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MONTE CARLO SIMULATION OF THE ELECTRICAL CONDUCTIVITY OF RUBBER COMPOUNDS DURING SILANIZATION

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Abstract

Monte Carlo simulation of temperature dependence of electric conductivity of a model mixture system, which involves reaction with first order kinetics, was carried out on the basis of chemical kinetics laws. The temperature dependence of the conductivity of rubber compounds during the process of silane treatment was studied experimentally. Simulated temperature dependence of conductivity was compared with measured experimental results. The obtained experimental results and the data derived from numerical simulation are in satisfactory agreement. Effective method for monitoring and control of silane treatment of rubber compounds directly during the material preparation process can be proposed on the basis of the abovementioned finding.

Key words

Monte Carlo simulation, chemical kinetics, reaction of first order kinetics, rate constant of reaction, silane treatment

Introduction

Rubber mixtures have attracted attention of materials technologists for several decades because these materials have found wide application in the manufacture of tires. Silane or silica treatment of resin composite is a very important technology step within the rubber mixture preparation which is oriented on cross linking and reinforcement of silica/silane-filled

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rubber compounds. The purpose of the presented paper is to find a method for investigation of the effect of silane treatment on rubber composites microstructure. Silanization to indirect resin composite enhances significantly higher bonds strength, and bonds strength are affected by the type of silane treatment ultimately. Application of a silane treatment improves the bond strength to indirect resin composite for repair. Main goal of the silanization process study is to find the most effective silane system. The experience suggests that the silane treatment should be considered to be a chemical reaction which is obeying laws of chemical kinetics. Chemical kinetics deals with the problem of the speed with which a chemical reaction occurs.

Theory of chemical reactions analyses the factors that affect the reaction speed and looks for the information useful for determining how the reaction process occurs. The speed of a reaction is the rate at which the concentrations of reactants and products change. It is well known that chemical reaction affects the physical and chemical properties of reacting system. In case the charge carriers are products of the reaction, it is expected that the electric conductivity of the system changes continuously during the reaction process, because values of electrical conductivity are considered to be sensitive to concentration of charge carriers. Nevertheless, there has been no experimental or theoretical study to determine the effect of chemical reaction process on the temperature dependence of electrical conductivity of system during the reaction. Our contribution deals with this problem in connection with the rubber compounds silanization process.

Theory

The study of dielectric properties of industrial rubber compounds is of great practical interest. As it is known, the electrical conductivity of rubber is caused by presence of impurities which transfer ions and thus electric current. The mechanism of electrical conductivity in the concerned materials was investigated in our earlier experiments [1, 2, 3, 4]. However, the mechanism of electrical conductivity in rubber compounds during the process of silane treatment is not even clear entirely. In the present paper, we investigate the problem of changes of electrical conductivity of such reactive dielectric system within the numerical approach. In most of transport mechanism models, the electrical conductivity is explained by means of concentration of charge carriers in structure. We suggest that the electrical conductivity of rubber compounds system during silane treatment reaction can by determined as:

$$\sigma = \sigma_{\mathrm{Pol}} + \sigma_{\mathrm{Sil}}, \tag{1}$$

where σ_{Pol} is electrical conductivity of reactionless compounds of structure and σ_{Sil} is a contribution of reactants to electrical conductivity. We expect that both contributions in (1) follow Arrhenius equation [5, 6, 7]:

$$\sigma_{\mathrm{Pol}} = \sigma_{01} e^{-\frac{E_A}{kT}}\,, \qquad \sigma_{\mathrm{Sil}} = \sigma_{02}\left(C_N\right) e^{-\frac{E_A^{(S)}}{kT}}\,, \tag{2}$$

where activation energy of charge carriers in reactionless compounds E_A and activation energy of charge carriers in reactants $E_A^{(S)}$ do not have to be equal. Pre-exponential factor σ_{02} depends on immediate concentration C_N of that reactant which contributes to electrical conductivity of the system. We expect that the factor σ_{02} is proportional to the reactant concentration C_N, i.e. the factor σ_{02} may be expressed as:

$$\sigma_{02} = K' C_N \,, \tag{3}$$

where K' is constant. For determination of σ_{02} it is essential to know how the concentration of the reactant C_N changes when reaction progress:

$$C_N = C_N\left(t,T\right) \,. \tag{4}$$

We start with the rate law for the reaction, which follows first-order kinetics [8]:

$$\frac{dC_{\mathrm{N}}}{dt} = -c_{\mathrm{r}} C_N \,, \tag{5}$$

where c_{r} is the reaction rate constant which depends on temperature T and follows Arrhenius equation in the form [9, 10]:

$$c_r = B e^{-\frac{E_{\mathrm{D}}}{kT}} \,. \tag{6}$$

E_D is activation energy of the reaction and B is constant. If we consider both the time and temperature dependence of concentration C_N we obtain:

$$\frac{dC_{\mathrm{N}}}{dt} = \frac{\partial C_N}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial C_N}{\partial t} = \eta \frac{\partial C_N}{\partial T} + \frac{\partial C_N}{\partial t} \,, \tag{7}$$

where η is the rate of temperature change. If we consider linear changes of temperature during reaction, then:

$$\eta = \frac{dT}{dt} = const \,. \tag{8}$$

After substitution (7) in equation (5) we obtain:

$$\eta \frac{\partial C_N}{\partial T} + \frac{\partial C_N}{\partial t} = -c_{\mathrm{r}} C_N \,. \tag{9}$$

Solution of equation (9) is expected in the form:

$$C_N = C_N\left(t,T\right) = \varphi\left(t\right)\chi\left(T\right) \tag{10}$$

and after substitution (6) and (10) to (9) we obtain:

$$\eta \frac{1}{\chi\left(T\right)} \frac{\partial \chi\left(T\right)}{\partial T} + B e^{-\frac{E_D}{kT}} = -\frac{1}{\varphi\left(t\right)} \frac{\partial \varphi\left(t\right)}{\partial t} \,. \tag{11}$$

Problem of solution of equation (11) leads to the next differential system:

$$\eta \frac{1}{\chi\left(T\right)} \frac{\partial \chi\left(T\right)}{\partial T} + B e^{-\frac{E_D}{kT}} = C'' \,, \tag{12}$$

$$-\frac{1}{\varphi\left(t\right)} \frac{\partial \varphi\left(t\right)}{\partial t} = C'' \,, \tag{13}$$

where C'' is constant. System (12), (13) is solvable and solution of this system can be written in the next form:

$$\chi(T) = e^{\frac{C''}{\eta}(T-T_0) - B\frac{1}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'}, \tag{14}$$

$$\varphi(t) = A''e^{-C''t} \text{ , where } A'' = const . \tag{15}$$

T_0 is initial value of reacting system temperature by which the reaction runs. Consequently, the concentration of the reactant C_N can be expressed as:

$$C_N = \varphi(t)\chi(T) = A''e^{\frac{C''}{\eta}T - \frac{C''}{\eta}T_0 - C''t - \frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'} = A''e^{C''\left(\frac{T}{\eta}-t\right) - \frac{C''}{\eta}T_0} e^{-\frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'} . \tag{16}$$

Assuming (8) the linear dependence of system temperature on time can be written as:

$$T = \eta t + b , \tag{17}$$

where b is constant, and next we find:

$$\Rightarrow \quad C''\left(\frac{T}{\eta} - t\right) = C''\left(\frac{\eta t + b}{\eta} - t\right) = C''\frac{b}{\eta} . \tag{18}$$

Thereby the solution (16) can be rewritten as:

$$C_N = Ae^{-\frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'} , \tag{19}$$

where:

$$A = A''e^{-\frac{C''}{\eta}T_0} e^{-\frac{C''}{\eta}b} = const. \tag{20}$$

Pre-exponential factor σ_{02} can be obtained by substituting (19) to (3).

$$\sigma_{02} = K'Ae^{-\frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'} = Ce^{-\frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT'} \text{ , where } \quad K'A = C = const. \tag{21}$$

Consequently assuming (21) in (2), we can find a contribution of reactant to electrical conductivity σ_{Sil} as:

$$\sigma_{\mathrm{Sil}} = Ce^{-\left(\frac{E_A^{(S)}}{kT} + \zeta(T)\right)} \qquad \text{where:} \qquad \zeta(T) = \frac{B}{\eta}\int\limits_{T_0}^{T} e^{-\frac{E_D}{kT'}}dT' . \tag{22}$$

Expression (20) indicates the temperature dependence of reactant contribution to electrical conductivity of reacting system under the condition of reaction with first order kinetics. In the frame of the model described above, we considered that only concentration of one reactant changes during the reaction involving only a one-step mechanism. In summary, we have proposed a simple model with emphasis on the chemical reaction effect on the electronic transport behaviour in a mixture system. This effect is reflected through the changes of charge carriers' concentration which is proportional to the concentration of reactant. Numerical simulation of temperature dependence of electrical conductivity can be realized by means of result (20). There are difficulties in evaluating the integral expression in (20) because the integral cannot be evaluated analytically. Highly effective Monte Carlo methods can be applied for its evaluation [11-18].

Experiment and simulation

Rubber compounds marked as SCR-3-X prepared in temperature range from 140 °C till 145 °C were investigated experimentally. Duration of silane treatment process of the prepared samples was from 0 till 7 minutes. Temperature dependences of AC electrical conductivity of prepared samples $\sigma(T)$ were persistently measured by GoodWill LCR 819 equipment at linear increasing temperature ($1°C\cdot min^{-1}$) until to 170 °C. Details of the investigated rubber mixture composition and experiment details can be found in [4]. In the next text, we will substitute the letter *X* in the sample identification symbol by the duration of thermal exposure of the sample. Comparison of the obtained results showed notable differences between the data of AC electrical conductivity measured during the first and the second cycles of heating process. The abovementioned differences can be seen in Fig. 1 which shows the graphs of temperature dependence of AC conductivity of SCR-3-7 sample. It is evident that the increase of AC electrical conductivity measured during the first cycle of heating process is caused by the silanization process since such increase is not measurable in the second cycle. The results showed that if the duration of silane treatment of a sample increases, then the size of the area below measured curves $\sigma(T)$ gradually decreases in both the first and the second cycles of heating. In case of some samples, we observed the abortion of silanization reaction at the first cycle of heating, and then the reaction continued during the second cycle. That fact was registered as a smaller maximum in $\sigma(T)$ curve measured in the second cycle. The values of electrical conductivity of non-silanized sample (SCR-3-0) were lower than we expected. It can be concluded on the basis of the mentioned results that if the increase of AC conductivity values (i.e. differences between values $\sigma(T)$ measured in the first and the second cycles of heating - see Fig.1) respond to the chemical reaction rate, then the size of the area below the curve represents the charge carriers concentration which is proportional to the size of the concentration of reactive substances. The dependence of the size of area below the measured $\sigma(T)$ curve on mixing duration is shown in Fig. 2. As it can be seen, the mentioned dependence of area on mixing duration decreases linearly (except the sample 0 min, which was mixed and heated only to 110 °C). This responds to the fact that the silane treatment was in progress during the mixing already and only finalization of treatment during the AC conductivity measurement was observed there consequently.

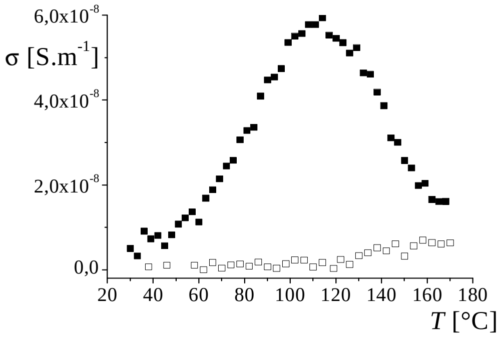

***Fig. 1** Temperature dependence of AC electrical*

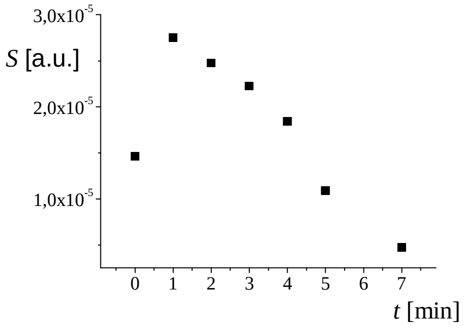

***Fig. 2** Dependence of size of area below*

conductivity of sample SCR-3-7 measured at 1 kHz and with heating rate 1°C·min^{-1}
■ *in case of the first cycle of heating*
☐ *in case of the second cycle of heating*

measured σ(T) curves on mixing duration

We simulated the measured σ(T) curves by the model presented above. That needs to determine some parameters contained in (20) and from these parameters σ_{SIL} can be calculated persistently. The best numerical fit of the measured temperature dependence of electrical conductivity of system during silane treatment must be obtained during the process of simulation. Results are shown in Fig. 3.

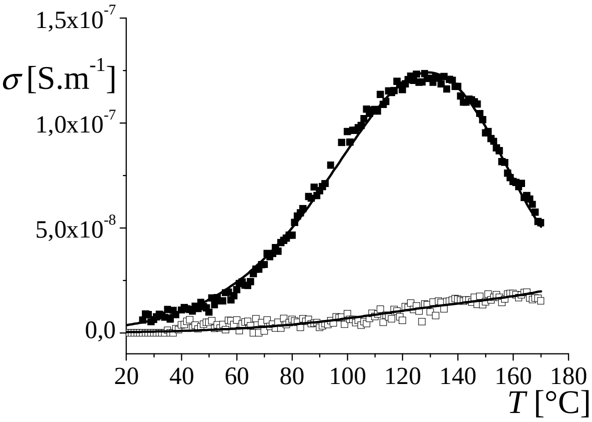

Fig. 3 *Temperature dependence of AC electrical conductivity of sample SCR-3-5 measured at 1 kHz and with heating rate 1°C·min^{-1}*
■ *in case of the first cycle of heating*
☐ *in case of the second cycle of heating.*
Solid lines represent simulated data

Conclusion

Potential applications of the presented method are in computer aided optimization of the rubber compounds silane treatment process. Presented numerical investigation indicates that the formula (20) could be usable for the process of rubber compounds silanization modeling. This make possible to use AC electrical conductivity as a measure of the extent of chemical reaction. Then we can realize an effective analysis and control of silane treatment process and find possibilities for the process improvement. This contribution was supported by the Slovak National Science Foundation under VEGA No.1/0645/10 and KEGA 327-010STU-4/2010 grants.

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