Polyolefin elastomer grafted unsaturated hindered phenol esters: synthesis and antioxidant behavior

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ABSTRACT

Monomeric antioxidants are synthesized from esterification of 3,5-di-tert-butyl-4-hydroxybenzoic acid and 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with unsaturated fatty alcohols. The antioxidant activity is evaluated both in blending and radical grafting processes. The effect of chain length and phenolic group is investigated on efficiency of antioxidants. It is demonstrated that the esters of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid exhibit significantly longer induction time. The results of radical grafting reaction shows synthesized antioxidants can be successfully grafted onto polymer chains and the phenolic moiety is functional after extraction process, while pure and commercially stabilized samples are degraded instantaneously. Also, different initiator systems are utilized to enhance the extent of grafting. Among MEK, DCP, and DHBP peroxides, DHBP can be more effective in increasing the antioxidant grafted onto polymer. In addition, possibility of rising in graft content is investigated in presence of redox initiator. Using this approach, polymer-bound antioxidant with prolonged thermal stability can be achieved.

1. Introduction

Oxidation reactions due to the presence of free alkyl radicals, which enhance during elevated temperature processing conditions, cause degradation and deterioration in physical and mechanical properties of polymeric materials.[1–3] Also, radicals and active oxygens from materials which are in direct contact with foods can be responsible for severe diseases or even cancer.[4] To address the issue, it has been suggested to add sufficient amounts of stabilizers based on material type to inhibit degradation. Antioxidants can be categorized as three types, namely primary, secondary, and thio-esters. The most important division is primary antioxidants (generally hindered phenols), which prevent thermal oxidation by donating a hydrogen atom.[5]

However, low molecular weight antioxidants exhibit a considerable physical loss through migration to surface and extraction by liquid media.[6–9] This phenomenon results in reduced life time and properties of polymeric materials and possible health risks due to unwanted release of such stabilizers when polymers used for food packaging.[1,2,9] There have been research efforts to develop supramolecular stabilizers with reduced mobility and volatility to improve the long-term stability of polymeric products, especially packaging films and pipes.[10–12] The reports generally categorized as two approaches: stabilizer immobilization and high molecular weight, olefin-based antioxidants[13] to provide homogeneous distribution in polymer. In 1991, Munteanu and Cunderlik reported the synthesis of three monomeric antioxidants bearing 3,5-di-tert-butyl-4-hydroxyphenyl as radical scavenging group and successful melt grafting onto polyethylene.[14] Also, free radical grafting of antioxidants based on maleimides onto PE and polypropylene, provided covalently bonded stabilizers to matrix.[1] Another approach is copolymerization of monomeric stabilizers with vinyl monomers through radical polymerization and ring-opening metathesis polymerization (ROMP).[11,15] Moreover, few studies have reported coordination copolymerization of monomers having antioxidant moieties with ethylene via organometallic catalysts.[16]

The other route concerns with preparation of antioxidants having alkyl chain with various length and functionality. It was proposed that phenolipids (lipophilized phenolic compound) efficacy may improve by increasing the length of unbranched fatty alcohols to a critical chain length.[17] Several studies on synthesized alkyl caffeates, coumarates and ferulates, caffeic acid phenethyl esters, and long chain alkyl hydroxycinnamates using esterification reactions have
proved the potential antioxidant ability and revealed that polarity and hydrophobicity of stabilizers can be determining factors in efficiency of antioxidants.[18,19] Torres and coworkers [4,20] investigated the antioxidant ability of a new class of lipophilic phenolic-based stabilizers and their fatty acid esters. The study showed superior antioxidant activity in cases of phenolic stabilizers derived from acylated palmitic acid and di-orthophenolic lipophilic antioxidants. Also, it has been proven that the alkyl chain attached to the phenyl ring can have a significant effect in stabilizing free radicals. Over the past decade, supramolecular architectures and dendritic macromolecules have gained interest in drug delivery, gene therapy and reacting with harmful substances due to precise control over structure and numerous possible sites for functionalization via covalent and non-covalent chemical groups.[21] Using dendrimer-like substances such as polyglycerols, phenolic acid-modified hyperbranched antioxidant compounds can be prepared.[22]

In this study, we investigate the design and synthesis of novel esters of 3,5-di-tert-butyl-4-hydroxybenzoic acid and 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid bearing unsaturated alcohol chains with various length and double bonds. The efficiency of synthesized antioxidants was evaluated using oxidation induction time both in blending and radical grafting solution-based processes. In addition, effects of different peroxides and presence of redox initiator on graft content of antioxidant monomers were studied.

2. Experimental section

2.1. Materials

3,5-di-tert-butyl-4-hydroxybenzoic acid (1) (98%), oleyl alcohol (technical grade, 85%), geraniol (98%), farnesol (95%), tin(II) 2-ethylhexanoate (Sn(Oc)t, ≥99–100%), and 4-(dim ethylamino)pyridine (DMAP, ≥99%) were purchased from Sigma-Aldrich and used as received. Dichloromethane (DCM, 99.8%), thionyl chloride (≥99%), triethylamine (TEA, ≥99%), and sodium bicarbonate (≥99%) were purchased from Merck. The DCM was refluxed over calcium hydride followed by distillation and storage over activated molecular sieve. 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (2) (>95%) was purchased from Sigma-Aldrich and used as received. Dichloromethane (DCM, 99.8%), thionyl chloride (≥99%), triethylamine (TEA, ≥99%), and sodium bicarbonate (≥99%) were purchased from Merck. The DCM was refluxed over calcium hydride followed by distillation and storage over activated molecular sieve. 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (2) (>95%) was purchased from Santa Cruz Biochemistry and used without modification. Dichem peroxide (DCP), methyl ethyl ketone peroxide (MEK), and 2,5-dimethyl-2,5-di(tert-butyl peroxy)hexane (DHPB) were obtained from AkzoNobel. POE, an ethylene 1-octene copolymer (LC 670) was supplied by LG Chem, Korea.

2.2. Instrumentation

Nuclear magnetic resonance (13C NMR) spectra were recorded on a Bruker Avance spectrometer using CDCl3 as solvent. Chemical shifts were reported downfield from 0.0 ppm using TMS as internal reference. FT-IR spectra were recorded on a FTIR Nicolet 5700 spectrophotometer using two KBr plates with a drop of compound between them for liquid samples and thin film (50–100 μm) for grafted polymers. Oxygen induction time (OIT) was determined according to ASTM D3895 and performed using Mettler Toledo DSC 1. The sample was equilibrated at 25 °C and then heated to 200 °C at the rate of 20 °C min−1 under nitrogen, and was held at 200 °C for 5 min before the gas was switched to high purity oxygen. The OIT was measured as a sharp increase in the heat flow.

2.3. Synthesis of esters of 3,5-di-tert-butyl-4-hydroxybenzoic acid and 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

In a round-bottom flask, 1 (0.5 g, 2 mmol) or 2 (0.56 g, 2 mmol) was dissolved in dry DCM (20 ml). The solution was cooled to 0 °C and thionyl chloride (10 mmol, 0.75 ml) was added under nitrogen atmosphere. Then, the reaction allowed continuing under reflux for 4 h. After completion, solvent and extra SOCl2 were separated under reduced pressure distillation and 3,5-di-tert-butyl-4-hydroxybenzoyl chloride or 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl chloride was suspended in 10 ml DCM. About 30 mg of DMAP, 0.7 ml of TEA, and 2 mmol of unsaturated alcohol (0.65 ml of oleyl alcohol, 0.35 ml of geraniol and 0.5 ml of farnesol) were added to 5 ml of DCM. Afterward, 3,5-di-tert-butyl-4-hydroxybenzoyl chloride or 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl chloride was added to the mixture under nitrogen atmosphere and the reaction was refluxed for 8 h. Ester products were washed by conc. HCl and extracted with 30 ml of DCM. The organic layer was extracted by saturated NaHCO3 solution and dried over Na2SO4 followed by evaporation of extra solvent under reduced pressure. The chemical structures of synthesized antioxidants along with 13C NMR spectra are shown in Figures 1 and 2.

2.3.1. Oleyl 3,5-di-tert-butyl-4-hydroxybenzoate (OB)

Yield 80%; pale yellow solid (m.p. 40 °C); IR (KBr, cm−1): 3627.2 (C–OH), 1780.15 (COO); 13C NMR (500 MHz, CDCl3, δ): 167.5 (–COO–), 158.5 (C–OH), 136.8, 130.3, 128.5, 127.4, 122, 65 (CH3OCO), 36.1, 34.7, 32.4, 31.8, 30.5, 30.2, 29.8, 27.6, 23.1, 14.5.

2.3.2. Geranyl 3,5-di-tert-butyl-4-hydroxybenzoate (GB)

Yield 87%; pale yellow oil; IR (KBr, cm−1): 3626.7 (C–OH), 1769.8 (COO); 13C NMR (500 MHz, CDCl3, δ): 167.6 (–COO–), 158.5 (C–OH), 141.9, 136.4, 132, 128.6, 127.5, 124.3, 122, 119.5, 61.9 (CH3OCO), 40, 34.7, 31.8, 30.8, 30.6, 26.8, 26, 18.1, 16.8.
2.3.3. Farnesyl 3,5-di-tert-butyl-4-hydroxybenzoate (FB)
Yield 84%; pale yellow solid (m.p. 38 °C); IR (KBr, cm⁻¹): 3628.4 (C–OH), 1778.5 (COO); ¹³C nMR (500 MHz, CDCl₃, δ): 167.5 (–COO–), 158.5 (C–OH), 141.8, 136.1, 135.7, 131.7, 131.4, 125, 124.8, 124.1, 122, 119.6, 61.9 (CH₂OCO), 40.1, 34.8, 31.8, 30.6, 27.2, 26.7, 26.1, 23.8, 18, 17, 16.4.

2.3.4. Oleyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (OP)
Yield 85%; yellow oil; IR (KBr, cm⁻¹): 3647.33 (C–OH), 1739.34 (COO); ¹³C nMR (500 MHz, CDCl₃, δ): 173.6 (–COO–), 152.7 (C-OH), 136.4, 131.7, 130.3, 125.2, 64.9 (CH₂OCO), 36.9, 34.8, 32.5, 31.6, 30.8, 30.2, 29.8, 27.7, 23.2, 14.6.

2.3.5. Geranyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (GP)
Yield 92%; pale yellow oil; IR (KBr, cm⁻¹): 3647.5 (C–OH), 1732.54 (COO); ¹³C nMR (500 MHz, CDCl₃, δ): 173.6 (–COO–), 152.6 (C–OH), 142.3, 139.4, 136.4, 132, 125, 124.3, 119, 61.8 (CH₂OCO), 40, 37, 34.7, 32.4, 31.5, 30.2, 26.8, 26.16, 18.1, 16.9.

2.3.6. Farnesyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate (FP)
Yield 88%; yellow to pale brown oil; IR (KBr, cm⁻¹): 3640 (C–OH), 1730.58 (COO); ¹³C nMR (500 MHz, CDCl₃, δ): 173.5 (–COO–), 152.6 (C–OH), 142.3, 136.4, 135.8, 131.7, 125,
Alkyl chain attached to phenolic ring in 1 exhibits more electron-withdrawing characteristic in comparison to 2, which causes worsening effect in antioxidant activity of 1 and corresponding derivatives.[5,24] However, the major affecting factor in antioxidant efficiency seems to be the type of alcohol chain since lipophilization is a vital approach to improve efficacy in non-polar systems.[25] Antioxidants substituted with oleyl alcohol were the most efficient stabilizers, where the OIT of oleyl 3-(3,5-di-tert-buty1-4-hydroxyphenyl)propionate reached almost 43 min. One probable explanation could be the higher lipophilicity and compatibility of fatty unbranched oleyl alcohol’s alkyl chain (C_18) with polymeric chains than solvent/non-solvent phase. Decrease in alcohol chain length and less compatibility with polymer matrix resulted in less radical scavenging potency for geraniol and farnesol-substituted compounds. For derivatives of 1, an increase in antioxidant activity was observed with increase in alcohol chain length from geraniol (C_10) to farnesol (C_15), whereas in case of 2 derivatives contradictory results were obtained.

2.4. General compounding and grafting procedure

All the manipulations were carried out under nitrogen and based on solution method using toluene under reflux condition. During first step, 10 g of POE was added to toluene and the temperature was fixed at 130 °C. After being solved, desired amount of the phenolic antioxidant (0.6 and 1 mmol of synthesized stabilizers in compounding and grafting, respectively) was added to the solution and mixed for 30 min. In case of grafting, prior to addition of antioxidant, the radical initiator system consists of 0.1 wt% MEK, DCP or DHBP and Sn(Oct)_2 (when used) as redox initiator with weight ratio 1:1 (w/w) was added to the mixture and maintained for 30 min. Then, the solution was poured in cold methanol and precipitate was filtered, washed with acetone, and dried in vacuum oven overnight.

2.5. Sample purification procedure

The functionalized POE samples were hot-pressed at 120 °C under 5 MPa for 5 min into sheets with the thickness around 200 μm. Prior to characterization, sheets were purified by soxhlet extraction using acetone as solvent for 72 h to remove unreacted antioxidant molecules and other by-products (24 h extraction in case of commercially stabilized sample). Finally, the purified sheets were dried by vacuum oven for 8 h.

3. Results and discussion

3.1. Thermal oxidative stability of POE blends

In order to examine the radical scavenging ability of synthesized antioxidants OIT method was utilized. As OIT is the required time for oxidation, the longer OIT time reveals more resistance to oxidation. The DSC curves of pure and stabilized POE with ester derivatives of 1 and 2 are shown in Figure 3. Oxidation of neat POE took place immediately after introduction of oxygen and addition of 1 couldn’t significantly contribute to improve resistance to oxidation in comparison with 2 (4.7 min). The higher efficiency of 2 is attributed to the alkyl group attached to phenyl ring based on polar paradox hypothesis.[4,18,23] The longer alkyl chain in 2 is responsible for better solubility and miscibility of phenolic antioxidant in polymer matrix. Similar findings in case of di-orthophenolic lipophilic antioxidants has been reported.[4] On the other hand, reactivity of antioxidants containing hindered phenolic moieties toward free radicals can be greatly affected by substitution in the para position of phenolic ring. Introducing electron-donating group results in enhanced efficiency of antioxidants.

Figure 3. Oxidation induction time curves of various POE samples prepared by solution blending.

Figure 4. FT-IR spectra of pure POE, GP, and POE-g-GP.
3.2. Radical grafting of antioxidants onto polymer

The synthesized antioxidant monomers were covalently bonded to polymer chains through grafting approach in presence of DCP/Sn(Oct)$_2$ initiator system and unreacted monomer was extracted. Grafting of 2 derivatives onto POE was confirmed by FT-IR and NMR spectroscopies. The infrared spectra of pure POE, GP and GP-grafted POE are shown in Figure 4. Two characteristic peaks at 1732 and 3648 cm$^{-1}$ related to carbonyl group of phenolic ester and C–OH group of antioxidant can be seen in spectrum of GP. For POE-g-GP the band at 3650 cm$^{-1}$ was the characteristic peak of phenolic group of stabilizer and the band at 1732 cm$^{-1}$ shifted to higher wave number zone (1740 cm$^{-1}$) due to association of antioxidant monomer and polymer chain. Compared with esters of 2, the intensities of carbonyl groups of antioxidants derived from 1 around 1780 cm$^{-1}$ (OB), 1770 cm$^{-1}$ (GB), and 1778 cm$^{-1}$ (FB) and C–OH bands around 3627 cm$^{-1}$ were insignificant as a result of low grafting content, thus no confirmation of grafting reaction was concluded from IR spectroscopy.

The structure of POE-g-GP and POE-g-GB were characterized with $^{13}$C NMR in comparison to pure polymer, as shown in Figure 5. The peaks at 31.7 and 38.6 ppm were assigned to methine groups of POE according to literature.[26–28] After radical grafting reaction, intensities of methine groups reduced (in case of POE-g-GP, peak at 38.6 ppm was not observed), while two new characteristic peaks were observed at 36.6 and 44.3 ppm in case of POE-g-GP and for POE-g-GB peaks appeared at 36.5 and 47.8 ppm, relating to formation of covalent bond between stabilizer monomers and polymer backbone. The detailed microstructures of GP and GB were not obvious due to low graft content and relatively large molar mass of synthesized stabilizers. However, five resonance absorption peaks were observed at 68, 125.7, 128.6, 129.4, and 137 ppm in case of POE-g-GP and four resonance bands at 68.1, 126.2, 130, and 136.1 were determined for POE-g-GB; since the samples were purified and unreacted monomer were extracted before NMR characterization, these peaks were attributed to CH$_3$OCO group of stabilizer, unincorporated double bond of GP and GB molecules and phenyl ring.

3.3. Thermal oxidative stability of antioxidant-grafted-POE

Figure 6 depicts the curves from OIT measurements for radical grafted antioxidants onto POE along with stabilized POE resulted from blending with commercial Irganox® 1076 (2500 ppm) before and after extraction. It can be seen that the extraction procedure was able to remove all the unbonded antioxidant monomers from polymer matrix as the stabilized POE degraded immediately over introduction of oxygen gas after extraction. It is evident that the most effective antioxidant was GP with OIT value...
temperature end-up in coupling reactions due to early stage dissociation. Moreover, initiators which form more free radicals after thermal decomposition can be considered as improver of grafting reaction. In order to evaluate the effect of initiator system on grafting of synthesized antioxidants, GP monomer was chosen because of the highest efficiency among synthesized stabilizers. Five initiator systems, namely MEK, DCP, DHBP, DCP/Sn(Oct)$_2$, and DHBP/Sn(Oct)$_2$ were tested and results of FT-IR and NMR spectroscopies are shown in Figures 7 and 8, respectively. As it can be seen the intensity of peak at 1740 cm$^{-1}$, related to the ester group in GP, seems to increase in the order of DHBP/Sn(Oct)$_2$ > DCP/Sn(Oct)$_2$ > DHBP > DCP > MEK which suggests higher extents of grafting of GP onto polymer. Several studies [29–31] have considered DCP as suitable peroxide both in grafting content and efficiency due to relatively high molar efficiency and decomposition temperature. However, in this study initiator systems containing DHBP showed higher degrees of antioxidant grafting, which can be attributed to the formation of two times more radicals than DCP.[32]

To achieve extensive amount of grafted monomer, redox initiator Sn(Oct)$_2$ was utilized with ratio of 1:1 wt% according to findings of Brito and coworkers.[33] Results showed considerable rise in intensity of band at 1740 cm$^{-1}$ in FT-IR spectra of DCP/Sn(Oct)$_2$, and DHBP/Sn(Oct)$_2$ systems compared to DCP and DHBP due to presence of reducing agent which prevents side reactions of free radicals by temporary trapping them. Further, by comparing NMR spectra (Figure 8) of stabilized polymers synthesized using DHBP/Sn(Oct)$_2$, DHBP, and DCP it was found that the intensities of methine peaks at 31.8 and 38.6 ppm tended to reduce with introduction of DHBP instead of DCP until no methine absorption was observed when DHBP/Sn(Oct)$_2$ was utilized. Also, increasing intensities of signals at 36.6 and 44.3 ppm along with arising in peaks at 68, 126, 130, and 137 ppm relating to $\text{CH}_2\text{OCO}$ group and phenyl ring

![Figure 7. FT-IR spectra of grafted POE using different initiator systems.](image)

![Figure 8. Effect of initiator type on structure of grafted samples.](image)

3.4. Effect of initiator system

Initiator type has a prominent role in radical grafting reaction. Free radicals from initiators with low decomposition
of stabilizer confirms higher extents of grafted monomers onto polymer chain in presence of redox initiator.

The effect of initiator type on oxidative stability of grafted POE samples with GP was analyzed by OIT and results are depicted in Figure 9. Findings revealed higher amounts of grafted antioxidant in case of DHBP peroxide with more stable radicals than DCP and MEK with premature structure dissociation as the OIT value of DHBP was nearly two to three times longer than DCP’s and MEK’s. Also, through the introduction of redox initiator the oxidation induction time could be delayed to almost 10 min when combination of DHBP and Sn(Oct)_2 was used.

4. Conclusions

In this study, unsaturated esters of 3,5-di-tert-butyl-4-hydroxybenzoic acid and 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propiionic acid were successfully synthesized and characterized using FT-IR and NMR spectroscopy. The efficiency of resulting stabilizers in polymer media was evaluated both in blending and radical grafting in solution. Results showed that 3,5-di-tert-butyl-4-hydroxybenzoic acid and its derivatives were not able to stabilize macroradicals from degradation process. Moreover, in blending approach oleyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate showed significantly high oxidation induction time as a result of better compatibility with polymer chains due to linear structure of oleyl alcohol. Since the synthesized stabilizers have double bond in their structure, they can be used in radical grafting to prevent antioxidant migration and loss from polymer matrix. Results of radical grafting revealed that GP was grafted onto polymer chains more than other stabilizers and resulting POE-g-GP showed satisfactory level of thermal oxidative stabilization after extraction process. Also, the effect of different initiation systems was studied on grafting reaction. It was found that addition of redox initiator Sn(Oct)_2 could increase the amount of antioxidant monomers grafted onto polymer.

Disclosures statement

No potential conflict of interest was reported by the authors.

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