# Monitoring of vulcanization process using measurement of electrical properties during linear increasing temperature

**E Seliga[1], O Bošák[1], P Koštial[2], Z Dvořák[3], M Kubliha[1,4], S Minárik[1] and V Labaš[1,5]**

[1] Department of Physics, Institute of Materials, Faculty of Materials Science and Technology SUT, J. Bottu 25, 917 24 Trnava, Slovakia

[2] Faculty of Metallurgy and Materials Engineering, VŠB – Technical University of Ostrava, 17.listopadu 15, 708 33 Ostrava – Poruba

[3] Department of production engineering, Faculty of technology, Thomas Bata University in Zlin, Nad Stráněmi 4511, 760 05 Zlín, Czech Republic

[4] Department of Physics, Faculty of Civil Engineering SUT, Radlinského 11, 813 68 Bratislava, Slovakia

[5] Department of Physics, Faculty of Education, Catholic University, Hrabovská cesta 1, 034 01 Ružomberok, Slovakia

E-mail: emil.seliga@stuba.sk, ondrej.bosak@stuba.sk, pavel.kostial@vsb.cz, zdvorak@ft.utb.cz, marian.kubliha@stuba.sk, stanislav.minarik@stuba.sk, vladimir.labas@stuba.sk

**Abstract**. The article presents the possibilities of diagnostics of irreversible chemical reaction - vulcanization in case of laboratory prepared rubber mixture based on styrene - butadiene (SBR) using measurements of selected physical parameters. Our work is focused on the measurement of current rheologic parameters (torque at defined shear deformation) and selected electrical parameters (DC conductivity) during linear increasing temperature. The individual steps of vulcanization are well identified by means of measurements of rheologic parameters, while significantly affecting the value of the electrical conductivity. The value of the electrical conductivity increases with the increasing of rate of the crossbridging reactions during vulcanization. The rate of the heating affects both types of measurements. When the rate of the heating is increasing the temperature of the beginning of networking step of reactions and also the rate of vulcanization grow. The sensitivity of the both types of measurements allows a good mathematical description of the temperature dependence of the torque and the electric conductivity during the vulcanization of rubber mixtures based on SBR.

## 1. Introduction

Most important process in elastomers production is vulcanization process. Three-dimensional network of polymer chains creates during vulcanisation. This network is generated by cross-bonds among linear rubber chains [1]. Significant increase of resistance against external forces caused by the origin and the increasing of number of cross-linking bonds can be observed. There is correlation between the number of cross-linking bonds and values of some mechanical properties manly Young modulus. It makes possible to observe and analyse the creation of cross-linking bonds indirectly by means of

measurement of amounts of mechanical units required for realization of the deformation. Generally used method is measurement of the time dependence of torque generating constant shear deformation at constant temperature (figure 1).



**Figure 1**. Scheme of time dependence of torque - vulcanization curve.
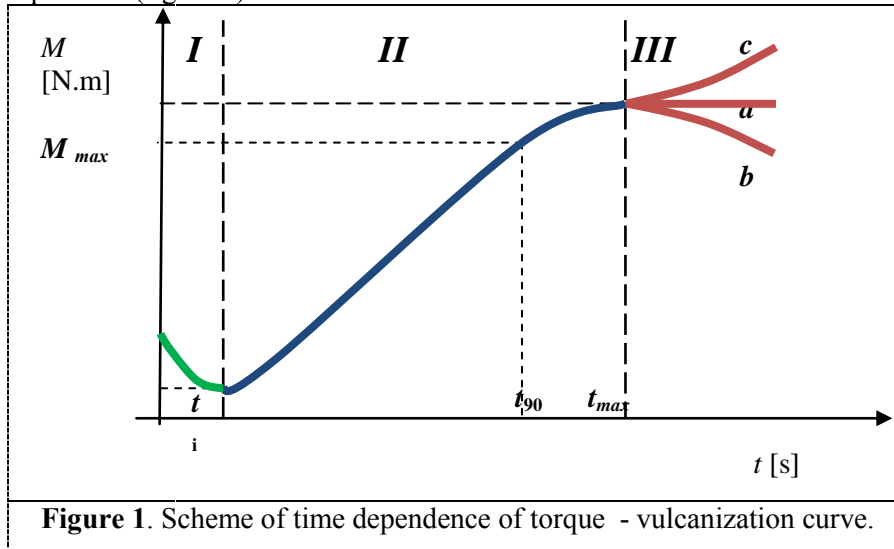
Whole vulcanization process can be divided on three stages which determine changes in material structure. The first of them is induction stage (I) during which preliminary chemical reactions in material are in progress. Next cross-linking bonds among linear chains are generated during second stage (II). The increasing of their number causes growth of value of measured torque. Depending on used kind of rubber the number of bonds can be slightly changed in third stage (III) (cases a, b, c) [2]. Requirement of defined samples preparation and impossibility of practical realization of these methods directly in technological equipment determined for real production are disadvantages of analysis of vulcanization process by means of measurement of chosen mechanical units. Content of this contribution is oriented on presentation of possibilities of the using of electrical methods for observation of vulcanization process in case of laboratory prepared rubber mixture based on styrene-butadiene (SBR) at linear increasing of temperature.

## 2. Experiment

Experimental measurements were carried out on laboratory prepared rubber mixture based on SBR with simple vulcanizing reagent based on sulphur. Mixing of the mixture shown in table 1 was realized in double-roller.

**Table 1.** Composition of the tested rubber mixture

| Components | pphr |
|---|---|
| SBR Rubber | 100.0 |
| Buna VSL 5025-0 | |
| 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 |

In order to the fact that the number of cross-linking bonds generated during vulcanization process increases values of mechanical units, rheological measurements were used as a basis for evaluation.

Values of torque needed for creation of constant value of shear modulus 0.5° [3] were measured. Measurements were realized by means of equipment D-MDR 3000 MonTech. Value of torque was observed for more values of heating rates (0.2°C/min; 0.4°C/min; 0.6°C/min; 0.8°C/min; 1.0°C/min; 2.0°C/min; 3.0°C/min; 4.0°C/min; 5.0°C/min; 7.0°C/min; 10°C/min). Mentioned measurements were realized repeatedly at increasing temperature ranged from 30 °C up to 200 °C. Heating rates were determined on the basis of possibilities of the measuring equipment and mathematical processing of results. Measurements of torque carried out during linear increasing temperature were supplemented by measurement of DC electrical conductivity realized by means of equipment Novocontrol concept 90. Measurements of DC electrical conductivity were realized by direct method in constant voltage 10V at the same heating rates as measurements of vulcanization curves during linear increasing temperature.

## 3. Results

Example of measured temperature dependencies of torque during heating rate 2 °C.min$^{-1}$ is shown in figure 2. The first measured curve can be divided on two areas while transition between them corresponds to the temperature ~155 °C. The change of torque is influenced by two factors in this case. The first one is the decrease of torque values of rubber mixture caused by the change of viscosity during the increasing of temperature (see area I in figure 2). The second one is the beginning and progress of cross-linking reaction – networking with relatively abrupt increase of torque values (see area II in figure 2). Results of repeated measurement are not already influenced by potential changes resulted from the subsequent cross-linking of rubber chains.
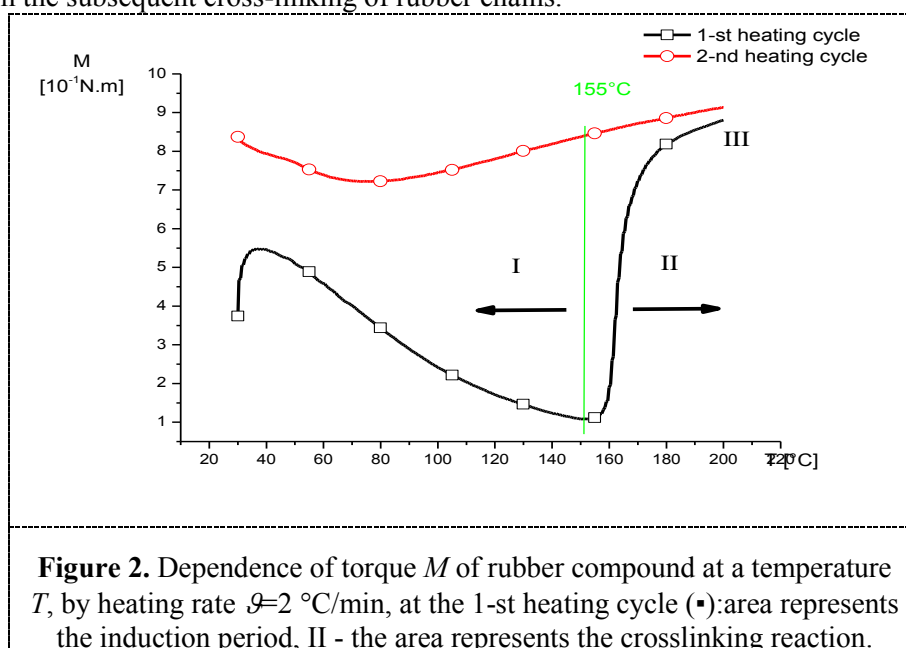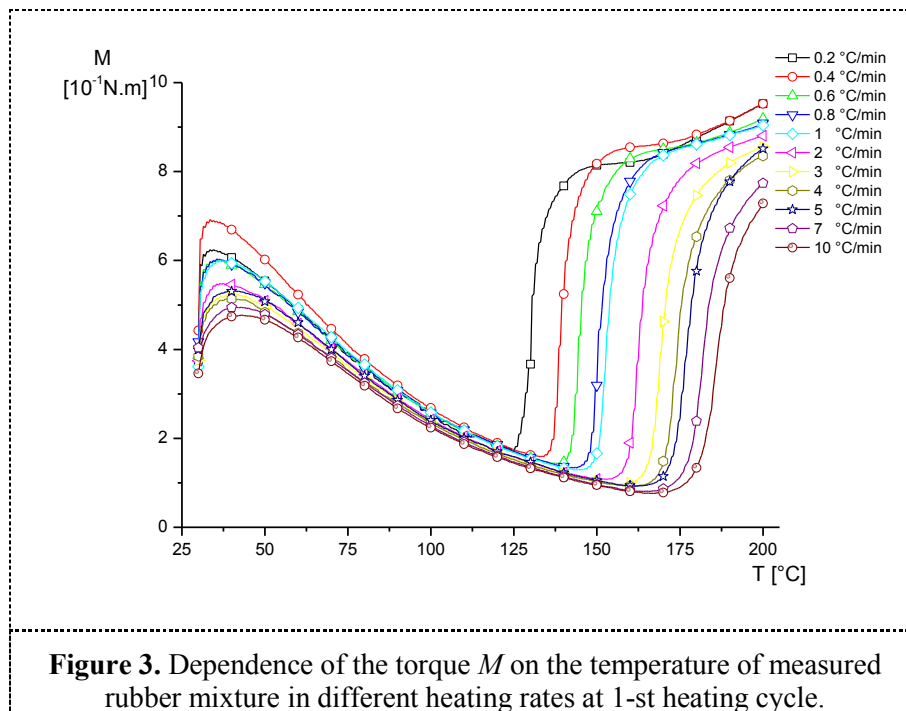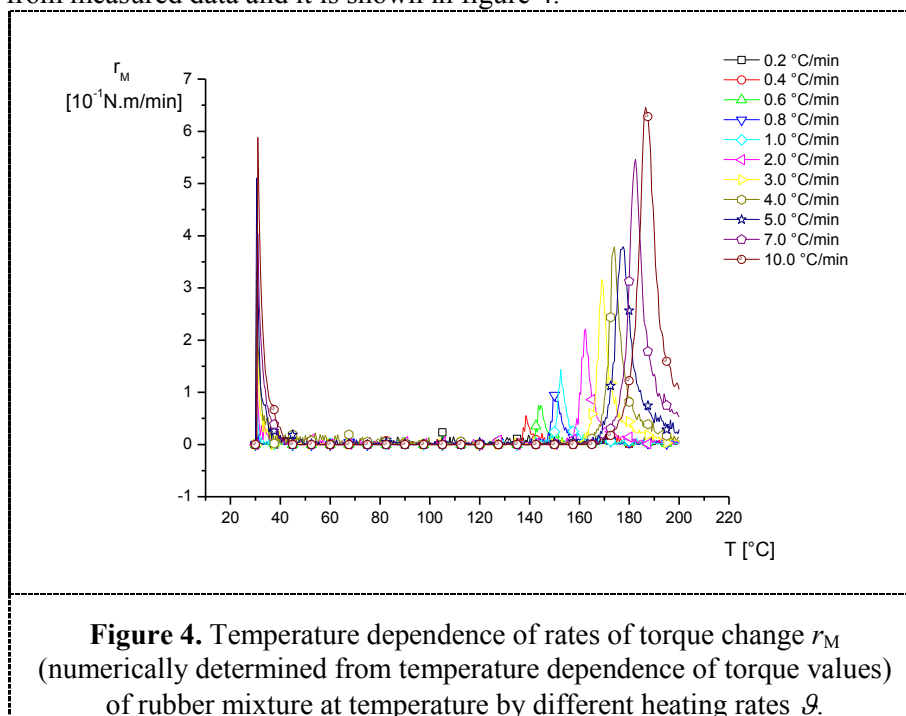


**Figure 2.** Dependence of torque *M* of rubber compound at a temperature *T*, by heating rate $\vartheta$=2 °C/min, at the 1-st heating cycle (▪):area represents the induction period, II - the area represents the crosslinking reaction.

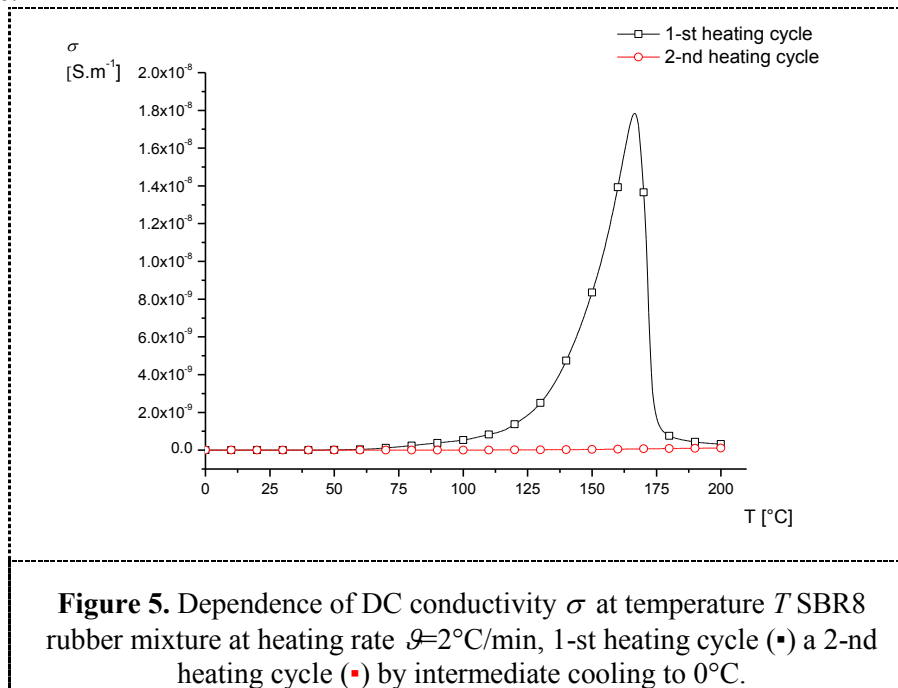There is observable influence of heating rate when temperature dependencies of torque are compared (see figure 3).

**Figure 3.** Dependence of the torque *M* on the temperature of measured rubber mixture in different heating rates at 1-st heating cycle.
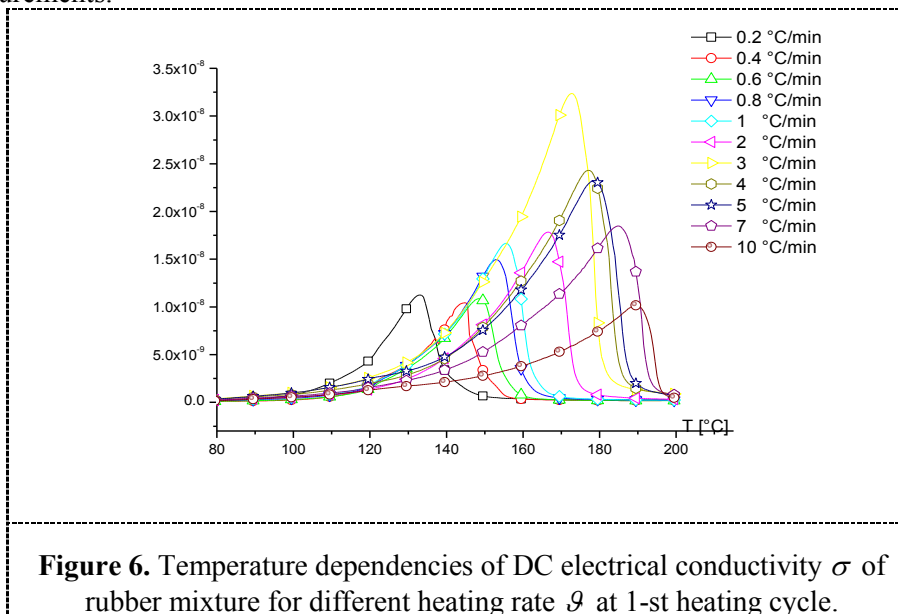
With regard to the fact that the increase of torque is in correlation with the increasing of number of generated cross-linking bonds [4], in case of linear increasing of temperature the temperature derivation of torque represents value correlating with the rate of cross-links creation $\frac{dM}{dT} \approx \frac{dN}{dt}$. Temperature dependence of the torque derivation (rate of cross-links creation) was determined numerically from measured data and it is shown in figure 4.



**Figure 4.** Temperature dependence of rates of torque change $r_M$ (numerically determined from temperature dependence of torque values) of rubber mixture at temperature by different heating rates $\vartheta$.
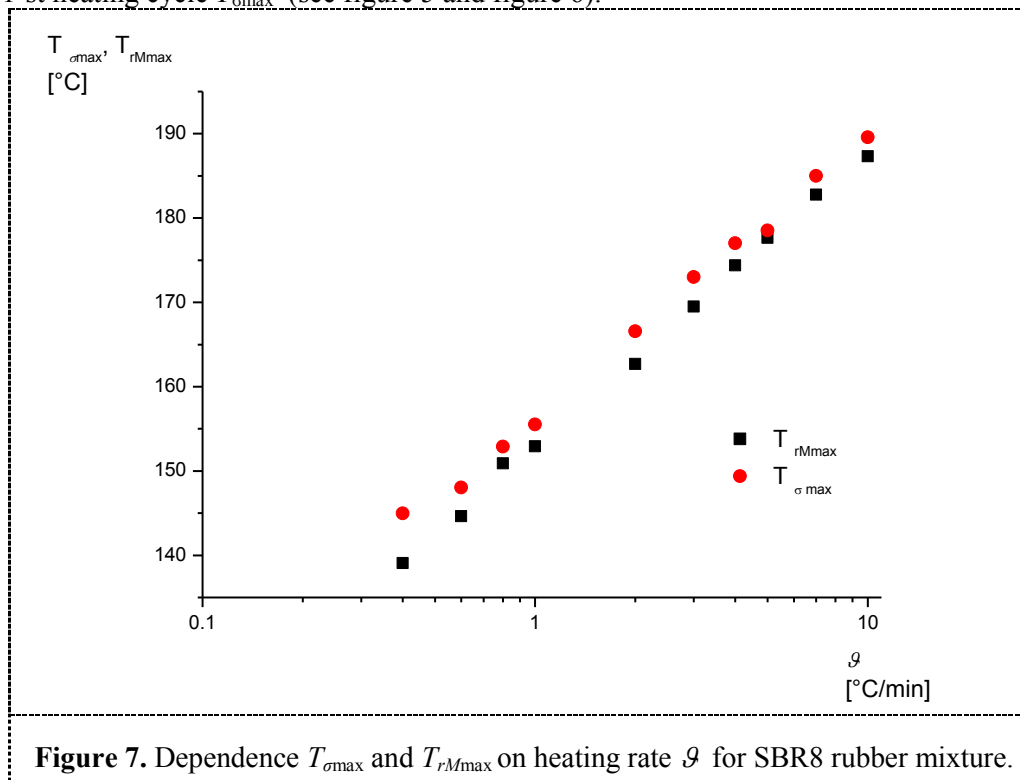
Rubber mixture based on SBR at which cross-linking bonds during vulcanization process are created via sulphur ions was used for experimental measurements. There is possibility of the increasing of the electrical charge transport during vulcanization process caused by mentioned ions occurrence. Influence of vulcanization reaction – crosslinking, in accordance with prediction, can be identified on measured curves of DC electrical conductivity as an increase of DC electrical conductivity during 1st. heating cycle which is observable at divers values of heating rate (see figure 5). Influence of another cross-linking of rubber mixture was not already observed during second heating cycle.



**Figure 5.** Dependence of DC conductivity $\sigma$ at temperature $T$ SBR8 rubber mixture at heating rate $\vartheta$=2°C/min, 1-st heating cycle (▪) a 2-nd heating cycle (▪) by intermediate cooling to 0°C.

In case of these measurements can be observed influence of heating rate similarly as in the case of torque measurements.



**Figure 6.** Temperature dependencies of DC electrical conductivity $\sigma$ of rubber mixture for different heating rate $\vartheta$ at 1-st heating cycle.

There is observable the significant correlation between temperature at which the torque value is maximal $T_{rM\max}$ and temperature corresponding with maximal value of DC electrical conductivity during 1-st heating cycle $T_{\sigma\max}$ (see figure 5 and figure 6).



**Figure 7.** Dependence $T_{\sigma\max}$ and $T_{rM\max}$ on heating rate $\vartheta$ for SBR8 rubber mixture.

Difference between $T_{\sigma\max}$ a $T_{rM\max}$ can be caused by different dimensions of samples as well as their temperature inhomogeinity. However, values of DC electrical conductivity increase also in temperature area of induction period (figure 5 up to 150°C) in which there is observed no increase of number of cross-linking bonds (figure 4 up to 150°C).

## 4. Conclusion

Observation of changes during cross-linking reaction of rubber mixtures and their subsequent quantification is one of the criteria for evaluation of final mechanical properties of rubber products.

Measurement of vulcanization characteristics at linear increasing temperature is of great importance for determination of transition temperature from induction period to area of cross-linking reaction. This transition is manifested by the increasing of mechanical properties when cross-linking bonds among rubber macromolecules are generated in the mixture. Measurement of vulcanization characteristics by means of rheometer is typical for evaluation of mechanical properties in technical practice.

Measurement of DC electrical conductivity at linear increasing temperature is non-standard measurement in technical practice. Value of temperature $T_{rM\max}$, at which largest speed of reaction is observed (largest value of derivation of torque) correlates with temperature $T_{\sigma\max}$, at which the maximal value of DC electrical conductivity is detected. We observed similar dependencies of temperatures $T_{rM\max}$ a $T_{\sigma\max}$ on used heating rate $\vartheta$.

Results presented in this work create good basis for development of material science in the area of rubber mixtures. Correlation between mechanical and electrical properties has been proven. The application of electrical methods at diagnosis of process of vulcanization appears as a possible alternative to non-destructive observation of cross-linking process.

**References**

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