very wide distribution of chain structure, from highly degraded short chains to partially cross-linked chains. The gel content increases with DCP and MAH loading but reaches a plateau value of ≈50 wt%; this is explained in terms of the competition between cross-linking and scission reactions. The extent of grafting in the functionalized EPR, as estimated by means of Fourier-transform infrared spectroscopy (*FT*i.r.), also increases with DCP and MAH loading but quickly reaches a limited plateau value; this is attributed to the immiscible nature and the low diffusion rate of MAH in EPR.

Gaylord *et al.*[8,9,16,17] observed that these peroxide-induced side reactions may be controlled by the addition of polar ingredients such as stearamide (SA) to the reaction mixture without serious deterioration of the efficiency of MAH grafting. As interfacial properties of EPR are expected to be improved with grafting of MAH, side reactions such as cross-linking and chain scission may certainly alter the rheological nature and the processing characteristics as well as the mechanical properties of the functionalized polymer. It is therefore of practical importance to control the extent of side reactions while maintaining the proper degree of grafting. The present paper reports observations on effects of incorporating a minor amount of SA into the reaction mixture on structural features of the melt-functionalized EPR.

EXPERIMENTAL

Materials

The ethylene–propylene rubber (EPR) used was Vistalon 404 (propylene content ≈60 wt%, i.e. nearly unitary ethylene/propylene molar ratio) from Exxon, the same as in the previous study[15]. All other chemicals and solvents including dicumyl peroxide (DCP, the initiator), maleic anhydride (MAH, the reactive monomer), and

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stearamide (SA, an ingredient for the suppression of cross-linking and scission reactions) were of reagent grade and were used without further purification.

Melt mixing

The composition of the reaction mixture was typically 40 g of EPR, 0 to 2 phr of MAH, 0 to 1 phr of DCP, and 0 to 0.2 phr of SA. The components were mixed in a Haake-Buchler Rheomix 600 internal mixer (equipped with a pair of high-shear rollers) connected to the Rheocord 40 main frame. The rotor rate was 10 rev $\min^{-1}$ in the first 1 min and then increased to 40 rev $\min^{-1}$ thereafter. The temperature of the mixing chamber was set at 140°C for the first 1 min and was then raised to 160°C; the actual melt temperature typically rose to and then remained at $\approx$170°C within the first 10 min of melt mixing. The total mixing–reaction time was $\approx$30 min. For a given composition, the reproducibility of the final torque value was within 0.5 N m.

Fourier-transform infrared spectroscopy (FT*i.r.*)

The reaction products were compressed at $\approx$120°C into thin films from which infrared spectra were taken using a Digilab FTS-40 Fourier-transform infrared spectrometer at 2 cm^{-1} resolution with the co-addition of 64 scans. The relative peak height of the anhydride absorption band at 1780 cm^{-1} (compared with the $(CH_2)_n$ rocking band at 720 cm^{-1}, serving as an internal standard) was taken as an approximate indicator of the extent of MAH grafting[15]. The confidence level of the peak ratio was in the vicinity of 0.05[18].

Gel content

Gel contents of the reaction products were determined by means of a typical extraction procedure of refluxing in boiling xylene (with 10 mg l^{-1} of 3,5-di-*t*-butyl-4-hydroxytoluene added as an antioxidant) for $\approx$3 h. The solution was subsequently filtered and the insolubles were combined and dried under vacuum at 140°C to constant weight. The gel content was operationally defined as the weight fraction of undissolved portion. Repeated runs indicated that the reproducibility of the present procedure was within 5 wt%.

Dynamic rheological analysis

Dynamic rheological properties, including storage modulus (G') and loss modulus (G''), of the reaction products were measured using a Rheometrics RDA-II instrument in the frequency range 0.3 to 300 rad s^{-1} at 135°C.

RESULTS

Figures 1 and *2* show representative torque curves for the present systems containing DCP as the peroxide initiator, MAH as the reactive monomer, and SA as the suppressor for side reactions. General features of these torque curves include an initial loading peak, followed by a broad maximum (attributed to the cross-linking reaction, which is expected to be more operative in the early stage of reaction, when the rate of radical generation is high), and a gradual decrease in mixing torque (attributed to the dominance of degradation reactions as the initiator is gradually consumed and radical concentration is lowered) until the end of mixing. *Tables 1* and *2* show the variations in the height of the cure peak (defined as the increase in mixing torque from the minimum after the loading peak to the maximum of the cure peak) as well as the gel content with system composition. The first thing to be noted is that, in the absence of SA, the height of the cure peak and the gel content of the final product increase with the DCP or MAH loading. This is attributed to the enhancement of DCP-initiated cross-linking reactions by the presence of MAH, as discussed previously[15]. Of more concern here, the addition of SA does indeed tend to reduce the height of the cure peak and the gel content, but its effectiveness decreases with increasing DCP level. Interestingly, even for the systems of lowest MAH and DCP contents (0.5 phr MAH and 0.25 phr DCP), the addition of SA up to 0.2 phr still does not entirely eliminate the cure peak.

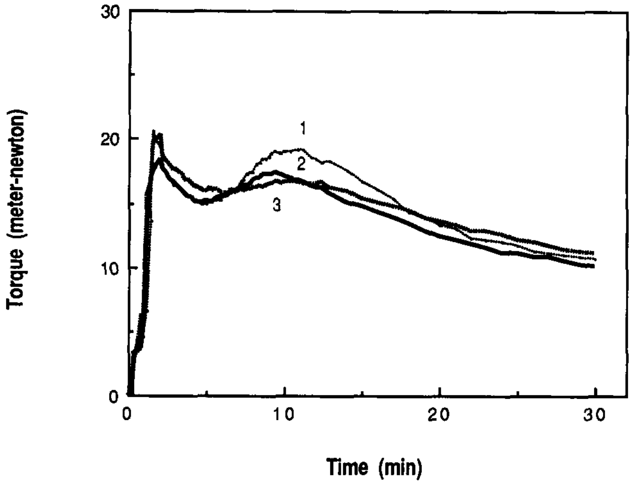


Figure 1 Representative torque curves at 1.0 phr MAH and 0.25 phr DCP. SA level (phr): (1) 0; (2) 0.05; (3) 0.15

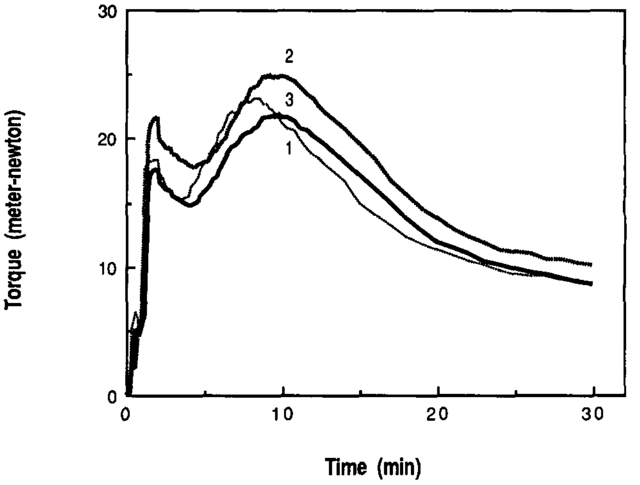


Figure 2 Representative torque curves at 1.0 phr MAH and 0.75 phr DCP. SA level (phr): (1) 0; (2) 0.05; (3) 0.20

As shown in *Figure 3*, the gel content of the final product appears to increase with the height of the cure peak, but the effect ceases at a gel content of $\approx$50 wt%. The fact that the gel content is closely related to the peak height strongly supports the previous proposal[15,19] that the cure peak results from cross-linking reactions. The levelling-off of the curve may be attributed to the competing DCP-induced scission reaction, especially in

Table 1 Final mixing torque, gel fraction and extent of grafting for systems of comparatively low DCP loading

DCP (phr)	MAH (phr)	SA (phr)	Height of cure peak (N m)	Final torque (N m)	Gel fraction	Relative peak height at 1780 cm^{-1}
0.25	0.5	0	1.2	7.7	0	0.26
0.25	0.5	0.05	1.0	9.8	0	0.30
0.25	0.5	0.15	1.0	9.4	–	0.41
0.25	0.5	0.20	0.5	8.6	–	0.22
0.25	1.0	0	4.4	10.6	0.46	0.62
0.25	1.0	0.05	2.2	10.1	0.32	0.46
0.25	1.0	0.10	1.7	10.3	0.07	0.48
0.25	1.0	0.15	1.0	11.0	0.04	0.49
0.25	1.5	0	4.9	9.6	0.53	0.56
0.25	1.5	0.05	2.2	10.8	0.19	0.58
0.25	1.5	0.10	1.0	10.6	0	0.51
0.25	1.5	0.20	1.0	11.5	–	0.55
0.25	2.0	0	6.2	11.5	0.57	0.57
0.25	2.0	0.05	3.2	13.0	0.33	0.69
0.25	2.0	0.15	1.7	11.5	0	0.59
0.25	2.0	0.20	1.0	11.3	–	0.64
0.5	0.5	0	4.0	7.4	0.34	0.36
0.5	0.5	0.05	3.4	8.4	0.20	0.29
0.5	0.5	0.15	3.4	8.4	–	0.34
0.5	0.5	0.20	3.4	9.1	0.29	0.22
0.5	1.5	0	7.7	10.6	0.49	0.63
0.5	1.5	0.05	6.3	11.0	0.57	0.55
0.5	1.5	0.10	5.1	9.8	0.51	0.55
0.5	1.5	0.20	2.1	8.6	0.44	0.55

Table 2 Final mixing torque, gel fraction and extent of grafting for systems of comparatively high DCP loading

DCP (phr)	MAH (phr)	SA (phr)	Height of cure peak (N m)	Final torque (N m)	Gel fraction	Relative peak height at 1780 cm^{-1}
0.75	1.0	0	7.3	8.6	0.47	0.60
0.75	1.0	0.05	7.3	10.1	0.48	0.47
0.75	1.0	0.15	7.6	9.4	–	0.44
0.75	1.0	0.20	7.3	8.6	0.44	0.52
0.75	1.5	0	9.3	11.8	0.52	0.60
0.75	1.5	0.05	8.5	11.5	0.47	0.49
0.75	1.5	0.10	8.8	11.8	–	0.54
0.75	1.5	0.20	7.8	11.5	0.47	0.53
0.75	2.0	0	9.8	10.8	0.51	0.61
0.75	2.0	0.05	9.0	10.1	0.47	0.57
0.75	2.0	0.15	7.3	10.8	–	0.67
0.75	2.0	0.20	7.3	10.3	0.46	0.63
1.00	1.5	0	9.5	9.1	–	–
1.00	1.5	0.05	9.8	10.3	–	0.72
1.00	1.5	0.10	9.3	9.8	–	0.61
1.00	1.5	0.20	9.0	11.5	–	0.61

the later stage of melt mixing (i.e. after the cure peak), when the scission reaction assumes prime importance.

Representative dynamic rheological properties of the final products are illustrated in *Figures 4* to *6*. At a high DCP level (*Figure 4*), no discernible difference due to the addition of SA may be identified. As may be expected, the corresponding gel content is also unaffected by the addition of SA (cf. *Table 2*). These observations indicate the predominance of DCP-induced side reactions (both cross-linking and chain scission) due to the excessive DCP loading. It is clear that SA is not effective at high DCP loadings.

At low DCP levels, the situation is more complicated: the G' curve may shift either down or up (depending on the MAH loading, see *Figures 5* and *6*) upon SA addition; the variation in G'' is similar in trend although less

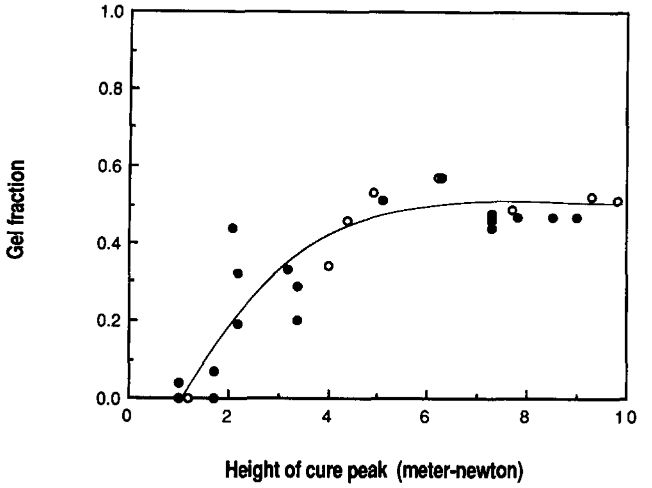


Figure 3 Relation between gel content and height of cure peak. (●) SA present; (○) SA absent

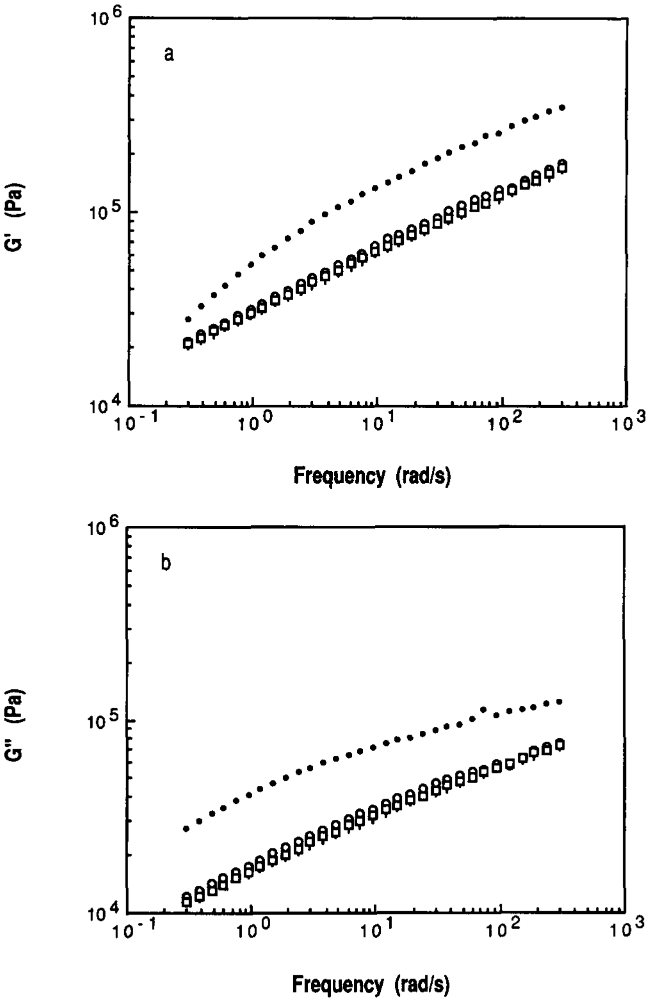


Figure 4 Variation of (a) storage modulus and (b) loss modulus with angular frequency at 135°C, 1.0 phr MAH and 0.75 phr DCP. (●) as-received EPR; (+) without addition of SA; (○) SA content 0.05 phr; (□) SA content 0.20 phr

apparent. The corresponding gel content, however, increases with MAH loading (at a fixed SA level) and decreases with the addition of SA (at a given MAH level) in a consistent manner. At low DCP content but high MAH loading (and therefore stronger MAH-enhanced cross-linking), *G'* tends to decrease upon the first addition of SA, but the effect decreases with further increase in the SA loading (*Figure 5a*). This is attributed to the initial suppression of cross-linking at low SA loadings and subsequently the simultaneous suppression of both cross-linking and chain scission.

At low DCP *and* MAH loadings (and therefore weak MAH-enhanced cross-linking but stronger DCP-induced scission due to the lower radical concentration), there appears to be an initial increase in *G'* upon first addition of SA, but the effect fades away with further increase in the SA loading (*Figure 6a*). The initial increase in *G'* may be attributed to the suppression of chain scission, and the subsequent decrease in *G'* to the simultaneous suppression of both the cross-linking and the scission reactions. The effect of SA does not appear to be intrinsically selective; it tends to suppress the more populated radical reaction path. In other words, SA may probably be considered as an almost non-selective chain transfer agent here. This is consistent with the observation that the addition of SA does not completely eliminate the presence of the cure peak even at the lowest DCP and MAH levels. In this case of predominating scission reaction, the added SA suppresses mainly the scission reaction.

To reconcile differences in the trends of variation of gel content and dynamic rheological properties, it is

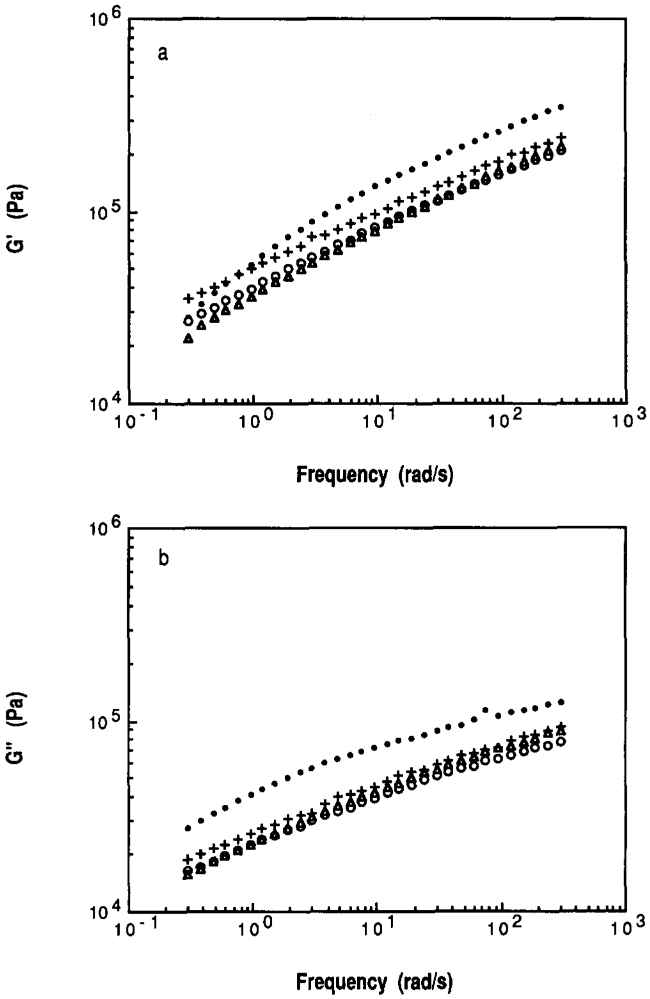


Figure 5 Variation of (a) storage modulus and (b) loss modulus with angular frequency at 135°C, 2.0 phr MAH and 0.25 phr DCP. (●) as-received EPR; (+) without addition of SA; (○) SA content 0.05 phr; (△) SA content 0.15 phr

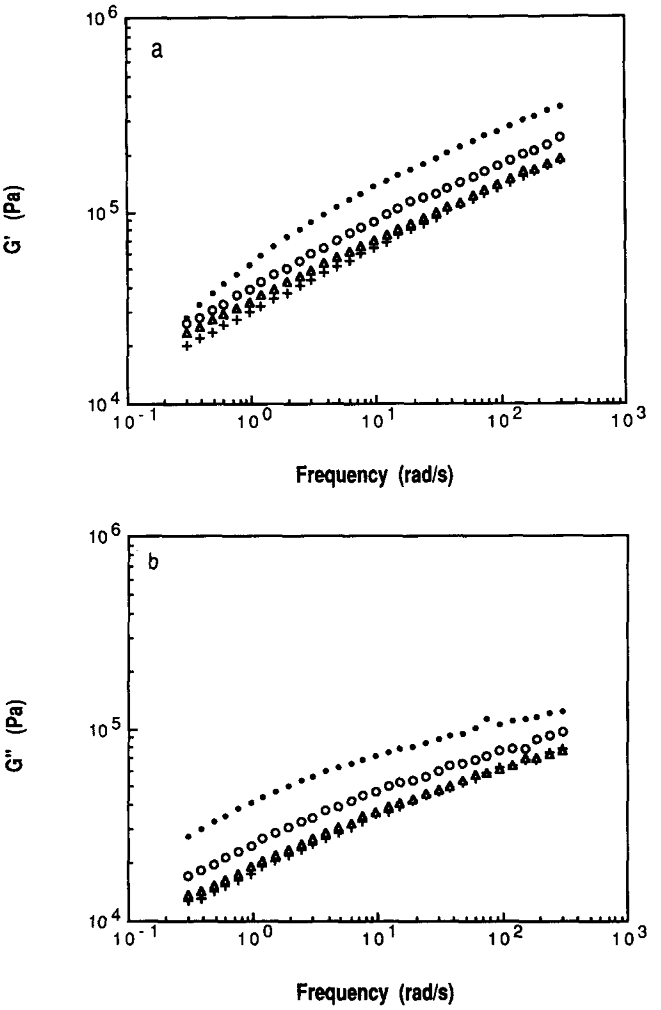


Figure 6 Variation of (a) storage modulus and (b) loss modulus with angular frequency at 135°C, 1.0 phr MAH and 0.25 phr DCP. (●) as-received EPR; (+) without addition of SA; (○) SA content 0.05 phr; (△) SA content 0.15 phr

suggested that the gel content and the dynamic properties represent different aspects of the structural features. The gel content is related to the spatial connectivity of chains; however, the total number (and therefore the density) of cross-linking is not necessarily the main concern. The dynamic rheological properties, on the other hand, reflect the combined molecular response to the periodic perturbation; the densities of both chemical cross-links and physical entanglements are directly responsible[20,21]. The two techniques give complementary information on the actual structure of the functionalized rubber.

Results for the extent of grafting, defined as explained under Experimental, are given in *Tables 1* and *2*. There appears to be a weak tendency for the extent of grafting to decrease with the addition of SA but, owing to the rather large error bounds of the present technique, no definite effect may be identified. The results agree reasonably well with the previous observation of Gaylord *et al.*[8,9,16,17] that SA is a good suppressor for the side reactions and does not interfere strongly with the grafting reaction.

DISCUSSION

The mechanistic paths of the grafting and the side reactions are not exactly clear from reports in the literature. It is generally agreed that a radical-type mechanism is involved; however, specific mechanisms proposed by different researchers differ from one another in the graft site, the intermediates involved, and structures of the final products. For example, Porejko *et al.*[22] proposed that grafting of MAH on to PE in a homogeneous xylene solution occurs by means of chain transfer to PE and the subsequent propagation of the macroradical with consecutive attachment of MAH molecules. On the basis of the observed unsaturation in grafted PE, Gaylord and Mehta[7] suggested formation of single grafts via disproportionation of grafted MAH radicals. More recent ^{1}H and ^{13}C n.m.r. results of Russell and Kelusky[23] indicated that MAH is grafted on to PE as single rings in presence of a large excess of MAH. Gaylord and Mishra[8] proposed that the grafting of MAH on to PP follows a complicated set of reaction paths which result in singly grafted rings as well as poly(maleic anhydride) branches. Minoura *et al.*[24] suggested that MAH is not grafted on to PP but is inserted between PP chains as a bridging unit. This proposal is supported by the more recent ^{13}C n.m.r. results of Rengarajan *et al.*[25], who grafted MAH on to PP by means of a solid-state process. Grafting of MAH on to EPR is generally considered as a hybrid of the mechanisms proposed for PE and PP; discrepancies in details of the mechanisms proposed by different researchers[9,26] are therefore not unexpected. It appears that the grafting of MAH on to polyolefins involves a variety of reaction paths; different synthetic processes adopted by different researchers resulted in different weightings to the kinetic routes and therefore apparent disagreement among the proposed mechanisms.

The possible reaction paths representing the present authors' simplified view of the present reaction system are as follows.

Initiation

Initiator dissociation: $I \rightarrow 2R^*$ (1)
Hydrogen abstraction: $P + R^* \rightarrow {}^3P^* + RH$ (2)
$P + R^* \rightarrow {}^2P^* + RH$ (3)

Side reactions (in the absence of MAH)

Chain scission: ${}^3P^* \rightarrow {}^2P^* + P$ (4)
Cross-linking: ${}^2P^* + {}^2P^* \rightarrow P$ (cross-linked) (5)
Chain transfer: ${}^2P^* + P \rightarrow P + {}^3P^*$ (6)

Grafting

Graft to secondary carbon: ${}^2P^* + M \rightarrow P\text{–}M^*$ (7)
Graft to tertiary carbon: $[{}^3P^* + M \rightarrow P\text{–}M^*]$ (8)

Further side reactions (in the presence of MAH)

Cross-linking: ${}^2P^* + P\text{–}M^* \rightarrow P$ (cross-linked) (9)
Chain transfer: $P\text{–}M^* + P \rightarrow P$ (grafted) $+ {}^2P^*$ (10)
$P\text{–}M^* + P \rightarrow P$ (grafted) $+ {}^3P^*$ (11)

Further transfer reactions (in the presence of SA)

Chain transfer to SA: ${}^2P^* + HS \rightarrow P + S^*$ (12)
$[{}^3P^* + HS \rightarrow P + S^*]$ (13)
$P\text{–}M^* + HS \rightarrow P + S^*$ (14)
Chain transfer to EPR: $S^* + P \rightarrow HS + {}^2P^*$ (15)
$S^* + P \rightarrow HS + {}^3P^*$ (16)

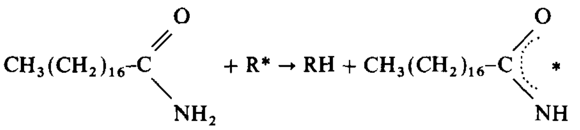
Here, ${}^2P^*$ and ${}^3P^*$ represent respectively secondary and tertiary EPR macroradicals, M and M* represent respectively MAH and the succinic anhydride radical, and HS and S* represent respectively SA and the corresponding amide radical. The brackets indicate reaction paths of probably lower rate due to reactivity considerations.

Important features of the proposed mechanism include chain scission via formation and dissociation of tertiary radicals on propylene units, cross-linking via combination of secondary radicals on ethylene units or grafted anhydride units, and grafting via propagation of radicals to the MAH monomer. It is assumed that the hydrogen abstraction by primary radicals from the tertiary carbon of the propylene unit is favoured more than those from the secondary carbon of the ethylene unit. However, the formation of secondary radicals is still considered significant, owing to combined effects of reactivity and population. (The EPR used in this work corresponds to a hydrogen population ratio, primary : secondary : tertiary, of 3 : 6 : 1.) On the other hand, the reactivity of tertiary radicals towards MAH is assumed relatively low, compared with that of secondary radicals. The homopolymerization of MAH is neglected, from ceiling temperature considerations[24]. It is further assumed that SA serves as a nearly non-selective chain transfer agent. Consequences of these assumptions include the following.

1. In the absence of MAH, the peroxide induces mainly degradation of EPR, although cross-linking may still persist to a somewhat limited extent.
2. In the presence of MAH, chain scission is alleviated (but not eliminated), whereas cross-linking is enhanced, since the presence of MAH provides (via formation of secondary radicals) several additional routes for cross-linking and one route (i.e. equation (8)) to avoid chain scission, whereas only one (i.e. equation (11)) of the additional reaction paths encourages scission.
3. The presence of SA tends to suppress the more populated radical reaction path (whether cross-linking or chain scission).

These assumptions are consistent with observations in the authors' previous and present studies. They also agree with further observations that another EPR sample of high ethylene content tended to cross-link more strongly with the addition of DCP, especially in the presence of MAH.

As far as is known, the mechanism of the chain transfer action of SA has not been extensively discussed in the literature. It is proposed that the chain transfer capability may possibly be related to the electron delocalization effect after the extraction of an amide hydrogen, i.e.



$$\mathrm{CH_3(CH_2)_{16}{-}C({=}O)NH_2} + \mathrm{R^*} \rightarrow \mathrm{RH} + \mathrm{CH_3(CH_2)_{16}{-}C(\cdots O)(\cdots NH)}\ {*} \qquad (17)$$

CONCLUSIONS

Functionalized EPR was prepared by melt mixing with various amounts of DCP, MAH, and SA, and analysed using gel content measurements, dynamic rheological analysis, and Fourier-transform infrared spectroscopy in combination with observations in the mixing torque behaviour. Effective suppression of side reactions was realized for systems of moderate or low DCP contents upon addition of SA, but no apparent changes could be identified at high DCP loadings. Within the confidence level of the *FT*i.r. measurements, the extent of grafting appeared to be little affected by the addition of SA. The role for each ingredient in the present reaction system was discussed from a mechanistic point of view. In particular, SA was considered as a chain transfer agent which tends to suppress the more populated radical reaction path, be it cross-linking or chain scission.

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