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THE EFFECT OF MECHANICAL, ELECTRIC, TEMPERATURE FIELDS AND PLASMA OF AN ELECTRIC DISCHARGE ON THE ELECTRET PROPERTIES OF POLYMER - FERRO-PIEZOCERAMIC COMPOSITES

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Abstract. This paper presents the results of a study on the effect of mechanical σ_n, electric E_n, temperature T_p fields and electric discharge plasma on the electret states of polymers and polymer - ferroelectric piezoceramic composites. It is shown that under the simultaneous action of T_p, E_p, and T_p, the concentration and spectrum of localized charges injected into the polymer during electrothermopolarization change significantly. It is shown that structural changes occurring under the action of an electric discharge plasma, accompanied by the appearance of polar groups with high electronegativity in them, lead to an improvement in the electret state of polymers. It has been experimentally found that the plasma of a barrier discharge is a more efficient way of modifying polymers and composites based on them.

Keywords: ferroelectric piezoceramic composites, electrothermopolarization, electric discharge plasma, modifying polymers.

AMS Subject Classification:

1. INTRODUCTION

It is known that when considering the electret state of polymers, they are mainly limited by the results of studies on the effect of electrothermopolarization of polymers and composites based on them. Note that the electret state, in particular, the electret property and effective polarization, can significantly improve the modification of the polymer matrix and their composites under the action of an electric discharge plasma.

In [3], it was found that stretching leading to orientation also improves the thermal stability of HDPE corona electrets due to a decrease in the molecular mobility of the chains. Note that after orientational stretching, it is necessary to hold the polymer at a certain temperature under the action of a tensile force for some time in order to remove the internal mechanical stress in the films and eliminate shrinkage. In contrast, we applied mechanical stress during thermoelectreting [3]. In addition, the mechanical load was chosen in the region of elastic deformation, that is, it does not lead to a residual orientation of the polymers. For comparison, the studies were carried out in two different modes:

a) polytetrafluoroethylene (PTFE) films were charged, thermopolarized and discharged under the action of a mechanical load;

b) PTFE films were charged and discharged without mechanical stress.

It should be noted that thermoelectreting under the simultaneous action of mechanical stress (σ_n) can initiate the development of structure formations of different nature in PTFE, change the development of polarization and orientation processes, as well as the molecular mobility of polymer chains, and the degree of change of these processes depends on the values of σ_p, E_p, и T_p. Therefore, by changing the values of σ_n, E_p, and T_p during charging (polarization), it is possible to regulate the electret state of polymers and composites based on them. It is known that the implementation of the process of electrothermopolarization of polymers and their composites under conditions of the simultaneous action of external factors (σ_p, E_p, T_p and barrier discharge plasma) leads to a noticeable increase in the electret state, in particular, the electret potential difference U. An analysis of numerous experimental results shows that the reason for the increase in the macroscopic characteristics of composites is mainly determined by the value of the charges stabilized in the process of electrothermopolarization at the interface. If we take into account that the value of stabilized charges is determined by the concentration of local energy levels in the quasi-forbidden zone of the polymer, then it can be concluded that external electromechanical factors should be associated with the electronegativity of monomers, radicals, and segments of the polymer phase. It is known that among the existing external factors, the plasma of an electric barrier discharge [3, 4], is more effective, that is, an electric discharge in the air gap limited by dielectrics [5]. Therefore, we have presented the preliminary treatment of polymers under the conditions of the action of an electric discharge plasma in order to increase the electronegativity of the macromolecules of the polymer matrix. As our numerous experiments have shown, of great interest are those studies that were obtained under the simultaneous action of the above-mentioned mechanical, electrical, temperature fields and discharges of different nature.

The aim of this work is to determine the effect of mechanical, electric, temperature fields and plasma of a barrier discharge on the electret state of polymer-ferroelectric piezoceramic composites.

2. METODICS EXPERIMENT

The process of creating any polymers and composites based on them includes at least three stages: I – preparation and selection of initial components; 2

– mixing the components until a homogeneous mixture is obtained; 3 - obtaining a composite material from a mixture. The choice of the components of the composite and the method for their preparation and study is dictated by a set of properties that the final material, in particular, electret, should have. Therefore, the selection of the individual components of the composites is based on the following considerations. Certain requirements are imposed on polymer matrices and piezophases, electret composites, namely: easy processability, high plasticity and mechanical strength, as well as minimal conductivity. The above analyzes of the thermophysical, electrical, and physicomechanical properties of polymers showed that thermoplastic polymers of the polyolefin series and halogen-containing polymers meet the above requirements in the most complete form [6]. The determining factor in choosing a polymer matrix for obtaining electret materials is the high bulk conductivity ρv and the existence of deep charge trapping centers in the composite. For electret and piezoelectric composites, the most effective ferroelectric piezoelectrics of various structures are used as an active filler [8]. Recent work in the field of piezoceramic materials research has led to the creation of four main groups of materials: based on barium titanate, zirconate-lead titanate, lead niobate and sodium-potassium niobate. It should be noted that materials based on PZT are most widely used [1]. Materials with a PZT structure were developed and manufactured at the Research Institute of Physics of the Rostov State University using hot pressing technology[8].

The method of obtaining composites, ultimately, consisted in the following: a homogeneous mixture is obtained from powder polymers and fillers in a mechanical mixer; from it, tablets are obtained by cold pressing; the tablets are kept for some time at the melting temperature under low pressure; at the same temperature, the pressure slowly rises to P_{pr}, at which the sample is kept for tпp; then the pressure is released and the sample is rapidly cooled in water or slowly cooled under pressure. The method for obtaining electret elements is described in more detail in the work [7].

The charge state of polymers and their composites was studied using the method of registration of thermal depolarization current [9]. The structure of the composites was studied using the method of IR spectroscopy. The electret state of composites was studied by recording the electret potential difference [10].

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Numerous experimental results obtained show that the electric field initiates free radical oxidation processes in the polymer [3, 4, 6, 7]. The combined effect of mechanical load, temperature and electric field intensifies the above processes and contributes to the ionization of deeper traps, which is very important in the development of effective piezo-, pyro- and electret composites [1, 2]. In the IR spectrum of HDPE subjected to the simultaneous action of temperature, electric field and mechanical load for 0.5 to 2 hours, a number of new absorption bands [10], appear, of which the most pronounced are the bands at 3400 - 3200 sm^{-1} (OH - groups), 1750 - 1720 sm^{-1} (C = O groups), 1280 sm^{-1} (complex ether groups), 1210-1180 sm^{-1} (ethers -C - O - C), 1650 sm^{-1} (C = C connection). In the IR spectrum of PTFE-n after its thermoelectreting under conditions of simultaneous action of mechanical load, weakly pronounced bands appear in the range of 3600–2800 sm^{-1} (RCF2OH), 1760–1650 sm^{-1} (~CF=CF~), 1500 sm^{-1} (~CHF=CF$_2$).

Changes in the IR spectra of PE and PTFE show that in these polymers, under the simultaneous action of σ_p, E_p, T_p and the plasma of a barrier discharge, polar groups or complexes are formed, which are active centers of trapping charge carriers. The formation of polar groups or complexes due to free radical oxidative processes developing in polymers, with the simultaneous action of σ_p, E_p, and T_p, more intensively leads to an improvement in the electret properties of polymers [4] and composites based on them [7].

In fig. 1 shows the dependence of the surface density of the stabilized charge of PTFE-based electrets at $\sigma_p = 0$ (curve 1) and $\sigma_p = 15$ MPa (curve 2). The value of the effective charge in the case of polarization under load is significantly greater than the charge in the case of polarization without mechanical load, and the electric field strength at which Q reaches its maximum value decreases significantly. A more interesting effect is a decrease in E_p and a shift in its value towards a relatively lower electric field. This effect is further enhanced in the case of mechanical loading of the composite. Indeed, at $\sigma_p = 0$, only E_p is involved in the formation of the electret charge. With a further increase, the strength of the electric field of polarization - E_p, the electret charge - Q decreases, passing through a maximum. It should be noted that in the case of $\sigma_p = 0$ and $E_p \neq 0$, the decrease in Q is associated with an increase in the electrical conductivity of the material.

Possible reasons for the development of these processes are determined, taking into account the effect of mechanical stress on the activation energy of stabilized charges in the process of electrothermopolarization. To determine the relaxation time and activation energy of charges, electrets were carried out at different temperatures, i.e., the dependences of the logarithm of the surface charge density on time after polarization at different temperatures were obtained. Similar experimental studies were carried out for composites polarized at different temperatures [10]. At all temperatures, the curves have a break, which indicates the presence of two relaxation processes (or relaxers). The relaxation time τ of the charge at a given temperature was determined from the slopes of the straight lines by the least squares method. Next, the dependence of $\ln\tau$ on the reciprocal temperature was plotted and the activation energy was determined from the slope of the straight lines. The values of the activation energy calculated in this way for electrets without a load is 1.27 eV, and for electrets obtained by the action of a mechanical load, 1.83 eV. Thus, it can be concluded that the mechanical load applied during the polarization of the electret not only leads to an increase in the magnitude of the electret charge, but also contributes to the formation of deep traps in the PTFE film [2]. This approach allowed us to modify the polymer matrix, which is used as the matrix of composites. To clarify the reason for the formation of new centers of charge trapping (modification), we studied changes in the IR spectra of PTFE after exposure to an electric field and mechanical load [5, 8].

An increase in the relaxation time and energy of the charge relaxation of polymer electrets obtained under the simultaneous action of mechanical stress shows that the mechanical field causes a change in the population of the capture levels, moving charge carriers from shallow traps to deep ones. It is also possible that the combined effect of the electric field and mechanical load during thermoelectreting contributes to the formation of more perfect crystallites, at the boundary of which charges are accumulated.

Similar experiments were performed for the aforementioned polymers with variation in the polarization temperature.

In fig. 2 shows the dependence of the surface charge density of PETF(curve 1) and PTFE (curve 2) electrets on the charging temperature when the films are placed on the cathode surface. As you can see, the dependence Q = f (T_p) at U_p = const has an extreme character. The highest surface charge density for PTFE and PETF electrets is achieved at temperatures of 328 K and 333 K, respectively. When polymer samples are placed on the anode (curve 3), the surface charge density of electrets is much lower and practically does not depend on temperature. Note that in the selected temperature range (293–413) K and the electric polarization field strength (2–5) kV, the Q value reaches saturation in 10–15 minutes.

Let us consider the process of charging polymers in the cathodic potential drop zone. After the onset of a glow discharge, positive ions are introduced into the film, and the electric field near the cathode is a superposition of two fields: external E_p and the field of embedded ions E_i, i.e (formula 1).

$$E=E_p+/-E_i \qquad \textbf{(1)}$$

It can be assumed that the process of polymer charging will practically stop when the equality of the embedded Eu and the polarizing field En is reached. With an increase in temperature during polarization, a decrease or compensation of the field of implanted ions occurs due to the intensification of the following ion-polarization processes:

1. The diffusion of ions into the interior of the sample is accelerated;
2. The diffusion of positive charges localized deep into the polymer is accelerated;

3. The orientational polarization of small polar groups, which compensate for the field of incoming ions, is facilitated.

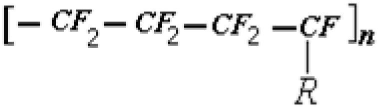
Of these factors, the dipole-group orientational polarization will obviously have the greatest effect on the effective surface charge density, since the first two factors, increasing the volume charge concentration, weakly change the surface density of the electret charge. The dipole - group orientation after polarization quickly relaxes and increases the effective electret charge. The choice of the temperature range for heating the sample is of particular importance here. We have found experimentally that if the polarization temperature of the polymer is selected in the temperature range of its dipole - group relaxation, then the magnitude of the electret charge increases with polarization [7].

Indeed, rapidly relaxing hetero charges, on the one hand, partially screening the field of embedded charges during charging, facilitate their further entry into the polymer volume, and on the other hand, after the termination of the glow discharge and heating, they quickly relax and thereby lead to an increase in the effective electret charge. With a further increase in the polarization temperature, a more stable, for example, dipole-segmental orientational polarization begins to play a role, the relaxation of which at room temperature is difficult. Therefore, the injected charge after electrification remains more compensated and the effective charge of the electret decreases (Fig. 2, b).

From the dependences of the logarithm of the relaxation time ($ln\tau$) of the charge on the reciprocal temperature (Fig. 3) for PET electrets charged in the zone of the cathodic drop of the glow discharge potential and under the influence of the positive corona, it can be seen that τ of the electret obtained by charging in the zone of the cathodic potential drop at 333 K, is noticeably longer than the relaxation time of the corona electrets. More interesting are the experimental results on the effect of the plasma of a barrier discharge on the property, in particular, on the dependence $ln\tau=f(1/T)$ of PETF electrets (Fig. 3, curve 4).

In fig. 4 shows the curves of the TSD currents of electrets made of PTFE (curves 3, 4) and PETF (curves 1, 2) charged at room temperature and 333 K, respectively. For PTFE electrets, the TSD current has a fairly wide maximum at room temperature, which indicates the presence of a wide range of filled traps in PTFE. Electrification at 333 K leads to a noticeable narrowing of the TSD spectrum width and a shift of the TSD maximum to high temperatures. This indicates that at 333 K shallow traps are practically not filled and charges are mainly stabilized on deep traps, which require a high activation energy to release. The same is observed in the spectrum of TSD currents of PETF electrets. In this case, two TSD current peaks are observed. The first maximum of a PET film charged at room temperature (curve 1) is wide and the maximum current value corresponds to a temperature of 353–368 K. During electrification at 333 K, this maximum narrows and its area slightly increases. The second maximum is observed at 393 K and its area increases strongly with an increase in the polarization temperature to 333 K.

Similar studies were carried out on a copolymer of tetrafluoroethylene with perfluorovinylethyl ether (TFE - PFVEE)



$$[-CF_2-CF_2-CF_2-\underset{\substack{|\\ R}}{CF}]_n$$

where

$$R= -O - CF_2 - CF_3$$

We have established for the first time that electrets from TFE - PFVEE copolymer with a content of 40 - 60 mol%. PHVEE has a significant value and stability charge [12]. In fig. 5 shows the dependence of the surface charge density Q of electrets from the TFE – PFVEE copolymer on the molecular content of the PFVEE in mol%. immediately after polarization (curve-a) and after 30 days (curve-b). It can be seen that with an increase in the molecular content of PHEEE, the surface charge density of the copolymer first increases and reaches a maximum at 50 mol%. PFVEE, and then decreases. In fig. 6 shows the dependences of Q of electrets from TFE – PFVEE with a PFVEE content of 50 mol%. (curve 1) and polytetrafluoroethylene (PTFE) (curve 3) on the strength of the polarization electric field. The polarization conditions for PTFE are chosen the same as in the case of obtaining an electret from TFE - PFVEE. It can be seen that the surface charge density of the proposed material is noticeably higher than Q of PTFE, and with an increase in Ep, the value of the effective charge grows almost linearly up to the breakdown of the sample.

The stability of composite corona electrets can also be improved if samples of the composite electret material are heated during the electrification process. In fig. 7 shows the dependences of the electret potential difference U_p of the corona electrets of the HDPE composite + 10% vol. PZT-2 on the polarization temperature. It can be seen that with an increase in the polarization temperature, the value of U_p at the selected value of the electric voltage of the corona electrodes first increases noticeably, and then its growth either stabilizes or slightly decreases. The value of U_p increases with an increase in the value of the electric voltage of the corona electrodes (Fig. 7, a). Stability of corona electrets of HDPE composites + 10% vol. PZT-2 charged at T_p = 353 K is noticeably higher than the stability of electrets electrets from the same composites electrifying at room temperature (Fig. 7, b).

The improvement in the stability of the corona electrets of the composite material in the case of heating in the first approximation should be attributed to the appearance of deep traps in the electret material, although the nature of these traps is not completely clear [9]. It seems to us that the field of oriented domains plays an important role here. Oriented domains can hold charges in their own field and thus serve as traps for injected charges. When the polarization temperature is low, the alignment of spontaneously oriented domains in the field is difficult, and therefore the domains cannot be active traps for injected charges. Indeed, with an increase in temperature, shallow surface and bulk traps are unable to retain charges, and for this reason, charges are re-captured in deeper traps, which can also be accompanied by an increase in the stability of the composite electret. An increase in the amplitude and temperature of the TSD current maximum of HDPE composites + 10% vol. PZT-2 in the case of charging it at a relatively high temperature, as well as a change in the half-width of the TSD curves (Fig. 7, c) are confirmation that heating of an electret material during corona electreting in a certain temperature range leads to the appearance of deeper traps in it and an increase in the concentration centers of captures in charged particles.

In accordance with the task at hand, in this work, we present comparisons of the characteristics of corona electrets and electrets previously modified under the action of a barrier discharge plasma. Figure 8 shows the dependence of the electret charge (Q) on the polarization temperature (T_p) for the following electrets: 1) HDPE; 2) HDPE + 10% vol. PZT - 1 (Pb (ZrTi) O_3); 3) HDPE + 10% vol. PZT - 1 (Pb (ZrTi) O_3) - corona electrets; 4) HDPE + 10% vol. PZT - 1 (Pb (ZrTi) O_3) - modified by barrier discharge plasma.

It can be seen that the modification of the aforementioned composites studied by us by the plasma of a barrier discharge leads to a noticeable change in the electret charge and is an effective method for modifying electret composites.

CONCLUSION

It is shown for the first time that the modification of composites by an electric discharge plasma is accompanied by a noticeable increase in the main electrophysical parameters of composite electrets. It has been experimentally established that plasma modification of composites is a more effective method for modifying composites in comparison with thermal, electrical, and mechanical methods. The reason for the high efficiency of plasma modification is the multifactorial nature of plasma processing in comparison with mechanical, electric and temperature fields. In the case of plasma treatment, the effects of electromagnetic radiation arise, that is, discharge radiation, which leads to a significant change in the spectrum of the band gap of the polymer matrix at the interface.

References

1. Galihanov M.F. Electret properties of compositions of polar polymer with dispersed filler.//Proceedings of universities. Chemistry and chemical technology. t. 49, vol. 11, 2006, pp. 53–55.

2. Galihanov M.F., Kozlov A.A., Karabaeva E.A., Deberdeev R.Y., Temnov D.E., Bobriskaya E.I., Krihtal I.V. Chemistry and chemical technology, 52 (4), 91 (2009).
3. Galihanov M.F., Kozlov A.A., karabaeva E.A., Deberdeev R.Y., Temnov D.E., Bobriskaya E.I., Krihtal I.V. Chemistry and chemical technology, 52 (4), 91 (2009).
4. Goroxovatskiy Y.A., Temnoe D.E. Electret properties of polymeric fibrous materials based on polypropylene.//Promising materials. № 1, 2006, pp. 68 – 72.
5. Kerimov M.K., Kurbanov M.A., Bayramov A.A., Mamedov A.I..Matrix Active Micro and Nanocomposites Based on the Polymer, Semiconductive and Ferropiezoceramic Materials. Nanocomposites and Polymers with Analytical Methods /Book 3. Book ed. by John Cuppoletti (INTECH Open Access Publisher, 2011) p. 375.
6. Kurbanov M. A., Ramazanova I.S., Dadashov Z. A., Yusifova U. V., Huseynova G. Kh., Azizova K. K. Farajzade I.A. Electret effect in polymer – ferroelectric piezoceramic composites with different electronegativity of the polymer matrix and piezophase cations. Physics and Technology of Semiconductors, Volume 52, Issue. 1, 2018, pp. 68-75
7. Kurbanov M. A., Sultanakhmedova I.S., Kulieva G.Kh, Aliev G.G., Geydarov G.M Electromechanical characteristics of matrix piezoelectric composites crystallized under the action of an electric discharge plasma. Electricity, № 7, 2009, pp. 39 – 45.
8. Kurbanov M.A., Sultanakhmedova I.S., Kerimov E.A., Aliev H.S., Aliev G.G., Geydarov G.M. Plasma crystallization of polymer-ferroelectric ceramics composites and their piezoelectric properties.SSP, t. 51,Vol. 6, 2009, pp. 1154-1160.
9. Pomogaylo A.D., Rozenberg A.S., Uflyand I.E. Metal nanoparticles in polymers (M., Chemistry, 2000).
10. Richkov A.A., Boytsov V.G. Electret effect in polymer-metall structures.-SPb.,2000.
11. Sherbachenko L.A., Borisov V.S., Maksimiva N.T., Barishnikov E.S., Karnakov V.A., Marchuk S.D., Yejova Ya.V., Rujnikov L.I., JTF 79 (9), 129 (2009).
12. Yakhyayev F.F., Kurbanov M.A., Sultanakhmedova I.S., Tatardar F.N., Kulieva G.Kh. A device for the complex study of the modes of crystallization and processing of polymeric composites under electric discharge plasma and temperature effects. Surface Engineering and Applied Electrochemistry, Vol. 46, № 2, 2010, pp. 160–164

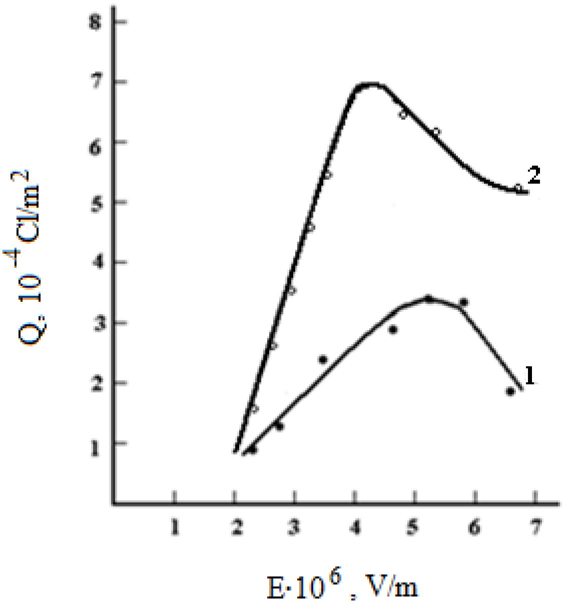


Fig. 1. Dependence *Q=f(E$_n$)* electrets from PTFE. 1-σ_n=0; 2-σ_n=15 MPa; T_n=393 K.

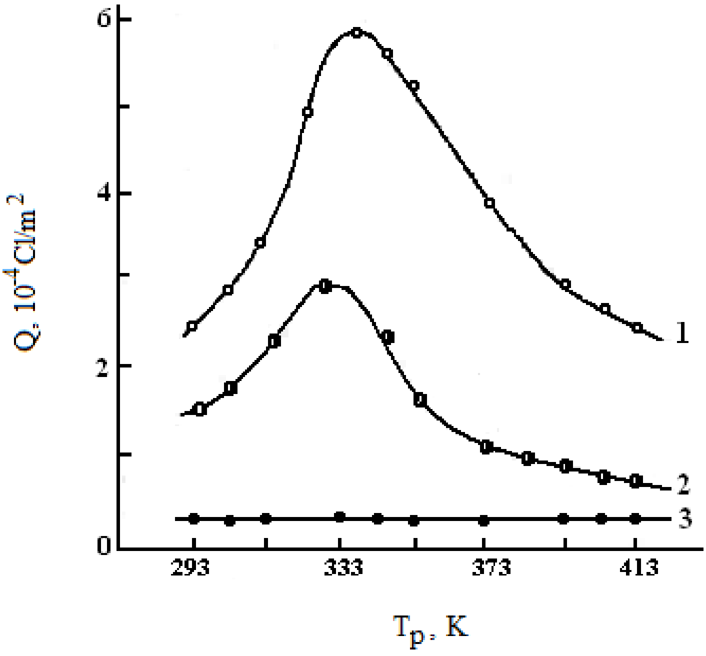


Fig. 2. Dependence $Q=f(T_n)$ at constant voltage on the polarizing electrode $U_u=3{\cdot}10^3$ B, $P=7{\cdot}10^{-6}$ MPa, $t_n=10$ min.

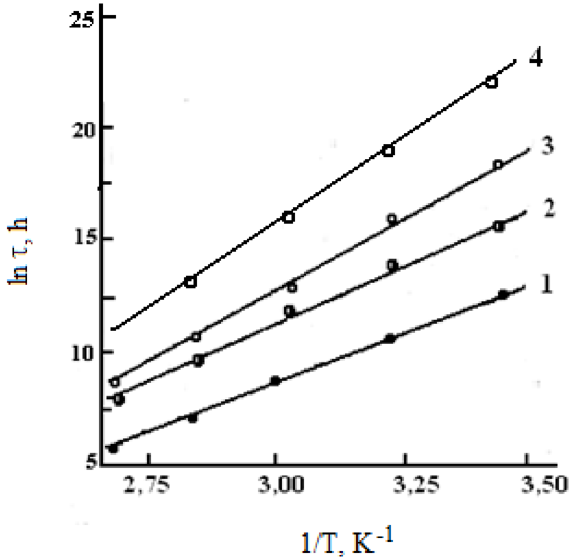


Fig. 3. Dependence $ln\tau=f(1/T)$ PET electrets $U_u=3\cdot10^3$ *B*, $P=7\cdot10^{-6}$ MPa, $t_n=10$ min. 1 – corona electret, $T_n=293$ *К*, 2,3 - in the zone of the cathode drop of the glow discharge potential at 293 K and 333 K, respectively, 4–$U_u=3\cdot10^3$ *B*, $t_n=10$ min., $T_n=293$ *К*.

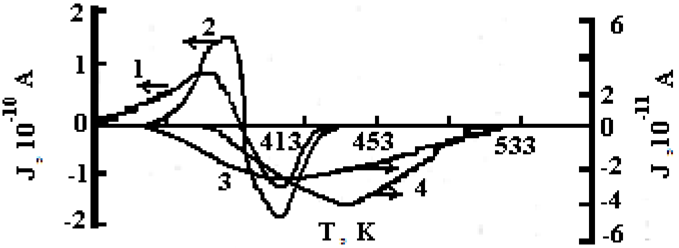


Fig. 4. TSD current of PET and PTFE electrets charged in the zone of cathode drop of the glow discharge potential. $P=7\cdot10^{-6}$ MPa, $U_u=3\cdot10^3$ *B*, $t_n=10$ min.

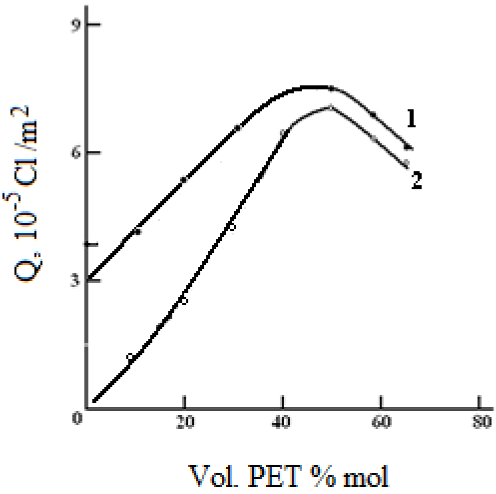


Fig. 5. Dependence of Q of electrets from TFE – PFVEE on the molecular content of PFVEE.

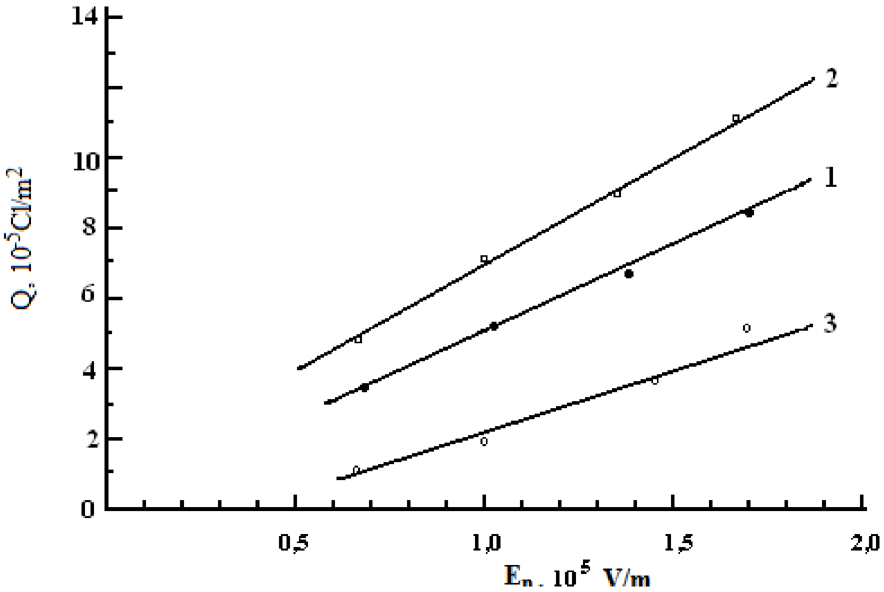


Fig. 6. Dependence at T_n =393 K.

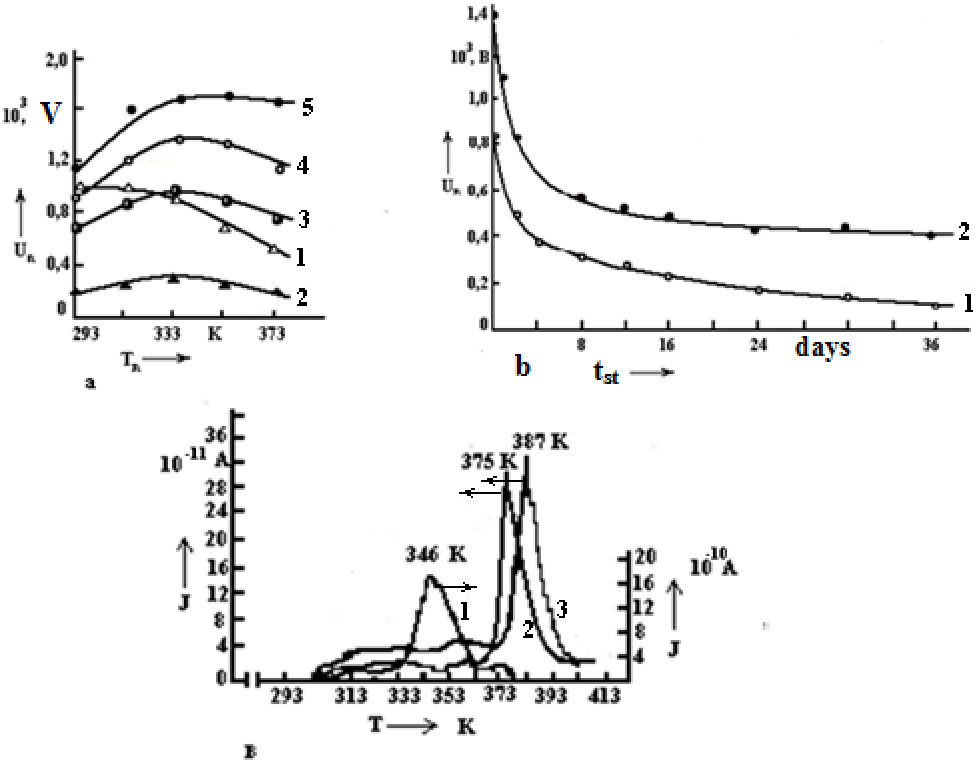


Fig. 7. a–$U_n=f(T_n)$ HDPE electrets + 10% vol. TsTS-2. 1 - the initial HDPE is charged at $U_n=5, 10\ B$; 2, 3, 4, 5– for compositions charged at $3\cdot10^3$, $5\cdot10^3$ and $6\cdot10^3$ respectively.

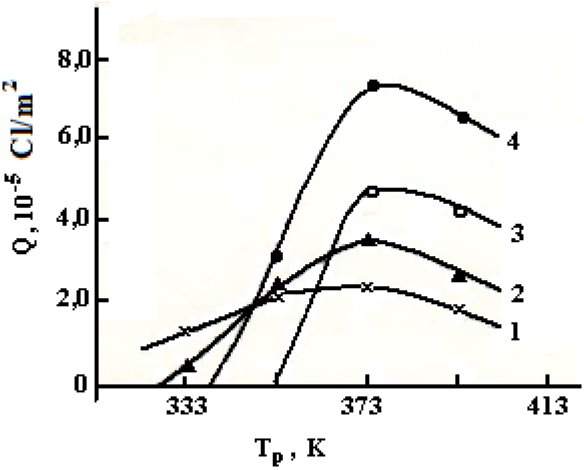


Fig. 8. Dependence of the electret charge (Q) on the polarization temperature (T_n). 1) HDPE; 2) HDPE + 10% vol. TsTS – 1 (Pb(ZrTi)O_3); 3) HDPE + 10% vol. DHS -1(Pb(ZrTi)O_3) - corona electrets; 4) HDPE + 10% vol. DHS - 1(Pb(ZrTi)O_3) - modified plasma of a barrier discharge.