A POLYMER ADDITIVE ESTIMATION BY DERIVATIVE SPECTROPHOTOMETRY

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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. Beer's law has been valid in the concentration range 0.25-10 μg MB/mL (by applying the second derivative) and 0.5-10 μg MB/mL (by applying the third derivative).

Introduction

The range of applications for polymeric materials is still increasing at an enormous rate and, as it does so, the number of additives available to modify polymer properties increases proportionately. 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. In view of the proper analysis, it seems inevitable that a preliminary separation of the antioxidant from the polymer is in most cases necessary. Many such separations which have been reported are concerned with solid/liquid extraction. The extract contains other additives besides the antioxidant. For this reason, the 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. That is why 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]. Recent studies report high techniques for antioxidants analysis at low levels: 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]; capillary liquid chromatography [13], pyrolisis and pyrolisis-GC techniques [14,15].

Another series of methods for antioxidants estimation are based on their spectrometric properties. From this point of view, by far the most popular method of estimating antioxidants is by coupling or oxidizing them to form coloured products and measuring the

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resulting absorbance in the visible region of the spectrum [16]. Also, 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, without the separation of the additives from each other after extraction form the polymer. For that, the derivative spectrophotometry was proposed. The derivative spectra allow to determine MB at λ = 304 nm (by applying the second derivative) and at λ = 308 nm (by applying the third derivative), in binary, ternary and multicomponent synthetic mixtures.

Experimental

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 the spectrophotometric software. This equipment allows a direct derivatization up to the third-order. Suitable settings were: slit width, 1 cm; scan speed, 200 nm/min.

Reagents

All the chemicals used were of analytical-reagent grade (Merck) and all the solutions were prepared in ethanol.

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.

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 commonly presented in mixtures (λ = 304 nm, for the second derivative and λ = 308 nm, for the third derivative).

Conformance to Beer's law

Into each of a series of 10 mL calibrated flasks, known volume of MB solution was transferred, diluted to the mark with ethanol and mixed. The absorption spectra of these solutions were recorded. Then, the value of the third-derivative was measured at $\lambda = 308$ nm.

Results and Discussion

Absorption spectra of the polymer additives

Fig. 1 shows the conventional spectra of MB, CBS, DPG and DOP. 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. The most common technique used for quantitative analysis is the zero-crossing method (ZCM)[18]. This method involves a measurement of the absolute value of the total derivative spectrum at an abscisa value (λ) corresponding to the zero-crossing point (ZCP) of the interfering component. At this wavelength, the amplitude of the derivative signal of the one of the two components passed through zero. Therefore, a measurement of the value of the derivative amplitude of a mixture, made at the ZCP of the derivative spectrum of one of the two components is a function only of the concentration of the other component. In our study, a large number of preliminary tests were made to select the more convenient order of derivative and working wavelength.

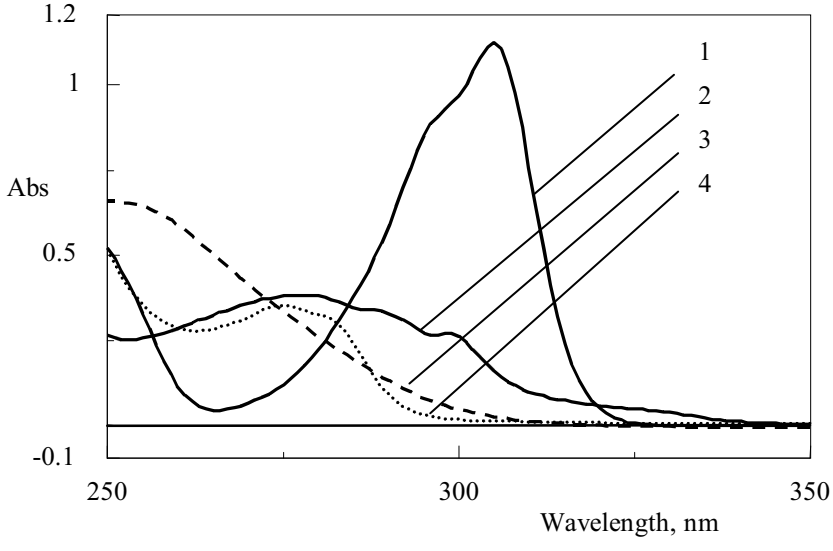

Fig. 1: *Conventional UV spectra of some polymer additives.*
1- MB; 2- CBS; 3- DPG; 4- DOP; $c_{DOP} = 20$ µg/mL; $c_{DPG} = c_{CBS} = c_{MB} = 5$ µg/mL.

Fig. 2 shows that 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 Figs. 3 and 4 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.

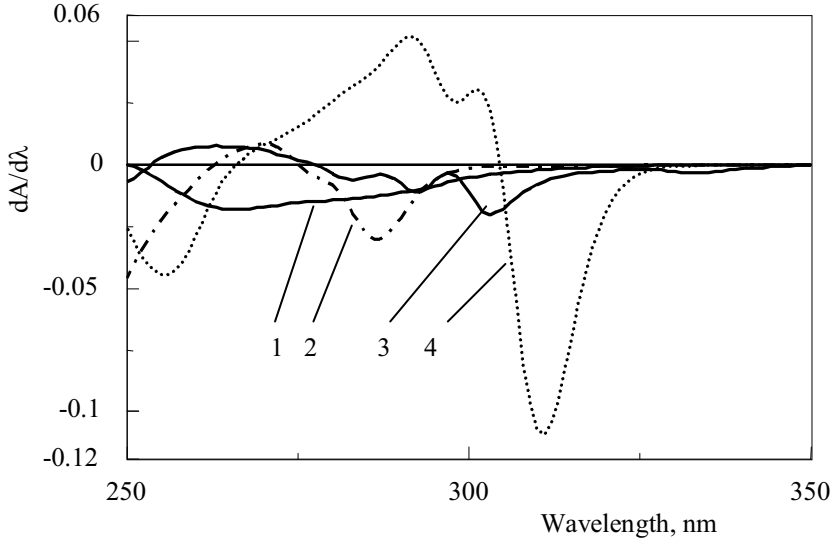

Fig. 2: *First derivative spectra of some polymer additives.*
1- DPG; 2- DOP; 3- CBS; 4- MB; c_{DOP} = 20 μg/mL; $c_{DPG} = c_{CBS} = c_{MB}$ = 5 μg/mL.

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.

Also, we have found that, by applying the second derivative at 304 nm, Beer's law has been valid in the concentration range of 0.25-10 μg/mL.

When the third derivative was applied at 308 nm, the calibration graph was obtained for a concentration of MB between 0.5 and 10 μg/mL.

As we have reported, the manufactured rubber samples contain stearic acid as one of the polymer additives. We verified that stearic acid, which could be extracted in acetone together with the other additives, does not interfere with the tested antioxidant.

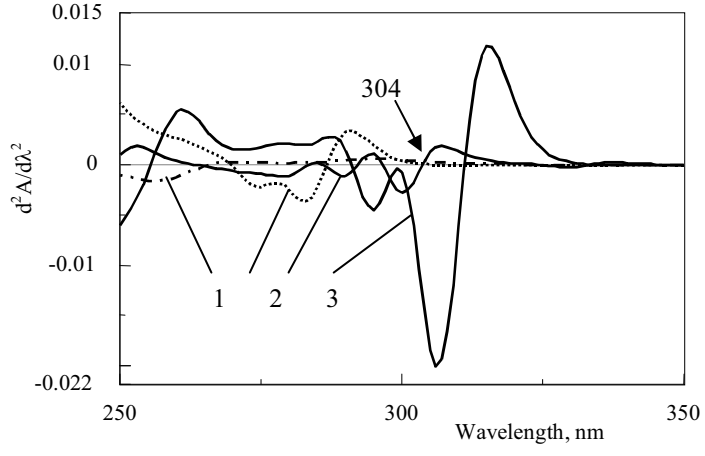

Fig. 3: *Second derivative spectra of some polymer additives.*
1- DPG; 2- DOP; 3- CBS; 4- MB; c_{DOP} = 20 μg/mL; c_{DPG} = c_{CBS} = c_{MB} = 5 μg/mL.

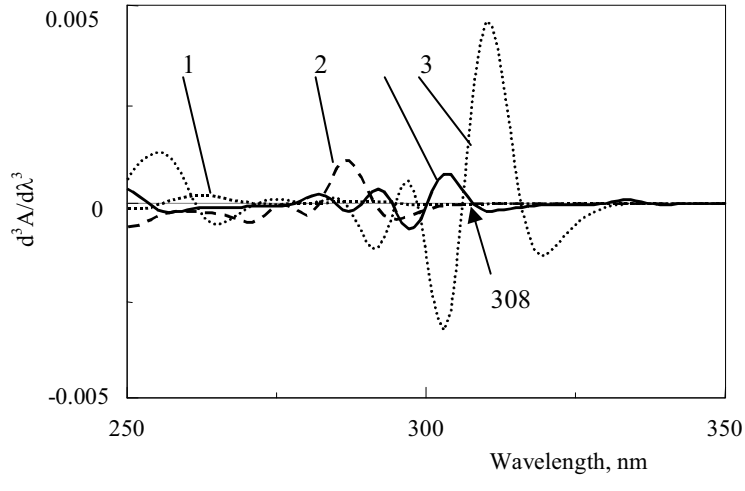

Fig. 4: *Third derivative spectra of some polymer additives.*
1- DPG; 2- DOP; 3- CBS; 4- MB; c_{DOP} = 20 μg/mL; c_{DPG} = c_{CBS} = c_{MB} = 5 μg/mL.

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. Maintaining a constant concentration of MB of 2.5 μg/mL and in the presence of the interfering species over a range of concentration between 2.5 and 10 μg/mL (1:1 to 1:4 MB:interferent), the second and third derivative spectra of binary mixtures were obtained. The MB content was determined from the second and third derivative spectra by automatically measuring the amplitude (at 304 nm for the second derivative and at 308 nm for the third derivative) and using the appropriate calibration graphs. As it can be seen from Table 1, by applying the second derivative, DPG has only a slight effect on the determination of MB at a 4-fold excess with respect to MB. Also, as we expected, DOP does not interfere in the MB estimation. CBS was found to interfere significantly at a 4-fold excess over MB, by applying the second derivative, but a slight interference was observed when the third derivative was applied.

Table 1. Results of MB determination in binary mixtures by the use of the second and third order derivative (mean values for three independent measurements; r_e = relative error)

MB in sample, μg/mL	MB found by second derivative[a], μg/mL	r_e, %	MB found by third derivative[b], μg/mL	r_e, %	Interferent,	μg/mL
2.50	2.43	-2.8	2.50	-		2.5
2.50	2.36	-5.6	2.50	-	CBS -	5
2.50	2.30	-8.0	2.36	-5.60		10
2.50	2.50	-	2.50	-		2.5
2.50	2.50	-	2.50	-	DPG -	5
2.50	2.40	-4.00	2.50	-		10
2.50	2.50	-	2.50	-		2.5
2.50	2.50	-	2.50	-	DOP -	5
2.50	2.50	-	2.50	-		10

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

On the basis of the obtained results and 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 PBN 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 2. 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.

Table 2. Results of MB determination in multicomponent mixtures by the use of the second and third order derivative (mean values for three independent measurements; r_e = relative error)

MB in sample, μg/mL	MB found by second derivative[a], μg/mL	r_e, %	MB found by third derivative[b], μg/mL	r_e, %	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.

Conclusion

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.

In a continuation of this study, the selective determination of MB will be carry out in real rubber samples.

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