Rapid Determination of Antioxidant Irganox 1076 in Polyethylene

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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 1738 cm⁻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.

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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℃, 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.

As can be seen from Figure 1, Irganox 1076 has a strong absorption peak at 1738 cm\(^{-1}\), there is no strong absorption peak around, and PE has basically no absorption at this wave number. Therefore, the absorption peak at 1738 cm\(^{-1}\) 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 1738 cm\(^{-1}\) 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.

As can be seen from Figure 2, the wave number 1738 cm\(^{-1}\) 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 2017 cm\(^{-1}\), 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.

As 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>
<thead>
<tr>
<th>Sample</th>
<th>Mass Fraction/%</th>
<th>True Value</th>
<th>Measured Value</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-1</td>
<td>0.05</td>
<td>0.051</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>PE-2</td>
<td>0.25</td>
<td>0.256</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>PE-3</td>
<td>0.45</td>
<td>0.479</td>
<td>6.42</td>
<td></td>
</tr>
<tr>
<td>PE-4</td>
<td>0.65</td>
<td>0.616</td>
<td>5.20</td>
<td></td>
</tr>
<tr>
<td>PE-5</td>
<td>0.85</td>
<td>0.820</td>
<td>3.55</td>
<td></td>
</tr>
</tbody>
</table>

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 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.

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