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Computer simulation of alternate conductivity of polymer system

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The classical model of electrical conduction was used for simulation of alternate conductivity frequency dependence $\sigma(\omega)$ of polymeric material at low frequency range. We assumed that the simple classical kinetic theory is applicable for description of drif mobility of the charge carriers bounded in the polymer material structure. Harmonic forced oscillators approximation was used for the simulation of the polymer AC conductivity in the framework of simple Drude`s approach. Dependence $\sigma(\omega)$ of polymehylmethacrylate (PMMA) was measured experimentally at the frequency range from 12 Hz up to 300 kHz and the observed experimental data was compared with the result of simulation. We concluded that it is necessary to optimize the applied simulation process for the reason of macromolecular character of polymer structure. Systems of different types of oscillating charge carriers with properties distinguishable each other coupled in the polymeric chains was considered and the superposition principle was used for the determination of simulated dependence $\sigma(\omega)$ optimization.Good agreement of the experimental data with the results of alternate conductivity frequency dependence simulation was reached in this way at the investigated frequency range.

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1. Introduction

The charge carriers transport in solids has been in the centre of interest of many research works for many years. The wide range of carriers mobility values in materials determined the appearance of a number of transport mechanism models, which are frequently used to analyse the charge transport in solids.

The most applicable models which enable to describe the electrical transport characteristics of solid systems are based on the concept of band conduction by free charges.

In the case of crystalline solids the three-dimensional architecture of an ideal crystal determined by the infinite repetition of the identical structure units in space is characterized by the long-range order and strongly coupled atoms. Just this strong coupling results in the formation of the long range delocalized energy bands separated by the forbidden energy gap in the energetic structure of solids. On the contrary the polymers do not have so well-ordered structural configuration as crystals. Polymer consists of macromolecular chains which can be disrupted by chemical or structural defects. The absence of an ideal periodic lattice in the disordered polymer structures complicates description of the charge transport in terms of standard models. The spatial and energetically disordered configuration and the absence of the translation symetry in the polymeric systems cause that the concept of the band conduction cannot be applied and different theoretical approachs are required. Over the past years an intense research has been carried out to explain the low mobility of charge carriers in disordered polymers. There were developed several transport models which show good agreement with experimental data of electrical measurements for some particular systems. In the present time no complete solution is available due to the diversity and the comlexity of disordered polymer systems.

In our work we simulate the frequency dependence of disordered polymer system alternate conductivity (AC) at low frequency range. The algorithm of the simulation is based on the classical theory which can be applicable in many cases to describe the transport mechanism in solids. For example such a classical approximation is Drude model which explains the transport properties of materials by the application of the classical kinetic theory [1, 2]. As it is known the electrical and the thermal conductivity of metals can be described sufficiently by so-called Drude-Sommerfield free electrons model. Classical Lorentz model [3, 4] can explain the frequency dependence of polarization in dielectrics. The mentioned classical models exhibits good agreement with experimental results in some specific cases.

2. Theory

During last few decades a large attention has been focused on electrical properties of polymer materials investigation within the context of extreme low carriers mobility in these materials. As was found the formation of localized states (Anderson localization) [5, 6, 7, 8, 9] is enhanced in the energetic structure of the polymer systems as a consequence of disorder. In order to participate to the transport, the charge carriers must hop between these localized states [10, 11, 12]. The mentioned process is concerned with inter- or intra-chain charge transitions. To overcome the energy difference between two localized states, the carriers absorb or emit phonons. This model of

the phonon-induced hopping mechanism of the charge transport usually leads to a very low carrier mobility and a very low value of material electrical conductivity consequently [13, 14, 15, 16]. The hopping mechanism of the charge transport in disordered systems was for the first time suggested by Conwell and Mott and later by Pines, Abrahams and Anderson [5, 6, 7].

Generally the resonant tunelling of charge carriers between pairs of localized states is allowed to be leading mechanism for the AC of localised systems. Several models of AC based on the hopping mechanism of the charge carriers transport were developed. Various types of distributions of localized states *N(E)* enable to explain a specific character of conductivity in various types of materials such as dopped semiconductors, disordered molecular crystals, conjugated polymer semiconductors e.t.c.

We carried out the frequency dependence of the polymer material alternate conduction of the computer simulation. Very long macromolecules in polymer structure usually consist of repeating structural units connected by covalent bonds. We assumed that the relative high density of localized states results from the complexity of these materials structure and we solved the problem of the frequency dependence of AC in the classical limit. The applicability of the classical approximation based on Drude`s approach to describe AC conductivity of polymer systems was investigated.

2.1 Forced oscillators approximation

For determination of the simulation process basis we assumed that the harmonic character of the measured current time dependence is the result of the harmonic motion of charge carriers in the material structure. For that reason we used the mathematical analogy with harmonic forced oscillating system at the charge carriers motion analysis.

In the Drude model of the conductivity the following formula can be written for the electrical current in the simplest case:

$$I(t) = nQSv(t), \tag{1}$$

where n is charge carriers number per unit volume, Q is electrical charge of the carrier, S is sample cross section and $v(t)$ is mean drift velocity of carriers in the direction of the electric field. We considered harmonical power supply voltage $U(t) = U_0 \sin(\omega t)$ connected to the material sample and generating alternating harmonical current $I(t) = I_0 \sin(\omega t - \delta)$. The charge carrier coupled in the material structure is exposed to an oscillating electric field $E(t) = E_0 \sin(\omega t)$ in that case. Thus the carrier will be forced to oscillate. There is an equilibrium restoring counter force, proportional to deviation for small deviations. We also allow for friction which we assume to be proportional to the carriers velocity $v(t)$. Therefore, the well-known equation of harmonic forced oscillating motion has to be solved and following mean drift velocity time dependence of charge carriers $v(t)$ can be written:

$$v(t) = \frac{Q\omega E_0}{\sqrt{\left(M\omega^2 - k\right)^2 + k_b^2\,\omega^2}} \cos(\omega t - \alpha), \tag{2}$$

where M is mass of the charge carrier, k is the spring constant of linear oscillator, k_b is the friction coefficient and:

$$\alpha = arctg\left(\frac{\omega k_b}{M\omega^2 - k}\right).$$

Consequently, it can be easyly shown by substituting (2) to (1) that the time dependence of current can be written in the form:

$$I(t) = I_0 \sin(\omega t - \delta), \tag{3}$$

where: $I_0 = \dfrac{nQ^2\omega S}{\sqrt{\left(M\omega^2 - k\right)^2 + k_b^2\,\omega^2}} E_0$

and $\delta = \alpha - \dfrac{\pi}{2}$.

If we consider the electric current has to obey Ohm`s law the frequency dependence of AC can be considered by means (3) in following form:

$$\sigma(\omega) = \frac{\sigma_0}{\sqrt{1 + \mu^2(\omega)}}, \tag{4}$$

where $\mu(\omega) = \dfrac{\omega^2 + \left(\alpha^2 - b^2\right)}{2b\omega}$ and $\alpha = \sqrt{\dfrac{k_b^2}{4M^2} - \dfrac{k}{M}}$,

$$b = \frac{k_b}{2M},\ \sigma_0 = \frac{nQ^2}{k_b}. \tag{5}$$

In order to conjugate character of polymer structure the major types of charge carriers with different properties can be coupled in the polymer chains. Superposition principle enable to find the total amount of polymer AC by:

$$\sigma(\omega) = \sqrt{\left(\sum_{i=1}^{m} \frac{\sigma_{0i}}{1 + \mu_i^2(\omega)}\right)^2 + \left(\sum_{i=1}^{m} \frac{\sigma_{0i}\,\mu_i(\omega)}{1 + \mu_i^2(\omega)}\right)^2}, \tag{6}$$

where $\mu_i(\omega) = \dfrac{\omega^2 + \left(\alpha_i^2 - b_i^2\right)}{2b_i\,\omega}$

and: $\alpha_i = \sqrt{\dfrac{k_{bi}^2}{4M_i^2} - \dfrac{k_i}{M_i}}$, $b_i = \dfrac{k_{bi}}{2M_i}$, $\sigma_{0i} = \dfrac{n_i Q_i^2}{k_{bi}}$.

Q_i, M_i, k_i, k_{bi} and n_i are parameters mentioned above for i-th type of charge carriers fixed in the polymeric chains. Index i alter from one up to m, where m is the total number of distinguishable types of charge carriers conjugated in the polymer structure.

The expression (6) determines the character of the frequency dependence of AC in the classical limit.

2.2 Simulation algorithm

The calculation of the frequency dependence of AC, which we used for the simulation is based on the formula (6). It is possible to determine the contribution to

conductivity of each one from m considered distinguishable types of charge carriers by means of the simple classical model and one can evaluate the total amount of $\sigma(\omega)$ at certain angular frequency ω by the superposition principle. The parameters m, σ_{0i}, α_i, and b_i (i = 1, 2, ... m) play the role of the fundamental parameters of the model. The presented classical model of conductivity applied to polymer system has $3m$+1 free parameters. The computer simulation consists of the quantification of the sums in (6). Whereas the values of the m, σ_{0i}, α_i, and b_i are unknown parameters typical for the specific polymeric material, it is necessary to optimize the simulation process by means of the suitable optimizing criteria. In the presented work we optimized the process of the $\sigma(\omega)$ computer simulation with regard to the measured experimental data. The experimental measurement of dependence $\sigma(\omega)$ of chosen polymer was carried out and we struggled to reach the best possible agreement of calculated $\sigma(\omega)$ with experimantal data varying the parameters m, σ_{0i}, α_i, and b_i during the simulation process. The mentioned agreement of the calculated data with results of electrical measurements was quantified by the least squares method. The least square method is the optimizing criteria which enables to repeat the calculation process under the conditions of the variable parameters m, σ_{0i}, α_i, and b_i till the coincidence of the simulation results with the experimental data is acceptable.

3. Experimental

The sample was cut out from PMMA material by means of the electrically heated wire and smoothed by series of the metallographic abrasive papers into the required dimensions (10 mm × 10 mm × 1 mm). The abrasive papers was cooled by water during the sample preparation and, finally, the conductive paste based on silver was deposited on the sample surface.

The prepared sample was inserted between the measuring electrodes in the shielded heating measuring cell. The investigation of the electrical properties was performed in the presence of air at the constant temperature. The frequency of applied electrical field was changed in the chosen way within the range from 12 Hz up to 300 kHz and resistivity of the sample was determined. AC of material was estimated by the well-known method [17, 18]. We repeated the same measuring process at the temperatures of 50 °C, 60 °C , 70 °C, 80 °C, 90 °C and 110 °C.

4. Results

The measured $\sigma(\omega)$ dependence of the sample prepared from PMMA material at fixed temperatures from the range (50 °C – 110) °C is shown in Fig. 1. We compared each measured $\sigma(\omega)$ dependence with the corresponding simulated results. Comparisons of simulated results with results of measured data for different m are shown in Figs. 2-7.

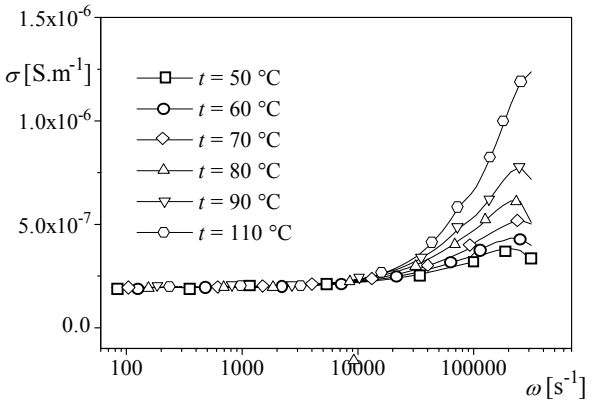

Fig. 1. σ(ω) of PMMA measured at different temperatures.

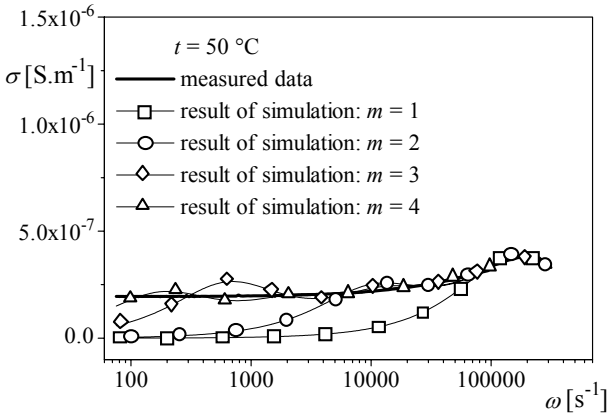

Fig. 2. σ(ω) of PMMA measured at temperature of 50°C. The comparison of experimental data with the result of the simulation for different m.

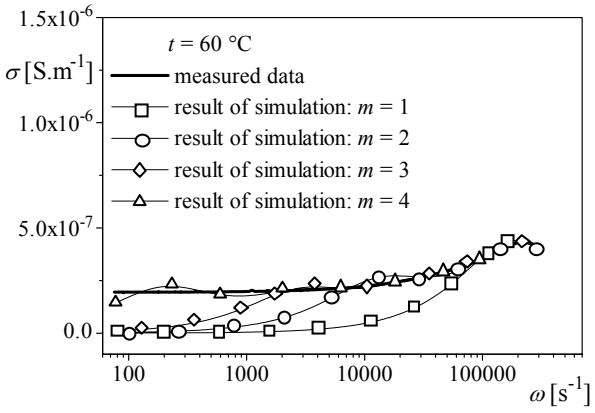

Fig. 3. σ(ω) of PMMA measured at temperature of 60°C. The comparison of experimental data with the result of the simulation for different m.

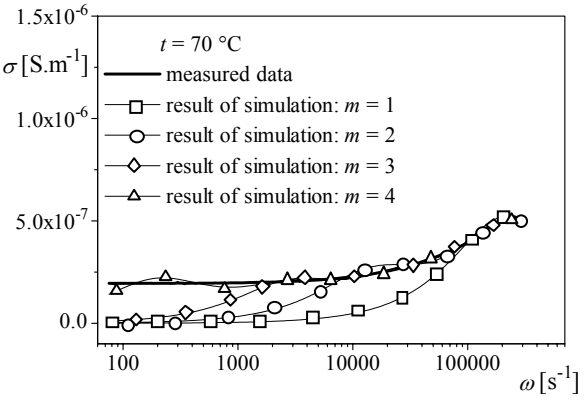

Fig. 4. σ(ω) of PMMA measured at the temperature of 70 °C. The comparison of experimental data with the result of the simulation for different m.

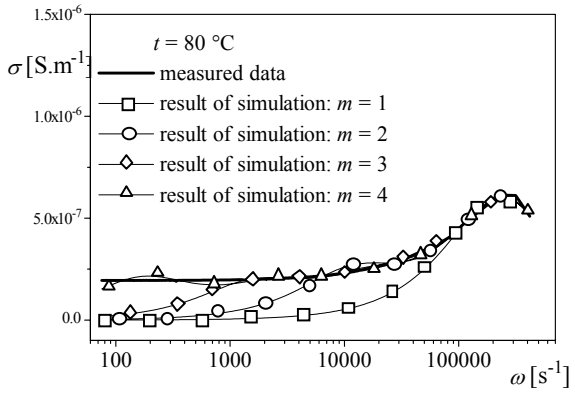

Fig. 5. σ(ω) of PMMA measured at temperature of 80 °C. The comparison of experimental data with the result of the simulation for different m.

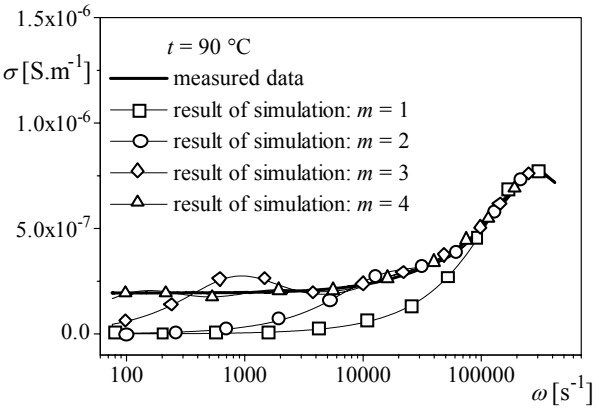

Fig. 6. σ(ω) of PMMA measured at temperature of 90 °C. The comparison of experimental data with the result of the simulation for different m.

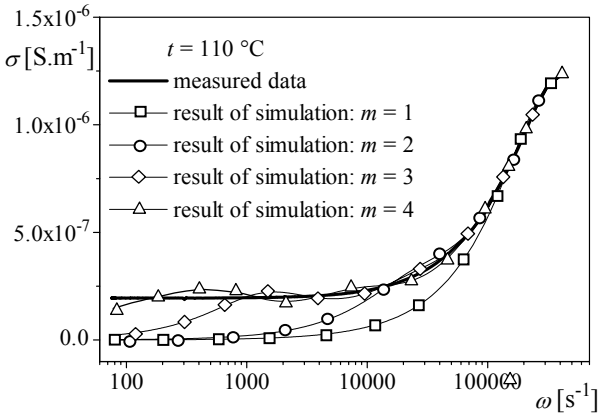

Fig. 7. σ(ω) of PMMA measured at temperature of 110 °C. The comparison of experimental data with the result of the simulation for different m.

5. Discussion

As it is evident from the results shown in fig.1 the measured $\sigma(\omega)$ dependences of PMMA are independent on temperature at low frequency range from 10 Hz up to 10 kHz. The mentioned temperature independences of the measured results suggest that the effect of phonon-induced charge carriers hopping can be considered as neglectable. If we assume the high density of the localized states of examined PMMA system under the given conditions the negligible quantum of energy is necessary to carriers overcome the difference between two localized states and the classical models of the transport mechanism should have been acceptable in this case. There were recognized considerable differences within the measured frequency dependences of AC at frequencies above 10 kHz. The mentioned differences can be described as a consequence of the temperature dependences of the model parameters m, σ_{0i}, α_i, and b_i within the frame of the proposed model when the frequency increases to the higher values of the investigated frequency range.

We can check the applicability of the classical model for the simulation of PMMA AC frequency dependence by means of the results shown in the figs.2-7. The graphs make it possible to evaluate the agreement of the calculated values with the experimental data.

As it can be seen from the presented results the measured $\sigma(\omega)$ dependences of PMMA show a maximum at the frequency above 100 kHz. The simulated results calculated with the parameter m = 1 agree with the experimental data in the frequency range above the mentioned frequency (100 kHz) in the case of all applied temperatures. The simulated values are located below the measured data at frequencies less than 100 kHz in this case. The coincidence of the simulated results with regard to the measured data improves when the parameter m increases. The acceptable agreement was observed in the frequency range above 10 kHz at the simulation with

the parameter m = 2 as well as in the frequency range above 1 kHz at the simulation with the parameter m = 3. As it can be seen from the presented results the parameter m determines the number of maxima uprising in the simulated function $\sigma(\omega)$. When m is greater then 1 the simulated values oscilate along the measured data and oscilations vanish when the parameter m increases. The best consistency of the simulation results with experiment was reached with the parameter m = 4 (see Figs. 2-7), when we observed the best agreement at whole investigated frequency range. We assume that the optimal value of m can be determined for the simulation of particular polymer system AC frequency dependence. The correlation between polymer structure and optimal m is a subject of discussion.

6. Conclusions

We carried out the computer simulation of $\sigma(\omega)$ of polymeric material at the low frequency range. AC data computation was based on the simple classical model when charge carriers are forced by the electric field to oscillate. We investigated the agreement of the simulation results with the experimental data measured of the PMMA sample. It can be concluded that optimization of the simulation process is necessary by the intermediate of the parameter m of the model. We suppose that the parameter m makes it possible to quantify conjugate character of the material in the model approach. The acceptable agreement with the experimental data was reached by the simulation and the relation of the presented results to current theories of AC conductivity [19, 20, 21] was investigated.

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