

Rapid Determination of Antioxidant Irganox 1076 in Polyethylene

Qiukai Zheng¹, Dan Hu², Jingjing Fan^{3,*}

¹ Chemistry & Chemical and Environmental Engineering College, Weifang University, Weifang, Shandong 26106 China

² Qidong Animal Disease Prevention and Control Center, Qidong, Jiangsu 226200 China

³ Biological and Agricultural Engineering College, Weifang University, Weifang, Shandong 261061 China

Abstract. A method was established to quickly determine the content of antioxidants in polyethylene by Fourier transform infrared spectroscopy. By analyzing the FTIR spectra of the antioxidant Irganox 1076 and PE, the characteristic peak of the antioxidant Irganox 1076 in PE was determined to be the absorption peak at 1738cm⁻¹. According to the standard curve of the antioxidant, the content of the antioxidant had a good linear relationship with the absorption intensity of its characteristic peak, and the linear regression coefficient of the equation was 0.97363. The relative error was less than 7%. The method is accurate and reliable, allowing for rapid quantitative analysis of trace antioxidant content in polyolefin.

1. Introduction

Polyolefin is widely used in the fields of household appliances, packaging and building materials because of its rich source of raw materials, low production cost and good comprehensive performance. It has become an indispensable material in human life and production and occupies an important position in the national economy [1]. Polyethylene (PE) is a kind of polyolefin which has been widely used in many fields. However, polyolefin in the preparation, storage and application is inevitably affected by factors such as heat, light, oxygen, heavy metal ions and mechanical shear [2], resulting in discoloration and mechanical physical properties degradation [3]. Its products turn yellow, hard and brittle, and even completely lose their use value [4, 5]. In order to inhibit its oxidative degradation, antioxidants are generally added to polyolefins [6, 7]. Antioxidants can be divided into main antioxidants, auxiliary antioxidants and metal passivators according to different action mechanisms. The main antioxidants are divided into hindered phenol type and hindered amine type according to the chemical structure formula. Among them, hindered amine type antioxidants are heavily polluted and dark in color. They are mostly used in black, dark plastic or rubber products. Auxiliary antioxidants mainly include phosphorus and sulfur antioxidants [8]. When used together with main antioxidants, they play a synergistic role [9]. On the one hand, they decompose the generated peroxide into alcohol compounds [10]; On the other hand, reduce the main antioxidant inactivated by oxidation [11]. Metal passivators form extremely stable complexes with active metal ions to prevent oxidative degradation of polymers [12-14]. Controlling the amount of antioxidants is conducive to improving the quality of polyolefin products, reducing costs and improving economic benefits. Therefore, it is necessary

to establish a simple, rapid and accurate analytical method for determining the content of trace antioxidants in PE. Due to the low antioxidant content in polyolefins, the pretreatment of samples is cumbersome. There are many methods for analyzing the additive content in polyolefins, such as ultraviolet spectrum [15], mass spectrometry [16], nuclear magnetic resonance [17] extraction [18], chromatography [19], thermal analysis [20], infrared spectroscopy [21], and so on. However, these methods have problems such as high cost, long test cycle, and difficult online analysis, which are hard to meet the needs of rapid analysis. Infrared spectroscopy is a simple, fast and accurate analytical method. In this paper, the qualitative and quantitative analysis of irganox 1076, a trace antioxidant in PE, was studied by infrared spectroscopy, which has important practical significance for analyzing the effect and modification of antioxidants in polyolefin.

2. Experimental Section

2.1 Raw materials and auxiliaries

High-density polyethylene (HDPE), GX-103, Hirst, Germany; Irganox 1076, commercial product; toluene, analytical purity.

2.2 Instruments and Equipment

Fourier transform infrared spectrometer (FTIR), Tianjin Gangdong Science and Technology Development Co., Ltd. The wave number of the spectrogram ranges from 4000 to 200 cm⁻¹, the resolution is 4 cm⁻¹, and the data is analyzed with software origin8.0.

* Corresponding author: zqiukai@163.com

2.3 Preparation of samples

The antioxidant Irganox 1076 was weighed with an electronic balance with an accuracy of 0.0001 g, dissolved in toluene, weighed different amounts of the solution and mixed well with PE, processed for 3 min on a hot table at 160°C, and pressed into a sample of a certain thickness with a mold.

3. Results and Discussion

3.1 Determination of characteristic absorption peaks

The antioxidant Irganox 1076, PE and PE samples with 0.8% Irganox 1076 were tested by infrared spectroscopy, and the appropriate absorption peaks were intercepted as shown in Figure 1.

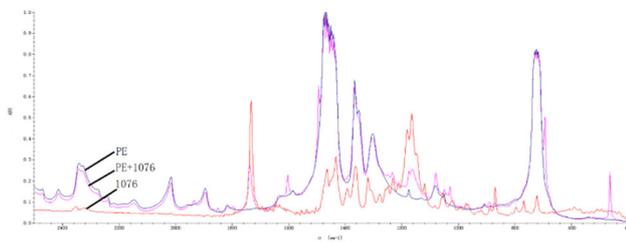


Figure 1. The FTIR curves of Irganox 1076, non-stabilized and stabilized PE with Irganox 1076

It can be seen from Figure 1 that Irganox 1076 has a strong absorption peak at 1738cm⁻¹, there is no strong absorption peak around, and PE has basically no absorption at this wave number. Therefore, the absorption peak at 1738cm⁻¹ is selected as the characteristic absorption peak of antioxidant Irganox 1076 for quantitative analysis. PE samples containing 0.8% Irganox 1076 have a significant absorption peak at the wave number 1738cm⁻¹ without being affected by the PE absorption peak, so it is desirable to take this absorption peak as a characteristic absorption peak of the antioxidant Irganox 1076.

3.2 The drafting of standard curves

The PE and Irganox 1076 solutions were mixed evenly and prepared into standard samples with antioxidant Irganox 1076 content of 0 to 1.0% (0, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, respectively). The specimens were pressed into samples with a thickness of 1 mm by a mold for infrared spectrum test and analysis. The characteristic absorption peaks of Irganox 1076 with different contents are shown in Figure 2.

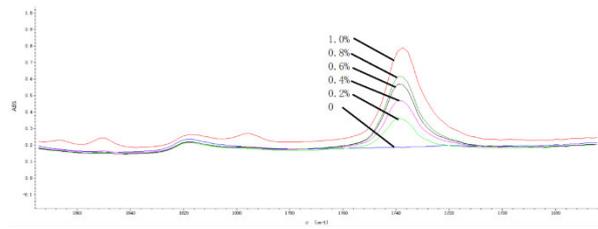


Figure 2. The FTIR curves of PE stabilized with Irganox 1076 in various concentrations at 1738cm⁻¹

As can be seen from Figure 2, the wave number 1738cm⁻¹ absorption peak area increases with the increase of antioxidant content. After baseline correction, the characteristic absorption peak area (A_1) of the antioxidant was calculated using Fourier infrared spectroscopy software. In order to eliminate the effect of sample thickness differences, the characteristic absorption peak of the PE sample needs to be selected as a reference. Comparing the spectra of the three samples in Figure 1, PE has an absorption peak at 2017cm⁻¹, while the antioxidant Irganox 1076 has no absorption peak here, and the absorption peak can be selected here as a reference. After baseline correction, the characteristic absorption peak area of the antioxidant (A_2) is calculated using Fourier infrared spectroscopy software. The mathematical model was established by using Origin8.0 analysis software to obtain the standard curve of A_1/A_2 and its mass fraction, as shown in Figure 3.

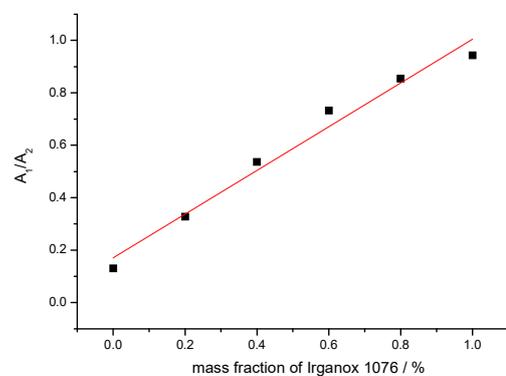


Figure 3. The standard curve of Irganox 1076 contents in PP

It can be seen from Figure 3 that the ratio of the characteristic absorption peak area of antioxidant Irganox 1076 to the reference absorption peak area of PE is positively correlated with the antioxidant content. The fitting equation is $y = 0.17007 + 0.83474x$, and the correlation coefficient of the equation is 0.97363. This indicates that the standard curve has a good correlation.

3.3 Accuracy verification

In order to verify the reliability of the fitting equation, five PE / antioxidant Irganox 1076 samples with different antioxidant contents were prepared for verification. The antioxidant Irganox 1076 characteristic peak absorption peak area and PE reference absorption

peak area were determined, and the ratio was calculated. The antioxidant content was calculated from the fitted equation, and compared with the true value, as shown in Table 1.

Table 1. Accuracy of test results

Sample	Mass Fraction/%		Relative Error /%
	True Value	Measured Value	
PE-1	0.05	0.051	1.30
PE-2	0.25	0.256	2.26
PE-3	0.45	0.479	6.42
PE-4	0.65	0.616	5.20
PE-5	0.85	0.820	3.55

As can be seen from Table 1, the relative errors are within 7%, and the reliability of the fitted equation is high, which basically meets the needs of the actual detection.

4. Conclusion

(1) The quantitative standard curve of the antioxidant Irganox 1076 in the PE/antioxidant Irganox 1076 sample is $y=0.17007+0.83474x$, and the correlation coefficient of the equation is 0.97363;

(2) The relative errors between the measured value and the calculated value of the antioxidant Irganox 1076 in the PE/antioxidant Irganox 1076 samples are less than 7%, and the maximum is 6.42%, which basically meets the needs of actual detection.

Acknowledgments

This work was financially supported by Shandong Provincial Natural Science Foundation ZR2020MC174.

References

- Mei G, Beccarini E, Caputo T, et al. Recent Technical Advances in Polypropylene [J]. *Journal of Plastic Film and Sheeting*, 2009, 25(2): 95 ~ 113.
- In-Jin S, Won C, Jae-Gyu S, et al. Experimental and Analytical Study of the DC Breakdown Characteristics of Polypropylene Laminated Paper with a Butt Gap Condition Considering the Insulation Design of Superconducting Cable [J]. *Japanese Journal of Applied Physics*, 2014, 53(83): 4 ~ 8.
- Wang X, Xing W, Tang G, et al. Synthesis of a Novel Sulfur-bearing Secondary Antioxidant with a High Molecular Weight and its Comparative Study on Antioxidant Behavior in Polypropylene with two Commercial Sulfurbearing Secondary Antioxidants Having Relatively Low Molecular Weight [J]. *Polymer Degradation and Stability*, 2013, 98(11): 2391 ~ 2398.
- Xie J, Xu R, Chen X, et al. Influence of Heat-treatment Temperature on the Structure and Properties of Polypropylene Microporous Membrane [J]. *Polymer Bulletin*, 2015, 73(1): 265 ~ 277.
- Maeda E A, Santos A F, Silva L G A, et al. Chemical, Physical, and Mechanical Properties Evolution in Electron Beam Irradiated Isotactic Polypropylene [J]. *Materials Chemistry and Physics*, 2016, 169: 55 ~ 61.
- Umile G, Spizzirri G C, Nevio Picci and Francesca Iemma. Recent Development in the Synthesis of Eco - Friendly Polymeric Antioxidants [J]. *Current Organic Chemistry*, 2014, 18: 2912 ~ 2927.
- Wang L, Li K, Zhu G, et al. Preparation and Properties of Highly Branched Sulfonated Poly(ether ether ketone)s Doped with Antioxidant 1010 as Proton Exchange Membranes [J]. *Journal of Membrane Science*, 2011, 379(1 ~ 2): 440 ~ 448.
- Pénzes G, Domján A, Tátraaljai D, et al. High Temperature Reactions of an Aryl-alkyl Phosphine, an Exceptionally Efficient Melt Stabiliser for Polyethylene [J]. *Polymer Degradation and Stability*, 2010, 95 (9): 1627 ~ 1635.
- Hassanpour S, Khoylou F. Synergistic Effect of Combination of Irganox 1010 and Zinc Stearate on Thermal Stabilization of Electron Beam Irradiated HDPE/EVA both in Hot Water and Oven [J]. *Radiation Physics and Chemistry*, 2007, 76(11-12): 1671 ~ 1675.
- Kriston I, Pénzes G, Szijjártó G, et al. Study of the High Temperature Reactions of a Hindered Aryl Phosphite (Hostanox PAR 24) used as a Processing Stabiliser in Polyolefins [J]. *Polymer Degradation and Stability*, 2010, 95(9): 1883 ~ 1893.
- Papanastasiou M, McMahon A W, Allen N S, et al. Atmospheric Pressure Photoionization Mass Spectrometry as a tool for the Investigation of the Hydrolysis Reaction Mechanisms of Phosphite Antioxidants [J]. *International Journal of Mass Spectrometry*, 2008, 275(1-3): 45 ~ 54.
- Allen N S, Barcelona A, Edge M, et al. Aspects of the Thermal and Photostabilisation of High Styrene-butadiene Copolymer (SBC) [J]. *Polymer Degradation and Stability*, 2006, 91(6): 1395 ~ 1416.
- Cogen J M, Hilmer A J. Crystal Polymorphism in Antioxidant- metal Deactivator 1,2-bis (3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine[J]. *Polymer Degradation and Stability*, 2008, 93(12): 2193 ~ 2198.
- Morlat-Therias S, Fanton E, Gardette J-L, et al. Photochemical Stabilization of Linear Low-density Polyethylene/clay Nanocomposites: Towards Durable Nanocomposites [J]. *Polymer Degradation and Stability*, 2008, 93 (10): 1776 ~ 1780.
- Métois P, Scholler D, Bouquant J, Feigenbaum A. Alternative test methods to control the compliance of polyolefin food packaging materials with the European Union regulation: the case of aromatic

- antioxidants and of bis(ethanolamine) antistatics based on $^1\text{H-NMR}$ and UV-visible spectrophotometry [J]. *Food Addit Contam*, 1998, 15(1): 100-111
16. Vit A I, Galbraith M N, Hodqkin J H, et al. Quantitative analysis of additives in polyethylene by MID mass spectrometry [J]. *Polym Degrad Stab*, 1993, 42(1): 69 ~ 73
 17. Schilling F C, Kuck V J. Determination of stabilizer concentrations in Polyethylene [J]. *Polym Degrad Stab*, 1991, 31(2): 141 ~ 152
 18. Pinto A M, Taylor L. Evolution of a method for quantitative supercritical fluid extraction 330 antioxidant from high density polyethylene [J]. *J Chromatoga, A*, 1998, 811(1 ~ 2): 163 ~ 170
 19. Thilen M, Shishoo R. Optimization of experimental parameters for the quantification of ploymer additives using SFE/HPLC [J]. *J Appl Polym Sci*, 2000, 76(6): 938 ~ 946
 20. Karlsson K, Assarqren C, Gedde U W. Thermal analysis for the assessment of antioxidant content in polyethylene [J]. *Polym Testing*, 1990, 6(9): 421 ~ 431
 21. Karstang T V, Henriksen A. Infrared spectroscopy and multivariate calibration used in quantitative analysis of additives in high-density polyethylene. *Chemometrics and Intelligent Laboratory Systems* [J]. 1992, 14(1 ~ 3): 331 ~ 339