

Journal of Material Sciences & Engineering

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

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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 chaindegradation 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

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Received September 20, 2017; Accepted November 14, 2017; Published November 24, 2017

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

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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]. Cross linked 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 (y-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 O_2 and moisture sensitive manipulations were carried out inside an argon-filled dry box. 3,5-Bis(tert-butyl)-4-hydroxy benzoic

4-N,N-dimethylaminopyridine, 1-(3-dimethylaminopropyl)-3ethylcarbodiimide, 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 antioxidant46 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- d_2 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 decahydronaphthalene (Decalin) dilute solution at 135°C with a Cannon-Ubbelohde viscometer. The viscosity molecular weight was calculated by the Mark-Houwink equation: $[\eta] = KM_v^{\alpha}$ where K=1.05 \times 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 μ m. 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 W_i . 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

acid, 3,5-bis(tert-butyl)-4-hydroxyphenylpropionic acid (Ciba),

weighted to get W_2 . The gel content was calculated by the difference between the two weights. Gel Content= $(W_1 - W_2)/W_1 \times 100\%$.

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)-4hydroxyphenylpropionic acid, were carried out in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) and 4-N,Ndimethylaminopyridine (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 noncrosslinkable 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)-4hydroxy 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 CH₂-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 CH₂-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 CH₂-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.



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Figure 1: H NMR spectra of (a) PP-OH with 1 mol	% OH content and (b) the corresponding PP-HP	P-L and (c) PP-HP-S copolymers.
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Polymer	[HP] (mol%)	M _v ª (×10⁻³ g/mol)	Т _m ^ь (°С)	∆H ^ь (J/g)	Т _с ь (°С)
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

^aEstimated by intrinsic viscosity of polymer/decalin dilute solution at 135°C.

^bDetermined by DSC curves at a heating rate of 20°C/min.

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 15C 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



Figure 2: The comparison of TGA curves (10C/min) measured in air, including (a) general grade PP, (b) capacitor grade PP (Borclean), (c) PP-HP-S polymer with 1 mol% of HP-S groups, and (d) PP-HP-L polymers with 1 mol% HP-L groups.



temperature for 24 h in air).

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 UVvis 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



Figure 4: Gel content test of x-PP-HP-L (1 mol% HP-L) with different heating conditions. Gel content is the insoluble portion after refluxing in xylene for 2 h. (a) Gel content as a function of temperatures (Heating at different temperatures for 24h under air condition). (b) Gel content versus time, heating treatment at 210°C in air.

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



(general-grade and capacitor-grade) and two PP-HP copolymers with 1 mol% of HP-S and HP-L groups, respectively, under similar heating conditions. The general-grade commercial PP polymer shows a rapid decomposition after heating the sample at 190°C in air for about 50 minutes. The stable time is significantly shortened to about 10 minutes at 210°C. The protection time is just enough for melt processing. The capacitor-grade Borclean PP shows slightly better endurance, about 300 minutes at 190°C, but only 20 minutes at 210°C. On the other hand, both PP-HP polymers (1 mol% HP content) shows significantly better performance, especially PP-HP-L polymer exhibiting a dramatic increase in thermo-oxidative stability. After constant heating at 190°C in air for 1000 minutes, the PP-HP-L polymer exhibits no-detectable weight loss. At 210°C, the weight loss of PP-HP-L polymer is also negligible.

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 sideby-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 (*Ea*) of each polymer weight loss (conversion during the polymer chain oxidation and degradation reaction), using the equation in ASTM 1877 test $Ea = -(R/b)^* \Delta \log \beta / \Delta (1/T)$; wherein $\Delta \log \beta / \Delta (1/T)$ =slope of the line obtained in Figure 7, β =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



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Figure 6: TGA curves under various heating rates in air for (top) PP (Borclean) and (bottom) PP-HP-L-1 copolymer (1 mol% HP-L content).



Figure 7: Log heating rate constant vs. inverse temperature kinetics plot for various conversions (weight loss) of (top) PP (Borclean) and (bottom) PP-HP-L-1 (1 mol% HP-L content).

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_n) with the

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	

Table 2: Activation energy in polymer weight loss for (a) PP (Borclean) and (b) PP-HP-L-1.



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 (Ea), we can estimate the material endurance time under a specific value of conversion and failure temperature, following the ASTM 1877 equation $T_c = Ea/(2.303 R[log t_c - 1.05])$ $\log{Ea/(R\beta)}+a$]); wherein a=approximation integral, t_i=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 condition, is near 105 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.

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Acknowledgments

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

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