

Scanning probe microscopic study of P(VDF-TrFE) based ferroelectric nanocomposites

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Abstract

Ceramic and polymer based nanocomponents combine the properties of their constituents, e.g. flexibility, elasticity, polymer reprocessability, hardness typical of glass, wear resistance and high light refraction index. This helps improving many properties of the materials in comparison with the source components. Since recently researchers have been manifesting interest to the properties of complex composite compounds. This is primarily caused by the unique properties of their structures as compared with conventional materials having homogeneous composition. Secondly, this interest is caused by the fact that these compounds may prove to be much cheaper than homogeneous structures provided the physical properties of the composite in a preset range of parameters (temperature, applied field frequency etc.) are identical to those of the respective homogeneous materials. For example, polyvinyl idenfluoride (PVDF) type ferroelectric polymers and copolymers on its basis have found wide application for functional elements of various electromechanic devices in advanced electronics due to their relatively good piezoelectric and pyroelectric properties. The strong random polarization and the formation of polar non-centrosymmetric crystals provide for the high piezoelectric and pyroelectric activity in these crystals. Scanning probe microscopy has been used for study of ferroelectric nanocomposites having different compositions. The matrix specimen for study of local polarization switching at a nanoscale level was vinyl idenfluoride and trifluoroethylene P(VDF-TrFE) copolymer possessing sufficiently high crystallinity. The composite fillers were barium titanate BaTiO₃ and deuterized triglycinsulfate DTGS ferroelectric powders and zirconate-titanate lead barium BPZT ceramic powder. We show these materials to show good promise for use in memory cells.

Keywords

nanocomposites, ferroelectric polymer, piezoelectric properties, scanning probe microscopy

1. Introduction

Composites are materials consisting of two or more phases with a clear phase boundary [1]. Practically they are systems containing reinforcement components (fibers, plates etc.) with different length to section ratios (providing for the reinforcing effect) contained in a polymer matrix. The specific mechanical properties of the compo-

sites (normalized to their density) are appreciably better than those of the source components. It is the reinforcing effect that makes composites differ from filled polymer systems where the filler makes the final product cheaper but significantly impairs the mechanical properties of the material. Composites differ by matrix types (organic or inorganic), matrix reprocessability (thermoplastic or thermosetting), type and orientation of reinforcing

elements (isotropic or uniaxially oriented) and continuity [2]. The mechanical properties of composites depend on the structure and properties of the phase boundary. For example, strong phase interaction between the matrix and the fiber filler provides for a high strength of the material, whereas much weaker phase interaction delivers good impact toughness. Phases in conventional composites have micron and submicron sizes. Currently dozens of nanocomposites with good physical and mechanical properties have been produced [3].

Polyvinyl idenfluoride (**PVDF**) type ferroelectric polymers and copolymers on its basis have found wide application for functional elements of various electromechanic devices in advanced electronics due to their relatively good piezoelectric and pyroelectric properties [4, 5]. Polymer materials have a number of advantages over other materials, e.g. low density, stable electrophysical properties, as well as simple and relatively cheap production. One should also note that a polymer film can acquire almost any shape without compromise in its mechanical strength and impact strength [6]. Due to this property polymer films to be used in all industry branches. Since recently researchers have been manifesting interest to the properties of complex composite compounds. This is primarily caused by the unique properties of their structures as compared with conventional homogeneous composition materials. Secondly, this interest is caused by the fact that these compounds may prove to be much cheaper than homogeneous structures provided the physical properties of the composite in a preset range of parameters (temperature, applied field frequency etc.) are identical to those of the respective homogeneous materials.

In this work we report experimental data on the piezoelectric properties of polymer ferroelectric composites. One can however hardly estimate dipole switching and local elemental diffusion in polymer films due to the presence of amorphous regions and low crystallinity [7–9]. Well-ordered films are required for studying nanoscale ferroelectric parameters. Therefore the test material for the study of local nanoscale polarization switching was vinyl idenfluoride and trifluoroethylene P(VDF-TrFE) copolymer possessing sufficiently high crystallinity.

2. Experimental

For producing the specimens we used P(VDF-TrFE) copolymer with a VDF/TrFE ratio of approx. 72/28 as the composite matrix. P(VDF-TrFE) copolymer crystallization from a solution or a melt leads to the formation of the crystalline ferroelectric phase (the β phase) with no additional treatment required, e.g. mechanical orientation stretching, annealing or strong electric fields. This copolymer has relatively high pyroelectric and piezoelectric indices and a high thermal stability of the physical parameters.

The composite fillers were barium titanate BaTiO_3 and deuterized triglycinsulfate (**DTGS**) ferroelectric powders and zirconate-titanate lead barium (**BPZT**) ceramic powder. BaTiO_3 and DTGS powders are classic model ferroelectrics with high piezoelectric and pyroelectric parameters. BPZT ceramic powder has a moderate ferroelectric hardness and at a Ba content of ~20% and a Ti content of ~40–50% it exhibits excellent piezoelectric and pyroelectric properties and has a low dielectric loss coefficient.

The specimens were produced by crystallization from a solution. The P(VDF-TrFE) copolymer powder was dissolved in a dimethylsulfoxide and acetone mixture. The filler powder was added to the solution after complete copolymer dissolution. The solution was ultrasonically treated in a bath for ~1 h until a homogeneous suspension. The resultant solution was poured into a special vessel for solvent evaporation and film structure formation. More detailed description of the composite specimen preparation process was reported elsewhere [10–13].

The specimens were studied by piezoresponse force microscopy in Kelvin mode on a scanning probe nanolab (NT-MDT, Russia). The surface structure, piezoelectric properties and surface potential of the films were studied for specimens of pure P(VDF-TrFE) copolymer and composites on its basis: P(VDF-TrFE) + 20%BPZT + Fe, P(VDF-TrFE) + 5% BaTiO_3 , as well as P(VDF-TrFE) + 0.5%DTGS and P(VDF-TrFE) + 10%DTGS.

3. Results and discussion

At the first stage we obtained semi-contact mode surface images [14] of the test films (Fig. 1). It can be seen from Fig. 1 that the surface structure of the polymers varies. This is caused by the different specimen preparation and synthesis process modes [15–17]. Higher doping leads to significant changes in the surface structure, see Fig. 1.

We carried out a series of experiments in order to study polarization in the copolymer films with different ferroelectric material additions. In these experiments, induced macrodomain regions were produced by scanning film areas at a direct voltage supplied to a conducting cantilever which served as the top electrode. We thus produced two $6 \times 12 \mu\text{m}^2$ polarized regions: bright (at –55 V) and dark (at +55 V). Figure 2 shows piezoresponse signal scans after polarization. The reverse switching effect (feeding a + signal yields a – signal) is only manifested in ferroelectrics with negative d_{33} piezoelectric module, e.g. polymers [7]. By way of comparison Fig. 2 also shows a scan of lead titanate-zirconate film (**PZT**) whose d_{33} piezoelectric module is positive, where the dark rectangle corresponds to polarization by negative voltage and the bright one, to polarization by positive voltage. It can be seen from Fig. 2 that the contrast of the induced regions varies depending on the ferroelectric material added to the copolymer. To illustrate the above we show all the

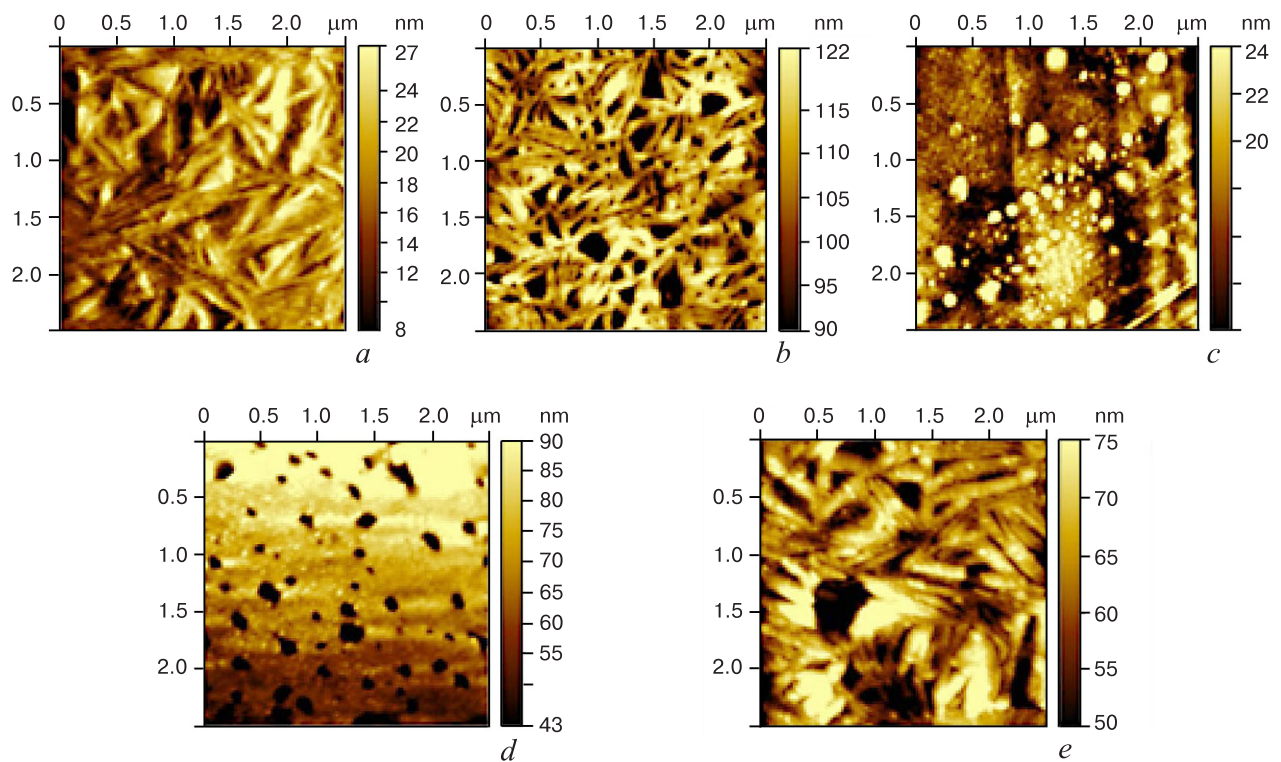


Figure 1. Semi-contact mode film surface images for P(VDF-TrFE) copolymer with different ferroelectric material additions: (a) P(VDF-TrFE); (b) P(VDF-TrFE) + 20%BPZT + Fe; (c) P(VDF-TrFE) + 5% BaTiO₃; (d) P(VDF-TrFE) + 0.5%DTGS; (e) P(VDF-TrFE) + 10%DTGS

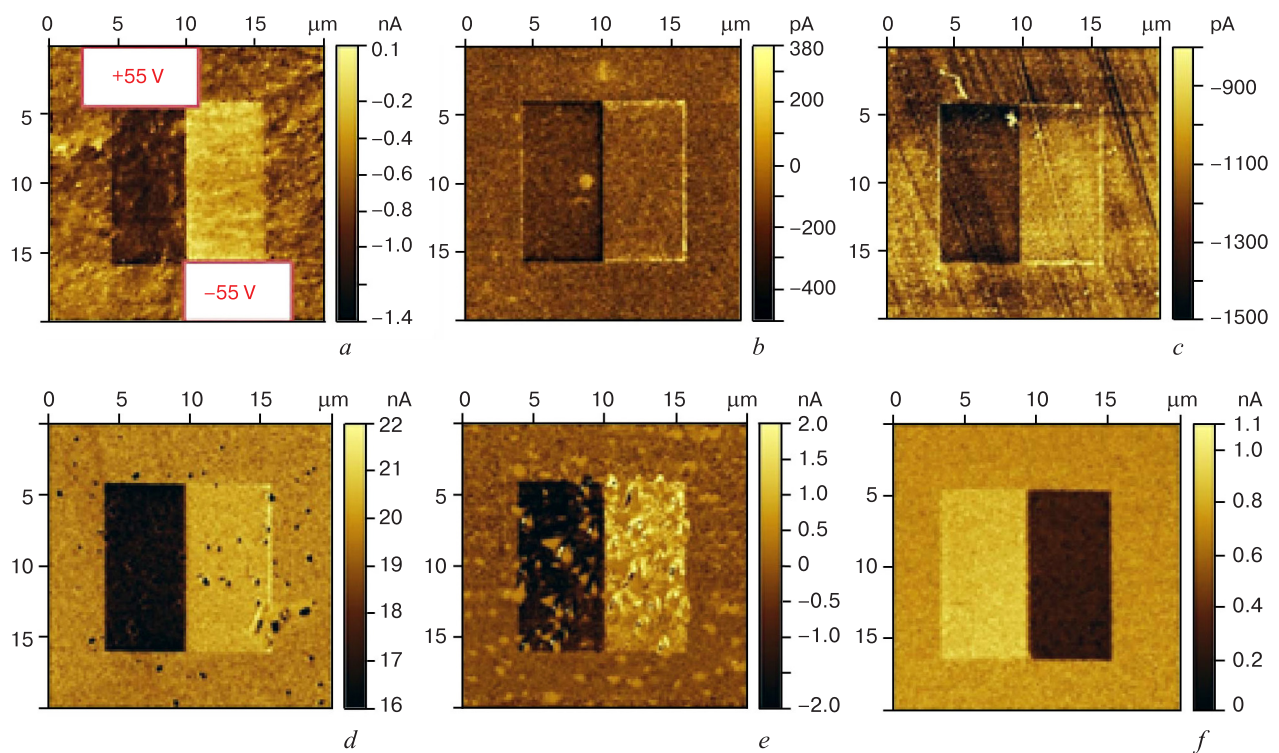


Figure 2. PFM images after polarization: (a) P(VDF-TrFE); (b) P(VDF-TrFE) + 20%BPZT + Fe; (c) P(VDF-TrFE) + 5% BaTiO₃; (d) P(VDF-TrFE) + 0.5%DTGS; (e) P(VDF-TrFE) + 10%DTGS; (f) PZT

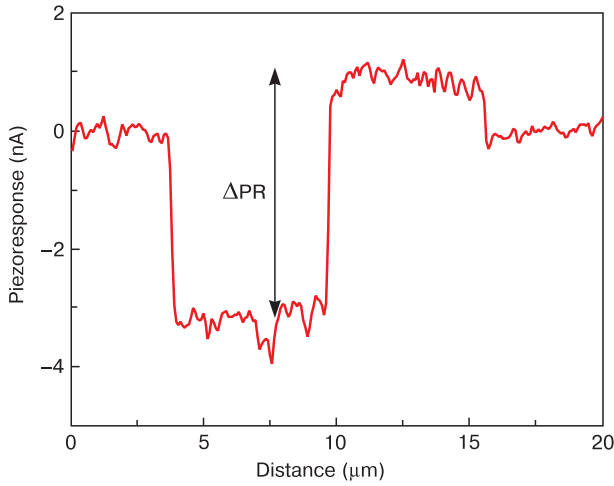


Figure 3. Piezoresponse signal profile in the middle of scan for P(VDF-TrFE) + 0.5%DTGS specimen.

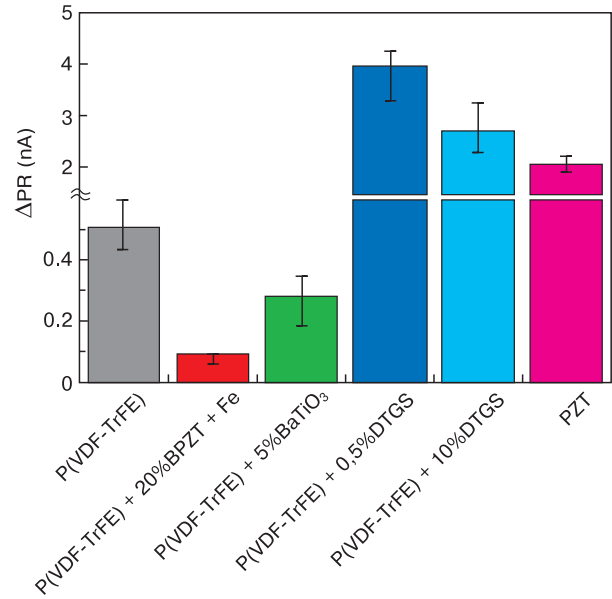


Figure 4. Residual piezoresponse for test samples.

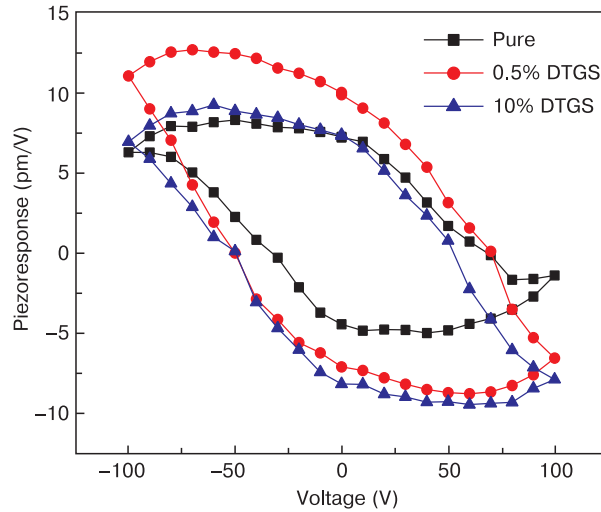


Figure 5. Residual piezoelectric hysteresis loops for pure copolymer (square) and copolymer with different DTGS percentages (circle, triangle)

images in Fig. 2 on the same vertical scale (contrast is equalized relative to the zero level).

To analyze the experimental data we suggested the following induced piezoelectric response calculation procedure.

Figure 3 shows a piezoresponse signal profile taken in the middle of the scan for the P(VDF-TrFE) + 0.5%DTGS film. The residual induced piezoresponse (ΔPR) was determined by the height of the “step” between the positive and the negative polarized regions. For the test specimen this height was ~ 4.1 nA. This procedure allows one to determine ΔPR for all the test samples. Furthermore there is a difference in the amplitudes of the polarized regions: the average piezoresponse for the region polarized at $+55$ V is ~ 3.1 nA whereas for the region polarized at -55 V it is ~ 1 nA. This asymmetric switching was observed in all the test samples.

Figure 4 shows a general diagram of residual piezoresponse as a function of copolymer composition. ΔPR is the highest for the P(VDF-TrFE) + 0.5%DTGS specimen and the lowest for the P(VDF-TrFE)+20%BPZT+Fe one.

Residual piezoelectric hysteresis loops (local deformation and piezoelectric signal phase as a function of direct voltage) were recorded in local polarization switching spectroscopic mode for the P(VDF-TrFE), P(VDF-TrFE) + 0.5%DTGS and P(VDF-TrFE) + 10%DTGS (Fig. 5).

The hysteresis loops demonstrate the effect of doping on the coercive strain, maximum effective piezoelectric coefficient and hysteresis loop area which corresponds to the effective switching work.

Piezoelectric hysteresis loops provide additional information on the behavior of domain structures during local polarization switching.

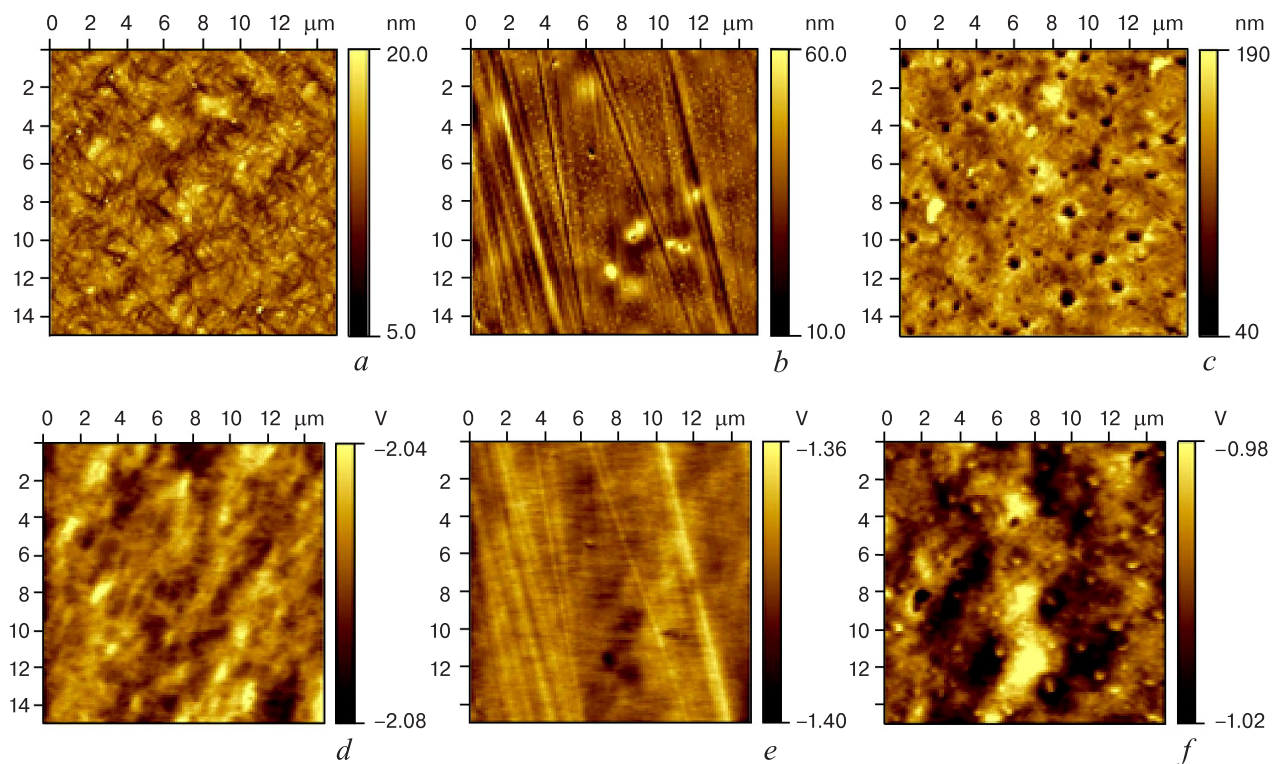


Figure 6. (a – c) topography and (d – f) surface potential for the test specimens: (a and d) pure P(VDF-TrFE) copolymer; (b and e) P(VDF-TrFE) + 5% BaTiO₃; (c and f) P(VDF-TrFE) + 10%DTGS

The experiments showed that the effective piezoelectric coefficient is the highest ($d_{33} = 12.6$ pm/V) for the P(VDF-TrFE) + 0.5%DTGS copolymer film.

We also obtained surface potential maps by Kelvin mode for the P(VDF-TrFE), P(VDF-TrFE) + 5% BaTiO₃ and P(VDF-TrFE) + 10%DTGS specimens.

As can be seen from Fig. 6, the copolymers exhibit a strong negative surface potential signal suggesting the presence of self-polarization in the samples, the random polarization vector being oriented from the bulk toward the film surface. Based on the surface potential maps we plotted distribution profiles (Fig. 7) which suggest the presence of natural unipolarity (self-polarization) in the test composite films.

An increase in the ferroelectric addition percentage shifts the distribution profile maximum and changes its width.

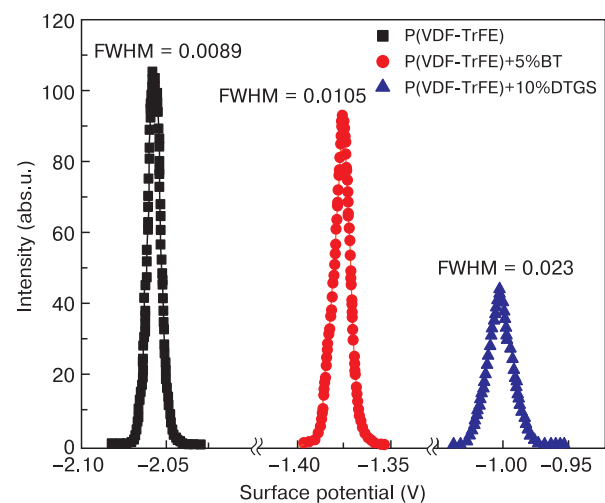


Figure 7. Surface potential signal distributions for the test copolymers.

4. Conclusion

Surface topography and local piezoelectric parameters of composites on the basis of ferroelectric vinyl idenfluoride and trifluoroethylene copolymer were studied using scanning probe microscopy. The surface topography of the composite films proved to vary. Natural unipolarity was observed in all the test samples. The highest residual polarization ΔPR and the highest effective piezoelectric coefficient $d_{33} = 12.6$ pm/V were observed in the P(VDF-TrFE) + 0.5%DTGS copolymer specimen.

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