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CONDUCTIVITY IN CURED EPOXY RESINS CONTAINING A BIPHENYL UNIT

Conductivity of two epoxy matrices based on the same monomer was compared. The epoxy monomer had symmetric structure and contained the biphenyl group which induced additional phase transitions in the pure material. Two amines responsible for different curing mechanisms were used to prepare the matrices. Wide ohmic regions were observed in both materials but quite high activation energy results in quick drop of conductivity at low temperatures and the materials can be treated as good isolators below 100°C. The obtained results are comparable with traditional epoxy resins.

Keywords: epoxy polymer network, DC conductivity, activation energy.

1. INTRODUCTION

Most polymeric materials have low electric conductivity and are classified as insulators although their specific conductivity changes in a very broad range depending on their chemical structure – from 10^{-16} S/m (anthracene) to even 10^2 S/m (graphite) – and polymers with high DC conductivity are in fact treated as semiconductor materials [1-5]. From the application perspective, polymer composites used in electronic, automotive and aerospace industry are required to dissipate static electric loads to avoid electrostatic charging and electromagnetic radio frequency interference [6,7]. This is a driving factor for continual studies on electric conductivity in polymeric materials and attempts to modify them through changes in manufacturing process, doping or adding nanofillers [4-9]. Although the conductivity mechanisms can be different in such materials, most

of the organic materials show exponential relation between conductivity and temperature [3,6]:

$$\sigma = \sigma_0 \cdot e^{-E/kT} . \quad (1)$$

In some cases, high activation energy may lead to a conductivity change with temperature by several orders of magnitude in the same material. Several publications discuss the conductivity mechanism in organic materials but the topic is rather complex because different charge carriers (e.g. ions or electrons) may be involved as well as various transport mechanisms [1-4,8]. For instance, attempts to adopt the band model directly for organic compounds did not give satisfactory results even in the case of organic crystals. One of the arguments against simple adoption of the band model was the fact that the conductivity rises after melting an organic crystal; another phenomenon observed in many compounds was constant activation energy in both the solid and liquid state [1-3].

Electric properties of polymeric materials depend on two processes: creation of charge carriers and their transport along the macromolecule as well as charge transfer between the molecules in a macroscopic sample. The first process is determined primarily by the chemical structure of the macromolecule, whereas the second process depends mainly on the chemical structure of the entire system [3,6,10,11]. From the perspective of a single molecule (precursor), the greatest impact on polymer conductivity has the coupling order of π -electrons and the presence of heteroatoms and functional groups [3,6,10,11]. It has been shown, for example, that presence of increased number of double conjugated bonds in the monomer leads to lowering of activation energy and growth of conductivity. This is confirmed by experiments on aromatic compounds in which the conductivity rises (from 10^{-7} to 10^{-5} S/m) with increasing number of aromatic rings (from 1 to 3) [10,11]. Aromatic rings, heteroatoms and functional groups also appear in epoxy networks studied in this work, both in the monomer and in the curing agent, which can influence the conductivity in these materials. Another contributing factor is the physical structure of the polymer, particularly molecular interactions. For example, growth of electric conductivity with increasing degree of crystallinity has been observed in many cases. Polymer networks are structurally inhomogeneous, though [1-3,12]. DC conductivity is in this case connected with strong cross-linking which enables overlapping of electron orbitals. Moreover, complexes with charge transfer between numerous aromatic groups and groups containing heteroatoms may appear in these systems [1-3].

Due to the exponential nature of the conductivity-temperature (Eq. 1) dependence in most organic materials, it is possible to determine and compare

thermal activation energy obtained from that dependence. Although physical interpretation of such empirical activation energy is not unequivocal, it is nevertheless a useful parameter characterizing organic materials.

In this work, electric conductivity of two types of polymer matrices based on the same epoxy monomer is studied. The observed conductivity changes significantly with temperature and exhibits high activation energy. Due to the presence of a mesogenic (biphenyl) group, the investigated materials may find future application as self-organizing matrices for nanofillers.

2. MATERIALS

Two polymer matrices obtained by curing an epoxy compound with DDM and DMAP amines were chosen for this study. The chemical structure of the epoxy material (based on a biphenyl mesogen) and the selected amines is shown below. The synthetic route and basic physical properties of the epoxy material – in particular, temperatures and types of phase transitions – can be found in the paper [13].

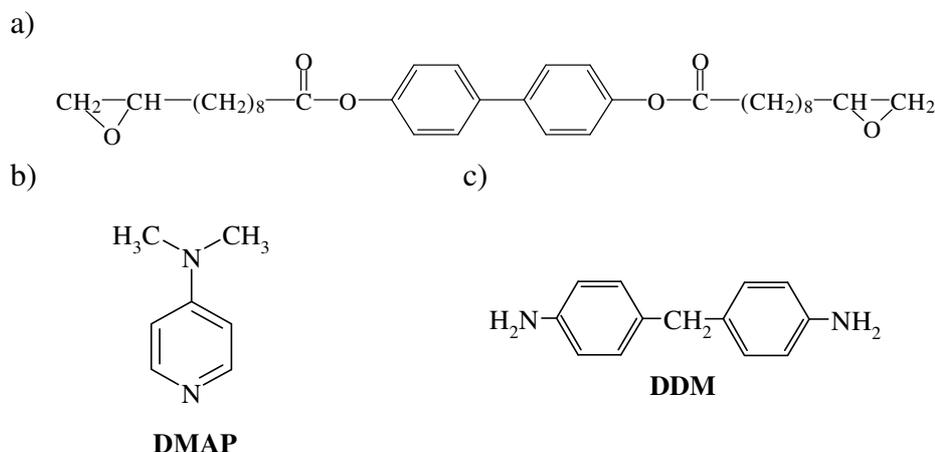


Fig. 1. Chemical structure of the used compounds: a) epoxy material, b) DMAP amine, c) DDM amine

The first studied material was obtained by curing the monomer with DMAP amine for 3 hours at 127°C. In this case, the amine was only needed to initiate the curing reaction and its mass fraction was only 1% of the mixture. The material was additionally annealed for 2 hours at 180°C in order to stabilize the structure before commencing the measurements. The second material was

obtained by curing the monomer with DDM amine for 3 hours at 138°C. In this case, the proportion of both substances in the mixture was stoichiometric. This material was also annealed for 2 hours at 180°C before the measurements.

3. EXPERIMENTAL

The samples of thickness 50 μm were placed between brass discs. The temperature of the samples was stabilized with the accuracy of 0.01 K using Unipan 620 temperature controller. The conductivity measurements were performed using a circuit consisting of an 8088A digital multimeter and an SDP 2603 DC power supply working as a programmable voltage source. The resolution of Fluke 8808A multimeter operating in the ammeter mode is limited to 1 nA. In order to increase the resolution for measurements carried out at low temperatures, the multimeter was switched to voltmeter mode and additional external reference resistors of 10, 100 or 1000 k Ω were connected in parallel with the voltmeter input. This circuit allowed us to reach resolutions of up to 1 pA. The conductivity measurements were also compared in some cases with results obtained using a Keithley 487 picoammeter/voltage source and very good agreement of experimental data was obtained.

Before capturing the current-voltage characteristics, some initial measurements of the current-time characteristics for a constant applied voltage were performed. This allowed us to estimate the stabilization time of the current measurements to be around 200 s for the highest considered temperature of 180°C. This time decreases with decreasing temperature and may be estimated at around 50 seconds for the lowest considered temperature of 100°C. The characteristics were captured by increasing the voltage gradually, and also by short-cutting the circuit after each voltage change. The second method appears to be more reliable because it prevents accumulation of charge in the material under influence of the electric field. It is also more time consuming so should only be used when one expects a significant accumulation of charge in the material.

4. RESULTS AND DISCUSSION

The first studied material was a matrix created with DMAP amine which only acts as a precursor of the curing reaction. The chemical structure of the obtained matrix is thus similar to the structure of the monomer. In the first step, changes in the current with time were studied at constant voltage in order to find the optimal time after which the current stabilizes. Those times were different at

various temperatures and they were longer at higher temperatures. An example current-time characteristics is shown in Fig. 2, where for the upper curve (140°C) stabilization is seen after 120 s whereas in the other case the stabilization time is longer than 300 s. In the second part of the work, current-voltage characteristics were studied (Fig. 3). For the voltage range used in this work, nearly linear dependencies were obtained. Only at temperature values around 180°C and higher values of voltage deviations from linearity were observed. It is not surprising, because validity of Ohm's law in moderate electric fields has already been verified for most organic compounds (including polymeric materials) [3]. Conductivity was determined for each value of temperature (Fig. 4) using the relationship

$$\sigma = \frac{S}{l \cdot R}, \quad (2)$$

where: l – distance between the electrodes, S – electrode surface, R – sample resistance.

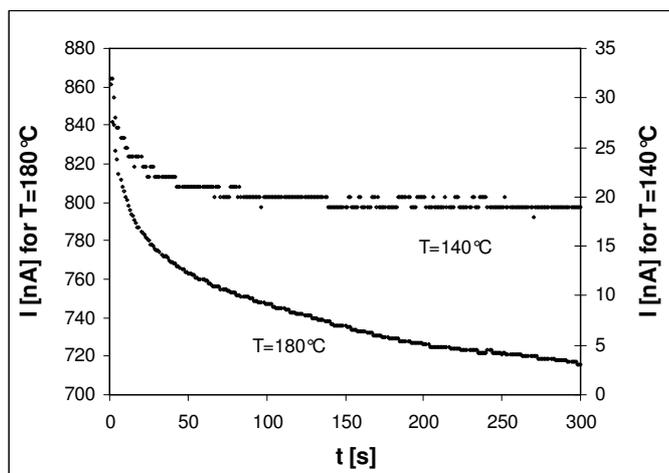


Fig. 2. Current-time characteristics for material 1 (product of curing with diamine DMAP) at temperatures 140°C and 180°C. Both curves are shown in one plot, but using two different scales indicated on the left and right axes

By looking at Fig. 3 one can already notice a significant change in conductivity with temperature. The plot of specific conductivity vs. inverse temperature and the activation energy calculated from that plot fully confirm that initial observation (Fig. 4). As it was mentioned earlier, most organic materials obey the exponential relation (1), which is also true in the studied case.

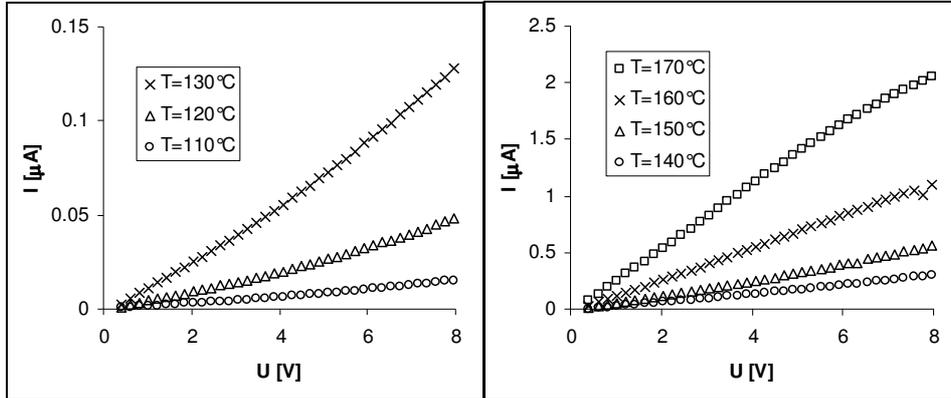


Fig. 3. Current-voltage characteristics for material 1. For most of the temperatures, linear characteristics were obtained in the considered voltage range. At the temperature 180°C the characteristics bends slightly at the high end of the voltage range

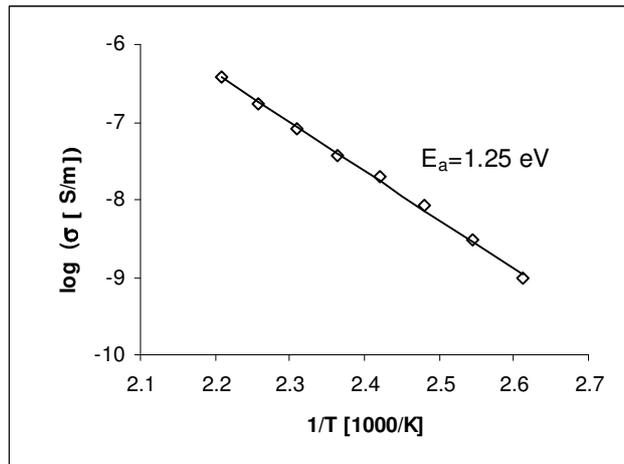


Fig. 4. Logarithm of conductivity vs. inverse temperature and activation energy for material 1. The conductivity changes in a broad range (10^{-6} to 10^{-9} [S/m]) during cooling from 180°C to 100°C

A similar behaviour was observed in the second material, with stoichiometric content of the DDM amine in the cured mixture. The current-voltage characteristics were also linear in most of the cases (Fig. 5). In order to avoid modifications of the results by charge accumulation at the electrodes, the measurements of this material were carried out with discharging the sample after each change of applied voltage. Plots of conductivity vs. inverse temperature and

the activation energy are shown in Fig. 6. Though the current-voltage characteristics are similar for both materials, conductivity is somewhat lower and activation energy somewhat higher in this case, compared with the first material.

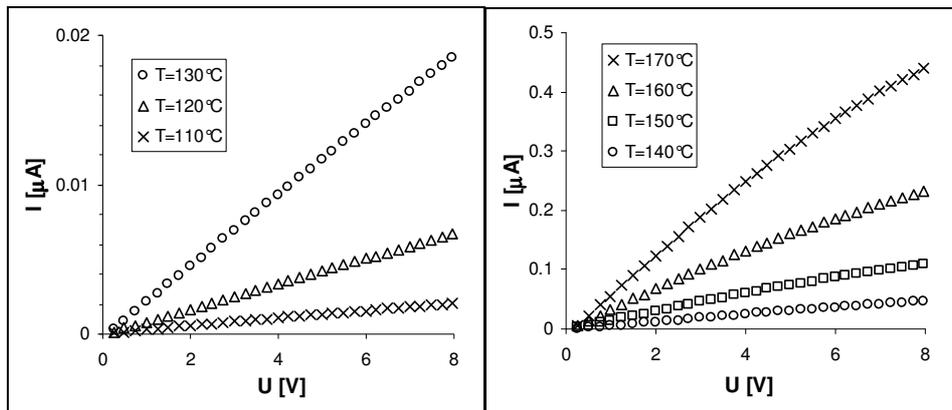


Fig. 5. Current-voltage characteristics for material 2. For most of the temperatures linear characteristics were obtained in the considered voltage range. For the temperature of 180°C the characteristic slightly bends at the high end of the voltage range

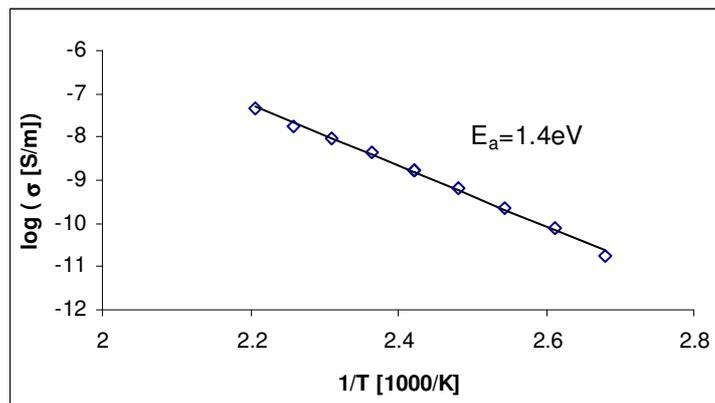


Fig. 6. Logarithm of conductivity vs. inverse temperature and activation energy for material 2. The conductivity changes in a broad range (10^{-6} to 10^{-11} [S/m]) during cooling from 180°C to 100°C

It is noteworthy that the structure of both network is a little different – the amine also contains aromatic bonds and nitrogen atoms, which contribute to increased conductivity in organic materials, but a different structure may result in higher energy barriers and, effectively, somewhat lower conductivity of the network containing the amine component.

Quite high values of conductivity at high temperatures (above 100°C) are also observed in traditional epoxy matrices, where drastic resistance drop (3 orders of magnitude) is observed around that temperature [2]. But since epoxy resins are typically used at temperatures close to the room temperature, these materials are treated as insulators [2].

5. CONCLUSIONS

In both epoxy matrices similar behaviour in a constant electric field was observed. The current-voltage characteristics were linear within the range of applied voltages (electric field up to $\sim 2 \cdot 10^5$ V/m). The electric conductivity changed significantly – from 10^{-11} to 10^{-6} S/m – in the investigated range of temperature (100°C – 180°C) and it was somewhat higher in the matrix obtained using the reaction-initiating amine as a curing agent. Relatively high values of the activation energy in both the cases (1.25 eV and 1.4 eV) mean that the studied materials practically become insulators at temperatures below 100°C.

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PRZEWODNICTWO USIECIOWANYCH ŻYWIC EPOKSYDOWYCH ZAWIERAJĄCYCH GRUPĘ BIFENYLOWĄ

Streszczenie

Porównano przewodnictwo dwóch matryc epoksydowych, opartych na tym samym monomerze. Monomer epoksydowy miał budowę symetryczną i zawierał grupę bifenylową, która wpłynęła na powstanie dodatkowych przejść fazowych w czystym materiale. Do wytworzenia matryc użyto dwóch amin odpowiedzialnych za różne mechanizmy sieciowania. W obu materiałach zaobserwowano szerokie przedziały przewodnictwa omowego, ale duża energia aktywacji powoduje szybki spadek przewodnictwa w niskich temperaturach i poniżej 100°C materiały te mogą być traktowane jak dobre izolatory. Otrzymane wyniki są porównywalne z tradycyjnymi żywicami epoksydowymi.