

ON MECHANISM OF THE ELECTRET EFFECT IN THE POLYMERS, DISPERSED BY THE PARTICLES OF THE PIEZOELECTRIC MATERIALS

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In this article the results of investigation for reveal of the formation mechanism of the electret effect in polymer-piezoelectric heterogeneous system are presented. It is shown, that a volume submicro- and microsections (the polymer domains) formed at the dispersion by piezoelectric particles of thermoplastic polymers (PE, PP, PVDF) are not the determining elements in the formation of the electret state of composites. Oriented domains of piezoparticles that form with injected boundary charges the quasistationary system are responsible for the formation of stable electret state of the composite

It is known, that thermoplastic polymer materials- polyethylene (PE), polypropylene (PP), polyvinylidene-fluoride (PVDF) have the low electret properties, although the inducted materials have high physico-mechanical and dielectric characteristics [1]. It is also known, that for the formation of stable electret state in dielectrics it is necessary to form in them the two types of charges: homo- and heterocharges [2]. Taking into account that indicated polymers are non-polar (PE, PP) and weakly polar (PVDF) dielectrics then it can make a conclusion that the formation in them a quasi-stable system consisting of the oriented dipole and injected charge is not possible practically. Despite of the fact that indicated polymer materials after electrothermopolarization have the high electret potential difference (U_e), or electret charge Q , but the dependences of U_e and Q on time interruptedly decrease (Fig.1). The non-stable electret state in indicated materials may be related with the absence in them the stable and easily relaxed dipole orientation polarization. Such polarization in polymers, as it is shown early was created by means of dispersion of ones by the strongly polar piezoelectric particles [3].

hedral structure (PCR-3M) at the certain volume fraction of piezophase have high electret properties.

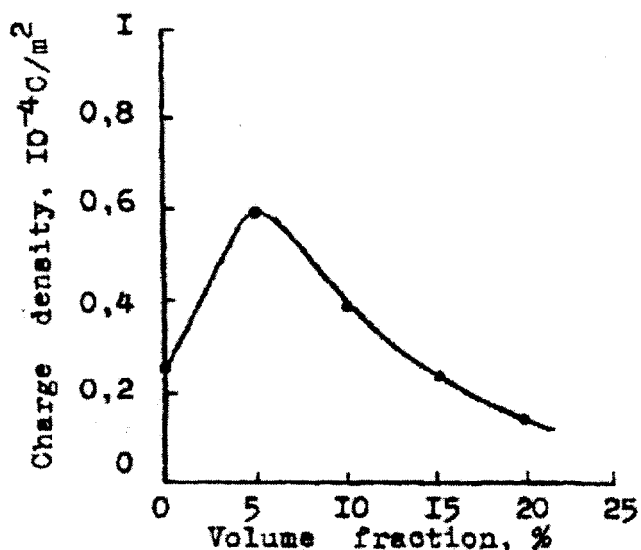


Fig.2. The dependence of the stabilized surface charge density (Q) on volume fraction (ϕ) of the piezoceramics for PP/PCR-3M composite.

On the base of earlier presented model we have shown, that the formation causes of stable electret effect in polymer-piezoelectric composites relate with the formation in them a quasi-neutral relaxed system of oriented domain-injected on the phase boundary charge.

However it may be assumed that in the case of (PVDF) the formation of stable electret state in PVDF/PCR-3M composite is not related with domain polarization of piezoparticles and the advent of micro- and submicropolar polymer domains in the volume of polymer matrix takes place. The absence of electric field on the piezoparticle in electrothermopolarization process due to the great value of dielectric constant of the piezophase confirms this proposition [2,3]. It is noted, that the problem of polarization of polymer-piezoelectric composites is reduced to the creation of maximal polarization of dispersed particles in a polymer phase and its retention in a long time. It is known, that piezoceramic polarization of PCR-3M type are made usually at the electric field strength order to 3-5 MV/m [4,5]. In this case the residual polarization value in the piezoceramics is equal to $0,3 \pm 0,4$

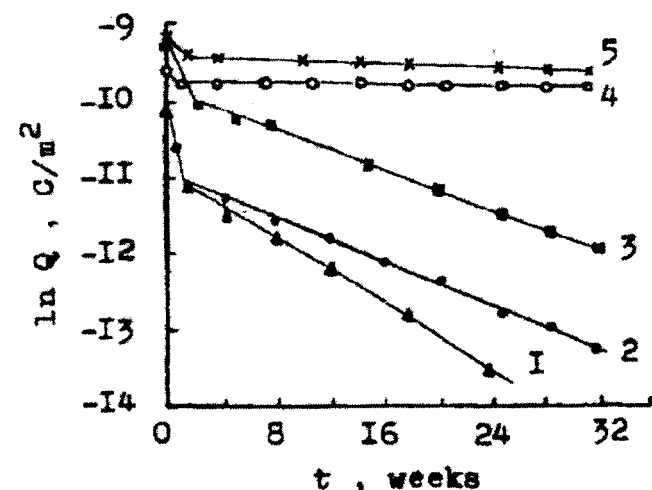


Fig.1. The dependence of effective surface electret charge density ($\ln Q_e$) on storage time (t). 1 - HDPE; 2 - LDPE; 3 - PP; 4 - HDPE/PCR-3M; 5 - PP/PCR-3M ($\phi = 10\%$ vol.).

From Fig.1 (curves 4, 5) and Fig.2 it is seen that composites on the basis of PE and piezoelectric ceramics of rhombo-

that it corresponds to the theoretically value. Polarization of the composite is carried out at the electric field strength of 3÷8 MV/m, i.e. it practically coincides with polarization conditions of piezoceramics used as piezofillers. The polarization temperature interval of the piezocomposite and PCR-3M practically coincides: 320÷433 K [4]. The electric field strength value on the piezoparticle the initial step of composite polarization was determined with the account of dielectric constant of phases and the ratio of H/D , where D - piezoparticle diameter, H - sphere interphase layer diameter with thickness of $H-D$, the structure of which is formed by the interphase interactions of various nature (Fig.3). The dielectric constant of interphase layer in the first approximation can be taken as dielectric constant of the composite. The piezoparticle is considered one-domain for simplicity. In [6] the problem of the electric field strength determination within one-domain crystallite surrounding by glassy-phase practically coinciding with our problem is considered. Using the solution of Laplas equation for the system given in Fig.3, under boundary conditions that take into account of the potential or tangential component of electric induction continuity at the

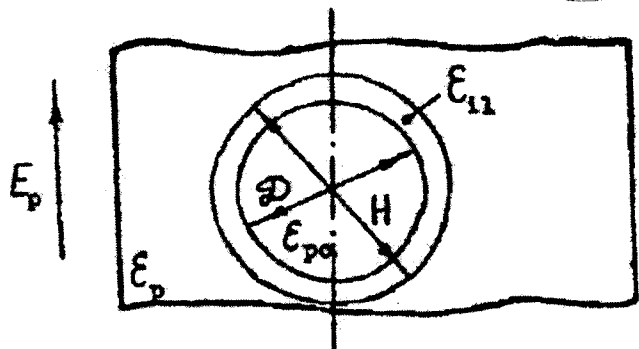


Fig.3. Spherical piezoparticle surrounding by the polymer phase $\epsilon_p, \epsilon_{pc}$ and ϵ_{11} - dielectric constants of the polymer, piezoparticle and interphase layer, correspondingly. E_p - polarization electric field strength

boundary transition in [8] it is obtained the expression for the field strength within one-domain crystallite

$$E = \frac{9\epsilon_p \epsilon_n E_p}{(2\epsilon_p + \epsilon)(2\epsilon + \epsilon_{pc}) + 2 \frac{H^3}{D^3} (\epsilon - \epsilon_{pc})(\epsilon_p - \epsilon)} \quad (1)$$

For domains the "c" axis of which coincides with E_p vector (180°-domains) $n_k=1$. If the value of H/D appreciably is more that 1, then the field within one-domain crystallite decreases distinctly. Using the piezoparticle of 200 μm diameter the thickness of the obtained composite sample on the base of PP changes from 220 to 280 μm . The value of E calculated by formula (1) for PP/PCR-3M composites of indicated thickness is equal to: $E \approx (0,012 \div 0,07) E_p$.

In [7] for composites it is introduced local field coefficient (L_E) of the electric field strength determined as the ratio of local field (E) in the internal piezoelectric sphere to the average field (E_p). For calculation of L_E it is presented the following expression

$$L_E = \frac{3\epsilon_p}{2\epsilon_p + \epsilon_{pc} + \Phi(\epsilon_p - \epsilon_{pc})} \quad (2)$$

where $\epsilon_p, \epsilon_{pc}$ and ϵ - dielectric constants of the polymer, piezoceramics and composite, correspondingly; E_p - polarization electric field strength; Φ - volume fraction of piezoparticles. $L_E=0,032$, $E=0,032 E_p$ at $\Phi=0,05$ for PP/PCR-3M composite. If E is determined using formulas (1) and (2), then we obtain $E=0,1 \div 0,2$ MV/m. It is seen that E on the piezoparticle by an order smaller as it's electric field strength polarization. The obtained results show that other electron-ion and polarization of piezoparticles dispersed in the polymer [3].

Table

Composites	Polarization regime		Electret potential difference U_a , V	Charge decay time to zero, hours
	E_p , MV/m	T_p , K		
HDPE/CaTiO ₃ $\Phi=5\%$ vol.	5	373	124	≤ 72
	10	373	145	
	14	373	182	≤ 100
	5	393	115	≤ 48
	10	393	135	"
HDPE/SiO ₂ $\Phi=5\%$ vol.	5	373	140	≤ 72
	10	373	170	
	5	393	117	≤ 75
	10	393	108	
	14	393	124	
PP/CaTiO ₃ $\Phi=5\%$ vol.	5	373	105	≤ 75
	10	373	122	
	14	373	140	
PVDF/TiO ₂ $\Phi=10\%$ vol.	6	413	150	≤ 9
PVDF/CaTiO ₃ $\Phi=20\%$ vol.	6	413	200	

Theoretical modeling of polarization process of piezoelectric or polymer domains in heterogeneous systems, polymer-piezoelectric in particular, is fraught many assumptions. Therefore we are chosen physical modeling method. For this purpose the polymer matrix is dispersed by inorganic fillers of various dielectric constants: TiO_2 , SiO_2 , CaTiO_3 . The study of electret properties of composites on the bases of polymers and indicated fillers shows that these electrets are not stable (Table).

The change of polymer structure after introduction of inorganic fillers is observed for diffractograms, IR and EPR-spectrums, DTA [8]. The obtained results show, that the dispersion of polymers by PCR-3M, TiO_2 , SiO_2 , CaTiO_3 particles leads to identical change of physicochemical polymer structure. If a disturbance of physicochemical structure of the matrix at the dispersion (the formation of polymer domains) maintains the electret charge stability, then the stable electret

state in composites is formed by filler type independent (which have metastable domain-orientation polarization or ones have not it). The electrets with high surface density and stability of the charge are formed from composites only dispersed by PCR-3M piezoceramics that has metastable domain orientation polarization and high Curie temperature. Hence are follows that the main factor of stable electret state formation of composites on the bases of polymers and piezoelectrics is non-polymer-domain polarization, and piezoelectric domain-orientation polarization takes place. Of course, the stabilized in various traps charges (external residual polarization) make great contribution in the stable electret state formation of composites. Namely these charges as we are shown earlier [8], form interrelated stable charge system with oriented domains of piezoparticles maintaining in the result the electret charge stability of composites.

- [1] G.A. Lucheykin. In "Polymer electrets", Moscow, 1984, 184.
- [2] B.I. Sazhin. In "Electric properties of polymers", Leningrad, 1986, 224.
- [3] M.A. Kurbanov, A.I. Mamedov, M.G. Shakhtakhtinsky, S.N. Musaeva. Fizika, 1, 3, 1995, 18.
- [4] A.Ya. Dantsiger. In "Ferroelectric solid solutions of multicomponent systems of complex oxides and high effective piezoceramics materials on their bases" Doctor thesis of physico-mathematical sciences, Rostov-on-Don, 1985, 480.

- [5] E.G. Fesenko, A.Ya. Dantsiger, O.N. Razumovskaya. In "New piezoceramics materials", Rostov-on-Don, 1986, 133.
- [6] E.G. Fesenko et al. In "Polarization of piezoceramics", Rostov-on-Don, 1986, 133.
- [7] T. Furukawa, K. Fujino, E. Fukada. Japan. Jour. Appl. Phys., 15, 1976, 2119.
- [8] A.I. Mamedov, M.A. Kurbanov, M.G. Shakhtakhtinsky, M.M. Kuliev. Preprint №7 of Institute of Physics of Azerbaijan Academy of Sciences, Baku, 1987, 69.

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ПЬЕЗОЭЛЕКТРИК МАТЕРИАЛЛАРИНИН НİССӘСİKЛӘРİ İLƏ ДİСПЕРСİYАLANМИŞ ПОЛİМЕРЛӘРДӘ ELEKTRET EFFEKTİNİN МЕХАΝІЗМİ

Məqalədə polimer-pyezoelektrik heterogen sistemində elektret effektinin formalaşması mexanizminin tədqiqatının nəticələri verilir. Göstərilir ki, termoplastik polimerlərin (PE, PP, PVDF) pyezohissəciklərin dispersiyası ilə yaranmış submikro- və mikrooblastları (polimer domenləri) kompozitin elektret halının formalaşmasında əsas rol oynadır. Pyezohissəciklərin injeksiya olunmuş sərhəd yükü ilə kvazistasionar sistem yaratmış istiqamətlənmiş domenləri kompozitlərin stabil elektret halının formalaşmasını təmin edir.

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МЕХАНИЗМ ЭЛЕКТРЕТНОГО ЭФФЕКТА В ПОЛИМЕРАХ, ДИСПЕРГИРОВАННЫХ ЧАСТИЦАМИ ПЬЕЗОЭЛЕКТРИЧЕСКОГО МАТЕРИАЛА.

В данной статье представлены результаты исследования механизма формирования электретного эффекта в гетерогенной системе полимер-пьезоэлектрик. Показано, что субмикро- и микрообласти (полимерные домены) термопластик полимеров (ПЭ, ПП, ПВДФ) сформированные дисперсией пьезочастиц не являются определяющими в формировании электретного состояния композита. Ориентированные домены пьезочастиц, которые образуют с инжектированными граничными зарядами квазистационарную систему, ответственны за формирования устойчивого электретного состояния композита.