Melt Free-Radical Grafting of Maleimides with Hindered Phenol Groups onto Polyethylene

Taek Hyeon Kim

Department of Applied Chemistry and Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, Korea

Received 21 November 2003; accepted 15 May 2004
DOI 10.1002/app.21003
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A monomeric antioxidant, bearing carbamate groups, was synthesized from the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol and azidomaleimide. Another antioxidant was prepared from the reaction of *N*-(4-hydroxyphenyl-)maleimide and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic chloride in the presence of triethylamine. These fictional antioxidants were grafted onto polyethylene (PE) via melt processing with free-radical initiators in a minimax molder. The IR spectra of the grafted PE showed that the monomeric antioxidants were added to PE. IR spectroscopy methods were used for the quantitative determination of the extent of grafting of the monomeric antioxidants. Also, the extent of crosslinking was determined from the gel content. To optimize the reaction conditions, we investigated the effects of the initiator concentration, monomeric antioxidant, reaction time, and temperature on the extent of grafting. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2117–2122, 2004

Key words: additives; polyethylene (PE); reactive processing; antioxidant

INTRODUCTION

Polyethylene (PE) is one of the most widely used polymers. One of the major drawbacks associated with this polymer, however, is its susceptibility to thermooxidative degradation. Oxidation reactions are enhanced at elevated temperatures during the processing of the polymer. To protect against the thermal oxidation of polymers, hindered phenol antioxidants, which contain the 2,6-di-*tert*-butylphenol group, are widely used as effective antioxidants.[1,2] Low-molecular-weight antioxidants, however, are easily lost from polymers through physical loss such as migration, evaporation, and extraction. The physical loss of antioxidants, therefore, is a major concern for environmental issues and safety regulations as well as the long-term use of polymers. Additional demands on the performance of both polymers and antioxidants have been increasing. Several efforts have been devoted to investigating the associated problems of the performance and physical loss of antioxidants. The grafting of functional antioxidants in polymer melts, particularly polyolefins, is one of the most important approaches.[3–8]

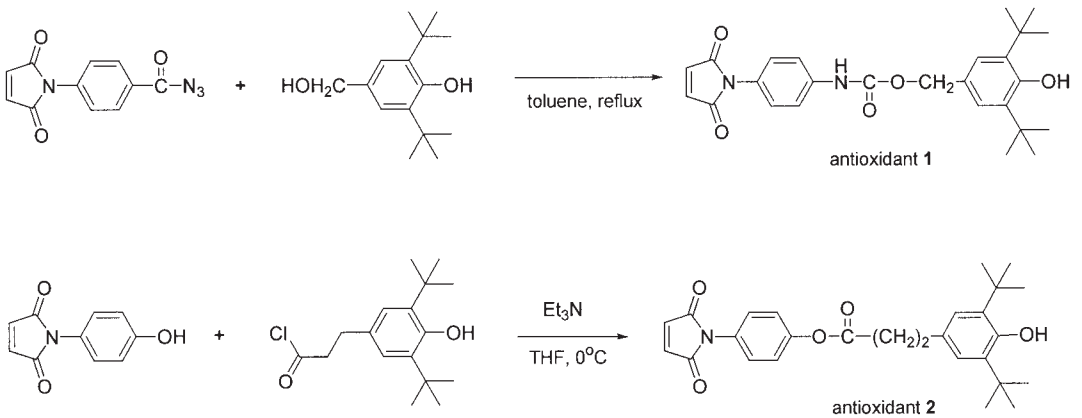
Munteanu and Csunderlik[7] reported the melt grafting of methacrylate, cinnamic acid, and styrene bearing the 2,6-di-*tert*-butylphenol group onto PE in the presence of an initiator. Al-Malaika and Suharty[8] also studied the melt grafting of acrylate onto polypropylene in the presence of a trifunctional coagent such as trimethylol propane triacrylate to improve the grafting yields. However, acrylic monomers in grafting reactions are easy to homopolymerize. Recently, we demonstrated the melt grafting of a maleimide onto PE[9(a)] because maleimide is not readily susceptible to radical homopolymerization. In this article, we report the melt-grafting polymerization of newly designed monomeric antioxidants **1** and **2** bearing maleimide onto PE to investigate their reactivity in grafting and the performance of grafted PE according to the functionality of the linker group, such as carbamate of antioxidant **1** and ester of antioxidant **2**.

EXPERIMENTAL

Chemicals and equipment

Unstabilized PE powder was supplied by Samsung General Chemicals, Ltd., Daejeon, Korea, with a melt-flow index of 0.8 g/10 min at 190°C and 2.16 kg and with a density of 0.948 g/cm^3. Reagent-grade dicumyl peroxide (DCP) and 2,2′-azobisisobutyronitrile (AIBN) were used without further purification. Benzoyl peroxide (BPO) was purified by recrystallization in ether. The melt-grafting reaction was carried out in a CS 183MM-065 minimax mixer from Custom Scientific Instruments, Inc.[10] IR spectra were recorded on a Nicolet Fourier transform infrared (FTIR) instrument (Madison, WI, USA).

Correspondence to: T. H. Kim (thkim@chonnam.ac.kr).



Scheme 1 Synthesis of the monomeric antioxidants.

Monomeric antioxidant synthesis

Monomeric antioxidants **1** and **2** were prepared as shown in Scheme 1 according to a previously published procedure.[9(b)]

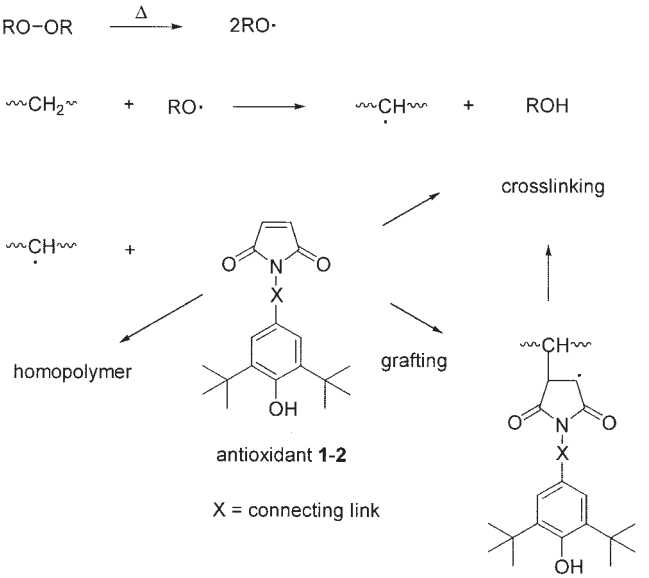
General grafting and purification procedure

All the components, including the PE powder, purely prepared monomeric antioxidants **1** and **2**, and initiator, were fully mixed. The resulting dry powder mixture was charged into the chamber of the minimax molder, which was processed at 60 rpm under a nitrogen atmosphere. For optimal reaction conditions, a series of exploratory grafting reactions were performed through changes in the initiator type (DCP, BPO, and AIBN) and concentration (0.5–2.0 mmol/100 g of PE), the monomer concentrations (0.05–0.20 mmol/100 g of PE), the reaction time (4–20 min), and the temperature (120–180°C). It is known that grafting reactions include some unavoidable homopolymerization and cause some degree of crosslinking (Scheme 2). The reaction product was purified by dissolution in refluxing xylene and precipitation in dichloromethane. The precipitated grafted PE was filtered, washed with more dichloromethane, and dried in a vacuum oven at 80°C. The ungrafted antioxidant, homopolymer, and peroxide were dissolved in the dichloromethane solution, whereas grafted and ungrafted PE were precipitated out. Successive reprecipitation showed that a one-time process was adequate for the removal of the homopolymer and monomer.

Estimation of the extent of grafting

The purified PE was analyzed by IR spectroscopy with films compression-molded at 170°C and 2000 psi for 5 min. To determine the degree of grafting, the peak at 2025 cm^{-1} from PE was chosen as a reference.[7] A carbonyl peak corresponding to the grafted antioxidant was chosen as the target. The integral ratios of the carbonyl peak to 2025 cm^{-1} were used as a convenient measure of the relative degree of grafting. The IR calibration curve for determining the grafting yield was established through the mixing of PE, the monomeric antioxidants at different concentrations, and DCP, and the IR spectra were recorded. The curve of the monomer concentration versus the integral ratios of the carbonyl peak to 2025 cm^{-1} was plotted under the assumption that the difference in the absorbance between the mixed and grafted monomers could be disregarded. The grafting yield was calculated as follows:

$$\text{Grafting yield}(\%) = M_g/M_i \times 100$$



Scheme 2 Outline of the free-radical-induced grafting reaction and side reaction.

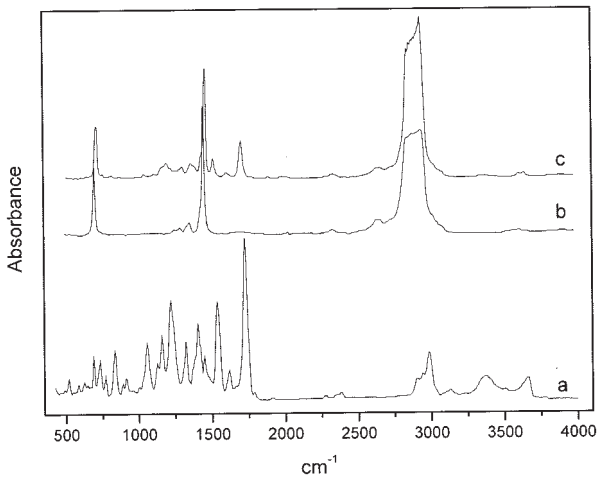


Figure 1 FTIR spectra of (a) monomeric antioxidant **1**, (b) pure PE, and (c) PE grafted with **1**.

where M_g and M_i present the mass of the monomer grafted onto PE and the mass of the initial monomer, respectively.

Degree of crosslinking and gel content

An indication of the extent of crosslinking was obtained from the measurement of the gel content (%) of grafted PE, which was assessed from the fraction by the extraction of samples with boiling xylene for 12 h according to ASTM D 2765-68 (method A). A higher gel content was an indication of more crosslinking.

Solvent extraction and thermal oxidation

The extraction of films with dichloromethane was performed in a Soxhlet extractor for 3 days. The thermal oxidation of the films before and after extraction was carried out in an oven at 120°C in air and was monitored with FTIR spectroscopy, with the peak height ratio of 1720 to 2025 cm^{-1} used to assess the extent of the oxidation of the polymers.[11,12]

RESULTS AND DISCUSSION

Grafting reaction and IR spectra of grafted PE

The most widespread method for adding an additive to polyolefin substrates by reactive extrusion involves free-radical-induced grafting. Hindered phenolic antioxidants are free-radical scavengers used to stabilize the radical in polyolefins formed in processing. However, Munteanu and coworkers reported that antioxidants containing hindered phenol are capable of homopolymerization[13] and grafting onto PE in the presence of free-radical initiators.[7] In general, hindered phenolic antioxidants may trap peroxy radicals (ROO ·) rather than alkyl radicals (R ·) in the stabilization mechanism.[14] Therefore, we expected that phenol might not hinder free-radical-induced grafting.

Our monomeric antioxidants (**1** and **2**), as expected, were grafted onto PE in the presence of free radicals. The grafting of **1** and **2** onto PE was confirmed by IR spectroscopy. Figures 1 and 2 shows the IR spectra of the monomeric antioxidants, the pure PE, and the grafted PE made under nitrogen. The spectrum of the grafted PE shows a band at approximately 1720 cm^{-1}, which is characteristic of the carbonyl group of the monomeric antioxidants. More distinct peaks due to the stretching of the carbamate of **1**, the C—O—C bond of ester group of **2**, and the —OH group also appear. The band of 1720 cm^{-1} may also have resulted from the thermal oxidation of PE during the grafting reaction. To test this probability, we performed the grafting reaction with 2 mmol of DCP/100 g of PE for 10 min at 170°C in the absence of the monomer. The IR intensity of the peak at 1720 cm^{-1} almost did not increase in comparison with that of the original PE. Thus, we confirmed that the peak at 1720 cm^{-1} after the grafting reaction was mainly from the monomeric antioxidant.

It is known that three competing reactions can occur during melt grafting, such as the homopolymerization of the monomer, PE crosslinking, and the desired graft reaction. We tried to optimize the reaction to maximize the grafting yields, minimizing main side reactions. An investigation of the effects of the initiator concentration, monomer concentration, and reaction time and temperature was necessary to obtain the optimal grafting reaction conditions.

Effect of the initiator type and concentration on the grafting reaction

Three initiators were tested: two peroxy initiators (DCP and BPO) and one azo initiator (AIBN). The

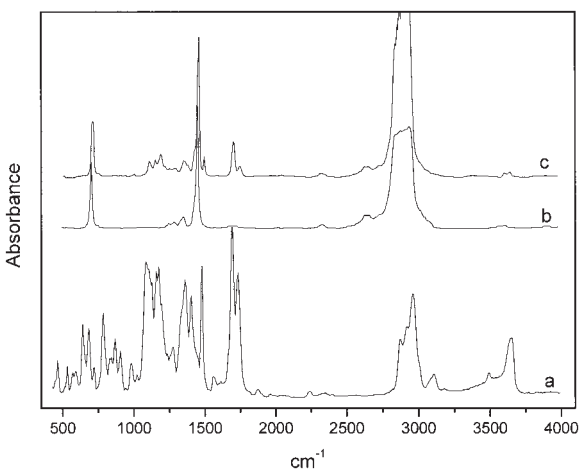


Figure 2 FTIR spectra of (a) monomeric antioxidant **2**, (b) pure PE, and (c) PE grafted with **2**.

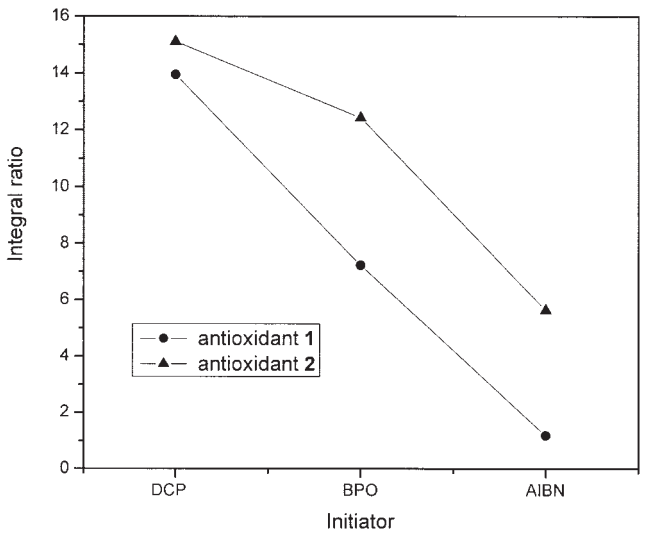


Figure 3 Influence of the initiators on the grafting yield (monomer concentration = 10 mmol/100 g of PE, reaction temperature = 180°C, time = 10 min).

graft reaction was performed with a monomer concentration of 10 mmol/100 g of PE for 10 min at a reaction temperature of 180°C. As shown in Figure 3, the extent of the grafting of monomers **1** and **2** with PE was in the order of DCP > BPO > AIBN. Thus, DCP was chosen to provide the best grafting yield. The grafting yield increased with the increasing half-lifetime ($t_{1/2}$) of the initiators. The $t_{1/2}$ values were as follows:[15] AIBN, 7.2 min at 100°C; BPO, 19.8 min at 100°C; and DCP, 1.7 h at 130°C. The grafting reaction in the absence of an initiator with the aforementioned reaction conditions did not occur. Thus, the thermally induced method did not produce grafting.

The influence of the DCP concentration on the grafting yield is shown in detail in Figure 4. For each grafting reaction, the DCP concentration was in the range of 0.5–2.2 mmol/100 g of PE. With monomeric antioxidant **1**, a rapid increase was observed at low initiator concentrations (<1 mmol). The grafting yield changed little with an increase in the DCP concentration after an initial increase. A well-known problem with grafting onto PE is crosslinking as a side reaction. The gel contents for DCP are illustrated in Table I. A higher DCP dose produced the more prominent crosslinking trend (entries 1–4). Therefore, the concentration of DCP was optimized at 1 mmol/100 g of PE.

Effect of the monomer concentration on the grafting reaction

Figure 5 shows the effect of the monomer concentration on the grafting yield. The reaction was performed at a DCP concentration of 2 mmol/100 g of PE at a reaction temperature of 160°C for 10 min. The grafting yield decreased substantially as the monomer concentration increased. This behavior was probably a result of the incompatibility between the PE and monomer. The polar monomer molecules tended to form aggregates dispersed into the PE matrix. Increasing the amount of the monomer also increased the proportion of the monomer located inside the phase and, consequently, inaccessible to the free-radical site of the polymer. However, the absolute amount of the grafted monomer increased as the monomer concentration increased. In monomer **1**, the gel contents in Table I largely increased with an increase in the amount of the monomer (entries 5–8). The carbamate group of monomer **1** probably decomposed into the isocyanate group,[16] which could then be used as the crosslinking reagent.

Effect of the reaction time and temperature

Figure 6 shows the influence of the reaction time. The concentrations of DCP and the monomer were fixed at 2 and 5 mmol/100 g of PE, respectively. The grafting yield increased with an increase in the reaction time up to 10 min. After 10 min, the graft yield decreased. The decrease in the grafting yield after 10 min could be a result of the degradation of longer formed grafts.[17] The gel contents of these products are shown in Table I. Crosslinking took place more prominently with an increase in the reaction time (entries 9–13).

The influence of temperature on grafting was also studied (Fig. 7). With **1**, grafting was obtained at 140°C. The grafting yield increased slightly from 150 to 160°C and then decreased as the temperature was further increased. With **2**, the optimal reaction occurred at 150°C. The grafting yield probably decreased at the high temperature because faster chain

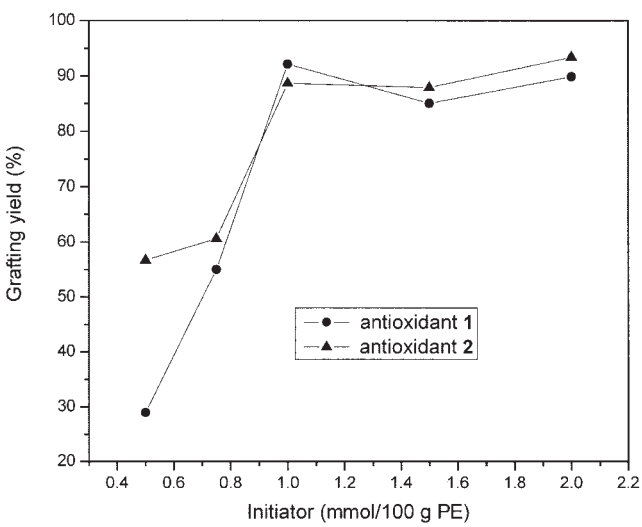


Figure 4 Influence of the initiator DCP concentration on the grafting yield (monomer concentration = 5 mmol/100 g of PE, reaction temperature = 160°C, time = 10 min).

TABLE I
Gel Content (%) of Grafted PE

Entry	Reaction time (min)	Reaction temperature (°C)	DCP (mmol/100 g of PE)	Monomer (mmol/100 g of PE)	Gel content of PE grafted with **1** (%)	Gel content of PE grafted with **2** (%)
1	10	160	0.5	5	1.2	0.8
2	10	160	1.0	5	3.5	1.3
3	10	160	1.5	5	7.8	2.5
4	10	160	2.0	5	10.3	3.2
5	10	160	2.0	5	4.2	3.5
6	10	160	2.0	10	11.4	4.3
7	10	160	2.0	15	24.7	4.9
8	10	160	2.0	20	25.1	10.4
9	4	160	2.0	5	1.8	1.1
10	8	160	2.0	5	2.3	1.2
11	12	160	2.0	5	4.9	2.2
12	16	160	2.0	5	6.3	3.3
13	20	160	2.0	5	10.3	6.7
14	10	120	2.0	5	—[a]	0.7
15	10	140	2.0	5	5.8	1.0
16	10	160	2.0	5	9.7	3.2
17	10	180	2.0	5	20.4	—[a]

[a] Not determined

termination at the high temperature led to a short graft length.[17] An increase in the temperature to 160°C with **1** and to 150°C with **2** led to increased grafting yields, but unfortunately the sensitivity of crosslinking, as shown in Table I, increased as well (entries 14–17).

Antioxidative effect of grafted PE before and after solvent extraction

The change in the peak height ratio of 1720 to 2025 cm^{-1} versus the aging time is illustrated in Figure 8 (before extraction) and Figure 9 (after extraction). The carbonyl content of unstabilized PE drastically increased, whereas monomers **1** and **2** and the PE grafted with the antioxidants showed no increase of the 1720/2025-cm^{-1} ratios for 5 days. After solvent extraction, only the films blended with monomers **1** and **2** exhibited an increased peak of the 1720/2025-cm^{-1} ratio, and this showed that the monomeric antioxidants were lost. These preliminary oxidative results confirm that the antioxidant moiety is chemically bound to the PE chains.

CONCLUSIONS

New polymer-bound antioxidants were successfully prepared by the melt grafting of new monomeric maleimides **1** and **2** onto PE in the presence of a DCP

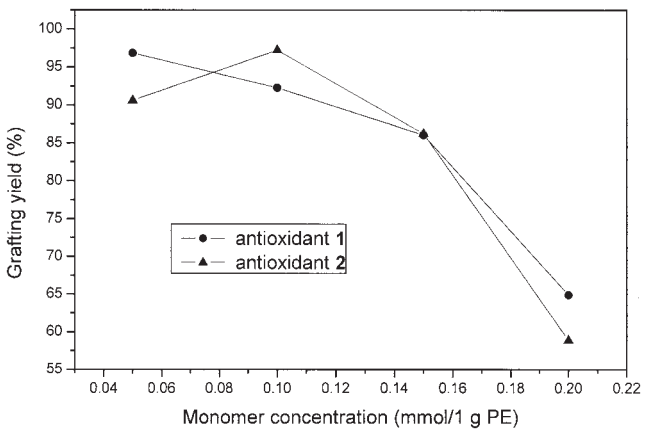


Figure 5 Influence of the monomer concentration on the grafting reaction ([DCP] = 2 mmol/100 g of PE, reaction temperature = 160°C, time = 10 min).

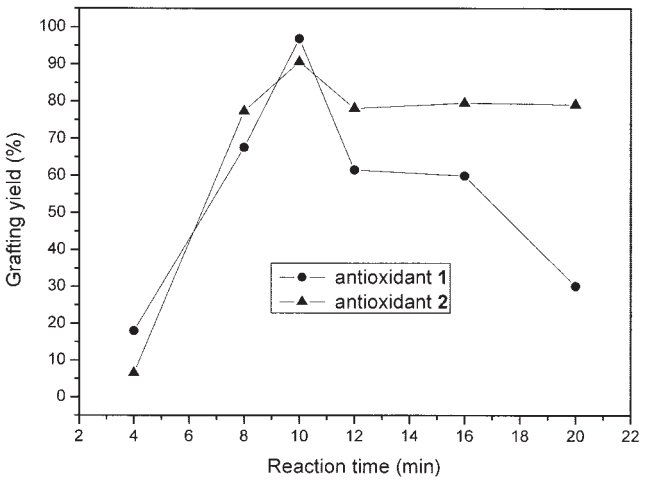


Figure 6 Influence of the reaction time on the grafting yield ([DCP] = 2 mmol/100 g of PE, monomer concentration = 5 mmol/100 g of PE, reaction temperature = 160°C).

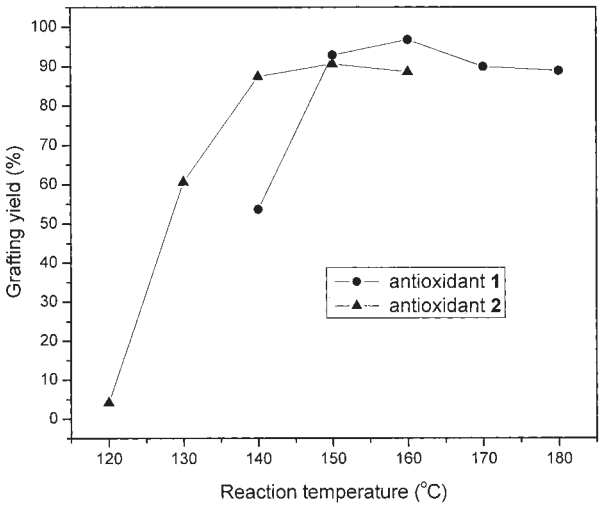


Figure 7 Influence of the reaction temperature on the grafting yield ([DCP] = 2 mmol/100 g of PE, monomer concentration = 5 mmol/100 g of PE, time = 10 min).

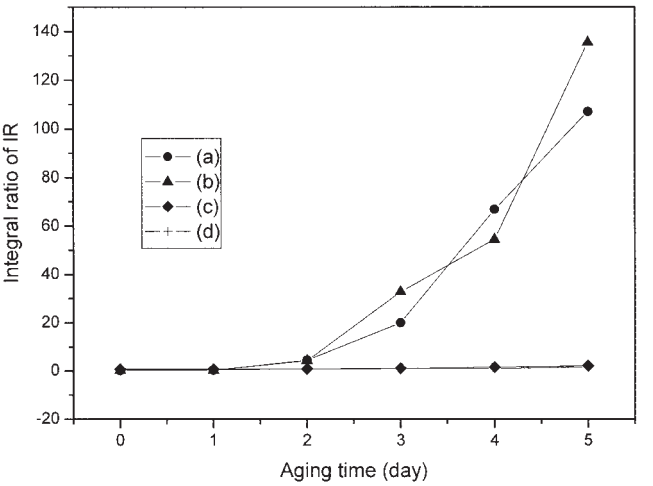


Figure 9 Antioxidative effect of grafted PE after extraction: (a) 0.2 wt % PE blended with **1**, (b) 0.2 wt % PE blended with **2**, (c) 0.2 wt % PE grafted with **1**, and (d) 0.2 wt % PE grafted with **2**.

initiator. Monomer **2** was a better grafting reagent than monomer **1** with respect to both the gel contents and grafting yields because the ester group was more thermally stable than the carbamate group. The 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate group of monomer **2** was more resistant to oxidation into the quinone moiety than the 3,5-di-*tert*-butyl-4-hydroxyphenylmethyl alcohol group of **1**, which gave less yellowness. The appearance of the IR peak of the carbonyl bond of the monomeric antioxidants in reacted PE confirmed the presence of grafting. The grafted PE possessed some stabilizing effect against thermal oxidation with oven aging in air at 120°C for 5 days, with no intensity change indicated in the IR peak at 1720 cm^{-1}.

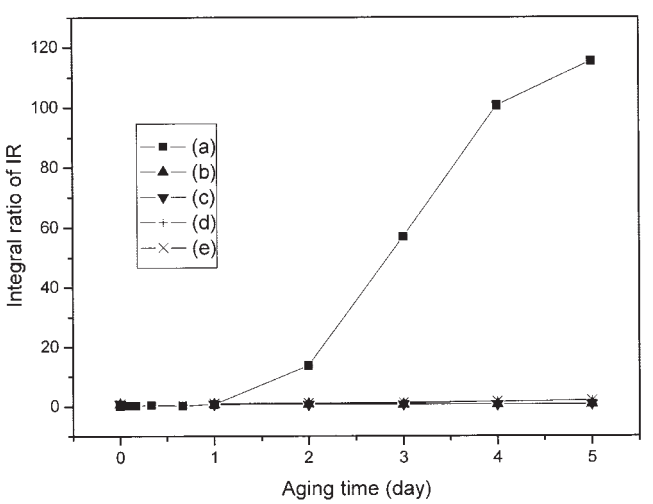


Figure 8 Antioxidative effect of grafted PE before extraction: (a) pure PE, (b) 0.2 wt % PE blended with **1**, (c) 0.2 wt % PE blended with **2**, (d) 0.2 wt % PE grafted with **1**, and (e) 0.2 wt % PE grafted with **2**.

References

1. Lutz, J. T., Jr. Thermoplastic Polymer Additives: Theory and Practice; Marcel Dekker: New York, 1989.
2. Gugumus, F. Plastics Additives, 3rd ed.; Oxford University Press: New York, 1990.
3. Al-Malaika, S. CHEMTECH 1990, 366.
4. Munteanu, D. In Developments in Polymer Stabilization 8; Scott, G., Ed.; Applied Science: London, 1987; Chapter 5.
5. Pospisil, J. Angew Makromol Chem 1988, 158, 221.
6. Kuczkowski, J. A.; Gillick, J. G. Rubber Chem Technol 1984, 57, 621.
7. Munteanu, D.; Csunderlik, C. Polym Degrad Stab 1991, 34, 295.
8. Al-Malaika, S.; Suharty, N. Polym Degrad Stab 1995, 49, 77.
9. (a) Kim, T. H.; Kim, H.-K.; Oh, D. R.; Lee, M. S.; Chae, K. H.; Kaang, S. J Appl Polym Sci 2000, 77, 2968; (b) Oh, D. R.; Kim, H.-K.; Lee, N.; Chae, K. H.; Kaang, S.; Lee, M. S.; Kim, T. H. Bull Korean Chem Soc 2001, 22, 629.
10. Marechal, P.; Chiba, T.; Inoue, T. Polym Networks Blends 1997, 7, 61.
11. Pan, J. Q.; Lau, W. W. Y. Polym Degrad Stab 1996, 53, 153.
12. He, M. B. Polym Degrad Stab 1991, 33, 3367.
13. Munteanu, D.; Mracec, M.; Tincul, I.; Csunderlik, C. Polym Bull 1985, 13, 77.
14. Matsumoto, A.; Yamagishi, K.; Aoki, S. J Polym Sci Part A: Polym Chem 1994, 32, 917.
15. Odian, G. Principles of Polymerization; Wiley: New York, 1991; p 215.
16. Chang, J. Y.; Kim, T. J.; Han, M. J.; Chae, K. H. Polymer 1999, 40, 4049.
17. Song, Z.; Baker, W. E. Angew Makromol Chem 1990, 181, 1.