

ON THE ROLE OF INTERPHASE SPACE CHARGES AND THEIR RELATED EFFECTS IN POLYMER-PIEZOELECTRIC COMPOSITES

S.N. MUSAYEVA, M.A. KURBANOV, I.A. FARAJZADE, R.I. NAJAFOV

Institute of Physics Azerbaijan Academy of Sciences

H.Javid, av. 33, Baku, 370143

In the present paper it is shown that an immediate information received from the phase boundary of the composite (in particular about the potential barrier) allows to explain the change of macroscopic characteristics of composites depending on properties of separate phases and their heat treatment conditions. It is also shown that all changes of parameters characterizing the boundary essentially change the piezoelectric properties of composites as a whole.

Before it was shown that in formation of the piezoelectric effect in polymer-piezoelectric heterogeneous system interphase space charges and their related effects play an important role [1]. Contribution of interphase charges was investigated by study of dielectric characteristics (ϵ , $\tau g\delta$) and charge state of the composite before and after thermopolarization. However, for more detail revealing of the role of interphase charges in formation process of effective domain-orientation polarization of piezoparticles it is necessary to receive an information from the phase boundary, where charges accumulate. To receive an immediate information from the phase boundary by physical methods is very difficult due to small extent of interphase layer [2,3]. We regard that a certain information about the phase boundary state, related with formation of interphase space charges in polymer-piezoelectric composites can be received by determination of the potential barrier value on the boundary and by research of its change under the action of external factors, in particular, the electric field, temperature and also the preliminary heat treatment of separate phase particles.

In the present paper the value of potential barrier on the phase boundary and its influence on the piezoelectric properties of polymer-piezoelectric composite are investigated. For this purpose a charge state by the thermally stimulated depolarization (TSD) method and dependences of steady-state current on electric field strength at different temperatures for composites on the base of polyvinylidene fluoride (PVDF), polypropylene (PP) and piezoceramics of different structure are investigated. As the piezoelectric phase the sintered and nonsintered

piezoceramics of lead-zirconate-titanate (PZT) type, in particular PCR-3M, PCR-11, PCR-26 are used.

Before on the base of the large number of experiments it was established that the dependences of steady-state current ($lg j$) on $E^{1/2}$ at different temperatures are expressed by straight line [4]. It is shown at the same place that the indicated dependence is described satisfactorily by Richardson-Schottky

mechanism. In this connection the dependence of $ln \frac{j}{AT^2}$

on $\frac{1}{T}$, calculated by results of $lg j = f(E^{1/2})$ dependences, is

expressed by straight line, the inclination of which allows to determine the value of potential barrier on the phase boundary under different electrophysical conditions and also properties of the composite separate phases [4]. The change

of the inclination of the dependence of $ln \frac{j}{AT^2}$ on $\frac{1}{T}$

before and after polarization is seemed to us as an important result of the role of interphase space charges and their related effects. It is noted that the initial value of potential barrier on the phase boundary and the degree of its change as for nonpolarized and as for polarized samples depend on matrix properties, structure and properties of filler, volume fraction of polymer and filler and also thermopolarization conditions and heat treatment of phases (table 1).

Table 1.

Composites	Polymer Structure	Filler structure	ϕ, eV	
			Before polarization	After polarization
PVDF + 50% vol.PCR-3M	polar	rhombohedral	0,65	0,54
PVDF + 50%vol.PCR-7M	polar	tetragonal	0,76	0,69
PP + 50% vol.PCR-3M	nonpolar	rhombohedral	0,7	0,62
PVDF + 60% vol.PCR-3M	polar	rhombohedral	0,63	0,48

We regard that the change of interphase potential barrier depending on the above mentioned factors in the first turn depends on electron-ion and polarization processes on the phase boundary.

Confirmation of this is the change of the boundary charge value, of the potential barrier and the thermally stimulated depolarization current (fig.1).

In fig.1 the TSD currents for PP+50% vol. PCR-3M composite at the first heating up to the temperature at which the minimum of the TSD current (at 443 K) was observed (curve 1) and with discrete line is shown the extension of the TSD curve obtained at the same another sample polarized under the same conditions are shown. After the first heating the value of potential barrier ϕ is determined, piezoelectric

modulus d_{33} is measured and the total charge Q from the TSD curves and the charge Q_1 at the first heating are calculated (table 2).

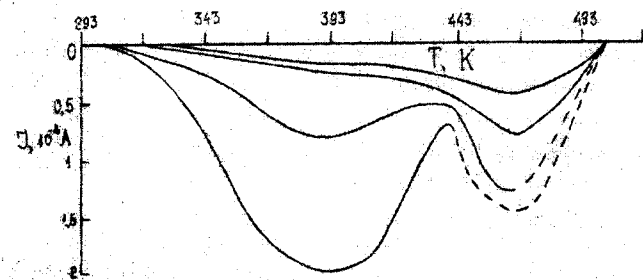


Fig. 1.

Then the same polarized composite after the first heating and cooling up to room temperature, the second time is heated up to the temperature of arising of the second maximum of the TSD current (468 K), then cooled up to room temperature. From fig.1 it is seen that after that the first maximum of the TSD current decreases significantly and

the second maximum (the discrete line 2) also several decreases. From measurements $\varphi=0,62$ eV, $d_{33}=30$ pC/N, $Q=1,15 \times 10^{-5}$ C, $Q_1=6,2 \times 10^{-6}$ C are obtained. Then the new same polarized and heat treated (the heating up to 468 K and cooling) sample is heated to 10 K higher than the temperature of the second maximum (478 K) and cooled up to room temperature. As it is seen from fig.1 (curve 3) the first maximum of the TSD current is absent and the second maximum amplitude significantly decreases. For this sample $\varphi=0,7$ eV, $d_{33}=15$ pC/N, $Q=5,55 \times 10^{-6}$ C are obtained. Further the polarized composite under the above mentioned conditions is heated to the temperature 20 K higher than the temperature of the second maximum of the TSD current. After that the values of piezoelectric modulus and charge were correspondingly, $d_{33}=10$ pC/N, $Q=3 \times 10^{-6}$ C and the value of the potential barrier completely restored. These results (Table 2) show that at the second heating a part of charged traps on the interphase boundary is released. Increase of the barrier at the every heat treatment and restoration of its value after the heating up to the temperature 488 K show that the cause of decrease of the potential barrier on the phase boundary is space charges on the polymer-piezoelectric boundary.

Table 2.

Regime of treatment	d_{33} , pC/N	φ , eV	Q , C	Q_1 , C
Before polarization	-	0,7	-	-
After polarization	72	0,56	$2,2 \times 10^{-5}$	$1,6 \cdot 10^{-5}$
After I heating (up to 443 K)	60	0,59	$2,2 \times 10^{-5}$	$1,6 \cdot 10^{-5}$
After II heating (up to 468 K)	30	0,62	$1,15 \times 10^{-5}$	$6,2 \cdot 10^{-6}$
After III heating (up to 478 K)	15	0,7	$5,5 \times 10^{-6}$	-
After IV heating (up to 488 K)	10	0,7	3×10^{-6}	-

Further influence of heat treatment, that is a sintering of piezoelectric phase particles on the ability of the composite to accumulate charges on the phase boundary in thermopolarization process was investigated. We note that a sintering of particles does not influence on piezophase structure. However, a sintering essentially influences on mobility of domain walls and domain sizes. Activity of the piezofiller particle surface also changes

and it, as known, determines as thickness and as physical structure of interphase layer. Change of interphase layer extent and its structure undoubtedly determines the height and width of the potential barrier on the phase boundary. In table 3 values of the potential barrier (φ) and piezoelectric modulus (d_{33}) for composites on the base of PVDF and different piezoceramics are presented.

Table 3.

Composites	Piezofiller particle size	Before polarization		
		φ , eV	φ , eV	d_{33} , pC/N
PVDF+PCR-11	<50 μ m, nonsintered	1,03	0,84	12
PVDF+PCR-26	<50 μ m, nonsintered	1,01	0,84	9
PVDF+PCR-11	<50 μ m, sintered	0,83	0,76	24
PVDF+PCR-11	160-200 μ m, sintered	0,73	0,57	80

The results show that under the same of polarization conditions, volume fraction and particle size of piezofiller the piezoelectric modulus of the composite with nonsintered ceramics is smaller than for composites with sintered ceramics. The value of interphase potential barrier, on the contrary, that

is φ in the case of nonsintered ceramics is higher for composites with sintered ceramics. One may regard that this is related with the change of surface state, volume conduction, domain structure and domain size of piezoceramics after its sintering [5]. Really, after sintering the electrical

conductivity of piezoceramics decreases and domain size several rises [6].

Summing up the can do a conclusion that the electron

and electrical properties of the phase boundary and therefore macroscopic properties (for example, d_{33} , Q) are determined by interphase space charges.

- [1] *A.I. Mamedov, M.G. Shakhtakhtinsky, M.A. Kurbanov, S.N. Musaeva.* Fizika, 1995, v.1, № 3, p.18-23.
- [2] *Hyeung-Gye Lee, Ho-Gi Kim.* Journal of Applied Physics, 1990, v.67, № 4, p.2024-2028.
- [3] *Yu.S. Lipatov.* Interphase phenomena in polymers. Kiev, 1980, p. 259.
- [4] *M.A. Kurbanov, M.G. Shakhtakhtinsky, A.I. Mamedov, S.N. Musaeva, Kh.S. Aliev, I.A. Farajzade, A.O. Orujov.* Fizika, 1997, v.3, № 3, p.23-26.

- [5] *A.Ya. Dantsiger* "Ferroelectric solid solutions of multicomponent system of complex oxides and high effective piezoceramic materials on their base". Thesis for a doctor's degree of physico-mathematical sciences. Rostov-na-Dony, 1985, p. 480.
- [6] *K.Okadzaki* Technology of ceramic dielectrics. Moscow, 1976, p. 336.

S.N. Musayeva, M.Ə. Qurbanov, İ.A. Fərəczada, R.İ. Nəcəfov

POLİMER-PYEZOELEKTRİK KOMPOZİTDƏ FAZALAR ARASI FƏZA YÜKLƏRİNİN VƏ ONLARLA ƏLAQƏLİ EFFEKTLƏRİN ROLU HAQQINDA

Bu işdə göstərilmişdir ki kompozitdə fazalar arası sərhəddən (xüsusən potensial çəpər haqqında) alınmış məlumat kompozitlərin makroskopik xarakteristikalarının ayrı-ayrı fazaların xassələrindən və onların termoeməltmə şəraitindən asılı olaraq dəyişməsinə izah etməyə imkan verir. Həmçinin göstərilmişdir ki, fazalararası sərhədi xarakterizə edən parametrlərin istənilən dəyişməsi kompozitlərin pyezoelektrik xassələrini xeyli dəyişdirir.

С.Н. Мусаева, М.А. Курбанов, И.А. Фараджаде, Р.И. Наджафов

О РОЛИ МЕЖФАЗНЫХ ПРОСТРАНСТВЕННЫХ ЗАРЯДОВ И СВЯЗАННЫХ С НИМИ ЭФФЕКТОВ В КОМПОЗИТЕ ПОЛИМЕР-ПЬЕЗОЭЛЕКТРИК.

В данной работе показано, что непосредственная информация, полученная из границы раздела фаз композита (в частности, о потенциальном барьере) позволяет удовлетворительно объяснить изменения макроскопических характеристик композитов в зависимости от свойств отдельных фаз и условий их термообработки. Показано, что всякие изменения параметров, характеризующих границы раздела фаз существенно изменяют пьезоэлектрические свойства композитов в целом.