

Radioisotopic Determination Methods of Sulfur Dispersion and Sulfur Blooming in Rubber Compounds

B. JURKOWSKI,^{1,*} E. KOCZOROWSKA,² W. GORĄCZKO,² and J. MANUSZAK¹

¹Division of Plastic and Rubber and ²Division of Radio- and Photochemistry, Poznań University of Technology, Institute of Mechanical Technology, Division of Plastic and Rubber Processing, 61-138 Poznan, Piotrowo 3, Poland

SYNOPSIS

Radioisotope methods have been analyzed to study the dispersion of sulfur in rubber compounds. The radioactivity of the ³⁵S isotope introduced into rubber compounds has been measured by volumetric and surface methods. These methods can be applied to investigate physical and chemical processes in rubber and to optimize technical conditions of tire production. It was found that the radioisotopic methods can be used in the studies of sulfur blooming. Experimental data of the effect of mixing and the storage temperatures of the rubber compound on these processes are presented. Rubber compounds containing soluble sulfur, insoluble Crystex sulfur, and T-accelerator were made for such investigations.

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INTRODUCTION

The phenomena taking place in a rubber compound during production are still little known. This is particularly true for such processes as dispersing of curatives in raw rubber or physical and chemical processes occurring during storage and vulcanization of a rubber compound. It is well known that the concentration of sulfur, which is one of the main components of rubber compounds, essentially affects the structure of the vulcanizate network. This determines also the range of applications of products made of these compounds. Much equipment has been designed to carry out standardized investigations of rubber compounds. However, the proposed methods for estimating the compound's quality still fail regarding different aspects of the problem.¹ For example, there are no efficient and accurate methods to estimate dispersion and migration of curatives in rubber compounds. An attempt was made to solve, at least partially, this problem during optimization of production and processing of rubber compounds. The aim of such an attempt is to meet specific needs in certain products.

In the manufacturing processes of rubber goods, particularly tires, it is important to retain the tack

building of materials to be stable and determined according to technological specifications, since weak tack causes great difficulties during the building of the tires and causes deterioration. Such deterioration appears as the bubbles between layers of the tire body and unsymmetrical location of the elements, etc. The migration of sulfur, paraffin, and other ingredients would form the so-called blooming on the surface of semi-finished raw rubber products.

Investigating of the mechanism and kinetics of the processes accompanying migration of ingredients toward the surface constitutes a difficult and complex problem. It should include the entire manufacturing process from compounding to vulcanization stages of rubber goods. The ratio of ingredients in the recipe and the method of preparation besides storage conditions of a compound and further processing play an important role here. This is because complex physical, physicochemical, and chemical processes depend on temperature to a different degree. In the present work, an attempt was made to estimate the influence of selected technological factors on the kinetics of sulfur blooming.

EXPERIMENTAL

To obtain radioactive sulfur, a soluble sulfur was activated by neutrons in quartz capsules. The flux

* To whom correspondence should be addressed.

of neutrons was 1×10^{13} neutrons $\text{cm}^{-2} \text{s}^{-1}$ and the activation time was 34 h. The obtained radioactive material was "cooled" for 200 days to reduce the concentration of the simultaneously formed ^{32}P isotope. The final preparation contained ^{35}S , with a specific activity of 12.2 MBq/g.^{2,3} Next, the radioactive sulfur was mixed with sulfur that was usually used in industry at a ratio of 1:100 to obtain a homogeneous mixture. The homogeneity of the ^{35}S isotope distribution in the whole mass of the preparation was statistically checked. Variation coefficients of the sulfur activity were found to be from 4.0 to 4.7%. In next stage, the prepared mixture of radioactive and nonradioactive sulfur was introduced into the rubber compound. The methods of the radiation intensity measurements were chosen from those reported in the literature,⁴⁻⁹ which are

- liquid scintillates,
- the proportional flow-through counter 2π ,
- the Geiger-Müller (G-M) counter, and
- an autoradiographic method.

The radiation intensity of samples containing ^{35}S were measured by volumetric and surface methods.

In the volumetric method, sulfur was isolated in the form of water-soluble sulfates. Samples were oxidized by nitric acid and bromine. The samples were then melted with anhydrous sodium carbonate.¹⁰ Under these conditions, sulfur, previously being in various forms, was brought into water-soluble sulfates. Radiation intensity measurements were conducted by two techniques: In the first one, a part of the solution under investigation was introduced into a liquid scintillate composed of 5.5 g 2,5 diphenyloxazole (PPO) and 0.1 g 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) per 1 L of a mixture of toluene and X-100 Triton (2:1).¹¹⁻¹⁴ Radiation intensity was measured by a LS-100C Beckman spectrometer. This method enables detection of the radioactive sulfur to about 10^{-7} g per 0.1 g of the rubber compound. In this case, the technique of liquid scintillates to aqueous solutions was applied. This system requires the presence of some detergents as additional components (e.g., X-100 Triton). Their role is to ensure the solubility of aqueous solution samples in a scintillate. For large amounts of water, the state of emulsion is achieved and the properties of the scintillate are significantly different than if a small amount of water is used. These differences are particularly well manifested as far as the degree of quenching and temperature dependence are concerned. The efficiency of measurements depends also

on the ratio of toluene to X-100 Triton. The reproducibility of results was not satisfactory.

The second procedure required converting the sulfates to $\text{Ba}^{35}\text{SO}_4$. The radiation intensity of the precipitate was measured by a special proportional ZR-16-type flow-through gas counter. This counter was designed to measure low activities of low-energy β -radioactive preparations, providing a good efficiency of 60.7% for a reference standard source of ^{35}S . In this method, the detectability of radioactive sulfur was 10^{-6} g/0.1 g of the rubber compound. For samples with $\text{Ba}^{35}\text{SO}_4$ precipitated, barium significantly absorbs the β -radiation emitted by the sulfur radioisotope. Although the precipitate was filtered off through a special funnel made of PMMA with a filter inside, it was still difficult to obtain reproducible results.

In the surface method, samples of the rubber compound were cut out from a 3 mm-thick plate by a chisel of 22 mm in diameter. The radioactive intensity was measured by the ZR-16 flow-through counter and the G-M counter.^{11,15-17} Emphasis was made that the relative activity measured in this way came from the surface layers of the sample to a depth of 0.3 mm. This was due to the β -radiation emitted by the ^{35}S radioisotope in the studied rubber compound. In this method, the detectability of radioisotope sulfur is also of 10^{-6} g/0.1 g of the rubber compound, ensuring the same geometry of measurements. Here, it is easy to obtain a very good reproducibility of results. The autoradiographic method was used to detect sites of ^{35}S radioisotope concentrations on the sample surface.^{3,18}

An assumption was made that if sulfur blooming takes place on the surface of semifinished products then its concentration has to increase both on this surface and in the layers near the surface. The rubber compound containing this radioisotope was made for our investigations in accordance with our disposal methods and apparatus.^{3,19,20} A soluble sulfur containing the radioisotope ^{35}S was added to the first batch. A Crystex insoluble labeled sulfur was added to the second sample, and the T-accelerator (including ^{35}S sulfur in its structure), to the next one. In each case, the above-mentioned conditions of activation were applied. To decrease the level of activity of the preparation and to reduce the costs of experiments, active and nonactive sulfur were mixed at a ratio of 1 to 100. The T-accelerator was introduced into the compound without dilution with a nonactivated accelerator. For intensity measurements, the method of constant geometry using a G-M BOH-45 type counter was chosen.

The investigated compounds were made in a batch laboratory mixer with a chamber capacity of 2 L and 40 rpm in the following way:

- First, the mixer chamber was heated to an adequate temperature. Tests were carried out at the chamber's temperatures of 110 and 150°C.
- Next, the mixer chamber was loaded with a master batch of a typical compound and masticated for 2.5 min.
- Subsequently, the labeled sulfur was put into a plastic masterbatch and mixed for 2 min.
- After terminating the mixing cycle, the compound was discharged. The temperature was measured by a thermocouple. The following temperatures were recorded:
 - A. For the compound with soluble sulfur: 106, 108, 125, 145, 158°C.
 - B. For the compound with Crystex sulfur: 108, 158°C.
 - C. For the compound with T-accelerator: 105, 118, 138, 160°C.

Each batch of the above compounds was passed through the gap of a mixing mill repeatedly until a relatively smooth plate of 3 mm thick was obtained. Samples with 22 mm diameter were cut out of the compound plate. The first portion of the samples was stored at a temperature of 20°C. The second portion was stored at a temperature of 40°C (or 42°C). The third portion was stored at 60°C. The

difference of 40–42°C resulted from real temperatures inside two different types of thermostating chambers. The intensity of radiation was measured at the surface by the G–M BOH-45-type counters after storage times of 6, 16, 24, 40, 64, 88, 112, 258, and 400 h.

RESULTS AND DISCUSSION

The above-described methods were used in a number of experiments performed in laboratory and industrial scales to estimate the dispersion degree of sulfur in rubber compounds. The effect of various technological parameters on the distribution of sulfur concentration was also studied.

The analyzed factors affecting distribution of sulfur in a rubber compound were the type of compound, number of passes through a mixing mill gap, temperature of the batch at the time of introducing curatives, conditions of vulcanization, time, and storage temperatures.

Measurements of radioactivity and treating results by methods of statistical analysis of the radioisotope-labeled rubber compounds were performed in laboratory experiments. Typical tread masterbatches were passed through the gap of the mixing mill, and soluble sulfur with radioisotope ^{35}S was added. Vulcanization of these compounds at 160°C was carried out (vulcanization time was 25 min). The radioactive intensity was measured by the ZR-16 flow-through and the G–M counter (surface method). For samples with precipitated $\text{Ba}^{35}\text{SO}_4$,

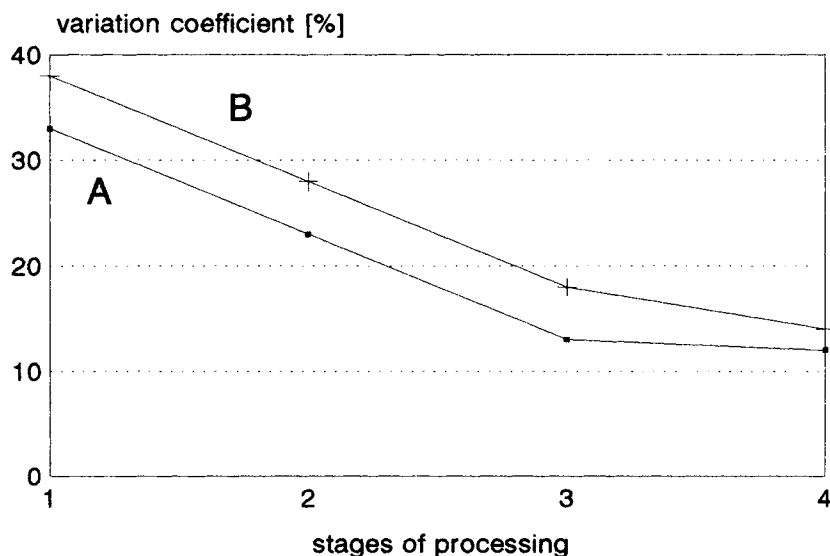


Figure 1 Comparison of variation coefficient at different stages of processing: (A) intensity of radiation measured by the G–M counter; (B) intensity of radiation measured by the flow-through counter.

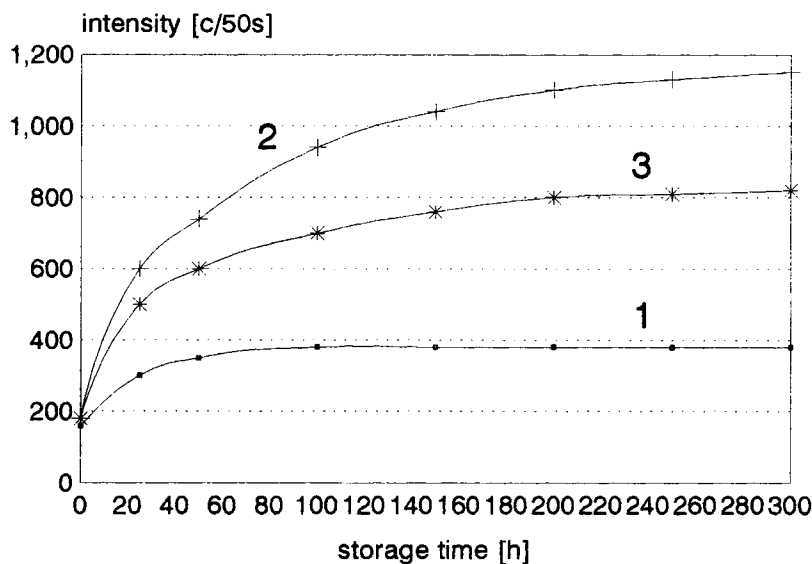


Figure 2 Rubber compounds stored at 20°C: (1) mixing at 106°C; (2) mixing at 125°C; (3) mixing at 145°C.

the volumetric method was used. The autoradiograms of the rubber surfaces were also performed. It was been observed that

- The standard deviation for each process has a characteristic value;
- After 5 and 10 passes through the gap, before and after vulcanization, the distribution of sulfur concentration was the best;
- The influence of the number of passes through the gap on results of radiation intensity was

more visible before vulcanization than after vulcanization;

- The radiation intensity distribution before and after vulcanization measured by surface and volumetric methods were similar to normal distribution; and
- The surface method can be applied to investigate the migration process.

During experiments on an industrial scale, on an extrusion line of treads, the samples were taken at

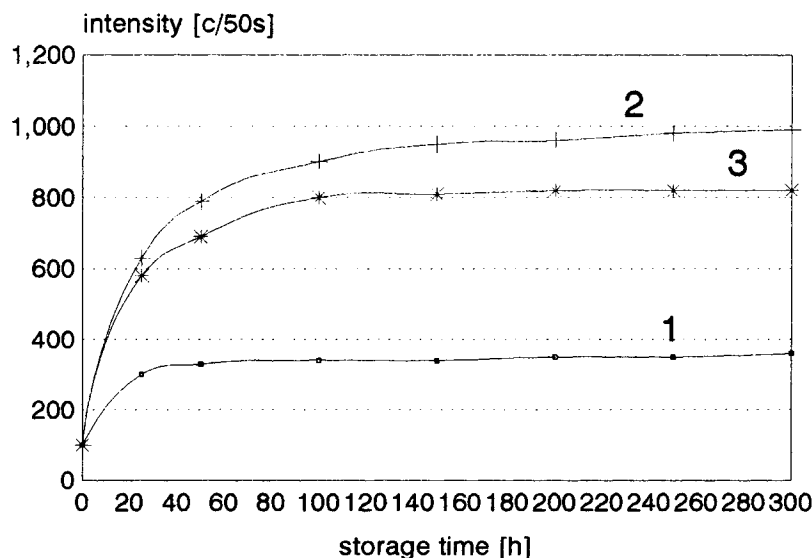


Figure 3 Rubber compounds stored at 40°C: (1) mixing at 106°C; (2) mixing at 125°C; (3) mixing at 145°C.

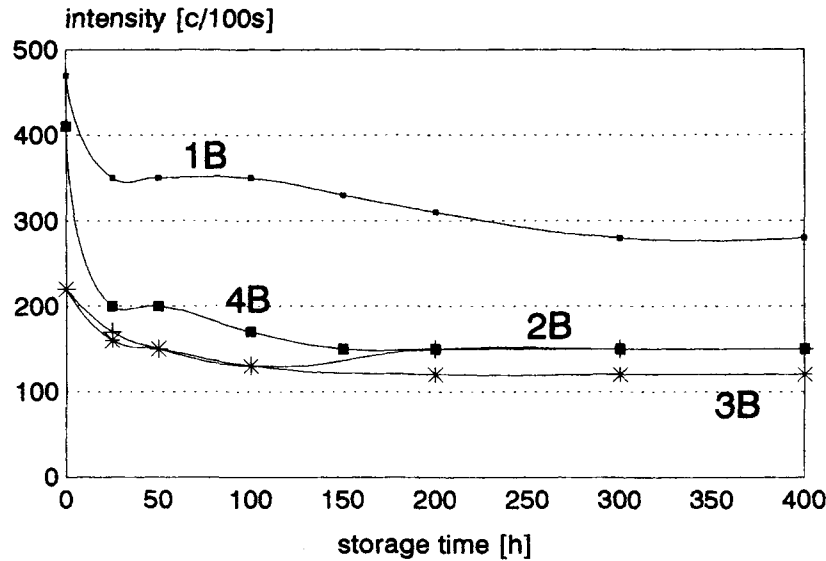


Figure 4 Rubber compounds stored at 42°C: (1B) soluble sulfur, mixing at 106°C; (2B) Crystex, mixing at 106°C; (3B) Crystex, mixing at 158°C; (4B) soluble sulfur, mixing at 158°C.

different stages of the process: (1) from the discharge mill under the mixer, (2, 3) from two subsequent homogenizing mills, (4) and from the extruded tread. The scatter of intensity results decreases after subsequent technological operations. This was confirmed by results obtained by the comparing of variation coefficients of the intensity measurements. These measurements were determined at different stages of the processing of two batches of the same rubber compound. Data are plotted in Figure 1. Experiments were repeated a few times. The obtained

variation coefficients proved that the considered technological process does not provide a satisfactory distribution of curatives in the rubber compound during production and processing in specified conditions. In the majority of the performed experiments, the surface methods were used to measure the radiation intensity as they were simpler, quicker, and cheaper and provided satisfactory reproducibility of results.^{3,19}

In Ref. 3, examples of autoradiograms were discussed as an instructive method. These autoradio-

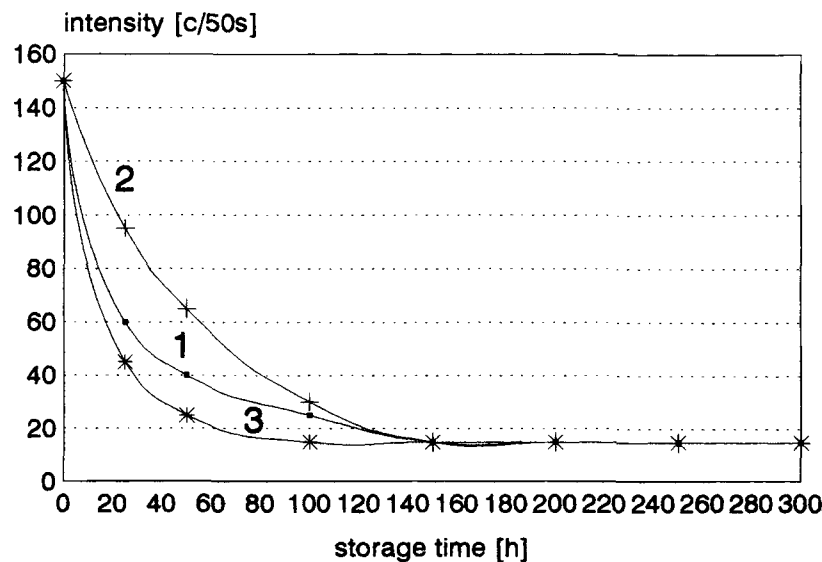


Figure 5 Rubber compounds stored at 60°C (soluble sulfur): (1) mixing at 106°C; (2) mixing at 125°C; (3) mixing at 145°C.

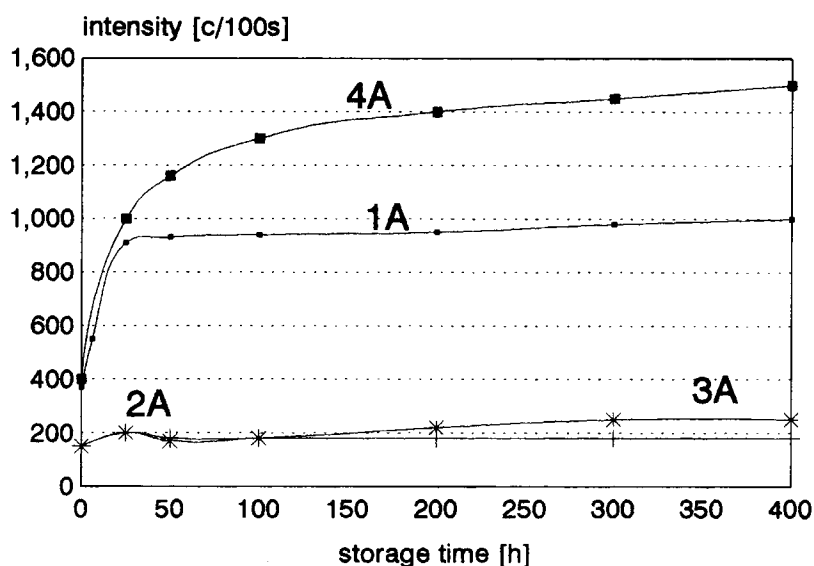


Figure 6 Rubber compounds stored at 20°C: (1A) soluble sulfur, mixing at 108°C; (2A) Crystex, mixing at 106°C; (3A) Crystex, mixing at 158°C; (4A) soluble sulfur, mixing at 158°C.

grams reveal sites of the radioactive sulfur concentration both in compounds and vulcanizates. Taking into account the fact that heating of the compound speeds up the diffusion of sulfur, which is then melted, a reduction in sulfur concentration in points where lumps of sulfur were after mixing is obtained.

Experiments on an industrial scale show that the surface method based on the use of G-M counters is suitable. Using the G-M counters significantly shortens the measuring time compared with other methods. This fact enabled the studying of a greater number of samples, which, in turn, gave results with better accuracy.

In this work, it was found that by using an appropriate radioisotope method local distributions of sulfur concentrations in rubber compounds may be estimated. The accuracy of this estimation is sufficient for a preliminary study of the effects of particular stages of the technological process on the degree of sulfur dispersion and the compound homogeneity.

Visible sulfur blooming on the surface of the compound samples containing labeled soluble sulfur stored at temperatures of 20 and 40°C (Figs. 2 and 3, respectively) were measured. This blooming was independent of the temperature at which the sulfur was put into the batch. At 42°C (Fig. 4), sulfur behaved differently. At first, there can be a sharp drop of the sulfur concentration on the surface. After 24–100 h, the decrease is slower until it reaches some stabilization. At that storage temperature, Crystex sulfur behaved in the same way. The above-described

behavior of sulfur contained in rubber compounds stored at temperatures higher than 42°C indicates that the processes occurring here are the reverse of blooming. It is confirmed by the fact that at a storing temperature of 60°C (Fig. 5) the decrease in concentration of the soluble sulfur on the surface is also very sharp.

Therefore, within a storing temperature between 20 and 60°C for rubber compounds, there is a certain limiting temperature (approximately 42°C) and the direction of the soluble sulfur displacement is reversed. For lower temperatures, sulfur blooming on the surface takes place. For higher temperatures, its motion inside the material is observed. Such behavior of sulfur has been inexplicable so far. That is the reason for attempting to explain these processes in further research.

At a temperature of 20°C, no change of concentration of the insoluble sulfur Crystex was noticed. This was proved by the fact that no blooming on the surface can be found (Fig. 6). In all samples of the rubber compounds containing T-accelerator, no changes of its concentration on the surface were noted. It is independent of the temperature of the compound preparation and the temperature of sample storage.

CONCLUSION

The above-described radioisotope methods can be applied to investigate physical and chemical pro-

cesses in rubber compounds (migration and sulfur blooming). Measurements performed using these methods may be employed for optimization of technological conditions of the production process. These methods permit detection of concentrations 10^{-6} g of radioactive sulfur per 0.1 g of rubber compound. The sensitivity of these methods enables the investigating of sulfur behavior in rubber compounds during processing on an industrial scale without any hazards for workers.

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