

Parameters Affecting the Free-Radical Melt Grafting of Maleic Anhydride onto Linear Low-Density Polyethylene in an Internal Mixer

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ABSTRACT: Our main objective of this study was to study the parameters affecting the free-radical melt grafting of maleic anhydride (MA) onto linear low-density polyethylene (LLDPE) with dicumyl peroxide (DCP) in an internal mixer. The degree of grafting (DG) was measured with titrimetry and Fourier transform infrared spectroscopy. The extent of chain-branching/crosslinking was evaluated with gel content and melt flow index measurements. The flow behavior and melt viscoelastic properties of the grafted samples were measured by using rheometric mechanical spectrometry. Feeding order, DCP and MA concentration, reaction temperature, rotor speed, and grade of LLDPE were among parameters studied. The results show that the reactant concentration (MA and DCP) played a major role in the determination of the grafting yield and the extent of the chain-branching/crosslinking as competitive side reactions.

The order of feeding also had an appreciable effect on the DG and the side reactions. Increasing the rotor speed increased the grafting yield and reduced side reactions by means of intensification of the mixing of reactants into the polyethylene (PE) melt. Chain-branching dominated the side reactions for lower molecular weight PE, whereas for higher molecular weight PE, chain-branching led to crosslinking and gel formation. The results of the melt viscoelastic measurements on the grafted samples provided great insight into the understanding of the role of influential parameters on the extent of side reactions and resulting changes in the molecular structure of the grafted samples. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 141–149, 2006

Key words: graft copolymers; polyethylene (PE); processing; viscoelastic properties

INTRODUCTION

In recent years, increasing activities have been directed toward the modification of existing polymers to produce new polymers with desirable properties.^{1–4} Polyolefins, despite their excellent combination of physical and chemical properties and processability, lack reactive groups in their structure, which may limit some of their applications, particularly where interfacial interactions with other materials are a determining parameter.^{1–9} The functionalization of polyolefins with polar monomers in particular maleic anhydride (MA) is one of the most common examples of polyolefin modification. Although many methods, including solution grafting, photografting, solid-phase grafting, and ultrasonic-initiated grafting of MA can be used, free-radical melt grafting of MA is usually preferred as the most reliable and successful method.^{1–3,10–18}

The free-radical melt grafting of MA onto polyolefins is usually accompanied by side reactions, including chain scission for polypropylene and chain-

branching/crosslinking for polyethylene (PE). For PE, unless the grafting reaction is controlled, free-radical-induced chain-branching and thermomechanical degradation can lead to crosslinking and gel formation, which may, in turn, cause severe problems in the processing of the grafted PE. Therefore, many attempts have been made to study the parameters affecting the MA grafting reaction and the competitive side reactions to direct the reaction toward a higher grafting yield with minimum side reactions. Gaylord and coworkers^{19–22} showed that in contrast to other monomers, MA intensifies the chain-branching/crosslinking reaction by the mechanism of MA excimer formation. These authors demonstrated that electron donor materials, which inhibit the formation of MA excimers, can reduce the extent of chain-branching/crosslinking. This process may occur at the expense of the grafting yield. Similar results were reported by White and coworkers.^{23–25} These authors also examined the effect of the presence of comonomers on the grafting reaction of MA onto PE and showed that the use of vinyl monomers can lead to a higher degree of grafting (DG) and less crosslinking. These results were supported by those of Chandranupap and Bhattacharya.²⁶

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TABLE I
Specifications of the PE Used

PE code	Commercial name	MFI (190°C/2.16 kg)	Form	Supplier
PE-1	LL209AA	0.9 g/10 min	Granule	Arack Petrochem Co. Iran
PE-2	LLM200024	20 g/10 min	Powder	Sabic Petrochem Co. Saudi Arabia
PE-3	LLMG500026	50 g/10 min	Granule	Sabic Petrochem Co. Saudi Arabia

Callais and Kazimerczak^{27,28} examined the effect of peroxide type on the grafting of MA onto different grades of PE in a single-screw extruder. They showed that tertiary alkyl peroxides provided the greatest DG, although these peroxides increased chain-branching/crosslinking. Hogt²⁹ showed that the DG increased with increasing MA content to some extent, above which it declined. Ganzveld and Janssen³⁰ reported a different trend for the variation of the DG as a function of MA content. Their results on the variation of the DG as a function of MA content showed an increase in DG, which after passing through a maximum, declined to a minimum and increased again with further increases in MA content. Recently, Covas and coworkers^{31,32} carried out an interesting study on the free-radical melt grafting of MA onto PE with an emphasis on the physicochemical phenomena developing along the screw axis of a twin-screw extruder for different PEs. They showed that an increase in the propene content of PE increased the DG.

The free-radical melt grafting of MA onto PE has been performed both in batch internal mixers^{19–26,29,33} and in extruders.^{24–29,34} Although extruders are usually preferred in industry, laboratory internal mixers are most appropriate for the physicochemical study of polymer modification. The main objective of this study was to examine the effects of influential parameters on the free-radical melt grafting of MA onto linear low-density polyethylene (LLDPE) with dicumyl peroxide (DCP) as a free-radical generator in a laboratory batch internal mixer. The feeding order, reactant concentration, reaction temperature, rotor speed, and base PE melt flow index (MFI) were among the parameters investigated.

EXPERIMENTAL

Materials

Three different commercial grades of LLDPE, all containing about 7% of the same comonomer (1-butene) but varying in MFI (with specifications summarized in Table I), were used. MA (Merck, Darmstadt, Germany) and DCP (Akzo Nobel, Amersfoot, The Netherlands) were used as received.

Melt-grafting processes

The free-radical melt-grafting processes were carried out in a 60-cc, roller-type rotor internal mixer (Bra-

bender W50, Duisburg, Germany). Variations of the internal mixer torque and chamber temperature were recorded for all samples. All samples were prepared at the same temperature (200°C) and with a rotor speed of 60 rpm unless otherwise specified. For PE-1, due to higher induced shear viscose heat, the initial temperature was adjusted to 20–30°C lower than the desired reaction temperature. The fill factor for all samples was kept constant at 78%.

Characterization

To remove ungrafted MA from the melt-grafted samples, 3 g of each sample was dissolved in 300 cc of boiling xylene and refluxed for 4.0 h. The xylene-insoluble portion of the samples was separated from the clear solution; then, 1000 cc of acetone was added to the clear solution, and the precipitated grafted PE samples were washed with excess acetone, vacuum-filtered, and then dried in a vacuum oven at 80°C for 12 h. The quantitative measurement of the DG was performed according to Gaylord and Mishra's³⁵ method with a small modification in the procedure. Purified MA-grafted sample (1.0 g) was dissolved in 200 cc of pure xylene and refluxed under stirring and a controlled temperature until a clear solution was obtained. The solution temperature was lowered below 100°C; then, 0.5 cc of distilled water was added to the solution, and refluxing was continued for about 1.0 h to ensure that the carbonyl groups were converted to acid groups. The solution was cooled to 80–90°C and titrated with 0.05N ethanolic KOH in the presence of thymol blue as an indicator until a deep blue color was obtained. Excess KOH was back-titrated by 0.05N isopropanolic HCl until a yellowish blue color appeared. The DG was calculated with the following equations:

$$\text{Acid number} = \frac{V_{\text{KOH}} (\text{mL}) \times N_{\text{KOH}} \times 56.1}{W_{\text{Polymer}} (\text{g})} \quad (1)$$

$$\text{MA (wt\%)} = \frac{\text{Acid number} \times 98}{2 \times 561}, \quad (2)$$

where V_{KOH} is the consumed volume of KOH solution, N_{KOH} is the normality of KOH solution and W_{polymer} is the polymer weight. Fourier transform infrared (FTIR) spectroscopy was performed on the thin

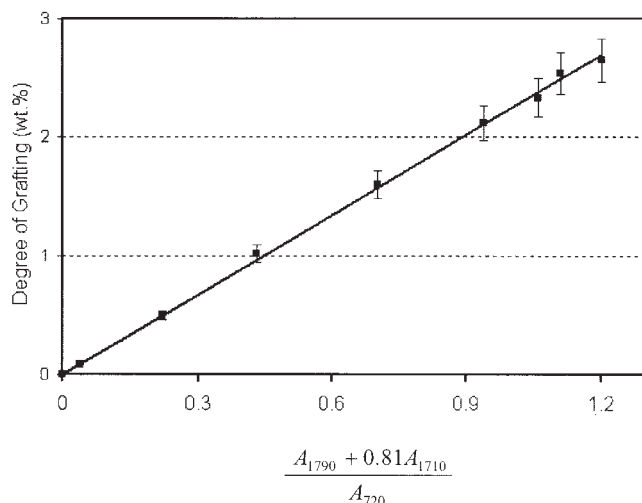


Figure 1 Calibration curve for the quantitative measurement of the degree of MA grafting onto PE obtained with titrimetry and FTIR results.

films prepared from the purified samples with a Bomem FTIR spectrometer. The intensity of the absorption peak at 1790 cm^{-1} , corresponding to the anhydride-type carbonyls, and 1710 cm^{-1} , for acid-type carbonyls, divided by that of the CH_2 absorption peak at 720 cm^{-1} was used as a measure of the degree of grafted MA. The DGs for all samples were determined with the calibration curve, obtained on the basis of the titrimetry and FTIR results, as shown in Figure 1.

The MFIs of the melt-grafted samples were measured according to ASTM D 1238 with a Davenport melt indexer (Hants, UK). The gel content (GC) of the samples was measured according to ASTM D 2765 procedure A. The flow behavior and melt linear viscoelastic properties of the neat PEs and melt-grafted samples were studied with rheometric mechanical spectrometry. Oscillatory rheological measurements were carried out at 190°C with parallel plate geometry with a gap of 1.0 mm and a diameter of 25.0 mm. A frequency sweep test from 0.1 to 1000 Hz was performed for each sample, with an amplitude of 1.0% to maintain the response of the material in the linear viscoelastic regime.

RESULTS AND DISCUSSION

Figure 2 shows the variation of the mixing torque versus time obtained for MA grafting onto PE-1 in the internal mixer. The first peak was due to the plastification of PE. The second pronounced increase in the mixing torque appeared after the addition of DCP was the result of chain-branching, which led to the crosslinking of PE as an undesirable competitive side reaction. At first glance, one may guess that the decrease in the mixing torque beyond the maximum was the result of a GC decrease and/or PE chain scission.

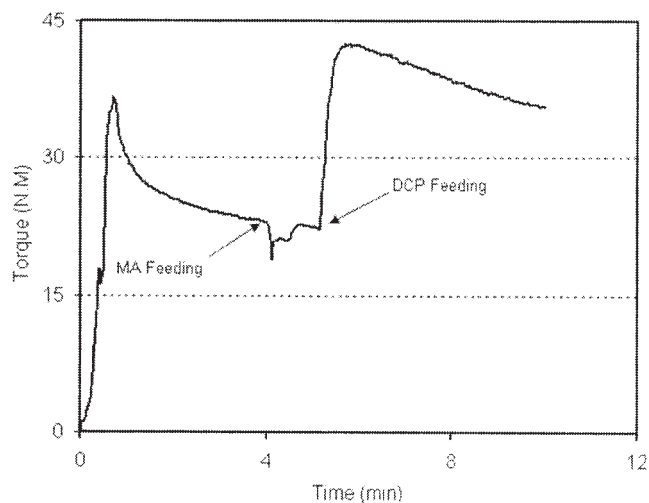


Figure 2 Variation of the mixing torque versus time obtained for the melt grafting of MA onto PE-1 in the internal mixer ($[\text{MA}] = 4\%$; $[\text{DCP}] = 0.25\%$).

However, as shown in Figure 3, the GC consistently increased with increasing reaction time. These results suggest that the chain-branching, which led to crosslinking and gel formation, was initiated and proceeded in parallel to the grafting reaction up to a reaction stage beyond which the big gels were broken down into smaller size gels, which may have continued to grow via reaction with the remaining macroradicals, especially with the MA-grafted macroradicals. This may be the reason that for PE-1, the DG tended to decline in the later stages of the reaction. In other words, the decrease in the mixing torque could be attributed to the breakdown of the formed gel networks into smaller but growable discrete gels distributed in the PE matrix, which may have acted like ball bearings. Also, as the branching occurred, the

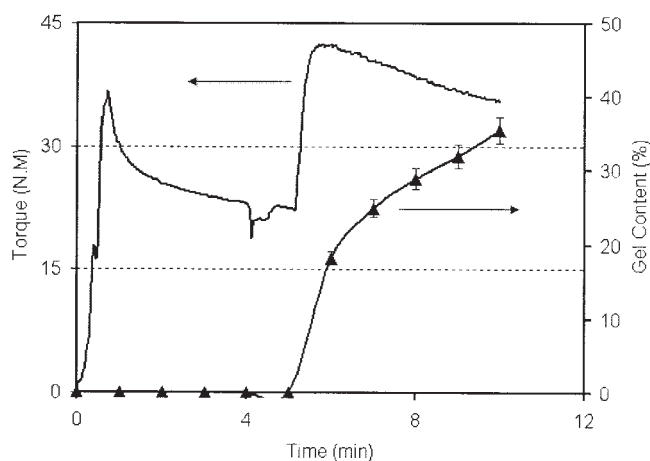


Figure 3 Variation of the mixing torque and GC as functions of reaction time for the melt grafting of MA onto PE-1 in the internal mixer ($[\text{MA}] = 4\%$; $[\text{DCP}] = 0.25\%$).

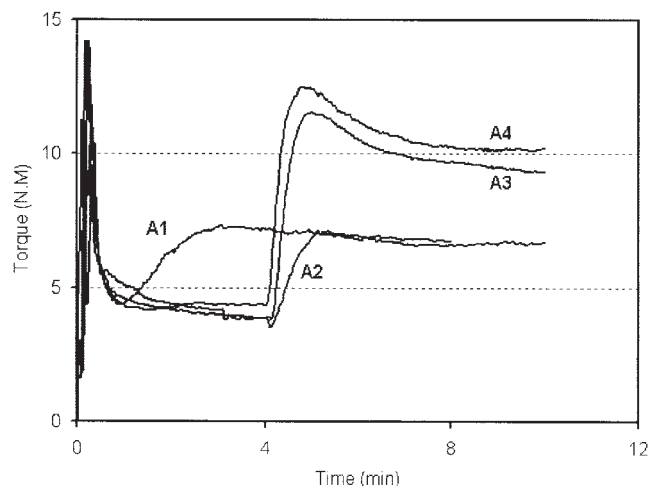


Figure 4 Variation of the mixing torque versus time for four different feeding orders (PE-2; [MA] = 4.0%; [DCP] = 0.25%).

polymer chains became less linear and more ball-like, which allowed molecules to flow past each other more easily.

Effect of feeding order

Although a considerable number of research works have been published on the melt grafting of MA onto PE, it has always been difficult to find close agreement between the results reported by different research groups, even for those who used the same reactant composition and melt-grafting processes.^{21,29,31,34,36} The feeding order is probably one of the processing variables that can play an influential role in the determination of the extent of the grafting reaction and the side reactions. Thus, to understand the effect of feeding order and to select the most appropriate order, four samples were prepared in the internal mixer with different feeding orders described as follows: for feeding A₁, all components (PE, MA and DCP) were fed simultaneously; for A₂, PE was fed first, and after the mixing torque reached its steady state (plateau), MA and DCP were added simultaneously; for A₃, PE was

TABLE II
Degree of Grafting and MFI Values Obtained for the Samples Prepared in the Internal Mixer with Four Different Feeding Orders

Sample	Degree of grafting (wt %)	MFI (g/10 min)
A ₁	1.31	1.4
A ₂	1.41	0.97
A ₃	2.33	0.17
A ₄	2.42	0.085

PE-2; [MA] = 4.0%; [DCP] = 0.25%.

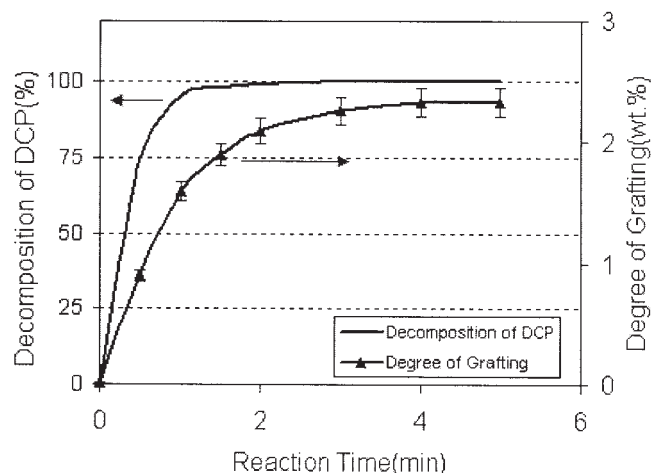


Figure 5 Degree of MA grafting and DCP decomposition versus reaction time (PE-2; [MA] = 4%; [DCP] = 0.25%).

fed first, and after the mixing torque reached a plateau, MA was charged, and 1 min later, DCP was added; and for A₄, PE and MA were fed first simultaneously, and after the mixing torque reached a plateau, DCP was added.

Figure 4 shows the variation of the mixing torque versus time obtained for the melt-grafting process for the previously described four feeding orders. The MA DG and MFI values obtained for these samples are given in Table II.

When these results are compared, it is clear that the variation of the mixing torque versus time for samples A₃ and A₄ followed the same trend with small differences in torque values. Samples A₁ and A₂ also showed the same trend of mixing torque versus time but were quite different from the other two samples. These results together with the results given in Table I indicate much greater DG and chain-branching for samples A₃ and A₄ compared to samples A₁ and A₂. In the case of the A₁ and A₂ feeding orders, in which the MA and DCP were charged together into PE, due to the greater affinity of DCP to MA compared to PE, the mixture of these two reactants into the PE melt required longer times. Therefore, it is possible that some portion of DCP and MA was consumed in some other side reactions. The primary radicals generated in the mixture of MA and DCP may have been wasted before they could abstract the hydrogen atoms from the PE backbone, which is necessary in the grafting reaction. This may have, in turn, led to a lower reactant content for participation in the melt-grafting and chain-branching reactions. This may have also been the reason for the small differences between the results obtained for samples A₁ and A₂. In sample A₁, the fusion of PE and the mixing of the reactants took a longer time than for sample A₂, where reactants (MA and DCP) were added after the fusion and homogeniza-

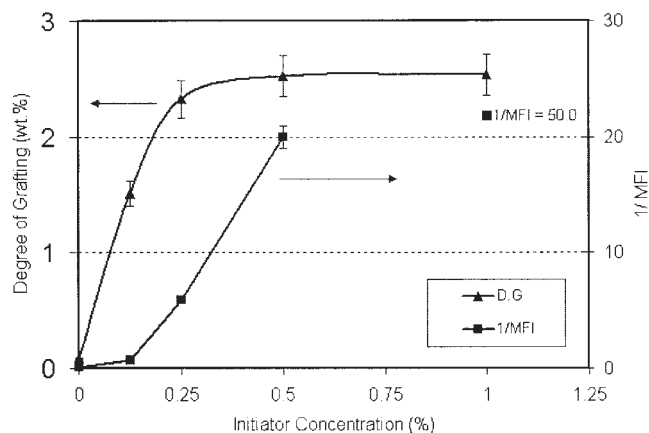


Figure 6 Dependence of the DG and 1/MFI on the initiator concentration (PE-2; [MA] = 4.0%).

tion of PE. Therefore, the extent of side reactions, such as homopolymerization, and cage reactions for sample A₁ was expected to be higher compared to that for sample A₂. From the previously discussed results, it is clear that the feeding order may have played a determining role in the control of the melt-grafting reaction of MA onto PE in an internal mixer. Similar results were found for the two other PEs (PE-1 and PE-3). With these results considered, the A₃ feeding order was used for the following experiments.

Figure 5 shows the results of the DG as a function of reaction time. The result of the percentage DCP decomposition, calculated with the information from the DCP decomposition rate constant and the recorded temperature profile, is also shown in Figure 5. These results indicate that although the grafting reaction followed the same trend as that of DCP decomposition, it leveled off at some time after the DCP decomposition was completed. This may have been partly due to the greater half-life of DCP in the highly viscous PE melt compared to that in the low-viscosity solution media, from which the half-life information was taken for calculation. This may have also been due to the generation of macroradicals by the thermomechanical breaking of the polymer chain, which could have continued the grafting reaction.

Effect of initiator concentration

Figure 6 shows the variation of the DG and 1/MFI of the grafted samples as functions of the initiator concentration. The reason we present the MFI results in the form of 1/MFI is that this format enabled us to follow the effect of the reactant concentration on the molecular weight of the grafted samples. As shown, the DG increased with increasing initiator concentration to some extent, above which it remained almost unchanged. Also, the 1/MFI of the MA-grafted samples increased with increasing initiator concentration.

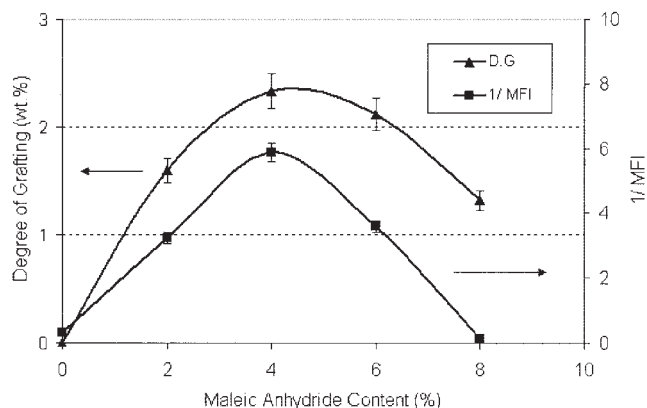


Figure 7 Dependence of the DG and 1/MFI on the initial MA content (PE-2; [DCP] = 0.25%).

These results were in agreement with those of Callais and Kazmierczak.^{27,28} These results indicate that there was an initiator concentration above which there was no appreciable effect on increasing DG, but it decreased the MFI as a result of a continuation of the chain-branching/crosslinking reactions.

Effect of MA content

Figure 7 shows the results of increasing MA content on the DG and 1/MFI of the grafted samples. These results imply that at a constant initiator concentration, increasing MA content led to an increase in the DG and 1/MFI. An increase in MA content increased the MA excimer formation,²⁰ which intensified the hydrogen abstraction from the PE backbone and, therefore, increased the DG and chain-branching/crosslinking. However, as clearly shown, there was some extent of MA content above which the DG and 1/MFI decreased. These results were attributed to the limited solubility of MA in the PE melt.³⁶ When the MA concentration exceeded the required amount for PE

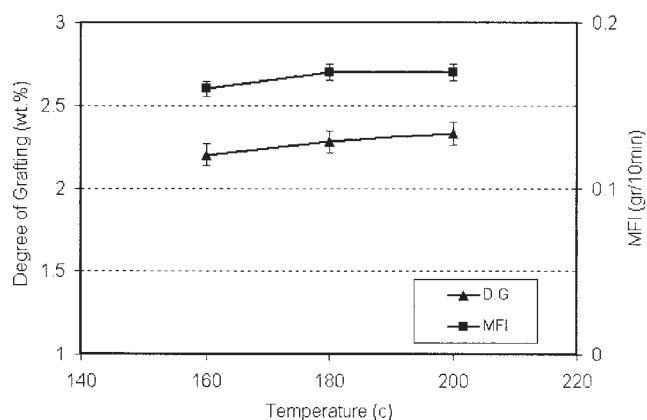


Figure 8 Effect of the set temperature on the DG and MFI of MA-grafted samples (PE-2; [MA] = 4.0%; [DCP] = 0.25%).

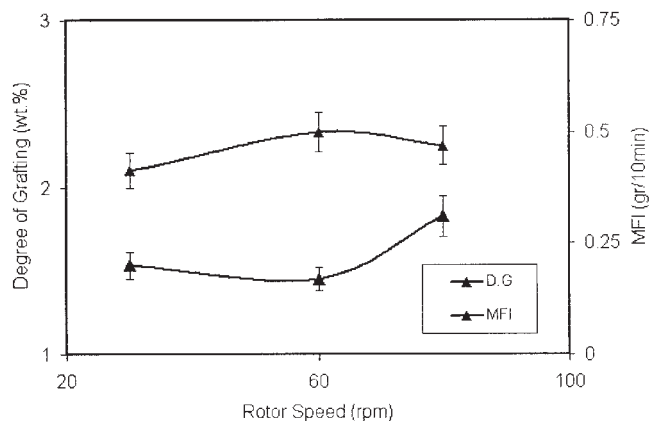


Figure 9 DG and MFI of the MA-grafted samples versus rotor speed (PE-2; [MA] = 4.0%; [DCP] = 0.25%).

melt saturation, the remaining MA formed a separate phase. This allowed the DCP to be absorbed in the separated MA phase due to its greater miscibility with MA compared to PE, which in turn, resulted in less DCP remaining for grafting and chain-branching/crosslinking reactions.

Effect of temperature

Figure 8 shows the effect of the set temperature on the DG and MFI of the grafted samples for PE-2. As shown, an increase in the set temperature had no appreciable effect on the DG or MFI of the samples, although it slightly increased the DG. Increasing the temperature favored hydrogen abstraction² and also increased the amount of macroradicals formed via thermomechanical degradation. Therefore, an increase in temperature should have increased the DG. On the other hand, increasing the temperature decreased the initiator efficiency and accelerated the evaporation of monomer and initiator. Thus, it was hard to clarify the role of temperature on the DG and the extent of chain-branching/crosslinking.

Effect of rotor speed

Figure 9 presents the results of the DG and MFI against the rotor speed for PE-2 grafted samples. As

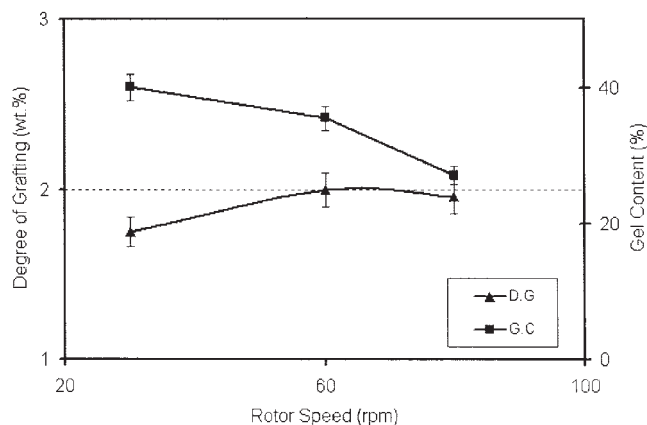


Figure 10 DG and GC of the MA-grafted samples versus rotor speed (PE-1; [MA] = 4.0%; [DCP] = 0.25%).

shown, increasing the rotor speed from 30 to 60 rpm resulted in an increase in the DG without appreciable effect on the MFI of the grafted samples. This can be explained in terms of increasing the mixing efficiency of reactants in the polymer melt. However, increasing the rotor speed above 60 rpm increased the reaction temperature as a result of increasing the shear viscose heat. This, in turn, accelerated the rate of reactant evaporation and, therefore, decreased both grafting and side reactions. Further, at rotor speeds above 60 rpm, the imposed deformation rate preferentially broke down the large branched macromolecules, resulting in an increase in the MFI of the grafted samples.

Figure 10 shows the results of the DG and GC as functions of rotor speed for the PE-1 grafted samples. When these results are compared with those shown in Figure 9, the effect of rotor speed on this sample is seen to be similar to that on PE-2. Therefore, the same explanation given for PE-2 can also be used to describe the results observed for PE-1.

Effect of PE molecular weight

The results of MFI and GC measured for three MA-grafted samples prepared from three different LL-DPEs varying in MFI are given in Table III. The results

TABLE III
MFI, Gel Content, and Degree of Grafting Values for Three Samples Prepared with Different Base PEs

PE	MFI (g/10 min) ^a	MFI (g/10 min) ^b	Gel content (wt %)	Degree of grafting (wt %)		
				Sol portion	Gel portion	Total
PE-1	0.9	0.0	35.5	2.06	2.26	2.13
PE-2	20.0	0.17	0.0	2.33	0	2.33
PE-3	50.0	0.85	0.0	2.41	0	2.41

^a Neat PEs.

^b MA-grafted PEs ([MA] = 4.0%; [DCP] = 0.25%).

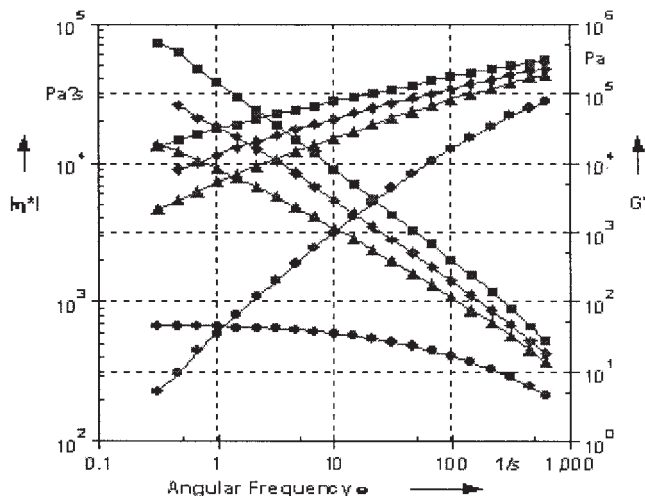


Figure 11 η^* and G' as functions of ω for (●) neat PE-2 and three MA-grafted PE-2 samples ([MA] = 4.0%): [DCP] = (▲) 0.125, (◆) 0.25, and (■) 0.5%.

of DG for both the xylene-soluble portion (sol) and xylene-insoluble portion (gel) are also given in Table III. As shown, the DG increases with decreasing PE molecular weight.^{31,32} These results, in conjunction with the results discussed earlier, suggest that in the free-radical melt grafting of MA onto PE-2 and PE-3 (lower molecular weight PEs), free-radical and thermomechanical degradation predominantly led to chain-branching, whereas in the case of PE-1 (higher molecular weight PE), crosslinking (gel formation) was the dominating reaction. The lower DG obtained for higher molecular weight PE (PE-1) was attributed to the lower diffusivity of MA and DCP into this PE. All of the base polymers used contained about 7% of the same comonomer.

Melt linear viscoelastic behavior of grafted samples

The chain-branching and/or crosslinking reactions taking place during the free-radical melt grafting of MA onto PE could have had significant effects on molecular structure and, therefore, the processability of the grafted PE. In this study, the effects of some influential parameters involved with the MA grafting reaction on the melt flow behavior and viscoelastic properties of the MA-grafted PE samples were studied.

Figure 11 shows the results of complex viscosity (η^*) and storage modulus (G') versus angular frequency (ω) obtained for the neat PE-2 and three MA-grafted samples prepared with the same MA content but various initiator concentrations. These results clearly indicate that PE-2 grafted samples exhibited a power-law-type flow behavior with greater shear thinning compared with the neat PE-2. Also, the viscosity and melt elasticity of the grafted samples increased with increasing initiator concentration; this was in good agreement with the results of the MFI measurements discussed earlier. These results justify the effect of increasing initiator concentration on the promotion of chain-branching and/or crosslinking as competitive side reactions. Figure 12 shows the results of relaxation time distribution [$H(\lambda)$] obtained for the same samples. Comparisons made between these results suggest that increasing the initiator concentration, in addition to increasing the molecular weight, had a significant effect on increasing the molecular weight distribution of the grafted samples.

Figure 13 shows the effect of MA content on the η^* and G' of the grafted samples. The results of $H(\lambda)$ obtained for the same samples are also shown in Fig-

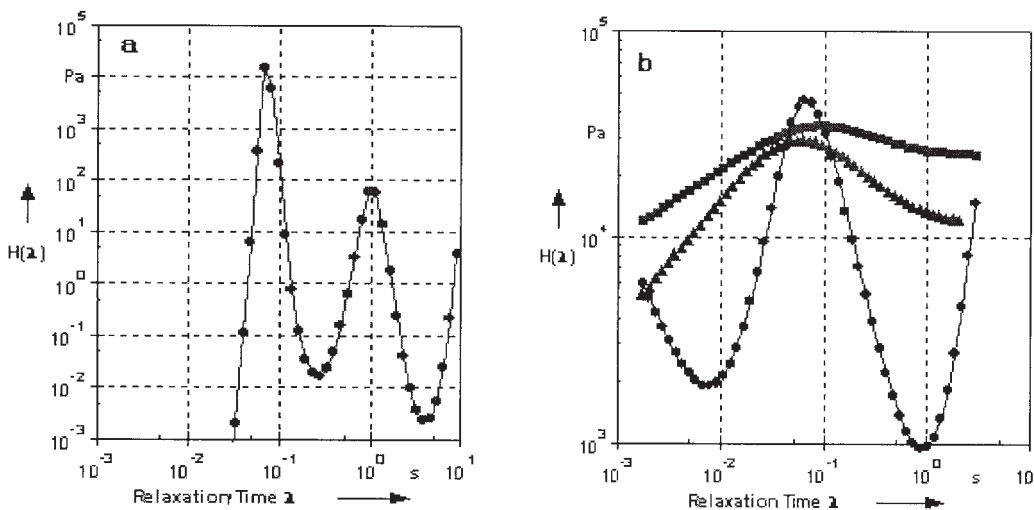


Figure 12 $H(\lambda)$ for (a) neat PE-2 and (b) three MA-grafted PE-2 samples ([MA] = 4.0%): [DCP] = (●) 0.125, (▲) 0.25, and (■) 0.5%.

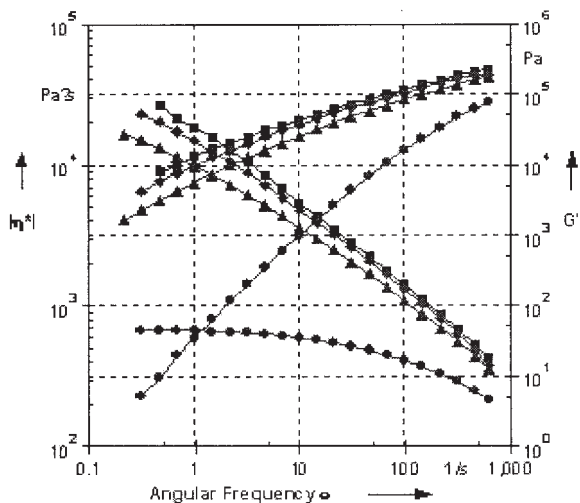


Figure 13 η^* and G' as functions of ω for (●) neat PE-2 and three MA-grafted PE-2 samples ([DCP] = 0.25%): [MA] = (▲) 1.0, (◆) 2.0, and (■) 4.0%.

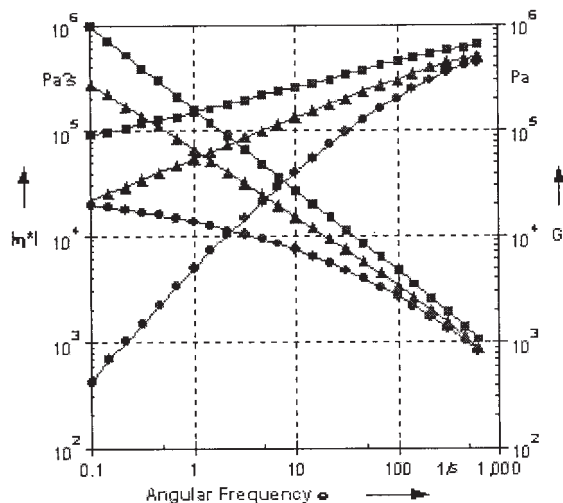


Figure 15 η^* and G' as functions of ω for (●) neat PE-1 and two MA-grafted PE-1 samples ([MA] = 4.0%): (▲) [DCP] = 0.125% and GC = 13.5% and (■) [DCP] = 0.25% and GC = 35.5%.

ure 14. When these results are compared with those shown in Figures 11 and 12, it is revealed that the effect of MA content (up to 4.0%) on molecular weight and molecular weight distribution of grafted samples was similar to that of the initiator concentration.

Figure 15 compares the melt viscoelastic properties of neat PE-1 with those obtained for two grafted samples varying in GC, which were prepared with the same MA content but different initiator concentrations. The results of $H(\lambda)$ obtained for the same samples are shown in Figure 16. The pronounced increase in viscosity and melt elasticity in particular at the low- ω range (low shear rates) obtained for these grafted samples were considered a strong indication for the presence of gel networks in these samples.

CONCLUSIONS

In the free-radical melt grafting of MA onto PE, the reactant concentration (MA and DCP) played a major role in the determination of the grafting yield and the extent of the chain-branching/crosslinking as competitive side reactions. The order of feeding also had an appreciable influence on the control of the grafting reaction and side reactions, which could be explained in terms of the mixture and the higher chemical affinity between the reactants compared with PE. Increasing the rotor speed increased the grafting yield and reduced the side reactions through the intensification of the mixing of reactants into the PE melt. Increasing the DG with time followed the same trend as that of

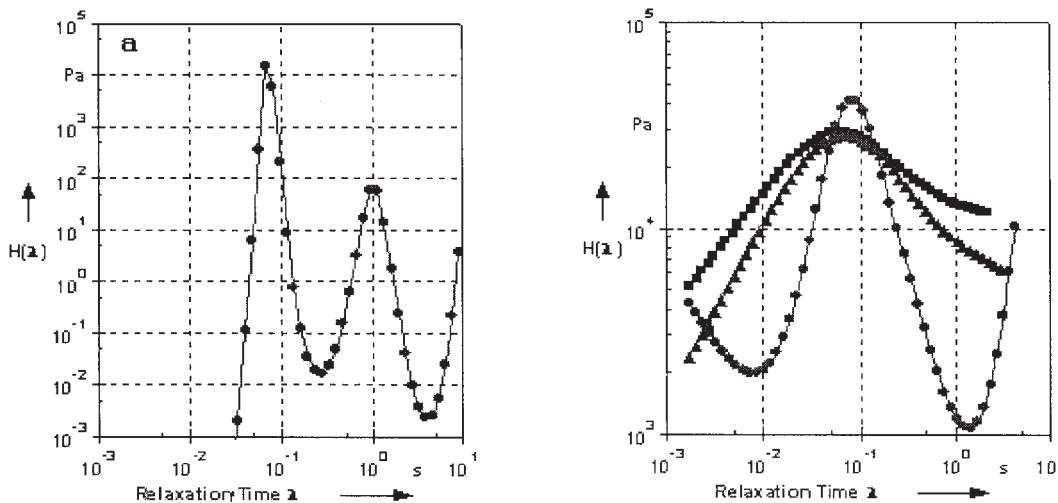


Figure 14 $H(\lambda)$ for (a) neat PE-2 and (b) three MA-grafted PE-2 samples ([DCP] = 0.25%): [MA] = (▲) 1.0, (◆) 2.0, and (■) 4.0%.

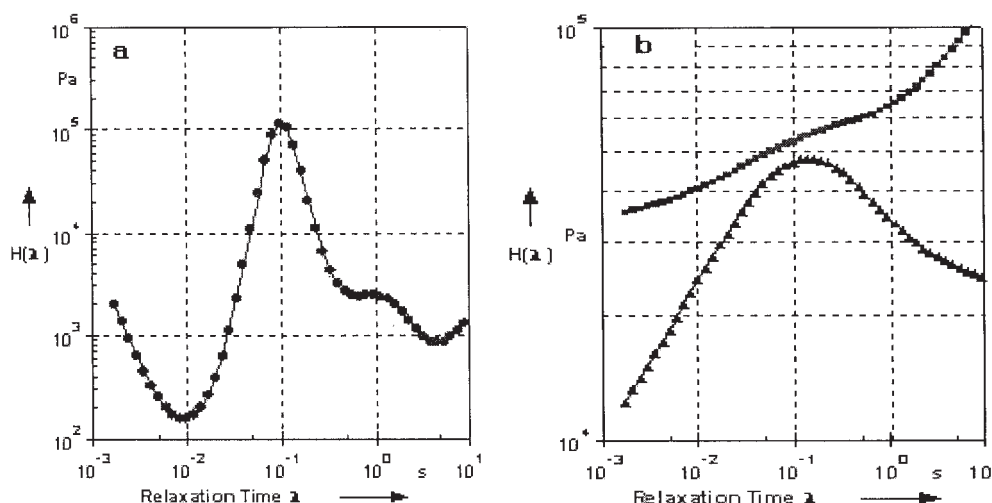


Figure 16 $H(\lambda)$ for (a) neat PE-1 and (b) two MA-grafted PE-2 samples ($[MA] = 4.0\%$): (\blacktriangle) $[DCP] = 0.125\%$ and $GC = 13.5\%$ and (\blacksquare) $[DCP] = 0.25\%$ and $GC = 35.5\%$.

DCP decomposition but leveled off at some time after the DCP decomposition was completed. Although for lower molecular weight PEs (PE-2 and PE-3) the chain-branching was the dominating side reaction, for high-molecular-weight PE (PE-1), the chain branching led to crosslinking and gel formation. The results of the melt viscoelastic measurements on the grafted samples provide great insight into the understanding of the role of influential parameters on the extent of the side reactions and resulting changes in the molecular structure of the grafted samples.

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