Electrical Properties of Piezo Organic Materials and Application

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Abstract – **Nanocomposite materials on the basis of vinylidene fluoride–hexafluoropropylene copolymer with organically modified nanoclays were obtained by co-precipitation method from its solution in dimethylsulfoxide. The addition of nanoclays was found to facilitate the transformation of the polymer crystals from α- to β- phase. The increase of the tensile strength and elongation at break of the nanocomposites, containing Cloisite®15A was higher at lower content of nanoclays, compared to that of the initial VDF−HFP copolymer, thus disclosing that the clay layers were better exfoliated. The results obtained showed that the nanocomposites prepared could be promising for the application as new piezo materials.**

Key words - **Electrical properties, Nanoclay, Nanocomposites, Vinylidene fluoride-hexafluoropropylene copolymer, Co-precipitation, Piezo effect, Organic piezo materials.**

I. INTRODUCTION

There are four basic methods for synthesis of polymer/silicate materials: from melt, from solution, by in-situ polymerization and sol-gel techniques. Every polymer system requires selection of proper method and treatment conditions to obtain the product wanted at highest efficiency. In the present paper, the experiments were limited to mixing from solution based on consideration on simplifying the technological procedures aiming at further implementation of the method directly in the industry.

The mixing from solution is based on a system where the polymer is soluble and silicate layers swell. Layered silicates swell in the solvent while polymer is dissolved.

The layered silicate suspension and the polymer solution are mixed, so polymer chains penetrate and substitute the solvent in the intermediate silicate layers. After the removal of the solvent, polymer nanocomposite is obtained [1].

Special attention should be paid to the proper selection of solvent. It should be suitable for the polymer and considered against the layered silicate and its organic modifier.

There is certain risk of solvent intercalation in the polymer which is unwanted process.

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The dimethyl sulfoxide (DMSO) is a common solvent for many polymers, suitable for the preparation of nanocomposites by co-precipitation method.

It is well known that films of vinylidene fluoride hexafluoropropylene copolymer (VDF–HFP) with different HFP contents indicate prominent piezo-, pyro-, and ferroelectricity comparable to that in PVDF [4-11].

It was found also that these properties are highly dependent on the crystal structure and polymer chain orientation of the VDF–HFP copolymer [12].

Casting from dimethylformamide solution [9, 10] or stretching of VDF–HFP films [8] leads to chain conformations that are similar to those of polar β- PVDF.

The addition of nanoclays is a prerequisite for the improvement of the mechanical, barrier, piezo-, pyro- and ferroelectric properties [13-15].

It was reported in ref. [14] that the addition of organically modified nanoclays to the VDF–HFP copolymer facilitated the transformation of the polymer crystals from α- to β-.

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 VDF–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 [15].

The aim of the present work is to obtain nanocomposite materials on the basis of vinylidene fluoride–hexa-fluoropropylene copolymer with organically modified nanoclays Cloisite®15A and Cloisite®30B by co-precipitation method from solution in dimethylsulfoxide and study the tensile, dielectric and piezoelectric properties of the nanocomposites obtained.

II. EXPERIMENTS

A. Materials

Vinylidene fluoride–hexafluoropropylene copolymer referred to as VDF–HFP is a copolymer (15 mol% HFP comonomer) with melting temperature 117ºC and melt index 6.52 g/10 min (220ºC, load 98 N) in the form of powder, kindly supplied from Arkema, France.

Cloisite®15A and Cloisite®30B, organically modified montmorillonite nanoclays from Southern Clay Products Inc. were used. Cloisite®15A is Na^+ montmorillonite clay modified with dimethyl, dehydrogenated tallow, quaternary ammonium (2M2HT) with d_{001} spacing – 31.5 Å and density – 1.66 g/cm^3. HT stands for a tallow-based compound (~65% C18, ~30%

C16, ~5% C14) in which the majority of the double bonds have been hydrogenated.

The modifier concentration of Cloisite®15A was 125 meq/100 g. Cloisite®30B is montmorillonite clay modified with methyl, bis-2-hydroxyethyl tallow, quaternary ammonium (MT2EtOH) with d_{001} spacing – 18.5 Á and density – 1.98 g/cm^3.

The modifier concentration of Cloisite®30B was 90 meq/100 g. The solvent used for the compositions was dimethylsulfoxide (DMSO), Sigma Aldrich.

All the materials described above were used directly without any further modification or treatment.

B. Sample Preparation

The co-precipitation method was used to prepare VDF–HFP copolymer nanocomposites containing 1, 2 and 3 mass% of Cloisite®15A or Cloisite®30B.

To obtain the nanoclay contents in the VDF-HFP copolymer mentioned, two premixes were made: one for the nanoclay and the other for the VDF–HFP, using DMSO as solvent. The two premixes were sonicated using a Branson 8510 ultrasonication bath at 30–40°C for approximately 5 min.

The final 10% solution was prepared by adding the contents of the nanoclay premix to the VDF–HFP copolymer premix and the product was sonicated again for 20 min.

The mixture obtained, 150 ml of deionized water were added. A stringy, white, translucent precipitate formed immediately. Then, the precipitate was removed and dried in a vacuum oven until constant weight.

For most physical testing, the precipitated samples were pressed into films on a laboratory press PHI (England) between aluminum foils under the following conditions: samples thickness about 0.3 mm, temperature 200ºC, melting period at 200ºC – 3 min, pressing pressure – 12 MPa; cooling rate – 40ºC/min.

C. Tensile Properties

The tensile strength, elongation at break and the other characteristics of the initial VDF–HFP copolymer and the nanocomposite materials based on it were measured on a dynamometer INSTRON 4203 (England) at speed of 100 mm/min and room temperature.

D. Electrical properties

Before studying the electrical parameters the samples should be metalized for ohmic contacts.

The electrodes could be made using two methods:

- Film deposition in vacuum of conductive materials (e.g. Al Al-Ni, Ag, Au);
- Printing of conductive layer (epoxy+Ag-powder).

The first method of vacuum deposition is sputtering [2, 3, 17], because is low temperature, not destructive with good adhesion.

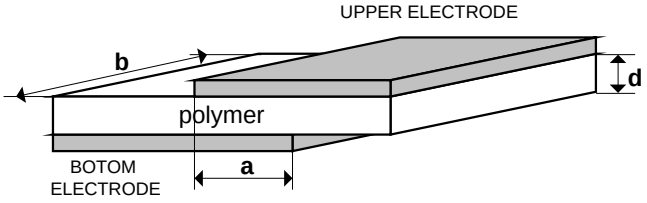
In these experiments conductive silver glue is used for easy preparation of the electrodes.

The process is screen printing and polymerization at 60÷80˚C for 20 minutes.

The shape of samples is shown in Fig. 1.

The next very important step for preparation of the samples is thermal and electrical polarization.

The electric field is applied (100 to 500 kV/cm) to align the dipoles at a temperature in the range of 90÷100˚C.



a)

b)

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

The next is cooling of the sample with electrical field thus freezing the polar alignment.

Before electrical testing the samples are numbered as follows:

1. Initial VDF-HFP copolymer;
2. VDF-HFP + 1 mass% Cloisite®15A;
3. VDF-HFP + 2 mass% Cloisite®15A;
4. VDF-HFP + 3 mass% Cloisite®15A.

TABLE I
DIELECTRIC CONSTANTS AND CRITICAL ELECTRICAL FIELD OF THE SAMPLES

PARAMETER	NUMBER OF SAMPLES			
	1	2	3	4
C(pF)	212	70	110	190
ε_r	9	15	22	25
U_{BR}(KV)	5.1	5.2	5.8	5.7
E(V/m)×10^7	6.0	5.7	3.0	-

The main electrical parameters such as dielectric constant ε_r, breakdown voltage of resistively are shown in Table I.

The experiments showed that the specific resistance (total ohmic resistance) rapidly drops after 50˚C. At room temperature (20˚C) the resistance of all samples is over the measuring range 200 MΩ. After temperatures between 70 - 80˚C the resistance is in the range between 9 – 30 MΩ. It could be seen that after the initial rapid changes there are stabilization of total resistance. It means that over temperature 55 - 60˚C there are saturation of current thermogeneration.

The conclusion is that these materials have semiconductor behavior with clear negative temperature coefficient of resistivity.

III. Results and Discussion

The initial VDF–HFP copolymer obtained by co-precipitation method contains mainly α- phase. With the addition of organically modified nanoclays (Cloisite®15A, Cloisite®30B) to the copolymer, α- phase was transformed into β- phase.

The presence of polar electroactive β- phase is the reason for the ferro-, pyro-, and piezoelectric properties of the materials based on this copolymer which makes possible to use them in control and measuring gauges, in microelectronics and other specific fields.

Because of the rigid structure of clay layers and their high aspect ratio, they have proven to be very effective in the improvements of the nanocomposites mechanical properties even at very lower nanoclay additions [16] in well dispersed state.

The tensile strength, elongation at break and Young modulus of the materials based on VDF–HFP copolymer with Cloisite®15A and Cloisite®30B are shown in Table III.

It can be seen that the increase of the values of tensile strength (to 38.7 and 34.3 MPa, respectively) and elongation at break (to 848 and 835%, respectively) was higher at lower content of the nanoclays used (0.75, 1.0 mass%), compared to that of initial VDF−HFP copolymer. It means that the clay layers are better dispersed in the polymer matrix. The reinforcing effect was lower for the nanocomposites with higher clay content (up to 3.0 mass%) owing to some clay platelets being agglomerated and stacked.

The formation of β - phase in the compositions studied is also beneficial to the improvements of mechanical properties of the materials obtained.

The Young modulus of the composite materials prepared by the co-precipitation method showed higher values, compared to that of initial copolymer.

IV. Application and Conclusion

Polymer nanocomposite materials containing up to 3.0 mass% organically modified montmorillonite nanoclays Cloisite®15A and Cloisite®30B were prepared by co-precipitation method. The nanocomposites obtained were characterized by their tensile, dielectric and piezoelectric properties.

TABLE III
TENSILE PARAMETERS OF THE INITIAL VDF-HFP COPOLYMER AND ITS NANOCOMPOSITES

NUMBER OF SAMPLES	TENSILE STRENGTH, MPa		ELONGATION AT BREAK, %		YOUNG MODULUS, MPa	
	Cloisite®15A	Cloisite®30B	Cloisite®15A	Cloisite®30B	Cloisite®15A	Cloisite®30B
1	27.2	27.2	795	795	125	125
2	38.7	34.3	823	835	215	184
3	35.2	32.9	805	770	156	165
4	33.6	30.7	750	700	154	155

The main application is transforming mechanical effect into an electric signal.

There are many variation of this effect but in two main configuration – bending and pressing – Fig. 2.

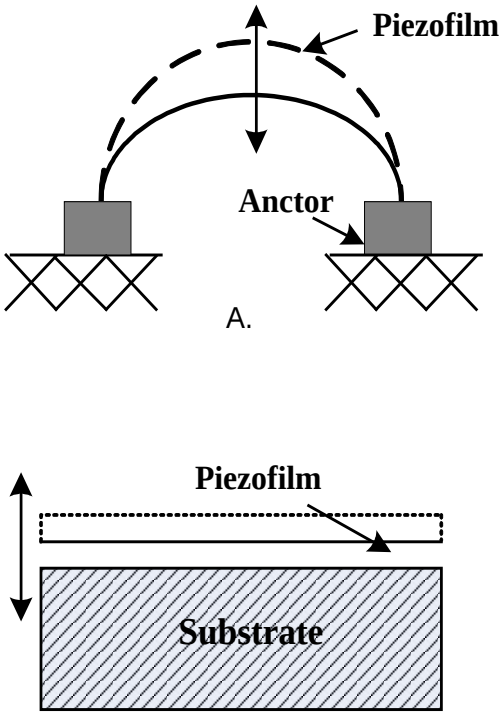


Fig. 2. Bending (A) and pressing (B) of piezomaterials.

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