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РОЗДІЛ 2

ХІМІЧНІ, ФІЗИЧНІ ТА МАТЕМАТИЧНІ МЕТОДИ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ТА АПАРАТІВ

FERROELECTRIC FILMS OF PVDF HOMOPOLYMER AND P(VDF-TFE) COPOLYMER

N.V.Gadzhileu, BSc student, the AMiR Faculty
Odessa National Academy of Food Technologies, Odessa

A comprehensive research on ferroelectric films of polyvinylidene fluoride (PVDF) and a copolymer of vinylidene fluoride with tetrafluoroethylene (P(VDF-TFE) is carried out at the Department of Physics and Materials Science of ONAFT. We study the uniaxial and biaxially oriented PVDF films and P(VDF-TFE) copolymer with different content of crystallites with α- and β-phase. The thickness of the polymeric films is in the range of 10-30 μm. PVDF samples were taken from experimental batches produced by extrusion. The films were subjected to thermal and mechanical processing consisting in a uniaxial or biaxial orientation (stretching) in the ratio 1-4 at a temperature of 100 °C followed by annealing (120 °C, 1 hr).

PVDF molecules consist of 10^3-10^4 unit cells (–CH_2–CH_2–) that corresponds to a molecular weight of about 10^5–10^6. PVDF and copolymers are semicrystalline materials, i.e. they contain an amorphous phase and dispersed therein crystallites in the form of thin lamella having size of about 10 nm. The lamellae areas of macromolecular chains are arranged in a zigzag manner, while the chain is folded repeatedly.

The same macromolecule can pass through crystalline and amorphous phases. It is known [1] that the crystalline lamellae have no shaped plates perpendicular to the direction of orientation, as it was previously thought, but on the contrary: they are extended in this direction. Thus, the crystallites are brick-like blocks disposed parallel to the stretching direction (1) and separated by very small gaps in the directions (2) and (3), consisting of only 1-3 polymer chains.

Dimensions of the crystallites and amorphous gaps between them, defined by two independent methods with a small degree of orientation are given in the Table. 1.

Table 1 – Crystallite size in PVDF (nm)

Direction	Crystal	Amorphous phase	Total size
1	5.7-7.6	4.0-4.3	9.7-9.9
2	3.5-3.7	4.0-5.0	3.9-4.2
3	2.4-2.5	5.0-7.0	2.9-3.2

PVDF is composed of repeated units of the polymer chain –CH_2–CF_2–, each having a high dipole moment of $\mu = 7 \cdot 10^{-30}$ C·m (2,1 D) due to the symmetric arrangement of the H positively charged H atoms and negatively charged F atoms. Since these dipoles are rigidly connected to the principal carbon chain, their mutual orientation depends on the molecular conformation and the chain packing. PVDF is characterized by polymorphism with two major crystalline α and β phases, corresponding to two types of conformation of the polymer chain. In the crystallites of the α-phase, which are formed by crystallization of PVDF from the melt under normal conditions, the polymer chains have a spiral shape with a trans-gauche-trans-gauche* conformation and preferred orientation of the dipoles along the chain. However, the chains in the crystals are stacked antiparallel, so that the total dipole moment per unit volume is zero. Thus, α-phase PVDF is non-polar one.

When the polymer is stretched or under the influence of a strong external field, the α-phase transforms and the crystallites of ß-phase are formed. The polymer chains in ß-phase have the form of a flat zigzag, to which corresponds the trans-trans conformation.

All molecular dipoles are oriented along the chain in one direction and in the chain crystallites are stacked parallel to each other. The result is a strongly polar structure having ferroelectric properties. The formed ß-phase has the spontaneous polarization, direction of which can be changed under the influence of the external electric field. Calculation shows that the magnitude of the spontaneous polarization in the ß-phase of PVDF is P_o = 130 mC/m^2.

Introduction of tetrafluoroethylene (TFE) leads to the fact that due to the difference in sizes of F and H atoms, trans-gauche-trans-gauche* conformation in the copolymers is not formed and crystallization occurs immediately in the polar β-phase. Concentration of elementary units $–CF_2–CH_2–$ in the P(VDF-TFE) copolymer is increased as compared to the homopolymer, so it can be regarded as a copolymer of PVDF with a certain percentage of "head to head" defects, which are not compensated by corresponding "tail to tail" defects.

Lattice constant in β-phase of PVDF and P(VDF-TFE) substantially identical and comprise a = 0.858 nm, b = 0,491 nm, and c = 0.256 nm. In real films, given the relatively low percentage of TFE in the copolymer (about 5-10 %), along with β-phase there is a certain amount of non-polar α-phase. The relationship between α- and ß-phase in PVDF is determined by the parameters of the stretching and the heat treatment.

By studying IR absorption spectra, we identified PVDF and P(VDF-TFE) films with different ratios and α- and β-phase. To determine the content of α- and β- phase, the peaks were tested in the vicinity of 510 cm^{-1} and 530 cm^{-1}. If we assume that the peaks of 510 cm^{-1} and 530 cm^{-1} are superimposed on the broad peak in the 400-560 cm^{-1} region, the α:β ratio should be calculated in relation to this broad peak taken as a baseline.

Table 2 – Interrelation between α- and β-phase crystallites in PVDF and P (VDF-TFE)

	Type of orientation stretching	Film thickness, μm	α-phase, %	β-phase, %
PVDF	uniaxial	20-30	57±2	43±2
P(VDF-TFE)	uniaxial	20-30	4±1	96±1

Experimental batches of PVDF and P(VDF-TFE) as powder and films were produced by the St. Petersburg concern "Plastpolymer" under the names of F2B and F2ME. Overseas manufacturers of PVDF and its copolymers are currently the Atochem (France) company and Pennvolt (USA). The same polymers are manufactured by Kureha (Japan) and Solvay (Belgium).

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