

Electrical Properties of Poly(Vinylidene Fluoride-CO-Hexafluoropropylene) Nanocomposites with Nanoclays

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Abstract – Polymer nanocomposite materials based on PVDF with 15 mol% content of hexafluoropropylene and Cloisite® 15A and Cloisite® 30B were prepared by melt-mixing at 200°C. In pure copolymer, the crystalline phase is the α - phase. Materials consisting organoclays Cloisite show significant increasing of β – phase from 30% to 55-60%. It is expected these materials to have piezoeffect but primery they are dielectrics. In this work the main parameters as dielectric constant ϵ_r and critical electric field E are investigated.

Key words - nanoclays, nanocomposites, poly(vinylidene fluoride-co-hexafluoropropylene), β - phase, electrical properties, piezoeffect, polymer piezo materials.

INTRODUCTION.

Poly(vinylidene fluoride) (PVDF) and copolymers on its basis have been some of the most researched polymers, due to their ferroelectric properties. These polymers have different unit cells of varying polarity, because its different crystal modifications. They are known at least four different crystal modifications of PVDF with different molecular conformations and lattice parameters [1–3]. The most common, easily obtainable and thermodynamically stable phase is the α -phase. It does not show a net lattice polarization due to its ant parallel chain arrangement (a trans-gauche conformation). In β -phase the molecules are configured in all-trans conformation. This gives the β -phase crystals a spontaneous lattice polarization, which is necessary to observe ferroelectricity in PVDF. The γ -phase is combination of alternating conformational units from the α - and β -phases, a δ -phase is a polar version of the α -phase. The crystal forms of PVDF homopolymer is retained in many copolymers of VDF containing small amounts of comonomer [4]. The fluorine atoms in the copolymers produce steric hindrance that prevents the molecular chains from assuming conformations similar to non-electroactive α -phase of PVDF.

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Many of the copolymers directly crystallize into the polar electroactive β -phase [3], which give the ferro-, pyro-, and piezoelectric behavior in PVDF and its copolymers [3, 5].

It is known, that films of poly (vinylidene fluoride hexafluoropropylene) copolymer (VDF–HFP) with different contains of HFP indicates prominent piezo-, pyro-, and ferroelectricity, comparable to that in PVDF [6–13].

It is established that these properties were highly dependent on the crystal structure and polymer chain orientation of the VDF–HFP copolymer [14].

Very high electrostrictive response was reported for VDF–HFP copolymer with content of 5 and 15 mol% HFP – 1700 pm/V and 1200 pm, respectively.

The remnant polarization of copolymer films with the same content of HFP was 60 mC/m² and 48 mC/m² [6, 8]. In the solution-cast sample the remnant polarization was found to be 80 and 50 mC/m² for VDF–HFP copolymer films with 5 and 15 mol% HFP content, respectively [8].

Casting from dimethylformamide solution [11, 12] or stretching PVDF-HFP films [10] leads to chain conformations that are similar to those of polar β -PVDF.

Over the past decade, many researchers have reported a possibility to stabilize β -phase in PVDF and copolymers with HFP in the presence of layered silicates well scattered within the polymer matrix.

The addition of 1 – 6 mass% nanoclays is a prerequisite for the improvement of the mechanical, barrier, piezo-, pyro- and ferroelectric properties [15–17].

In the work [16] is reported that the addition of organically modified nanoclays to the VDF–HFP copolymer facilitated the transformation of the polymer crystals from α - to β -phase.

The nanocomposite materials obtained showed increased values of elongation at break compared to the initial copolymer, as well as high dielectric permeability in wide temperature interval.

The piezoelectric β -phase in PVDF–HFP nanocomposites with layered silicate was retained after swift heavy ion irradiation, indicating that the nanocomposites can be used as radiation-resistant materials at high temperature [17].

The aim of the present work is to obtain nanocomposite materials on the basis of poly (vinylidene fluoride-co-hexafluoropropylene) with organically modified montmorillonite nanoclays Cloisite®15A and Cloisite®30B and study the content of β -phase, dielectric and piezoelectric properties of PVDF-HFP modified copolymers.

The piezoeffect of these materials could be used for many applications very attractive in this way for transforming noise energy into electrical.

II. EXPERIMENTS

Materials preparation

Poly(vinylidene fluoride-co-hexafluoropropylene) referred as PVDF-HFP is a copolymer (15 mol% HFP comonomer) with melting temperature 117°C and melt index 6.52 g/10 min (220°C, load 98 N) as powder was kindly supplied from Arkema, France.

Two organically modified montmorillonite nanoclays (Cloisite®15A and Cloisite®30B) from Southern Clay Products Inc. were used. Cloisite®15A was dimethyl, dehydrogenated tallow ammonium - exchanged montmorillonite. Cloisite®30B was bis (hydroethyl) methyl tallow ammonium-exchanged montmorillonite.

Sample Preparation

The compositions of these nanoclays were mixed with PVDF-HFP and homogenized as powder by stirring at 50 – 60°C for 10 min, and then twice in a “Brabender” at 200°C. They were pressed on a laboratory press PHI (England) between aluminium foils under the following conditions: samples thickness about 1 mm, temperature 200°C, melting period at 200°C – 3 min, pressing pressure – 12 MPa; cooling rate – 40°C/min.

X-ray Structure Analysis

The X-ray diffraction patterns were taken by X-ray diffractometer with generator Iris-M (Russia) and goniometer URD-6 (2θ) (Germany) at atmospheric pressure, room temperature, Ni-filtered Cu target K_{α} radiation in the interval $2\theta = 4 \div 50^{\circ}$.

Fourier Transform Infrared Spectroscopy (FT-IR)

Samples prepared as films were analyzed using spectrophotometer produced by “Bruker” (Germany) in the interval 4000–400 cm^{-1} with Tensor 27. To determine the relative quantity of the β - phase, the heights of the series of peaks were determined by simulation of the spectrum observed.

This was done using OPUS – 65 software which automatically corrects the baseline. For each sample, the fraction of the β -crystalline phase (F_{β}^{IR}) was calculated by the formula:

$$F_{\beta}^{IR} = A_{\beta} / (1.26 A_{\alpha} + A_{\beta}) \quad (1)$$

where: A_{α} и A_{β} – are the heights of the peaks at 764 and 840 cm^{-1} , respectively while the coefficient 1.26 represents the ratio of the absorption coefficients at 764 and 840 cm^{-1} [18].

Electrical measurement

As expected these materials initially must act as dielectrics. For these measurements universal digital multimeter is used with capacitance range ($C_{\min} > 1\text{pF}$) and resistors ($R_{\max} < 200\text{M}\Omega$).

The sample for easy measurements are prepared as capacitors (single layer) with two silver electrodes – Fig. 1.

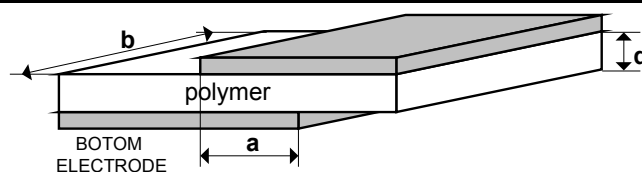
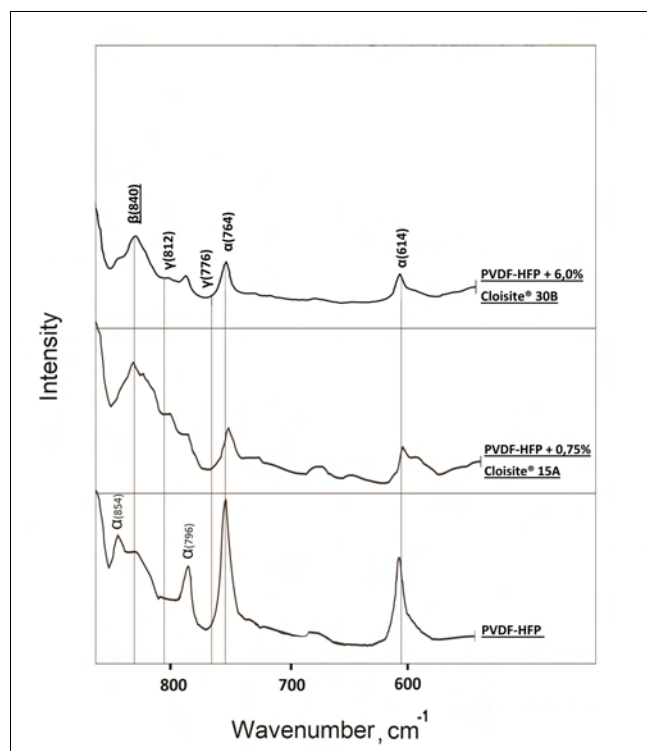


Fig. 1. The shape and dimension of samples.
 $S = a \times b$ – common surface between upper and bottom electrodes (Ag); d – thickness of samples.

III. RESULTS AND DISCUSSION

The XRD diffractograms of VDF-HFP copolymer were analyzed in reference to the standard XRD patterns for PVDF [19], in this way small quantity of HFP (15 mol %) in VDF-HFP copolymer does not change significantly the lattice symmetry of PVDF [20]. Fig. 1 shows the XRD patterns of the PVDF-HFP, organoclays Cloisite® 15 A and Cloisite® 30 B and nanomaterials on their basis.

Fig. 2. X-ray diffraction patterns of the initial PVDF-HFP and



nanocomposite materials containing Cloisite®15A and Cloisite®30B.

The peaks at $2\theta = 17.7, 18.4, 19.9$ and 26.6° correspond to 100, 020, 110 and 021 diffractions of the PVDF α - phase while the peaks at $2\theta = 20.2, 20.6, 20.7$ and 20.8° – to 110 and 200 β - phase diffractions [21].

The change in the diffractograms and the appearance of a basic peak above 20° together with a smaller one at $2\theta = 18 - 19^{\circ}$ directly proved the formation of a pure and prevalently oriented β -phase in the obtained nanocomposite materials (Fig. 2). In the initial VDF-HFP copolymer, the crystalline phase is predominantly the non-polar α - phase. Since the

peaks characteristic for the α - and β -phases are somewhat overlapped in the X-ray diffractogram, the XRD- analysis of PVDF-HFP and its nanocomposites was supplemented by Fourier transform infrared spectroscopy (FT-IR).

The values calculated for F_{β}^{IR} by the FT-IR method for VDF-HFP copolymer and its nanocomposites with Cloisite® 15 A and Cloisite® 30 B showed that the increase of nanoclay content gave increased β - phase content from about 30 % in the initial PVDF-HFP to 55÷60 % in the composite materials containing organoclays Cloisite® 15A and Cloisite® 30B.

Before electrical testing of samples they are numbered as follows (type of material and sizes see Fig. 1):

1. PVDF-HFP, pure S=16×15 mm, d=81 μ m;
2. PVDF-HFP+0.5%, Cloisite® 15A, S=15×12 mm, d=98 μ m;
3. PVDF-HFP+0.75%, Cloisite® 15A, S=11×13 mm, d=250 μ m;
4. PVDF-HFP+6%, Cloisite® 30B, S=12×20 mm, d=207 μ m;

The first measurement are for estimation of dielectric constant ϵ_r [22] - Table I.

TABLE I
DIELECTRIC CONSTANTS OF SAMPLE

PARAMETER	NUMBER OF SAMPLES			
	1	2	3	4
C(pF)	212	135	60	180
ϵ_r	9	8.5	12	20

TABLE II
CRITICAL ELECTRICAL FIELD OF THE SAMPLES

PARAMETER	NUMBER OF SAMPLES			
	1	2	3	4
$U_{BR}(kV)$	5.1	5.35	6.3	5.8
$E(V/m)$	6.00×10^7	5.30×10^7	$>2.10 \times 10^7$	3.00×10^7

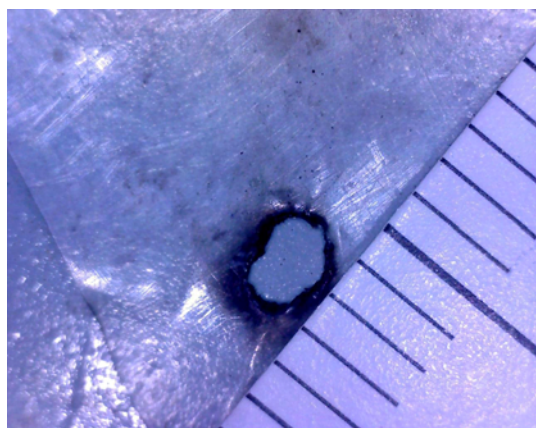


Fig. 3. Destruction pictures of samples (a).

Investigation of breakdown voltage and type of distriction are shown in Table II and Fig.3,a,b

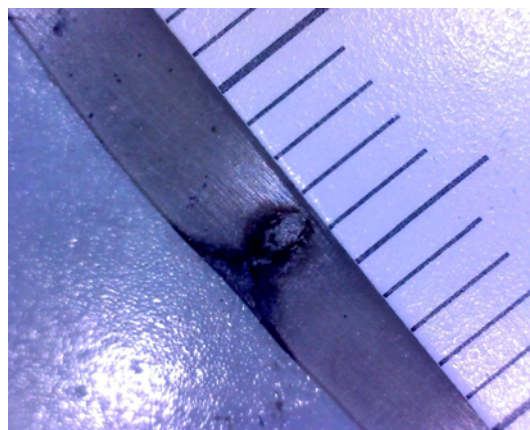


Fig. 3. Destruction pictures of samples (b).

The presence of piezoeffect is detected only as a phenomena. Bending and pressing the samples the voltages about 8÷20 mV appear between two electrodes.

The interest are the results from temperature dependence of the isolation resistivity R_{sample} – table III. It could be seen significant drop after 50°C.

TABLE III
TEMPERATURE CHANGES OF THE SAMPLES

T(°C)	NUMBER OF SAMPLES			
	1	2	3	4
	R(M Ω)			
40	200	198	-	-
45	176	153	-	>200
50	88	87	-	170
55	50	49	-	85
60	24	25	200	60
65	13	17	150	40
70	9	12	62	30
75	-	-	43	21
80	-	-	30	-

CONCLUSION

Nanocomposite materials on the basis of poly (vinylidene fluoride-co-hexafluoropropylene) with Cloisite® 15A and Cloisite® 30B were obtained.

The materials obtained were analyzed by X-ray diffraction, FT-IR analyses and electrical measurements.

The addition of organically modified nanoclays changes the structure of the crystalline phase and facilitate the transformation of the polymer crystals from α - phase to more polar β -phase.

Analyzing electrical parameters several conclusion could be made:

❖ These materials have more semiconductor for behavior than dielectric. The drop of resistance in heating is a result of thermo generation of electrical carriers]

❖ The changes of ε_r are significant with the additives in polymers;

❖ The shape of destroyed area is approximately 1×1 , 2×2 mm. That leads to the conclusion the breakdown mechanism is not very sharp and has slowly increased current.

Dielectric semiconductor behavior, piezoeffect, probably photo effect could be used for different sensors and new energy sources.

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