

PIEZOCOMPOSITES ON THE BASE OF THE TWO-COMPONENT MATRIX

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Electrophysical and piezoelectric properties of composites on the base of two matrix: polar-polar polar-non-polar and non-polar-non-polar polymers are investigated. It is experimentally shown that by the elaboration of multiphase composites it is better to use the combination of polar and non-polar polymers than that of only non-polar or only polar polymers.

We showed before that electret, piezo- and pyroelectric properties of composites depend mainly on conditions of the injection and stabilization on various charge capture centers in the polymer phase at the electrothermopolarization [I-3]. Various structural defects, heavy-polar, low-molecular compounds in the bulk, oxide chains of the macromolecule and boundaries between amorphous and crystal phase of polymers might enter the charge capture center[1-4].It is natural to assume that the value of stabilized charges, which determines the degree of the domains orientation in composites, depends on the activation energy of stabilization centers.

It is known, that the boundaries of incompatible polymers may be effective charge capture centers (4,5). In this respect, we used the mixture of two polar and non-polar polymers, in particular, PE+PP, PE+PVDF, PP+PVDF as a matrix. Composites on the base of two-component matrixes and the piezoelectric of various structures are obtained by the method of the hot pressing.

Piezoceramics of the rhombohedral (Rh) and tetragonal (T) structure are used as a piezoelectric phase and PP, HDPE, PVDF and F₃ as a polymer phase. Electrodes of aluminum foil are applied in the process of the hot pressing. Temperature-temporary and temperature-pressure regimes of crystallization are varied with the aim of the polymer phase receipt with the various supermolecular structures (SMS). Sizes of electric phase particles are varied in the interval 50÷100 μm. Piezoelectric parameters of composites are determined by quasi-static methods.

The matrix compatibility and new phase formation in composites are determined by the research of the posistor effect. The research of the posistor effect in indicated composites allowed to determine the optimal conditions of polar composites.

Value of piezomodulus d_{33} and composites piezosensitivity g_{33} on the base of two-component matrix HDPE+PP, dispersional PCR-11 and PZT-2 versus the volume content of HDPE and PP in the matrix are shown in

the Table I. It is seen, that the polymer composite with the volume relationship HDPE to PP, equal to 2:3, has the maximal value d_{33} and g_{33} .

The dependence of various composites piezomodulus, polarized at optimal values of the electric field voltage E_p and the polarization temperature T_p on the volume content F of the piezoceramics is shown on fig.1. It is seen that the piezomodulus value at all filler contents grows at the use as a matrix of the mixture HDPE and PP.

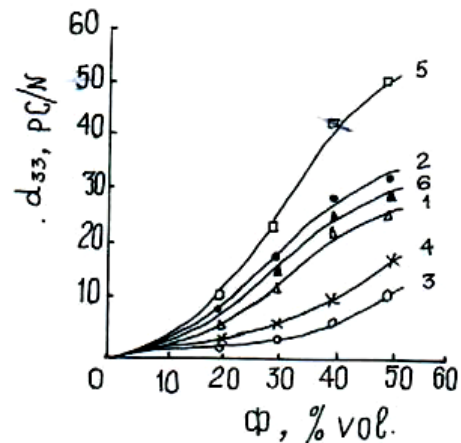


Fig.1. Piezomodulus dependence on the bulk content of the Piezoceramics: I- HDPE+PCR-11; II- PP+PCR-11; III- HDPE+PZT-2;IV- PP+PZT-2; V- HDPE+PP+PZT-2; VI- HDPE+PP+PCR-11.

The dependence of d_{33} on E_p for composites from polyolefin and PCR-11 is shown on fig.2,a. The maximal value d_{33} of HDPE+PP+PCR-11 composite is in 2 times more than the piezomodulus composite HDPE+PCR-11 and in 1,7 times more, than the piezomodulus PP+PCR-11. The d_{33} composite of HDPE+PP+PZT-2 is approximately in 2 times more, than d_{33} composite on the base of one-component matrix of HDPE+PZT-2.

Table 1.

The value of piezomodulus and composite piezosensitivity on the base of the two-component matrix.

| Piezocomposites | Volume relationship HDPE:PP | Volume content of piezofillers in % | d_{33} pC/N | g_{33} Vm/N |
|-----------------|-----------------------------|-------------------------------------|---------------|---------------|
| HDPE+PP+PCR-11 | 1 : 4 | 50 | 34,7 | 0,14 |
| | 2 : 3 | 50 | 50,3 | 0,12 |
| | 3 : 2 | 50 | 33,8 | 0,15 |
| | 4 : 1 | 50 | 31,5 | 0,13 |
| HDPE+PP+PZT -2 | 1 : 4 | 50 | 19,2 | 0,091 |
| | 2 : 3 | 50 | 30,4 | 0,145 |
| | 3 : 2 | 50 | 21,6 | 0,103 |
| | 4 : 1 | 50 | 17,1 | 0,081 |

The research results of the charge state of the indicated components show, that at other equal conditions of the polarization (at the stability of E_p , T_p and t_p is the polarization time) the value of stabilized volume charges (Q) in composites on the base of the two-component polymer matrix is visually more in comparison with the charge value of composites on the base of one-component polymer matrix (Table 2).

Table 2.

The charge value on the thermostimulated depolarization (TSD) and the composites piezomodulus on the base of one-component and two-component matrix.

| Composites | $Q, 10^{-3}C/m^2$ | $d_{33}, pC/N$ |
|-----------------|-------------------|----------------|
| HDPE+PCR – 11 | 0,65 | 21 |
| PP+PCR – 11 | 0,75 | 33,6 |
| PP+HDPE+PCR– 11 | 1,9 | 50,6 |

It is shown that more favorable conditions for the charge stabilization are realized in two-component systems. Obviously, additional centers of the charge stabilization at the electrothermopolarization occurs from non-polar polymers in the polymer-ferropiezoelectric system on the base of the matrix.

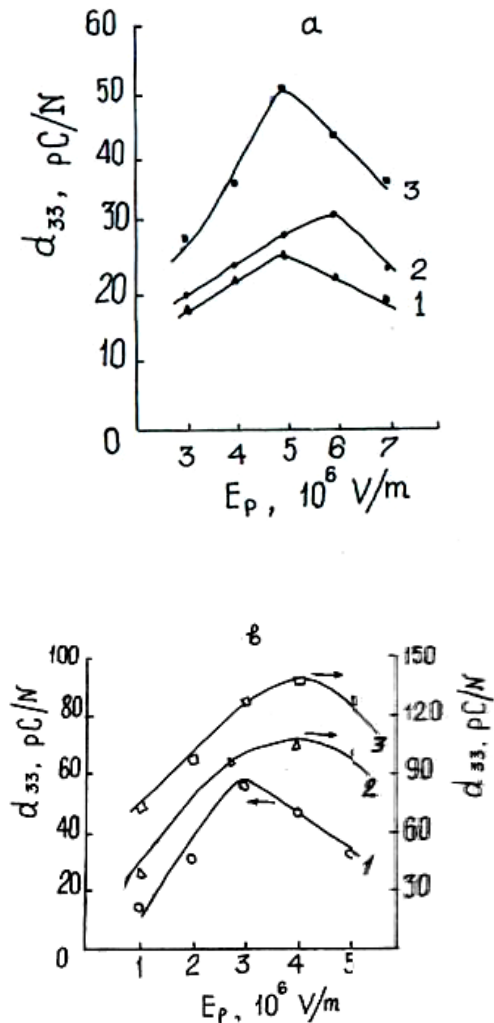


Fig.2. The dependence of piezomodulus d_{33} on the electric field voltage of the polarization E_p .
 a) I- HDPE+PCR-11; II- PP+PCR-11;
 III- HDPE+PP+PCR-11;
 b) I- PP+PCR-I; II- PVDF+PCR-I; III- PP+PVDF+PCR-I.

The dependence of d_{33} on E_p for composites as the matrix, in which polar polymer PVDF and non-polar polymer PP are used, is presented on fig. 2,b. The comparison of optimal values d_{33} versus $d_{33}=f(E_p)$ shows, that in this case the piezomodulus increment (Δd_{33}) is more, than for composites on the base of the matrix from polar or non-polar polymers. The piezomodulus increment (Δd_{33}) at the transition on the multicomponent composites was determined by optimal values of the piezomodulus dependence d_{33} on E_p and by the comparison of the piezomodulus of two matrix and more effective one-matrix composites.

Dependences of d_{33} on E_p for composites on the base of the matrix from the polar fluorine-containing polymers are shown on fig. 3 (a,b). It is seen, that d_{33} of the composite on the base of the matrix PVDF+F₃ is equal to the composite piezomodulus on the base of only PVDF (fig. 3,b) or a bit lesser (fig. 3,a).

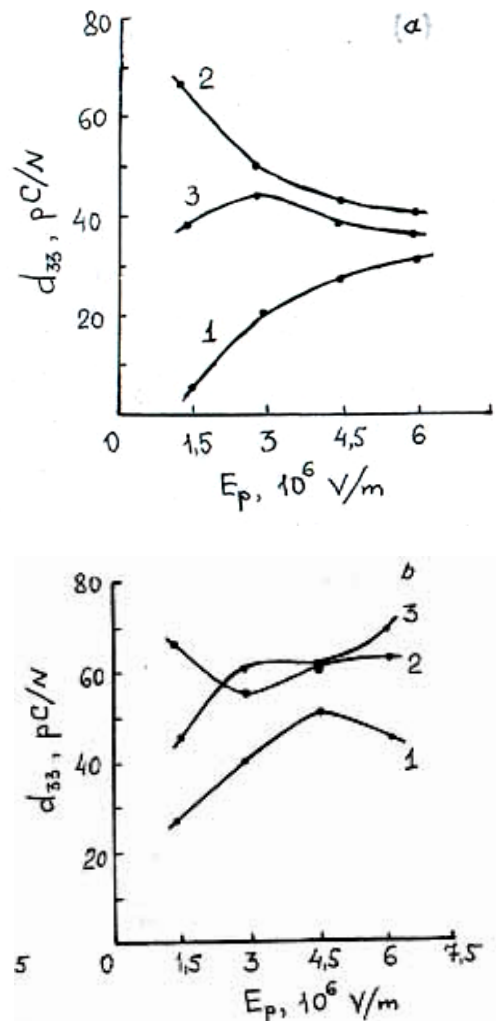


Fig. 3. The dependence of the piezomodulus d_{33} on the electric field voltage of the polarization E_p . $T_p = 140^\circ C$ (a)
 I – F₃+PZT-I9; II – PVDF+PZT-I9; III – PVDF+F₃+PZT-I9
 $T_p = 180^\circ C$ (b)
 I – F₃+PZT-I9; II – PVDF+PZT-I9; III – PVDF+ F₃+PZT-I9

Therefore, it may be concluded, that at the elaboration of multiphase composites, it is better to use the combination of the polar and non-polar polymer, than to use that of only non-polar or only polar polymers.

Obtained results, obviously, at first approximation may be explained with regard of changes of the supermolecular structure of matrix at their mixture and the composites receipt, and also by the compatibility of polar and non-polar polymers.

The SMS change may mainly occur in the transient layer of polymer phases. And it, in its turn, is determined by the compatibility of used polymer couples, in particular, PE+PP or PP+PVDF. As it is known, the thickness of this layer, is more exactly, the thickness of the segmental solubility layer makes dozens or hundreds Å [6]. The formation of such layer imposes limitations on the SMS formation in amorphous-crystal polymers in the direct proximity to the layer.

The thickness of the boundary layers with the changed

SMS and properties on the contact surface of polymers may reach many hundreds and even thousands Å. Boundary layers may be additional phase for the change filler in the process of the composite polarization. Really, as it is seen from the table 2 at identical conditions the electrothermopolarization in the two-matrix system accumulates more changes, than in one-matrix composite. The value of the accumulated in the electrothermopolarization change, as it was proved before, determines the piezomodulus value of the composite [3]. Obviously, in two-matrix composites on the base of polar (PVDF) and non-polar (PP) polymers, a new phase, formed on the contact boundary of polymer segments has an ability to strong accumulate changes at the electrothermopolarization.

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İKİKOMPONENTLİ MATRİSA ƏSASINDA PYEZOKOMPOZİTLƏR

Polyar-polyar, polyar-qeyri polyar və qeyri polyar-qeyri polyar polimerlər kimi iki matrisa əsasında kompozitlərin elektrofiziki və pyezoelektrik xassələri tədqiq edilmişdir. Eksperimental olaraq göstərilmişdir ki, çoxfazlı kompozitlər hazırlayarkən yalnız polyar və ya yalnız qeyri-polyar polimerlərdən deyil, matrisa kimi polyar və qeyri-polyar polimer qarışığından istifadə etmək lazımdır.

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ПЬЕЗОКОМПОЗИТЫ НА ОСНОВЕ ДВУХКОМПОНЕНТНОЙ МАТРИЦЫ

Исследованы электрофизические и пьезоэлектрические свойства композитов на основе двух матриц: полярный-полярный, полярный-неполярный и неполярный-неполярный полимеры. Экспериментально показано, что при разработке многофазных композитов следует использовать сочетание полярных и неполярных полимеров, чем использовать сочетание только неполярных, или же только полярных полимеров.

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