

ELECTRET EFFECT IN HIGHLY HETEROGENEOUS POLYMER-PIEZOELECTRIC COMPOSITE SYSTEM

S.N. NIFTIEV, M.A. KURBANOV, M.C. SHAKHTAKHTINSKII, A.O. ORUJEV, KH.S. ALIEV

Institute of Physics of Academy of Sciences of Azerbaijan

H. Javid, av. 33, Baku, 370143

It has been shown that the dispersion of nonpolar polymers of the polyolefinic series by the piezoelectric particles (a ferroelectric particle) leads to the formation of the electret state characterized by a high electret potential difference and the surface charge density. The role of the domain-orientation polarization as the main factor in the formation of the stable electret effect has been determined. The additional amorphization of the polymer phase is shown not to be a determining factor in the electret effect in a heterogeneous polymer-piezoelectric system due to its dispersion by piezoelectric particles.

1. INTRODUCTION

The modern theory of the electret effect proceeds from the fact that for providing the significant relaxation times the interaction inside the electret, if only of two different types of the change each of which has its own mechanism and hence the relaxation time, is necessary [1-3]. Therefore, one can suppose that in the case of creating somehow the stable orientation polarization and the localization centers for injected charges in polyethylene and polypropylene free of the deep traps and the stable dipole polarization, the electrets with high electret potential difference and the surface charge density can be obtained on their basis. Such a state can be achieved through their dispersion by piezoelectric particles.

2. EXPERIMENTAL

The polymer matrix has to exhibit the features of stabilizing the injected charges and the structure variation in the case of the change of temperature-time conditions of crystallization. The simple thermoplastic polymers, polyethylene and polypropylene, fulfill the above requirements.

The following requirements are imposed upon the piezoelectric fillers: a high quasistationary domain orientation polarization; a low electrical conduction and migrational polarization.

The piezoceramic materials of the zirconate-titanate-lead (ZTL) family conform to these requirements. The piezoceramics of ZTL of tetragonal $[Pb(Ti_{0.6}Zr_{0.4})O_3]$ -ZTL-1; $Pb(Ti_{0.4}Zr_{0.6})O_3$ -ZTL-2 and rhombohedral $[Pb(Ti_{0.4}Zr_{0.6})O_3]$ -ZTL-3; $Pb(Ti_{0.46}Zr_{0.58})O_3$ -ZTL-4] structures were used.

The process of obtaining the electret composites includes the following technological operations: the dispersion, the drying and dosage of the basic components; mechanical mixing of components; the obtaining of nonporous, mechanically and electrically, strong, high-ohmic and metallized on one side the composite materials by hot pressing and based on the above mixture.

The polarization temperature (T_p) was chosen below the melting point of the polymer matrix. The electric field of polarization (E_p) was limited to the composite breakdown strength.

The surface effective charge density (Q) and the charge relaxation time (τ) were determined on the base of induction methods with the compensation of electret potential difference and thermostimulated depolarization methods [1,2].

3. RESULTS AND DISCUSSION

The dependence of the effective surface charge density of the composition based on polyethylene of high density on the volume content of the ZTL piezoceramics with different structure is shown in Fig. 1. The electrets of composites with

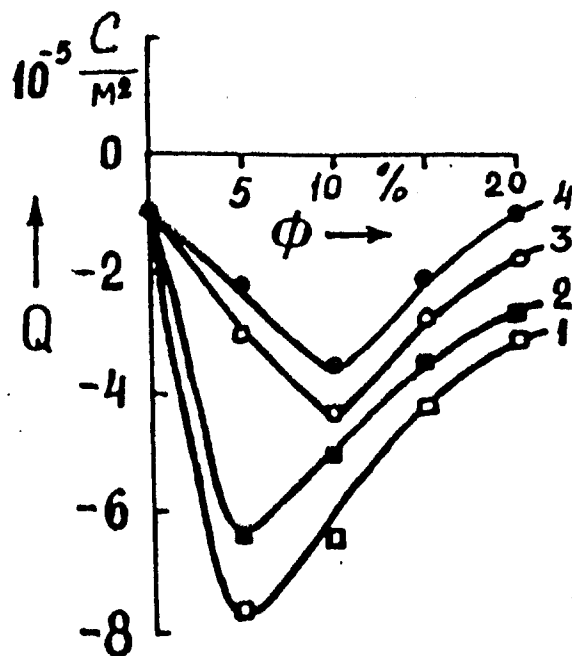


Fig. 1. The change of the electret charge (Q) versus the volume content of the piezoelectric filler. 1 – PE+ZPL-3; 2 – PE+ZTL-4; 3 – PE+ZTL-1; 4 – PE+ZTL-2.

rhombohedral and tetragonal piezoceramics have the effective charge maximum value at the volume content (ϕ) of 5 % and 10 %, respectively. Within the limits of one structure the Q value decreases with increasing the ferroelastance. The results of studying of the composites based on the polyethylene with a low density (PELD) and the polypropylene (PP) are given in Table 1. The experiments show that the dispersion of nonpolar polymers (PP and PE) by piezoelectric particles considerably increases their electret properties, i.e. the effective charge value and the stability of the life time of electret state increase (Fig.2).

Table 1

The characteristics and polarization conditions of composite electrets

Composition	Polarization conditions		$Q \cdot 10^{-4}$, c/m ²	Life time τ , years
	E_p , MV/m	T_p , K		
PELD+ZTL-1	8	373	0.12	11.0
PE+ZTL-3	7	393	0.88	9.0
PELD+ZTL-1	8	373	0.6	10.5
PP+ZTL-1	7	393	0.78	8.5
Polypropylene	8	373	0.22	0.5
Polyethylene of low density	6	353	0.28	0.2

Now consider the peculiarities of the formation of electret effect in polymers dispersed by piezoelectric particles. The model on which the electret properties of composites can be considered is shown in Fig. 3.

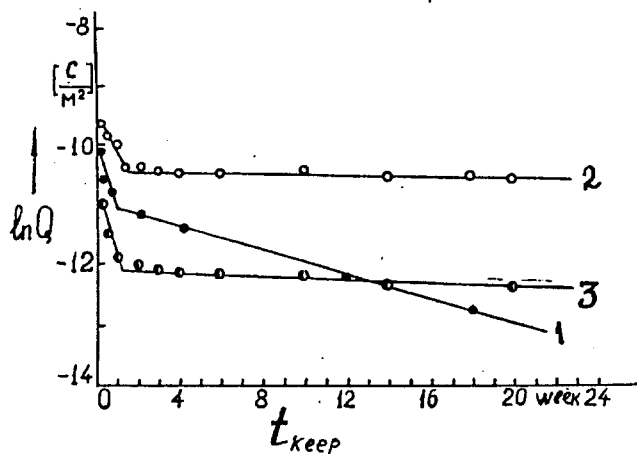


Fig. 2. The time dependence of the electret charge. 1 – the PE electrets; 2 – the electrets of the PE+ZTL-3 composites; 3 – the electrets of the PE+ZTL-2 composites.

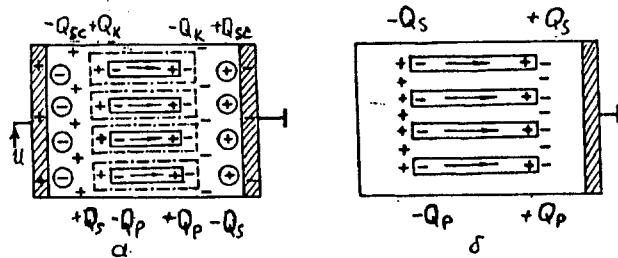


Fig. 3. The model of the composite electret.

When polarization in the temperature region below the melting temperature of polymer phase and the Curie temperature of the piezoelectric filler, the domain orientation polarization (P_d) schematically shown on the model with the bound charges Q_d is established in the composite. Part of injected charges Q_k screens the domain-orientation polarization. The injected charges trapped by the domains of piezoelectric particles and polymer traps Q_t behave as the bound charges and form "an external remanent polarization" (P_{ex}). The untrapped injected charges behave as free charges (Q_f). The existence of the domain orientation polarization and injected charges leads to occurrence of certain initial effective charge Q . This resultant charge creates the electric field inside the electret and promote the development both of slowly established orientation polarization (P_s) and the Maxwell relaxation of intrinsic and injected free charges. The electronic processes attributed to the migration, for a macroscopic distance, of intrinsic charges both of polymer matrix and the piezoelectric boundaries lead to the formation of the space-charge remanent polarization P_{sc} macroscopically manifesting itself as heterocharge (Q_{sc}). The relationship of the values of injected charges the domain-orientation and the space-charge polarization's and their time variation determine the value and the sign of the electret charge and electret potential difference. Thus, the electret state of the polymer-piezoelectric composite is attributed to relaxation of internal (P_d, P_{sc}, P_s) and external (P_{ex}) remanent polarizations and free charges (Q_f) in the internal electret field. The separation of contributions of every type of the above polarizations has been realized through the model experiments. Primarily, the role of the domain-orientation polarization

Table 2
The characteristics and polarization conditions of composite electrets

Composition	Polarization conditions		Electret potential, V	Charge type	Decay time of the charge to zero, hours
	E_p , MV/m	T_p , K			
PE+CaTiO ₃ volume fraction of CaTiO ₃ , 5%	10.0	393	135	homo	100
PE+SiO ₂ volume fraction of SiO ₂ , 5%	10.0	393	117	homo	75
PP+CaTiO ₃ volume fraction of CaTiO ₃ , 5%	10.0	393	140	hetero	75

should be noted. For this purpose the inorganic fillers, Ca-TiO₃ and SiO₂, leading to amorphization of the polymer

phase but being free of the domain-orientation polarization were introduced into the polymer.

The electrets based on PE and PP and also on CaTiO_3 and SiO_2 fillers are extremely unstable (Table 2). It follows from this that the change of the polymeric phase structure due to introduction of inorganic fillers is not the major factor.

One can assume that in the composites based on PE or PP and CaTiO_3 with a relatively high electrical conduction the intensive migrational polarization due to the mixing of low-molecular ionic impurities of the polymer phase and the filler will take place. However, these composites do not have the high-electret properties. Thus, the analysis of the experimental results shows that the additional disarrangement of the physical structure and migrational polarization do not provide the electret change stability. The formation of electrets with high density and charge stability is typical only of composites based on polymers and ZTL piezoceramics.

The comparison of the regularity of the change of electret charge Q and the piezoelectric modulus d_{33} of the PE-ZTL-3 composite versus the volume content of the piezophase speaks in favor of the domain-orientation polarization (Fig.4). As seen in Fig.4, with increasing the volume fraction of the piezophase the Q value primarily increases, passes through the maximum, then decreases and tends to zero. The piezoelectric modulus increases slowly at first and as the Q value approaches zero, the d_{33} increases more rapidly than according to the linear law. This fact indicates that with increasing the volume fraction of the piezoelectric phase, the field of the injected charges is completely compensated by oriented domain field, and therefore the resultant charge and hence the field inside the electret is equal to zero. The mechanical load breaks the quazineutrality of the oriented domain-injected charge system and therefore the composite shows the piezoelectric effect [4]. The study of the piezoelectric effect in the composite is the subject of particular investigation.

Thus, the composite electret charge can be considered to change due to the following three processes: the decrease of "internal" remanent domain-orientation polarization due to a thermal motion and the change of internal electret field; the decrease of "external" remanent polarization $P_{ex}(t)$ due to ejection of the injected bound charges coming from the outside in the internal field.

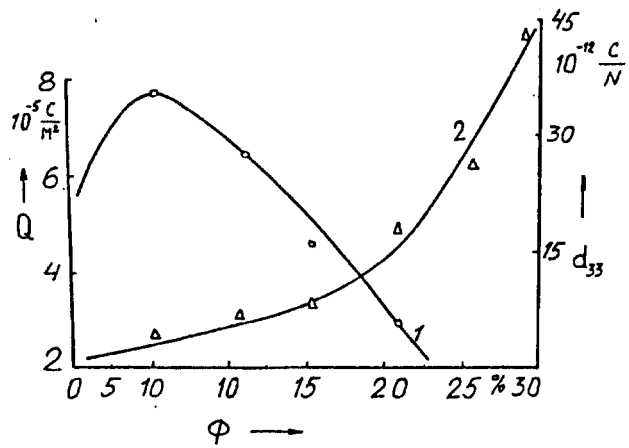


Fig. 4. The dependence of the effective charge and the piezoelectric modulus of the PE+ZTL-3 composite on the ZTL-3 volume content. 1 - $Q=f(\phi)$; 2 - $d_{33}=f(\phi)$.

The mechanism providing a large value of the stable effective charge in nonpolar polymers dispersed by piezoelectric particles is the following: the domains oriented in the thermopolarization process form with the injected charges stabilized at the interface the quazineutral system; simultaneously the stabilization of the part of injected charges on traps in the polymer phase volume takes place; the inevitable relaxation of the effective charge is compensated by relaxation of the domain-orientation polarization; at the constant value of the injected charges forming with the oriented domains the quazineutral system the domain relaxation due to a thermal motion is compensated by the relaxation of their related free charges. All the above-mentioned provides the constant effective charge value and hence the constant value of the electret potential difference.

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4. CONCLUSION

The high effective electret composite material can be obtained by the dispersion of nonpolar polymer PE and PP by piezoelectric particles of the ZTL family.

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S.N. Niftiyev, M.Ə. Qurbanov, M.H. Şahtaxtinski, A.O. Orucov, H.S. Əliyev

POLİMER-PYEZOELEKTRİK HETEROGEN KOMPOZİT SİSTEMDƏ ELEKTRET EFFEKTİ

Göstərilmişdir ki, poliolefin sırasından qeyri-polyar polimerlərin pyezoelektrik hissəciklərlə disperqasiyası yüksək elektret potensialı fərqi və yüklərin səthi sıxlığı ilə xarakterizə olunan elektret halını formalaşdırmağa gətirir. Stabil elektret halını formalaşdırmağında domen-orientasiya polarizasiyasının rolu təyin edilmişdir. Göstərilmişdir ki, polimer fazasının amorflaşması pyezoelektrik hissəciklərlə disperqasiya edildiyinə görə polimer-pyezoelektrik sistemdə elektret effektinin yaranmasında təyinedici faktor deyil.

С.Н. Нифтиев, М.А. Курбанов, М.Г. Шахтактинский, А.О. Оруджев, Х.С. Алиев

**ЭЛЕКТРЕТНЫЙ ЭФФЕКТ В СИЛЬНО ГЕТЕРОГЕННОЙ КОМПОЗИЦИОННОЙ СИСТЕМЕ
ПОЛИМЕР-ПЬЕЗОЭЛЕКТРИК.**

Показано, что диспергирование неполярных полимеров полиолефинового пьезоэлектрическими частицами приводит к формированию электретного состояния, характеризующегося высокой электретной разностью потенциалов и поверхностной плотностью зарядов. Определена роль доменно-ориентационной поляризации как главного фактора в формировании стабильного электретного состояния. Показано, что аморфизация полимерной фазы не является определяющим фактором в электретном эффекте в гетерогенной системе полимер-пьезоэлектрик, благодаря их диспергированию пьезоэлектрическими частицами.

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