

THE TITRATION OF SOLUBLE SULFUR CONTENT OF THE INSOLUBLE SULFUR AS RAW MATERIAL IN THE RUBBER INDUSTRY

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abstract: The aim of present paper is to present a spectral method to determine the amount of soluble sulfur contained in the insoluble sulfur used as raw material in rubber industry. The soluble sulfur extracted in an organic solvent presents an UV absorption band at 263nm.

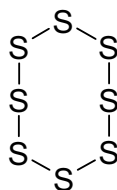
Introduction

In rubber industry there are used two common polymorphic sulfur forms as vulcanization agent of unsaturated polymers. These two forms are the rhombic sulfur, soluble ($S\alpha$) and insoluble sulfur ($S\mu$) respectively.

Both $S\alpha$ and $S\mu$ powders can cause dust explosions (static, spark, etc.) and hence they are oil-coated form 1.5-20% oil. In our polymer the pre- dispersed sulfur is bound, these hazards being in this way completely removed.

Both $S\alpha$ and $S\mu$ are difficult to mix and a good dispersion of sulfur powder in mixing is not achieved.

$S\alpha$ exists as eight atom ring:



and $S\mu$ is a polymeric $[S_8]_n$ [1,2] which is an unstable form and even at ambient temperature $S\mu$ tends to revert to $S\alpha$. This process is accelerated by the temperature rising. At 50°C, $S\mu$ will revert to $S\alpha$ with 1% per day and it will revert even faster in presence of alkaline materials (hence insoluble sulfur) powders are not recommended to be weighed and mixed with such chemicals. Polymer bound in soluble sulfur does not have these problems.

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At moulding temperature, S_{μ} reverts totally to S_{α} and behaves similarly in the sulfur crosslink mechanisms. There are used stabilizers to delay this reversion.

Practically, the rubber chemists with an eye on cost savings usually opt for Semi-EV cure system i.e. S dosage of 1.5 ± 0.2 PHR. This is very close to the maximum solubility of 1.5 PHR S in NR/SBR/BR at 25°C. If our S-80 is used to replace S at 1:1 weight basis, then the actual active S dosed is only 1.2 PHR in such Semi-EV cure systems and in most cases, no S bloom is encountered. For supplementary safety, we recommend the use of our economical ISE-60 or ISE-75. Factories are also encouraged to stock with both our S-80 and IS-65 grades and they can experiment with whatever combinations of these substances to suit their formulations.

The use of insoluble sulfur in rubber industry involves many aspects, such as oil content, density, acidity and soluble sulfur content. Sulfur and its compound titration is very present in chemical literature [3,4,5,6,7,8].

Experimental

Reagents

All reagents used were of analytical purity (crystallized sulfur, n-hexane).

Apparatus

The spectra were recorded using n-hexane as solvent and a Jasco V-550 UV-VIS spectrometer. 25cm³ measuring bottle has also been used. A standard reference solution was prepared solving crystallized sulfur in n-hexane with 0.4g/l concentration. Diluting this solution with solvent there were prepared the working sample solutions with concentrations comprised within the range $1.06 \cdot 10^{-2}$ and $2.55 \cdot 10^{-2}$ g/l used for calibration curve.

Results and discussion

It was recorded the 200÷450nm absorption spectra using sulfur in n-hexane standard solution. The maximum absorbance was found for 263nm.

The calibration curve was made measuring the absorbance of standard solutions obtained from stock solutions diluted with n-hexane.

Table 1 summarizes the experimental data.

The data from Table1 were used to plot the calibration curve [19], using the least squares regression:

$$C = -0.000154 + 0.038715 \cdot A^{263} \quad (1)$$

The obtained correlation coefficient is $r = 0.998983$ showing a good curve linearity.

The calculated detection limit is $1.1 \cdot 10^{-3}$ g/l sulfur and the determination limit is $2.2 \cdot 10^{-3}$ g/l. It was calculated soluble sulfur in insoluble sulfur rate using the relationship

$$C_2 = C \cdot 100 / C_q \quad (2)$$

C_2 is the concentrated value calculated using the eqn (1) and C_p is the concentration of the sample assumed from calibration curve whose absorbance is fitted in eqn (1).

Table 1. The calibration curve for *n*-hexane as solvent.

Nr. crt.	Concentration (g/l)(x10 ⁻²)	Abs (%)
1	1.06	0.275
2	1.18	0.310
3	1.32	0.350
4	1.44	0.375
5	1.57	0.405
6	1.69	0.435
7	1.82	0.475
8	1.94	0.510
9	2.07	0.550
10	2.19	0.570
11	2.31	0.600
12	2.43	0.625
13	2.55	0.665

Interference study

a. Refined oil influence as insoluble sulfur stabilization factor

It was utilized extra refined mineral oil (soluble in *n*-hexane) for the preparation of synthetic mixtures of soluble sulfur with different proportions. The spectra were recorded and the soluble sulfur matter was calculated from eqn (1).

Table 2 presents the obtained results.

Table 2. Influence of refined oil on the soluble sulfur determination.

Nr. Crt.	C _{soluble} (g/l) (introduced)	C _{oil} (g/l) (introduced)	C _{oil} /C _s	C _{found} (g/l)	C(g/l)
1	0.0269	0.0135	0.51	0.0273	0.0004
2	0.0202	0.0202	1.00	0.0208	0.006
3	0.0162	0.0242	1.45	0.0169	0.0007
4	0.0135	0.0269	1.99	0.0140	0.0005

It is obvious that the influence of the refined oil on soluble sulfur graduation is insignificant (compare C_{soluble} with C_{found})

b. Influence of temperature

It was followed the influence of the operating temperature on soluble sulfur dissolution. Five sample sets were prepared with the same concentration of sulfur solved in *n*-hexane at the room temperature and at 60°C. After cooling of the samples until the room temperature is reached, their absorbance has been recorded and the sulfur concentration calculated.

The Table 3 presents the average concentrations for each temperature.

Table 3. Temperature influence on the soluble sulfur determination.

No.	T(°C)	C _{soluble} (g/l)·10 ⁻²	C _{found} (g/l)·10 ⁻²
1	Room temperature	2.100	2.110
2	30	2.030	2.010
3	40	2.180	2.180
4	50	2.260	2.263
5	60	2.380	2.282

The Table 3 reveals a gently increase of soluble sulfur content with temperature.

It is recommended that the dissolution of the sample which contains soluble and insoluble sulfur at maximum 50°C do not affect the soluble sulfur stability.

c. Error calculation

The standard deviation was calculated from the formula:

$$S = \left[\frac{\sum (\Delta C_{\text{founded}})^2}{n} \right]^{\frac{1}{2}} = \left(\frac{0.16}{6} \right)^{\frac{1}{2}} = 0.16 \quad (3)$$

The variation coefficient, σ is:

$$\sigma = \frac{100S}{n} = 100 \cdot \frac{0.16}{6} = 2.7\% \quad (4)$$

It was calculated P=95% and the trust interval for C_{found} is of ±0.2%.

d. Proposed protocol

It is measured an amount of approximately 0.01g of sample that contains insoluble sulfur (S_μ) and soluble sulfur (S_α). The sample is solved in n-hexane at a temperature of 40-50°C, cooled at the room temperature and then filtered in a 25cm³ measuring flask. It fills out to 25cm³ with n-hexane. The absorbance is measured at 263nm. The corresponding sulfur amount is found from etalon curve. The found values are put in the following equation:

$$C_{\text{soluble}} = (-0.000154 + 0.38715 \cdot A^{263}) \cdot 100 / C_p \quad (5)$$

where C_p is the value extracted from the etalon curve and C_{soluble} is the concentration of soluble sulfur from the analyzed sample.

Conclusions

A method for the determination of soluble sulfur from insoluble sulfur has been studied and proposed for the use of sulfur as raw material in rubber industry for fabrication of tires. The base of this method is the molecular UV absorption spectroscopy. The method uses n-hexane as solvent instead of CS₂, which is toxic and very volatile. Thus, the reactive costs are substantially lowered.

The influence of additional oil on the method accuracy is insignificant (accuracy of 95%).

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