JOINT INSTITUTE FOR NUCLEAR RESEARCH
Flerov Laboratory of Nuclear Reactions

FINAL REPORT ON THE SUMMER STUDENT PROGRAM

Study of electrets based on track membranes by the thermally stimulated current method

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Abstract

Nowadays, interest has grown in nanoporous structures with electret properties for medical use, especially in the production of implants, artificial blood vessels, etc. Track membranes are thin films (PET) with nanopores. In this work, we studied the effect of UV radiation on films of polyethylene terephthalate (PET) and their relaxation over time by the contact angle method, as well as track membranes obtained on the basis of PET with a layer of titanium and titanium dioxide with titanium by the method of thermally stimulated currents. The latter showed the presence of electret properties in layered structures with track membranes.

Introduction

An electret is a dielectric material that has a quasi-permanent electric charge or dipole polarisation. An electret generates internal and external electric fields, and is the electrostatic equivalent of a permanent magnet.

If a substance whose molecules have constant dipole moments is melted and placed in a strong constant electric field, the molecules are partially oriented along the field. When the melt is cooled to solidification and the electric field is turned off in the solidified substance, the rotation of the molecules is difficult, and they retain their orientation for a long time. Electret made in this way can remain in a polarized state for quite a long time (from several days to many years). The first such electret was made of wax by the Japanese physicist M. Eguchi in 1922.

The electrets are characterized by hetero and homo charge. Homo charge appears due to injection from the electrodes into the dielectric charge carriers of the same sign as that on the electrode. Hetero charge caused electric polarization in the dielectric volume because of the orientation of the dipoles, ionic (or electronic) polarization or displacement of the space charge.

Almost all known organic and inorganic dielectrics can be transferred to the electret state. Stable electrets produced from waxes and resins (kanowski wax, beeswax, paraffin, etc.), from polymers (polymethyl methacrylate, polyvinyl chloride, polycarbonate, polytetrafluoroethylene, etc.), polycrystalline inorganic dielectrics (titanates of alkaline earth metals, steatite, porcelain and other ceramic dielectrics), single-crystal inorganic dielectrics (e.g., halides of alkali metals, corundum), glass and ceramics, etc [1].

An electret state can occur in a dielectric as a result of the action of an electric field, lighting, heating, irradiation, friction, mechanical deformation, a laser beam, etc., as well as various combinations of these factors. The dielectric is polarized or charged as a result of such influences. There are a lot of possible combinations of influence, and consequently, methods of obtaining electret state. Consider the main methods of obtaining electret [2].

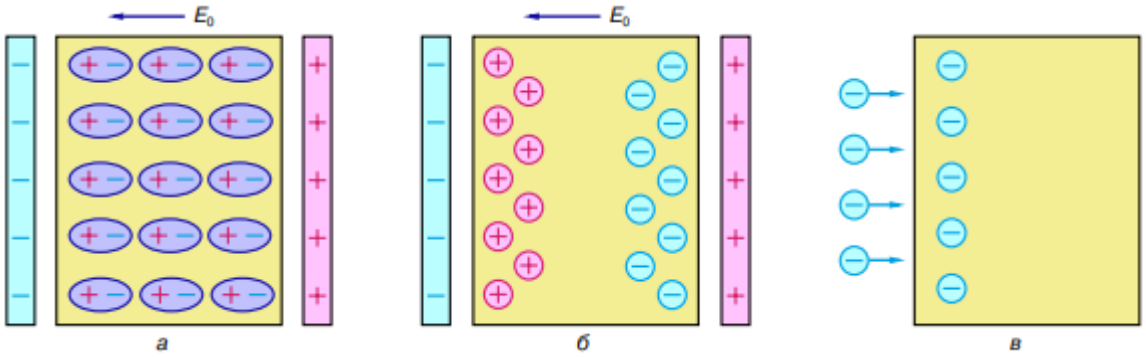

Fig. 1. The main mechanisms of formation of the electret state of the dielectric [2]

The method of thermoelectricity is reduced to placing a dielectric in an electric field at some elevated temperature, followed by cooling in this field. Initially, it was believed that the thermoelectric power obtained in this way has only a dipole (in the extreme case, a volume-charge) residual polarization. Further studies have shown that using relatively high polarizing electric fields are possible or breakdown of air gaps between the clamping electrodes and the dielectric, or injection of charge carriers from the sputtered electrodes into the dielectric.

The corona discharge method is based on the charge transfer from the electric discharge region in the air (gas) gap to the dielectric surface. In this case, the ions either transfer their dielectric charge and return back to the air, or penetrate into the near-surface region of the dielectric, where they are fixed by ion traps. It is clear that in the manufacture of cronobacter in principle may be violated electroneutrality of the dielectric. The advantage of the crown electroterapia are the simplicity of equipment and high performance (includes installation of continuous electroterapia polymer film, peremestivsheesya from one coil to another). The method of corona discharge is by far the most common in the production of film electret [3,4].

Method of creating electret by electron beam action. The effect of the electron beam on the dielectric leads to the injection of electrons into the material with the formation of negatively charged layers. The electron beam irradiation of fluorinated polymers allows to obtain on their basis the so-called radioelectric with the lifetime of an electret state, reaching at room temperature for decades [3]. Radioelectric obtained in this way usually are monoelectronic. The undoubted advantage of the method is the possibility of creating the necessary surface charge distribution of the electret by scanning the electron beam.

To create photoelectrees, materials, usually photoconductive, are coated on one or both sides with transparent electrodes (for example, thin films of gold or tin oxide) and irradiated with ultraviolet (sometimes visible) light in the presence of an electric field. After switching off the light and removing the voltage in the dielectric persisting over time polarization is detected [3, 1]. There are two main mechanisms of formation of photoelectric state. The first is the generation of charge carriers by light due to the transition of electrons from one allowed zone to another and their spatial separation along the thickness of the dielectric under the action of an external electric field. The second mechanism of the formation of the

photoelectric state is due to the photo-injection of charge carriers from the electrodes into the dielectric and their subsequent capture into deep traps.

The capture levels of injected charge carriers in the band gap of a dielectric or semiconductor are called traps. The nature, depth and concentration of traps strongly depend on the structure and nature of the dielectric and the conditions of its production. Thus, traps in dielectrics can be various imperfections of the crystal lattice, for example, impurity atoms, vacancies, etc. [5]. The main supplier of injected charge carriers is also the interface of the amorphous and crystalline phases near the polymer surface. This process is defined as Maxwell-Wagner polarization. Traps also include functional groups of macromolecules with positive electron affinity, deformed chemical bonds in the macromolecule skeleton, and free macroradicals [6].

The band theory is applicable for crystalline substances. The energy level, which lies in the forbidden zone of the dielectric, from the point of view of this theory, corresponds to the trap, and is sufficiently remote from the "bottom" of the conduction band or the "ceiling" of the valence band (Fig. 2). If the energy "gap" is less than 1 eV trap is considered small, while values greater than 1 eV deep. The energy" depth " of the trap is often referred to as the trap activation energy (E_a). This is the minimum energy that must be reported to the charge carrier in the trap for its release-the transition to the conduction band. The division of traps on small and deep enough conditional support. Deep traps at room temperature can hold a carrier at this level for months or even years. As the temperature rises, the probability of the carrier escaping the trap (w_t,) increases:

$$w_t \sim \exp\left(-\frac{E_a}{kT}\right),$$

where k is the Boltzmann constant, T is the absolute temperature, E_a is the activation energy of the trap.

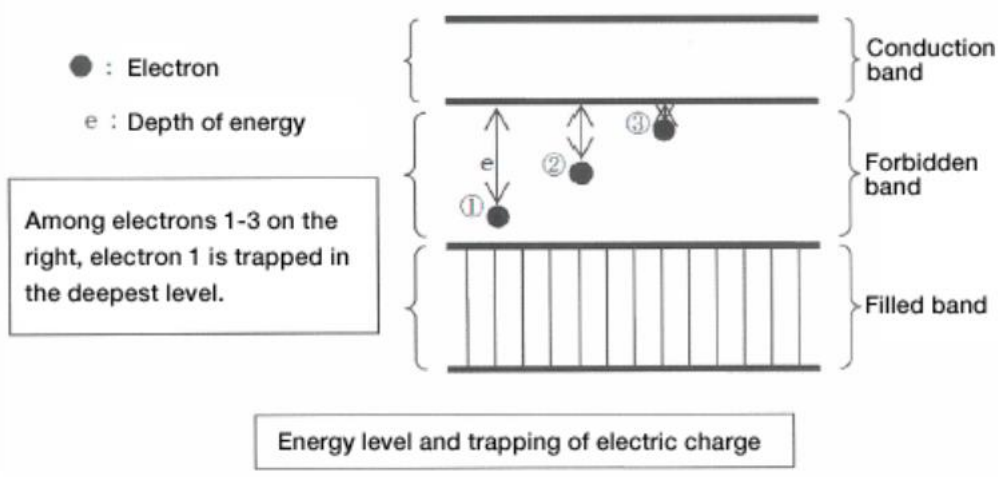

Fig. 2. Electret Traps [7]

Application of electret

- converters of mechanical, thermal, acoustic, optical, radiation and other signals into electrical (current pulses),
- storage devices, electric motors, generators, etc • ;
- filters and membranes;
- anti-corrosive structures;
- friction units; − systems of sealing;
- medical applicators, antithrombogenic implants, etc.

Bioelectrets

For a long time it was believed that electret, unlike ferromagnets, does not exist in nature. However, it appeared that a tissue of a living organism are in an electret state, i.e., they are bioelectrets. The potential created by bioelectrets is called ζ-potential. The internal walls of blood vessels, leukocytes, erythrocytes and other blood elements have a negative charge; in this regard, there is an assumption that it is due to the presence of charge that blood easily passes through the thinnest capillaries, despite its high molecular weight [4].

A new field in medicine, which is based on local electrostatic fields to stimulate biological processes in the human body, has been formed and is being actively developed. Electric fields are created by selffunctioning electret films deposited onto implants intended for various purposes. A biocompatible implant having improved host tissue ingrowth capability and enhanced blood compatibility com prises at least one tissue-contacting surface of an electrically charged material. The electrically charged material can be further chemically modified with covalently bonded activator molecules which further promote host tissue ingrowth and adhesion to the implant and/or enhance blood compatibility [8].

Polyethylene terephthalate (PET, PETE, PETP or PET-P) is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins.

PET consists of polymerized units of the monomer ethylene terephthalate, with repeating (C10H8O4) units (Fig. 3).

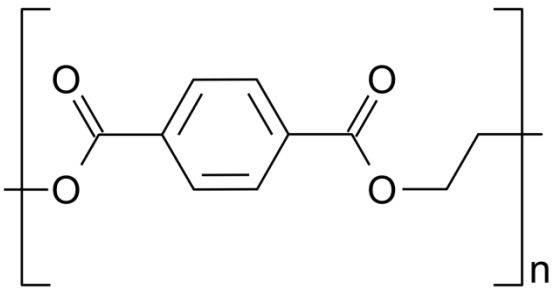

Fig. 3. Polyethylene terephthalate structure [9]

Polymers, as the main material for creating electret, in many cases do not have the mechanical, thermal and other properties necessary for their practical application. At the same time, life requires materials with new properties. Therefore, to obtain electret materials with desired properties, it is advisable to use compositions consisting of a polymer binder and fillers of different nature. When polymers are filled with dispersed fillers, new structural elements arise in composite materials that can serve as charge carrier traps, which causes a change in the electret characteristics of dielectrics.

Track-etched membrane — thin crystalline layers, metal foils or films (usually polymer with a thickness of 5 to 25 microns), whose pore system is formed by irradiation of initial non-porous materials with high-energy particles and subsequent etching of latent tracks of such particles to form through pores of a given diameter.
Such particles (Xe ion producing latent tracks can include accelerated heavy charged ions, flows of high-speed nano-and microparticles or products of their division, as well as beams of synchrotron radiation (ion-track technology). Colloidal particles flowing at speeds of 5-10 m/s form pores at once, without etching. The main differences between track-etched membranes and traditional membranes are the correct geometry of pores, ability to control their number per unit of membrane surface area and narrow pore size distribution. The pore sizes of track-etched membranes with scientific or practical value are in the range from 1 nm (primary track channel of high-energy particles) to several hundred nanometres (track-etched ultra and micro-filtration membranes). [10] Development of methods for creating electret membranes is an urgent task in recent years [11], [12].
В данной работе перед травлением трековые мембраны сенсибилизировали УФ излучением для увеличения скорости травления [13].

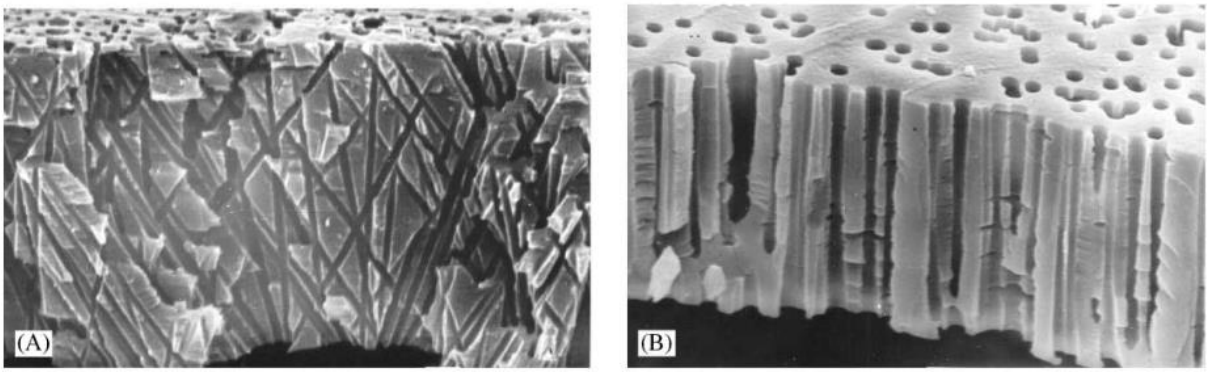

Fig. 4. Examples of pourus structures produced in thin polymeric films [14]

Methods

Drop shape analysis

Contact angles of PET surface and water were measured at room temperature using goniometer equipped with system of drop shape analysis (DSA100, Kruss, Germany). The liquid drop was placed onto the polymer surface by a microsyringe. The drop image was recorded by video camera and digitalized. The profile of single drop was numerically solved and filtered by mathematical functions. Each contact angle is the average of minimum 4 measurements.

Thermostimulated currents

Thermally stimulated discharge (TSD) is a technique that has contributed significantly to the current understanding of charge decay and charge storage processes in electret. TSD is the study of charge decay by heating the Electret at constant rate. These decay processes are investigated as a function of temperature. At room temperature the charge decay measurements are time consuming. The TSD technique shortens the time for measurements. So it is playing a vital role in Electret research. TSD of polymer has become a widely used experimental technique for the investigation of various material parameters such as charge storage properties, determination of mean depth of the internal charge, activation energies of traps and trap structure of the material. The thermally stimulated discharge conductivity is induced by thermal release of dipoles, ions and trapped electrons [2]. The thermally stimulated conductivity is applied to dielectrics in which a store of non-equilibrium carriers can be performed by nuclear radiations. In electrets made from polar materials the disorientation of dipoles plays a prominent role. This disorientation tends to destroy the persistent dipole polarization by redistribution of all the dipoles at random. The disorientation of dipoles involves the rotation of coupled pair of positive or negative charges and requires certain activation energy per dipole. The activation energy is not same for all the dipoles. The current-temperature plot will then consist of several peaks, because the dipoles with low activation energy will disorient at low temperatures, while those with high activation energy will only respond at higher temperatures. So, the activation energy is a great factor to study depolarization effect and also the conduction.

TSD setting

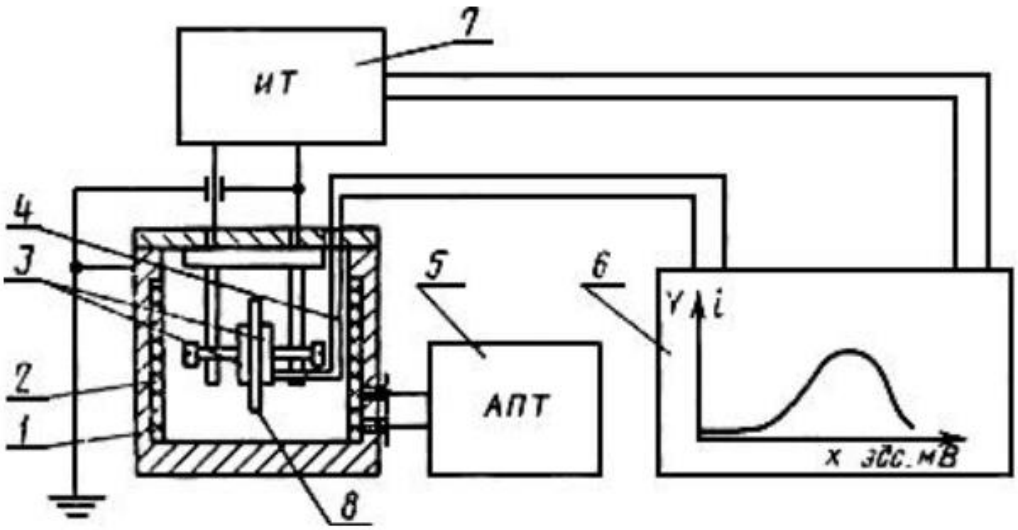

Fig. 5. 1-heat chamber housing; 2-heat chamber heating; 3-electrodes; 4-thermocouple; 5-automatic temperature programmer; 6-two-coordinate recorder; 7-current meter; 8-electret [15]

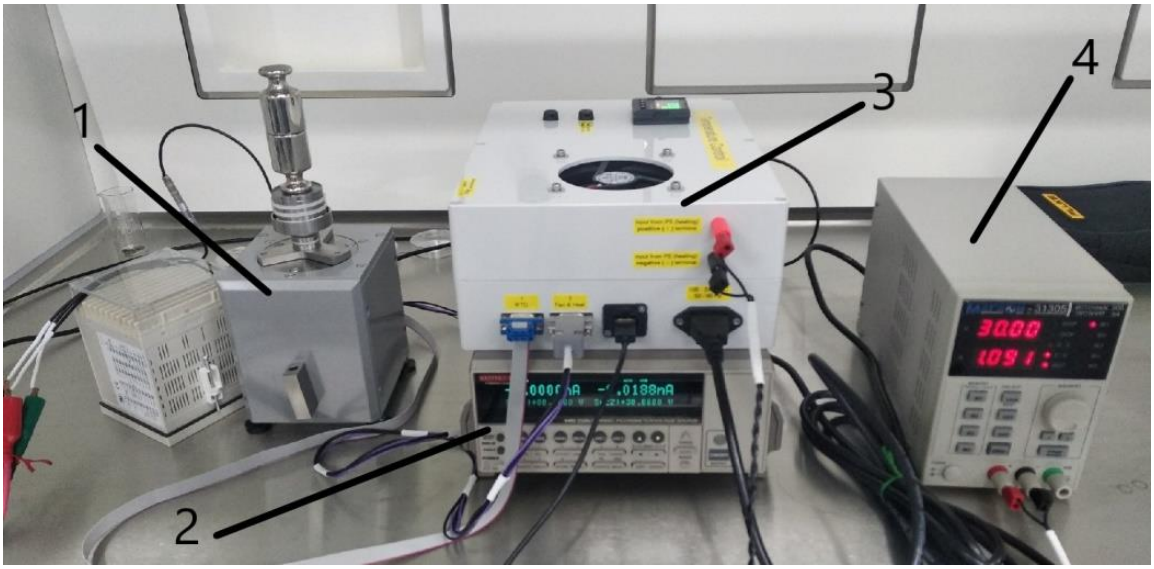

Fig. 6. 1 – Heat chamber; 2 – current meter; 3 – automatic temperature programmer; 4 – power sourse

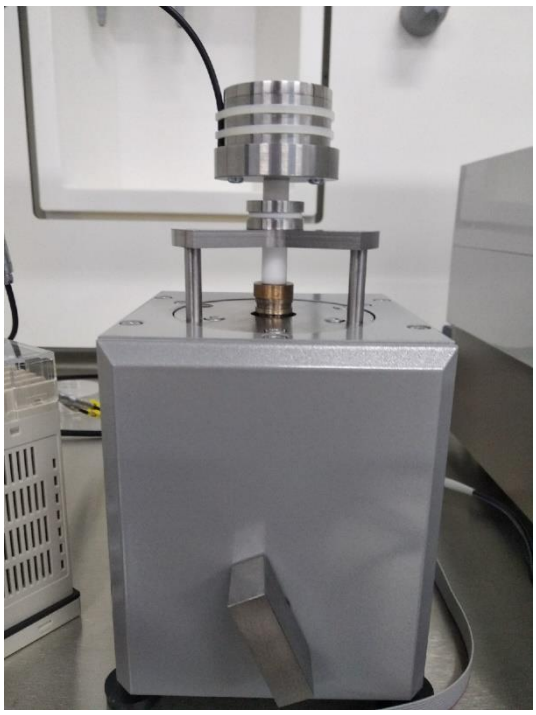

Fig. 7. Electrodes

The electret sample is clamped between electrodes, which are placed in a heat chamber, providing uniform heating in the temperature range (30-140) °C. with the help of a programming device, the desired rate of temperature increase is set. Currents of thermally stimulated depolarization are measured in time and recorded on a recorder depending on the temperature (thermocouple EMF). Get a thermogram based on current thermodepolarization temperature (Fig. 8).

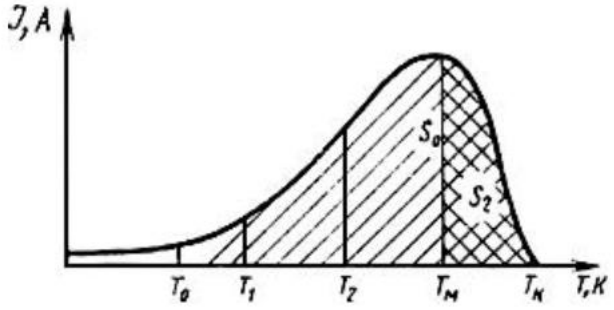

Fig. 8. TSD scale [15]

Processing of measurement results

1. The area under the curve (S_0) of the thermogram in mm^2 is calculated by the Fig. 8.
2. The residual charge of electret Q_r in C. is calculated by the formula:

$$Q_r = \frac{S_0 * M_1 * M_2}{\nu}$$

Where S_0 is the area under the curve of the thermogram in mm^2;
M_1 - the scale along the x-axis, K/mm;
M_2 - the scale on the y-axis, A/mm;

ν - rate of temperature rise, C / s.

3. The residual charge density of the electret is calculated by the formula:

$$\sigma_r = \frac{Q_r}{S_1}$$

where S_1 - electrode area, mm^2

4. The charge remaining at the time of reaching the maximum current in the C is calculated by the formula:

$$Q_M = \frac{M_1 * M_2 * S_2}{\nu}$$

where S_2- area under the thermogram curve in the temperature range above the maximum temperature, mm^2.

5. The charge relaxation time in seconds at maximum temperature is calculated by the formula:

$$\tau_M = \frac{Q_M}{I_M}$$

where I_M - maximum current, A.

6. The activation energy of the charge relaxation at the maximum current in J / mol is calculated by the formula:

$$W_M = \frac{R * T_M^2}{\tau_M * \nu}$$

where R=8,31 gas constant, J / mol·K;

T_M - current maximum temperature, K.

7. The activation energy of the charge relaxation with increasing current in J / mol is calculated by the formula:

$$W_y = \frac{R * 2{,}3 * (lgI_1 - lgI_2)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

where I_1, I_2 - depolarization current in the region of increasing current to a maximum at temperatures T_1 and T_2, A [15].

Experimental results and discussion

Samples of polyethylene terephthalate (PET) RNK with a thickness of 12 μm. were irradiated under UV light on one side for 15, 30, 45, 60, 90,120 minutes.

The contact angles of these samples were measured immediately after preparation, and also after relaxation of 1 and 4 days. The measurement results are presented in Fig. 9, 10, 11.

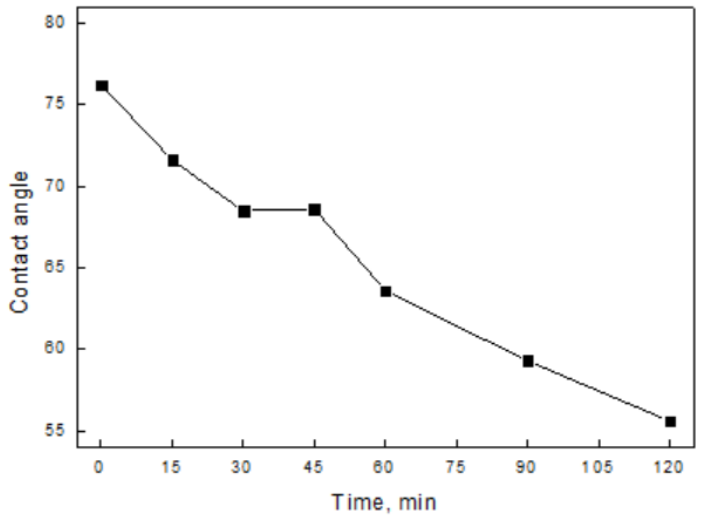

Fig. 9. The contact angles (°) of water on PNK PET after UV-irradiation during 0–120 min.

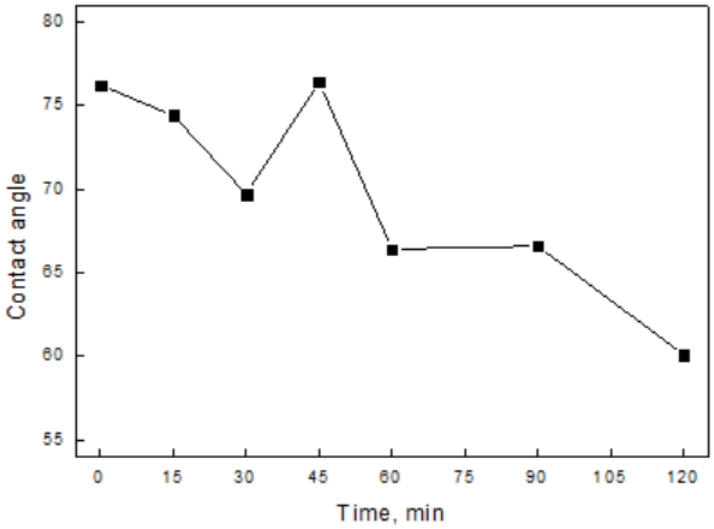

Fig. 10. The contact angles (°) of water on PNK PET after UV-irradiation during 0–120 min. after 1 day storage

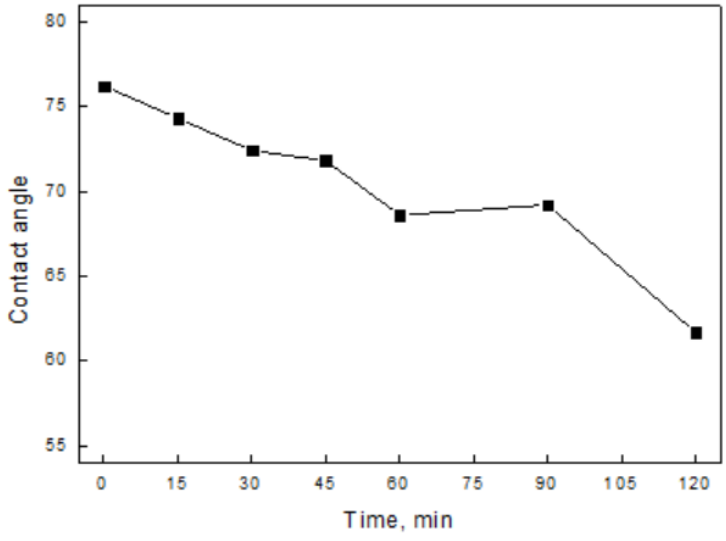

Fig. 11. The contact angles (°) of water on PNK PET after UV-irradiation during 0–120 min. after 4 day storage

The TSD currents of the samples obtained from track membranes with a Ti and TiO2 with Ti layer were measured. The measurement results are shown in Fig. 12, 13 ,14. As can be seen from Figure 12, an electret with a Ti layer completely loses its electret properties; therefore, during the cooling, TSD currents do not flow through the sample. In the second sample (Fig. 13.14), the maximum point of the TSD currents is above 140 ° C; therefore, the activation energy (Ea) was calculated from the increase in current. The activation energy of the track membrane sample with a Ti layer is Ea ~ 0.35 eV, and with a TiO2 with Ti layer - Ea ~ 0.86 eV.

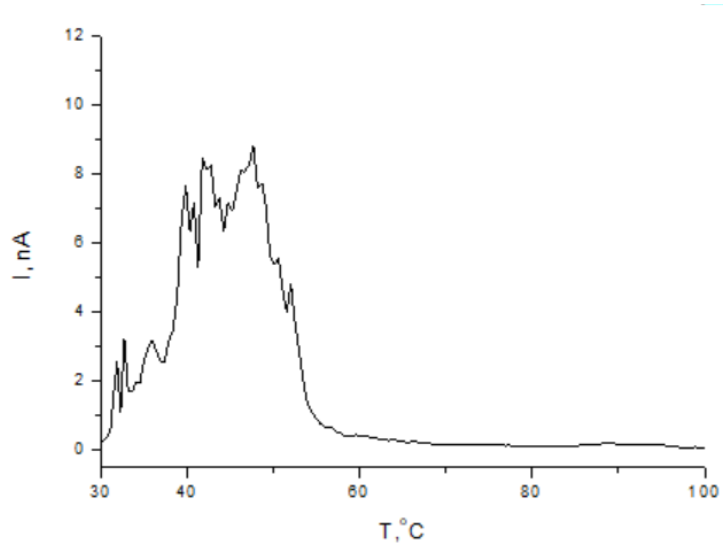

Fig. 12. Thermostimulated depolarization currents of a track membrane sample with a Ti layer during sample heating

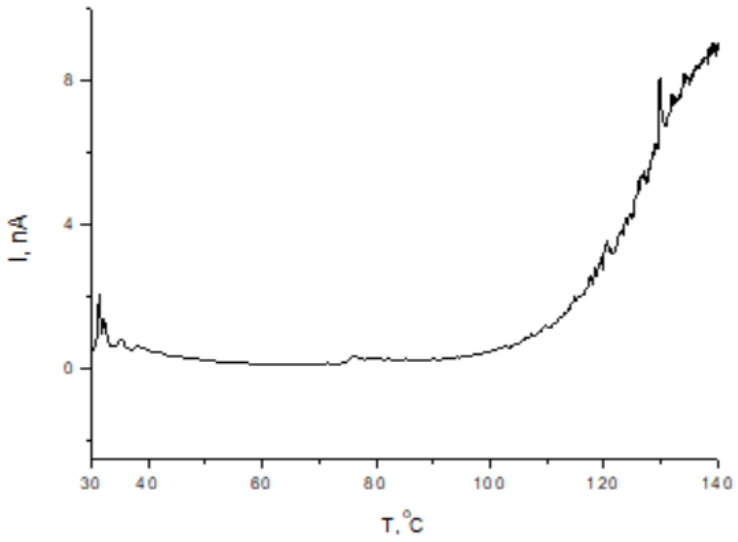

Fig. 13. Thermostimulated depolarization currents of a track membrane sample with a Ti + TiO_2 layer during sample heating

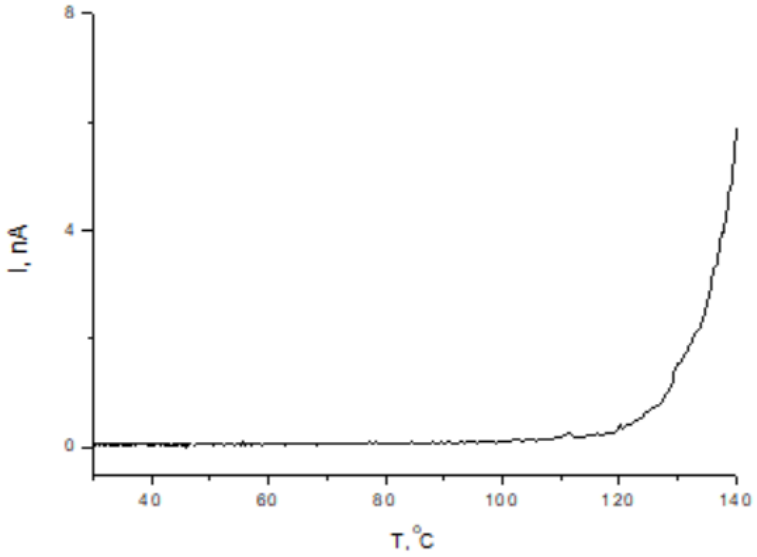

Fig. 14. Thermostimulated depolarization currents of a track membrane sample with a Ti + TiO_2 layer during sample cooling

Conclusions

During this work, I studied the electret properties of UV-irradiated PET samples and track membranes based on PET with a layer of Ti and TiO2 with Ti. I have gained skills in working with a setup for measuring thermally stimulated currents, also with a system of drop shape analysis (DSA100, Kruss). The dependences of the contact angles on the irradiation time were obtained and relaxation graphs for RNK PET samples were presented. Currents of thermally stimulated depolarization were obtained and activation energies for track membrane samples with a Ti and TiO2 with Ti layer were calculated.

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