

UDC 537.521.7:621.315.6

INFLUENCE OF THE MODIFYING AGENT NANO-POWDER OF NICKEL ON BASIC ELECTROPHYSICAL CHARACTERISTICS OF POLYVINYLIDENE FLUORIDE

O.S. Gefle, S.M. Lebedev, S.N. Tkachenko

The High Voltage Research Institute of TPU

E-mail: polymer@hvd.tsk.ru

Results of the study of temperature-frequency relationships of dielectric permittivity and dielectric loss tangent, electric strength and permolecular structure of polyvinylidene fluoride, modified nano-powder of nickel are presented in this paper. It was shown that load nano-particles of nickel in polyvinylidene fluoride lead to change of structure and electrophysical characteristics one.

Introduction

One of the most perspective ways of electrical engineering material is design of new polymeric composite materials (PCMs) with high specific stored energy (more than 10^5 J/m³) for high voltage impulse equipment. Such materials can find their application as an insulation of capacity storage devices operating under the impulse voltage. Similar materials should have the following electrophysical characteristics: high values of permittivity (ϵ), electric and mechanical strength, specific resistance volume as well as low value of dielectric loss angle tangent ($\text{tg}\delta$) in the wide range of external field frequency and operating temperature.

Design of PCM with necessary electrophysical parameters is possible only under the condition of good compatibility of polymeric matrix and filler. Polyvinylidene fluoride (PVDF) can be a sufficiently effective polymeric matrix, which is referred to semi crystalline polymers with the crystallinity degree approximately 50 % [1]. The given polymer has high operating temperature (to 423 K) and permittivity $\epsilon=9$ at frequency 10^6 Hz, that has to provide homogeneous distribution of the local field in PCM volume and less dispersion of complex permittivity. Besides, PVDF is stable to ultraviolet and ionizing radiation, possesses piezo- and pyroelectric properties that can be improved by filling with soot of ferroelectric ceramics [2].

Filling a polymeric matrix with fine filler of inorganic origin modifies sufficiently the structure and properties of PCM owing to interfacial interaction and formation of boundary nanolayer in the vicinity of filler particles [3]. For example, adding 3,5 wt. of nickel powder into polypropylene spherulites become two times less in comparison with pure polypropylene, where in the centre of each spherulite there are the particles of nickel powder initiating the formation of polymeric nucleus on their surface [4]. In this case the increase in polypropylene film strength is observed. Hence, stabilisation and improvement of PVDF electrophysical characteristics can be obtained by artificial production of crystallization centres when filling polymer with fine metal fillers, e. g., nickel (Ni). In this connection, the purpose of the given paper is to study the influence of Ni nanoparticle concentration on electrophysical characteristics and permolecular structure of PVDF.

Experimental technique and samples

The object of examination was PVDF and compositions on its base with different concentration of modifying filler. Nanopowder Ni with an average particle size 200 nm of spherical shape was used as a filler. The technique of nanopowder production is described in details in [5].

Composition of composites under study is presented in Table 1.

Table 1. Designation and composition of examined PVDF polymer composites

| № of composition | Content of Ni in PVDF, wt. % |
|------------------|------------------------------|
| K1 | 0 |
| K2 | 0,5 |
| K3 | 1,0 |
| K4 | 2,0 |

Measurements of relative permittivity ϵ' and $\text{tg}\delta$ were performed by means of measuring instrument Solartron Analytical [6] under AC voltage 3 V in the frequency range from 10^{-4} to 10^6 Hz and that of temperature from 293 to 373 K. In the frequency range from 10^{-4} to 1 Hz relative measuring error of ϵ' and $\text{tg}\delta$ was not more than 5 and 8 %, respectively. At frequency $F > 1$ Hz relative measuring error of these parameters amounted not more than 1 and 3 %. Measurements were carried out by the method [7]. Investigation of ϵ' and $\text{tg}\delta=f(T,K)$ at fixed frequency $F=10^{-4}$ Hz was performed separately due to long duration of measurement procedure. Measurements of parameters were made under stationary temperature condition, in which accuracy of specification and maintenance of temperature at each temperature step was ± 1 K.

Electrical strength for the given materials was defined at AC voltage $F=50$ Hz at smooth raise of voltage with the velocity 2 kV/sec. The rapture was made in the cell filled with transformer oil in the semi-sphere – plane electrode system. The radius of semi-sphere rounding was 12,5 mm. The thickness of the tested samples amounted 100 ± 5 mkm, diameter – 70 mm. The average value of electrical strength was calculated by the formula:

$$E_{\text{np, cp}} = \bar{U}_{\text{np}} / \bar{\Delta},$$

where \bar{U}_{np} is the average value of disruption voltage, $\bar{\Delta}$ is the average thickness of the samples. Not less than 20 samples were tested. The confidence interval for $E_{\text{np, cp}}$ (ΔE) was calculated by the formula:

$$\Delta E = t_{0,05} \frac{\sigma_E}{\sqrt{N}},$$

where $t_{0,05}$ is the Student's criteria at the confidence probability 0,95; σ_E is the root-mean-square deviation, $N=20$ is the total number of the tested samples.

To reveal the influence of fine filler on permolecular structure the sections of the samples were prepared of the compositions K1–K4, which were studied under polarized light by means of microscope MIM-7 at different magnification.

Experimental results and discussion

The dependencies of $\text{tg}\delta=f(F, T)$ for PVDF in the frequency range from 10^{-2} to 10^6 Hz are presented in Fig. 1. It is seen that at the frequencies $F < 10$ Hz there is the maximum $\text{tg}\delta$, which shifts toward the higher frequencies (HF) with the temperature increase. At frequencies $F > 1$ kHz the values of $\text{tg}\delta$ are not more than 0,3 over the whole temperature range.

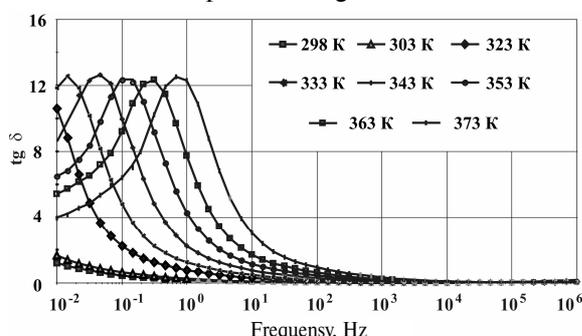


Fig. 1. Dependences of $\text{tg}\delta=f(F, T)$ for PVDF in the frequency range from 10^{-2} to 10^6 Hz

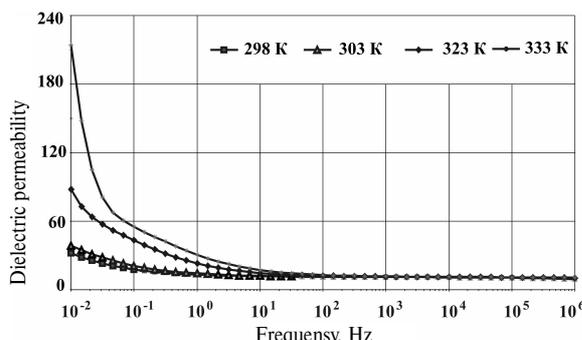


Fig. 2. Dependences of $\epsilon'=f(F, T)$ for PVDF in the frequency range from 10^{-2} to 10^6 Hz

In Fig. 2 the dependences of $\epsilon'=f(F, T)$ for PVDF in the frequency range from 10^{-2} to 10^6 Hz are shown. It is obvious that at the frequencies $F < 10$ Hz the non-linear growth of real component of the complex permittivity is observed. In the frequency range from 100 to 10^6 Hz there is no significant change of ϵ' , for example, at the frequency 10^6 Hz the values of ϵ' amount 9,0 and 10,6 at $T=298$ K and 373 K, respectively.

Filling of polymeric matrix with 0,5 wt. % Ni results in not only the shift of $\text{tg}\delta$ maximum position toward the lower frequencies (LF), but also the change of its value at

$T > 343$ K (Fig. 3). Thus, at $T=373$ K the maximum value of $\text{tg}\delta$ is approximately 15 % more than PVDF, and it corresponds to the frequency 0,11 Hz instead of 0,7 Hz for PVDF. However, filling with modifying filler does not influence essentially the values of $\text{tg}\delta$ at the frequencies $F > 10^3$ Hz. In the given frequency range the values $\text{tg}\delta$ for composition K2 as well as for pure PVDF are not more than 0,3 for all investigated temperatures.

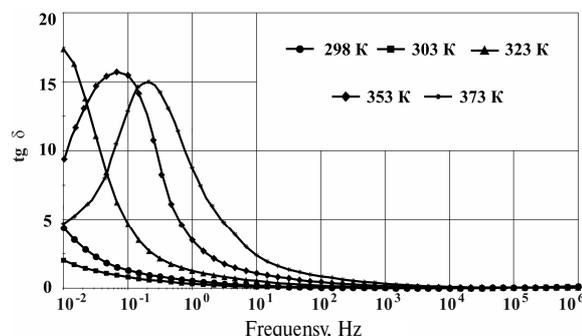


Fig. 3. Dependences of $\text{tg}\delta=f(F, T)$ for PVDF+0,5 wt. % Ni

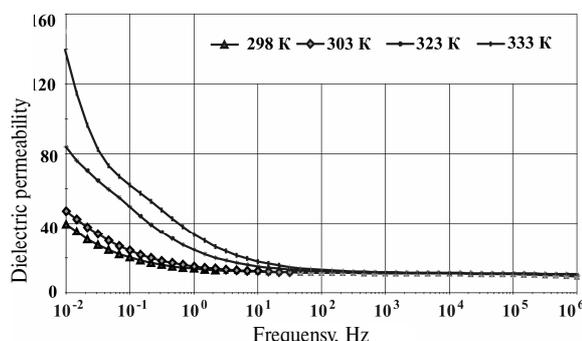


Fig. 4. Dependences $\epsilon'=f(F, T)$ for PVDF + 0,5 wt. % Ni

Fig. 4 shows the dependence of $\epsilon'=f(F, T)$ for PVDF+0,5 wt. % Ni that indicates that the behaviour of ϵ' is the same as for pure PVDF.

Increasing concentration of Ni in the polymer from 1 to 2 wt. % leads to even more growth of $\text{tg}\delta$ maximum values, moreover, in comparison with composition K2 the shift of $\text{tg}\delta$ maximums occurs not toward the lower frequencies, but to HF. For example, at $C=1$ vol. % Ni (Fig. 5) and $T=373$ K the maximum position of $\text{tg}\delta$ corresponds to $F \approx 0,3$ Hz, but its value is approximately 1,4 and 1,6 times more than PVDF+0,5 wt. % Ni and pure PVDF, respectively. As for ϵ' , as it is the case with PVDF and K2, the changes in values of this parameter is not sufficient on the temperature in HF and amounts not more than 5%. At frequencies $F < 10$ Hz the decrease of ϵ' values in comparison with pure PVDF and composition K2 is observed.

At $C=2$ vol. % Ni the maximum position shifts toward the even higher frequencies and at $T=373$ K it approximates to $F \approx 0,7$ Hz, that is to the frequency of relaxation maximum of $\text{tg}\delta$ of non-modified PVDF.

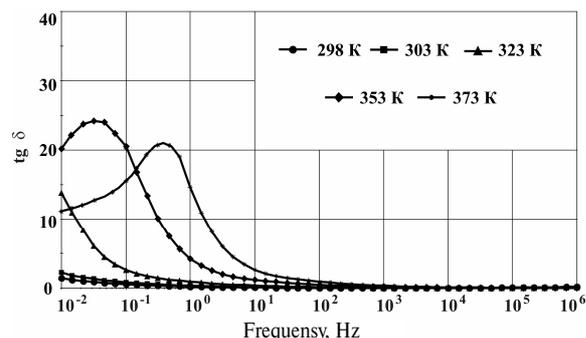
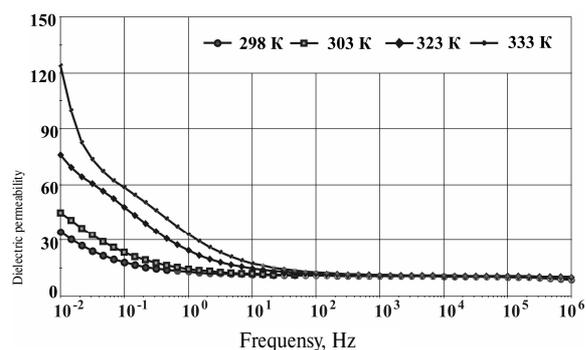
Investigation of complex impedance of the given polymeric composites at frequency $F=10^{-4}$ Hz was performed for calculation of specific volume resistance value

$$\rho_v = Z_a \cdot S / \Delta, \text{ Ohm} \cdot \text{m},$$

Table 2. Dependence of ρ_v on nano-dielectric temperature on the basis of PVDF with different content of Ni nano-powder on temperature at $F=10^{-4}$ Hz

| № of composition | ρ_v , Ohm·m at T, K | | | | | | | | |
|------------------|--------------------------|---------------------|---------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | 298 | 303 | 313 | 323 | 333 | 343 | 353 | 363 | 373 |
| K1 | $2,1 \cdot 10^{12}$ | $2,2 \cdot 10^{11}$ | $3,1 \cdot 10^{10}$ | $4,4 \cdot 10^9$ | $1,0 \cdot 10^9$ | $4,6 \cdot 10^8$ | $2,1 \cdot 10^8$ | $1,5 \cdot 10^8$ | $5,4 \cdot 10^7$ |
| K2 | $4,5 \cdot 10^{12}$ | $4,5 \cdot 10^{11}$ | $5,1 \cdot 10^{10}$ | $6,8 \cdot 10^9$ | $1,0 \cdot 10^9$ | $5,4 \cdot 10^8$ | $2,3 \cdot 10^8$ | $9,8 \cdot 10^7$ | $4,9 \cdot 10^7$ |
| K3 | $2,9 \cdot 10^{11}$ | $2,7 \cdot 10^{11}$ | $3,1 \cdot 10^{10}$ | $4,0 \cdot 10^9$ | $6,5 \cdot 10^8$ | $2,9 \cdot 10^8$ | $1,3 \cdot 10^8$ | $6,6 \cdot 10^7$ | $3,3 \cdot 10^7$ |
| K4 | $2,6 \cdot 10^{12}$ | $2,9 \cdot 10^{11}$ | $3,6 \cdot 10^{10}$ | $5,2 \cdot 10^9$ | $8,0 \cdot 10^8$ | $3,3 \cdot 10^8$ | $1,3 \cdot 10^8$ | $6,5 \cdot 10^7$ | $2,9 \cdot 10^7$ |

where Z_a is the experimental value of active component of complex impedance at $F=10^{-4}$ Hz; S is the square of measuring probe; Δ is the sample thickness.


Fig. 5. Dependences of $tg\delta=f(F, T)$ for PVDF+1,0 wt. % Ni

Fig. 6. Dependences of $\epsilon'=f(F, T)$ for PVDF+1,0 wt. % Ni

The results of calculation of ρ_v for investigated PCM are listed in Table 2. It is seen from Table 2 that in the temperature range from 293 to 323 K at nickel concentration $C=0,551$ vol. % the specific volume resistance of modified PVDF (K2) increases in comparison with K1 approximately 2,2...1,5 times. At $T>353$ K the value of ρ_v decreases in comparison with PVDF approximately 1,3 times. With increase of Ni concentration there begins the decrease of ρ_v in

comparison with compositions K1 and K2 at $T>333$ K, but at $T=373$ K the value of ρ_v of K3 and K4 compositions is approximately 1,6 and 1,9 times less than for K1.

Dependences of $\ln\rho_v=f(1/T)$ represents two crossing lines with different slope angle, where points of the line crosspoint correspond to the glass-transition temperature T_c of PVDF, which lies within the limits 338...343 K [8]. The values of activation energy W_i , corresponding to different slope angles were determined as following

$$W=[\Delta \ln\rho_v/\Delta(1/T)] \cdot K,$$

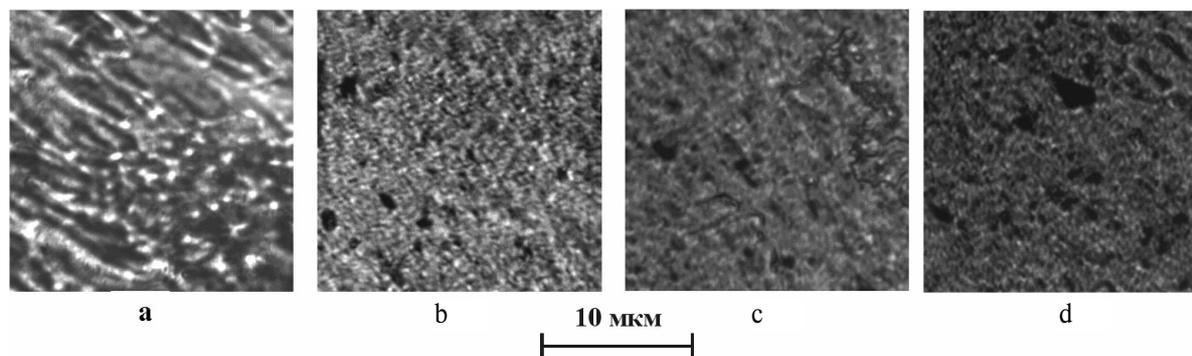
where $\Delta \ln\rho_v$ is the difference of value logarithms ρ_v at corresponding low- and high temperature regions; $\Delta(1/T)$ is the difference of inverse temperatures at these temperature regions; T is the absolute temperature; K is the Boltzman's constant.

The results of calculation of activation energy values presented in Table 3, show that activation energy of modified and non-modified PVDF in glassy state (at $T<T_c$), is approximately 2 times higher than in high-elasticity state. In this case the maximum values of W_1 (at $T<T_c$) and W_2 (at $T>T_c$) are observed for the composition K2 (PVDF+0,5 wt. % Ni).

Table 3. Energies of activation and glass-transition temperature of the examined polymer compositions

| № of composition | W_1 , eV | W_2 , eV | T_c , K |
|------------------|-----------------|-----------------|-----------|
| K1 | $1,66 \pm 0,02$ | $0,78 \pm 0,01$ | 338 |
| K2 | $1,77 \pm 0,01$ | $0,88 \pm 0,02$ | 340 |
| K3 | $1,75 \pm 0,04$ | $0,80 \pm 0,03$ | 333 |
| K4 | $1,70 \pm 0,05$ | $0,85 \pm 0,03$ | 333 |

The following values of PVDF electrical strength and compositions on its basis have been obtained: for K1: $E_{np, cp} \pm \Delta E = 70,40 \pm 2,77$ kV/mm; for K2 – $71,06 \pm 3,01$ kV/mm; for K3 – $68,53 \pm 2,07$ kV/mm; for K4 – $67,82 \pm 2,59$ kV/mm. It is seen that when filling PVDF with 0,5 vol. % Ni the electrical strength of the


Fig. 7. Microphotography of the sample sections: a) K1; b) K2; c) K3; d) K4

produced PCM does not change essentially in comparison with polymeric matrix. At further increase of Ni nano-powder concentration in the polymer there is a tendency for decrease of PCM electric strength.

In Fig. 7 the picture of sample sections of the examined polymeric compositions are presented. It is seen from Fig. 7 that filling with Ni results in sufficient changes of PVDF permolecular structure. Macro-spherulite structure of PVDF is transformed into micro-spherulite one, moreover, the most homogeneous structure is observed for the composition K2. With increase in filler concentration the structure of modified PVDF becomes more heterogeneous due to increase in agglomerate size of Ni nanoparticles. For example, at $C=0,5$ vol. % average size of agglomerates amounts approximately 0,6 mkm, but at $C=2,0$ vol. % – 2,5 mkm.

The analysis of the experimental results has shown that in the LF region of the investigated temperature range the anomalous high values of $\text{tg}\delta$ are observed for both non-modified and modified PVDF. It means that Ni particles are active filler for PVDF and high values of $\text{tg}\delta$ are explained by, first of all, non-linear growth of ϵ' . As a rule, the values $\text{tg}\delta > 1$ are presented in ferro- and magnetoelectrics, so that dispersion of complex permittivity in the LF range of external electric field can be conditioned by the orientation of «domain» electric moments, which are macrocrystalline structures with high proper dipole moment [9]. Since PVDF is referred to semi-crystalline polymers, the increase in its conductivity can greatly contribute in growth of $\text{tg}\delta$ at $T \geq 333...343$ K, conditioned by molecule dissociation in the amorphous layers [9]. The shift of $\text{tg}\delta$ maximum to LF region for the composition K2 in comparison with pure PVDF correlates with the change in the form of crystalline structure and the energy of their cohesive interaction: the higher the energy of cohesive interaction is, the higher the values of conductance activation energy are (see Table 3), the more is the shift of $\text{tg}\delta$ maximum toward the low frequency region at the same temperature of the environment.

Besides, increase in concentration of Ni in polymer changes its T_c . Decrease of T_c indicates the loosening of package and appearance of internal stress, but increase of T_c is conditioned by restrictions in chain mobility as a

result of their connection with the filler surface [10]. Small spread of T_c for the examined compositions shows the mutual influence of these two factors.

Since in the LF range the investigated polymer compositions have the values of $\text{tg}\delta > 1$, they cannot be applied as isolation of capacity storage devices at the frequency of external electric field $F < 10$ Hz. The given materials can be of interest from the point of view of their pyro- and piezoelectric properties.

In the frequency range from 10^3 to 10^6 Hz in the whole investigated temperature range the values of $\text{tg}\delta$ for all examined PCM are not more than 0,3 at insufficient change of permittivity. Hence, the given materials can be used as a polymeric matrix to design PCM with high specific energy content. However, among the studied materials the composition K2 possesses the best properties. This indicate that optimal concentration of Ni should lie within the range from 0,1 to 0,5 wt. %. In determination of optimal concentration of Ni particles there is an essential possibility of designing PCM with stable properties in the frequency range from 10^3 to $3...5 \cdot 10^6$ Hz, that invites further investigation.

Conclusion

1. Filling PVDF with Ni nanoparticles results in transformation of its permolecular structure and glass-transition temperature owing to the formation of artificial nuclei of structure formation.
2. Changes in permolecular structure influence the PCM electrophysical characteristics and conductance activation energy in weak electric fields.
3. The examined PCM possess quasi-high values of the real and imaginary components of complex permittivity at the frequencies $F < 10$ Hz, therefore they can find application in the devices based on pyro- and piezoelectric effect.
4. PCMs on the basis of PVDF are perspective polymer materials for design of materials with high values of specific stored energy in the frequency range from 10^3 to 10^6 Hz in the temperature range from 293 to 373 K, in this case the optimal concentration of Ni has to be within the range from 0,1 to 0,5 wt. %.

REFERENCES

1. Reference on electro-engineering materials / Ed. by Yu.V. Koritskiy et al. – Moscow: Energoatomizdat, 1986. – V. 1. – 368 p.
2. Chan H.L.W., Chan W.K., Zhang Y., Choy C.L. Pyroelectric and piezoelectric properties of lead titanate/polyvinylidene fluoride-trifluoroethylene 0-3 composites // IEEE Trans. Dielect. Electr. Insul. – 1998. – V. 5. – № 4. – P. 505–512.
3. Tanaka T. Dielectric nanocomposites with insulating properties // IEEE Trans. Dielect. Electr. Insul. – 2005. – V. 12. – № 5. – P. 914–928.
4. Gul V.E., Turkova N.N., Golubeva M.G. On increasing the strength of metal-filled conductive polymeric films under the influence of static magnetic field // Doklady AN of USSR. – 1971. – V. 199. – № 1. – P. 135–137.
5. Tikhonov D.V. Electroblasting production of ultra-fine powders of complex composition. Dis. ... Cand. of Tech. Scien. – Tomsk, 2000. – 240 p.
6. Solartron Analytical. Impedance/Gain-Phase Analyzer 1260 and Dielectric Interface 1296, Operating manual. – 2001; <http://www.solartronanalytical.com>.
7. Tkachenko S.N., Khramtsov S.E. Measurement of dielectric electrophysical characteristics by the method of dielectric spectroscopy // Modern Technology and Engineering: Materials of the 12th Intern. Scient.-Pract. Conf. Of Students and Young Scientists. – Tomsk, 2006. – V. 1. – P. 62–63.
8. Physics of polymers / Ed. by M.V. Volkenstein. – Moscow: Inostrannaya Literatura, 1960. – 552 p.
9. Sinha D., Muralidhar C., Pillai P.K.C. Dielectric behaviour in lead zirconate titanate (PZT) polyvinylidene fluoride (PVDF) composite // Proc. 2 Intern. Conf. Dielec. – Erlangen, 1986. – P. 227–231.
10. Solomko V.P. Filled crystallisable polymers. – Kiev: Naukova Dumka, 1980. – 264 p.

Received on 23.11.2006