

ANORMAL PIEZOELECTRIC EFFECT IN POLYMER-PIEZOELECTRIC COMPOSITE SYSTEM

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On the basis of analysis of theoretical and experimental investigations of properties of active polymer-piezoelectric composites it has been shown, that interaction between the phases plays a significant role for formation of the piezoelectric effect in these materials. The successive registration of different kind interactions on a phase interface is specificity of physics of the compositional structures. It has been shown, that the effects connected with the electrothermopolarization of a piezophase in the polymer-piezoelectric system are explained on the basis of model, demonstrating the creation of the quasineutral system of the oriented domain and the charge stabilized on the phase interface in the polymer.

The most common representation of composites feature formation is based on account of characteristics of the constituents. In this case the geometry (size, shape) and their initial position are taken into account. The interaction between the phases is considered negligible, i.e. integral characteristics of composites are taken additive [1-3]. However, one cannot neglect the interaction between the phases formed the composites as far as it becomes decisive in formation of their properties for many cases [4,5]. Below we shall make an attempt to show the necessity to take consideration the interface interaction, the electron states of phase interface and charge stabilizations in it in formation of the composite properties on the example of the disordered polymer-piezoelectric system.

A theoretical consideration of two phase system based on a polymer dielectric dispersed by piezoelectric particles uniformly distributed in the volume, gives [1]

$$d_{33} = \Phi \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2 + \Phi(\epsilon_1 - \epsilon_2)} \cdot \frac{5C_2 \cdot {}^2d_{33}}{3C_1 + 2C_2 - 3\Phi(C_1 - C_2)} \quad (1)$$

where ϵ_1 and ϵ_2 are dielectric constants of the polymer matrix (phase I) and piezoceramic (phase II), accordingly, C_1 and C_2 are appropriate elasticity modules Φ is the volume fraction of piezofiller, ${}^2d_{33}$ is a piezocoefficient of piezofiller. Taking into account $\epsilon_2 \gg \epsilon_1$ and $C_2 \gg C_1$ one obtains

$$d_{33} = \frac{15\Phi}{(1-\Phi)(2+3\Phi)} \cdot \frac{{}^2d_{33}}{\epsilon_2} \cdot \epsilon_1 \quad (2)$$

It is seen, that the piezocoefficient of composite is proportional to ϵ_1 of polymer phase and piezoceramic sensitivity (${}^2d_{33}/\epsilon_2$). The comparison of the piezoelectric properties of the composites based on the same polymer with different piezoelectric fillers (table 1) shows that piezocoefficients of composites (fig.1) are not proportional to the ratio ${}^2d_{33}/\epsilon_2$, as it is predicted by theory.

Table 1.
Sensitivity (${}^2d_{33}/\epsilon_2\epsilon$) and piezocoefficient (${}^2d_{33}$) of multicomponent piezoceramics of lead zirconate-titanate family.

The used piezoceramics and there foreign analogues in bracket	PCR-1 (PZT-5A)	PCR-3M (PZT-7A)	PCR-5 (PZT-75)	PCR-7M (PZT-5H)	LZT-19 (PZT-19)
${}^2d_{33}/\epsilon_2\epsilon$, Vm/N	0,033	0,024	0,029	0,0158	0,024
${}^2d_{33}/\epsilon_2$, pC/N	236	99	110	760	340

Numerous experimental results [5-7] for composites based on piezoceramics and polymers with various structures and polarities verify facts listed above and point to necessity for different approach in explanation of piezoelectric properties in formation of composites. In particular, all these facts may be explained if one takes into account an interconnection of charge accumulation processes in the polymer matrix and the piezophase polarization of the composite. Such interconnection may be explained on the basis of the simplified model showed in fig.2. According to this model the polarization process goes on by the following way. At $E_y=0$ a total polariza-

tion of piezoparticles is equal to zero (fig.2,a). During electrothermopolarization in the initial moment the charges are injected from electrode to the composite and at the same time insignificant polarization of piezoparticles takes place (fig.2,b). This insignificant polarization compensates a fraction of an per particle external field in accordance to the dielectric constants and phase conductivities for choosed T_p and E_p . Later on the injected charges drift towards the piezoparticle and are localized on the traps near the phase interface. This leads to the amplification of the local field on a piezoparticle and increase its polarization (fig.2, c). A formation of the quasi-

neutral complexes injected charges - oriented domain favours the further injection and drift of the charges towards the piezoparticles and their appropriate to polarizations (fig.2, d). It would seem that process must be continued till a total polarization of the particles. However, in practice a number of facts may disturb it, for instance a deficiency of amount of the deep traps on the interface, a screening of the piezoparticles by accumulated charges and etc.

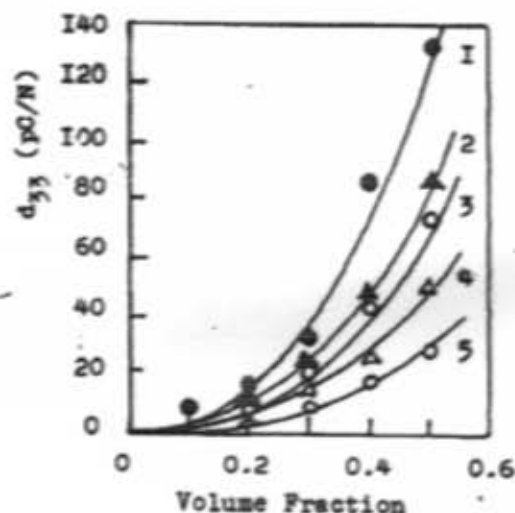


Fig. 1. Piezocoefficient d_{33} as a function of a piezoceramic volume fraction for composites on the basis of polypropylene and piezoceramics with different $d_{33}/2$. PP/PR-3M (1), PP/PCR-5 (2), PP/PCR-7M (3), PP/PCR-1(4), PP/PCR-8(5).

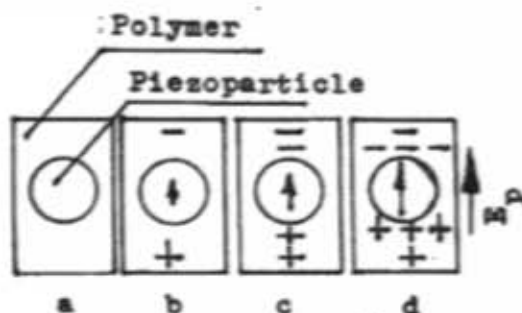


Fig. 2. Model of flowing of injected charges to polymer-piezoparticle and polarization of piezophase in the field of injected charges.

This interaction leads to seemed anomalous dependences of composite properties on a composition. In fig.3 as example the dependence of d_{33} on volume fraction for composites PVDF/PCR-3M, PVDF/PCR-7M and PVDF/PCR-37 is shown. It is seen, that the amount of the composite piezocoefficients for the certain compositions becomes greater than d_{33} of both components. If the interface interaction would not play a significant role in the formation of piezoelectric effect, then such maximum

must be absent. In the case, when the interaction between the charges localized in a polymer phase and particles polarization as taking into account, this maximum points to the best polarization of piezoface in a composite compared to a base ceramic. In general case the appearance of maxima on diagrams composition-composite properties shows the significant role of the interaction on the interface.

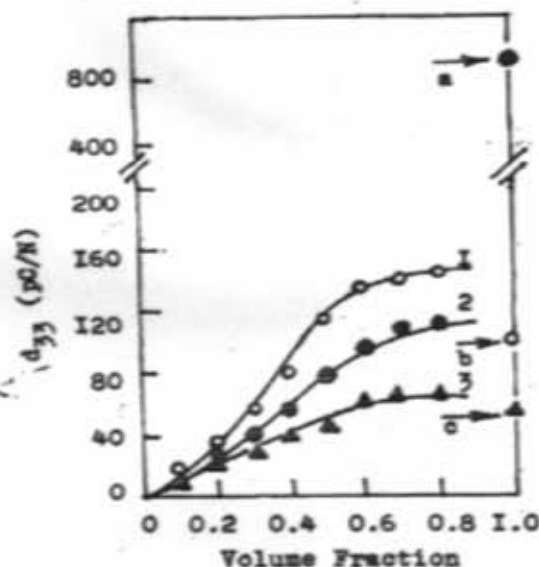


Fig. 3. Variation of piezocoefficient of composites with piezoceramic volume fraction of different structure for composites on the basis of polyvinylidene fluoride. PCR-3M, PCR-37 - rhombohedral; PCR-7M - tetragonal. PVDF/PCR-3M (1), PVDF/PCR-7M (2), PVDF/PCR-37 (3), a(●), b(○) and c(▲) points correspond to the value of piezocoefficient of starting ceramics of PCR-7M, PCR-3M and PCR-37. $E_p = 3.5$ MV/m, $T_p = 393$ K, time of polarization - 1 hour.

In literature [8] a high value of the piezocoefficient of tetragonal piezoceramics is associated with a large amount of a dielectric constant ϵ and the known relation is used:

$$d_{13} = Q_{12} \epsilon P, \quad (3)$$

where Q_{12} is the electrostriction coefficient, P , is an amount of the reorientational polarization of domains different from those of 180° . Dielectric constant in composites is significantly smaller than it in the piezoceramics because ϵ is a low value of at a polymer phase. Therefore a main role plays P , that is greater in the rhombohedral ceramics. On the other hand in the rhombohedral ceramics a mobility of the domain walls is great, that leads to the increase of a charge movement to the interphase boundaries. This is a cause of a great magnitude of boundary charge Q . Taking into account a major role of the interface charges in piezoparticles polarization it should be used Q , instead of P , in formula (3).

Thus the above model explains dependence of the composite piezocoefficient on the piezofiller structure accordingly. In this connection a definition of the composi-

tional materials as heterogeneous system with the kept phase individualities becomes nonrigorous. At least on the boundary layer there is occurred a significant change of the structure and microscopic parameters, such as for instance density, thermal expansion coefficient, thermoconductivity, heat capacity [9] and etc. On the other hand a Coulomb interaction on the phase interface leads to a great polarization of piezoparticles as a whole. There may be many kind of interactions. A contributions of different interactions naturally will be depend on considered properties. One of a principal problems of a compositional materials physics must be location of major types of interactions on the phase interface and their proper allowance in formation of the corresponding effects.

Conclusions.

It is shown, that piezoelectric properties of polymer-piezoelectric composite and their change on conditions of electrothermopolarization, an individual characteristics and cubic content of phase is consultationly explained by the formation of interconnected system polarized piezoparticle - localized on the phase boundary charge in polymer.

Physics of composition structures must be based on consistent account of contributions of different type of interactions between the phases in the formation of special properties of composites.

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POLİMER-PYEZOELEKTRİK KOMPOZİT SİSTEMİNDƏ ANOMAL PYEZOELEKTRİK EFFEKTİ

Polimer-pyezoelektrik aktiv kompozitlərin xassələrinin nəzəri və təcrübi tədqiqi əsasında müəyyən edilmişdir ki, fazalar arasında qarşılıqlı təsir bu materiallarda pyezoelektrik effektinin formalaşmasında mühüm rol oynayır. Kompozit strukturlar fizikasının əsas xüsusiyyəti fazalar sərhədində müxtəlif qarşılıqlı təsirləri ardıcıl nəzərə almaqdan ibarətdir. Göstərilmişdir ki, polimer-pyezoelektrik sistemdə pyezofazanın elektrotermopolyarizasiyası ilə əlaqədar effektlər oriyentasiya olunmuş domen-fazalar arası sərhəddə stabilizə edilmiş yük kimi kvazineytral sistemin eməli gəlməsini göstərən model əsasında izah olunur.

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АНОМАЛЬНЫЙ ПЬЕЗОЭЛЕКТРИЧЕСКИЙ ЭФФЕКТ В КОМПОЗИЦИОННОЙ СИСТЕМЕ ПОЛИМЕР-ПЬЕЗОЭЛЕКТРИК

На основании анализа теоретических представлений и экспериментальных исследований свойств активных композитов полимер-пьеzoэлектрик показано, что взаимодействие между фазами играет существенную роль в формировании пьезоэлектрического эффекта в этих материалах. Спецификой физики композиционных структур должен являться последовательный учет различного вида взаимодействий на границе фаз. Показано, что эффекты, связанные с электротермополяризацией пьезофазы в системе полимер-пьеzoэлектрик объясняются на основании модели, демонстрирующей образование квазинейтральной системы - ориентированный домен и стабилизированный на границе раздела фаз в полимере заряд.

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