V.V. Krivtsov, B.S. Kolupaev

# PURPOSEFUL REGULATION OF THERMOELECTRET EFFECT IN POLY(VINYLCHLORIDE) SYSTEMS

*Rivne State Humanitarian University,*
*31, Ostafov Str. , 33000 Rivne, Ukraine*

## Introduction

Despite of successes, bound with modifying of systems on the basis of linear polymers low and (or) high-molecular ingredients, and also fields of the different physical nature, many problems of formation of such composites in T-p condition by a mode of an electrostatic field remain still opened [1]. To them thermoelectretic of a phenomenon are referred, with which are connected the possibilities of creation of electrets that possess the particular characteristics, which depend on obtaining, preservation and usage of a polarization charge of the composite. Thus, the special concern is aroused by the possibility of obtaining thermoelectrets on the basis of charged and (or) plasticized polymers both from the point of view of fundamental science, and by virtue of the developed numerous applications [2].

In this work the experimental results of investigation of obtaining those systems are presented. It turned out that thermoelectric and characteristics of the received composite can be purposely regulated by the type and substance of the filler, plasticizer, by the tension of outer electric field in the precise polymeric matrix. To crown it all, it gives opportunities of receiving composites with more stable and high electrets characteristics.

## Experimental procedure

With the help of thermally stimulated depolarization method (TSD) the impact of electrical conductive fillers (dispersive powders of wolfram, zinc, graphite), fillers-dielectrics (dispersive powders of talcum, emery) and plasticizer dibutyl phthalate (DBP) on the electrets effect in industrial poly vinylchloride (PVC) suspension polymerization is investigated. The form and the size of the particles of the fine dispersed filler were estimated by examining photos of surfaces and polished cuts of the sample (fig. 1). We managed to get the electrets with volumetric substance of electrical conductive filler 0.5 vol.% where effective size of the particles doesn't exceed 7 μm with the normal coefficient $\varepsilon \approx 1$. We could not receive electrets of PVC composition with 0.5 vol.% Cu were unable to be received because of the inner electric breakdown (particles size Cu ~18 mkm, fig. 1,e).

The investigated samples with diameter (29±1) mm and thickness (0.2±0.02) mm were made with the help of the hot press 130°C temperature and 10.0 MPa pressure. For reaching a reliable electric contact within the electrets and the sample, it was pressed between two aluminum foils.

The sample's polarization was being made in electric field with constant intensity for five minutes. After that the sample was being cooled for thirty minutes to the indoor temperature in the same intension field. TSD current changes and parameter calculations of electric relaxation of the composites were conducted according to the GOST 25209-82. Current of discharge was recorded with the help of electrometric booster U 5-9. The parameters of electric relaxation, calculated on the basis of TSD current's curves (speed of heating is the 3°C/min), are shown in the table 1, where $\sigma$ is the surface solidity of an electric charge, $E_a$ is the energy of activation of charge relaxation, $\tau_e$ is the minimal time of charge relaxation under exploitation circumstances. The measuring of volume electric resistance ($\rho_v$) was done with the help of voltmeter-ammeter according to the GOST 6433.2-71.

The samples for the microscopic observations were made by samples' polishing till roughness elimination, exceeding in their high 0,1 mkm. On the digital photos the particles of fine dispersed filler look like dark sports on the white background of PVC (fig. 1). Investigation of particles' destruction in the polymeric matrix and estimation of volume unction of the filler were done by the quantity metallographic method. Errors

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calculation doesn't exceed 2% observatio, which was done with the help of stereoscopic microscope, allows finding out the existence of 3D space system of the fine dispersed filler under its substance more than 6%.

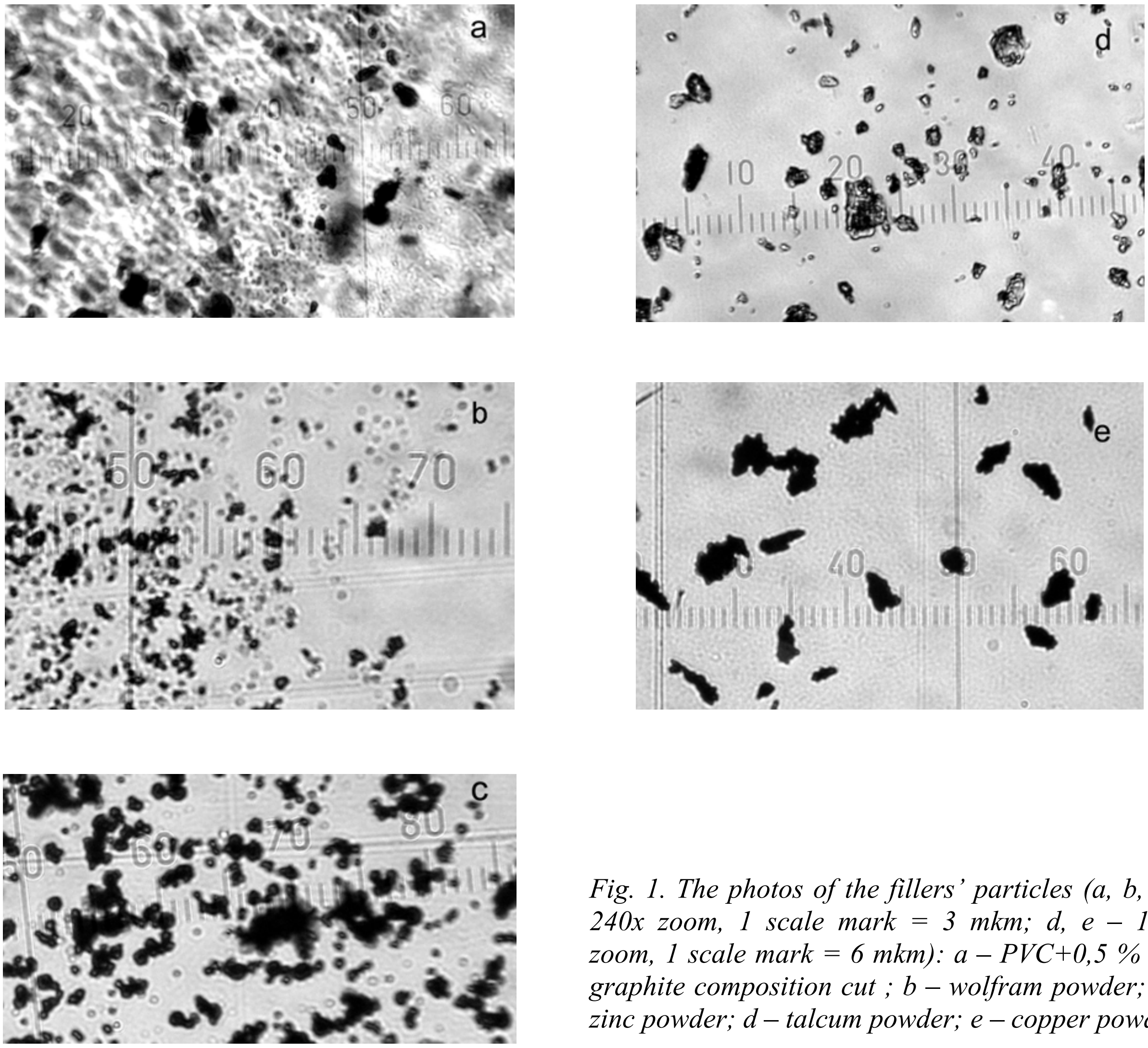


*Fig. 1. The photos of the fillers' particles (a, b, c – 240x zoom, 1 scale mark = 3 mkm; d, e – 120x zoom, 1 scale mark = 6 mkm): a – PVC+0,5 % vol. graphite composition cut ; b – wolfram powder; c – zinc powder; d – talcum powder; e – copper powder*

## Results and discussion

The current's investigation of TDS and PVC showed (fig. 2) that in temperature range (20–110)°C on depolarization spectrum maximum in the area of 40°C and α-relaxation transition of current's quantity is fixed. Polarization was done under $T_g$ (110°C) and electric field's intensity $E$=1,5·10 V·m$^{-1}$. This very temperature of polarization leads to appearance of two maximums on the current's curves of TSD and PVC. Both maximums correspond to heterocharge.

The first maximum (interval 30–50°C) is caused, however, by the losses of Maxwell-Vagner-Sillardovsky type [3], the second one (interval 70–90°C) – oriented PVC-segments polarization (α-relaxation) [4]. The first maximum appears both in original PVC-samples and in filled PVC-composites (fig. 3). It can be seen on the thermal dependence lg$\rho_v$ for PVC-electrets, obtained under described conditions (fig. 4). As we can see, the charge derivated in such conditions appears to be unstable (Ea ≈ 0,2–0,5 eV) and completely disappears at 50 °C in some day of storage at room temperature. The first maximum on current curves of TSD can be avoided, carrying out samples' polarization at $T = T_g$ (fig. 5). The second maximum in all cases is in the field of temperature of a glass transition PVC and is preconditioned by a dipole – segmental relaxation. Its form depends on tension of the applied electrical field (fig. 5).

Reducing of $E$ quantity up to 0,5·10$^6$ V·m$^{-1}$ leads to decreasing of size and stability of heterocharge. The increasing of $E$ up to 3,0·10$^6$ V·m$^{-1}$ increases the surface charge of PVC-electrets, reducing its stability a little bit. So the optimal mode of PVC polarization is established, with a maximum in the range (20–110)°C and appropriate time of relaxation (α-relaxation). This corresponds to $E$=1.5·10$^6$ V·m$^{-1}$ where the temperature of polarization is $T_g$.

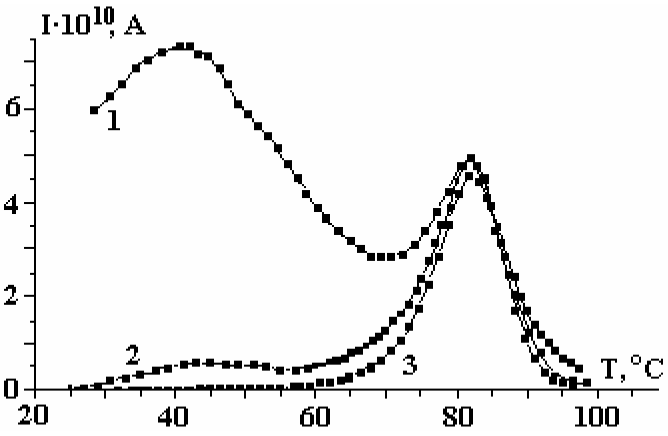
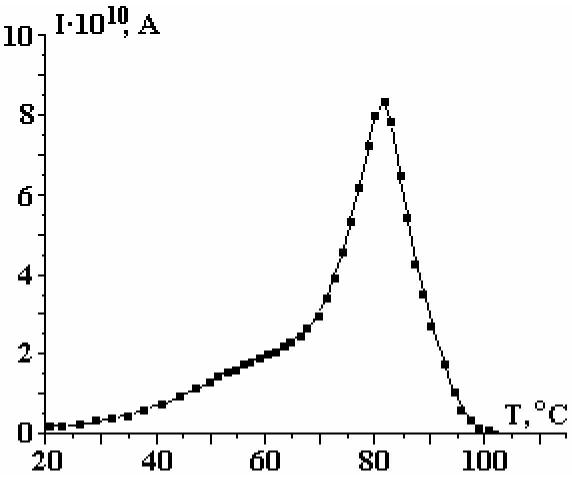


*Fig. 2. TSD currents of PVC obtained in half an hour (1), in 24 hours (2) and in 72 hours (3) after polarization*



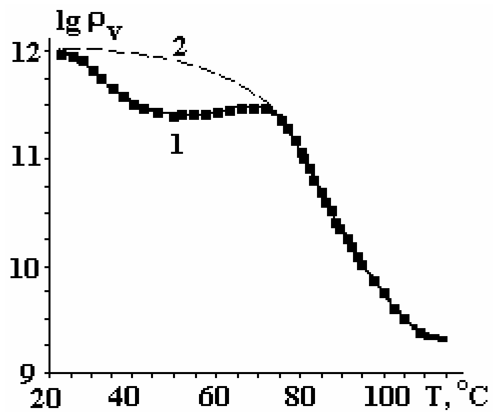


*Fig. 3. TSD currents of PVC with 0.5 vol. % Zn*

*Fig. 4. The thermal dependence lg$\rho_v$ for 1 – PVC-electret; 2 – original PVC*

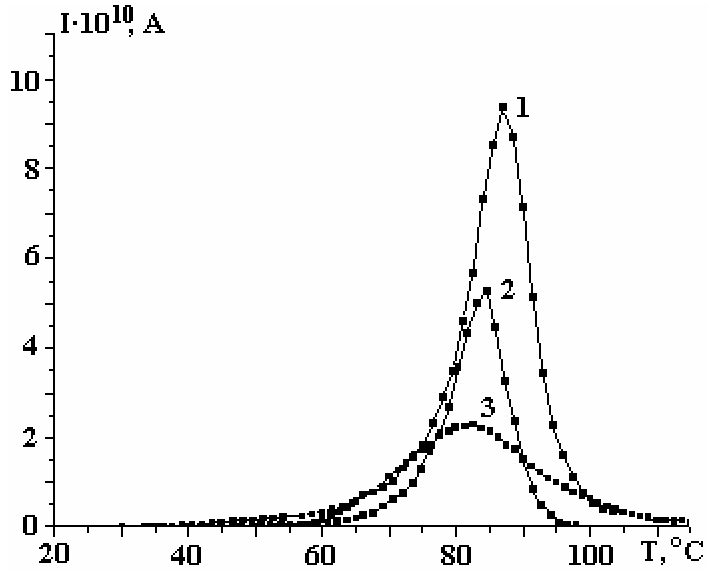


*Fig. 5. The curves of current of TSD of PVC for different modes of depolarization. E =3.0·10$^6$ V·m$^{-1}$ (1); 1.5 ·10$^6$ V·m$^{-1}$ (2); 5.0 ·10$^5$ V·m$^{-1}$ (3))*

When adding into PVC DBP pacificator α-maximum changes to lower temperatures in accordance with $T_g$ decline of flexible PVC (fig. 6). The rise of DBP substance increases the original quantity σ but the decline of charges precipitates because of that.

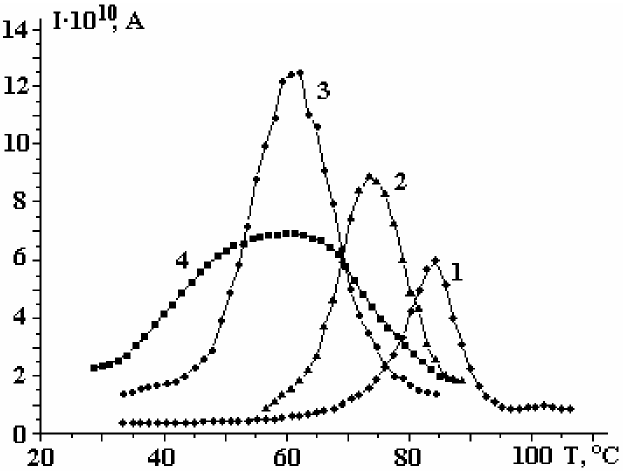


*Fig. 6. TSD currents of PVC (1) and of PVC with the component of DBP 5 vol. % (2), 10 vol. % (3) and 15 vol. % (4)*

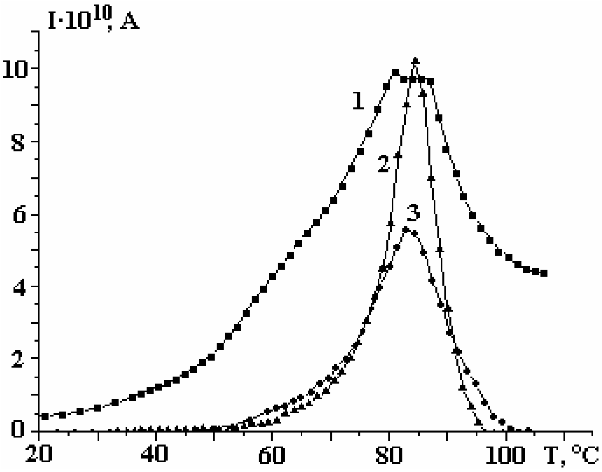


*Fig. 7. TSD currents of the following samples: PVC+0,5 vol. % C (1); PVC +0,5 vol. % W (2); PVC +0,5 vol. % talcum (3)*

In the composites with volumetric substance of DBP <15% electric effect is rather stable. PVC samples with great volumetric substance of DBP (>15%) can be polarized very quickly in outer electric field as well as depolarized. In this case the increase of the DBP plasticizer concentration in PVC-composites leads to decline of activation energy, making the process of polarization and depolarization easier. Actually, it can be noticed in the samples, where DBP substance is over 15%, where natural PVC plasticization takes place. It should be admitted, that the maximum under 83 °C can't be found in any of the curves of TDS of plasticized PVC, that illustrates a really good mixture of the ingredients and receiving of homogenous composites.

The current's curves of TDS for PVC with fillers of different physical-chemical nature are presented on fig. 7.

The analysis of quantitative comparison (table) of calculated quantities with the experimental results (fig. 2–7) illustrates that the temperature dependence $I=f(T)$ TDS is determined by the structural composites factors.

*Table. Parameters of electric relaxation of PVC-systems*

| Samples' components | σ, nC/m$^2$ | *Ea*, eV | $\tau_e$, s |
|---|---|---|---|
| PVC | 22,94 | 1,96 | $10^{8}$ |
| PVC, W (0,5 vol.%) | 45,39 | 1,74 | $10^{7,4}$ |
| PVC, DBP (5 vol.%) | 52,65 | 1,63 | $10^{6,5}$ |
| PVC, DBP (10 vol.%) | 96,06 | 1,21 | $10^{5}$ |
| PVC, DBP (15 vol.%) | 105,62 | 0,45 | $10^{3,5}$ |
| PVC, Zn (0,5 vol.%) | 43,13 | 1,66 | $10^{7}$ |
| PVC, C (0,5 vol.%) | 135,61 | 0,65 | $10^{4}$ |
| PVC, talcum, (0,5 vol.%) | 38,22 | 1,13 | $10^{5,5}$ |
| PVC, emery (0,5 vol.%) | 40,35 | 1,08 | $10^{5}$ |

So, in PVC case, that contains organic filler, there is slight adhesive interaction on the brink of phase division [5]. Because of outer polarized electric field influence the PVC macromolecule segments can refer towards considerable initial heterogeneous charge. Though, such charge is unstable and its quantity declines quickly because of disorientation under the influence of outer electric field. It is defined that if there are metallic fillers (Zn, W) in PVC the oxide films are not loose and they have inconsiderable thickness, in ion-dipole interaction (1–2%) of the ions of metal surface can take part [6]. Many authors mention the possibilities of chemical intercourse between the PVC and metals in their works [7]. Everything mentioned above leads us into conclusion that during the formation of PVC+ 0.5 vol. % Zn and PVC+ 0.5 vol. % W composite, we deal with an active filler, and the mass transfer of PVC macromolecule turns to its surface, that facilitates composites' energetic interaction on the brink phase division PVC – metal. When the electric field is given to such composites, the charge of certain quantity and sign is inducted on the surface of metallic fillers [8]. The composites acquire electric charge that remains stable after outer electric field removal, because mobility of polymer segments is restrained not only by steric but also by energetic effects in a brink film. The theoretical analysis of different cover types of particles of the fine dispersed metal in PVC shows that under their availability 0.5 % vol. unbroken chain of low-molecular ingredients doesn't exist. For this existence average number of contacts on a particle must be 1.42–1,55. In this case it is situated in $(5.0–7,0)\cdot 10^{-1}$ scope. While pressing composites in T-p regime, PVC is melting and filling all the volume around filler's particles, forming three-phase system which has a number of improved physical-chemical qualities.

In the case of dielectric fillers is defined that their surface contains structure bounded hydroxyl groups and a film of absorbing damp as well [9]. When $T>T_g$ at the beginning of composite formation, the polar PVC molecules according to their ion-dipole bounds steadily surround talcum or corundum surface. Dielectric fillers unlike conductive ones don't influence inner electric field of the composite. While using outer electric field towards such systems ($T=T_g$), disorderliness of those dipoles whose electric dipole moment opposes $E$ will happen. According to this, when $E=0$ acquired heterogonous charge will be disordered by the filler's surface, that's why the time of its living is not considerable.

Thus, the formation of the additional system heterogeneity, due to the fine dispersed filler and plasticizer on the basis of PVC, as the most typical representative of the linear polymers, opens possibility of the directed adjustment of their thermalelectretic properties with stable and high temporally-power characteristics.

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## Summary

The experimental results of the research of thermoelectrets on the basis of the filled and plasticized poly (vinylchloride) (PVC) are presented. It is proved, that the thermoelectret effect and properties of these composites can be purposely regulated by the type and concentration of the fillers, plasticizer, by intensity of the outer electric field in a certain polymeric matrix. As the result, it enables to get composites with the improved electret's characteristics.