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# STRUCTURE INTERPRETATIONS OF POLYMERS PROPERTIES

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**Abstract-** The investigation results of interconnection of structure and polyvinylidene fluoride properties (PVDF) under the influence of glow flare discharge interaction in the medium of residual gases of free air, argon and $SF_6$ is presented in this paper. It is shown that quantity of accumulated electric charges in the samples under electric discharge influence depends on the defects and sample defect degree. The investigations of thermally stimulated relaxation of charges from PVDF samples are carried out. It gives the possibility to estimate qualitatively the defect size change and sample defect degree by the way of changing material properties.

**Keywords:** Polymer Dielectrics, Electrical Discharge, Gas Inclusions, Insulation, Electric Charge, polyvinylindene Fluoride, Crystallization.

## I. INTRODUCTION

Polymer-dielectric materials are widely used as electric insulation in products and devices of electric power and other industries as insulate or ones (capacitor production, cable industry, transformer devices, etc.) often involving gas inclusions, the presence of which is due to manufacturing process, which in turn also determines the supramolecular structure of the insulate material.

In gas inclusions of high-voltage insulation, depending on the magnitude of the applied voltage and sizes of gas inclusions, there have been developed ionization processes of a certain intensity, the presence of which is the main cause of its destruction in strong electric fields [1-5].

In connection with above - mentioned, it is of interest to study certain physical processes occurring both on the surface and in the volume of crystallizing polymers, according to the supramolecular structure of the samples being studied.

To put the other way round, in this work an attempt is made to reveal the role of the supramolecular structure in the process of ageing of the polymer dielectric exposed to electric discharges.

We also investigate the processes of polyvinylidene fluoride (PVDF) taking place in a film exposed to the electric discharge in the medium of residual gases of atmospheric air, argon and $SF_6$.

## II. EXPERIMENTAL METHOD

It is known that the number of accumulated charges in samples exposed to the electric discharge depends on the size and degree of presence of sample defects. Therefore, in order to estimate the number of relaxed charges, we use the method of thermally stimulated relaxation (TSR) of charges from samples. The sample in review by the effect of the electric discharge is brought to the non-equilibrium state at room temperature. Then by the uniform increase of temperature, there has been stimulated, the sample transition from the excited (non-equilibrium) state to the equilibrium one. Later, plotting the temperature-time dependence of the recording current caused by the relaxation processes, we calculate the area enclosed by the curve $i=f(t)$, where $t$ is the relaxation time), which is equal to total charge relaxed in sample. The basic circuit diagram is presented in Figure 1.

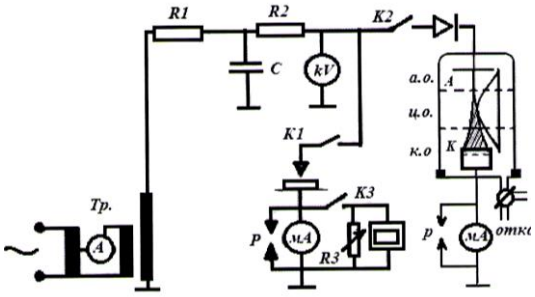



Figure 1. The circuit diagram of the experimental facility and contracted glow discharge including the anode region, cathode region and the central region [6, p. 40]

The pressure of the residual gas in the reactor with the sample before the plasma-forming gas puffing is $10^{-4}$ Pa. The pressure of plasma-forming gases (argon, air, $SF_6$) is 1.35 Pa, and is kept throughout the experiment.

The electrode power supply of the flare discharge reactor is carried out by the alternating voltage 6 kV by high-voltage transformer TBO-140. For continuous adjust of high voltage at the input of the transformer, the autotransformer has been incorporated. The discharge current in the inter-electrode space is 80 mA.

The design including the "needle-plane" electrode system has been used for investigation in highly inhomogeneous fields. The system of reactor electrodes like this makes it possible to create in the inter-electrode gap a sharply inhomogeneous field and excite an electric discharge of the corona type in it, and when the needle surface is limited by the dielectric material, the powerful flare discharge covering a wide section of the sample surface is kept from tip of needle in discharge volume.

The electrode system consists of 14 mm hollow cathode, the flat round anode of 27.5 mm radius. The distance between them is $d$=140 mm. The discharge regime in the processing processes is kept constant, by checking the discharge current more than (60 mA) and pressure (1.35 Pa) in the evacuated volume. The exposure time varies from 60 up to 120 sec.

The gas composition of the destructive emission from the polymer dielectric surface is tested by the time-of-flight mass spectrometer MS-4.

Preliminary mass spectrometric studies show that among the types of discharges in use, glow and flare discharges exert the most intense effect on polyvinylidene fluoride polymer film. Therefore, in this the effects of these two types of discharges have been investigated.

When studying the processes of electric charge accumulation in PVDF samples exposed to gas discharge (plasma), PVDF samples measuring 20×15×0.2 mm, the radius of spherules also increases. Further, they have been subjected to the uniaxial tension $\varepsilon$~0%, 400% at $T$=293 K. The effect of the gas discharge on the samples is carried out in the medium of $SF_6$ gas, Argon (Ar), and residual gas of atmospheric air. The sample treatment has been carried out in the cathode, anode and central parts of the gas discharge. The results of mass spectrometric studies show that the discharge carried out in the atmosphere of $SF_6$ gas has a significant effect on PVDF film surface.

## III. RESULTS AND DISCUSSION

The mass spectrogram characterizing the process of destructive emission from PVDF film surface exposed to the cathode region of the glow discharge in $SF_6$ gas is shown in Figure 2.

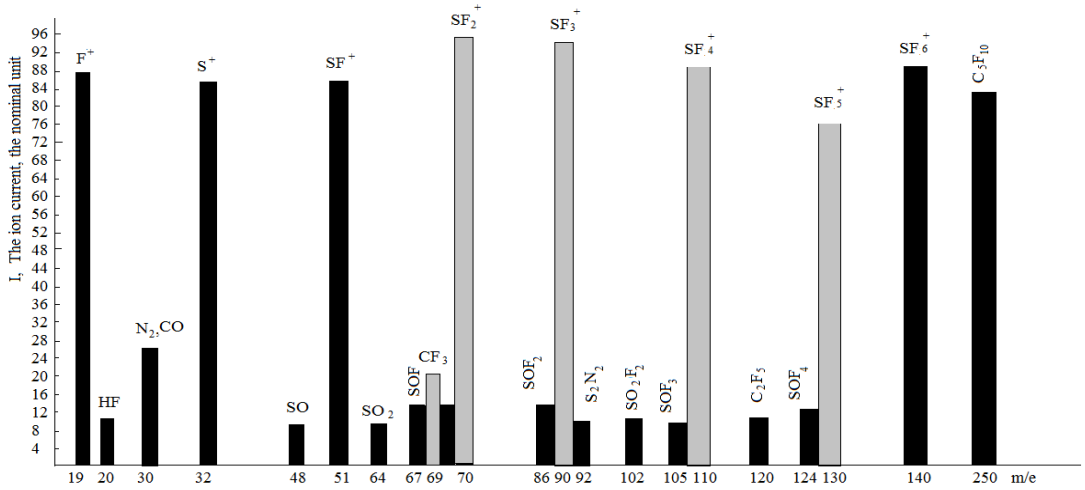



Figure 2. Mass spectrogram of destructive emission PVDF film gases exposed to the glow discharge in $SF_6$ atmosphere [7, p. 30]

The choice of $SF_6$ placing and forming gas is due to the fact that, being in neutral state, its chemical structure is compact enough (stable) and as a result $SF_6$ rarely enters the chemical reaction with any elements. However, ions, products of electric discharge in $SF_6$ gas, become aggressive and when exposed to a number of materials, including polymers, cause the of polymer destruction. Under the action of $SF_6$ ions on the polymer, atoms, molecules or polymer macromolecules spalls fall into the working volume. The mass spectrogram of neutral $SF_6$ gas at pressures in $10^{-2}$ Pa system is shown in Figure 3.

The starting material is PVDF in the form of powder. PVDF films are manufactured at $T$=523 K, at pressure 5,106 Pa; Then the samples are quenched in water at $T_1$=293 K, $T_2$=323 K and $T_3$=373 K, in this case PVDF films have a fine spherules structure in $K$=2-5 mkm sizes.

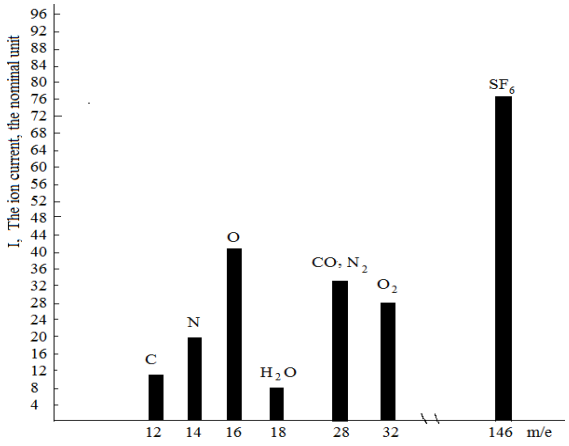



Figure 3. Mass-spectrogram of neutral $SF_6$ gas at pressure $10^{-2}$ Pa

In order to find out the duration of the conservation of PVDF film electrically charged state acquired by electric discharge, due to the short-term exposure to them we have conducted test experiments. The test experiment results indicate that the PVDF films maintain their charge state for at least six months. By increasing the crystallization

The $SF_6$ spectrogram exposed to the glow discharge at the same pressures in the system is shown in Figure 4. The spectrogram shows fluorine, sulfur and $SF_6$ ions. By exerting discharge products on PVDF sample, the increase of pressure in the system is observed, that is associated with the destruction of the sample material. The effect of different types of discharge and different regions of the same type of discharge, as well as their treatment in different discharge modes, are distinguished by the degree of medium ionization.

Therefore, in this paper there has been presented mass-spectrogram of PVDF sample destructive emission exposed to the glow discharge in $SF_6$ atmosphere, where the process of material destruction proceeds intensively enough.

The number of charges calculated on the basis of charge relaxation thermo grams from PVDF samples preliminarily exposed to glow discharge under different conditions is shown in Table 1.

Table 1. The number of charges accumulated in PVDF samples exposed to different regions of glow discharge [6, p. 126]

| Gaseous medium | Amount of charge $Q\times10^{-7}$ Kl | | |
|---|---|---|---|
| | In cathode region | In central Part | In anode region |
| $SF_6$ | 8.4 | 4.8 | 3.8 |
| Ar | 4.6 | 3.9 | 2.6 |
| Atmospheric air | 3.2 | 2.5 | 2.0 |

Analyses of investigation results shows that in the case of PVDF sample treatment in the cathode part of the discharge, and in $SF_6$ medium, the amount of accumulated charges is the greatest.

Thermo grams of charge relaxation from PVDF samples exposed to various glow discharge regions in the atmosphere of residual gas are shown in Figure 5 for argon and $SF_6$ gas.

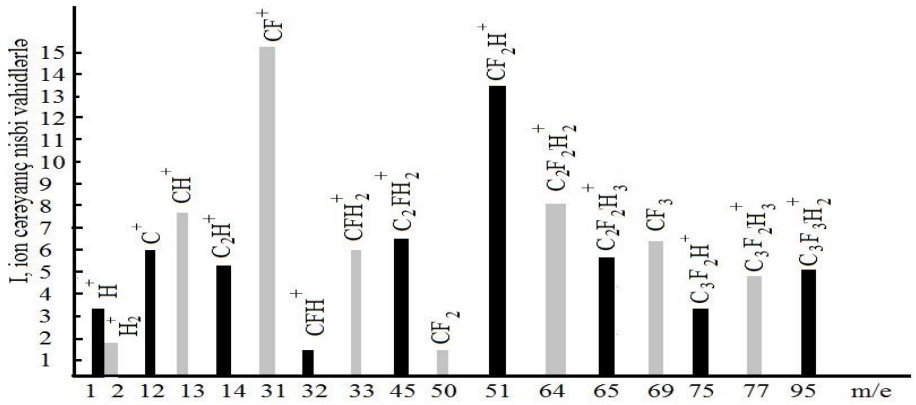



Figure 4. Mass spectrogram of $SF_6$ exposed to the glow discharge [7, p. 356]

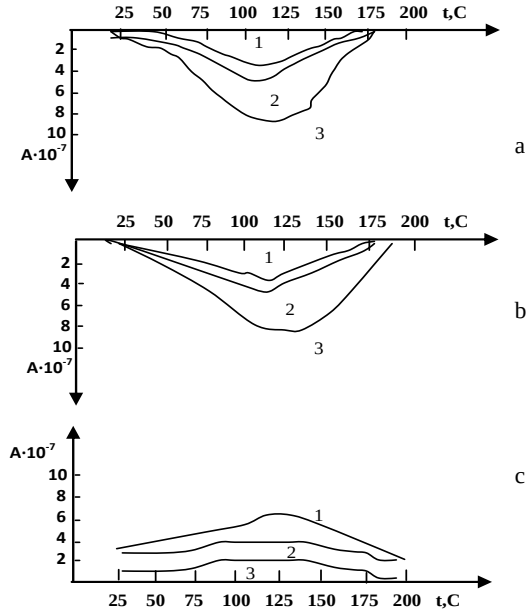



Figure 5. Thermo grams of PVDF charge relaxation exposed to (a) cathode, (b) middle and (c) anode regions of glow discharge 1-atmospheric, air. 2-Argon (Ar), 3-Elegas ($SF_6$) [6, p. 125]

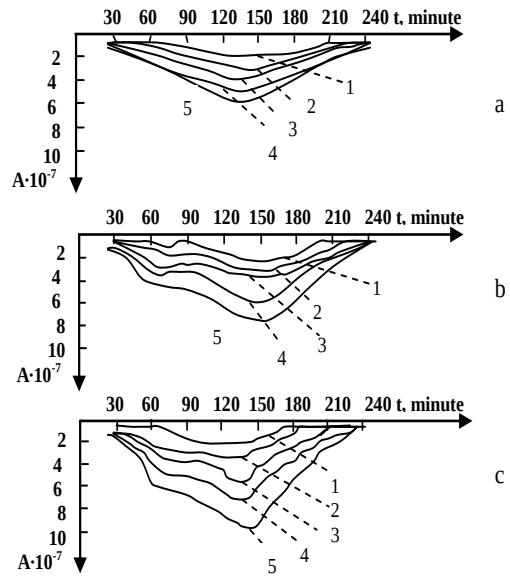


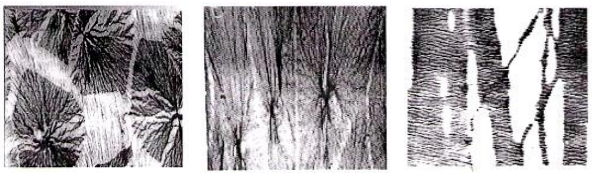

Figure 6. Thermo grams of charge relaxation of PVDF samples crystallized at different temperatures and exposed to uniaxial deformation, (a) $T_{cr}$=293 K, (b) 323 K, (c) 373 K 1- $\varepsilon$=0%, 2- 100%, 3- 200%, 4- 300%, 5- 400% Samples are exposed to flare discharge in $SF_6$ medium [8, p. 47]

It indicates that positive ions $SF_6^+$ affect a significant effect on the materials, that causes a host of defects in the sample, which enables the condition for the of partial discharge development to be realized. In reference [4, 5] it is noted that these or other properties of polymer materials largely depend on the manufacturing process.

In this connection, investigations of electric charge accumulation processes in PVDF samples crystallized under various conditions and exposed to various degrees of mechanical deformation have been carried out. Samples with different structural properties are exposed to the flare discharge in $SF_6$ medium.

Thermo grams of charge relaxation of PVDF samples crystallized at $T$=293 K, 323 K and 373 K and exposed to the uniaxial mechanical deformation $\varepsilon$~0%, 100%, 200%, 300% and 400% are shown in Figure 6.

It should be noted that by uniaxial mechanical deformation of non–oriented samples, significant structural changes take place in the material, i.e. in fact, the process of mechanical recrystallization has been taken place. In this case, the initial spherule structure breaks in and a new febrile structure is formed in the sample as shown in Figure 7.



(a) (b) (c)

Figure 7. Electron microscope image of non-oriented PVDF samples, (a) spherule structure, (b) change of the structure at uniaxial deformation of the initial samples by $\varepsilon$~6%, (c) change of the structure at $\varepsilon$~400% [9, p. 13, p. 14]

We note that in this work there has been made the deformation of the samples up to 400 is the intermediate stage of deformation (the limiting one for given samples is 600%, then the samples fail). By breaking the initial structural elements in the intermediate stage of deformation, a host of additional defects are formed in the sample. In this case, the larger the initial structural elements, are the greater the defects are. There have been presented the results characterizing the of charge accumulation in PVDF.

The investigation results of the studies are shown in Table 2. The crystallization temperature increase and degree of uniaxial deformation, the number of accumulated charges in the samples increases, which is explained by the fact that in both cases the number and size of the defects in these regimes rise due to the increase of structural formation size in the samples.

Table 2. Results are presented, characterize the accumulation exposed to flare discharges in $SF_6$ medium [8, p. 47]

| Deformation degree<br>Crystallization temperature | Amount of charge $Q\times10^{-7}$ KPa | | | | |
|---|---|---|---|---|---|
| | $\varepsilon$, 0% | $\varepsilon$, 100% | $\varepsilon$, 200% | $\varepsilon$, 300% | $\varepsilon$, 400% |
| $T_{cr}$ = 293 °K | 1.4 | 2.5 | 3.6 | 5.3 | 7.2 |
| $T_{cr}$ = 323 °K | 2.6 | 3.5 | 4.7 | 6.4 | 7.8 |
| $T_{cr}$ = 373 °K | 3.8 | 4.6 | 5.3 | 7.2 | 8.4 |

## IV. CONCLUSION

By method of relaxation electric charge measurements, it is established that the sizes and degree of presence of defects in PVDF samples depend on the production cycle of sample manufacturing, which in turn determines the supramolecular structure of the material. On the base of obtained results, it is possible to choose certain technological conditions for of PVDF film production under which the degree of presence of defects and size of the defects are minimum and the development of partial discharges leading to electrical breakdown of the material appear to be impossible for the low power of the discharge taking place in defects with minimum sizes.

The results of studies of the relationship between the structure and properties of polyvinylidene fluoride (PVDF) samples exposed to the interaction of glow and flare discharges in ambient atmospheric air, argon and $SF_6$ atmospheric gases are presented. It is shown that the amount of accumulated electric charges in a sample subjected to an electric discharge depends on the defects and the degree of defectiveness of the samples. The processes of thermally stimulated charge relaxation from PVDF samples were studied. This makes it possible to qualitatively evaluate the change in the size of the defects and the degree of defectiveness of the samples by changing the material properties.

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