CHARACTER OF DISTRIBUTION OF LOCAL LEVELS IN THE QUASI-FORBIDDEN BAND OF POLYMER PHASE OF POLYMER-PIEZOELECTRIC COMPOSITE

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On the basis of the analysis of temperature dependences of electrical conductivity, values of activation energy it is found, that electrothermopolarization results in change of a position of Fermi level in the quasi-forbidden band of a polymer phase of a polymer-piezoelectric composite. Dynamical position of Fermi level, related in it a decrease of an activation energy testify for the benefit of a monotonic distribution of local levels on energy in the quasi-forbidden band of polymer. It is considered, that in process of filling traps Fermi level rises and gets in region of local levels with a smaller activation energy.

The effect of deduction of charges inside volume of a polymer phase at electrothermopolarization of a polymer-piezoceramic composite is caused by presence in energy structure of polymer of set of the located levels being traps of injected charges. Infringements of structure of a polymer phase, conformation of macromolecules, connected with their inevitable deviation from a correct linear arrangement at dispersion polymer by piezoelectric particles are the precondition to this. Really, for a linear polymer circuit it is shown [1], that defect of it, depending on a sign on potential energy, causes eliminating a level from a strip of the allowed states of electron, or from its bottom, or the top edge, in immediate proximity from its space arrangement. Presence of such states in energy structure of polymer causes downturn of potential energy of the entrapped electron (carrier) and, as consequence, its fastening in one of low possible energy states and localization in spatial area which sizes correspond to extent of infringement of potential energy generated this state. Movement of the carrier is probably only by or tunnel jump on other located state with suitable energy, or its activation in area of located states. That the interval of the forbidden energies in polymer is very wide (E~10 eV), both opportunities do not result in the appreciable contribution to mobility of carriers. In immediate proximity from the occupied level there can be a free level with suitable energy, presence of such level far from occupied inefficiently as overlapping of wave functions of such states is not enough and probability of tunnel transition decreases. Activation in area of located states demands rather high energy, approximately 0,5E. To have such energy action with phonons or an electric field practically it is not possible.

Features of distribution of energy levels in the quasi-forbidden band and localization of charges in them, and also the effects connected to them (the piezo-, piroelectric effects) are an object of research of given article. Interest to studying questions touched in the given article is dictated first of all by the purpose of perfection of piezo-, piroelectric properties and an ensure of their stability at various mechanisms of ageing in that physical and chemical conditions which corresponds to conditions of their work.

Composites on the basis of polyvinylidenftoride (PVDF), polypropylene (PP) and piezoceramics of lead-zirconate-titanate families (PZT) such as PCR were investigated. Composites are received by the hot pressing method at temperature 493K and pressure 30 MPa. Composite samples were polarized at the temperature T_p=393K, the electric field intensity $E_p=1\div3MV/m$ and time of polarization t_p=0,5 hour.

Let's note, that though in polymer there are carriers of a charge, but it remains good dielectric and the relaxation of charges in it demands big enough time. Consideration of electrothermopolarization process demands composites to understand character of change stationary electrical conductivity of phases by action of a polarizing strong field E_p and the high polarizing temperature T_p, working simultaneously. There are certificates of an opportunity of the electronic mechanism of conductivity of polymer in case of injection of carriers from electrodes and orientation of dipoles under action E_p and T_p [2-4]. By virtue of specificity of the conditions realized at electrothermopolarization of a composite, it is possible to count, that electronic conductivity is inherent in the character of this process. The conditions accompanying of piezo-, piroelectric states of a composite with the generated volume charges are the base of above mentioned. Formation of volume charges is connected to development of the following processes: injection of electrons and their transport to the phase boundary under action E_p; stabilization of electrons at local levels of the quasi-forbidden band of a polymer phase; occurrence of the strong local field acting on piezoparticles. Only injection of electrons, their transport to the phase boundary and the orientation of domains connected to these phenomena in piezophase it is possible to explain formation of high piezo- and piroelectric effects in composites [5-7] (fig. 1 and fig. 2).

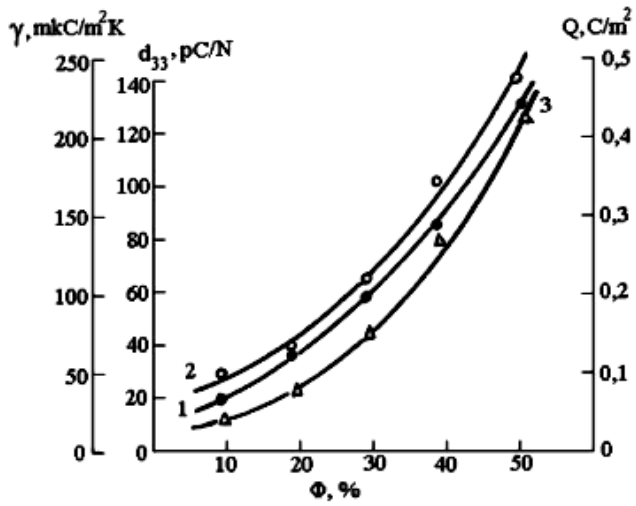

Fig. 1. Dependences of piezomodule d_{33} (1), pyrocoefficient γ (2) and electric charge Q (3) on volume contents Φ of piezoceramics in the composite PVDF+PCR-3M.

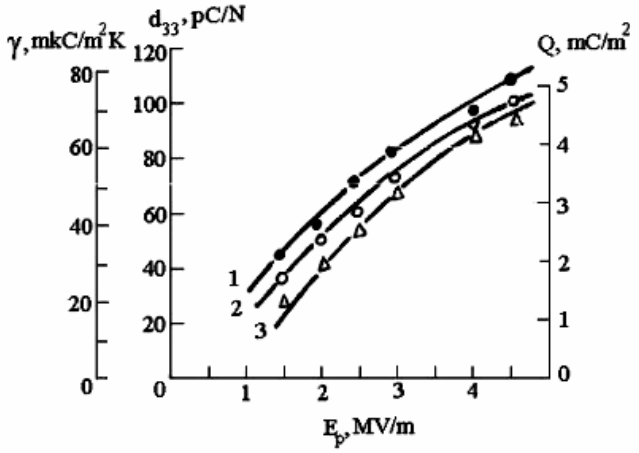

Fig. 2. Dependences of piezomodule d_{33} (1), pyrocoefficient γ (2) and electric charge Q (3) on polarization electric field intensity E_p for the composite PVDF+PCR-3M.

In table 1 values of activation energy W_A, calculated from the temperature dependence of electrical conductivity of the composite PVDF+PCR-3M are presented. It is experimentally found, that at a constancy of time and temperatures of polarization with increase of polarization electric intensity the activation energy decreases (fig. 3). It is possible to believe, that such change W_A is connected to change of Fermi level in the quasi-forbidden band of a polymer phase in process of filling local levels at electrothermopolarization.

Table 1.

Composites	Polarization voltage, V	Activation energy, eV	Piezomodule d_{33}, 10^{-12} C/N
PVDF+PCR-3M	50	0,69	18
	200	0,63	32
	400	0,57	56
	600	0,47	106
PP+PCR-3M	50	0,72	12
	200	0,68	28
	400	0,63	59
	600	0,45	120
PP+PZT-19	50	0,68	10
	400	0,64	48
	600	0,59	66

Let's consider the possible mechanism of this effect. For the disorder structures two models of density of states are known. It is model CFO (Cohen - Fritzshe-Owshinsky) and model Mott [8,9]. In both models there are tails of density of states of conduction and valence bands, coming into the forbidden zone. In model CFO tails of bands can be blocked without qualitative change of the general form of density of states in the field of overlapping. In model Mott tails of bands can not penetrate into the forbidden zone very deeply, however, in this area the peak of density of states to which Fermi level is adhered is formed. At a choice of model for composites at which the polymer phase is disorder, it is possible to use the model CFO. However, in this case it is necessary stability of Fermi level in an interval of energy where tails of bands are blocked also. Thus, in case of model Mott and areas of overlapping of tails of bands enable to allow presence of peak of density, that during polarization where there is a strong injection of carriers of charges, Fermi level should not change. The results of research resulted in the table 1, and also change of values of the injected charges (fig.2) and the activation energy (fig.3) at polarization show, that Fermi level changes after electrothermopolarization. Dynamism of Fermi level testifies that at polarization in a polymer phase charges are stabilized and in process of filling local levels of the quasi-forbidden band of this phase Fermi level rises and gets in area of local levels with rather smaller activation energy. Such it is possible if to assume, that distribution of local levels on energy in the quasi-forbidden band of a polymer phase is monotonous. If to consider models Mott or CFO appreciable change of activation energy and the big accumulation of charges in the quasi-forbidden band of a polymer phase was impossible. Appreciable change of activation energy, and also formation of high piezo-, piroelectric effects and electret states in composites testify for the benefit of monotony of distribution of local levels on energy in the quasi-forbidden band of polymer.

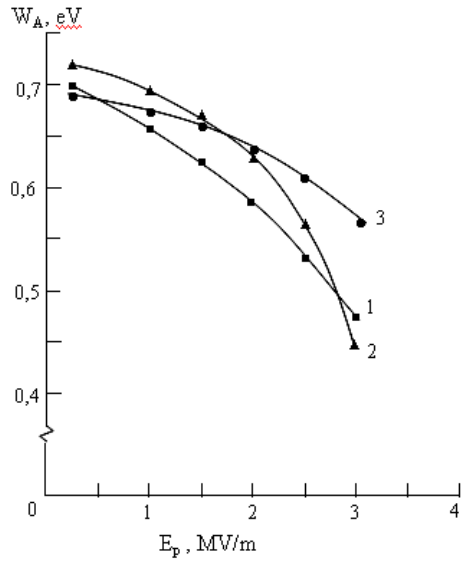

Fig. 3. The dependence of the activation energy on polarization electric field intensity. 1- PVDF+PCR-3M; 2 - PP+PCR-3M; 3 - PP+PZT-19.

Temperature dependences electrical conductivity on the basis of which the activation energy is determined (table 1) and experimental results on piezo-, piroelectric properties of composites (fig. 1, 2) show, that more comprehensible model for polymer - piezoelectric composites is monotonous distribution of local energy levels in the quasi-forbidden band. Really, to growth of concentration of the traps of charge carriers a seized at levels there is a rise of Fermi level and its approach a level of course. In process of rise of Fermi level there is its hit in area of local levels of the big density, but to smaller activation energy of charges in it. Only such distribution of local states on energy will allow the big accumulation of charges on the phase boundary that experimentally proves. All this allows to suppose, that the density of states in the quasi-forbidden band of a polymer phase monotonously falls down from edge of mobility deep into the quasi-forbidden band.

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POLİMER-PYEZOELEKTRİK KOMPOZİTDƏ POLİMER FAZANIN KVAZİQADAĞAN OLUNMUŞ ZONASINDA LOKAL SƏVİYYƏLƏRİN PAYLANMA XARAKTERİ

Polimer-pyezoelektrik kompozitlərdə elektrikkeçiriciliyinin temperatur asılılığına və aktivləşmə enerjisinin araşdırılmasına əsasən müəyyən edilmişdir ki, kompozitin elektrotermopolyarizasiyası polimer fazanın kvaziqadağan olunmuş zonasında Fermi səviyyəsinin vəziyyətinin dəyişməsinə səbəb olur. Fermi səviyyəsinin dinamikliyi və onunla əlaqədar olaraq aktivləşmə enerjisinin azalması polimerin kvaziqadağan olunmuş zonasında lokal səviyyələrin enerjiyə görə monoton paylanmasının göstərir. Fərz edilir ki, lokal səviyyələr dolduqca, Fermi səviyyəsi yuxarı qalxır və daha az aktivləşmə enerjisinə malik lokal səviyyələr oblastına düşür.

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ХАРАКТЕР РАСПРЕДЕЛЕНИЯ ЛОКАЛЬНЫХ УРОВНЕЙ КВАЗИЗАПРЕЩЕННОЙ ЗОНЫ ПОЛИМЕРНОЙ ФАЗЫ В КОМПОЗИТЕ ПОЛИМЕР-ПЬЕЗОЭЛЕКТРИК

На основании анализа температурной зависимости электропроводности и значений энергии активации найдено, что электротермополяризация приводит к изменению положения уровня Ферми в квазизапрещенной зоне полимерной фазы композита полимер-пьезоэлектрик. Динамичность положения уровня Ферми и связанное с ней уменьшение энергии активации свидетельствуют в пользу монотонности распределения локальных уровней по энергии в квазизапрещенной зоне полимера. Считается, что по мере заполнения ловушек уровень Ферми поднимается и попадает в область локальных уровней с меньшей энергией активации.

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