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INVESTIGATION OF VULCANIZATION OF RUBBER BLENDS BY USING ELECTRIC METHODS

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ABSTRACT: The paper shows the results of the measurement of time and temperature dependences of dielectric parameters measured during the vulcanization of the industrial rubber blend. Obtained results were compared to measurements made by rheometer. By using electric methods, it is possible to investigate the quantity and the quality of the processes running during the vulcanization.

KEY WORDS: rubber blends, vulcanization, dielectric properties

1. INTRODUCTION

It is important and useful to know the processes going on during the development and the production of new materials, as well as the influence of these processes on inner structure and their requested properties. Vulcanization, by chemically crosslinking long, flexible rubber chains to form a three-dimensional network, converts the rubber from a plastic substance of a very low strength into a highly elastic material of a considerable strength. The most frequently applied method for evaluation of the vulcanizing parameters consists of taking measurements by using several types of rheometers. These devices measured the time dependence of torque during the vulcanizing rubber blends. Evaluation of crosslinking isotherms obtained by rheometer test is the time law of crosslinking reaction [1]:

$$r_M = \frac{dM}{dt} = k(M_{\max} - M)^n \quad (1)$$

where k is rate constant of curing, n order of reaction, M torque at time t , M_{\max} final torque. Time differential of torque corresponds with cure rate r_M . Solution of differential equation (1) for $n = 1$ (1st order) is

$$M = M_{\max} - (M_{\max} - M_{\min}) \cdot e^{-k(t-t_i)} \quad (2)$$

and for $n \neq 1$ is

$$M = M_{\max} - \sqrt[n]{(M_{\max} - M_{\min})^{1-n} + k(t-t_i)(n-1)} \quad (3)$$

where t_i induction period and M_{\min} is initial torque uncross-linked sample.

In complex systems such as plastics and rubber, as well, it is possible to use methods of measurements of electrical parameters in order to detect changes in the structure of a material [2]. Electric conductivity corresponds to number of electrical charge [3].

$$\sigma = \sum N_i q_i u_i, \quad (4)$$

where N_i is number of electrical charge in elementary volume, q_i is electric charge, u_i mobility of charge.

During the crosslinking reaction, values of electrical conductivity increase due to the number of activated vulcanizing agents (sulfur). After creation of bonds between macromolecules of a rubber, mobility of charge is finished and electrical conductivity decreases [4]. The cure rate r_M corresponds to changes of conductivity during the vulcanization ($\Delta\sigma \sim r_M$). [5].

2. EXPERIMENTAL PROCEDURE

Rubber blends are usually vulcanized at 140-180 °C with a combination of sulfur, one or more accelerators, zinc oxide and a fatty acid. The mix formulation also contains other components, e.g., fillers, processing aids, antioxidants, and antiozonants, but these are incidental for the vulcanization process.

Investigated material was rubber blend in the non-vulcanizing state before the curing. The rubber blend was prepared by the known technological process with the formulation given in Tab 1.

Tab.1: Formulation of experimental material

I. st. [g]				II. st. [g]	
Rubber 1	889	Antioxidant 1	12.2	Denax DPG	15.7
Rubber 2	218	Antioxidant 2	10.5	Sulfenax CBS	16.6
Silica filler	567	Paraffin 60/62	10.5	Duslin G80	2.5
Carbon black	131	Aktiplast PP	33.1	Sulfur	20.2
X-50S	101	Stearin III	13.1		
Oil	65.4	Korezin	13.1		
ZnO	26.1				

The course of vulcanization was recorded by MDR 2000E Rheometer, whereby the torque values were found out by Alpha 2000R software. These standard measurements were performed at the constant temperatures of 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C and 200 °C. The samples of the same weight of 5.0 g were prepared for measuring of these values.

Procedure of the measurement of electrical properties was chosen on the basis of analogy with methods of torque moment measurements. The measurements were performed at the constant temperatures of 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C and 200 °C. The determination of dielectric properties by means of the measurements of time dependencies of alternate conductivity ($\sigma_{AC} = \sigma(t)$), was performed by using GoodWill LCR 819 LCR meter at the frequencies of 20 Hz - 100 kHz. The samples of the prism shape with dimensions 20×20×2 mm were contacted by using stainless electrodes at the opposite sides of samples.

3. RESULTS AND DISCUSSION

Processes running during the simulation of the vulcanizing conditions (change of temperature) were investigated. Dependencies of the time-torque measured at various temperatures for the sample are plotted in Fig.1. The nature of the vulcanizing curve changed with the increase of temperature, but mainly such important parameters in rubber technology like scorch time and optimum of vulcanization were decreased. Time dependencies of time differential of torque are plotted in Fig. 2. The cure rate increases with the increase of measurement temperature.

Time dependences which alternate conductivity $\sigma_{AC} = \sigma(t)$ measured at various temperatures are plotted in Fig. 3. The vulcanization processes are characterized by maximum value of conductivity at temperature range of about (130-180) °C. Position of this maximum on time axis relates to the rate of

vulcanization processes and the height of the maximum relates to the intensity of investigated processes. Area of local maximum at $\sigma_{AC} = \sigma(t)$ could correspond to number of crosslinks after curing.

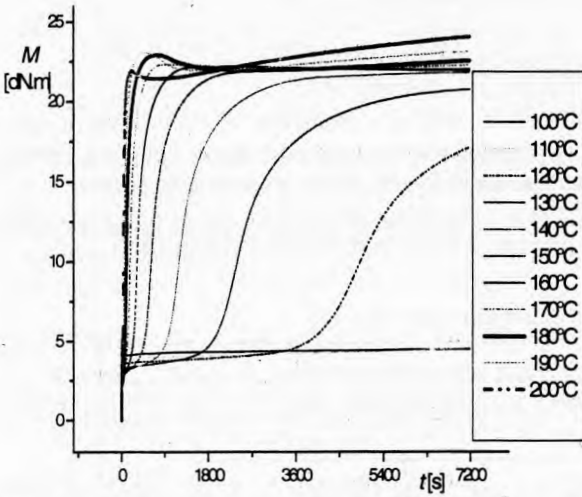


Fig. 1: Time dependencies of the torque measured at 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, 200 °C by using MDR 2000E Rheometer

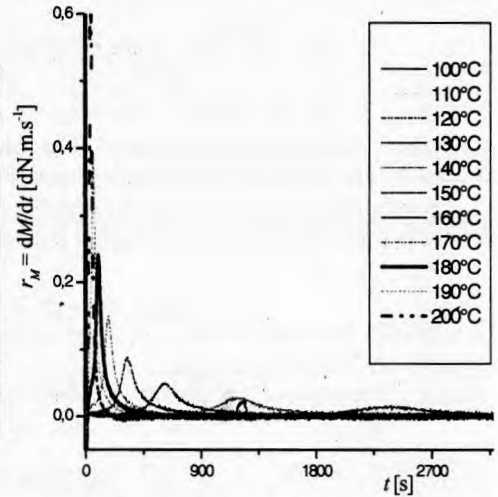


Fig. 2: Time dependencies of the time derivative of torque measured at 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, 200 °C

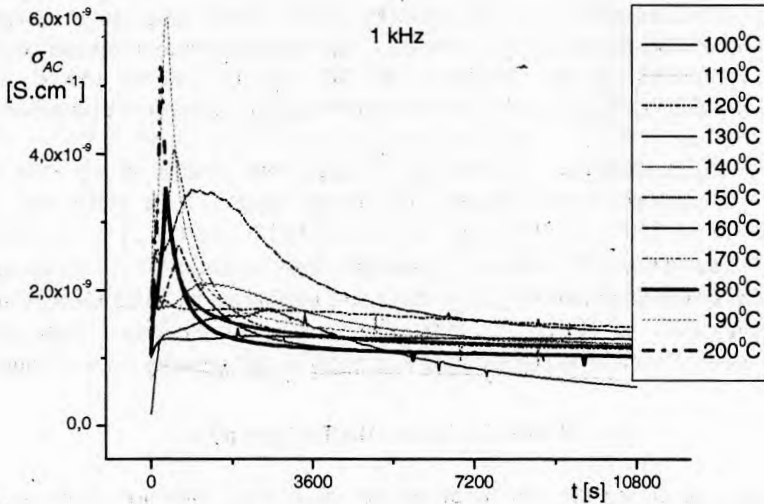


Fig. 3: Time dependencies of alternate electrical conductivity measured at 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, 200 °C by using LCR 819 LCR meter

To confirm this idea another experiment was performed. The samples of rubber blend were preheated for 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 and 160 minutes at 120 °C, and in the next step they were preheated two hours at 160 °C with measurement of alternate conductivity. Selected results are plotted in Fig. 4. During the preheating at 120 °C are crosslinks created slowly, but

with increasing time their number increases. The effect of a vulcanization reaction at 160 °C decreases with the increase of the time of preheating. In Fig. 5 there are dependencies of area of local maximum (A) and rate constant (k) calculated from measured data of time dependencies of alternate conductivity measured at 160 °C after the process of preheating at 120 °C. Rate constants were calculated by using differential of equation (2) from the decreasing parts of curves. These parameters decrease with the time t_{120} of preheating of the samples at 120 °C.

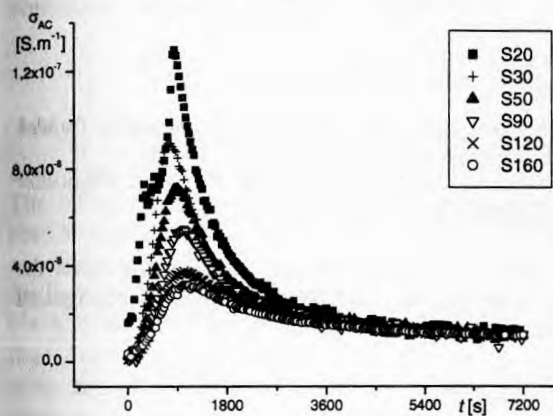


Fig. 4: Time dependencies of alternate electrical conductivity measured at 160 °C after heating for 20 min, 30 min, 50 min, 90 min, 120 min and 160 min at 120 °C

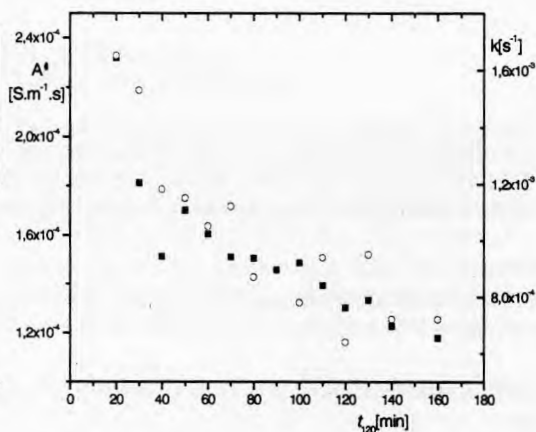


Fig. 5: Dependencies of area (\blacksquare) of local extreme and rate constant (\circ) calculated by using time dependencies alternate conductivity at 160 °C after the process of preheating at 120 °C

4. CONCLUSION

Electric measurements seem to be useful for the investigation of the processes running during the vulcanization of the rubber blend. Changes of conductivity could be connected to changes of the number of vulcanizing agents, which is sulfur in this case.

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