

Parameters Affecting the Grafting Reaction and Side Reactions Involved in the Free-Radical Melt Grafting of Maleic Anhydride onto High-Density Polyethylene

H. R. Z. Sheshkali, H. Assempour, H. Nazockdast

Polymer Engineering Department, Amir Kabir University of Technology (Tehran Polytechnic), Tehran, Iran

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ABSTRACT: The parameters affecting the grafting reaction and side reactions in free-radical melt grafting of maleic anhydride (MA) onto high-density polyethylene with the aid of 2,5-dimethyl-2,5-di(*t*-butyl peroxy)hexane peroxide (DTBPH) have been studied using an internal mixer. MA grafting degree of the maleated samples was measured with titrometry and FTIR spectroscopy methods. The extent of chain-branching/crosslinking side reactions was evaluated with gel content and MFI determination. The flow behavior and melt viscoelastic properties of the samples were measured using a rheometric mechanical spectrometer. DTBPH and MA concentrations, reaction temperature, rotor speed, the type and concentration of coagents were among the studied parameters. The results show that MA and DTBPH concentration has a major role on the grafting reaction, chain-branching/crosslinking side reactions and also the grafts microstructure in the final product. The reac-

tion temperature has a complex effect on the maleation reaction. Increasing the rotor speed causes an increase in MA grafting degree of the samples and reduces the competitive side reactions. By using Gaylord additives, gel formation reduces at the expense of a dramatic decrease in the grafting degree. MA grafting degree is increased by the use of comonomers in the reaction and this is accompanied with a decrease in crosslinking side reaction when the vinyl type styrene comonomer is used. The results of processing torque in combination with the measurements of the melt viscoelastic property and gel content of the samples provide a great insight into understanding the gel formation mechanism. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1869–1881, 2007

Key words: polyethylene; graft copolymers; viscoelastic properties; reactive processing

INTRODUCTION

In recent years, increasing activities have been directed toward graft modification of polyolefins with polar/reactive monomers for improving paintability, adhesion, and compatibility of these commodity polymers with other materials.^{1–5} The most common monomers used for the graft modification are maleic anhydride (MA), glycidyl methacrylate,^{6–11} acrylic acid,^{11–13} and diethyl maleate.^{14–16} By far, MA modified polyolefins are the most important class of functionalized polymers, which have found wide commercial applications such as interfacial modifier in polymer blends,^{1–4,17–27} composites containing fiber or nanofiller,^{28–30} multilayer paper sheets,³¹ metal coating,³² metal–plastic laminates,³³ and also as a precursor for ionomer production.³⁴

Maleation of polyethylene (PE), as one of the most important commodity polymers which exhibits a higher grafting efficiency towards reaction with MA comparing to the other polyolefins,^{35,36} has been an attractive subject for polymer researchers. Although many methods, including grafting with the aids of

free-radical initiator (in the melt,^{23,37–46} solution,^{27,47} or suspension⁴⁸ state), melt-grafting through ultrasonic²⁸ or thermomechanical²² initiation, and also photografting^{49,50} have been adopted for maleation of PE, free-radical melt grafting of MA is the most important method from the economical and environmental points of view. However, this method suffers from simultaneously occurrence of undesirable side reactions, such as chain-branching and/or crosslinking of PE, which can damage the processability and properties of the resulted product. The homopolymerization of MA may also occur during the maleation reaction, which results in coloration of the grafted product⁴¹ and may alter the physical and mechanical properties of the original polymer substrate.² Therefore, an optimization is required to direct the functionalization process towards MA grafting as a selective reaction over the undesirable side reactions. In this respect, many studies have been carried out for understanding the influences of the reactant parameters (type and amount of peroxide,^{39–43,51} MA concentration,^{37–44,51} and PE structure³⁶) on MA grafting degree and the extent of chain-branching/crosslinking side reactions occurred during the maleation of PE. The influences of processing conditions, such as temperature and mixing, on the free-radical maleation reaction have also been investigated both in

Correspondence to: H. Assempour (assempour@aut.ac.ir).

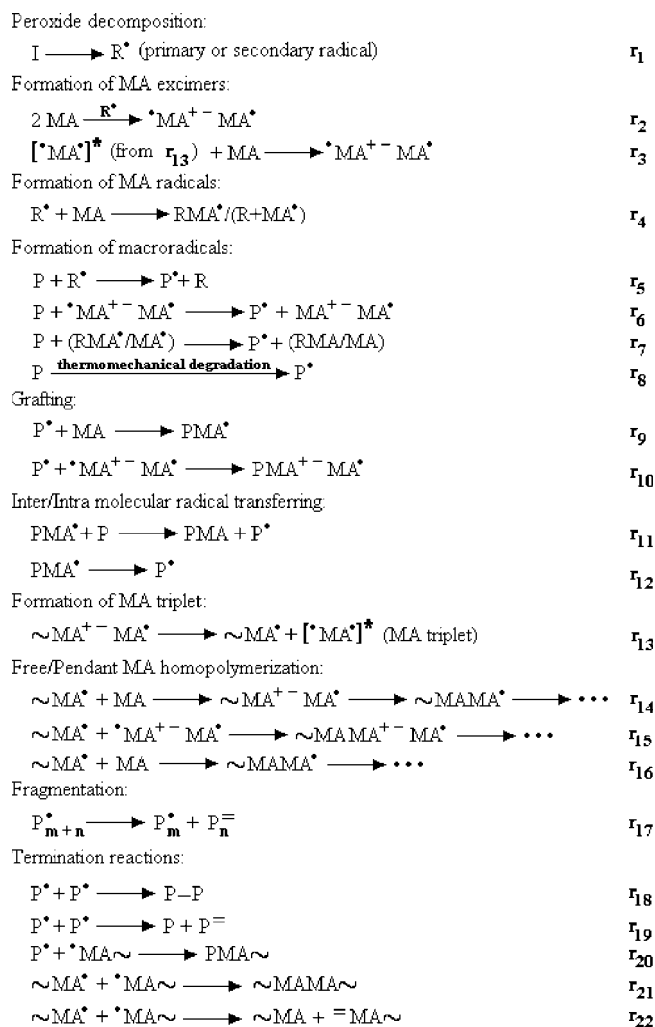


Figure 1 The overall mechanism suggested for MA grafting onto PE.

batch internal mixers^{40–42} and extruders.^{23,43–45} Moreover, studies on the effects of various coagents on the selectivity of the maleation reaction have shown that Gaylord additives (the electron donor compounds containing N, P, or S atoms) reduce PE chain-branching/crosslinking at the expense of decreasing MA grafting degree^{39–41,52–54} while the use of vinyl type comonomers leads to a higher MA grafting degree and less crosslinking.^{8,55,56} Furthermore, many works have been devoted to study the kinetics of the maleation reaction^{57–59} and the microstructure of grafts formed on the maleated PE chains^{60–62} to provide more information on the reaction optimization. However, in spite of these efforts, the condition for optimizing the grafting reaction over the side reactions have not been entirely understood due to the inherent complexity of the maleation reaction and, therefore, the lack of true insight about the reaction mechanism. While Gaylord and coworkers^{40,41,52,53,63,64} showed that MA increases the radical generation through the

mechanism of excimer formation, many investigators have suggested other mechanisms for the maleation reaction in which the radical species are produced only from dissociation of the peroxide initiator, including normal radical grafting reaction,^{2,51,57,65} chemisorption,⁶⁶ and intramolecular hydrogen abstraction.^{58,62} According to the above-mentioned various reports, one may summarize the overall mechanism of the free-radical MA grafting onto PE as shown in Figure 1.

In the present work, the effects of the influential parameters on the trends of grafting reaction and side reactions involved in the free-radical melt grafting of MA onto PE were investigated in details to gain more insight into understanding the reaction mechanism and the process optimization.

EXPERIMENTAL

Materials

A commercial polyethylene used in this study was a high density polyethylene (HDPE) in the granular form supplied by Arak Petrochemical Company (Iran, 6070EA). The polymer has a melt flow index of 17.9 g/10 min (190°C, 5 kg). MA (99%) was supplied from Merck (Darmstadt, Germany) and DTBPH (92%), produced by Akzo Nobel (Amersfoort, Netherlands), was used as a suitable free-radical initiator.^{43,67} Dimethyl formamide (DMF, 99%) and acetanilide (AAn, 99%) were supplied from Merck (Darmstadt, Germany) and used as Gaylord additives. Styrene (St, 99%) and trimethylolpropane triacrylate (TMPTA, 99%) comonomers were provided from Merck (Darmstadt, Germany) and Aldrich (USA), respectively. All materials were used as received.

Grafting reaction

All grafting reactions were carried out in a 60-mL laboratory-type internal mixer equipped with Banbury type rotors (Brabender Plasticorder W50, Duisburg, Germany). HDPE was first fed into the preheated mixing chamber, and after PE plastication, MA, coagent (when being used), and peroxide were added to the molten PE after 2, 3, and 4 min intervals from the starting point, respectively, unless otherwise specified. The mixing was continued for 6 or 9 min after the peroxide addition to the reaction media in the case of presence or absence of comonomer, respectively, when the processing torque reached to a steady state. The samples were prepared at a fixed fill factor of 0.8, at a rotor speed of 60 rpm and temperature of 185°C, unless otherwise specified. The amount of HDPE for obtaining a fixed fill factor in the grafting reactions was determined using Simha and Olabisi Equation.⁶⁸

Characterization

To remove unreacted chemicals from the grafted samples, 5 g of the grounded sample was placed in a 120-mesh stainless steel pouch and heated in 300 mL refluxing xylene for 7 h. The xylene soluble fraction (sol) was precipitated in 900 mL acetone, filtered, and washed with excess acetone. The insoluble fraction (gel) was removed from the pouch and washed with hot xylene. The purified sol and gel fractions were dried in a vacuum oven at 75°C for 24 h.

The MA grafting degree of the purified samples was determined on the basis of titrimetry and FTIR results. Film of 65–73 μm thickness was prepared by hot pressing about 1 g of the purified sample between two PTFE films at 180°C for 20 s under a pressure of 26 MPa. The prepared film was removed from the press after cooling to 60°C with a rate of 10°C/min. For titration of complete xylene-soluble samples, 1 g of the sample film was dissolved in 200 mL refluxing xylene (containing 0.5 mL distilled water) by heating for 1.5 h. The hot solution was titrated with 0.05N ethanolic KOH using three drops of 1% thymol blue in DMF as indicator. Then, an excess volume (0.3 mL) of the alcoholic KOH was added to the solution and after heating for 5 min, the deep blue color was back-titrated immediately to a yellow end point by the addition of 0.05N isopropanolic HCl. For titration of samples having gel portion, 1 g of the sample film was heated in 200 mL refluxing xylene (containing 0.5 mL distilled water) for 2.5 h. An excess volume of the alcoholic KOH (as determined experimentally) was added and heating was continued for another hour under the reflux condition. Then, the hot solution was back-titrated in the same manner described for the sol samples. Ungrafted HDPE sample processed at 185°C was also titrated using the same procedure described earlier and the result in which 0.1 mL of KOH solution was consumed for 1 g of the sample was used as reference. Therefore, MA grafting degree of the maleated samples was calculated according to the following equation:

$$\text{MA}(\text{wt}\%) = \frac{N \times (\text{mL}_{\text{KOH}} - \text{mL}_{\text{HCl}} - 0.1) \times 98.06}{2 \times W(\text{g}) \times 1000} \times 100\% \quad (1)$$

where N is the normality of KOH solution and W is the quantity of titrated sample. For each sample, the reported grafting degree is the average of two titrations. It is noteworthy that MA grafting degree of the samples prepared in the presence of coagents were determined only by the use of titration method.

The FTIR spectra of the samples films were recorded at 45°C on a Bomem FTIR spectrometer (Canada) from 4000 to 600 cm^{-1} with a 1 cm^{-1} resolution in the transmittance mode. A typical FTIR spectrum

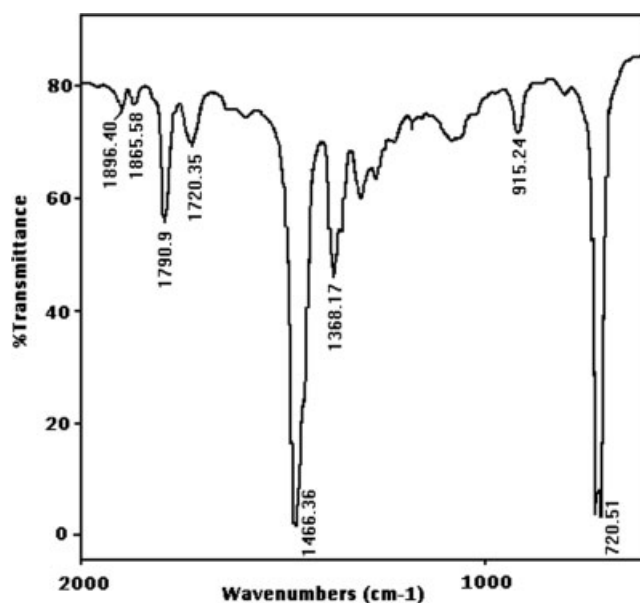


Figure 2 A typical FTIR spectrum of maleated PE.

of a maleated PE film is presented in Figure 2. The MA grafting degree of all samples prepared in the absence of coagents was measured by the aid of a calibration curve, obtained using a combination of titration and FTIR data, as shown in Figure 3(a). According to the Samay et al.⁵⁵ as well as Kozel and Kazmierczak⁶⁹ methods, the intensity of carbonyl absorption bands due to the anhydride (1830–1750 cm^{-1}) and carboxylic acid (1750–1660 cm^{-1}), and also the absorption band intensity of CH_2 sequences of PE (760–680 cm^{-1}), as the internal standard, were used for determination of MA grafting degree. It should be mentioned that the FTIR spectrum of the ungrafted HDPE showed an absorption band at 1720 cm^{-1} , which is the characteristic of the carbonyl band resulted from thermooxidation of PE during processing.²⁸ This result was taken into account for constructing the calibration curve. As it is seen in Figure 3(b), the intensity of CH_2 sequences absorption band can be used as the internal standard as long as the normalized absorption band for the sample film thickness (d) is not affected by the process; the results which is in agreement with that reported by Grigoryeva and Kocsis.⁷⁰

The gel content of the samples was determined according to ASTM D2765, procedure A. The MFI of the purified samples was measured in accordance with ASTM D1238 (190°C, 5 kg) with a Davenport melt indexer (Hants, UK). The rheological behavior and melt linear viscoelastic properties of the samples were studied by the aid of a rheometric mechanical spectrometer (Paar Physica USD200) with a parallel plate geometry (plates diameter = 25 mm; gap = 1 mm). The dynamic frequency sweep tests were performed

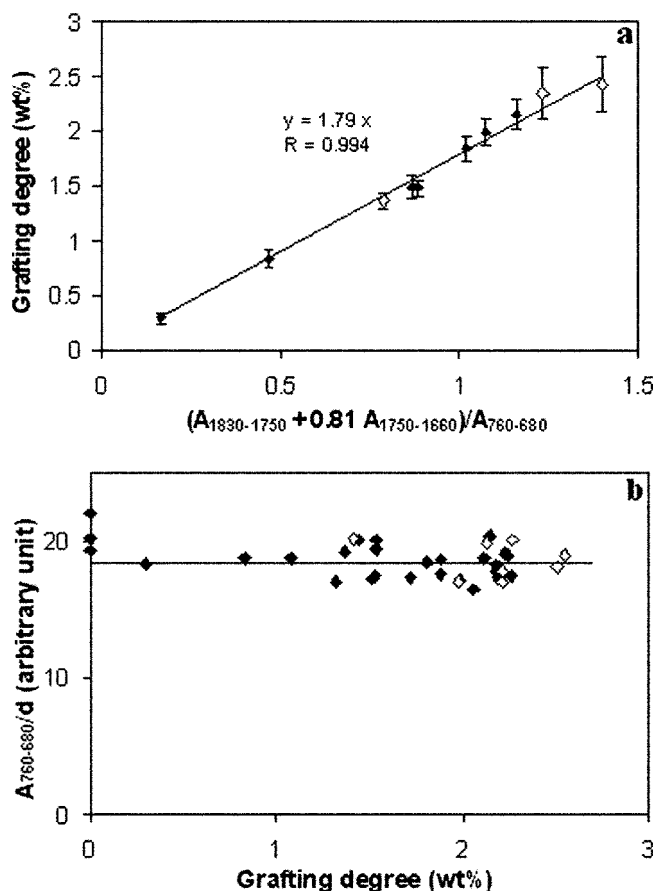


Figure 3 FTIR calibration curve for determination level of MA grafting (a) and the variation of normalized CH_2 absorption band as a function of MA grafting degree (b). \blacklozenge : complete xylene soluble samples; \diamond : samples containing gel portion.

at 200°C , in a frequency range of $0.1\text{--}1000\text{ s}^{-1}$ using strain amplitude of 1%.

RESULTS AND DISCUSSION

Effect of MA and DTBPH concentration

Figure 4 compares the torque variation versus processing time for the molten PE processed in the presence and absence of MA and DTBPH peroxide. As it is seen, in the absence of MA and peroxide (curve a), the torque of the PE melt almost remains unchanged throughout the mixing time. When peroxide is used (curve b), the torque increases rapidly due to the polymer chain-branching/crosslinking, and after reaching to a maximum, it decreases to a steady state level, as a result of the mechanical breakage of the branched/crosslinked chains formed during the reaction. Comparing the curves of b and c indicates that MA, apart from contributing in grafting onto PE, can also accelerate increasing the torque value.

The variations of gel content and maximum torque as a function of DTBPH concentration for the samples

prepared in the presence and absence of MA are presented in Figures 5(a) and 5(b), respectively. The effect of the peroxide concentration on the MA grafting degree of the maleated samples is also shown in Figure 5(c). As it is seen, MA has a strong effect on increasing the maximum torque and gel content of the processed samples and causes the gel formation to be occurred at a lower concentration of the peroxide. It is also observed that the variations of gel formation and maximum torque follow a similar trend with respect to the peroxide concentration; both increase rapidly with increasing the peroxide concentration up to some extent above which their rates decrease. This result is similar to that reported for the peroxide modification of PE in the absence of MA.^{71,72} Moreover, MA grafting degree increases with increasing the peroxide concentration up to some extent above which (0.4 phr) it declines.

An increase in the peroxide concentration increases the gel formation and MA grafting degree as a result of the higher macroradical generation. However, as the rate of grafting reaction with respect to radical concentration is equal or less than first order and that of termination reactions are of the second order,⁵¹ an increase in the amount of the peroxide directs the reaction towards the radical consuming termination reactions over the grafting reaction, which, in turn, can reduce MA grafting degree at high peroxide concentration due to decreasing the occurrence of graft propagation ($r_9 + r_{11}/r_{12}$) and/or graft homopolymerization (r_{16}) reactions. Reducing the rate of gel formation at high peroxide concentration [Fig. 5(a)] can be discussed as follows. At high peroxide concentration, in contrast to its low concentration, a more fraction of the radicals generated from the peroxide decomposition are consumed through recombination reaction (due to the cage effect) prior to form macroradicals. Also, increasing the crosslinking reaction reduces the diffusion rates of macroradicals,^{73,74} decreasing the rate of macroradical termination and,

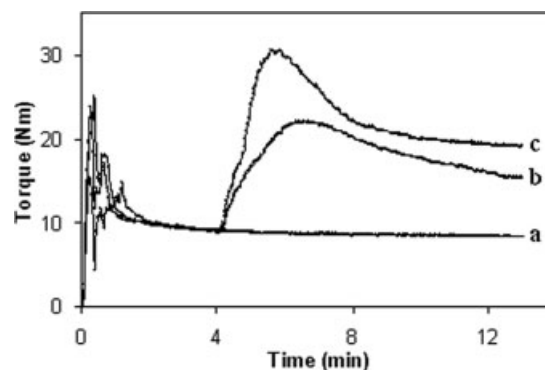


Figure 4 The variations of torque versus processing time for (a) PE, (b) PE containing 0.4 phr DTBPH, and (c) PE containing 0.4 phr DTBPH and 1.5 phr MA.

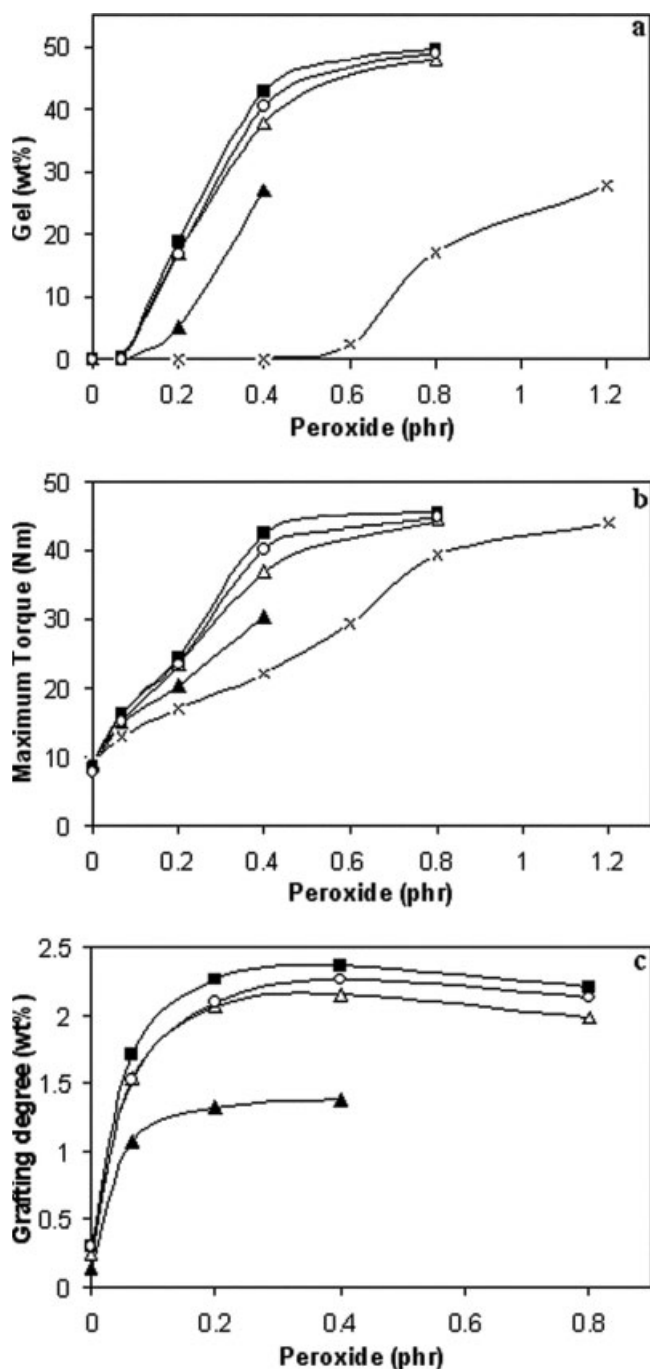


Figure 5 The variations of gel formation (a), maximum torque (b), and MA grafting degree (c) as a function of DTBPH concentration. x: MA = 0 phr, ▲: MA = 1.5 phr, Δ: MA = 3 phr, ■: MA = 4.5 phr, ○: MA = 6 phr.

hence, the rate of gel formation. Moreover, the ease of hydrogen abstracting by radicals from the tertiary carbon atoms existing in the gel fraction causes an increase in the crosslinking density without a further increase in the gel content. Another reason for this observation is that the highly branched and/or cross-linked chains formed at high peroxide concentration are more prone to the mechanical breakage.

Figure 6(a) shows the results of increasing MA concentration on the gel content and $1/\text{MFI}$, as a measure of the crosslinking side reaction, of the grafted samples. The effect of MA concentration on the MA grafting degree of these samples is also presented in Figure 6(b). As it is apparent, at a constant peroxide concentration, MA grafting degree follows a trend similar to that of gel formation, both increase with increasing MA concentration up to some extent above which (4.5 phr) they decline, indicating that the grafting reaction is accompanied with the chain-branching/crosslinking side reactions.

According to the mechanism proposed by Gaylord and coworkers,^{40,41,52,53} the acceleration effect of MA on increasing the gel formation is the result of increasing the macroradical generation through the mechanism of MA excimer formation (r_2, r_3). However, we believe that this effect could also be explained in terms of the greater efficiency of the grafted macroradicals (PMA^*) than PE macroradicals (P^*) for contribution in the gel forming reactions. To provide more insight into understanding the real mechanism of gel formation, three sets of samples were prepared in the presence and absence of MA. The formulation recipes and characteristics of these samples are presented in Table I. The variations of torque versus processing time and viscoelastic properties of the samples are also shown in Figures 7(a) and 7(b), respectively. By comparing the results in Figure 7 with the results given in Table I, it is noticed that while sample S1 has the same gel content of sample S2, it shows a higher storage modulus and a greater torque value than those of sample S2. Also it is apparent that although both samples S2 and S3 show almost a similar torque value throughout PE processing, the gel content of sample S2 is greater than that of sample S3. The results of melt viscoelastic properties of the samples S2 and S3 clearly show that the storage modulus and complex viscosity of sample S2 are much greater than those of sample S3. Moreover, while sample S4 has a greater gel content and storage modulus than those of sample S3, it shows a lower maximum torque value comparing to that of sample S3. This behavior could not be interpreted in terms of increasing macroradical generation through the mechanism of MA excimer formation in combination with considering Heinen et al.⁶⁰ idea in which MA does not act as a crosslinker between two polymer chains.

The above-discussed results suggest that the gels formed in the presence and absence of MA have not necessarily the same structure and show different hydrodynamic effect on the viscoelastic properties of the samples, indicating that the radicals generated in the presence of MA contribute in a termination pathway different from that occurs in the absence of MA. In the absence of MA, it seems that the chain-exten-

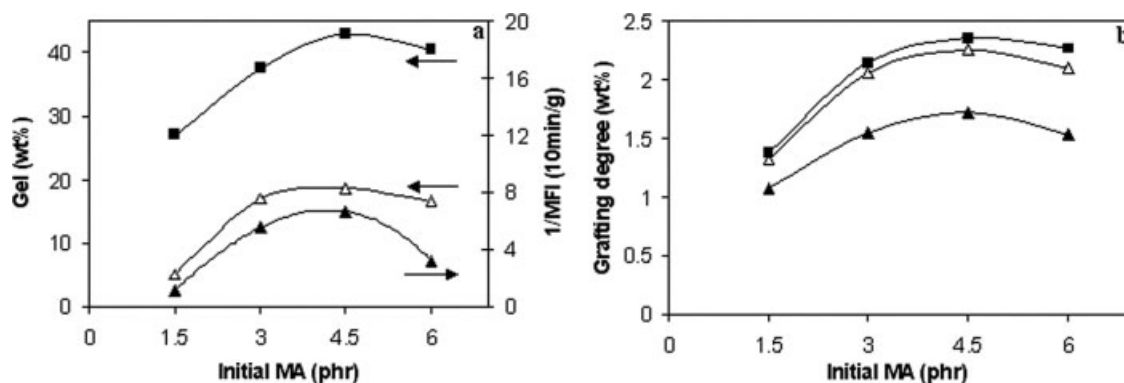


Figure 6 The variations of gel content as well as 1/MFI (a) and MA grafting degree (b) as a function of MA concentration. ▲: DTBPH = 0.067 phr, △: DTBPH = 0.2 phr, ■: DTBPH = 0.4 phr.

sion and chain-branching are more important than the crosslinking termination reaction, which the formers have remarkable influence on increasing the viscosity of the modified polymer but do not show appreciable effect on promoting the gel formation. In this case, the gel formation occurs as a result of producing highly branched molecules or crosslinking between two branched/extended chains during the polymer modification. In the presence of MA, the grafted macroradicals (PMA•) formed during the maleation reaction predominantly take part in the crosslinking termination reaction (r_{20}) rather than the reactions of chain-extension, chain-branching, and disproportionation termination (r_{22}). Also, the grafted macroradicals, unlike PE macroradicals, are unable to undergo intramolecular chain scission. These explanations could be considered for the acceleration effect of MA on increasing the gel formation.

It should be noticed that the ratio of termination reaction via recombination of PE macroradicals (r_{18}) to that occurs between the grafted and ungrafted macroradicals (r_{20}) is influenced by the peroxide and MA concentrations. When a low concentration of MA and a high concentration of the peroxide are used, due to the formation of considerable amounts of PE macroradicals, the termination reaction follows a route similar to that occurs in the absence of MA. However,

by increasing MA concentration, the probability of producing MA grafted macroradicals is increased so that the crosslinking reaction between the grafted and ungrafted macroradicals is expected to become the predominant termination reaction. This is evidenced by comparing the processing torque and viscoelastic property of the samples S2 and S4 presented in Figure 7. In the case of sample S4, using a high amount of MA (3 phr) accelerates the crosslinking type termination reaction during the maleation of PE, which leads to a high storage modulus of the final product. However, the higher peroxide concentration and lower MA content used in preparation of sample S2 comparing to those of sample S4 cause the chain-extension and chain-branching also become important in addition to the crosslinking reaction, which, in turn, result in an increase in the maximum torque compared to that of sample S4. However, the torque value is decreased abruptly as a result of the mechanical breakage of the formed branched/crosslinked chains. Thus, although different maximum torque are observed for the samples S2 and S4, the final torque values of these samples are almost the same. It is interesting that the final torque observed for the sample prepared in the presence of 0.067 phr of the peroxide and 1.5 phr of MA (grafting degree = 1.08 wt %) is only about 1 Nm higher than that of the sample pre-

TABLE I
The Formulation Recipes and Characteristics of Three Sets of Samples Prepared in the Presence and Absence of MA

Sample	Peroxide (phr)	Initial MA (phr)	Grafted MA (phr)	Gel (wt %)	Final processing temperature (°C)
S1	1.2	0	0	27.7	215
S2	0.4	1.5	1.4	27.1	203
S2	0.4	1.5	1.4	27.1	203
S3	0.6	0	0	2.5	201
S3	0.6	0	0	2.5	201
S4	0.2	3	2.1	17.1	203

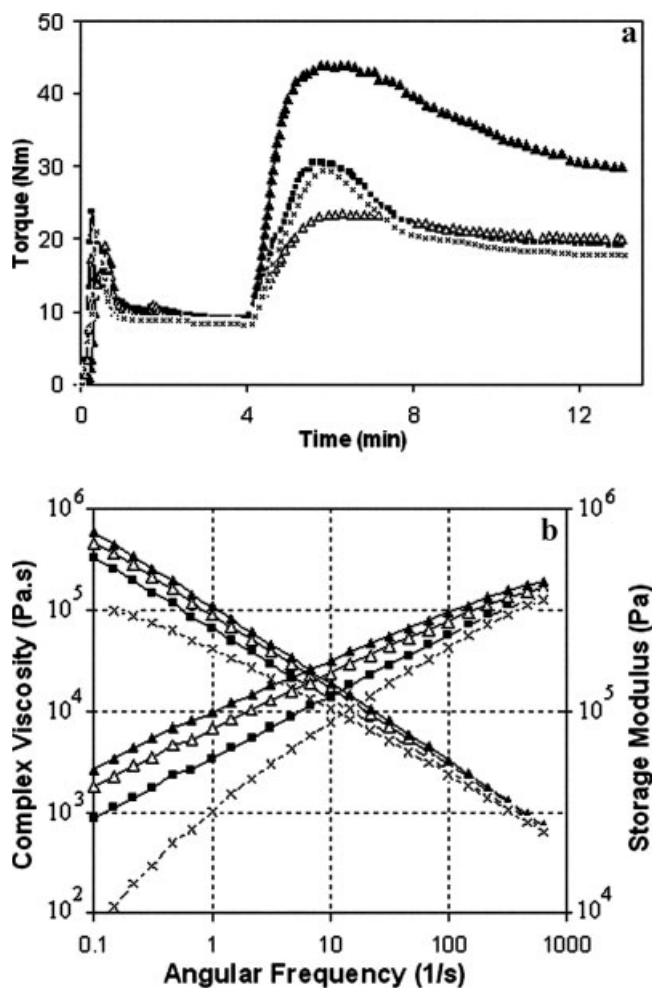


Figure 7 The variations of torque versus processing time (a) and viscoelastic properties versus angular frequency (b) of the samples S1–S4. ▲: S1, ■: S2, ×: S3, △: S4.

pared using 0.067 phr peroxide and 4.5 phr of MA (grafting degree = 1.72 wt %). Therefore, interaction between the polar side groups on the maleated PE chains only play a minor role in increasing the processing torque of the maleated products.

The positions of the FTIR absorption peaks due to the stretching of anhydride carbonyl bonds (W_{CO}) observed for maleated PE samples are listed in Table II.

TABLE II
The Positions of FTIR Absorption Peaks Due to Anhydride Carbonyl Bonds Observed for Maleated PE Samples

Initial MA (phr)	Peroxide (phr)	W_{CO} (cm ⁻¹)
0.5	0.067–0.2	1791.1
1.5	0.067–0.4	1790.9 ± 0.2
3	0.067–0.8	1790.9 ± 0.2
4.5	0.067–0.8	1786.2 ± 0.2
6	0.067	1786.15
6	0.2–0.8	1784.8 ± 0.2

According to Roover et al. observations,⁷⁵ the FTIR spectra of *n*-octadecyl succinic anhydride, poly(MA), and citraconic anhydride exhibit absorption peaks, due to anhydride carbonyl bonds, at 1792, 1784, and 1780 cm⁻¹, respectively. Table II shows that W_{CO} of the maleated samples prepared by using 1.5 and 3 phr of MA are very close to that of *n*-octadecyl succinic anhydride and also similar to that of the grafted samples prepared by using 0.5 phr of MA, in which it seems MA being soluble in the polymer melt. These results suggest that under the experimental condition used (185°C, 60 rpm), MA with concentrations up to 3 phr is soluble in the molten PE and is grafted onto the polymer chains mainly as single succinic anhydride. The shifting of W_{CO} toward lower wave number observed for the samples prepared in the presence of 4.5 phr and 6 phr of MA (Table II) could be assigned to the overlapping of absorption bands due to poly(MA) and single succinic anhydride grafts formed in these samples. Formation of poly(MA) grafts above 3 phr of MA concentration, which is accompanied with the coloration of maleated samples, can be attributed to the formation of MA phase separated droplets during the maleation reaction as a result of the weak miscibility of MA with PE (Fig. 8). It should be noticed that the presence of poly(MA) grafts in maleated PE samples prepared at 170°C has also been observed by Heinen et al.,⁶⁰ although the ceiling temperature of MA is reported to be 150°C.⁷⁷

When MA concentration exceeds 3 phr, the effective peroxide concentration and, hence, the number of radicals required for MA grafting is reduced as a result of greater affinity of the peroxide with the formed MA droplets comparing to PE, which is in favor of decreasing the gel formation. However, in this case, MA droplets, like the droplets in the emulsion polymerization,⁷⁸ can also act as a source of MA monomer for the maleation reaction, which, in turn, can increase MA grafting degree mainly through the formation of poly(MA) grafts and also increase the

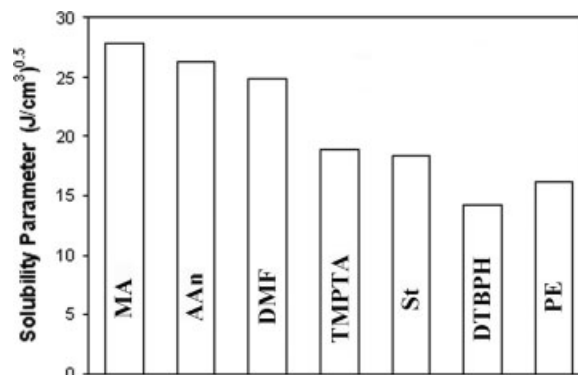


Figure 8 The solubility parameters of the reactants used in the grafting reactions (reported/calculated according to Ref. 76 and Small's group contribution method).

TABLE III
The Grafting Ratio of the Maleated PE Samples (DTBPH = 0.4 phr)

Initial MA (phr)	Grafting ratio
1.5	1.04
3	1.05
4.5	1.12
6	1.19

gel formation as a result of the generation higher amounts of the grafted macroradicals. The above-mentioned opposite effects of MA concentration on the gel formation and MA grafting degree can be taken into account for the maxima observed in Figures 6(a) and 6(b). On the basis of the above discussed results, we could suggest that MA concentration above which the grafting degree decreases is not necessarily the same concentration at which MA phase separation occurs.

The ratio of MA grafting degree in a given amount of gel fraction to that of sol fraction (grafting ratio) for a number of grafted samples are presented in Table III. As it is seen, at MA concentrations up to 3 phr, the grafting ratio is close to 1, while it continuously increases with increasing MA concentration even above 4.5 phr of MA where the grafting degree is reduced. This observation could be attributed to the trapping of macroradicals in the gel fraction which, in turn, can reduce the rate of termination reactions in this phase and provide a higher opportunity for the grafting reaction and formation of long MA grafts onto the polymer chains.

It was mentioned previously that, in the presence of MA, the gel formation increases as a result of creation a new termination pathway wherein crosslinking is favored over chain scission and disproportionation. It is also shown in Figure 6 that the gel formation has a trend similar to that of MA grafting degree. Thus, by considering the role of MA on the gel formation, a modified form of Narkis and Miltz method,⁷⁹ which is based on Charlesey and Pinner equation,⁸⁰ were developed as follows to study the crosslinking efficiency of peroxide in the maleation reaction:

$$s + \sqrt{s} = \frac{p}{q} \times \frac{1}{\exp(k_1[\text{MA}]^a)} + \frac{1}{2M_n E \exp(k_2[\text{MA}]^a)[\text{Po}]} \quad (2)$$

where s is the soluble fraction of the modified sample, $[\text{MA}]$ is the grafting degree, M_n is the number-average molecular weight of the virgin PE, $[\text{Po}]$ is the effective peroxide concentration, which is considered as the initial amount of the peroxide used for the reaction when its loss in the phase separated MA droplets can be neglected, p/q and E are the ratio of probability of chain scission to crosslinking and the number of

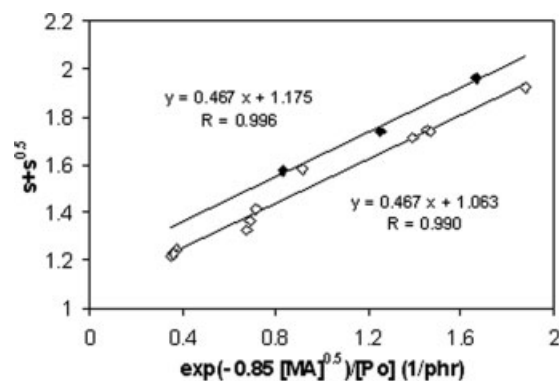


Figure 9 Modified form of Charlesey-Pinner plot for PE samples prepared in the presence (\diamond) and absence (\blacklozenge) of MA.

crosslinks per decomposed peroxide molecule, respectively, which are obtained from the peroxide modification of PE in the absence of MA. As it is seen in Figure 9, there is a good agreement between our experimental results and the results obtained from Equation 2. It should also be noticed that $p/(q \exp(k_1[\text{MA}]^a))$ is almost a constant value, indicating that k_1 is small.

Effect of temperature

The results of MA grafting degree and gel formation of three samples prepared at different temperatures are shown in Figure 10. As it is seen, although MA grafting degree almost remains unchanged with increasing the processing temperature, the gel formation shows an abrupt decrease above 185°C. Increasing the processing temperature has a complex effect on the maleation reaction. It reduces the peroxide half-life and, hence, increases the rate of radical generation. It also causes an increase in the probability of the occurrence of the reactions with high activation energy such as chain scission and disproportionation

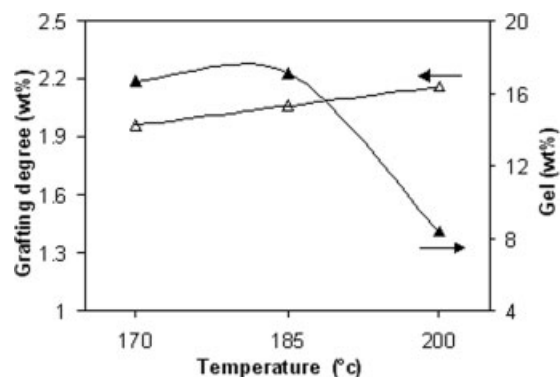


Figure 10 The variations of MA grafting degree and gel formation as a function of processing temperature (DTBPH = 0.2 phr, MA = 3 phr).

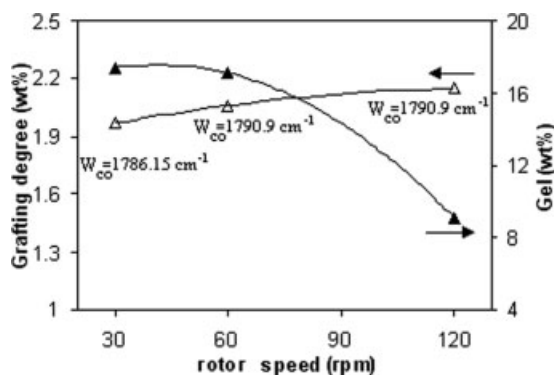


Figure 11 The variations of MA grafting degree and gel formation as a function of rotor speed (DTBPH = 0.2 phr, MA = 3 phr).

type termination reactions.⁸¹ Moreover, increase in the processing temperature affects the diffusivity and solubility of MA in the molten PE. Decreasing in the gel content of the samples prepared above 185°C could be mainly attributed to the greater extent of the peroxide evaporation and the higher probability of occurrence disproportionation reactions at the higher processing temperature. It should be noted that increasing of MA diffusion into the molten polymer resulting from increasing temperature can compensate the reducing effect of the peroxide evaporation on the grafting reaction.

Effect of rotor speed

The results of MA grafting degree and gel formation of three samples prepared at different rotor speeds are shown in Figure 11. The W_{CO} of these samples are also presented in Figure 11. As it is seen, although MA grafting degree almost remains unchanged with increasing the rotor speed, the gel formation shows an abrupt decrease above 60 rpm. Increasing the rotor speed increases the mechanical breakage of PE molecules, resulting in radicals which act in favor of MA

grafting. Moreover, it assists the breakage of branched/crosslinked polymer chains throughout the maleation process, hence, reducing the gel content. Increasing the rotor speed can also improve the mixing of MA in molten PE, directing the reaction towards formation of single succinic anhydride grafts. This is evidenced by the results of FTIR spectra shown in Figure 11.

Effect of Gaylord additives

Figure 12(a) compares the effects of DMF and AAn concentrations on the MA grafting degree of four samples. The gel content of these samples is also shown in Figure 12(b). As it can be seen, the grafting degrees as well as the gel content of the samples are decreased with increasing the concentration of both additives. It should be mentioned that increasing the concentration of the both additives are accompanied with development a deep brown color in the resulted product, which remains even after purification.

The gel content of PE samples prepared in the presence of the same mole amount of DMF and AAn but in the absence of MA is given in Table IV. The results indicate that these additives in the absence of MA decrease the gel content of the peroxide modified PE samples, which is in agreement with Al-Malaika idea stating that Gaylord additives act as radical deactivator.²

The extent of gel formation and MA grafting degree of two sets of samples prepared with the same MA concentration but varying amounts of both peroxide and Gaylord additives are given in Table V. By comparing these results, one may notice that the samples prepared in the presence of DMF and AAn have less MA grafting degree and higher gel content compared to those samples prepared in the absence of these additives but using a lower concentration of the peroxide. As the solubility parameters of DMF and AAn are close to that of MA (Fig. 8), it is possible that these

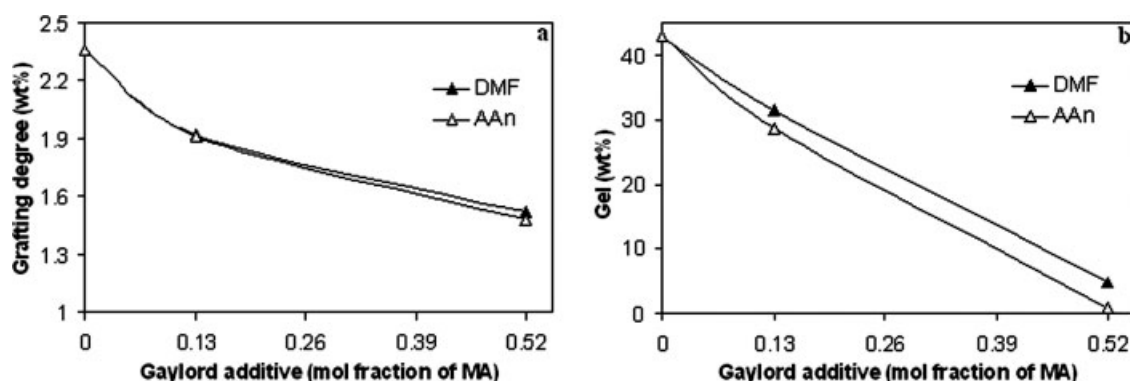


Figure 12 The effects of DMF and AAn concentrations on MA grafting degree (a) and gel content (b) of maleated PE samples (DTBPH = 0.4 phr, MA = 4.5 phr).

TABLE IV
The Effects of DMF and AAn on Decreasing the Gel Content of PE Samples Prepared in the Absence of MA

DTBPH (phr)	AAn (phr)	DMF (phr)	Gel (wt %)
1.2	—	—	27.7
1.2	3.23	—	19.4
1.2	—	1.74	22.8

additives migrate into the phase separated MA droplets, resulting in a reduction of local MA concentration in the system. This can be taken into account for the stronger effect of these additives on the reactions in which MA is involved, such as MA grafting and MA homopolymerization, in comparison with the other free-radical reactions such as chain-branching and/or crosslinking.

From the above discussion, it could be suggested that to reduce the gel formation during the maleation of PE, it is preferred to conduct the reaction using a lower concentration of peroxide instead of employing Gaylord additives.

Effect of comonomers

Figure 13 compares the variation of torque versus processing time of the molten PE processed in the presence and absence of MA and styrene comonomer. As it is seen, in the absence of peroxide (curve a), styrene comonomer has no appreciable effect on the processing torque. Also, in a given peroxide concentration, the processing torque of the maleation reaction in the presence of styrene (curve c) is higher than the peroxide modification processing torque (curve b), but lower than that of maleation reaction in the absence of styrene (curve d).

Figure 14(a) compares MA grafting degree of a number of PE samples prepared in the presence and absence of styrene. The gel content and 1/MFI of these samples are also shown in Figure 14(b). As it is seen, using styrene comonomer in the maleation reaction increases MA grafting degree and decreases the crosslinking side reaction.

Styrene as an electron donating monomer makes a charge transfer complex with an electron attracting MA molecule (Fig. 15), which has a more reactivity toward macroradicals and, hence, grafting comparing to MA molecule itself.² The high reactivity of styrene comonomer towards macroradicals can also result in producing a more stable styryl macroradicals (PSt[•]), which can increase MA grafting onto the polymer chains. Moreover, improvement in the solubility of MA due to the presence of styrene may delay MA phase separation. This can lead to a higher MA grafting degree and also continuous increasing in the level of MA grafting even above 4.5 phr of MA, which decrease in the grafting degree was observed in the absence of styrene. It should be noticed that the presence of styrene in the reaction system can also prevent MA homopolymerization and, hence, coloration of the final product.

The lower gel content of the maleated samples prepared in the presence of styrene compared to those samples prepared in the absence of styrene comonomer can be attributed to the consumption parts of radicals/macroradicals in the production of free St-MA copolymer. It should be noticed that at a given peroxide concentration, maleated samples prepared in the presence of styrene have a higher gel content and greater torque value comparing to the peroxide modified PE samples. This can be attributed to the higher tendency of PMA[•] and PSt[•] macroradicals towards the crosslinking reaction comparing to the ordinary PE macroradicals (P[•]).

From the above discussion, one may conclude that the higher MA grafting degree obtained in the presence of styrene comonomer is a result of the formation of grafts containing more than one St-MA moiety.

The variations of torque versus processing time for molten PE processed in the presence of different amount of TMPTA but in the absence of peroxide and MA are shown in Figure 16. As it is seen, TMPTA has a significant effect on increasing the processing torque of PE melt; the result which is in agreement with those reported for the effect of TMPTA on the viscos-

TABLE V
Comparing MA Grafting Degree and Gel Content of Two Series of Maleated Samples Prepared in the Presence and Absence of Gaylord Additives (MA = 4.5 phr)

DTBPH (phr)	DMF		AAn		Grafted MA (wt %)	Gel (wt %)
	phr	Mol fraction of MA	phr	Mol fraction of MA		
0.2	—	—	—	—	2.26	18.8
0.4	—	—	0.81	0.13	1.91	28.7
0.4	0.44	0.13	—	—	1.92	31.5
0.067	—	—	—	—	1.72	0.3
0.4	—	—	3.23	0.52	1.48	0.8
0.4	1.74	0.52	—	—	1.52	4.8

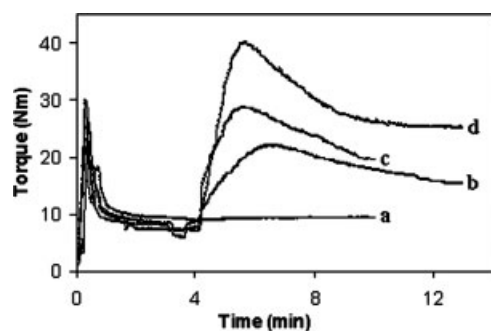


Figure 13 The variations of torque versus processing time for (a) PE containing 6.4 phr styrene; (b) PE containing 0.4 phr DTBPH; (c) PE containing 0.4 phr DTBPH, 6 phr MA, and 6.4 phr styrene; and (d) PE containing 0.4 phr DTBPH and 6 phr MA.

ity and processing torque of polystyrene⁸² and (ethylene-propylene) copolymer.⁹

TMPTA has three highly active double bonds which could act as a source of free radicals at high processing temperature, leading to the formation of PE macroradicals in addition to those formed through thermomechanical degradation of PE. It is also possible for TMPTA to be grafted onto the PE macroradicals from one of its double bonds to form TMPTA macroradicals which, in turn, can interfere in either PE chain-branching or crosslinking through the remained two double bonds. The low gel content of the prepared samples (≤ 5 wt %) indicates that the increase in the torque of these samples is mainly due to the formation of highly branched PE molecules rather than crosslinking of the polymer.

Figure 17(a) shows the results of torque variation versus processing time of molten PE during maleation reaction conducted at a constant peroxide concentration but varying amount of TMPTA comonomer. In all of these reactions, similar to Al-Malaika and Kong method used for glycidyl methacrylate grafting onto (ethylene-propylene) copolymer,⁹ the

monomer and peroxide were added into the polymer melt 1 min after the addition of TMPTA comonomer. The influence of TMPTA concentration on the MA grafting degree and gel content of these samples is also shown in Figure 17(b). As it is seen, the cross-linked formed during the maleation reaction can have a significant effect on increasing the torque of the samples containing TMPTA, particularly at low concentration of TMPTA. Also, increasing TMPTA concentration promotes MA grafting degree and gel content of the samples. Following the order of feeding used, TMPTA is grafted first onto the PE chains, which, in turn, can act as the active sites to react with MA. Also, the copolymer formed between TMPTA and MA can be grafted onto PE chains through the TMPTA highly reactive remaining double bonds. This causes not only increases in MA grafting degree but also minimize the free TMPTA-MA copolymers remained as impurity in the final product. Moreover, the remarkable decrease in maximum torque during the maleation reaction conducted in the presence of TMPTA, compared to the grafting reaction carried out in the absence of TMPTA [Fig. 17(a)], could be considered as an indication for production of a higher number of macroradicals due to the mechanical breakage of the produced highly branched PE chains, which are in favor of the grafting reaction.

It should be noticed that although TMPTA has a significant effect on increasing the processing torque, however, in the case of products having more than 2 wt % of MA grafting degree, the gel content of the samples prepared in the presence of TMPTA is close to that of samples prepared in the absence of TMPTA but in the presence of a higher peroxide concentration (Figs. 6 and 17) and the former samples have a less yellowish color.

It is worth mentioning that although both using TMPTA and styrene comonomers increase MA grafting degree, TMPTA in contrary to styrene, accelerates the chain-branching/crosslinking side reactions. Also,

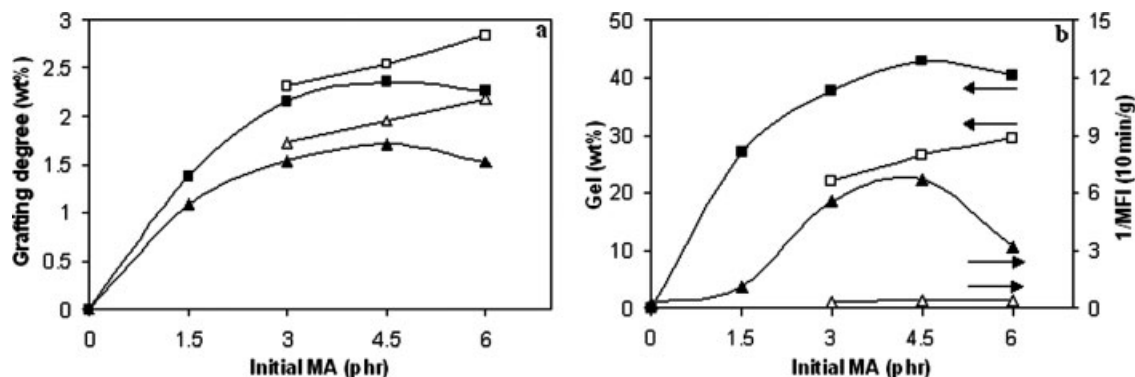


Figure 14 MA grafting degree (a) and gel content as well as 1/MFI (b) of the maleated samples. ▲: DTBPH = 0.067 phr and St = 0 phr, Δ: DTBPH = 0.067 phr and molar ratio of St/MA = 1, ■: DTBPH = 0.4 phr and St = 0 phr, □: DTBPH = 0.4 phr and molar ratio of St/MA = 1.

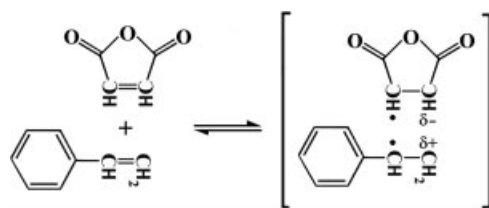


Figure 15 Formation of a charge transfer complex between styrene and MA.

the results shown in Figures 14(a) and 17(b) indicate that to achieve the same MA grafting degree, a higher concentration of styrene comonomer is required comparing to TMPTA.

CONCLUSIONS

In the free-radical melt grafting of MA onto PE, the reactants concentration (MA and DTBPH) has a major role on MA grafting degree, the extent of chain-branching/crosslinking side reactions and also the grafts microstructure in the final product. MA, apart from contributing in the grafting reaction, also accelerates the crosslinking side reaction, leading to the same variations of gel formation and MA grafting degree in terms of MA concentration. The reaction temperature has a complex effect on the maleation reaction. Increasing the rotor speed increases the grafting degree and reduces the side reactions, particularly at high shear rates, as a result of improving MA mixing in the polyethylene melt and increasing the mechanical breakage of the branched/crosslinked chains formed during the reaction. When Gaylord additives (DMF and AAn) are used in the maleation reaction, the gel formation is reduced at the expense of a dramatic decrease in MA grafting degree, indicating that these coagents are not suitable additives for the maleation reaction. The grafting degree is increased by using TMPTA and styrene comonomers in the maleation reaction and this is accompanied

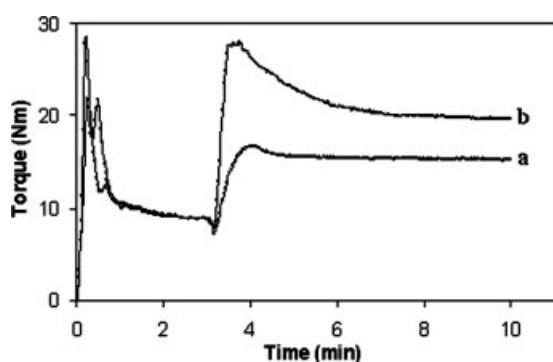


Figure 16 The variations of torque versus processing time for (a) PE containing 0.9 phr TMPTA, (b) PE containing 1.8 phr TMPTA.

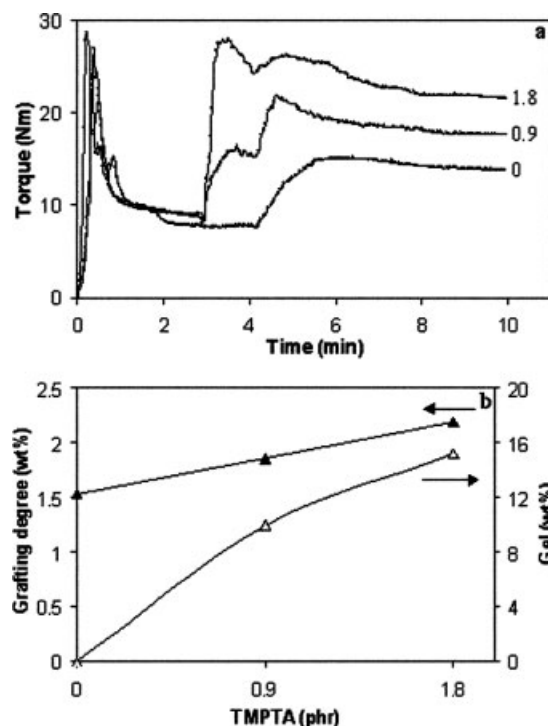


Figure 17 The variations of torque versus processing time (a) and MA grafting degree as well as gel content (b) of maleated PE samples prepared at varying amount of TMPTA (DTBPH = 0.067 phr, MA = 6 phr). The numbers shown on the curves are TMPTA concentrations used in the maleation reaction.

with a decrease in the crosslinking side reaction when the vinyl type styrene comonomer is used. The results of processing torque in combination with the measurements of the melt viscoelastic property and gel content of the samples show that the gels formed in the presence of MA have different structure from those obtained in the absence of MA, indicating that different mechanisms are involved in the formation of these two types of gels.

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