

Studies of Sulfur Behavior in Rubber Compounds

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ABSTRACT: The influence of temperature and storage time of polymeric sulfur from different producers on its behavior in rubber compounds was studied. Also, the influence of activation by neutron irradiation on a quantity of an insoluble fraction in polymeric sulfur was investigated. To better understand the reason of the small difference in properties of tested polymeric sulfur, its topological structures were evaluated using a thermomechanical method. It was confirmed by a previous conclusion that these kinds of polymeric sulfur have very similar topological structure, and as a result, their behavior in rubber compounds should be practically the same. Studying the reason of blooming in the mineral sulfur it was found that at normal storage conditions, sublimation and oxidative degradation of soluble sulfur could be negligible. For these measurements radioisotopic methods were used. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1531–1536, 1998

Key words: sulfur; rubber compound; blooming; dispersion

INTRODUCTION

Some processes related to a presence of sulfur and taking place during manufacturing and processing of typical rubber compounds were described in other articles.^{1–5} Neutron activation analysis is especially useful to evaluate a trace quantity of sulfur introduced into the rubber compound. This method is characterized by very good detectability (1 ppm in 0.1 g of the rubber compound). It is practically free from the blank test because here we measure a characteristic radiation of the isotope ³⁵S resulting from nuclear reaction. This isotope, emitting a beta radiation with maximum energy of 169 keV, has a half-life time for disintegration equal to 87.1 days.⁵ Both these values appear advantageous for experimental application. The advantages of this method among other methods of the trace analysis are simple

calibrations, a possibility to analyze very small samples, easy identification, and control of sources of random and systematic errors. It was also found that measurements by use of a G-M counter type BOH-45 of surface radiation intensity of samples containing ³⁵S are characterized by good repeatability and precision (variation coefficient 4%). Method simplicity and short measurement time allow an increase in the number of samples to be tested and, related to it, more complex statistical analysis of results. G-M counters were equipped with specialized measurements cards and a computer. Due to this studying sulfur dispersion and sulfur blooming, 1 h after manufacturing of the rubber compound and short intervals during storage of samples is possible.

In the activation method the important problem is to evaluate the influence of thermal neutrons and temperature in the reactor's tunnel on properties of activated material. It is well known that polymeric sulfur is a metastable form and it could be reversed into soluble sulfur. Due to this, one can expect that during activation accompa-

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nied by heating, insoluble sulfur could be transformed into the soluble form.⁶ As a result, one basic question was not answered—Is it possible to accept that activated sulfur is a representative of a nonactivated? Before the next study, to answer this question is very important because storage conditions influence transition of insoluble sulfur into soluble. As a result, they change the solubility degree, which could change the behavior of sulfur in a rubber compound.

It was shown earlier that blooming of soluble sulfur on the surface of a typical rubber compound based on unsaturated rubbers is observed up to 40°C of the storage temperature. This bloom at higher temperatures gradually disappears.⁴ Why? To clarify this problem investigation of sulfur to find the tendency to substantial sublimation and/or oxidation during storage at temperatures of 40–60°C is necessary.

Among sulfur properties the most important is solubility in rubber. For some rubber compounds introducing 3–4 phr of sulfur is necessary. This concentration is above solubility of mineral sulfur in rubber at storage temperature and it causes a bloom. To avoid problems related with blooming, in such a recipe polymeric sulfur is commonly used or, cheaper, a blend of mineral and polymeric sulfur in a ratio related to a content of an insoluble fraction in a polymeric commercial product. Due to this, a control of an insoluble fraction content in polymeric sulfur is needed.

There are some producers of polymeric sulfur. By analogy to polymers, which differ depending on technology of their synthesis, asking is reasonable: has sulfur from different producers the same structure and properties or not?

EXPERIMENTAL

Materials

Polymeric granulated sulfur containing 30–35% of processing oil, made by three producers, and mineral sulfur containing 5% of processing oil were tested.

RESULTS AND DISCUSSION

Testing of Stability of Polymeric Sulfur

Polymeric Crystex OT 33 sulfur from Kali-Chemie AKZO was activated by thermal neutrons in quartz capsules. The flux was $1 \cdot 10^{13}$ neu-

trons $\cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, and the activation time was 34 h. During this process sulfur was heated up to a temperature of 100°C. Next, the obtained radioactive material was “cooled” for 120 days at room temperature to reduce the concentration of the simultaneously formed ³²P radioisotope.¹ The final preparation containing ³⁵S has a specific activity of 5.8 MBq/g.

Knowing the influence of neutron irradiation on the stability of insoluble sulfur is important. The analysis showed that during nuclear activation and cooling for 120 days (Table I) the reduction in the average insoluble sulfur content in Crystex OT 33 was ~5%. It resulted from neutron irradiation and transition during storage. However, it is known that at a temperature storage of 50°C the rate of transition of insoluble sulfur into soluble is ~1% per day. At room temperature it is lower. On the other hand, not all amounts of sulfur in a rubber compound must be in the insoluble form. Usage of 50% of sulfur content in a rubber compound in the insoluble form often ensures safety processing against its blooming.⁷ Therefore, observed here, a reduction in insoluble sulfur has usually no essential influence on the existence of blooming. This was confirmed by the number of experiments. These investigations show that polymeric sulfur is stable enough. This conclusion was also confirmed by testing samples from two other producers of polymeric sulfur.

The changes in the content of the insoluble in CS₂ fraction of sulfur in sulfur, irradiated in a nuclear reactor using high intensity flux, were investigated earlier.⁸ The complicated pattern of the kinetics and annealing curves suggests a complex composition of the insoluble in CS₂ fractions, which contains at least S_μ allotropic modification. During the first stage of the activation process some lowering of insoluble fraction content and, next, its growth to some limit was observed during an irradiation time of 6 h. However, this limit does not reach the initial level. Due to this, changes in the amount of the sulfur allotropic modifications usually depend on the history of investigated samples. This shows that using activated preparations in the appropriate way as a representative of sulfur added into raw rubber during compounding is possible. Following this conclusion, the radioisotopic method could be used to study some physical–chemical processes also taking place during rubber compounding and processing. The difference in soluble sulfur content (Table I) resulting from activation is too small to change the conclusions from our previous experiments when

Table I

	Successive Number of Measurements						Average
	1	2	3	4	5	6	
Before activation	62.1	65.3	63.2	64.9	63.8	59.9	
After activation and "cooling" for 120 days	57.4	56.8	60.5	59.8	55.8	59.9	58.4

blooming and dispersions of sulfur in rubber compounds were studied.¹⁻⁴ However, the reason for changes in the kinetics of blooming was not explained there. Due to this, checking whether sublimation and oxidation processes during storage of rubber compounds are the reasons of the lowering of the sulfur concentration on the surface of rubber compounds during storage over 42°C is necessary.

Sublimation and Oxidative Degradation of Sulfur during Storage

Trying to solve this problem, additional model experiments on sublimation and oxidative degradation of sulfur during storage at different temperatures were done as follows: 0.1 g of mineral sulfur was put into the measuring bowl (1) of the special sublimation glass assembly (Fig. 1). During the test the bowl (1) is inside the lower glass dish (2). The bottom of this dish was heated in the water bath. The second bowl (4) was placed upside down and stuck together with the bottom of a dish (3), which was cooled by water flowing inside a space (5). Space between the dishes (2) and (3) is closed hermetically. The decrease in mass of the bowl (1) and an increase in a mass of the bowl (4) were analyzed using results of the radioisotopic (³⁵S) test. Changes in surface radiation intensity of the bowls were an indirect measure of the weight with accuracy of $\pm 1 \cdot 10^{-7}$ g. To control these results, the changes in weight of the bowls were also measured using analytical balance.

In sublimation and oxidation model experiments it was observed that during heating at 20 and 35°C by 150 h the mass decrement was too small to be measurable. At 40°C the mass decrement was 2%, at 45°C it was 4%, and at 60°C it was 6.5%. Only at 60°C the mass of the bowl (4) increased by 2%. The latter evidences some sulfur sublimation. An oxidation of sulfur inside the sub-

limation assembly also took place because the increase in weight of the bowl (4) is lower than the decrease in weight of the bowl (1). Considering that in rubber compounds sulfur concentration is smaller than that during the above-discussed model experiments, the influence of sulfur sublimation and oxidation on surface concentration of the sulfur being varied during the storage of rubber compounds at a temperature up to 60°C is too small to substantially change our conclusions shown in the next section and previous⁴ results of experiments on the blooming process.

Sulfur Blooming

In experiments aimed to study the phenomenon of sulfur blooming on the surface of rubber com-

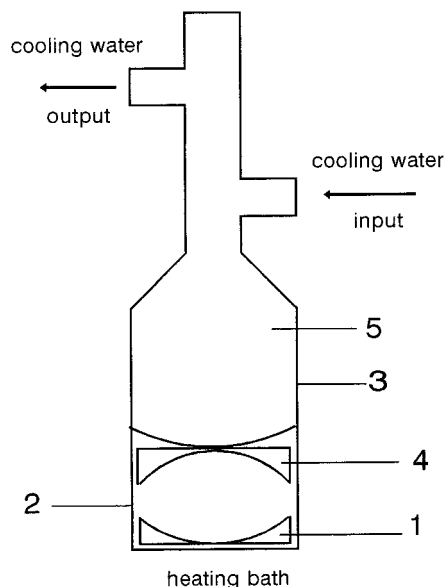


Figure 1 Schematic illustration of a glass assembly for measuring of weight loss during heating and for adsorption of volatile solid components; 1—a lower measuring bowl, 2—a lower glass dish, 3—an upper glass dish, 4—an upper measuring bowl, 5—space inside an upper glass.

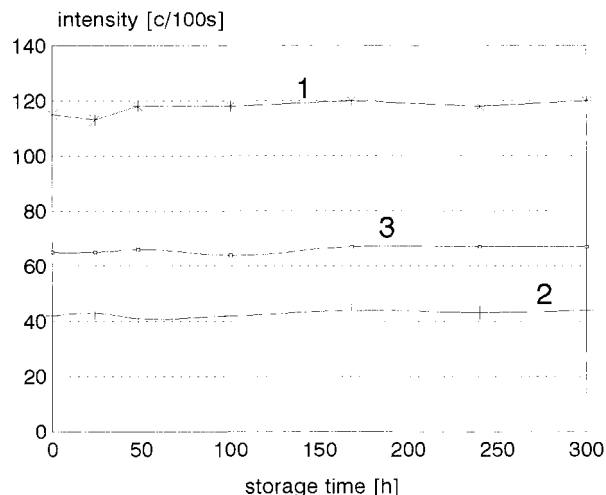


Figure 2 Surface radiation intensity of rubber compounds stored at 20°C, sulfur from the different producers (1), (2), and (3).

pounds during storage, a typical recipe for the rubberizing of a steel cord was used. Three compounds containing polymeric sulfur from three producers were prepared. Six parts by weight of labeled polymeric sulfur (with ^{35}S) were mixed with 182 parts by weight of rubber compound on a mixing mill at 105°C. After measuring their initial radioactivity with a G-M BOH-45 counter, the samples taken from these compounds were stored at temperatures of 20, 35, and 47°C. Successive measurements were made after 24, 48, 72, 144, 216, and 360 h of the storage. Results of these experiments are shown in Figures 2–7. The differ-

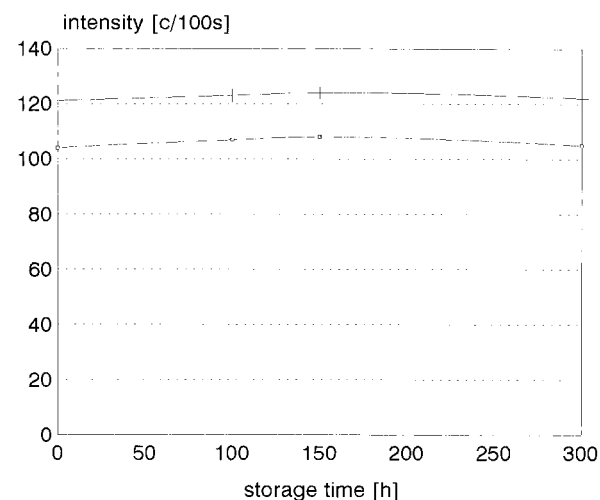


Figure 3 Confidence intervals for 95% probability for rubber compounds containing sulfur from the producer (1), storage temperature 20°C, (+)—upper limit, (□)—lower limit.

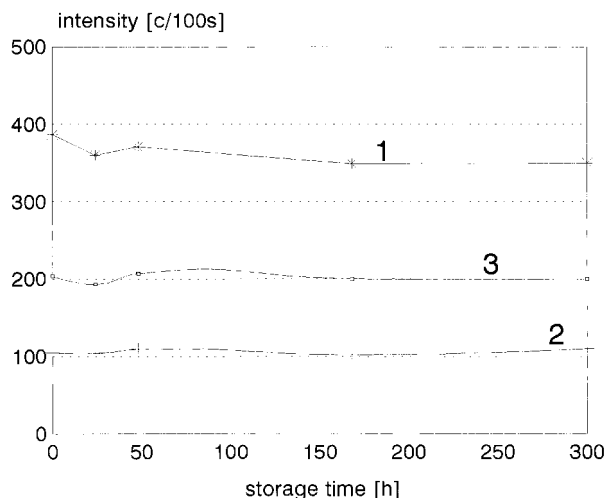


Figure 4 Surface radiation intensity of rubber compounds stored at 35°C, sulfur from different producers (1), (2), and (3).

ence in the initial intensity of radiation (point zero in these figures) is a result of variation in the irradiation inside a nuclear reactor channel where sulfur was placed for activation.

An Initial Stage

A difference in distribution of sulfur in the volume and on the surface of rubber compounds was found. The highest variation coefficient (27.5%) was for a sample (3). However, during storage it is reduced to 13.2%. This shows some diffusion

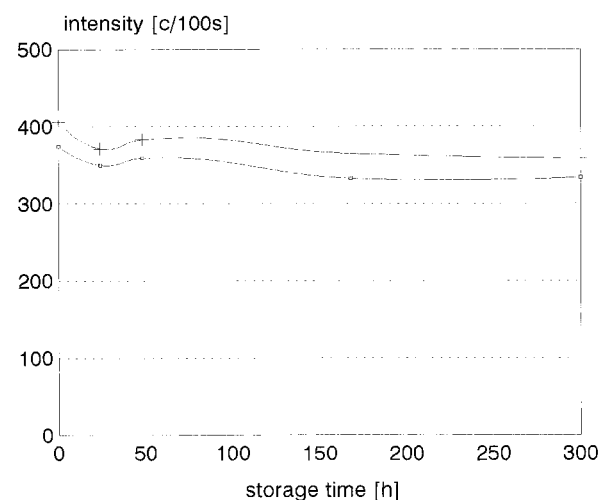


Figure 5 Confidence intervals for 95% probability for rubber compounds containing sulfur from the producer (1), storage temperature 35°C, (+)—upper limit, (□)—lower limit.

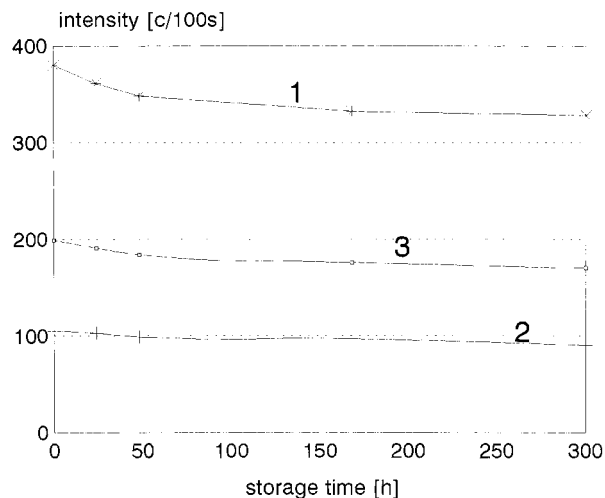


Figure 6 Surface radiation intensity of rubber compounds stored at 47°C, sulfur from different producers (1), (2), and (3).

processes taking place inside the samples. Sulfur taken from the producer (2) was better distributed—variation coefficient 10.8%. Sulfur from the producer (1) was the most uniformly distributed—variation coefficient 6.4%. These coefficients were calculated from 180 measurements. This suggests that tested sulfur samples were granulated in a different way because their structure is similar.

Storage at 20°C

No blooming for all tested kinds of polymeric sulfur was noticed during storage (Fig. 2). Changes in sulfur surface concentration were inside the range of the radiation background of the applied G-M counter. This phenomenon is characterized by a wide confidence interval. As a typical example, in Figure 3 are shown calculation results for sulfur from the producer (1).

Storage at 35°C

No blooming for all tested preparations of sulfur was observed (Fig. 4). A slight decreasing of the sulfur concentrations on the sample surfaces during storage was noticed only for sulfur from the producer (1). Measurements here are characterized by a narrow confidence interval. As a typical example, in Figure 5 are shown calculation results for this sample of sulfur. Tested samples from different producers taken for this investigation behave similarly.

Storage at 47°C

Decrease in sulfur concentration on the surface of tested rubber compound samples (Fig. 6) in comparison to results for storage temperature 35°C and narrow confidence intervals (Fig. 7) were noticed.

Differences in blooming behavior of tested samples of sulfur are so small that this gives an indirect evidence on their similar structure.

Solubility

The solubility degree of sulfur could be measured using different methods.^{5,9-12} In this study polymeric sulfur from different producers was investigated using the well-known method based on measurements of solubility in CS₂ at room temperature.⁹ Amounts of insoluble sulfur were found: 40% for the producer (1), 48% for the producer (2), and 63% for the producer (3). It was noticed that from solubility in the CS₂ view point all these samples of polymeric sulfur could be used, however in a different share in the total amount of sulfur in the rubber compound.

Topological Structure

A thermomechanical method was used to study topological and molecular structure of mineral and polymeric sulfur.¹³ This method is based on testing of the solid (not dissolved) material at temperatures variable against time. Now it was

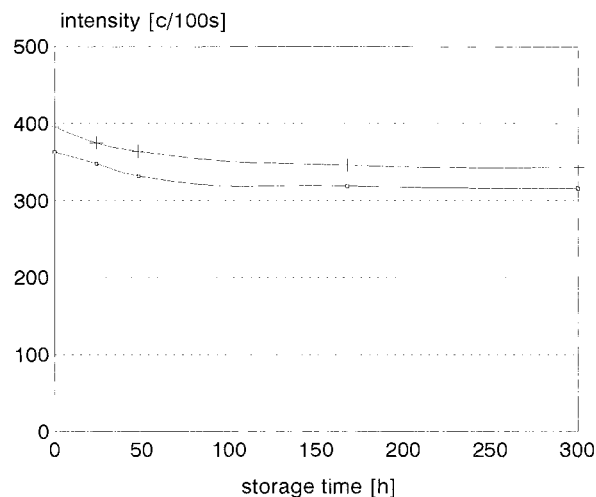


Figure 7 Confidence intervals for 95% probability for rubber compounds containing sulfur from the producer (1), storage temperature 47°C, (+)—upper limit, (□)—lower limit.

found that all tested samples of polymeric sulfur were amorphous (without a crystalline fraction) with a comparable coefficient of molecular weight polydispersity between 2.0 and 2.1. A difference in molecular weight distributions exists, but is small.

CONCLUSIONS

Method of analysis of activated ingredient distribution helps to study phenomena taking place during processing of rubber compounds. Neutron activation of Crystex OT 33 does not change solubility of sulfur substantially and, as a result, general conclusions from earlier blooming investigations. Also, the sublimation and oxidative degradation of soluble sulfur do not influence conclusions of previous investigations of blooming with the help of radioactive measurements. Tested samples of polymeric sulfur (having different concentrations of an insoluble fraction between 40 and 63%) behave similarly from a blooming point of view. Distribution of these samples in a tested rubber compound for rubberizing steel cord is characterized by different variation coefficients from 6.4 to 13.2%, and is expected that this does not create any technological problems.

REFERENCES

1. J. Komosiński and E. Koczorowska, *Isotopenpraxis*, **26**, 61 (1990).
2. B. Jurkowski and E. Koczorowska, *Polimery*, **35**, 217 (1990).
3. B. Jurkowski, E. Koczorowska, W. Gorączko, and J. Manuszak, *Polimery*, **37**, 163 (1992); full English translation: *Int. Polym. Sci. Technol.*, **20**, T/82 (1993).
4. B. Jurkowski, E. Koczorowska, W. Gorączko, and J. Manuszak, *J. Appl. Polym. Sci.*, **59**, 639 (1996).
5. M. Mozisek, *Rubber Chem. Technol.*, **44**, 1307 (1971).
6. H. Bartzsch, A lecture given at the meeting of the Lower Saxony district group of the German Rubber Society, February 13, 1986, Hanover, Germany.
7. E. N. Bielayewa et al., *Promyšlennost SK*, **8**, 31 (1987).
8. D. S. Todorovsky, K. N. Kostadinov, and G. B. Donchev, *Nukleonika*, **24**, 12, 7 (1979).
9. H. Bartzsch, *Gummi Asbest Kunststoffe*, **27**, 72 (1974).
10. M. D. Morris and A. G. Thomas, *Rubber Chem. Technol.*, **66**, 794 (1995).
11. P. Hendra et al., *Kautschuk Gummi Kunstst*, **46**, 694 (1993).
12. A. Brimblecombe et al., *Kautschuk Gummi Kunstst*, **49**, 354 (1996).
13. Y. Olkhov and B. Jurkowski, *J. Appl. Polym. Sci.*, **65**, 499 (1997).