Determination of ZnO Dispersion in Rubber Compounds

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SYNOPSIS

It was found that radioisotopic methods can be adapted for analysis of ZnO dispersion in rubber compounds. This method is characterized by a sensitivity of 10^{-6} g ZnO/1 g rubber compound. This fact enables application of this method in technological and research problems. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A review of the literature and the results obtained so far of our own studies involving the application of radioisotopic methods for assessment of dispersion and migration of curatives in rubber compounds[1–4] prompted us to try adapting these methods for analysis of ZnO dispersion in polymer compositions. Zinc oxide is usually added to rubber compounds in the amount of 2–3%. Upon heating, it is transformed into zinc salt of stearic acid, which activates the network. Zinc stearate acts as a lubricant facilitating the processing, especially extrusion.[5]

The aim of the studies reported in this work was to develop a method permitting assessment of ZnO dispersion in rubber compound by tracing the distribution of ^{65}Zn radioisotope.

EXPERIMENTAL

Measurements of the radiation intensity of ZnO and rubber compound samples including ^{65}Zn radioisotope were carried out on an automatic γ-spectrometer Tesla type with an NaJ (T1) crystal. A studied sample was mounted inside the crystal, which ensured the 4π geometry of measurement. Intensity of radiation was measured four times for each sample, the counters' operating voltage was 1200 V and the mean background for the whole cycle of measurements was 6 imp/40 s.

In the first phase of the experiment we worked out the conditions of ZnO activation.

As products of the (n, γ) reaction, we obtained radioisotopes of practical importance: ^{65}Zn emitting γ radiation and β particles (half-life period $T_{1/2}$ = 246 days), and ^{69m}Zn emitting γ-radiation ($T_{1/2}$ = 14 h). Two weeks after the activation the irradiated ZnO contained for the most part only ^{65}Zn nuclides.

To reduce the cost of the studies the activated ZnO was mixed with the unactivated compound (1.633 g ^{65}ZnO + 13,367 g ZnO) till a homogeneous mixture was obtained.[1] In this obtained preparation the variation coefficient of the activated ^{65}ZnO concentration in the sample of nonactivated ZnO was 5.7%.

Under laboratory conditions we prepared a rubber compound, introducing into the averaged production tread batch the obtained mixture with the ^{65}ZnO. The compound was homogenized until the preparation with ^{65}ZnO was homogeneously distributed. From the obtained rubber compound plate we cut out samples in the form of disks 12 mm in diameter and 10 mm in thickness.

The series of cut samples was divided into four subseries. In one of these subseries the studies of ZnO dispersion were performed immediately after the samples were obtained, and the samples of the other three subseries were kept at 22, 45, and 65°C. Each sample prior to measurements was sliced into 1-mm-thick layers. Intensity of radiation was measured for each layer, which were carefully weighted prior to measurements. The results enabled calcu-

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Table I Statistical Parameters of Activity Results in Rubber Compound

Sample Size	Average (c/40s/g)	Standard Deviation (c/40s/g)	Skewness	Kurtosis	Variation Coefficient (%)	Confidence Interval (c/40s/g)
240	3645	126	−1.3	3.5	3.5	3589–3701

lation of specific activities of the samples. Measurements of the samples stored at different temperatures were performed at the following time intervals 0, 3, 9, 21, 45, 69, and 93 h.

RESULTS AND DISCUSSION

On the basis of the collected data, we assessed dispersion of ZnO in the studied rubber compound and checked the possibility of the appearance of blooming on the sample surface as well as traced the ZnO concentration changes in a few layers of the compound depending on the temperature of their storage. Table I presents the basic statistical parameters of these results of measurements performed at 24 sites randomly chosen in the compound bulk. The intensity of radiation was measured for 10 samples taken from each of these sites.

According to Table I data, as far as the ZnO dispersion in the studied compound is concerned, the scatter of results is rather low, characterized by a variation coefficient of 3.5%. This low value of the variation coefficient is indicative of a high precision of the method applied.

As follows from a comparison of results obtained in a few subsequent experiments, the reproducibility of results was good, with a variation coefficient of 3.5–3.9%.

It is well known that during the rubber compound storage, the diffusion of plasticizers takes place, and blooming of stearine, sulfur, and some other components is observed. The question is whether these components take ZnO with them. Table II lists basic statistical parameters characterizing the data collected upon storing of the compound at 22°C (statistical parameters of the date at 45 and 65°C—like at 22°C). We have analyzed only the data for the top layers of each sample in order to get a picture of ZnO concentration changes on the sample surface depending on the temperature of storage. The measured changes in ZnO concentration in the studied rubber compound stored at the temperatures from 22 to 65°C for up to 93 h can be treated as random since according to the Student's t-test they do not differ on the level of significance of 0.05. The proposed radioisotopic method of ZnO content determination in rubber compound is characterized by a sensitivity of 10^{-6} g ZnO/1 g rubber compound. This fact enables application of this method in solving many technological problems related to estimation of ZnO dispersion, as well as other components including Zn atoms, in polymer compositions. Our further studies will concern zinc stearate.

Analysis of the changes in intensity of radiation of the top layers of samples stored at different temper-

Table II Statistical Parameters of the Data for the Storage Compound at 22°C

	First Samples	Storage Time 3 h	9 h	21 h	45 h	69 h	93 h
Sample size	10	10	10	10	10	10	10
Average (c/40s/g)	3618	3560	3697	3805	3599	3563	3682
Standard deviation (c/40s/g)	145	94	164	244	181	153	91
Skewness	0.63	−0.09	−0.18	−0.54	1.23	1.49	0.55
Kurtosis	−1.23	−0.68	0.88	−0.02	2.27	4.48	0.13
Variation coefficient (%)	4.02	2.64	4.45	6.43	5.04	4.30	2.47
Confidence interval (c/40 s/g) (95%)	3514–3722	3493–3628	3579–3815	3630–3980	3469–3729	3453–3673	3617–3747

atures permits concluding that the process of zinc blooming on the compound surface does not occur during the sample storage for up to 93 h. No changes in intensity of radiation and ZnO concentration were observed in subsequent layers of all samples. Thus, it can be concluded that in the studied temperature range there are no changes in ZnO concentration in the whole volume of the compound. In other words storage does not improve the homogeneity of ZnO distribution. Such behavior of ZnO in polymers makes it suitable for quantitative determination of efficiency of mixing devices and the effects of the mixing parameters on homogeneity of polymer compositions.

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