THE HYBRIDE COMPOSITES BASED NEW MATERIALS FOR THE ELECTROMECHANICAL AND ACOUSTICO-ELECTRICAL CONVERTERS

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In this article the basic parameters of various types of materials for electromechanical transducers as well as acoustic-electric converters on the basis of piezoceramic, piezoelectric polymeric composites, substances with features of high electrical striction and hybrides of nano-micro piezoceramic with polymeric matrix have been studied. Also, frequency dependences of amplitude and sensitivity of acoustic converters have been investigated and the areas of their possible applications were revealed.

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1. Introduction

The segneto-piezo-ceramics possess higher Curie temperature and higher piezoelectric modulus d_{ij}, but low dielectric permitivity ε_{ij} and hence a greater d_{ij}/ε_{ij} ratio.

Owing to structural and technological reasons it is impossible the reasonable variation of these parameters for inorganic segneto-piezo-electric materials [1], whereas the synthesis of organic piezoelectric materials is definitely promising.

More effective of these materials are copolymers of polyvinylideneflorine (PVDF), vinylidenefluorine (VDF) and tetraflourineethylene (TFE) . For all polymeric piezoelectrics the main negative feature is a small stability interval in the dependence of elasticity modulus versus temperature.

For this reason the effect of mechanical hysteresis is more pronounced for polymers. In the temperature range from $-80^{\circ}C$ to $+90^{\circ}C$ in fluorine containing polymers three types of relaxations are observed [2].

Activation energy and relaxation spectrum have been determined on the basis of spectrum of thermally stimulated depolarization current. It has been found that the $\beta-$relaxation is associated with the Brownian movement of macro-molecules in amorphous phase and the dependence of the relaxation period on the temperature is taken into account. The α_1 and α_2 relaxations depend mainly on the effects which occur as a function of temperature in the chemical structure and crystalline phase .

In the synthesis of piezo-electric materials on the basis of polar polymers the main condition is the higher temperature being responsible for formation of phase transitions . With this purpose there is importance to increase intermolecular interaction and reduce the intensity of thermal movement of polymeric chain in amorphous-crystalline phases.

Finally, an influence of mechanical and thermal areas causes the change in the volume of polymers with piezo- and pyroelectric properties. However a change in the volume should be reversible process [2]. Mechanical hysteresis is a property of polymeric piezo-, pyroelectric materials and it should be taken into consideration upon processing of different multifunctional convertors and sensors on their base.

Piezoelectric composites promise large perspectives. Piezocomposites are mainly obtained by the technique of thermal compressing the mechanical mixture of organic and

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inorganic materials. These materials have properties such as synergistic effect and a wide operating temperature range. However individual components of those materials do not demonstrate these properties.

Negative feature of composite materials is that their efficiency as the generator of acoustic waves is less as compared to the multi component segneto-piezo-ceramic materials from $Pb(ZrTi)O_3$ family.

Recently with the purpose of increasing of the bulk piezo modulus the 3 – 1 and 3 – 3 types of interphase bonds are obtained. To create the mentioned interphase bonds the $PbZrO_3$ – $PbTiO_3$ piezoceramic rods should be placed with definite order in the polymeric matrix.

The purpose of the present study is to compare basic parameters of various types of materials on the basis of piezoceramic, piezoelectric polymeric composites :YSPE + SiO_2 + PKR-7M , YSPE + PKR-7M , PVDF + PKR – 3M, . PVDF +$BaTiO_3$ + PKR – 3M, ASPE + PKR – 8, ASPE + $BaTiO_3$ + PKR-8, PP + PKR – 8 and PP + $BaTiO_3$ + PKR – 8 hybride composites under different polarization conditions.

It should be noted that this technology is quite complex: a cylindrical or rectangular rods are cooked at temperature of 1300^0C and were uniformly placed in the matrix after polarization under special conditions.

2. Results and discussion

Calculations of the effective values of d_{33}, g_{33} and ε_{33} parameters for composites having the 3-1 type bond structure are carried out by the formulas:

$\varepsilon_{33}= {}^1\nu \cdot {}^1\varepsilon_{33}+{}^2\nu \cdot {}^2\varepsilon_{33}$;
$d_{33}= ({}^1\nu\, {}^1d_{33}\, {}^2\varepsilon_{33}+{}^2\nu\, {}^2d_{33}\, {}^1\varepsilon_{33})/ ({}^1\nu \cdot {}^2\varepsilon_{33}+{}^2\nu \cdot {}^1\varepsilon_{33})$;
$g_{33} = d_{33}/\varepsilon_{33}$

here ν – indicates the volume share , Main attention in the use of such composites is paid to the choose of piezoceramic with high piezoelectric modulus (phase 1) and elastic (phase 2) components. For these components ${}^1d_{33}> {}^2d_{33}$, ${}^1\varepsilon_{33}>{}^2\varepsilon_{33}$, ${}^1S_{33}>{}^2S_{33}$, where S- is the ability of elastic deformation. For instant, in case of ${}^1\nu$=0,1 və ${}^2\nu$= 0,9 we get : $d_{33}= {}^1d_{33}$; $g_{33}=10({}^1g_{33})$.

From the simple analysis it becomes clear that to increase the piezoelectric sensitivity of composite the volume share of piezoceramic phase should be reduced. In this case the d_{33} factor of composite remains constant and ε_{33} is reduced to a certain degree. For the 3 – 1 and 3 – 3 structural piezo-composites, in the first review, the d_{33} should be remained constant and be equal to the respective parameters of piezo ceramic rods.

However mesurements carried out by different methods have shown that the d_{33} coefficient of composites considered is about 60 – 75% of the respective parameter of piezo rods used as the piezo- phase.

-it is impossible to provide perfect orientation of domains being responsible for polarization of piezoceramic rods and this effect is more pronounced with increase in the height of rods.

-transmission of mechanical stress to the piezorods fixed in the polymeric matrix and the variety of complexity of deformation created due to its affect

-to be different from one another the geometrical sizes and electromechanical parameters of piezorods.

As it was noted the hybride piezo electric materials must have higher specific power for their applications as the acoustic receivers, transmitting antennas, piezo transformers, filters and piezo motors.

- constantly remaining of its quality factor (Q_m) due to effect of higher exciting electric field.
- exsistence of the higher operational temperature range
- stability of $K_{ij}Q_m$ factor under influence of the higher static and dynamic mechanical stresses.

We have solved this problem by two ways:

1.Crystallization of composites with different piezo phase ($PbTiO_3$ – $PbZrO_3$ – $PbNb_{2/3}Mn_{1/3}O_3$ – $PbW_{1/2}Mg_{1/2}$) and polymer matrix in the conditions of electric gas discharge.

2. Obtaining the piezo electric materials on the base of hybrides of composites having polymeric matrix with nano- and micro size piezo phases.

Investigations performed has shown that obtaining structures with polymer matrix and SiO_2 or $BaTiO_3$ nanoparticles by use of the suggested technology significantly increases the electro-mechanical, mechanical as well as the piezo electric properties of composites (for instant, PE – PKR-7M) on their basis. For this reason increase in amplitude and widening in the frequency band of the output signal of electro-acoustic convertors obtained on the basis of above mentioned composite are observed (Fig.1) Here is a brief explanation of the experimental results: Since interaction between distributed SiO_2 or $BaTiO_3$ nanoparticles and macromolecules of PE matrix are so high that they reduce the mobility of polymer segments.

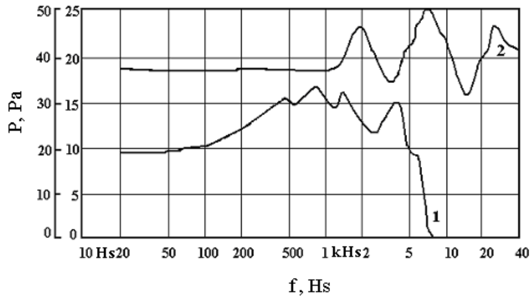

Fig.1. Frequency dependence of output signal amplitude in Pascal's for acoustic converter on the basis of YSPE – 0,4 volume, SiO_2 – 49,6 volume PKR-7M hybride composite. 1 – The P = f (f) dependence for YSPE – 50% volume PKR-7M micro composite(scale 1); 2 – The P = f (f) for YSPE – 0,4 volume SiO_2 – PKR-7M phase hybride composite (scale 2). For the YSPE – 50% volume PKR-7M microcomposite U_1 = 25V, for the YSPE – 0,4% volume SiO_2 – 49,6 PKR-7M hybride composite U_2= 5V. Polarization conditions: E_p= 4,5 MV/m, T_p = 393K, t_p= 0,5 hour.

The mechanical strength and Young's modulus of hybrid composite close to its surface layer is higher than the same parameters of micro-composite.

Higher mechanical properties of hybrid composites appear on the formation of their piezoelectric, electromechanical and electrical characteristics: they increase the amount of electric charge stabilized in interphase boundary, temperature of relaxation and activation energy. Factor which must be taken into account is the conversion of the nanoparticles' location places to the stabilization centers for the electrical charge carriers injected during electro-thermal polarization.

Such spaces are equivalent to the creation of local levels in the quasi forbidden band of polymeric matrix. As we noted earlier, an increase in piezoelectric, mechanical and electromechanical effects also shows itself in the receiving mode of acoustic waves as in generator regime of the acoustic waves (Fig. 2).

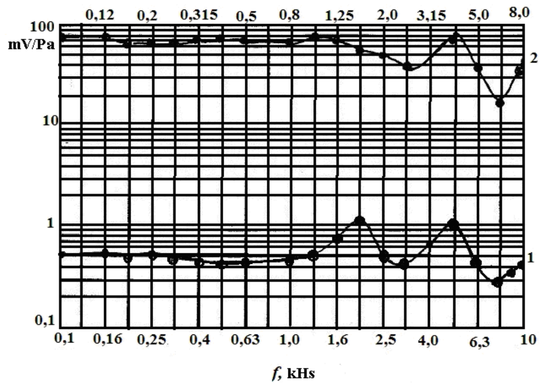

Fig.2. Frequency dependence of sensitivity(mV/Pa) of acoustic electrical convertor on the basis of hybride piezoelectric material 1. PVDF – 50% PKR – 3M microcomposite. 2. PVDF – 1,5% volume nanophase $BaTiO_3$ – 48,5% PKR – 3M hybride composite ; Polarization conditions: E_p = 4,5 MV/ m, T_p= 393 K, t_p =0,5 hour.

According to the Fig.2, by the comparison of the amplitude and the frequency range of converters on the basis of various hybrid composite piezo-materials one can concluded that the hybrid composites are more effective transducers: having a wide frequency range , larger signal amplitude and shifting of the nearly stable section of volt - ampere characteristics towards a higher frequencies , as well as decrease in nonlinearity of amplitude - frequency characteristics.

In Fig. 2 is demonstrated the frequency characteristics of sensitivity of the PVDF – 1,5% $BaTiO_3$ – 48,5% PKR-3M hybride compoisite for the receiving regime of acoustic waves(curve 2). Here also is given the similar characteristics of PVDF - 50% PKR-3M micro composite (curve 1). In the given dependence it seems to be very clear that only in the rectilinear parts of characteristics the sensitivity (mV / Pa) is differ approximately by 10^2 times.

To determine the influence of composite piezo-substrates on the properties of multifunctional acoustic electrical converters designed on their surface, the amplitude - frequency characteristics of hybride composites on the basis of ASPE, PP and PVDF matrices are plotted (Fig. 3).

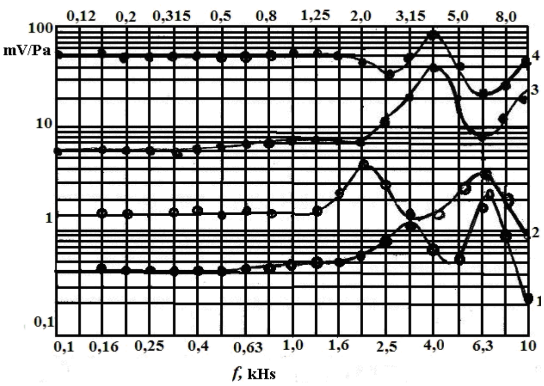

Fig. 3. Frequency dependence of sensitivity (mV/Pa) of acoustico-electrical convertor on the basis of hybride piezo-electrical materials 1. The ASPE and (PKR – 8) micro-phase based composite.; 2. The ASPE – 1,5% volume $BaTiO_3$ nanosize and 48,5% PKR – 8 phase based hybride composite; 3.The PP – 50% PKR – 8 microcomposite; 4. The PP – 1,5% volume , $BaTiO_3$ nanoparticle, and 48,5% PKR – 8 phase. Polarization conditions: E_p = 4,5 MV/ m, T_p= 393 K, t_p =0,5 hour.

It is clear from comparison of results given in Fig.2 and Fig.3 that depending on structure of the piezo-composite substrate the ranges of both amplitude and frequency characteristics of acoustic transducers are quite different.

4. Conclusions

From these results one can conclude that the PVDF as well as PP which was previously modified under the effect of electrical gas discharged plasma are more effective as the piezoelectric substrate at the first approach. We have experimentally found that the piezoelectric substrate which is the main phase of the hybrid composites must have the following properties:

1.A structure of composite piezo-substrate and piezo-ceramic phase should be rhombohedral(R_e) or heterogeneous(R_e+T)

2.The reorientation polarization formed in the process of polarization should be higher and stable.

3.The orientation degree of domains (71^0, 90^0 and 109^0) being differ from piezo-phase domains of 180^0 should be higher.

4. Diameter of piezo-phase domains should be larger as possible .

5. Importance of sharply increase in a quantity of electric charge (Q_r) stabilized in the composite interphase boundary and piezo-modulus(d_{33}) with increase in diameter of domains .

6. A homogeneous spontaneous deformation (η) of piezophase perovskite cell should be increased with increase in diameter of domains.

7.Higher mutual interactions in the interphase boundary of the composite’s piezoelectric substrate

8.Existence of polar polymeric matrix in the composite’s piezoelectric substrate.

9.Activation energy of electric charge carriers stabilized during the polarization process in the interphase boundary of composite’s piezoelectric substrate should be higher as compared to the activation energy of domains of piezo-electric phase o in the piezosubstrate.

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