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Changes of durable properties and physical structure of polymer and composites on its basis caused by electrical treatment

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Have been stated the results of influence of electrical treatment on durable properties of polyethylene (PEVP), polyvinylidenfluoride (PVDF) and piezocomposites on its basis. Have been presented the results of IR and EPR spectroscopy of these polymers. AFM research revealed that electrical treatment brings to change of frontier lay structure and it leads to changes of composites durable properties.

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Keywords: Polymer, Composite, Piezcomposite, Electrical treatment, PEVP, PUDF

1. Introduction

The wide application of composite on the polymeric piezoceramics basis in various sensors and transducers requires investigation of pyroelectrical, piezoelectrical and electret as well as durable characteristics. This research presents the results of influence of preliminary electrical treatment in alternating field which is below than breakdown strength of composite on electrical and mechanical durability of composite on the basis of PEVP, PVDF and piezocomposites PKR5 (composition: zirconate-titanate-lead ZTL with rhomboidal structure). Have been studied the IR and EPR spectra of these polymers before and after treatment.

2. Experimental part

Composites were prepared by hot-pressing method of mechanical mixture piezoceramics powders of PEVP, PVDF at the melting point of polymeric matrix under the pressure of 15 MPa during 10 minutes with further cooling (2000^0 C/min) by immersion between aluminum foils in the ice -water mixture. The samples of composites (diameter = 40 mm, thickness = 0.2 mm) were placed between two electrodes (diameter = 30 mm) with applied alternating electrical current for making the electrical treatment.

3. Results and discussion

The electrical E_{tr} and mechanical σ durability of composition PEVP +30% PKR5 were defined at 293K in accordance the methods, described in [1,2]

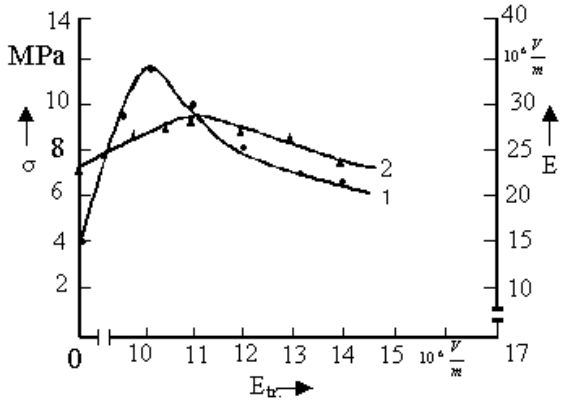

Fig.1. Dependence of electrical E_{tr} and mechanical σ durability of composition PEVP +30% PKR5 with particle size d≤50 μm on electrical treatment strength during 1 hour.

In Fig. 1 is given the dependence of electrical E_{tr} and mechanical σ durability of composite PEVP +30% PKR5 with particle size d≤50 mkm on preliminary electrical treatment strength during 1 hour. It is clear from picture that maximum increasing of electrical durability is observed after electrical treatment strength at $E=10^7$V/m and maximum increasing of mechanical durability is observed after electrical treatment strength at $E=10^6$V/m. At the same time the treatment of samples with more field strength leads to diminution of electrical and mechanical durability of composite.

Increasing of electrical and mechanical durability of composites PEVP +30% PKR5 is very probably connected with thermal warming up process of polymeric matrix.

It was also studied the influence of preliminary electrical treatment on IR spectra of PEVP and PVDF. On the Fig. 2 is presented IR spectra PEVP before and after

treatment in electrical field. The research was carried out in 700-3600 cm^{-1} wave length intervals. As it is seen from the pic. 2 after treatment there are absorption band at 2800-2500 cm^{-1} and 1710 cm^{-1} wave length intervals. However with increasing E the absorption band of deformation oscillation δ (CH_3, CH_2) at 1450-1460 cm^{-1} also increases. Relatively initial PEVP the intensity of absorption band at 1085 cm^{-1} with increasing E also increases. The intensity of band at 720-740 cm^{-1} actually doesn't change, however a narrowing of the band is observed. Starting from these facts one can draw the conclusion that there is no chemical structural change after the treatment in IR spectra of PEVP, and the intensity of individual bands changes with the treatment in the electrical field.

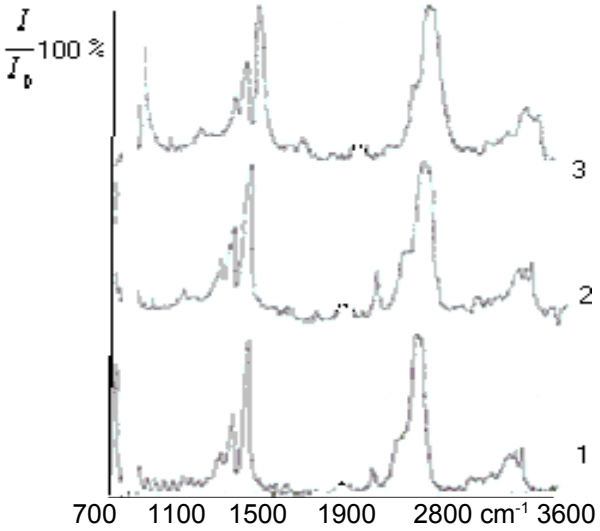

Fig. 2. Dependence of IR spectra PEVP on strength of field of electrical treatment: 1-E=O; 2-E=3×10⁶V/m; 3-E=5×10⁶V/m.

In Fig. 3. there are presented changes of IR spectra of PVDF as a function of the strength of electrical field value. After treatment the vibration interval of CH_2 and CH_3 (3000-2800 cm^{-1}) decreases with breaking of chemical bonds and appearance of a band at 2970 cm^{-1}. There are some changes in intensity of band at 2920-2970 cm^{-1} as well as splitting of maximum at 1500 cm^{-1}.

Earlier in [3,4] it was shown the generation of two types of free radicals as the result of strong electrical field due to local warming up as well as extension of blast wave. The first type radicals concentrated in pirolyzed by-electrode areas, the second – in dendrimerous formations along incomplete breakdown of polyethylene.

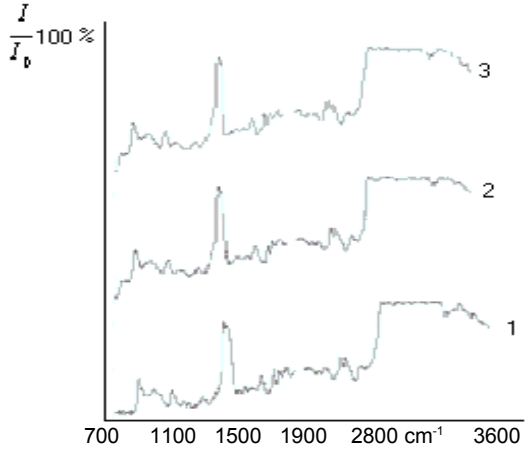

Fig. 3. Dependence of IR spectra PVDP on strength of field of electrical treatment: 1. E=O; 2. E=3 × 10⁶V/m; 3. E=5 × 10⁶V/m.

The formation of two types of radicals preceding to breakdown, accelerates the decomposition of polymer. In order to clarify the influence of electrical treatment on radical formation and excitation paramagnetic centers have been studied the compositions on the basis PEVP + 30% PKR5. On the Fig 4 there are presented EPR spectra of PEVP+30% PKR5 as a function of strength of field of electrical treatment. It is seen from the picture that electrical treatment of composition strongly influences on EPR spectra. There are two maximums in magnetic field 1.6×10^6 and 1.6×10^6 Gauss at E=0 at identical amplitudes. After the treatment at $E=10\times10^6$ V/m amplitude at $H=2.2\times10^6$ Gauss decreases. Comparison of spectra given on Fig. 4 and spectra from [5,6] reveals the allylic radicals. Proceeding from Fig. 4 g-factor was calculated for composition at E=0 and was shown that g=2.9; half-width ΔB≈0.7 mTl; g-factor after treatment at $E=8\times10^6$ V/m for the first maximum $g_1=4.2$ and for second maximum $g_2=2.9$; $\Delta B_1\approx0.4$ mTl, $\Delta B_2\approx0.2$ mTl.

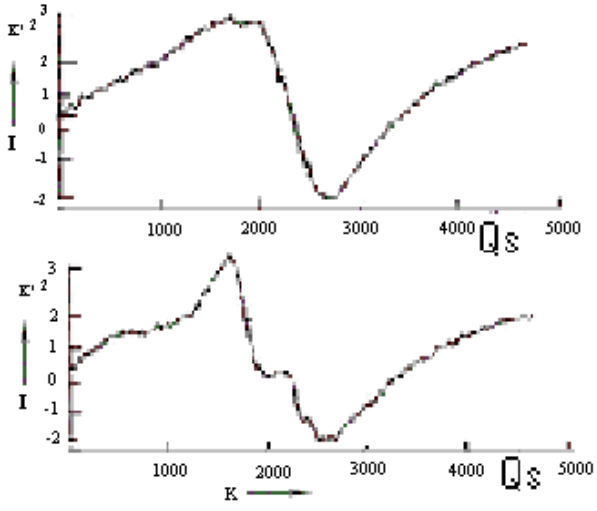

Fig.4 EPR spectra of PEVP+30% PKR5 as a function of the strength of electrical field.1.E=O; 2. E=8×10⁶V/m.

EPR triplet belongs to allylic radicals $^{-}C_{\alpha}H\cdots C_{\alpha 0}H\cdots C_{\alpha}H^{-}$ in which spin density of unpaired electron is distributed between carbon atoms. Formation of allyl radicals is perhaps the result of micro discharge, produced on the boundary of polymer-piezoelectric phases. The formation of free radicals is able to change the phase interactions between component and composite. The phase interactions are able to change the durable properties of the composite. Also it is supposed to produce quasi stable radicals, that influence the durable properties of composite. Depending the strength of electrical treatment the concentration of quasi stable radicals can increase and it is supposed to lead to deterioration of durable properties. Hence it is seen from the spectra that electrical treatment of composites leads to formation of free, quasi stable radicals and change the concentration of paramagnetic centers for composite PEVP + 30%PKR5.

It was scanned the relief changes of composites by SEM method in AF mode.

Have been studied the relief of PEVP +30%PKR5 treated at E=0 and E=8×10^{6}V/m.

There are AFM images of composite before and after electrical treatment on Fig. 5.

It is seen from the picture that relief of the composite strongly changes after treatment.

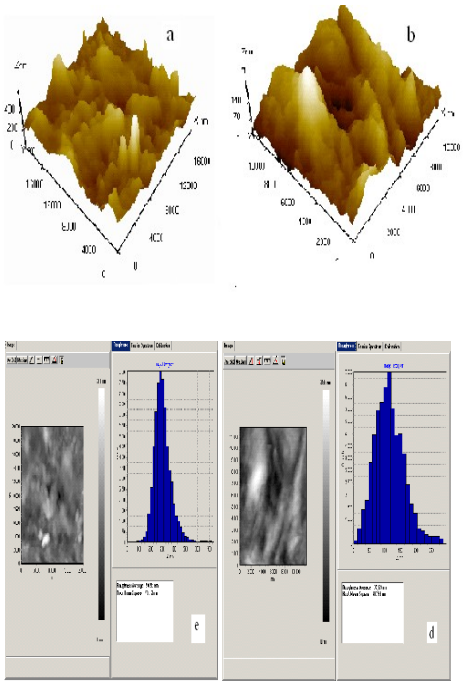

Fig.5. AFM 3D image of composite PEVP +30%PKR5 a)E=0, b)E=8·10⁶V/m, d)histogram E=0, e)histogram E=8×10⁶V/m.

The histogram of AFM image reveals that homogeneity of relief depending of treatment changes in 400 nm – 2500 nm interval. AFM research shows that after treatment crystallites sizes are crumbled in the composite up. It should be noted that crumbling up of crystallites sizes observed after electrical treatment at E= 8×10^{6}V/m leads to promoting of physical structure and this consequently contributes to the increasing of electrical and mechanical durability, what is experimentally observed (see Fig. 1).

Hence AFM research revealed that electrical treatment changes the boundary structure and leads to changes of composites durable properties.

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