

# MATHEMATICAL MODELLING OF TEMPERATURE DEPENDENCES OF DIRECT ELECTRICAL CONDUCTIVITY OF STYREN-BUTADIEN RUBBER BLENDS FROM TIME DEPENDENCES OF TORQUE VALUES DURING VULCANISATION

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## Abstract

*This contribution presents a procedure of numerical modelling of temperature dependences of direct conductivity of styrene-butadiene rubber (SBR) blends, using the knowledge of vulcanisation curves (time dependences of torque). The cross-linking rate determined from measurements of mechanical values is proportional to the number of electrical charge carriers and also proportional to the increase in electrical conductivity. Considering heat transfer during vulcanisation, the modelled courses of temperature dependences of direct conductivity display a good conformity with real measurements.*

## Key words

*vulcanisation, rubber blends, electrical properties*

## Introduction

The most important technological operation in preparation of rubber is the process of vulcanisation, i.e., transformation of rubber blend, most often induced by higher temperature [1]. This process determines in a decisive manner the final values of useful properties. For the process description and optimisation, measurements of selected mechanical values [2] are used in most cases. In some types of vulcanisation systems, the process of vulcanisation can also be observed by carrying out measurements of selected physical values. In styrene-butadien (SBR) rubber blends vulcanised by means of sulphur, we can observe the increase in direct conductivity values during the process of cross-linking reaction [3]. This increase is connected with the creation of temporary electrical charge carriers whose number is proportional to the rate of cross-linking reaction.

This contribution is focused on the modelling of direct conductivity (DC) values by means of measurements of mechanical properties and the knowledge of cross-linking reaction kinetics. The modeled values are compared with experimentally obtained values of direct conductivity.

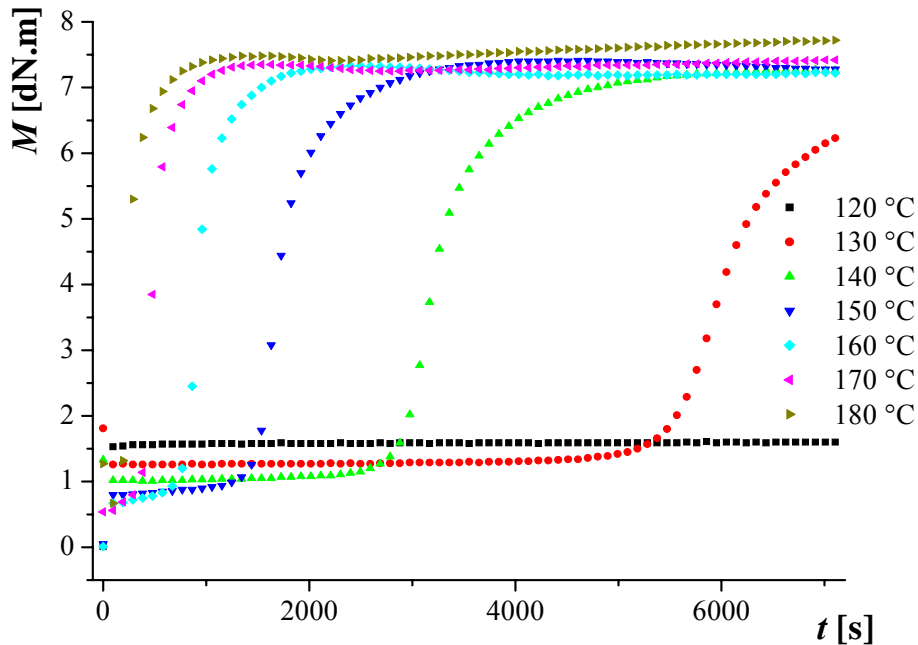
### Experimental part

Vulcanisation curves (i.e. time dependences of torque value at a constant temperature) measured by the MDR 2000 Rheometer [4] were used for modelling of direct conductivity values during SBR rubber blend vulcanisation . The direct conductivity measurements were realized by the volt-ampere method, i.e. by the measuring of the value of electrical current flow at a constant electrical voltage 10 V by the Keithley 6485 device.

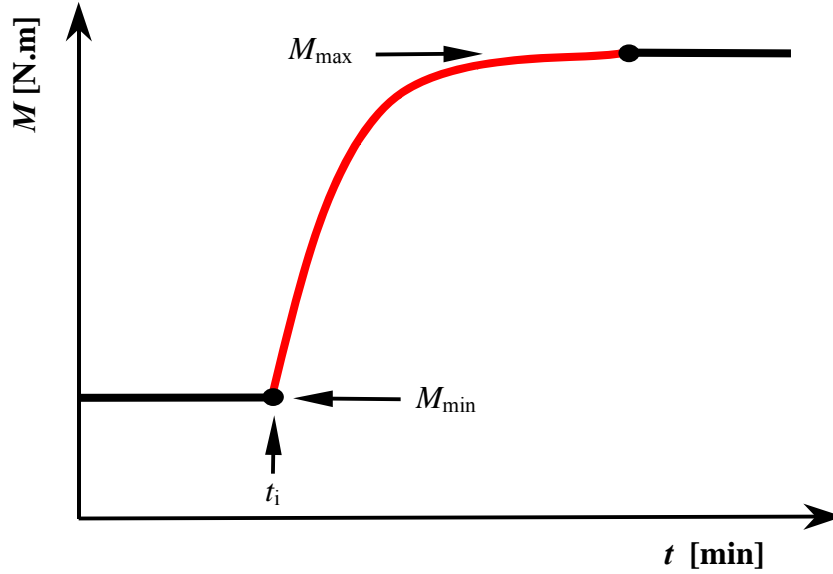
Based on the measurements of time dependences of torque (Fig. 1) and using least squares numerical method approximation, in the cross-linking area (Fig. 2) were determined constant values ( $M_{\max}$ ,  $M_{\min}$ ,  $S_1$ ,  $S_2$ ,  $E_1$ ,  $E_2$ ) needed for a description of temperature-time dependences of cross-linked bond creation rate  $r_M$  during vulcanisation, using relation [1, 5]

$$r_M = e^{\frac{S_1 - E_1}{RT}} \cdot (M_{\max} - M_{\min}) \cdot \exp \left[ -e^{\frac{S_1 - E_1}{RT}} \left( t - e^{-S_2 + \frac{E_2}{RT}} \right) \right], \quad (1)$$

where  $T$  is temperature,  $t$  is time and  $R$  is a universal gas constant.



**Fig. 1** The time dependence of torque for selected temperatures of SBR rubber blend vulcanization



**Fig. 2** Schematic representation of time dependence of torque at temperature  $T$  with the cross-linking reaction area (marked in red)

Relation (1) enables a description of vulcanisation even at temperatures that cannot be used in experimental observations (too long or short periods of vulcanisation). The value of electrical conductivity of rubber blend is affected by cross-linking because the number and mobility of the existing electrical charge carriers change. Cross-linked bonds between macromolecules have minimal effect on the electric charge transport because the number of abridged segments of a macromolecule is very small compared to the number of unabridged segments during the cross-linking process. We assume that the increase of DC conductivity during the cross-linking process is connected only with the creation of new temporary charge carriers.

The electrical conductivity value caused by cross-linking reaction can be described by the relation

$$\Delta\sigma = N_s \cdot q_s \cdot u_s , \quad (2)$$

where  $u_s$  is a magnitude of mobility of temporal electric charge carriers, the magnitude of which is minimally affected by cross-linking,  $q_s$  is a constant magnitude of temporal electric charge carriers, and  $N_s$  is the number of carriers which is proportional to the rate of cross-linked bond creation. This means that the change of the value of electrical conductivity during the cross-linking reaction is proportional to the rate of the cross-linking stage ( $\Delta\sigma \approx c_1 r_M$ ).

If we find this proportion, determine constant  $c_1$  and consider Arrhenius relation [6,7,8], we can determine temperature dependence of electrical conductivity of rubber blend during cross-linking without the influence of vulcanisation in the next form

$$\sigma = \sigma_{0,\text{blend}} \exp(-E_{\text{blend}} / kT) + c_1 \cdot (r_M)_T , \quad (3)$$

where  $k$  is the Boltzman constant,  $E_{\text{blend}}$  is activation energy of electrical conductivity of rubber blend without considering cross-linking, and  $\sigma_{0,\text{blend}}$  is a pre-exponential factor of electrical conductivity of rubber blend without considering cross-linking.

It is the problem to determine value of the cross-linking reaction rate  $r_M$  in relation (3). Namely, the initial time of cross-linking during vulcanisation does not depend only on the

temperature, but it is also dependent on the grade of induction stage completion (stage before cross-linking, without creation of cross-linked bonds). It follows that if we expose the rubber blend to lower temperature for a sufficiently long period, we can observe a consequent shortening of the period of induction stage  $t_i$  at higher temperature (Fig. 2). Simply said, a preceding induction of the blend affects the shortening of the induction period value at a given temperature. Thus, during gradual heating of rubber blend it is necessary to consider the reached degree of the induction period. A similar situation also occurs in the case of cross-linking reaction rate whose value depends on the reached number of cross-linked bonds – the degree of cross-linking. The main idea of the model is to describe the course of vulcanisation by assembling the process from very small time segments  $\Delta t$  in which the temperature can be considered to be constant. The change in the degree of induction period  $S_{IP}$  in the range of 0 to 1 can be described by the equation

$$(\Delta S_{IP})_T = \left( \frac{\Delta t}{e^{-S_2 + \frac{E_2}{RT}}} \right)_T . \quad (4)$$

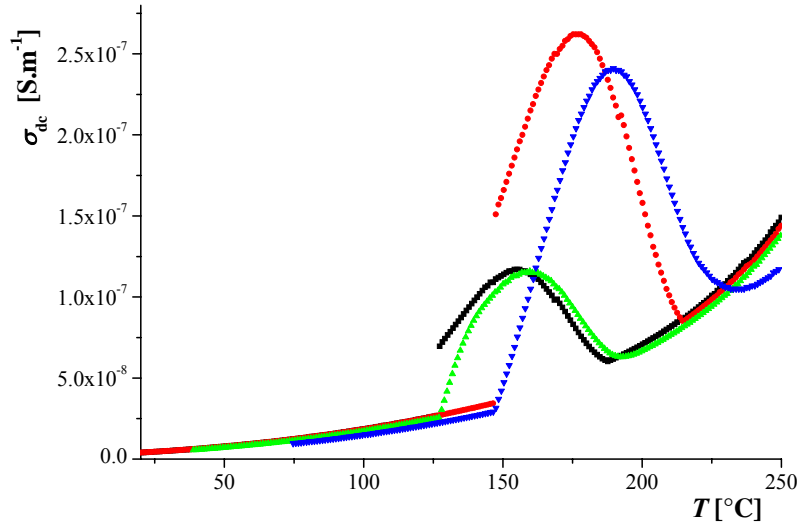
On reaching  $S_{IP} = 1$ , the cross-linking stage of vulcanisation begins. Similarly, in the case of the degree of cross-linking period  $S_{SP}$  in the range of 0 to 1, it is possible to use the equation

$$(\Delta S_{SP})_T = (\Delta t \cdot r_M)_T , \quad (5)$$

where  $r_M$  is the immediate value of cross-linking rate whose value depends not only on temperature  $T$ , but also on the immediate degree of vulcanisation  $S_{SP} = \frac{M - M_{\min}}{M_{\max} - M_{\min}}$ . Hence, for  $r_M$  in relation (5) can be used the relation

$$r_M = e^{\frac{S_1 - E_1}{RT}} (M_{\max} - M_{\min})(1 - S_{SP}) . \quad (6)$$

The value  $r_M$  expressed by means of relation (6) can be now used in the model of the changes in rubber blend electrical conductivity during its heating as a substitute into relation (3). We also considered the change of electrical conductivity during linear heating of the sample due to a delay in thermal heating in the sample volume. Although this phenomenon has a significant influence mainly at higher temperatures, it was used in the entire temperature interval. In modelling, there was also implemented a thermal factor  $\Delta T_z$  expressing thermal difference between the sample surface and its centre. We considered a linear change of temperature in dependence of the distance from the sample surface to its centre. The relation (3) was used for the determination of values of direct electrical conductivity in the model. The rate of the cross-linking reaction  $r_M$  was determined by means of relation (6). Methods of numerical mathematics [9, 10] were implemented into the prepared programme equipment. Fig. 3 shows the example of modelled dependences of the direct electrical conductivity with considering the delay in heating inside the sample for two rates of heating. As it can be seen from results, the effect of the heating rate and the considered delay on direct electrical conductivity can be observed. Considering an ideal case without a delay, the beginning of the cross-linking reaction is accompanied by the jumping change in the cross-linking rate, which is also manifested by the jumping change in the value of direct conductivity.



**Fig. 3** Representation of thermal dependences of electrical conductivity for approximated values  $M_{min} = 3 \text{ dN.m}$ ,  $M_{max} = 20 \text{ dN.m}$ ,  $S_1 = 14,16388$ ,  $S_2 = 12,64122$ ,  $E_1 = 70103,843 \text{ J.mol}^{-1}$ ,  $E_2 = 70690,16 \text{ J.mol}^{-1}$ ,  $E_{blend} = 0,18 \text{ eV}$ ,  $\sigma_{0,blend} = 5.10^{-6} \text{ S.m}^{-1}$  for two heating rates  $v_2 > v_1$ : without considering the delay ■  $v_1$ , ●  $v_2$  and with considering the delay ▲  $v_1$ , ▼  $v_2$

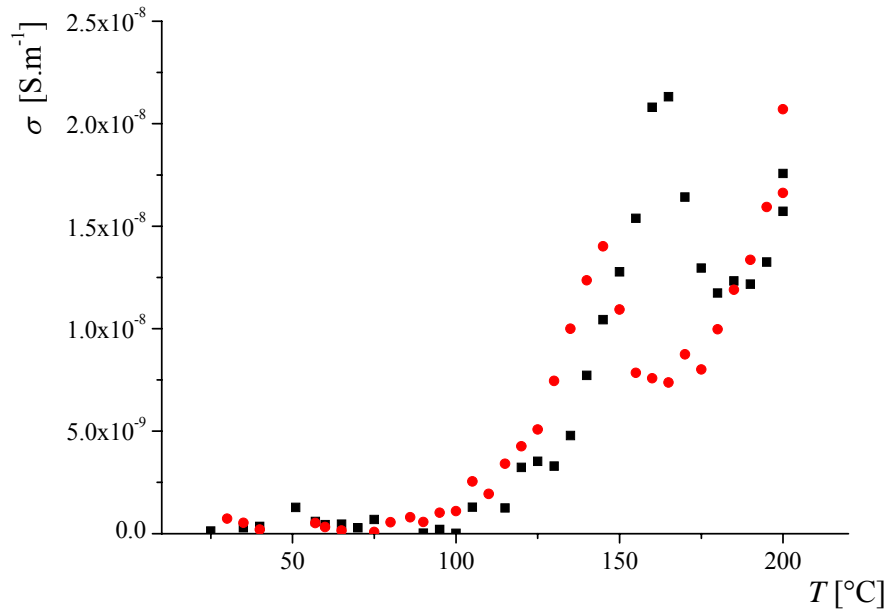
The reaction rate increases with the increasing of temperature, although the degree of cross-linking reaction continually decreases, particularly due to the exponential growth with the change in temperature. There is also an influence of the heating rate whose values affect the beginning and the course of cross-linking reaction. With the increasing of heating rate, the start of linking reaction shifts to higher temperatures, whereby the process of cross-linking is accompanied by higher values of reaction rate. This thermal shift is caused by the reaching of degree  $S_{ip} = 1$ , at a lower heating rate being reached at lower temperatures, and the following cross-linking reaction is slower due to lower temperatures.

Considering the delay, we modelled the temperature dependences of direct conductivity characterised by the loss of discontinuity at the beginning of cross-linking. Shift of cross-linking at higher temperatures with the lowered values of reaction rate, mainly at higher heating rates was modelled. Comparing the modelled values of the direct conductivity (Fig. 3) in case of the considering delay (▲, ▼) with the measured values of direct conductivity (Fig. 4), we can see a remarkable similarity.

## Conclusion

In the determining the conformity between the modelled direct electrical conductivity based on the assumption of creation of temporary charge carriers and the real measurements, there is a remarkable correlation regarding mainly the exertion of heating delay in the sample volume towards its surface and the influence of the heating rate magnitude. The delay effect is understandable regarding the fact of low thermal conductivity of polymers, to which rubber blends with a lower fulfilment are converging. The influence of the heating rate is primarily given by finishing of the induction period. At a lower heating rate, the finishing occurs at lower temperature, and the resulting cross-linking reaction displays the lower values of the reaction rate. The modelled dependences were determined provided the linear decreasing of temperature from the surface toward the centre of the heated sample during its heating. In fact, the time dependence of temperature delay from the centre towards the volume of sample

is another factor which can affect the shape of the modelled dependences. As it is shown in our recent papers dealing with this problem, it is mainly the shape of the modelled dependences of direct conductivity in the area of cross-linking that is influencable by the sample shape and by the shape of functional dependence of the volume temperature delay toward the sample surface.



**Fig. 4** Representation of thermal dependences of electrical conductivity of the measured rubber blend based on SBR during its vulcanisation for two heating rates  $v_2 > v_1$ : ■  $v_2$ , ●  $v_1$

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