Expanding Polypropylene Applications in High Temperature Conditions

Developing Polypropylene Bonded Hindered Phenol Antioxidants for Expanding Polypropylene Applications in High Temperature Conditions

Zhang G, Nam C and Chung TCM*
Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania, USA

Abstract

Polypropylene (PP) represents about a quarter of commercial plastics produced around the world. Despite its huge commercial success, PP polymer is not suitable for the applications that require long-term exposure to high temperatures (>80°C), due to its chemical and physical stability. The PP chain is prone to the oxidative chain-degradation and exhibits a relatively low material softening temperature. This paper discusses a new research approach by developing the PP-bonded hindered phenol (PP-HP) antioxidants to address this scientifically challenging issue. We have investigated two PP-HP structures, one with two methylene units adjacent to the hindered phenol group (HP-L) and one without this spacer (HP-S). In general, PP-HP polymers are advantaged with the ability to incorporate a suitable concentration of HP antioxidant groups with homogeneous distribution along the polymer chain, which provide effective protection to the PP chains from oxidative degradation. In addition, the specific PP-HP-L structure can also engage in a facile crosslinking reaction to form a 3-D network during the oxidation reaction. In one accelerated oxidation test in air at 190-210°C, the regular commercial PP polymer (containing common antioxidants and stabilizers) degrades within a few minutes; a PP-HP-L copolymer with about 1 mol% HP-L group shows almost no detectable weight loss after 24 hrs. In an ASTM endurance test at 140°C in air, the commercial PP shows 1% weight loss within about 10 days. On the other hand, the PP-HP-L polymer lasts for more than 30 years. Overall, the experiment results present the potential of expanding PP applications into a much higher temperature range (>140°C) under oxygen oxidative environments.

Keywords: Phenol antioxidants; Polypropylene polymer; Stabilizers

Introduction

Polypropylene (PP) polymer is inherently unstable under high temperature or long-term UV exposure conditions due to the presence of a labile tertiary proton in each monomer unit [1-3]. Scheme 1 illustrates the oxidative chain degradation mechanism. After removing a tertiary proton by heat or UV radiation, the formed polymer radical (I) spontaneously reacts with an oxygen molecule in air to produce the peroxy radical (II). This peroxy radical then removes another tertiary proton to form a hydroperoxide (C-O-O-H) intermediate (III) that is decomposed under heat. Two possible decomposition pathways, cleaving either O-O or C-O bonds in the C-O-O-H moiety, lead to the PP chain degradation to form PP with a terminal aldehyde group (IV) or PP with a terminal olefinic group (VI), respectively. On the other hand, the newly formed polymer radicals (V) and (VII) continue proton extraction and autoxidation-degradation cycle. In other words, this is a catalytic reaction mechanism with rapid degradation of the polymer chain [4].

It is a common practice in the industry to introduce a small amount (<1 wt%) of antioxidants or stabilizers in the PP products, which have the ability donating hydrogen atom to the polymeric radicals (I) to halt the oxidation-degradation cycles [5], especially during melt processes and outdoor applications. The most common antioxidants used in polyolefin are hindered phenol molecules, including octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076) and pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) (Irganox® 1010) [6,7] as illustrated in Scheme 2. However, there are several concerns of small organic HP molecules in the PP matrix, which often limit their effectiveness and the product’s long-term performance. The poor solubility of the polar HP molecules in the semi-crystalline nonpolar PP matrix can lead to the inhomogeneous distribution of antioxidant with less than minimum effective concentration in the PP matrix. As a result, the concentrated antioxidants on the polymer surfaces also accelerate the loss when exposed to solvents, heat, or strong electric fields.

There have been some research efforts to develop polymer-bonded antioxidants that offer reduced volatility to improve the long-term stability of polymer products [8-11]. This approach is particularly acute in thin film and coating applications. However, there are only few reports [12-15] discussing PE and PP-bonded hindered phenol antioxidants. Most synthesis routes are based on free-radical mediated copolymerization and grafting reactions with monomers containing hindered phenol moieties [16-21]. The free radical grafting reactions on PE and PP polymers are usually accompanied with many side reactions [22], including the chain degradation shown in Scheme 1, low yield, by-products, and colored material. There are only few reports discussing polyolefin-bonded stabilizers prepared by direct Ziegler-Natta catalyst mediated copolymerization reaction of olefin and functional co-monomers, due to the limitations of catalyst poison and different co-monomer reactivity ratios [23].

So far, most experimental results in polymeric antioxidants have been focused on the issues of antioxidant compatibility, migration, and oxidative stability. There is almost no attention in the antioxidant...
groups that can also serve as crosslinking agents to provide physical (structural) integrity of polyolefin products under elevated temperature conditions. Commercial PP polymers usually exhibit a broad melting endotherm, starting at as low as 70°C and peaked at around 165°C, due to a broad distribution of crystal sizes. As expected, they gradually lose the mechanical strength (softening) at a relatively low temperature. The general recommended application temperature for PP products is below 80°C. On the other hand, the polymer network is known to increase product mechanical strength, temperature stability, and resistance to solvents, creep, and stress-cracking [24-28]. Crosslinked polyethylene (x-PE) is used everywhere today in water piping and high voltage electrical cables [29]. However, PP cannot be effectively cross linked due to the lack of a suitable crosslinking chemistry. The crosslinking reaction for PE involves high energy irradiation (γ-rays and electron beams) [30-33], peroxide induced radical reactions [34-38] and silane-moisture cure mechanism [39-41]. Most of these methods are not suitable in the PP case due to the prompt degradation of the PP backbone under free radical conditions [42-45].

**Experimental Section**

**Materials and instrumentation**

All O₂ and moisture sensitive manipulations were carried out inside an argon-filled dry box. 3,5-Bis(tert-butyl)-4-hydroxy benzoic acid, 3,5-bis(tert-butyl)-4-hydroxyphenylpropionic acid (Ciba), 4,N,N-dimethylaminopyridine, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide, and calcium hydride (VWR Scientific), were used as received. Toluene (Wiley) was distilled over sodium benzophenone under argon. Two commercial PP polymers, including Daploy (general-purpose grade) with <1 wt% Irganox® 1076 and Borclean (capacitor grade) with <0.5 wt% Irganox® 1010 antioxidant and Melt Index 0.5, were produced by Borealis Co. All high temperature 1H NMR spectra were recorded on a Bruker AM-300 spectrometer, with the polymer samples dissolved in 1,1,2,2-tetrachloroethane-d₂ at 110°C. Thermogravimetric (TGA) analysis was performed on the TA Instruments Q600. The molecular weights of the polymers were determined by intrinsic viscosity of polymer measured in decahydrornaphthalene (Decalin) dilute solution at 135°C with a Cannon-Ubbelohde viscometer. The viscosity molecular weight was calculated by the Mark-Houwink equation: n = KM⁰ where K = 1.05 × 10⁻⁴ and α=0.80 [46,47]. UV-visible spectroscopy was investigated by Perkin-Elmer Lambda 950 UV-VIS-NIR Spectrophotometer. The samples were prepared as film form with a thickness around 20-30 µm. For the gel content test, all the samples were put into an oven for 24 h at various temperatures from 150-210°C under air condition. Then the samples were weighted to get W₁. Then, the samples were treated with refluxing xylene for 2 h to remove all the soluble part. After that, the samples were put into vacuum oven over night to dry and then...
weighted to get \( W_g \). The gel content was calculated by the difference between the two weights. Gel Content = \( \frac{(W_1 - W_2)}{W_1} \times 100\% \).

### Synthesis of PP-HP copolymers

The PP-OH copolymer, containing 10-undecen-1-ol comonomer units, was prepared by the published procedures [48]. The subsequent esterification reactions of the PP-OH copolymer, with 3,5-bis(tert-butyl)-4-hydroxy benzoic acid or 3,5-bis(tert-butyl)-4-hydroxyphenylpropionic acid, were carried out in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) and 4-N,N-dimethylaminopyridine (DMAP). In a typical reaction run, under an argon atmosphere, 5 g of PP-OH copolymer with 1 mol% of OH content was mixed with 1.9 g of 3,5-bis(tert-butyl)-4-hydroxy benzoic acid, 0.19 g of DMAP, and 100 mL of toluene in a 500 mL round bottom flask equipped with a stirrer and a condenser. After adding 1.15 g of the EDC reagent, the esterification reaction was carried out at 110°C for 12 hours. The resulting PP-HP copolymer was precipitated in 600 mL of methanol, and then washed with methanol a few times before drying the polymer overnight in a vacuum oven at 70°C.

### Results and Discussion

#### Polymer synthesis

This paper investigates two PP-HP copolymers containing non-crosslinkable hindered phenol (HP-S) and crosslinkable hindered phenol (HP-L) groups, respectively. Scheme 3 illustrates the synthesis routes, starting with the same PP-OH copolymer with the OH groups homogeneously distributed along the polymer chain. The subsequent Steglich esterification’s [49,50] of OH groups with 3,5-bis(tert-butyl)-4-hydroxy benzoic acid or 3,5-bis(tert-butyl)-4-hydroxyphenylpropionic acid, are very effective (quantitative) to form the corresponding PP-HP-S and PP-HP-L copolymers, respectively. Both resulting PP-HP-S and PP-HP-L copolymers have the pre-determined HP group content and the same homogeneous polymer structures.

Figure 1 compares the \( ^1H \) NMR spectra of a PP-OH copolymer and two corresponding PP-HP-L and PP-HP-S polymer antioxidants. All spectra exhibit three major chemical shifts at 0.95, 1.35 and 1.65 ppm, corresponding to the methine, methylene and methyl groups in polypropylene. After both esterification reactions, the triplet chemical shift at 3.65 ppm, corresponding to CH\( _2-OH \) group, completely disappeared with the appearance of several new chemical shifts. In the PP-HP-L case (Figure 1b), three triplet chemical shifts at 2.61, 2.89, and 4.10 ppm, corresponding to three methylene units near ester group linkage in the PP-HP-L sample. The 1:1 peak intensity ratio between the chemical shift at 4.10 ppm for CH\( _2-O-C=O \) and a singlet chemical shift at 7 ppm for two aromatic protons in the hindered phenol moiety clearly indicate the quantitative esterification reaction to obtain a highly pure PP-HP-L product. The same effective esterification reactions were also observed in the PP-HP-S cases. In Figure 1c, the appearance of two new chemical shifts, including a triple chemical shift at 4.28 ppm for CH\( _2-O-C=O \) and a singlet chemical shift at 8 ppm for two aromatic protons in the HP-L moiety. Both chemical shifts also show a 1:1 peak intensity ratio, indicating the complete esterification to obtain a pure PP-HP-S product.

Table 1 show several PP-HP-L and PP-HP-S copolymers used in this comparative study. Comparing with the starting PP-OH copolymer, both corresponding PP-HP-L and PP-HP-S copolymers show no significant change in polymer molecular weight, melting temperature, crystallization temperature, and degree of crystallinity. Both Steglich esterification reactions were very effective without any significant side reaction. They are all high molecular weight polymers with the melting temperature and the degree of crystallinity reversely proportional to the side chain (co-monomer) concentration.
Figure 1: H NMR spectra of (a) PP-OH with 1 mol% OH content and (b) the corresponding PP-HP-L and (c) PP-HP-S copolymers.

| Polymer      | [HP] (mol%) | $M_n$ ($\times 10^3$ g/mol) | $T_m$ (°C) | $\Delta H$ (J/g) | $T_c$ (°C) |
|--------------|-------------|-----------------------------|------------|------------------|------------|
| PP-OH        | 1.0         | 650                         | 152        | 70               | 115        |
| PP-HP-S-1    | 1.5         | 446                         | 143        | 86               | 107        |
| PP-HP-S-2    | 3.5         | 314                         | 116        | 27               | 67         |
| PP-HP-S-3    | 4.7         | 223                         | 112        | 12               | 62         |
| PP-HP-L-1    | 1.0         | 617                         | 150        | 65               | 114        |
| PP-HP-L-2    | 2.0         | 407                         | 145        | 47               | 103        |

*Estimated by intrinsic viscosity of polymer/decalin dilute solution at 135°C.

Table 1: Summary of several PP-HP-S and PP-HP-L copolymers with a PP-OH copolymer.

It is important to note the difference between HP-S and HP-L moieties. Although both HP moieties can engage in a facile protonation reaction with the polymeric radical ($R^*$), formed in the PP chain upon the oxidation reaction (Scheme 1), the HP-L moiety offers higher efficiency. In fact, the same HP moiety is also present in many commercial antioxidants, such as Irganox® 1010 and 1076 (Scheme 2). As illustrated in the oxidation mechanism (Scheme 4), two HP-L moieties can react with three $R^*$ radicals and finish with a dimerization reaction between two oxidized HP-L groups to form a long conjugated bis-quinonemethide group containing two benzoquinones [51]. In PP-
HP-L case, the dimerization reaction will create a crosslinking structure between PP polymer chains, as illustrated in Scheme 5. Therefore, it is logical to think that PP-HP-L shall afford superior thermo-oxidative stability.

**Thermal/oxidative stability**

Figure 2 compares TGA curves of PP-HP-S and PP-HP-L (1 mol% HP groups) with two commercial (general and capacitor grades) PP polymers, measured under the same condition at a heating rate of 10°C/min in air. The capacitor-grade PP (Borclean) shows the onset of weight loss at around 250°C, which is about 15°C higher than that of general-grade PP. The PP-HP-S copolymer starts the weight loss at almost the same temperature (250°C) but with a slower degradation rate. However, the PP-HP-L copolymer exhibits a significantly higher thermal/oxidative stability, with the starting weight loss temperature above 320°C, about 70°C higher than the high quality (capacitor grade) commercial PP polymer.

As illustrated in Scheme 5, the PP-HP-L polymer engages in a thermal/oxidation reaction with oxygen to form a crosslinked x-PP-HP-L network that contains some conjugated bis-quinonemethide (x-linker) moieties. UV-visible spectroscopy and gel content were used to monitor the thermal/oxidative induced crosslinking reaction in forming the x-PP-HP-L network. Figure 3 shows the UV-visible spectra of a PP-HP-L polymer containing 1 mol% HP-L group during constant heating at various high temperatures for 24 h under air flow condition. The absorption peak at λ=275 nm, corresponding to the hindered phenol moiety, is gradually reduced with the presence of a new peak at λ=310 nm, corresponding to the conjugated bis-quinonemethide (x-linker). Based on the peak intensity ratio, about 90% of HP groups in PP-HP-L polymer are converted to x-linkers after the heating at 150, 170, 190, and 210°C for 24 h each in air. On the other hand, the commercial PP and PP-HP-S films show no P2 peaks after the same heating condition. In fact, both polymers cannot hold the shape at the temperature higher than 160°C.

The crosslinked x-PP-HP-L networks were also examined by gel content. The samples were treated with refluxing xylene for 2 h to remove the entire soluble fraction. The gel content was calculated by the percentage of insoluble weight fraction in the sample. Figure 4 shows the gel contents for all heat-treated x-PP-HP-L samples from the same PP-HP-L polymer with 1 mol% HP-L group content. Figure 4a shows the gel content as a function of temperature from 150 to 210°C, after heating for 24 h. The gel content systematically increases with the increase of heating temperature. The higher the temperature we treated PP-HP-L polymer, the greater the crosslinking density in
the resulting x-PP-HP-L polymer. At 210°C for 24 h in air, the resulting x-PP-HP-L sample is completely insoluble. A small% of polymer may be lost during the solvent extraction, filtration, and isolation process. Figure 4b shows the gel content of the same PP-HP-L polymer heating at 210°C for various time periods. After 1 h of heating treatment, the PP-HP-L polymer began to crosslink with about 1% insoluble fraction. After 17 h of heating treatment, the PP-HL polymer was nearly fully crosslinked, with 95% insoluble fraction. Overall, the experimental results between UV-vis and gel content are quite consistent. It is expected that the experimental result in the gel content value (insoluble polymer fraction) shall be higher than the value of HP-L interconversion to the x-linker. It only needs several x-linkers in each polymer chains to form an insoluble network. The combination of UV-vis and gel content results clearly shows the presence of crosslinking reaction in the x-PP-HP-L polymers, with the kinetic rate controlled by the heat treatment condition.

**Endurance under elevated operation temperatures**

Polymer aging and endurance time under certain operational conditions are essential information in considering polymer applications. As discussed, it is highly desirable to broaden the PP application temperature and maintain constant performance for a long period time. With the newly developed PP-HP polymers, we are very curious to know what the new operational window is and what the endurance time is at an operational temperature >100°C, which is important in many high energy applications, but not attainable in current PP materials.

Figure 5 compares the weight loss under isothermal conditions. Since PP melt processing is usually operated at between 190°C and 210°C in air, we compare TGA curves of two commercial PP polymers...
Citation: Zhang G, Nam C, Chung TCM (2017) Developing Polypropylene Bonded Hindered Phenol Antioxidants for Expanding Polypropylene Applications in High Temperature Conditions. J Material Sci Eng 6: 393. doi: 10.4172/2169-0022.1000393

We also employed the ASTM 1877 method to determine PP-HP-L endurance time under various heating in air conditions [52]. The failure is defined at 1 wt% polymer weight loss. This method involves a TGA measurement (Figure 6) with various heating rates. For comparison, the high quality capacitor-grade Borclean PP was also examined side-by-side as the control runs. Figure 7 shows the plots of log (heating rate) vs. heating temperature (1/T) under various specific polymer weight loss (conversion) conditions, based on the TGA curves in Figure 6. The slope of each line was used to calculated the activation energy ($E_a$) of each polymer weight loss (conversion during the polymer chain oxidation and degradation reaction), using the equation in ASTM 1877 test $E_a = -\left(\frac{R}{b}\right) \Delta \log \beta / \Delta \left(1/T\right)$; wherein $\Delta \log \beta / \Delta \left(1/T\right)$ =slope of the line obtained in Figure 7, $\beta$=heating rate (K/min), $T$=temperature (K) at constant conversion, gas constant $R=8.314$ J/(mol.K), and $b=0.457/K$ on the first iteration.

Table 2 summarizes the activation energy ($E_a$) for both Borclean PP and PP-HP-L-1 polymers with various polymer weight loss conditions. In all side-by-side comparisons, PP-HP-L-1 polymer shows significantly higher activation energy than Borclean PP. In the details, it is interesting to note that the different trend in activation energy vs. polymer weight loss (Table 2) occurs between two cases. Borclean PP shows a systematical reduction of activation energy ($E_a$) with the
Table 2: Activation energy in polymer weight loss for (a) PP (Borclean) and (b) PP-HP-L-1.

| Conversion (%) | Activation Energy Ea (kJ/mol) |
|---------------|-------------------------------|
|               | PP                           | PP-HP-L-1  |
| 1.0%          | 126.8                        | 209.1      |
| 2.5%          | 117.6                        | 185.1      |
| 5.0%          | 104.7                        | 163.5      |
| 10.0%         | 97.0                         | 145.8      |
| 15.0%         | 93.6                         | 150.8      |
| 20.0%         | 91.7                         | 171.8      |

increase of polymer weight loss due to the continuous polymer chain degradation that results in lower polymer molecular weight and higher chain mobility. On the other hand, in the PP-HP-L-1 case, the initial reduction of activation energy is recovered at a higher conversion level, which may be related to the in situ formation of crosslinkers in the resulting x-PP-HP-L-1 network.

With the activation energy ($E_a$), we can estimate the material endurance time under a specific value of conversion and failure temperature, following the ASTM 1877 equation $T_f = rac{E_a}{2.303 R} \log\left(\frac{t_f}{t_i} + a\right)$, wherein $a$=approximation integral, $t_f$=estimated life time, and $T_f$=failure temperature for a given value of conversion. Figure 8 plots the estimated endurance (lifetime) vs. application temperature in air for both commercial Borclean PP and PP-HP-L-1 with 1 wt% polymer weight loss, assuming this weight loss level is acceptable in the application. It is clear that PP-HP-L-1 polymer shows much higher endurance than all commercial PP products in the whole elevated temperature range. The perpendicular line in Figure 8 indicates that the material lifetime for Borclean PP is about 10 days under 140°C in air. On the other hand, the lifetime of PP-HP-L-1, under the same temperature oxidative conditions, is much greater than that of the Borclean PP. It is clear that PP-HP-L-1 polymer shows much higher endurance than all commercial PP products in the whole elevated temperature range. The perpendicular line in Figure 8 indicates that the material lifetime for Borclean PP is about 10 days under 140°C in air. On the other hand, the lifetime of PP-HP-L-1, under the same temperature, is about 100 days. The four-order increase in endurance is astonishing, which clearly reinforces the idea of PP-bonded HP-L groups with the combination chemical and physical protections, not only preventing PP chain from thermo-oxidative degradation but also forming a crosslinking (3-D) network structure. The experimental results raise the strong possibility that this new PP-HP-L polymer may address the concern of a thermal and oxidative stability (aging issue) of PP polymer operated at elevated temperature conditions.

Conclusion

This study investigates two new functional polypropylene (PP-HP) polymers, containing two type hindered phenol (HP antioxidant) moieties homogeneously distributed along the polymer chain. Both PP-HP polymer structures provide an ideal mechanism to introduce suitable concentration of antioxidants that are homogeneously distributed in the PP matrix to provide long-term protection of PP products under severe application conditions. Evidently, the PP-HP-L polymers with two methylene unit spacer (HP-L moiety) show significantly better thermal/oxidative stability than the corresponding PP-HP-S copolymers (without spacer). All experimental results support the oxidation/coupling mechanism of HP-L moieties in PP-HP-L polymer, which not only offer the effective antioxidant protection for PP chains but also form a cross linked PP network structure. Meanwhile, PP-HP-S can only provide one hydrogen donation during the PP protection process. In other words, instead of weakening mechanical strength in most commercial PP products, PP-HP-L polymers become stronger materials upon exposure to high temperature oxidative conditions. They are suitable for applications that require constant high temperatures (>100°C) conditions. This work also opens a new approach in designing new high temperature polymers.

Acknowledgments

The authors gratefully acknowledge the financial support of this work through a grant from ABB.

References

1. Emanuel NNM, Buchachenko AL (1987). Chemical physics of polymer degradation and stabilization. VSP 1.
2. Al-Malaika S (1989) Effects of antioxidants and stabilizers. Pergamon Press plc Comprehensive Polymer Science 6: 539-578.
3. Billingham NC, Calved PD (1983) An Introduction-Degradation and Stabilization of Polyelectroins.
4. Cook CD, Woodworth RC (1953) Oxidation of hindered phenols II The 2, 4, 6-tri-i-butylnphenox radical. Journal of the American Chemical Society 75: 6242-6244.
5. Tobolsky AV, Nortin PM, Frick NH, Yu H (1964) On the mechanism of autodestruction of three vinyl polymers: Polypropylene, ethylene-propylene rubber, and poly (ethyl acrylate) J Am Chem Soc 86: 3925-3930.
6. Scheirs J, Pospisil J, O’Connor MJ, Bigger SW (1996) Characterization of conversion products formed during degradation of processing antioxidants, pp: 359-374.
7. Stillton GH, Sawyer DW, Hunt CK (1945) The hindered phenols. J Am Chem Soc 67: 303-307.
8. Cirillo G, Lemma F (Eds.) (2012) Antioxidant Polymers: Synthesis, Properties, and Applications. John Wiley & Sons.
9. Wilen CE, Auer M, Strandén J, Näsman JH, Rotzinger B, et al. (2000) Synthesis of novel hindered amine light stabilizers (HALS) and their copolymerization with ethylene or propylene over both soluble and supported metalloene catalyst systems. Macromolecules 33: 5011-5026.
10. Menichetti S, Vigliani C, Ligouri F, Cigliati C, Boragno L, et al. (2008) Ethylene-based copolymers with tunable content of polymerizable hindered phenols as nonreleasing macromolecular additives. Journal of Polymer Science Part A: Polymer Chemistry 46: 6393-6406.
11. Wu W, Zeng X, Li H, Lai X, Li F, et al. (2014) Synthesis and characterization of a novel macromolecular hindered phenol antioxidant and its thermo-oxidative aging resistance for natural rubber. J Macromol Sci Part B: Phys 53: 1244-1257.
12. Wilen CE, Nasman JH (1994) Polar Activation in Copolymerization of Propylene and 6-tert-Butyl-[2-[2-[1, 1-dimethylhept-6-enyl]-4-methylphenol over a Racemic [1, 1’-Dimethylsilylethylene] bis [ 1. 5-4, 5, 6, 7-tetrahydro-1-indeny][] zirconium Dichloride/Methyllalumoxane Catalysit System. Macromolecules 27: 4051-4057.
13. Wilen CE, Lutfikhedde H, Hjertberg T, Näsman JH (1996) Copolymerization of Ethylene and 6-tert-Butyl-2-(1, 1-dimethylhept-6-enyl)-4-methylphenol over Three Different Metallicene-Alumoxane Catalyst Systems. Macromolecules 29: 8569-8575.

14. Auer M, Nicolas R, Rosling A, Wilen CE (2003) Synthesis of novel di-α-tocopherol-based and sterically-hindered-phenol-based monomers and their utilization in copolymerizations over metallocene/MAD catalyst systems. A strategy to remove concerns about additive compatibility and migration. Macromolecules 36: 8346-8352.

15. Zhang Y, Li H, Zhang Y, Li Q, Ma Z, et al. (2014) Synthesis and Properties of Polyethylene-Bound Antioxidants. Macromol Chem Phys 215: 763-775.

16. Kim TH, Kim HK, Oh DR, Lee MS, Chae KH, et al. (2000) Melt free-radical grafting of hindered phenol antioxidant onto polyethylene. J Appl Polym Sci 77: 2968-2973.

17. Munteanu D, Cusniderik C (1991) Polyethylene-bound antioxidants. Polymer degradation and stability 34: 295-307.

18. Dolatkhani M, Cramail H, Defieux A, Santos JM, Ribeiro MR, et al. (2003) Functionalisation of Polyolefins: Grafting of Phenol Groups on Olefin/S, 7-Dimethylocta-1, 6-diene Copolymers. Macromol Chem Phys 204: 1889-1897.

19. Wu W, Zeng X, Li H, Xie H (2015) Synthesis and antioxidative properties in natural rubber of novel macromolecular hindered phenol antioxidants containing thiocarbonate and urethane groups. Polymer Degradation and Stability 111: 232-238.

20. Kim TH, Oh DR (2004) Melt grafting of maleimides having hindered phenol antioxidant onto low molecular weight polyethylene. Polym Degrad Stab 84: 499-503.

21. Kim TH (2004) Melt free-radical grafting of maleimides with hindered phenol groups onto polyethylene. J Appl Polym Sci 94: 2117-2122.

22. Chung TM (2002) Functionalization of polyolefins. Academic press.

23. Chung TC (2002) Synthesis of functional polyolefin copolymers with graft and block structures. Prog Polym Sci 27: 39-85.

24. Rodriguez-Perez MA (2005) Crosslinked polyolefin foams: Production, structure, properties, and applications. Adv Polym Sci 184: 97-126.

25. Appleby RW, Busfield WK (1994) Post-gamma irradiation cross-linking of polyethylene tape by acetylene treatment. J Mater Sci 29: 227-231.

26. Chodák I (1995) Properties of crosslinked polyolefin-based materials. Prog Polym Sci 20: 1165-1199.

27. Zhu Y, Yoon HG, Suh KS (1999) Electrical properties of silane crosslinked polyethylene in comparison with DCP crosslinked polyethylene. IEEE Trans Dielectr Electr Insul 6: 164-168.

28. Taddi P, Affatato S, Fagnano C, Toni A (2006) Oxidation in ultra-high molecular weight polyethylene and cross-linked polyethylene acetalube cups tested against roughened femoral heads in a hip joint simulator. Biomacromolecules 7: 1912-1920.

29. Pollet P, Liotta CL, Eckart CA, Verma M, Nixon E, et al. (2011) Radical-mediated graft modification of polyethylene models with vinyltrimethoxysilane: a fundamental study. Ind Eng Chem Res 50: 12246-12253.

30. Rijke A, Mandelmink L (1971) Irradiation of Linear Polyethylene. Partitioning between Sol and Gel. Macromolecules 4: 594-599.

31. Mitsui H, Hosoi F, Kagiya T (1972) Acceleration of Fluorine-Containing Monomer-Acetylene System for the γ-Radiation-Induced Cross-Linking of Polyethylene. Polymer Journal 3: 108-110.

32. Onishi H, Kuno M, Tsuji E, Fujisawa A (1997) The optimum dose of gamma radiation-heavy doses to low wear polyethylene in total hip prostheses. J Mater Sci Mater Med 8: 11-18.

33. Shen FW, McKelvey HA, Salovey R (2001) Crosslinking of polyethylene for low wear using radiation and thermal treatments. US Patent 6,228,900.

34. Miller AA (1960) A kinetic analysis for the free-radical crosslinking of saturated polymers. J Polym Sci 42: 441-454.

35. Bartof J, Lazar M (1967) Intractions of Macroradicals in Polyethylene-Polyethylene Blends. J Polym Sci Part C: Polym Symp 16: 361-368.

36. De Boer AP, Pennings AJ (1976) Polyethylene networks crosslinked in solution: preparation, elastic behavior, and oriented crystallization. I. Crosslinking in solution. J Polym Sci Polym Phys Ed 14: 187-210.

37. Phillips PJ, Lambert WS (1990) Regime transitions in a non-reptating polymer: crosslinked linear polyethylene. Macromolecules 23: 2075-2081.

38. Shen FW, McKelvey HA, Salovey R (1996) Irradiation of chemically crosslinked ultrahigh molecular weight polyethylene. J Polym Sci Part B: Polym Phys 34: 1063-1077.

39. Akutsu S, Isaka T, Ishioka M (1981) Process for producing electric conductors coated with crosslinked polyethylene resin. US Patent 4,297,310.

40. McCormick JA, Royer JR, Hwang CR, Khan SA (2000) Tailored rheology of a metallocene polyolefin through silane grafting and subsequent silane crosslinking. J Polym Sci Part B: Polym Phys 38: 2468-2479.

41. Shieh YT, Chuang HC, Liu CM (2001) Water crosslinking reactions of silane-grafted polyethylene blends. J Appl Polym Sci 81: 1799-1807.

42. Busfield WK, O'Donnell JH (1979) Effects of gamma radiation on the mechanical properties and crystallinity of polypropylene film. Eur Polym J 15: 379-387.

43. Kunert KA, Sozyrliksa H, Piliwenski N (1981) Structural investigation of chemically crosslinked low density polyethylene. Polymer 22: 1355-1360.

44. Ruggeri G, Agliotta M, Petragrani A, Ciardelli F (1983) Some aspects of polypropylene functionalization by free radical reactions. Eur Polym J 19: 863-866.

45. Lazo M, Rado R, Rychly J (1990) Crosslinking of polyolefins. Polymer Physics 149-197.

46. Zhang G, Nam C, Chung TM, Petersson L, Hillborg H (2017) Polypropylene Copolymer Containing Cross-Linkable Antioxidant Moieties with Long-Term Stability under Elevated Temperature Conditions. Macromolecules 50: 7041-7051.

47. Lu B, Chung TC (2000) Synthesis of maleic anhydride grafted polyethylene and polypropylene, with controlled molecular structures. Journal of Polymer Science Part A: Polymer Chemistry 38: 1337-1343.

48. Jagur-Grodzinski J (1992) Modification of polymers under heterogeneous conditions. Progress in polymer science 17: 361-415.

49. Zhang G, Li H, Antensteiner M, Chung TM (2015) Synthesis of functional polypropylene containing hindered phenol stabilizers and applications in metalized polymer film capacitors. Macromolecules 48: 2925-2934.

50. Neises B, Steglich W (1978) Simple method for the esterification of carboxylic acids. Angewandte Chemie International Edition 17: 522-524.

51. Kozlowski RR, Gallagher TK (1997) A practical guide to the identification of monomeric plasticizers in flexible PVC compounds. Journal of Vinyl and Additive Technology 3: 249-255.

52. Vasconcelos GDC, Mazur RL, Ribeiro B, Botelho EC, Costa ML (2014) Evaluation of decomposition kinetics of poly (ether-ether-ketone) by thermogravimetric analysis. Materials Research 17: 227-235.