

Synergistic Effect of Phosphite with Fullerene C₆₀ and Fullerenol C₆₀(OH)₂₄ as Antioxidants in Polypropylene^{*}

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Abstract Polypropylene samples with fullerene C₆₀, fullerenol C₆₀(OH)₂₄, 1010, C₆₀/168, C₆₀-OH/168 and 1010/168 as antioxidants were prepared by extrusions. MFR, YI, TGA and OIT of all the samples were tested. According to the results of MFR, during the melt extrusion, fullerene showed excellent stability effect on PP. The antioxidative ability of fullerene was comparable to the traditional antioxidant 1010. The antioxidative ability of fullerenol was not significant in the first extrusion and it accelerated the degradation of PP in the second and the third extrusions. TGA and OIT tests showed that the stability effects of fullerene and fullerenol were slightly lower than antioxidant 1010. In the first time, antioxidant 168 was reported to show great synergistic effects with fullerene and fullerenol as antioxidants, which suggested a simple way to enhance the antioxidative abilities of fullerene and fullerenol.

Keywords: Antioxidant; Degradation; Fullerene; Fullerenol; Polypropylene; Stability.

INTRODUCTION

Recently, fullerene C₆₀ was reported^[1–3] as an efficient radical scavenger. It can delay or inhibit radical reaction, and thus reduce the thermo-oxidative degradation of polymers. For instance, thermo-oxidative tests of polystyrene and polydimethylsiloxane with fullerene as antioxidant demonstrated that C₆₀, C₆₀/C₇₀ and C₇₀ could stabilize the polymers, whose performance was comparable to that of the well-known hindered phenolic stabilizer *n*-octadecyl-β-(4-hydroxy-3,5-di-tert-butyl-phenyl)-propionate (1076)^[4, 5]. The stabilizing effects of fullerenes C₆₀ and C₇₀ were also shown in the thermal and thermo-oxidative degradations of poly(2,6-dimethyl-1,4-phenyleneoxide) and its blends^[6], natural rubber (*cis*-1,4-polyisoprene) and synthetic *cis*-1,4-polyisoprene^[7], poly(methyl methacrylate)^[8] and poly(*n*-alkylacrylate)s^[9]. Fullerenol C₆₀(OH)₂₄, the derivative of fullerene C₆₀, has been proved an efficient radical scavenger in biological systems^[10–15]. While, the antioxidative activity of fullerenol for polymers was not investigated.

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In traditional antioxidant systems for polymers, hindered phenolic, such as [pentaerythritol tetrakis 3-(3,5-ditert-butyl-4-hydroxyphenyl)-propionate] (1010, Fig. 1), was used as main antioxidant and phosphite, such as tri-(2,4-di-tert-butyl)-phosphite (168, Fig. 1), was used as auxiliary antioxidant which showed great synergistic effect with hindered phenolic. These antioxidants were widely used to stabilize polymers, such as polypropylene (PP). PP is used in a wide variety of commodity and commercial applications. However, these kinds of polymeric materials are highly sensitive to degradation processes, due to the numerous tertiary carbon atoms in the structures which are easy to generate carbon radicals under thermal and thermo-oxidative conditions. Therefore, efficient stabilization of PP products with antioxidants is essential to preserve their physical and mechanical properties for long periods. The antioxidative effects of fullerene and fullerenol on polypropylene are still unknown.

In this paper, we first investigated the influence of fullerene C_{60} and its derivative fullerenol $C_{60}(OH)_{24}$ on the thermal and thermo-oxidative degradations of polypropylene and compared with antioxidant 1010. We found that phosphite, such as antioxidant 168, had great synergistic effect with fullerene and fullerenol to stabilize PP. As we know, fullerene and fullerenol are very expensive. The synergistic effect of cheap phosphite means that less consumption of fullerene and fullerenol and less cost. These results are valuable for polymer systems.

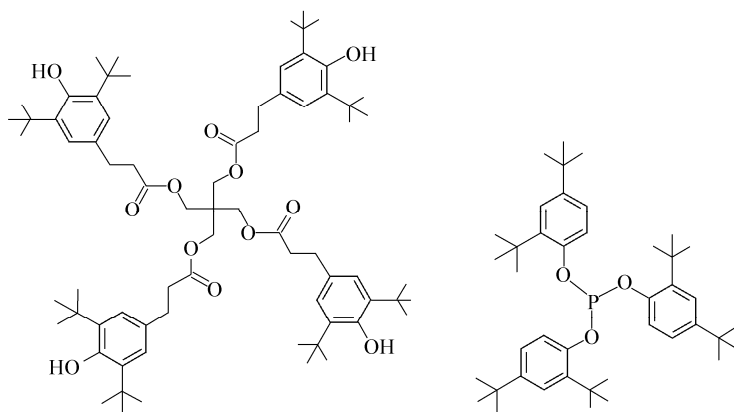


Fig. 1 Antioxidant 1010 (left) and antioxidant 168 (right)

EXPERIMENTAL

Materials

Fullerene C_{60} and fullerenol ($C_{60}(OH)_{24}$, $C_{60}-OH$) were prepared according to the previous reports^[16–19]. Antioxidants 1010, 168 and calcium stearate were supplied by Linyi Sunny Wealth Chemical Co., Ltd. PP particles without any additives were supported by Shenhua Ningxia Coal Industry Group Co., Ltd.

Sample Preparation

PP particles, antioxidants, calcium stearate (300×10^{-6} g/g of PP) were mixed in ratio. The antioxidant composition of each sample is listed in Table 1. The mixture samples were melt extruded three time using twin-screw torque rheometer (Polylab OS, HAAKE). The temperatures of cylinder were: TS1: 205 °C, TS2-TS9: 210 °C, TS10: 200 °C. The screw speed was 100 r/min.

Table 1. The antioxidant composition of each polypropylene sample

No.	Antioxidants	Content $\times 10^6$ (g/g)
1	—	—
2	1010	400
3	C_{60}	400
4	$C_{60}-OH$	400
5	1010/168	400/800
6	C_{60} /168	400/800
7	$C_{60}-OH$ /168	400/800

Measurements

Melt flow rate (MFR) of polypropylene samples was tested at 230 °C, 2.16 kg after 4 min preheating. Yellow index (YI) of polypropylene sample was tested by automatic colorimeter (Beijing Kangguang Instrument Co., Ltd). Thermogravimetric analysis (TGA) was performed under air atmosphere on a Perkin-Elmer TGA 7 series instrument from 50 °C to 600 °C at a heating rate of 20 K/min. Oxidation induction time (OIT) was tested by differential scanning calorimetry (DSC) on a Q2000 instrument in the temperature range of 60 °C to 200 °C at a heating rate of 20 K/min under nitrogen atmosphere at 20 mL/min. The samples were at 200 °C for 5 min and then nitrogen was changed to oxygen (20 mL/min). The test was stopped after thermo-oxidative degradation for 2 min.

RESULTS AND DISCUSSION

MFR Analysis

During the melt extrusion process, polypropylene polymer chains are thermo-oxidatively degraded and broken, resulting in the decrease of molecular weight and increase of melt flow rate (MFR). Therefore, MFR is one of the most important parameters to indicate the thermo-oxidative stability. In general, PP is stabilized by hindered phenolic antioxidant such as 1010 and phosphite auxiliary antioxidant such as 168. Therefore, we first investigated the processing stabilities of PP with 400×10^{-6} g/g of fullerene or fullerenol, by comparison with the performance of antioxidant 1010. And then the synergistic effect of antioxidant 168 with the above three antioxidants was tested. The MFR results after three extrusion processes were listed in Table 2.

It can be seen from Table 2 that the MFR values of PP samples increase with the increase of extrusion times. Compared with the PP sample without any antioxidant (sample 1) with MFR from 13.9 g/10 min to 17.5 g/10 min, the MFRs of PPs with fullerene are lower (sample 3, 9.1 g/10 min to 13.3 g/10 min). Fullerene shows thermo-oxidative stability effect on PP melt processing and its activity is comparable to that of antioxidant 1010 (sample 2, 10.2 g/10 min to 11.5 g/10 min). Under same condition, fullerenol shows slight antioxidative activity for the first extrusion (sample 4, 12.0 g/10 min). While during the second and third extrusions (18.8 g/10 min and 22.2 g/10 min), there is a faster increase of MFR than that of PP sample without any antioxidant (sample 1), which indicates the acceleration of the thermo-oxidative reaction.

Generally, phosphite auxiliary antioxidant has dramatically synergistic effect with hindered phenolic antioxidant. It can reduce hydroperoxide ROOH generated by oxidation reaction to stable ROH. The synergistic effect can be seen by the comparison of sample 5 with sample 2 in Table 2. With the addition of 168, MFR of PP decreases greatly. Similar synergistic effect of 168 with fullerene (sample 6) is shown in Table 2, which has not been reported yet. The antioxidative ability of C₆₀/168 is comparable to 1010/168. Antioxidant 168 has synergistic effect with fullerenol as well, although the antioxidative performance of C₆₀-OH/168 is not as good as C₆₀/168. These results mean that the consumptions of expensive fullerene and fullerenol could be reduced. It is valuable for the applications of fullerene and fullerenol in polymer systems.

Table 2. MFR tests of PP with fullerene and fullerenol as antioxidants

No.	MFR (g/10 min)		
	MFR 1	MFR 2	MFR 3
1	13.9	16.5	17.5
2	10.2	10.9	11.5
3	9.1	11.8	13.3
4	12.0	18.8	22.2
5	6.7	7.5	9.1
6	7.7	8.7	10.3
7	9.9	12.7	19.3

YI Analysis

In hindered phenolic/phosphite antioxidant system, when radical is scavenged, hindered phenolic will change to quinone compound which is yellow. Thus, the yellow index (YI) also acts as an index for the antioxidative ability of antioxidant. PP particles, antioxidant 1010 and 168 are white, fullerene is black and fulleranol is dark brown, as a result, the PP samples with fullerene or fulleranol show high YIs. The antioxidant 168 shows synergistic effect in YI for antioxidant 1010 and fullerene. The results are listed in Table 3.

Table 3. YI tests of PP with fullerene and fulleranol as antioxidants

No.	YI		
	YI 1	YI 2	YI 3
1	0.00	3.86	6.68
2	3.54	6.60	9.72
3	40.34	64.29	84.51
4	10.78	16.49	18.99
5	2.58	5.27	8.27
6	25.04	58.47	83.86
7	12.12	20.23	21.26

TGA Analysis

The thermo-gravimetric rate of polymer samples in air can also characterize the stabilizing ability of antioxidant. Samples 1–7 were tested by TGA in air. The results are shown in Fig. 2. The initial degradation temperature of the samples are listed in Table 4. It can be seen from Fig. 2 and Table 4 that the PP samples without additives (sample 1) and with 1010 (sample 2), C₆₀-OH (sample 4) and C₆₀-OH/168 (sample 7) have similar initial degradation temperature at about 272 °C, which is higher than that of C₆₀ (sample 3) and C₆₀/168 (sample 6, about 267 °C) and lower than that of 1010/168 (sample 5 about 279.8 °C). In the TGA testing, fullerene accelerates the thermo-oxidative degradation.

Table 4. The initial degradation temperature (IDT) of PP samples determined by TGA

No.	1	2	3	4	5	6	7
IDT (°C)	272.7	271.9	267.8	272.8	279.8	266.5	273.3

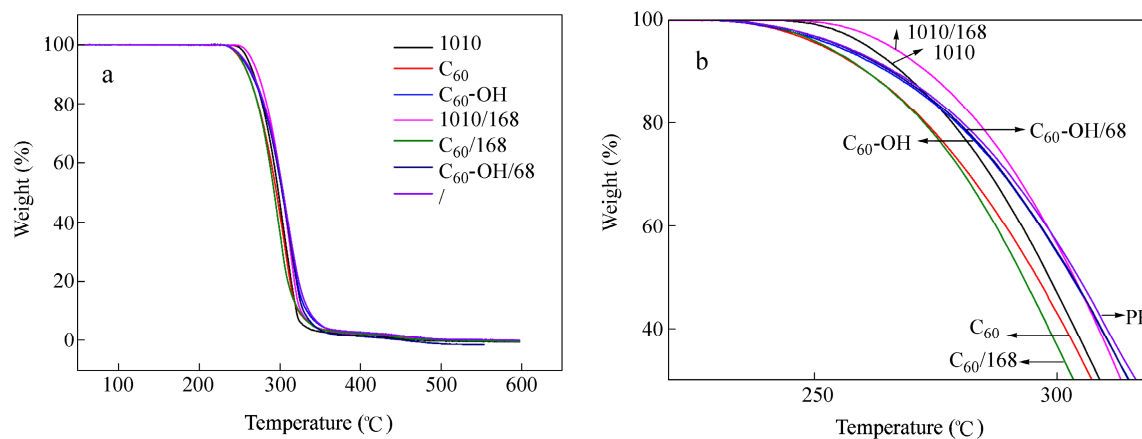


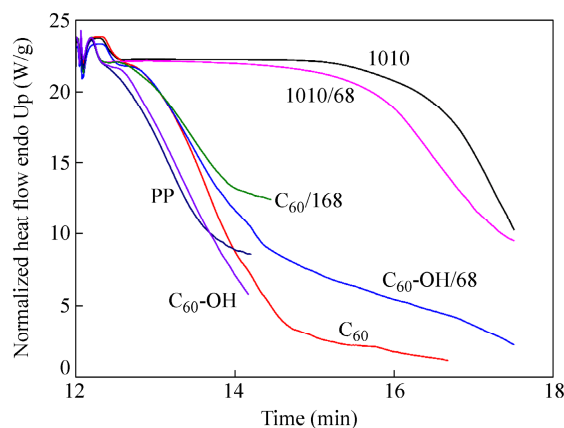
Fig. 2 TGA (a: full, b: partial) curves of PP samples with fullerene and fulleranol as antioxidants

OIT Analysis

All OITs of PP samples were tested by DSC, and the results are shown in Fig. 3 and Table 5. It can be seen that fullerene and fulleranol can increase the OIT of PP sample from 0.68 min to 1.07 and 1.01 min, respectively, while antioxidant 1010 greatly increases the OIT of PP sample from 0.68 min to 4.37 min. However, the addition of antioxidant 168 decreases the OIT of PP samples.

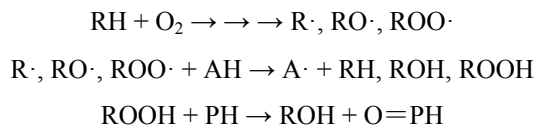
Table 5. The OIT of PP samples determined by DSC

No.	1	2	3	4	5	6	7
OIT (min)	0.68	4.37	1.07	1.01	3.81	0.87	0.64

**Fig. 3** OIT testing curves of PP samples with fullerene and fullerenol as antioxidants by DSC

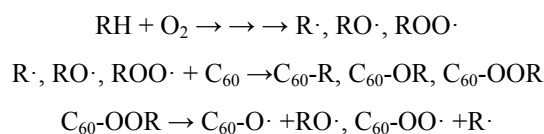
Mechanism Discussion

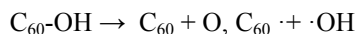
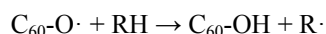
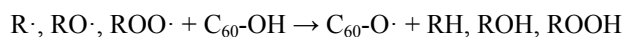
The antioxidative mechanism of hindered phenolic antioxidant and phosphite auxiliary antioxidant are usually believed as Scheme 1 shows^[20], where RH is the polymer, AH is hindered phenolic antioxidant, PH is phosphite auxiliary antioxidant. Under thermal, light and/or oxygen, polymers generate R·, RO· and ROO· radicals, which can react with phenolic antioxidant to produce stable A· radical, RH and ROH. ROOH could react with phosphite to produce stable ROH and O=PH.

**Scheme 1** The antioxidative mechanism of hindered phenolic antioxidant and phosphite auxiliary antioxidant

According to the reports^[1–15], the antioxidative mechanism of C₆₀ and C₆₀-OH is similar and is believed as Scheme 2 shows. The C=C double bonds in C₆₀ could react with R· and RO· radicals to generate C₆₀-R and C₆₀-OR. ROOH generated here could react with phosphite. As a result, phosphite shows great synergistic effect with C₆₀ and C₆₀-OH. To our knowledge, the reaction between C₆₀ and ROO· radical has not been reported. Based on the reaction of C₆₀ and RO·, we hypothesize that C₆₀ could react with ROO· radical to produce C₆₀-OOR which is unstable and will decrease new radicals. That is, C₆₀ could not block efficiently the ROO· radical, which may cause the less antioxidative capacity of C₆₀ than 1010.

According to the mechanism of hindered phenolic, we thought the antioxidative mechanism of C₆₀-OH has another path which is similar to that of hindered phenolic as Scheme 2 shows. However, the C₆₀-O· maybe is not stable enough under high temperatures and initiates new radical reactions, which can be proved by the several extrusion tests as mentioned above. In the other hand, it was reported that fullerenol could generate reactive oxygen species under both visible and ultraviolet light sources^[21]. C₆₀-OH may release reactive oxygen species in the thermo extrusion process, which accelerates the thermo-oxidative reaction of PP.





Scheme 2 The antioxidative mechanism of C_{60} and $C_{60}\text{-OH}$

CONCLUSIONS

The antioxidative effects of fullerene C_{60} and its derivate fullerenol $C_{60}\text{-OH}$, as well as the synergistic effects of antioxidant 168 on melt process of polypropylene were investigated. According to the results of MFR, during the melt extrusion, fullerene showed excellent stability effect on PP, and the antioxidant 168 showed great synergistic effect. The antioxidative ability of fullerene was comparable to that of the traditional antioxidant 1010. The antioxidative ability of fullerenol was not significant in the first extrusion and accelerated the degradation of PP in the second and the third extrusions. TGA and OIT tests showed that the stability effects of fullerene and fullerenol were slightly lower than those of antioxidant 1010.

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