2-MERCAPTOBENZIMIDAZOLE USED AS ANTIOXIDANT IN POLYMERIC MATERIALS. ESTIMATION BY DERIVATIVE SPECTROPHOTOMETRY

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Abstract

A method for the determination of 2-mercaptobenzimidazole (MB) in mixtures by derivative spectrophotometry has been developed. MB is used as antioxidant in the manufacture of industrial rubber. Derivative spectrophotometry has been applied for the elimination of the mutual interferences of the other polymer additives in the MB estimation. Thus, the procedure works whitout any separation step of MB from the other polymer additives. The second derivative spectrum of MB was measured at 304 nm while the third derivative was measured at 308 nm. At these wavelengths, the spectra of the other additives cross the zero line or are insignificant. The derivative spectrophotometric procedure was applied for MB determination in synthetic mixtures of polymer additives and in rubber samples.

Introduction

Manufacture of industrial rubber requires an elastomer, sulphur, one or more vulcanization accelerators, an antioxidant and filling material. Many studies have been done on the identification and determination of the antioxidants. A preliminary separation of additives from each other after extraction from the polymer is often necessitated by the lack of sufficiently specific methods for the identification of individual antioxidants in the presence of the other components. A lot of separatory techniques for antioxidants analysis were reported, such as: liquid/liquid extraction,[1] paper chromatography,[2] thin layer chromatography,[3] high pressure liquid chromatography (HPLC),[4-6] gas chromatography (GC),[2] electrophoresis,[7] gas chromatography coupled with mass spectrometry (GC-MS,[8] supercritical fluid and enhanced solvent extraction,[9] supercritical fluid extraction combined with GC-MS,[10] mass spectrometry coupled with HPLC (MS-HPLC),[11] size exclusion chromatography with on line UV, RMN and MS detection,[12] capilary liquid chromatography,[13] pyrolisis and pyrolisis-GC techniques.[14,15] Another series of methods for antioxidants estimation are based on their spectrometric properties.[16] As it is known the antioxidants absorb UV radiations and therefore they have characteristic UV spectra.[17] But, the UV spectrophotometry is not particularly specific for antioxidants and is liable to be in error owing to other highly absorbing additives in the sample.

In an attempt to overcome this difficulty, we have proposed in our study a spectrophotometric method for determination of the antioxidant in presence of the other polymer additives (2-cyclohexylbenzothyazil sulphenamide (CBS) and diphenylguanidine (DPG) as vulcanization agents and dioctylphtalate (DOP) as plasticizer), without the separation of the additives from each other after extraction form the polymer.

Results and discussion

Aborption spectra of the polymer additives

Figure 1 shows the conventional spectra of MB, CBS (2-cyclohexylbenzothyazil sulphenamide), DPG (diphenylguanidine) and DOP (dioctylphtalate). Because of the overlap of these spectra, the determination of MB in presence of the other polymer additives is subject to considerable difficulties.

Derivative spectral characteristics of the investigated additives

In order to prevent the effect of the spectral interferences in MB estimation, the derivative spectrophotometry was proposed.[18] The determination of MB by first-order derivative cannot be performed because of the overlap of the spectrophotometric signals attributed especially to MB and CBS. In Figures 2-3 the second and third order derivatives spectra are shown. Among the number of points where the derivative spectra cross the zero line, the most interesting were:

- 304 nm, by applying the second derivative; at this wavelength, the values of the second derivative of DPG and DOP are equal zero while the signal of CBS is very low.

- 308 nm, by applying the third derivative; at this wavelength, the third derivative of DPG, CBS and DOP are equal zero, allowing to analyse MB in the presence of those additives.

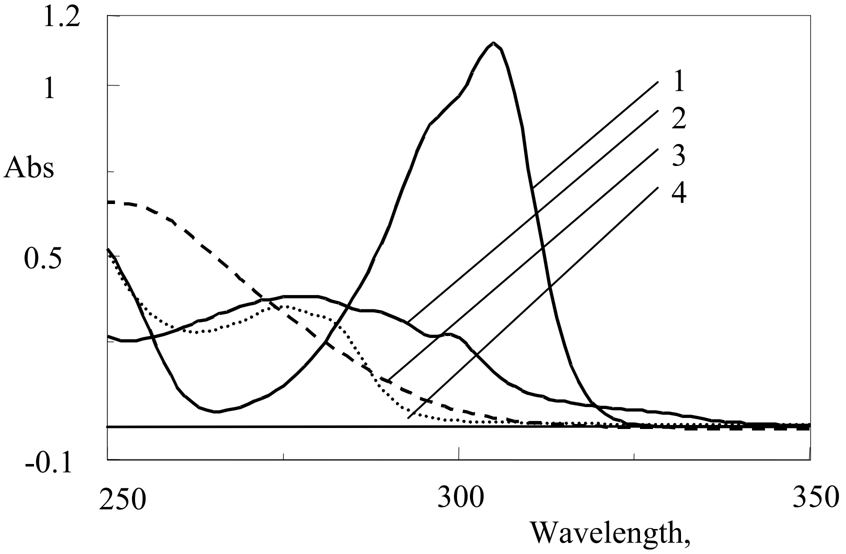

Figure 1. Conventional UV spectra of some polymer additives.
1- MB; 2- CBS; 3- DPG; 4- DOP; c_{DOP} = 20 μg/mL; c_{DPG}=c_{CBS}=c_{MB}= 5 μg/mL.

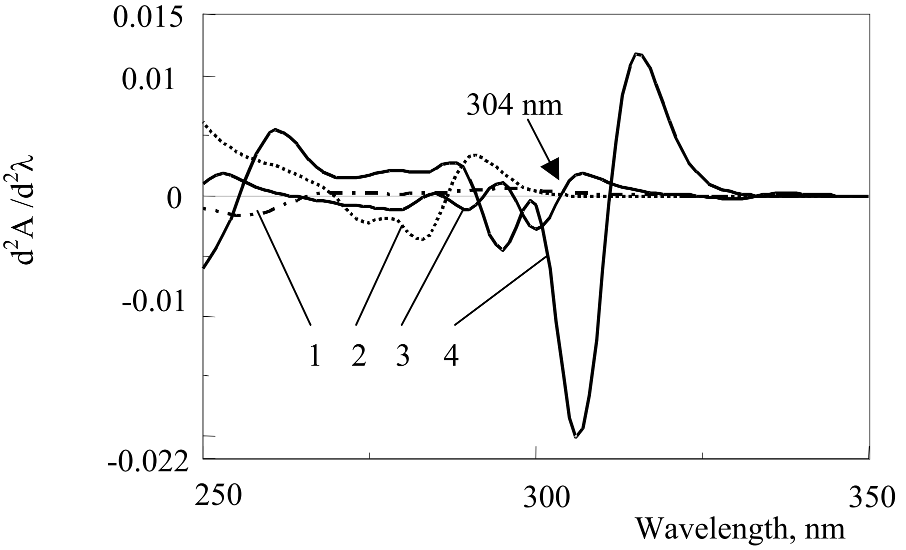

Figure 2. Second derivative spectra of some polymer additives.
1- DPG; 2- DOP; 3- CBS; 4- MB; c_{DOP}= 20 μg/mL; c_{DPG} = c_{CBS} = c_{MB} = 5 μg/mL.

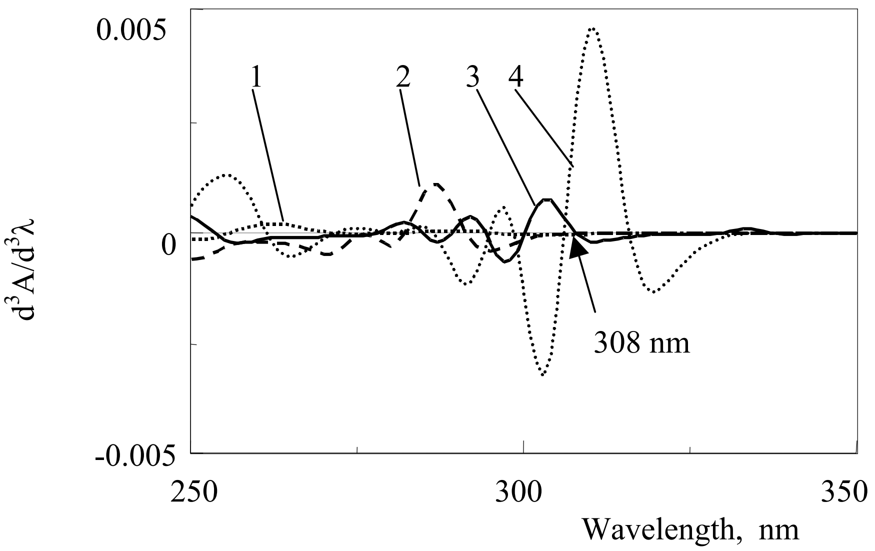

Figure 3. Third derivative spectra of some polymer additives.
1- DPG; 2- DOP; 3- CBS; 4- MB; c_{DOP}= 20 μg/mL; $c_{DPG}=c_{CBS}=c_{MB}$= 5 μg/mL.

We mention that these points can be used for MB estimation in multicomponent mixtures but the derivative signals attributed to MB are measured outside the maximum range located at 306 nm, in the case of the second derivative and at 311 nm when the third derivative is used.

Determination of MB in synthetic mixtures

With the aim of eliminating the above-mentioned interferences and on the basis of the second and third derivative spectra of the reference additives selected for this study, the proposed spectrophotometric methods have been tested to the analysis of MB in several synthetic mixtures. Taking into account that in real rubber samples all the mentioned additives are introduced, a series of synthetic multicomponent mixtures were prepared and the proposed method applied for MB estimation. In the prepared mixtures, the MB-to-interferents ratios were as follows: MB-CBS-DPG-DOP = 1:2:2:3. A ratio of MB-vulcanization accelerators (CBS, DPG) = 1:4 and a ratio of MB-plasticizer = 1:3 were chosen in order to test the proposed method for MB determination in presence of excess amounts of the other additives. The results obtained are summarized in Table 1. As we observe, the second order derivative spectrophotometry applied to complex mixtures of rubber additives allows the determination of MB in the presence of three other constituents, in the concentration range 0.25-5 μg MB/mL; by applying the third derivative, the accuracy achieved in the determination of MB was obtained in the concentration range 0.50-5 μg /mL. At concentrations higher than 5 μg/mL, a considerable decrease of the derivative signals was observed.

Application

To evaluate the analytical applicability of the proposed method, it was tested to the determination of MB in real samples, manufactured, extracted and then prepared according to the general procedure. As is shown in Table 2, similar content of MB in both raw and vulcanized rubber samples was found by the proposed method. So, the proceeding of vulcanization does not affect the content of MB found spectrophotometrically. However, the amount of MB extracted from rubber samples and found spectrophotometrically is less than the amount of MB introduced in the rubber samples.

Table 1. Results of MB determination in multicomponent mixtures by the use of the second and third order derivative (mean values for three independent measurements)

MB in sample, [μg/mL]	MB found by second derivative[a] [μg/mL]	Relative error [%]	MB by found third derivative[b] [μg/mL]	Relative error, [%]	Interferents [μg/mL]		
					CBS	DPG	DOP
0.25	0.25	-	0.20	-20.00	0.50	0.50	0.75
0.50	0.50	-	0.50	-	1.00	1.00	1.50
1.00	1.00	-	1.00	-	2.00	2.00	3.00
2.50	2.65	+6.00	2.50	-	5.00	5.00	7.50
5.00	5.30	+6.00	4.66	-6.60	10.00	10.00	15.00
10.00	7.25	27.50	6.50	-35.00	20.00	20.00	30.00

Measurements were performed at: a) λ = 304 nm; b) λ = 308 nm.

It could be assumed that this behaviour arise from the fact that antioxidants are labile unstable compounds;[19] so, any loss of material is liable to be significant since the quantitiy of antioxidant present are initially so low. This has resulted in a decrease of unmodified MB in extract.

Table 2. Results of MB determination in real samples[a]

Sample	MB, g/100g of sample	
	in sample	found[b]
Raw rubber	1.14	1.07 ± 0.01
Vulcanized rubber	1.14	1.05 ± 0.02

a) The rubber samples were manufactured according to the general procedure;
b) The second derivative order spectrophotometry was applied, at 304 nm.

Conclusions

A simple and inexpensive derivative spectrophotometric method for determination of 2-mercaptobenzimidazole (MB) has been developed. The proposed method permits the estimation of the antioxidant (MB) in multicomponent mixtures without separation from the other polymer additives. In presence of two vulcanization agents (namely 2-cyclohexylbenzothyazil sulphenamide (CBS) and diphenylguanidine (DPG)) and a plasticizer (dioctylphtalate (DOP)), the determination of MB can be made with good results by using both the second and the third derivative spectrometric method. The selective determination of MB was carried out in real rubber samples. As we reported, the described procedure can be used for the estimation of the percent of MB unmodified after separation of the additives, by extraction, from the polymer matrix.

Experimental

Materials

All the chemicals used were of analytical-reagent grade (Merck) and all the solutions were prepared in ethanol. One type of elastomer was used, namely nitrile rubber (NR). The specimen of elastomer was manufactured specifically for this study. The rubber extraction was made in acetone. The following vulcanization accelerators were selected: 2-cyclohexylbenzothyazil sulphenamide (CBS) and diphenylguanidine (DPG). The antioxidant used was 2-mercaptobenzimidazole (MB). As plasticizer, dioctylphtalate (DOP) was used. Stock solutions containing 100 μg polymer additive/mL were prepared in ethanol. Working solutions were obtained by appropriate dilutions of the stock solutions with ethanol.

Apparatus

All absorption spectra and derivatives were recorded with a Jasco-V 530 UV-VIS double beam spectrophotometer, equipped with a pair of 1-cm path length quartz cells and interfaced to a compatible computer running a spectrophotometric software. This equipment allows a direct derivatization up to the third-order.

Procedure for spectra measurements

Suitable volumes of stock solutions containing 100 µg polymer additive/mL were placed into the 10-mL calibrated flasks and brought to volume with ethanol. Also, mixtures of stock solutions containing suitable amounts of the investigated polymer additives were placed into the 10-mL standard flasks and diluted to the mark with ethanol. The absorption spectra of the samples were recorded between 250 and 350 nm, against ethanol. For the estimation of MB, the values of the derivatives were measured at the selected “zero-crossing” wavelength of the derivative spectra of the other additives prsented in mixtures.

Preparation of rubber mixtures

The rubber mixtures were manufactured with the additives in a certified formula, in the following proportions: elastomer (nitrile rubber), 100; stearic acid, 1.5; zinc oxide, 5; silicon oxide (Zeosil 45), 40; chalk, 20; sulphur, 1.2; CBS, 1; DPG, 0.5; DOP, 4; MB, 2. One half of the sample was vulcanized and the other half left raw to show the effects of vulcanization on the constituents of the mixtures.

Extraction

Extraction was performed on a weighed amount of the rubber specimens (2.5 g, cut into small pieces), in a Soxhlet extractor for 24 hours, with a defined volume of acetone, at the boiling temperature of the solvent. In order to minimize the decomposition and loss of the antioxidant during extraction, this was made under nitrogen. Then, it was filtered and diluted to 100 mL into a calibrated flask. A 0.5 mL portion of this solution was diluted to 25 mL with ethanol and the third derivative spectrum recorded. The raw rubber samples were extracted with acetone for 24 h, in closed container, in the dark, at room temperature. After filtration and elimination of the solvent, the residue was manufactured and analysed as before.

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Povzetek

Razvili smo metodo določanja 2-merkaptobenzimidazola (MB), ki je kot antioksidant v uporabi v proizvodnji industrijske gume, s pomočjo derivativne spektrofotometrije. Z določitvijo vrednosti drugega odvoda absorpcijskega spektra pri 304 nm, oziroma tretjega pri 308 nm, lahko odstranimo vpliv drugih v matriki prisotnih antioksidantov, ki lahko motijo določitev MB brez predhodne ločitve. Pokazali smo, da so pri teh valovnih dolžinah vrednosti odvodov absorpcijskih spektrov drugih dodatkov bodisi nič ali zanemarljive. Derivativni spektrofotometrični postopek smo uporabili za določitve MB v pripravljenih zmeseh polimernih dodatkov ter v vzorcih gum.