Melt Free-Radical Grafting of Hindered Phenol Antioxidant onto Polyethylene

TAEK HYEON KIM, HYUN-KYU KIM, DONG RYUN OH, MOO SUNG LEE, KYU HO CHAE, SHINYOUNG KAANG

Faculty of Applied Chemistry, College of Engineering, Chonnam National University, Kwangju 500-757, Korea

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ABSTRACT: A monomeric antioxidant (**3**) was prepared by reacting 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (**1**) with *N*-[4-(chlorocarbonyl) phenyl] maleimide (**2**). This reactive antioxidant was grafted onto polyethylene (PE) by melt processing with free-radical initiators in a mini-max molder. The IR spectra of the grafted PE showed that the monomeric antioxidant was introduced onto the PE. IR spectroscopic methods and titration were used for the quantitative determination of the extent of grafting of the monomeric antioxidant. Also, the extent of crosslinking was indicated by the gel content. Grafting occurred in the following order: dicumyl peroxide (DCP) > benzoyl peroxide > 2,2′-azobisisobutyronitrile. The influences of the DCP concentration and monomeric antioxidant on the extent of grafting were studied. The effects of the reaction time and temperature were also determined. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2968–2973, 2000

Key words: hindered phenol antioxidant; melt free-radical grafting; polyethylene; dicumyl peroxide; polymer-bound antioxidant

INTRODUCTION

Polyethylene (PE) is one of the most widely used polymers. One of the major drawbacks associated with PE, however, is its susceptibility to thermal oxidative degradation. Oxidation reactions are enhanced at elevated temperatures during the processing of the polymer. The addition of antioxidants is the most convenient and effective way to protect the thermal oxidation of polymers. Hindered phenol antioxidants, which contain the 2,6-di-*tert*-butylphenol functional group, are very effective primary antioxidants.[1,2] However, low molecular weight antioxidants are easily lost from polymers through migration, evaporation, or extraction. Physical loss of antioxidants therefore constitutes a major concern in environmental issues and safety regulation, as well as in long-term use of polymers. Several approaches to a more permanent antioxidant have been reported, and among these the polymer-bound antioxidants provide the most attractive answer to guarantee their performance in the polymer matrix.[3–8]

Thus far, polymer-bound antioxidants use acrylic substances in grafting reactions, which is easy to homopolymerize.[7,8] In this article we report the melt graft polymerization of a newly designed antioxidant (**3**) onto PE in a mini-max molder. A new monomeric antioxidant has a dual functionality: the hindered phenol group, which shows an intrinsic antioxidative property, and the maleimide group, which allows grafting onto PE. Preliminary studies on the antioxidative effect of this grafted polymer are also reported.

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

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EXPERIMENTAL

Chemicals and Equipment

The unstabilized PE powder was supplied by Samsung General Chemicals, Ltd. with a melt flow index of 0.8 g/10 min at 190°C/2.16 kg and a density of 0.948 g/mL. Reagent grade dicumyl peroxide (DCP) and 2,2′-azobisisobutyronitrile (AIBN) were used without further purification and benzoyl peroxide (BPO) was purified by recrystallization in ether. The melt grafting reaction was carried out in a mixer (mini-max model CS 183MM-065, Custom Scientific Instruments Inc.).[9] IR spectra were recorded on a Nicolet FTIR spectrometer and ^{1}H-NMR spectra on a Bruker FT DPX 300 (300 MHz) spectrometer. Elemental analyses were performed at the Korea Basic Science Institute (Seoul, Korea).

Synthesis of Designed Monomeric Antioxidant 3

To a stirred solution of *N*-[4-(chlorocarbonyl) phenyl] maleimide[10] (**2**, 1 g, 4.24 mmol) in dry toluene (20 mL) was added a solution of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol[11] (**1**, 1.1 g, 4.65 mmol) in toluene (30 mL) and triethylamine (0.6 mL) in an ice bath. The reaction mixture was stirred for 2 h in the ice bath, poured into water, extracted with ether, dried, filtered, and evaporated. The crude product was purified by flash column chromatography to give the desired monomeric antioxidant in a 55% yield.

^{1}H-NMR ($CDCl_3$): 8.17 (2H, d, Ar), 7.49 (2H, d, Ar), 7.26 (2H, s, Ar), 6.87 (2H, s, vinyl), 5.29 (1H, s, OH), 5.28 (2H, s, CH_2), 1.46 (18H, s, CH_3); IR ($CDCl_3$, cm^{-1}): 3524, 2957, 1716. ANAL. Calcd for $C_{26}H_{29}NO_5$: C, 71.69%; H, 6.72%; N, 3.22%. Found: C, 71.37%; H, 7.16%; N, 3.36%.

Grafting and Purification Procedure

All components, including the PE powder, purely prepared monomeric antioxidant, and initiator were fully mixed in ether using a rotary evaporator at room temperature and then the ether was evaporated. The resulting dry powder mixture was charged into the chamber of a mini-max molder, which was processed at 60 rpm under a nitrogen atmosphere. To get the optimal reaction conditions, a series of exploratory grafting reactions was performed by changing the initiator type (DCP, BPO, and AIBN) and concentrations (0.25–4 mmol/100 g PE), monomer concentrations (2–10 phr resin), reaction time (1–40 min), and temperature (130–210°C). It is known that a grafting reaction includes some unavoidable homopolymerization and causes some degree of crosslinking. The reaction product was purified by dissolving it in refluxing xylene and precipitating it in dichloromethane. The precipitated polymer 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 while grafted and ungrafted PE were precipitated out. Successive reprecipitation showed that a one-time process was adequate to remove the homopolymer and monomer.

Analysis

The purified PE was analyzed by FTIR using films compression molded at 170°C and 2000 psi for 5 min. To determine the degree of grafting, the peak at 2025 cm^{-1} for the PE was chosen as a reference.[7] A carbonyl peak at 1720 cm^{-1} corresponding to the grafted antioxidant was chosen as the target. The peak height ratios of 1720/2025 cm^{-1} were used as a convenient measure for the relative degree of grafting. The IR calibration curve for determining the grafting yield was established by the titration. The grafted PE was dissolved in hot xylene, cooled to about 80°C, and titrated with methanolic NaOMe using thylmol blue as an indicator. The grafting yield was calculated as follows:

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

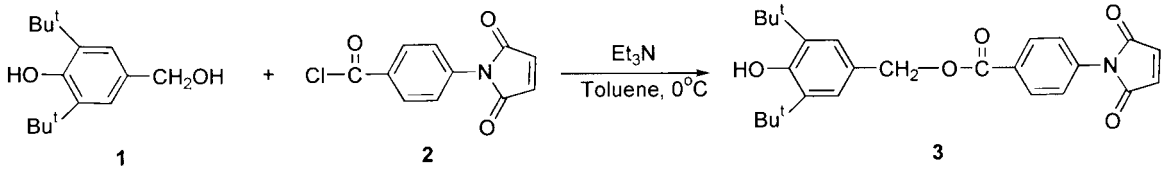
where M_g and M_i represent the mass of the grafted monomer onto PE and initially used monomer, respectively.

Degree of Crosslinking and Gel Content

An indication of the extent of crosslinking was obtained by measuring the gel content (%) of the grafted PE, which was assessed from the fraction by the extraction of respective samples with boiling xylene for 12 h by ASTM D2765-68 (method A). A higher gel content is an indication of more crosslinking.

Thermal Oxidation

Thermal oxidation of the sample was carried out in an oven at 130°C in air and monitored with



Scheme 1 Synthesis of a monomeric antioxidant.

FTIR spectroscopy using the peak height ratio of 1720/2025 cm^{-1} to assess the extent of oxidation of the polymers.[12,13]

RESULTS AND DISCUSSION

Monomeric Antioxidant Synthesis

Antioxidant **3** was prepared by the reaction of **1** and **2** in the presence of triethylamine in 55% yield (Scheme 1). The hydroxy group (—OH) of **1** and acyl chloride (—COCl) of **2** were combined to form an ester. The structure was confirmed with spectroscopy (NMR and IR) and elemental analysis. The IR spectrum of a monomeric antioxidant showed the strong carbonyl band at 1716 cm^{-1} [Fig. 1(a)].

IR Spectra of Melt Grafted PE

Hindered phenolic antioxidants as free-radical scavengers may interfere with the radical initiator. However, Munteanu and coworkers reported that the antioxidants are capable of homopolymerization[14] and grafting onto PE in the presence of free-radical initiators.[7] It is known that hindered phenolic antioxidants trap the peroxy radicals ($ROO^{\bullet}$) rather than the alkyl radicals ($R^{\bullet}$) in the stabilization mechanism.[15]

As expected, our monomeric antioxidant **3** was grafted onto PE in the presence of free radicals. The grafting was confirmed by IR spectroscopy. Figure 1 shows the IR spectra of the monomeric antioxidant, the pure PE, and the grafted PE made under nitrogen. The spectrum of the grafted PE shows a very strong band at 1720 cm^{-1}, which is characteristic of the carbonyl group of the monomer. Two more distinct peaks due to stretching of the C—O—C bond of the ester group and —OH group appears at 1120 and 3647 cm^{-1}, respectively [Fig. 1(c)]. The band at 1720 cm^{-1} can result from the thermal oxidation of PE during the grafting reaction. To test this probability, without the presence of the monomer, the grafting reaction was performed with 2 mmol of DCP/100 g of PE for 10 min at 170°C. The intensity of the peak at 1720 cm^{-1} almost did not increase in comparison with the original PE. Thus, we confirmed that the peak at 1720 cm^{-1} after the grafting reaction was mainly from the monomeric antioxidant. A further confirmation of grafting was achieved from the elemental analysis.

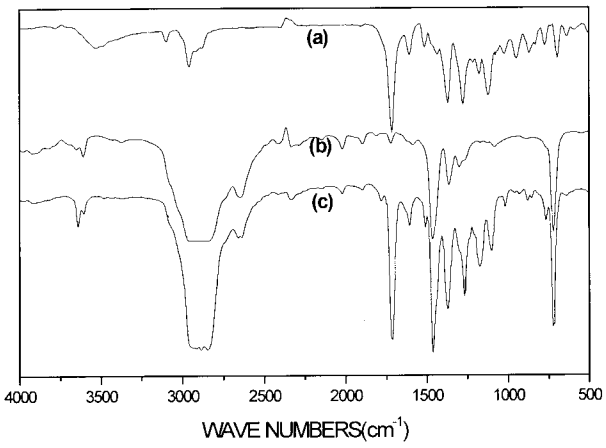


Figure 1 FTIR spectra of (a) the monomeric antioxidant, (b) pure PE, and (c) grafted PE.

Effect of Initiator Type and Concentration on Grafting Reaction

Three initiators were tested: two peroxy initiators (DCP and BPO) and one azo initiator (AIBN). The grafting reaction was performed with a monomer concentration of 4 phr for 15 min at a reaction temperature of 170°C. The grafting yield depended on the initiator type and is shown in Figure 2. DCP was preferable to BPO and AIBN and provided the best grafting yield. The grafting yield increased with an increasing half-life time ($t_{1/2}$) of the initiators. The $t_{1/2}$ values are as follows[16]: 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 without the presence of the initiator with the above reaction conditions did not occur.

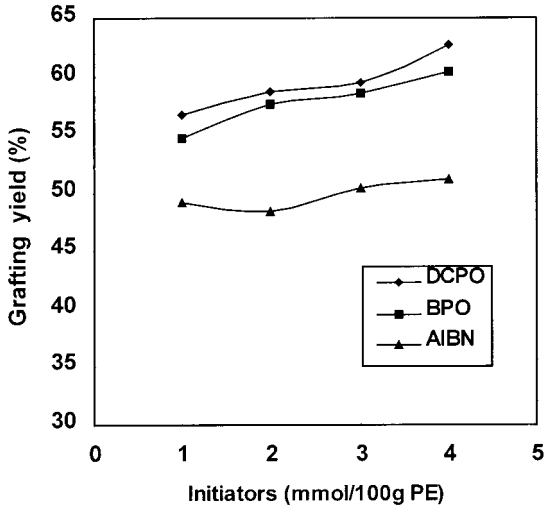


Figure 2 The influence of the initiators on the grafting yield and monomer concentration (4 g/100 g PE) at a reaction temperature of 170°C for 15 min.

A well-known problem in grafting onto PE is crosslinking as side reactions. The gel contents in the case of DCP and BPO are illustrated in Table I. Crosslinking of PE occurred in all cases studied. DCP resulted in less crosslinking, but a higher DCP dose produced the more prominent crosslinking trend. In the above results we found that three competing reactions could occur during the melt grafting, such as the homopolymerization of the monomer, PE crosslinking, and the desired graft reaction. Therefore, an investigation on the effects of DCP concentration, monomer concentration, and reaction time and temperature was necessary to get the optimal grafting reaction conditions. The influence of the DCP concentration on the grafting yield is shown in detail in Figure 3. For each grafting reaction the DCP concentration was varied over the range of 0.275–4.0 mmol/100 g of PE. A rapid increase was observed at low initiator concentrations (<2 mmol). The grafting yield was changed a small amount with an increase in DCP concentration after an initial rapid increase, but increasing the initiator concentration resulted in considerably more crosslinking. Therefore, the concentration of DCP is optimized with 2 mmol/100 g of PE.

Effect of Monomer Concentration on Grafting Reaction

Figure 4 shows the effect of the monomer concentration on the grafting yield. The reaction was performed in a DCP concentration of 2 mmol/100 g of PE at a reaction temperature of 170°C for 15 min. The grafting yield was substantially decreased as the monomer concentration increased

Table I Gel Content of Grafted PE

Reaction Time (min)	Reaction Temp. (°C)	Initiator (mmol)	Monomer (phr)	Gel Content (%)
15	170	DCP (1)	4	1.2
15	170	DCP (2)	4	1.2
15	170	DCP (3)	4	1.3
15	170	DCP (4)	4	3.8
9	170	DCP (2)	4	1.0
15	170	BPO (1)	4	1.3
15	170	BPO (2)	4	2.3
15	170	BPO (3)	4	5.6
15	170	BPO (4)	4	8.3
1	170	DCP (2)	2	1.1
3	170	DCP (2)	2	1.8
5	170	DCP (2)	2	3.6
7	170	DCP (2)	2	3.9
9	170	DCP (2)	2	6.8
11	170	DCP (2)	2	9.7
13	170	DCP (2)	2	13.7
15	170	DCP (2)	2	15.6
20	170	DCP (2)	2	23.9
40	170	DCP (2)	2	31.9
15	130	DCP (2)	2	2.3
15	150	DCP (2)	2	8.7
15	190	DCP (2)	2	18.8
15	210	DCP (2)	2	25.7

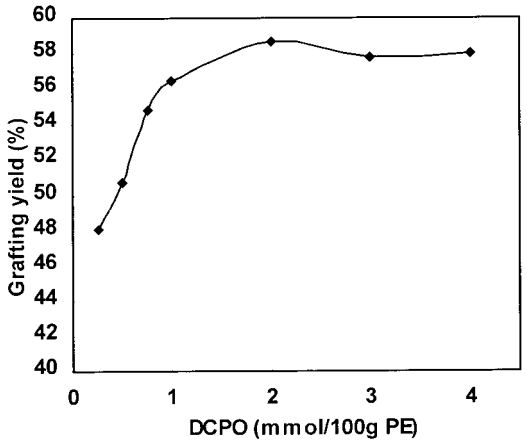


Figure 3 The influence of the initiator DCP concentration on the grafting yield and monomer concentration (2 g/100 g PE) at a reaction temperature of 170°C for 15 min.

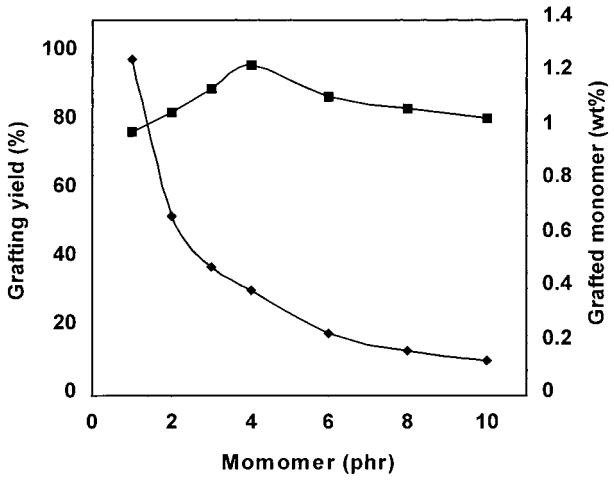


Figure 4 The influence of the monomer concentration on the grafting reaction and DCP concentration (2 mmol/100 g PE) at a reaction temperature of 170°C for 15 min.

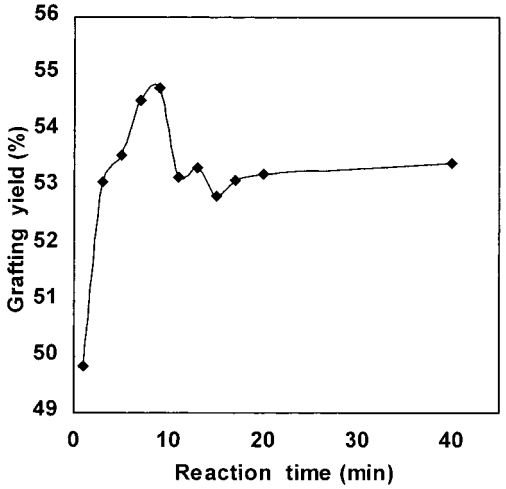


Figure 5 The influence of the reaction time on the grafting yield, DCP concentration (2 mmol/100 g PE) and monomer concentration (2 g/100 g PE) at a reaction temperature of 170°C.

(Fig. 4), but the absolute amount of the grafted monomer was varied over the small range of 0.99–1.2 wt % (Fig. 4). The absolute amount of grafted monomer increased as the monomer concentration increased to 4 phr, and a higher concentration resulted in a slight decrease. Therefore, a monomer dosage of 4 phr is optimum grafting conditions. This behavior is probably a result of the incompatibility between the PE and monomer. The polar monomer molecules tend to form aggregates dispersed in the PE matrix. Increasing the amount of monomer also increases the proportion of monomer located inside the phase and, consequently, is inaccessible to the free-radical site of the polymer.

Effect of Reaction Time and Temperature

Figure 5 shows the influence of reaction time. The concentration of DCP and monomer is fixed at 2 mmol/100 g of PE and 2 phr, respectively. The grafting yield increased with an increase in reaction time up to 9 min. After 9 min the graft yield decreased and then reached equilibrium. The decrease in the grafting yield after 9 min could be a result of degradation of longer formed grafts.[17] The gel contents of the product are shown in Table I. Crosslinking took place more prominently with an increase in the reaction time.

The influence of temperature on grafting was also studied (Fig. 6). Grafting was obtained at 130°C. The grafting yield increased slightly from 150 to 190°C and then decreased as the temperature was further increased. The grafting yield probably decreases at the high temperature because faster chain termination at a high temperature leads to a short graft length.[17] An increase in temperature until about 190°C led to an increased grafting yield, but unfortunately the sensitivity of crosslinking increased as well (Table I).

Antioxidative Effect of Grafted PE

The change in the peak height ratio of 1720/2025 cm^{-1} versus aging time is shown in Figure 7. The

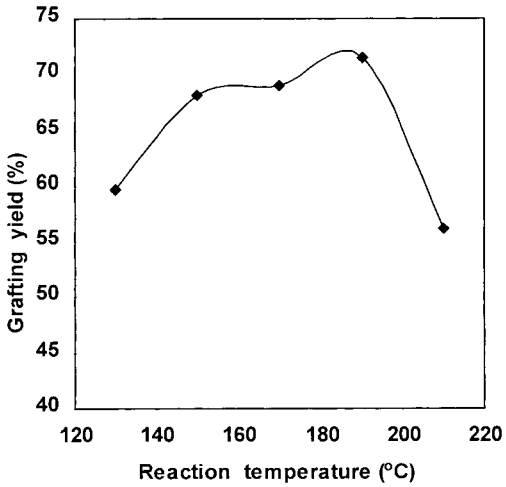


Figure 6 The influence of the reaction temperature on the grafting yield, DCP concentration (2 mmol/100 g PE), and monomer concentration (2 g/100 g PE) for 15 min.

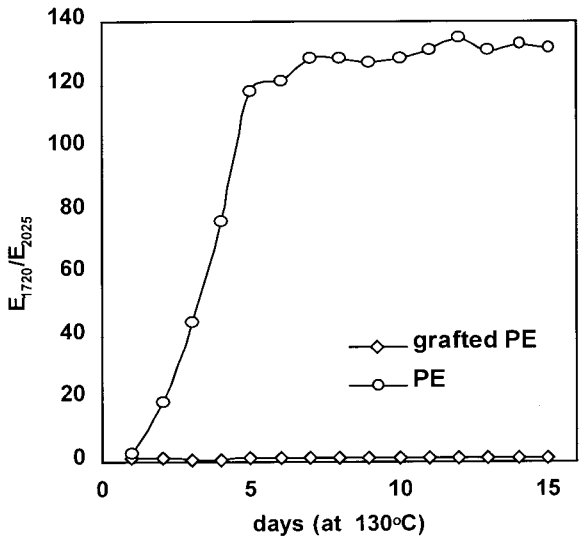


Figure 7 The antioxidative effect of the grafted PE.

carbonyl content of the unstabilized PE drastically increased, while the PE-bound antioxidant showed no increase of the 1720/2025 cm^{-1} ratio for 360 h. This preliminary oxidative result confirmed that antioxidant moiety was chemically bound to the PE chains.

CONCLUSIONS

1. A new polymer-bound antioxidant was successfully prepared by melt grafting a new monomeric maleimide onto PE in the presence of a DCP initiator.
2. The appearance of an IR peak of the carbonyl, —OH, and C—O—C bond stretching of a monomeric antioxidant in the reacted PE confirmed the presence of grafting.
3. The optimum grafting reaction conditions in the mini-max molder was a DCP concentration of 2 mmol/100 g of PE, a monomer concentration of 4 phr, a reaction time of 9 min, and a reaction temperature of 170°C.
4. The grafted PE possessed some stabilizing effect against thermal oxidation with oven aging in air at 130°C for 360 h, indicating no intensity change of the IR peak at 1720 cm^{-1}.

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