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The Relationship Between Mechanical and Electrical Properties During Vulcanisation of SBR Based Rubber

Introduction

Development of polymer materials is in the centre of interest of many research works in engineering practice. The materials based on rubber compounds are used in many technical applications, mainly in the transport for the production of different type tyres. New opportunities to improve the quality of raw materials and their processing are important due to diversity of application requirements and the increasing requirements on the specific characteristics of these materials. The final properties of materials based on rubber compounds are significantly affected by processing of raw materials. Vulcanization is a crucial part of these treatment processes. Traditional diagnostics is usually based especially on the tracking of the mechanical parameters [Salgueiroa a kol. 2007; Rusnákova a kol. 2014]. It is important to develop new methods based on the monitoring of such physical properties that are usually connected directly with changes of the material structure [Kubliha 2009; Bošák a kol. 2007; Seliga a kol. 2015].This paper is focused on the possibility of non-standard characterization of the curing processes realized under condition of the linear increasing of temperature by means of scanning mechanical (torque measurement) and electrical (conductivity studies) parameters.

Experiment

The experiment was realized under conditions of the linear heating, which is suitable for subsequent mathematical description of the studied process. Monitoring of temperature changes during cure has practical use in the rubber industry.

The experimental procedure was chosen in view of the simplicity of linear and isothermal heating. We used the modified rubber compounds in which the number of accelerators (sulphur, fillers...) has been established with respect to the configurations used in industrial practice. But their content was reduced to minimum to simplify the subsequent mathematical processing. The composition of used mixtures based on butadiene-styrene prepared in a standard way for two-cylinder system is described in Table 1.

Table 1

Composition of the tested rubber mixture

Compound	pphr
Rubber	100.0
Vulcan C-72 R	8.0
ZnO	3.0
Sterin III	1.0
Dusantox IPPD	1.0
Sulfenax CBS	1.5
Sulphur	1.5
Total	116

Results

Isothermal measurement of rubber compounds at various temperatures is listed in the preceding paragraph. Figure 1 shows the graph obtained by measurement of the time dependence of torque.

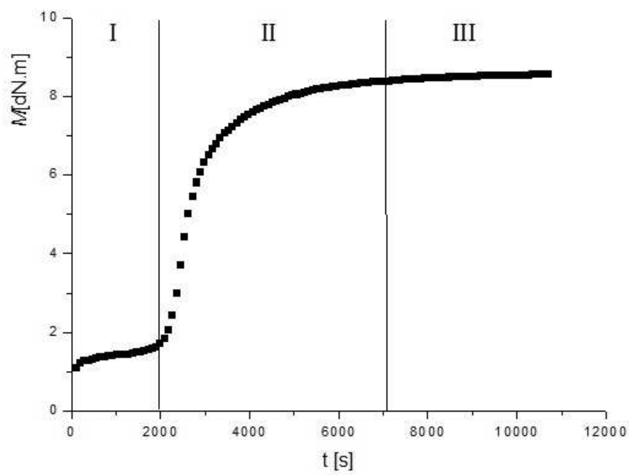

Fig. 1. Time dependence of the torque at the temperature 135 °C

There can be well recognized three areas (see Fig. 1) in the dependence, the area of the induction period (I), the area of self-crosslinking reaction (II) and vulcanization plateau region (III).

The area of self-crosslinking reaction can be described using the equation:

$$M = M_{\max} - \left(M_{\max} - M_{\min}\right) \cdot e^{-k(t-t_i)}, \quad (1)$$

After consideration of the thermal dependence of induction period and rate constant we obtain:

$$M = M_{\max} - \left(M_{\max} - M_{\min}\right) \cdot \exp\left[\text{-e}^{S_1 - \frac{E_1}{RT}} \left(t \text{ - e}^{-S_2 + \frac{E_2}{RT}} \right) \right] \tag{2}$$

The rate of vulcanization can be determined by time derivative of previous equation:

$$r_M = \frac{dM}{dt} = \text{e}^{S_1 - \frac{E_1}{RT}} \cdot \left(M_{\max} - M_{\min}\right) \cdot \exp\left[\text{-e}^{S_1 - \frac{E_1}{RT}} \left(t \text{ - e}^{-S_2 + \frac{E_2}{RT}} \right) \right] \tag{3}$$

In equations (1)–(3) $M_{\max}$ represents maximum value of torque, $M_{\min}$, minimum value of torque, k vulcanization rate constant, t_i time of induction period. S_1 is kinetic constant independent on temperature, E_1 is activation energy of vulcanisation. S_2 is kinetic constant independent on temperature and E_2 is activation energy of initiation. These parameters are described in [Seliga a kol. 2015].

Processing of the values measured at different temperatures shows the impact of rising temperatures on the curing parameters (time period of induction, self-crosslinking reaction), as reflected by shortening the induction period and increasing the rate of self-crosslinking reaction, as it can be seen in Fig. 2.

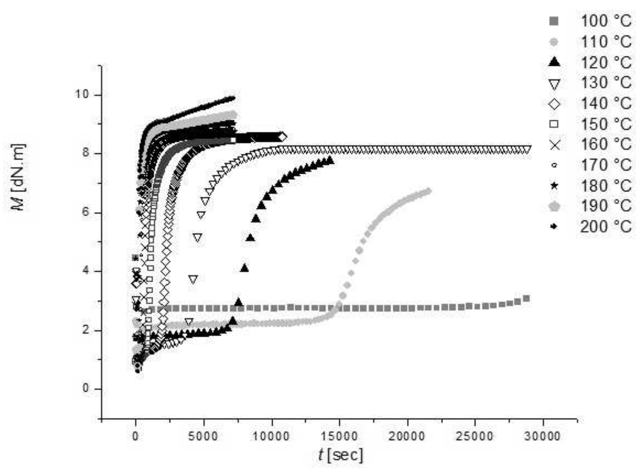

Fig. 2. Time dependence of torque of the rubber mixture M at temperatures from 100 °C to 200 °C

Measurement of vulcanization curves at linear temperature increase was realized after verifying the basic parameters of rubber compounds. We monitored the process of vulcanization under linear heating by pursuing of mechanical and electrical properties. Mechanical properties monitored by the time dependence of torque allow to determine the degree of cure using a constant angle of 0.5°

and the frequency of 1667 Hz. Measurements were realized at temperatures between 30–200 °C. Figure 3 shows the result of the measurement of the temperature dependence of the torque at the heating rate 2° C.min^{-1} during the first measuring cycle. The graph can be divided into two main parts. In the first part is the change of torque is affected by the change of viscosity at increased temperature (I – part of Fig. 3) and by the onset and course of crosslinking reaction that creates crosslinks between the rubber macromolecules (II – part of Fig. 3). The boundary between the parts corresponds to a temperature of about 150 °C.

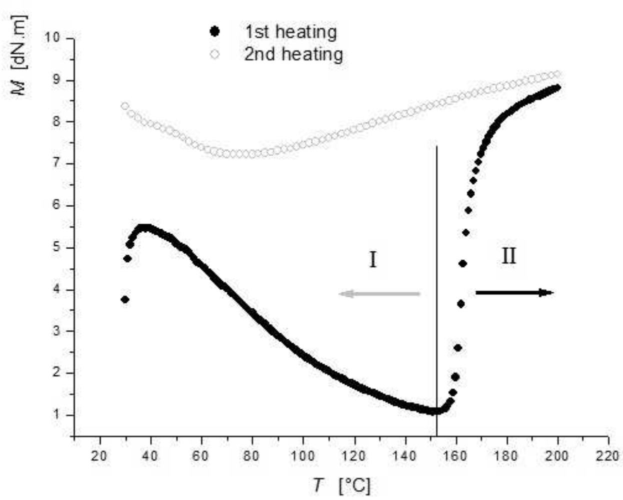

Fig. 3. Temperature dependence of the torque M, heat rate of 2°C/min

Investigations of changes of mechanical properties (torque) during linear increasing temperature have been realized by monitoring of electrical parameters. Our experiences with the measurement of direct electrical conductivity (DC) are based on the research work and projects solved in the past [Kubliha 2009; Bošák a kol. 2007]. Conductivity measurements were performed by using KEITHLEY 6517B device at the same heating condition as torque measurement. The measurements consist of two heating cycles with cooling to 0 °C after first cycle.

Temperature dependence of DC conductivity of the rubber mixture during the 1st and 2nd heating cycle can be seen in Fig. 4. The significant increase of the DC conductivity values could be connected with vulcanization reaction. The second heat cycle confirms the finish of the vulcanization. We observed no significant changes of DC conductivity, connected with charge transport during investigation process.

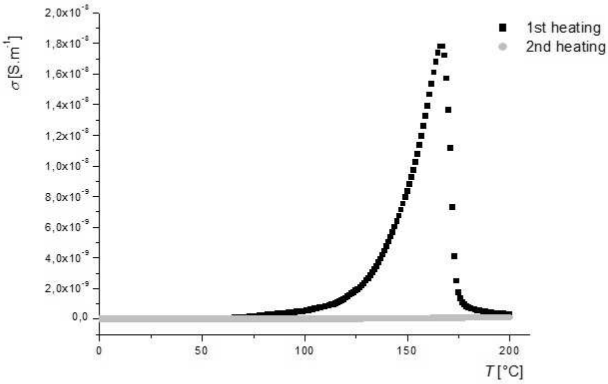

Fig. 4. Temperature dependence of the DC electrical conductivity σ of the rubber mixture, heat rate of 2 °C/min

Measured values of the electrical conductivity corresponding to the process of cure at different heat rate still require further analysis. Analysis of these results is important for good description of vulcanization processes. This part of investigation we plan for the next time.

Conclusion

The article is focused on monitoring and analysis of the process of vulcanization of rubber compounds at linear heating at different temperatures. Description has been used for torque measurement in isothermal heating. Mechanical and electrical properties were analyzed by means of obtained data. Measurement showed that the rubber mixture behaves as expected. Increasing of the temperature affects the mechanical and electrical properties. Monitoring of the electrical properties can be used to investigate the process of vulcanization, since they are identical to the standard tests.

Acknowledgements

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Abstract

The aim of this paper is description of vulcanization process by monitoring of selected electrical and mechanical parameters. The experiments have shown that the vulcanization process can be qualitatively and quantitatively evaluated on the basis of measurements of mechanical (standard procedure in rubber industry) and also electrical parameters. The results obtained for model system SBR rubber mixture under conditions of linear heating are presented also.

Keywords: electrical conductivity, torque, curing, linear heating.