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**MAGDALENA WŁODARSKA,[1] MICHAŁ PARTYKA[1]
GRZEGORZ W. BĄK,[1] BEATA MOSSETY-LESZCZAK[2]
HENRYK GALINA,[2] ZBIGNIEW FLORJAŃCZYK[3]
KRZYSZTOF ŁOKAJ[3]**

[1] Institute of Physics, Lodz University of Technology, ul. Wólczańska 219, 90-924 Łódź, Poland. e-mail: magdaw@p.lodz.pl
[2] Department of Industrial and Materials Chemistry, Rzeszow University of Technology, 35-959 Rzeszów, Poland. e-mail: mossety@prz.rzeszow.pl
[3] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa

ELECTRIC CONDUCTIVITY IN EPOXY MATRIX WITH NANOPARTICLES

This work presents results of DC conductivity measurements obtained for epoxy matrices with different concentration of the nanofiller. In the first step, optimal curing conditions were determined – which turned out to be similar to those established for a plain epoxy matrix. In order to confirm stability of the matrix, measurements of the current-time dependency were made, which clearly show both the chemical and electric stabilization at the given temperature. All the obtained materials appeared to be good insulators with high activation energy. It was observed that the activation energy decreases slightly with increasing concentration of the nanofiller.

Keywords: epoxy polymer network, nanocomposites, conductivity.

1. INTRODUCTION

Polymer composites are often used as construction materials. Their final mechanical properties are influenced not only by physicochemical properties of the components but also by the contact surface size between the contiguous and dispersed phase and by the nature of interactions between them. Hence, a lot of interest is in composites with nanofillers, in which these factors have a particularly high impact. Polymer nanocomposites find diverse applications in construction industry, or as coating materials – depending on the types of the nanofillers and the polymer [1, 2]. Adding nanoparticles to a composite may also modify the electric properties of the obtained material.

This work was focused on studying the electric conductivity of an epoxy matrix as a function of the amount of added nanofiller. The experiments were performed using epoxy matrices with unidimensional nanofillers. 1D nanoparticles can have the form of nanofibers, nanotubes or nanorods. They are characterized by high shape coefficient, i.e. their length to diameter ratio [1, 2].

2. MATERIALS

Mixtures prepared for the electric measurements where made of two basic components: AU12 epoxy monomer and DDM amine (Fig. 1) in stoichiometric ratios [3]. The third component, added to the mixtures in concentrations 0%, 1%, 2% and 10%, were aluminium diphenylphosphate nanorods with diameter of 100-200 nm and length of 1-5 µm. Detailed description of the synthesis and properties of the nanorods can be found in papers [2, 4, 5].

All the prepared samples were cured for 3 hours at the temperature of 130°C. Samples were already solid after curing at these conditions, but they still were not fully stable during the measurements. Due to that, the samples were additionally post-cured at the temperature of 180°C before commencing the conductivity measurements.

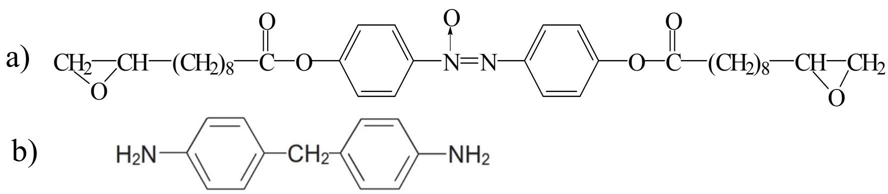

Fig. 1. Chemical structure of the used compounds: a) epoxy material, b) DDM amine.

3. EXPERIMENTAL

The samples of thickness 50 µm were placed between metal discs. The conductivity measurements were performed using a circuit consisting of a Fluke 8808A digital multimeter (which enables measuring currents above 1nA) and an SDP 2603 DC power supply working as a voltage source. The temperature of the samples was stabilized with the accuracy of 0.01 K using Unipan 620 temperature controller.

The curing process carried out at 130°C turned out to be insufficient for the reaction to reach completion. An additional process stabilizing the obtained polymer matrix was required in all the cases. It was achieved by annealing the samples at the temperature of 180°C. In order to determine the time needed for matrix stabilization, the post-curing process was monitored in a DC setup by collecting current-time characteristics at a constant applied voltage.
Moreover, some initial measurements of the current-time characteristic were carried out before capturing the final characteristics at particular temperatures. The circuit stabilization time at each temperature was estimated and it ranged from 25 to 100 seconds. An example plot of I(t) dependency at 160°C for the sample with 10% concentration of nanorods is shown in Fig. 2.

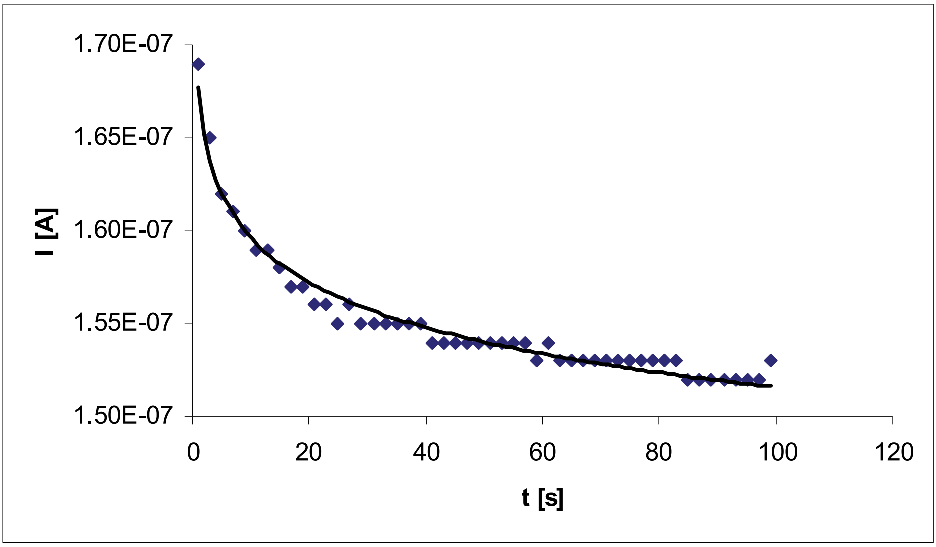

Fig. 2. Changes in the current during the initial period after closing the circuit. Exemplary results for the matrix with 10% concentration of nanoparticles at the temperature of 160°C.

4. RESULTS AND DISCUSSION

Current-time characteristics were collected for all the obtained materials in the temperature range from 120°C to 180°C. Below 120°C, the DC conductivity substantially and suddenly decreased in all the samples. Exemplary characteristics for the material with 1% concentration of nanoparticles is shown in Fig. 3. Noteworthy is the linear dependency I(U) and large differences in the values of the current with increasing temperature. Similar characteristics were observed in the majority of the studied materials and all they were linear in the investigated range of voltage and temperature. As a result, it was possible to determine the electric conductivity at almost all the selected temperatures by using the relation:

$$\sigma = \frac{l}{SR} \tag{1}$$

where l is the distance between the electrodes, S is electrode area, R is ohmic resistance determined from the current-voltage characteristics.

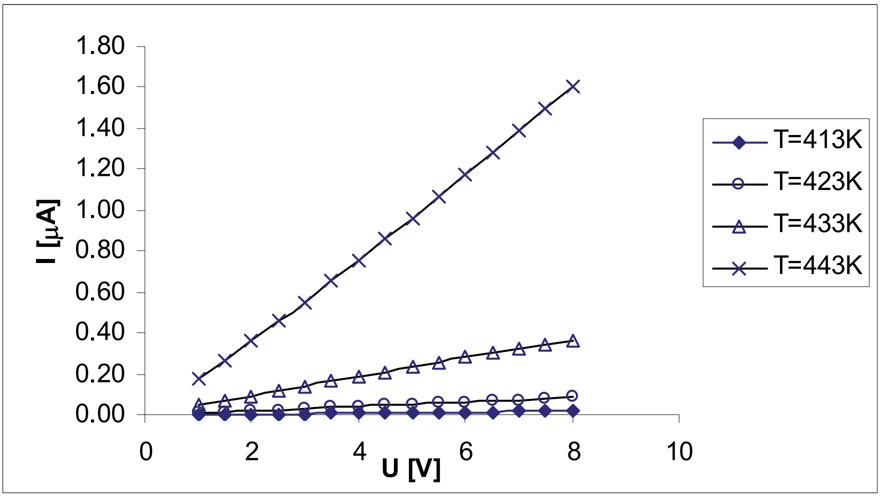

Fig. 3. Current-voltage characteristics at various temperatures, obtained for the epoxy matrix with 1% concentration of nanoparticles.

An example of the relation between the logarithm of the conductivity and the inverse temperature was shown in Fig. 4. Using this logarithmic relation, energy activation was determined for all the four materials. All the obtained values of the conductivity at various temperatures – along with their activation energy values – were collected in Table 1. However, it was not possible to determine the conductivity in some temperatures. This stems from the fact that the currents were sometimes too low for carrying out the measurements properly at low temperatures, whereas at high temperatures the measurements' stability or linearity was not sufficient in some cases (in plain matrix or at low concentration of nanoparticles). Low stabilization could be observed particularly in current-time characteristics (at constant voltage). By comparing the values of the activation energy presented in the table one can notice their similarity. However it can also be observed that the matrix with 1% concentration of nanoparticles has the highest activation energy, the plain matrix also exhibits high activation energy and with increasing concentration of nanofillers the activation energy decreases. Hence it can be concluded that high concentration of nanorods decreases the barrier for charge conductivity in the studied substance.

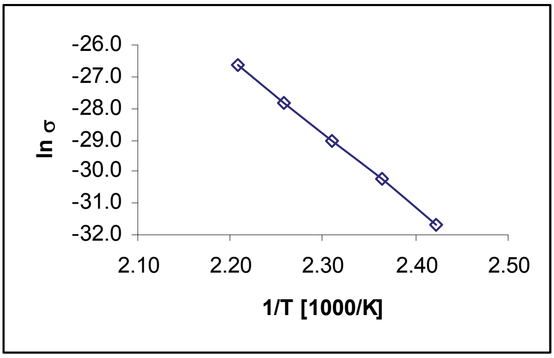

Fig. 4. Example of the logarithmic dependence of the electric conductivity on inverse temperature, obtained for the epoxy matrix with 2% concentration of nanoparticles.

Table 1. Electric conductivity at various temperatures and activation energy

T[°C]	σ_o [S/m]·10^{-14} 0% concentration	σ_1 [S/m]·10^{-14} 1% concentration	σ_2 [S/m]·10^{-14} 2% concentration	σ_{10} [S/m]·10^{-14} 10% concentration
120	1.89	-----	-----	-----
130	8.91	-----	-----	-----
140	40.5	3.99	1.78	7.20
150	173	17.1	7.20	29.0
160	631	73.2	24.6	68.6
170	-----	326	79.9	214
180	-----	-----	274	529
Ea [eV]	2.14	2.31	2.01	1.71

5. CONCLUSIONS

The conductivity values obtained for all the composites qualify them as insulators ($\sigma = 10^{-14} \div 10^{-12}$ [S/m]). Increased concentration of the nanoparticles did not improve conductivity of the materials, but it enabled carrying out stable measurements at higher temperatures. The activation energy is lowest for the highest concentration of nanorods though the differences between the computed values of the activation energy are generally small.

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PRZEWODNICTWO ELEKTRYCZNE W MATRYCACH EPOKSYDOWYCH Z NANOCZĄSTKAMI

Streszczenie

W pracy zaprezentowano wyniki pomiarów przewodnictwa stałoprądowego uzyskane dla matryc epoksydowych z różnym stężeniem nanonapełniacza. Początkowo ustalono optymalne warunki sieciowania, które były podobne do tych ustalonych dla samej matrycy. W celu potwierdzenia stabilności matrycy przeprowadzono pomiary zależności prądu od czasu, które dobrze obrazują zarówno stabilizację chemiczną, jak i elektryczną w danej temperaturze. Wszystkie uzyskane materiały okazały się dobrymi izolatorami z dużą energią aktywacji. Zauważono, że wraz ze wzrostem stężenia nanocząstek energia aktywacji nieznacznie maleje.