Infrared Spectroscopy Method for Detecting the Content of Antioxidant Irganox 1076 in Polypropylene

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Abstract. A method for rapid determination of antioxidant Irganox 1076 in polyolefin by Fourier transform infrared spectroscopy was established. By comparing the infrared spectra of Irganox 1076 and polypropylene, the absorption peak of Irganox 1076 at 1738 cm^{-1} was selected as the detection peak. Within the concentration range involved, the standard curve equation of Irganox 1076 in PP is y = 0.00593 + 0.12681x, and the linear regression coefficient is 0.98742. The standard curve was used to determine the content of Irganox 1076 in the actual sample, and the maximum relative error was 6.85%. The method is accurate, rapid and sensitive, which can be used for on-line monitoring of processing and using polyolefin products.

1. Introduction

Polyolefin is a kind of polymer material with the largest amount at present. In view of its excellent performance, low price, rich raw materials and easy processing, polyolefin is widely used. Food packaging materials are called "special food additives". It is the last process of modern food industry. Food packaging materials industry is developing rapidly with a rapid momentum. Plastic packaging is the main material of food packaging because of its convenient carrying and processing. On the other hand, polyolefins are easily affected by various environmental factors such as high temperature, ultraviolet, high load and microorganisms during processing, storage and use. The main reason for aging is that the structure or components have weaknesses that are easy to cause aging, such as unsaturated double bonds, branched chains, carbonyls, hydroxyl groups at the end, and so on. The molecular chain will break and form free radicals. If this free radical is not eliminated in time, it will further cause the fracture of plastic molecules, and finally make the relative molecular weight of plastics become very low and lose value. The macroscopic performance is the color changes and mechanical properties decline, that is, the degradation or aging of polymer materials [1].

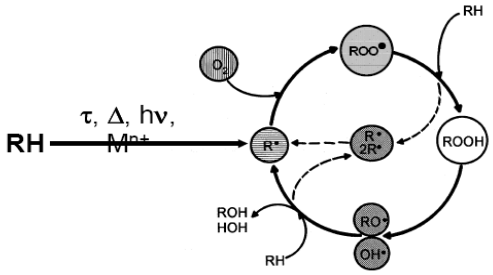

Figure 1. The Automatic oxidation of polymers

Without changing the original processing technology, adding antioxidant is the most effective means to slow down the aging of polyolefins [2~5]. The most common is phenolic antioxidants, which mainly capture free radicals by releasing hydrogen atoms. Common phenolic antioxidants include BHT, BHA, TBHQ, Irganox 1076 and Irganox 1010 [6]. However, almost all antioxidants are toxic. In particular, antioxidants used in food packaging materials will gradually penetrate into food and damage health if they contact with food for a long time in the preservation process [7~9]. As a kind of environmental estrogen, phenolic antioxidants can accumulate in human body. It has been studied that high-dose BHA can cause cancer [10], BHT can inhibit the activity of human biotransferase and affect the metabolism of organisms [11], TBHQ has adverse effects on human liver, spleen and stomach, and has acute toxicity and chronic carcinogenic effects [12]. Therefore, the addition of such antioxidants in food packaging materials has attracted more and more attention and has been strictly controlled. EU regulations Commission Directive 2002/72/EC, Commission

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Directive 2004/19/EC and China's GB 9685-2008 hygienic standard for the use of additives for food containers and packaging materials stipulate that the specific migration limits (SML) of BHA, BHT and irganox1076 are 30.0, 3.0 and 6.0 mg/kg respectively. Whether it is the quality control of polymer products or the safety detection of food packaging materials, the rapid detection of antioxidant content in polyolefins is of great significance. At present, the commonly used detection methods of antioxidant content in polymer materials are chromatography [13~17], mass spectrometry [18,19], spectroscopy [20], but most of these methods have the problems of long time-consuming, cumbersome operation, destructive pretreatment of samples and so on. Fourier transform infrared spectroscopy (FTIR) overcomes the above problems and has the advantages of easy sample preparation and rapid analysis results. In this study, the representative polyolefin material polypropylene (PP) was selected, the content of antioxidant Irganox 1076 was determined by Fourier transform infrared spectroscopy, the standard curve was established, and the precision and accuracy of the results of this method were verified.

2. Materials and Methods

FTIR-650 Fourier transform infrared spectrometer, Tianjin Gangdong Technology Development Co., Ltd; PP-045 powder, Maoming Shihua Dongcheng Chemical Co., Ltd; Antioxidant Irganox 1076, BASF Ag; Toluene, analytically pure.

Antioxidant Irganox 1076 was held in toluene to prepare a solution with a mass fraction of 1%. The solutions of different quality were well-mixed with PP. The samples were processed on a hot bench at 180 ℃ for 3 min before being pressed into thickness of 1mm transparent sheets to be tested. In this process, toluene volatilizes completely. The testing results showed the contents of Irganox 1076 at different positions of the samples were uniform. The mass fractions of Irganox 1076 in the prepared samples were 0, 1.0%, 2.0%, 3.0%, 4.0% and 5.0%, respectively.

3. Results and Discussion

3.1 Characteristic peak of Irganox 1076

Fourier transform infrared spectrometer was used to detect the spectra of antioxidant Irganox 1076, PP samples with and without Irganox 1076. The obtained spectra are shown in Figure 1. Comparing the spectra of three samples, the antioxidant Irganox 1076 has an obvious absorption peak at 1738cm^{-1}, which is the characteristic absorption peak of carbonyl structure in antioxidant, while PP sample has no obvious absorption peak near this wavenumber.

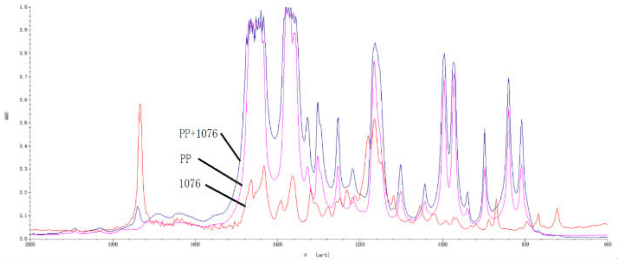

Figure 2. The FTIR curves of Irganox 1076, non-stabilized and stabilized PP with Irganox 1076

3.2 Standard curve of antioxidant Irganox 1076 in PP

Fourier transform infrared spectrometer was used to detect PP samples containing Irganox 1076 with mass fractions of 0, 0.2%, 0.4%, 0.6%, 0.8% and 1.0% respectively. The absorption peaks at 1738cm^{-1} in the obtained spectrum are shown in Figure 2.

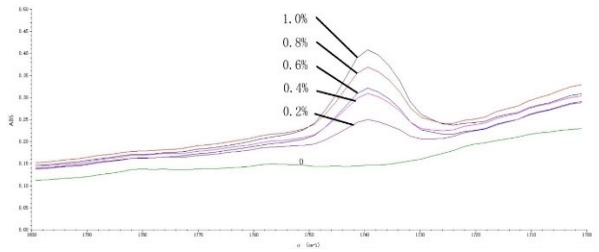

Figure 3. The FTIR curves of PP stabilized with Irganox 1076 in various concentrations at 1738cm^{-1}

Although all the samples were made in the same mold, there were still unavoidable nuances in the thickness of different samples. In order to eliminate the influence of the difference of sample thickness on the intensity of characteristic absorption peak of Irganox 1076, the characteristic absorption peak of PP sample needs to be selected as a reference. Comparative analysis of the spectra of the three samples in Figure 1 showed that PP has an obvious absorption peak at 841cm^{-1}, while the antioxidant Irganox 1076 has no absorption peak near this wavenumber. This absorption peak was selected as the reference. The mass fraction of antioxidant Irganox 1076 in PP sample was taken as the abscissa, and the ratio of the characteristic absorption peak area A_1 of antioxidant Irganox 1076 at 1738cm^{-1} to the reference absorption peak area A_2 of PP at 841cm^{-1} was drawn as the ordinate to establish the standard curve, as shown in Figure 3.

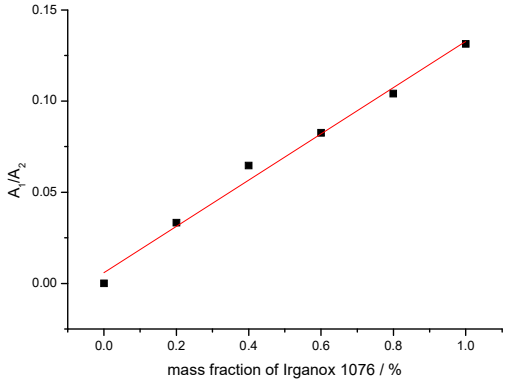

Figure 4. The standard curve of Irganox 1076 contents in PP

As shown in the figure above, the ratio A_1/A_2 of the characteristic absorption peak of antioxidant Irganox 1076 to the reference absorption peak area of PP had a linear relationship with the addition amount of antioxidant Irganox 1076 in PP. The linear regression equation is y = 0.00593 + 0.12681x, the linear regression coefficient is 0.98742.

3.3 Precision and accuracy verification

PP samples with Irganox 1076 content of 0.25% were prepared and tested for 5 times by Fourier transform infrared spectrometer. The determination results were calculated according to the standard curve. It can be shown that the minimum relative error of the determination result of Irganox 1076 content in PP sample is 1.58% and the maximum is 6.85% in Table 1.

Table 1. Precision of test results

Sample	mass fraction/%		Relative Error/%
	True value	Measured value	
1	0.25	0.246	1.58
2	0.25	0.258	3.33
3	0.25	0.245	1.98
4	0.25	0.256	2.57
5	0.25	0.233	6.85

PP samples with Irganox 1076 content of 0.05%, 0.25%, 0.45%, 0.65% and 0.85% were prepared and detected by Fourier transform infrared spectrometer. The determination results were calculated according to the standard curve according to the above method. It can be shown that the minimum relative error of the determination result of Irganox 1076 content in PP sample is 0.25% and the maximum is 4.32% in Table 2.

Table 2. Accuracy of test results

Sample	mass fraction/%		Relative Error/%
	True value	Measured value	
1	0.05	0.048	4.32
2	0.25	0.256	2.35
3	0.45	0.436	3.16
4	0.65	0.648	0.25
5	0.85	0.837	1.58

4. Conclusion

A method for rapid detection of antioxidant Irganox 1076 in PP by Fourier infrared spectroscopy was established. The ratio of the characteristic absorption peak area of Irganox 1076 to PP was used as the response parameter to eliminate the influence of sample thickness on the test results. The detection method is simple and fast, and is suitable for the rapid detection of various polyolefin products.

Acknowledgments

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