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THE INFLUENCE OF ELECTRONIC EXPOSURE AND HEAT TREATMENT ON THE ELECTRICAL CONDUCTIVITY OF EPOXY POLYMER MATERIALS

***Yuliia Udovytska*[1], *Sergiy Luniov*[2], *Vitalii Kashytskyi*[3], *Volodymyr Maslyuk*[4], *Ivan Megela*[5]**

[1]ORCID: 0000-0003-4707-6363
Science and Research Department
Lutsk National Technical University
[2]ORCID: 0000-0003-0737-8703
Department of Basic Sciences
Lutsk National Technical University
[3]ORCID: 0000-0003-2346-912X
Materials Science Department
Lutsk National Technical University
[4]ORCID: 0000-0002-5933-8394
Department of Photonuclear Processes
Institute of Electronic Physics, NAS
[5]ORCID: 0000-0003-3388-3535
Department of Photonuclear Processes
Institute of Electronic Physics, NAS

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A b s t r a c t

The effects of high energy (12 MeV) electron irradiation and heat treatment on the electrical properties of epoxy polymers with PEPA content of 11, 12, and 13 wt. h. per 100 wt., including epoxy resin, were investigated. It was found that the electrical conductivity of epoxy polymers increases with electron irradiation, especially for doses higher than 10 kGy. It was also demonstrated that extra

Correspondence: Yuliia Udovytska, Lutsk National Technical University, Lvivska Str., 75, Lutsk, 43018, Ukraine, e-mail: yulgb123@gmail.com.

heat treatment of irradiated samples with a hardener content of 12 wt. h. leads to a further increase in their electrical conductivity. The nature of the obtained dependencies of electrical conductivity is determined by the processes of cross-linking and irradiation/thermal destruction, as well as the mass fraction content of the hardener. The radiation-stimulated increase in the conductivity of epoxy polymers can be used in the manufacture of conductive protective coatings and electronic components of sensors.

Introduction

The tasks of getting new and expanding the scope of composite materials by modifying structure and stability have always been pressing problems of science and technology (Clough 2011, Akhmedov et al. 2013, Pinchuk et al. 2009, Verma et al. 2020, 2019a, 2019b). In this sense, it is promising to use polymer composite materials based on epoxy resins, which have high adhesion to many materials and unique physical and mechanical properties that explain their wide range of applications in aerospace, engineering, and other fields of technology (Abakarov et al. 2007). In particular, conductive composites are widely used to produce conductive coatings, thermal and radiation screens, grounding conductors, and the development of many electronics and microsensors (Ishkov, Sagalkov 2006, Petrov, Gagulin 2001, Gaskov, Rumiantceva 2000, Galiamov et al. 2000, Zou et al. 2010, Bai, Shi 2007). The most common way to create electrically conductive composite materials based on polymer dielectrics is to introduce a variety of electrically conductive fillers (Blait, Blur 2008).

Also, as the review of modern works (Verma et al. 2017, 2018a, 2018b, 2019c) shows, promising structural materials are materials whose structure is a combination of bio and epoxy composites. The study of the conductive properties of such systems is just beginning. On the other hand, the results of the development of electrically conductive composite materials must meet some of the special requirements, such as manufacturability, economy, the efficiency of operational properties.

Most of the materials developed in such a way do not meet these requirements at the same time. For example, soot-filled polymer composites become conductive in soot content, which is much larger than with the introduction of carbon nanotubes, which, in turn, is difficult to distribute uniformly in the polymer matrix (Kuryptya et al. 2016).

For solving this problem, one requires finding new methods and technologies. In this respect, the processing of polymer composite materials by external physical fields (radiation, temperature, magnetic, electrical) will allow purposefully changing the electrical properties of these materials. In (Akhmedov et al. 2013, Pinchuk et al. 2009, Fouracre et al. 1991, Demkiv et al. 2015, Nychyporenko

et al. 2016, SHESHIN, DENISOVA 2016), ionizing radiation's influence on the physicochemical properties of polymer composite materials were investigated. It has been shown that the treatment of polymer composites by X-ray, gamma, or beta-radiation beams improves mechanical, electrical, and photoelectric properties. In (SAVCHUK et al. 2008, STUKHLIAK, KARTASHOV 2011), optimal temperature-time modes of heat treatment and low-frequency alternating magnetic field treatment were established, which provided an increase in the mechanical characteristics of epoxy composites. But, the combined effect of different physical fields on the physical, including electrical and chemical properties of epoxy polymers, has not yet been studied.

Thus, an urgent applied task is to study the effect of high-energy electron irradiation and heat treatment on the electrical properties of epoxy-based polymeric materials.

Experimental technique

This study's objective was to investigate the effect of different doses of high energy (12 MeV) electron irradiation on the specific conductivity of ED-20 brand epoxy resin with polyethylene polyamine hardener (11, 12 and 13 parts by weight per). According to theoretical estimates of (KNYAZEV 1977), the optimal content of PEPA hardener in the resin ED-20 is from 5 to 15 parts by weight per. As shown in (SAVCHUK et al. 2008, 2014), a decrease or increase of the proportion of hardener weakens the mechanical, tribotechnical and operational properties in varying degrees. For example, epoxy resin hardens unevenly and the physical and mechanical properties of the absolutely identical samples obtained on its basis will differ, when the content of a hardener PEPA more than 15 wt. h. Such material is not suitable for serial use. The most homogeneous structure and the best physical and mechanical properties are achieved when the content of the PEPA hardener in the neighborhood of 12 wt. h. This argued our choice of such mass fractions of PEPA hardener. The composition was poured into special shapes, resulting in rectangular parallelepiped specimens, 6×10×14 mm in size (see Fig. 1).

The initial curing process went on 24 hours under normal conditions (the air temperature in the laboratory was 20°C, atmospheric pressure – 750 mm Hg, and relative humidity – from 40 to 50 percent). The samples of the first group were irradiated with different electron dozes. The samples of the second group after irradiation were further heat treated. The heat treatment was a stepwise drying process in a furnace at temperatures of 70… 130°C for 6 hours (heat treatment at 70°C took place during the first hour, at 80°C, 90°C, 100°C, 110°C, 130°C – during the second, third, fourth, fifth and sixth hours, respectively). Radiation experiments were performed on the microtron M30 of IEP NASU

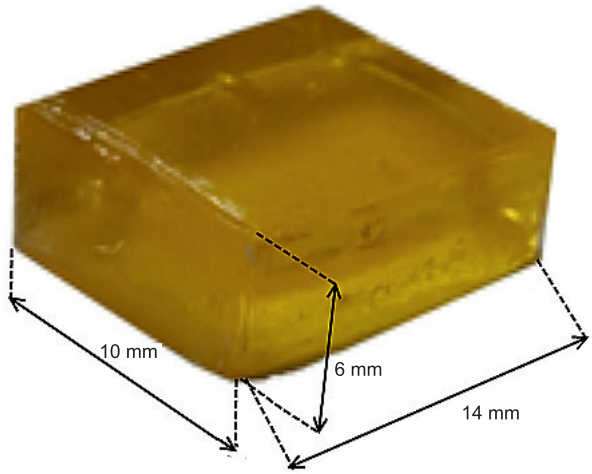

Fig. 1. The photograph of a epoxy resin sample for studies of the specific conductivity

with the electron's energy of 12 MeV, and they are monoenergetic of 0.01%. The inhomogeneity of the irradiation field did not exceed 10%. To ensure the stability of the room temperature of irradiation, which was recorded by a copper-constant differential thermocouple, the test samples were blown with nitrogen vapor. The epoxy polymer samples were irradiated to doses from 5 kGy (total fluence 1.56×10^{13} el./cm^2) to 100 kGy (total fluence 3.12×10^{14} el./cm^2) at electron flux rate 8.7×10^{10} el./(cm^2·s). The electron energy was chosen for the reason in order to the average linear electron path in the epoxy polymer was larger than the linear dimensions of the investigated samples. As is known (PAVLENKO et al. 2015, YASTREBINSKI et al. 2016), this parameter for the electron energy of 10 MeV is 1-4 cm for polymers, depending on their structure. In this case, the defects creation will be relatively uniform in the volume of a composite and there will be no significant resistance gradients that affect on the electrical conductivity of the epoxy resin. The processes of radiation destruction and creating of microcracks (PAVLENKO et al. 2010) will become significant at doses greater than 100 kGy. This will be affect the reducing of various physical and mechanical properties of the investigated epoxy polymer, including electrical properties. Measurements of the electrical resistance of epoxypolymers were performed on a universal voltmeter-electrometer B7-30, which allows measurements of the resistance of materials in the range from 10^5 Om to 10^{18} Om. If the cross-sectional area of the sample is epoxy polymer S, and the length is L, then its specific conductivity:

$$\sigma = \frac{L}{RS} \tag{1}$$

R – is the resistance of the epoxypolymer [Om].

Experimental results and discussion

In Figures 2–4 presents the dependences of the electrical conductivity of the epoxypolymer with different content of PEPA hardener on the irradiation doses of 12 MeV electrons. As one can see, the specific conductivity of epoxypolymers (both in the absence and in the presence of extra heat treatment after irradiation) decreases with increasing radiation dose to 10 kGy and then rapidly increases. Irradiation of samples of epoxypolymers with a hardener content of 12 wt. h. with a dose of 100 kGy, their special heat treatment increases the electrical conductivity by 1.7 times (Fig. 2, curve *1*). For samples of epoxy-dianic resin with a hardener content of 11 and 13 wt. h. the most significant effect of increasing the electrical conductivity of 1.2 times (for samples of epoxy-dianic resin with a hardener content of 11 parts by weight) and 3.9 times (for samples of epoxy-dianic resin with the content of hardener 13 parts by weight) is achieved after irradiation of these samples with a dose of 100 kGy, without extra heat treatment (Fig. 2 and Fig. 3, curve *1*). According to Figure 2 and Figure 3, the extra heat treatment of these samples after irradiation leads to a decrease in their electrical conductivity.

The two different processes occur in the irradiated polymers composites. The first one consists (AKHMEDOV et al. 2013, BLAIT, BLUR 2008) in the cross-linking of their chain structures under irradiation. In this case, it takes place the enlarging of the polymer macromolecules due to the formation of transverse chemical bonds between linear macromolecules. Another process is the destruction of macromolecules, the creation of the smaller macromolecules with some volatile products. The intensities and characters of the cross-linking and destruction processes of epoxypolymers depend on conditions of radiation treatments, especially on their doses and values of energy of the electrons.

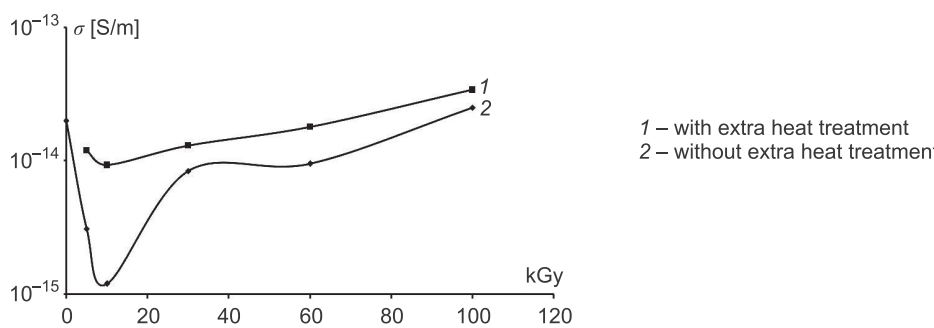

Fig. 2. The dependencies of the specific electrical conductivity on the absorbed electron irradiation doses for epoxypolymers with the content of PEPA hardener 12 parts by weight:
1 – irradiated samples of epoxypolymer which had been extra heat-treated,
2 – the same irradiated samples without extra heat treatment

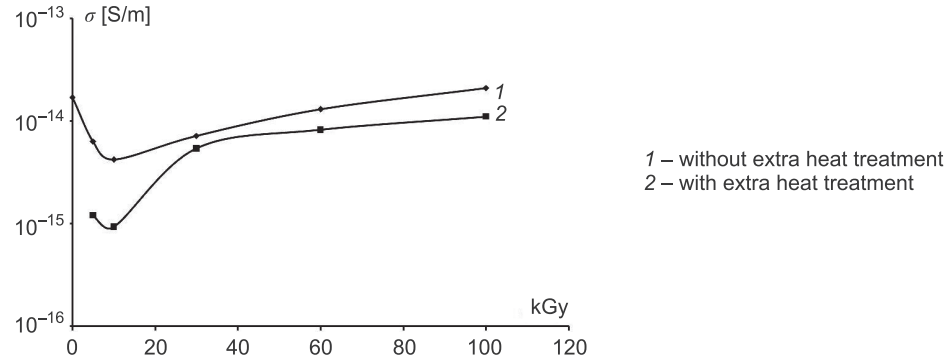

Fig. 3. The dependencies of the specific conductivity on the absorbed electron irradiation doses for epoxypolymers with the content of PEPA hardener 11 parts by weight:
1 – irradiated samples of epoxypolymer without extra heat treatment,
2 – same irradiated samples which had been extra heat-treated

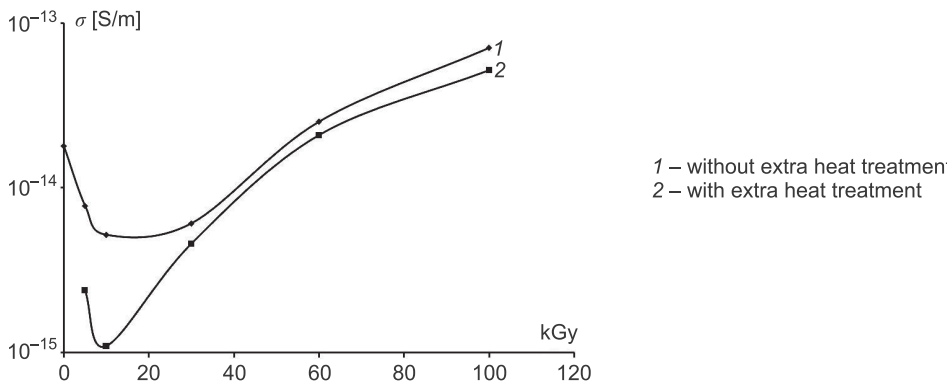

Fig. 4. The dependence of the specific conductivity on the absorbed electron irradiation doses for epoxypolymers with the content of PEPA hardener 13 parts by weight:
1 – irradiated samples of epoxypolymer without extra heat treatment,
2 – same irradiated samples which had been extra heat-treated

The effectiveness of such mechanisms of radiation-chemical transformations in composite materials will depend on the additional heat treatment and the mass fraction of the hardener, which explains the dependencies obtained in Figures 1-3. According to (ABAKAROV et al. 2007, BLAIT, BLUR 2008), three mechanisms of electrical conductivity are possible in polymer dielectrics: ionic, polarizing, and electronic. Besides, the dissociation and ionization of polymer molecules and processes of recombination of current carriers must also be taken into account. Today there is no only theory that able to explain the electrical conductivity of polymeric materials. For most polymer dielectrics, ionic conductivity is inherent (BLAIT, BLUR 2008). The specific conductivity

of the polymer is determined by the presence of free ions that are not chemically bonded to the macromolecules. In this case, the polymer chain is not involved in the transfer of electric charges, and the magnitude of the conductivity of the polymer depends on the presence of low molecular weight impurities, which can be a source of ions (AKHMEDOV et al. 2013). The expression for ionic conductivity can be written as (BLAIT, BLUR 2008):

$$\sigma = q\left(\sum_{i=1}^{n} m_i n_i \mu_i + \sum_{j=1}^{k} m_j n_j \mu_j\right) \tag{2}$$

where:

q – is the electron charge modulus,
m_i – is the charge of the i-th positive ion in electron charge units,
n_i – is their concentration,
μ_i – is the mobility,
m_j, n_j, μ_j – are the corresponding values for the j-th negative ion.

Cross-linking polymer macromolecules lead to the formation of a spatial grid and, consequently, a decrease in ion mobility. The decreasing of the ion mobility, according to equation 2, cause the reduction of the specific electrical conductivity of the polymer. Thus, for samples of epoxy-dianic resin with different PEPA harden content with electron irradiation doses up to 10 kGy, the probability of cross-linking is higher than that destruction of macromolecules, which explains the decrease of the electrical conductivity (see Figs. 2-4). For irradiation doses greater than 10 kGy, the destruction becomes more efficient.

Conclusions

The results of studies of the electrical properties of the electron-irradiated epoxy-dianic resin demonstrate their complicated nature. The specific electrical conductivity of these materials is determined by the domination of the macromolecules' cross-linking or destruction mechanisms, as well as the mass fraction of the curing agent into an epoxy-dianic resin.

The aggregation of macromolecules of the epoxypolymer due to their cross-linking leads to decreasing electrical conductivity. Extra heat treatment is effective only for irradiated epoxy resin samples with a hardener content of 12 wt. h. and leads to an increase in their electrical conductivity. Heat treatment of irradiated epoxy resin samples with a hardener content of 11 and 13 wt. h. leads to a decrease in their electrical conductivity. A purposeful change in the mass fraction of the hardener and the electron irradiation dose will control the electrical properties of the epoxy composite materials, which can be used to create conductive protective coatings and sensor electronics based on them.

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