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Structure effect of benzofuranone on the antioxidant activity in polypropylene

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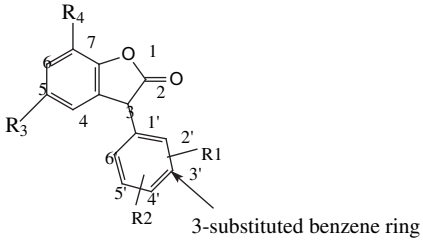
ABSTRACT

This work deals with the antioxidant activity of benzofuranone compounds in polypropylene (PP). The antioxidant activities of ten benzofuranone compounds in PP were compared using melt flow index (MFI) values of PP stabilized by benzofuranone compounds primarily. The results show: firstly, that the increase of electron donating ability of substituent in 3-substituted benzene ring is beneficial to the improvement of antioxidant activity. Secondly, it has been verified that the steric hindrance of 2′-position substituent can weaken the antioxidant activity of benzofuranone. But when 2′-position substituent forms a hydrogen bond with 3-position reactive hydrogen, the steric hindrance is offset efficiently. Finally, the methyl and *tert*-butyl groups in the 5 and 7-position of parent benzene ring do not affect the antioxidant activity of benzofuranone compounds in PP obviously.

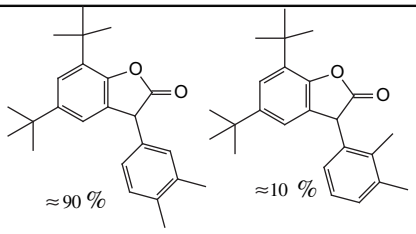
1. Introduction

It was reported that 3-aryl-benzofuranone compounds display strong scavenging ability to oxygen-centered and carbon-centered radicals [1]. Irganox HP-136, a new mixture of 3-aryl-benzofuranone, has been used as an effective antioxidant to increase the stability of hydrocarbon polymers in the melt processing at high temperature [2].



Generanl Structure of Benzofuranone

However, there have been few reports on the structure effect of benzofuranone compounds on the antioxidant activity in polymers to date, which results in the application of benzofuranone compounds being limited [3]. Furthermore, the antioxidant mechanism research shows that 2′-position substituent prevents the attack of 3-position reactive hydrogen toward radicals, which makes the reaction rate of benzofuranone with radicals lower [4]. As a result, most of the research and applications on this kind of antioxidant are only limited to the structures without 2′-position substituent [5,6], although lots of benzofuranone compounds with different chemical structures have been synthesized over the past years [7,8]. Recently, we studied the structure effects of benzofuranone compounds on the scavenging ability to 2,2-Diphenyl-1-picrylhydrazy (a.b.DPPH) radical, and found that benzofuranone compound with 2′-position hydroxyl group has stronger DPPH radical scavenging activity compared to other compounds [9]. Based on our findings, we propose that the benzofuranone compound will display good antioxidant activity in polymers. In order to confirm our proposal, further research is needed.



Irganox HP-136

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In this work, the structure effects of 3-aryl-benzofuranone compounds on the antioxidant activity in PP were studied using multiple extrusion methods. The relationship between the structures and the antioxidant activity in polypropylene is established, which will help people choose and design this kind of antioxidant according to different demands efficiently in the future.

2. Experimental

2.1. Materials

PP (T30S) powder not stabilized by antioxidant was donated by Jiujiang Petrochemical Limited Company.

Benzofuranone compounds were synthesized in our lab, the process is as follows:

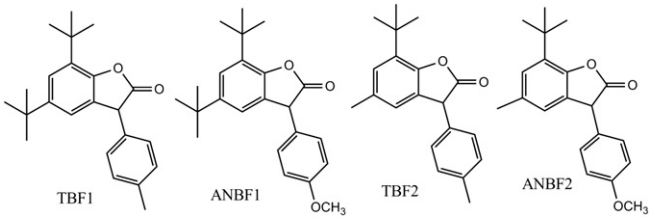
Preparation of 5,7-di-*tert*-butyl-3-(4-methylphenyl)3H-benzofuran-2-one (compound TBF1): a mixture of 20.5 g of 2,4-di-*tert*-butylphenol, 12 ml of 50% aqueous gloxylic acid and 0.05 g of p-toluenesulfonic acid in 30 ml of 1,2-dichloroethane was refluxed under nitrogen for 3 h on a water separator. Then 0.2 mol of toluene was added and the mixture was refluxed for 1 h. The excess toluene was removed on a vacuum rotary evaporator. Crystallization of the residue from 50 ml of methanol yielded white power [10].

In analogy to the preparation of compound TBF1, other compounds were prepared from other 2,4-di-substituted-phenol, di-methylbenzene, as well as anisole. The structures were fully characterized in references [11] and [12]. The structures of benzofuranone compounds were shown in Schemes 1, 2 and 4, respectively.

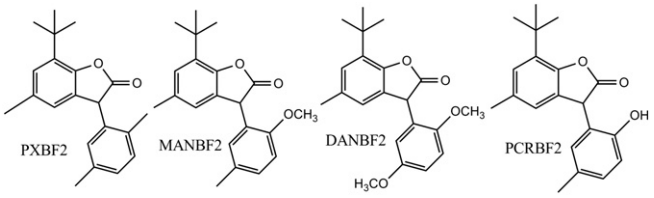
2.2. Sample preparation

The great hydrogen donating ability is the first character of chain-breaking antioxidant and the antioxidant activity has a very close relationship with the concentration of reactive hydrogen of antioxidant molecule [13]. Because of the difference in the molecular weight of benzofuranone compounds, the molar concentration of antioxidant was chosen when antioxidant was added in PP. In the past several years, we ever studied the effect of benzofuranone concentration on the anti-oxidation in PP. It was found that anti-oxidation increased obviously when the concentration was in the range of 1 mmol/Kg to 3 mmol/Kg, and that anti-oxidation displayed no evident change when concentration was larger than 3 mmol/Kg. In order to get better anti-oxidation at lower concentration, 3 mmol/Kg benzofuranone compounds were added in PP.

The PP powder and different concentrations of benzofuranone compounds were mixed using a mixer at low and high speed, respectively, and then the mixtures were extruded multiply in an SHJ-20B twin screw extruder having cylinder diameter of 20 mm and a length of 400 mm at 100 rpm (Nanjing Giant Machinery Company, China). The first extrusion was carried out with PP as powders and the remainders were carried out with PP as pellets.



Scheme 1. Chemical structures of TBF1, TBF2 and other benzofuranone compounds.



Scheme 2. Chemical structures of PXBF2, MANBF2, DANBF2 and PCRBF2.

Irganox HP-136, a new mixture of 3-aryl-benzofuranone, was used to provide excellent processing stability in PP. When the extrusion temperature was at 250 °C, the superior control of melt flow and low color in PP appeared simultaneously [14]. Based on the results, the temperature of 250 °C was chosen in this work.

2.3. Measurements

MFI values were measured using an RL-11B melt flow indexer at an extrusion temperature of 230 °C with a 2.16 Kg load using a small die (Φ 2.095 mm) according to ASTM D-1238.

FT-IR spectra were recorded on HI503701 FT-IR (Bruker Optics, Germany). The pieces of PP samples incorporated by different benzofuranone compounds were pressed into thin films at about 170 °C and then the thin films were to be analyzed. The samples were scanned in absorbance mode from 400 to 4000 cm^{-1} by signal averaging 32 scans at a resolution of 4 cm^{-1} at 250 °C and their spectra were recorded every other 5 min. The extent of oxidation of PP was evaluated by determining the relative amount of carbonyl group and double bond. The carbonyl group observed at 1720 cm^{-1} was normalized by dividing by an observed peak at 2720 cm^{-1} (carbonyl index = $A_{1720\ cm^{-1}}/A_{2720\ cm^{-1}}$). The double bond is observed at 1650 cm^{-1} and was normalized by dividing by an observed peak at 2720 cm^{-1} (double bond index = $A_{1650\ cm^{-1}}/A_{2720\ cm^{-1}}$) [15].

Thermal analysis was performed on a TA SDT-Q600. 20 mg of benzofuranone samples were placed in a sample pan and heated from 50 to 400 °C at 10 °C/min in nitrogen atmosphere.

3. Results and discussion

3.1. Effects of substituent in 3-substituted benzene ring

For phenol antioxidants, the presentation of oxygen para reactive hydroxyl group has been found to stabilize the phenoxyl radical through the delocalization of unpaired electrons of oxygen over benzene ring. In addition to this, the substituent having double bond or unpaired electrons such as alkoxy allows strong electron delocalization [16]. As a result, when the substituents having strong electron donating ability are incorporated in antioxidant molecules, the antioxidant activity will be improved obviously [13,17–19]. Thus, in this work, the ANBF1 and ANBF2 (The structures were shown in Scheme 1), which contain stronger electron donating substituent —4′-position methoxyl group— compared to methyl group, were designed, and the antioxidant activity in PP were compared with TBF1 and TBF2 having 4′-position methyl group using MFI values and FT-IR of PP stabilized by those benzofuranone compounds. The effect of electronic property of substituents in the 4′-position on the antioxidant activity was investigated. The results are shown in Figs. 1 and 2, respectively.

Compared the (a) and (b) of Fig. 1, it can be found that the MFI values of PP stabilized by ANBF1 and ANBF2 are smaller than those of PP stabilized by TBF1 and TBF2, which indicates that the presentation of methoxyl group is beneficial to the improvement of