

Novel Polymeric Composite Materials with High Specific Storage Energy¹

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

*High-Voltage Research Institute of Tomsk Polytechnic University, 2a, Lenin ave., Tomsk, 634028, Russia
Tel./Fax: +7(3822) 41-91-57; E-mail: polymer@hvd.tsk.ru*

Abstract – Temperature-frequency dependencies of the complex permittivity of composite materials with high permittivity on the basis of polyvinylidene fluoride were studied in this paper. The main parameters of dielectric relaxation spectra such as characteristic frequency and relaxation time of new composites with high specific storage energy were estimated in this work by means of the dielectric spectroscopy method.

1. Introduction

One of the advance fields of the material science is the development of novel polymeric composite materials (PCM) with high permittivity for HV techniques. These materials may be widely used for HV energy storage devices for the pulse power engineering. The front duration of voltage impulses of such HV energy storage devices may be changed from some nanoseconds to some seconds. Therefore PCM should have stable electrical properties over the frequency range. Filling of a polymeric matrix with ultra-disperse inorganic fillers results in the essential modification of the structure and properties of PCM due to both the interface interaction at the boundary matrix/filler and formation of nano-layers at this boundary [1–5]. It can result in the redistribution of the local field inside PCM and frequency dispersion of the complex permittivity. On designing these HV energy storage devices, the knowledge of the frequency spectrum of the complex permittivity of polymeric matrixes and fillers is necessary.

The study of temperature-frequency dependencies of the complex permittivity of polymeric nanodielectrics with high specific storage energy was the aim of this work.

2. Experimental procedure and samples

Polyvinylidene fluoride (PVDF, “Plastpolymer” Corp. Ltd., Russia, St.-Petersburg) was used as a matrix in this study. Nano-powders of nickel (Ni) and lead zirconate titanate (PZT) with average dimension of particles 200 and 800 nm were used as fillers. Compositions used in this study are listed in Table 1.

Measurements of the real part ϵ' of the complex permittivity and $\tan\delta$ were carried out under AC voltage 3 V at temperatures 20–100 °C in the frequency range from 10^{-2} Hz to 1 MHz by using the Solartron Instrument (Impedance/Gain-Phase Analyzer Solartron

1260 + Dielectric Interface Solartron 1296) [6]. From five to ten measurements per decade over the frequency range were carried out for all samples.

Table 1. Polymeric compositions used in this study

Type	Composition
C1	PVDF
C2	PVDF + 0.5 wt % Ni
C3	PVDF + 1.0 wt % Ni
C4	PVDF + 2.0 wt % Ni
C5	PVDF + 0.5 wt % Ni +25 wt % PZT
C6	PVDF + 0.5 wt % Ni +50 wt % PZT
C7	PVDF + 0.5 wt % Ni +65 wt % PZT

The measurements of ϵ' and $\tan\delta$ at the fixed frequency $F = 10^{-4}$ Hz were carried out separately because of long duration of the measuring procedure. The accuracy of the temperature adjustment at each temperature step was ± 1 °C.

3. Experimental results and discussion

The experimental results of study of temperature-frequency dependencies of $\tan\delta$ for PVDF are shown in Fig. 1.

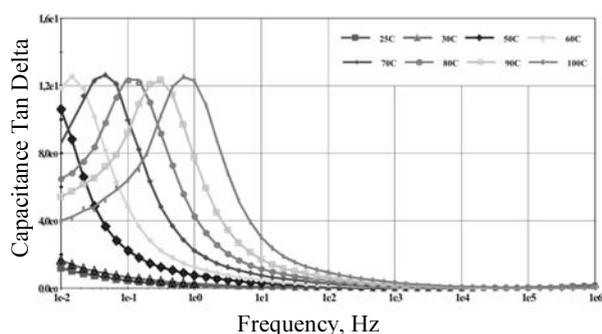


Fig. 1. Dependencies $\tan\delta = f(F, T)$ for PVDF

It can be seen that for PVDF the $\tan\delta$ peak is shifted towards the higher frequency with changing temperature from 20 to 100 °C. For example, the change of temperature from 60 to 100 °C results in the shift of $\tan\delta$ peak position from 0.015 up to 0.7 Hz (Fig. 1).

Figure 2 shows the dependencies of $\epsilon' = f(F, T)$ for PVDF. It is obvious that at $F < 10$ Hz a non-linear increase in ϵ' is observed. Modification of PVDF by

0.5 wt % Ni results in not only the shift of $\tan\delta$ peak position towards the lower frequency but also the change of its value at $T \geq 70^\circ\text{C}$ (Fig. 3).

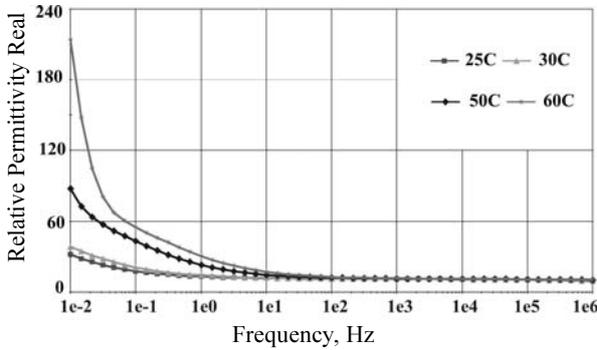


Fig. 2. Dependencies $\epsilon' = f(F, T)$ for PVDF

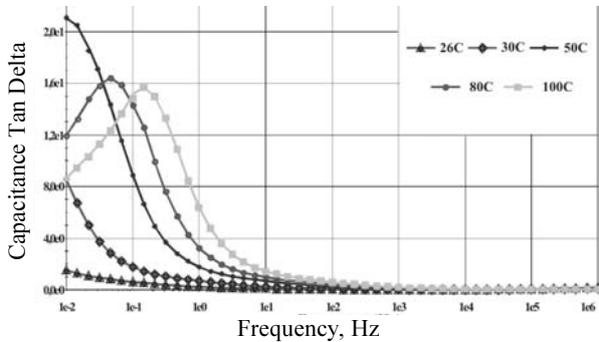


Fig. 3. Dependencies $\tan\delta = f(F, T)$ for PVDF modified by 0.5 wt % Ni

The value of $\tan\delta$ at $T = 100^\circ\text{C}$ is increased by 15% compared to that for PVDF. However, the value of $\tan\delta$ for the modified PVDF does not change at $F > 1\text{ kHz}$. The dependencies of $\epsilon' = f(F, T)$ for C2 have the same character (Fig. 4) just like for PVDF.

The $\tan\delta$ value is increased with increasing nickel content in PVDF matrix up to 2 wt %. However in this case, the shift of the $\tan\delta$ peak position towards the higher frequency is observed compared to that for C2. For example, the $\tan\delta$ peak position for C3 (Fig. 5) at $T = 100^\circ\text{C}$ is observed at $F \approx 0.3\text{ Hz}$ and its

value is increased by a factor of 1.4 and 1.6 compared to that for C2 and C1, respectively. The value of ϵ' in this case at $F < 10\text{ Hz}$ is decreased compared to that for C1 and C2. For comparison, the $\tan\delta$ peak position for C4 at $T = 100^\circ\text{C}$ is shifted to $F \approx 0.7\text{ Hz}$ just like for PVDF.

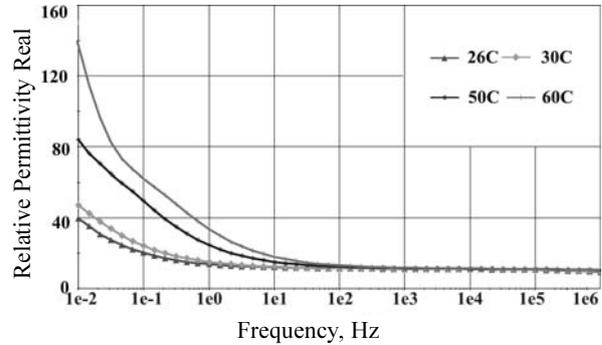


Fig. 4. Dependencies $\epsilon' = f(F, T)$ for PVDF modified by 0.5 wt % Ni

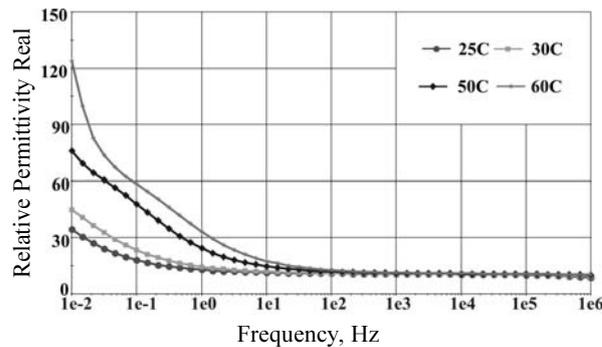


Fig. 5. Dependencies $\epsilon' = f(F, T)$ for PVDF modified by 1.0 wt % Ni

Measurements of the complex impedance Z^* for compositions C1...C4 at $F \approx 10^{-4}\text{ Hz}$ were carried out for the calculation of the specific resistance $\rho_v = Z_a S / \Delta$ [ohm · m], where Z_a is the real part of the complex impedance; S is the measuring electrode cross-sectional area; Δ is the sample thickness. The calculating results for ρ_v are represented in Table 2.

Table 2. The values of ρ_v at different temperatures and $F = 10^{-4}\text{ Hz}$

Composition Type	ρ_v , Ohm · m, at different temperatures $^\circ\text{C}$								
	20	30	40	50	60	70	80	90	100
C1	$2.1 \cdot 10^{12}$	$2.2 \cdot 10^{11}$	$3.1 \cdot 10^{10}$	$4.4 \cdot 10^9$	$1.0 \cdot 10^9$	$4.6 \cdot 10^8$	$2.1 \cdot 10^8$	$1.5 \cdot 10^8$	$5.4 \cdot 10^7$
C2	$4.5 \cdot 10^{12}$	$4.5 \cdot 10^{11}$	$5.1 \cdot 10^{10}$	$6.8 \cdot 10^9$	$1.0 \cdot 10^9$	$5.4 \cdot 10^8$	$2.3 \cdot 10^8$	$9.8 \cdot 10^7$	$4.9 \cdot 10^7$
C3	$2.9 \cdot 10^{12}$	$2.7 \cdot 10^{11}$	$3.1 \cdot 10^{10}$	$4.0 \cdot 10^9$	$6.5 \cdot 10^8$	$2.9 \cdot 10^8$	$1.3 \cdot 10^8$	$6.6 \cdot 10^7$	$3.3 \cdot 10^7$
C4	$2.6 \cdot 10^{12}$	$2.9 \cdot 10^{11}$	$3.6 \cdot 10^{10}$	$5.2 \cdot 10^9$	$8.0 \cdot 10^8$	$3.3 \cdot 10^8$	$1.3 \cdot 10^8$	$6.5 \cdot 10^7$	$2.9 \cdot 10^7$
C5	$8.7 \cdot 10^{12}$	$1.1 \cdot 10^{12}$	$1.3 \cdot 10^{11}$	$2.0 \cdot 10^{10}$	$3.2 \cdot 10^9$	$8.1 \cdot 10^8$	$3.1 \cdot 10^8$	$1.9 \cdot 10^8$	$1.1 \cdot 10^8$
C6	$2.8 \cdot 10^{12}$	$7.9 \cdot 10^{11}$	$2.2 \cdot 10^{11}$	$6.5 \cdot 10^{10}$	$2.2 \cdot 10^{10}$	$7.2 \cdot 10^9$	$2.5 \cdot 10^9$	$1.0 \cdot 10^9$	$4.3 \cdot 10^8$
C7	$3.9 \cdot 10^{12}$	$1.1 \cdot 10^{12}$	$3.7 \cdot 10^{11}$	$1.2 \cdot 10^{11}$	$4.0 \cdot 10^{10}$	$1.3 \cdot 10^{10}$	$5.2 \cdot 10^9$	$2.2 \cdot 10^9$	$9.7 \cdot 10^8$

It is obvious that the specific resistance for C2 is increased by a factor of 2.2...1.5 with changing temperature from 20 to 50 °C compared to that for C1. At $T > 80^\circ\text{C}$ the value of ρ_v is decreased by a factor of 1.3 compared to that for C1. The decrease in ρ_v begins at $T > 60^\circ\text{C}$ with increasing a nickel content compared to that for C1 and C2. The value of ρ_v is decreased at $T = 100^\circ\text{C}$ by a factor of 1.6 and 1.9 for C3 and C4 respectively compared to PVDF (C1).

Dependencies $\ln\rho_v = f(1/T)$ are two crossing lines with different slopes. The intersection point of these straight lines gives the value of the glass transition temperature T_g , which for PVDF is equal to 65...70 °C [7].

The experimental values of the dielectric strength for composites studied are represented in Table 3. It is obvious that the dielectric strength is unchangeable for all PCMs compared to that for C1.

Table 3. The dielectric strength for composites

Type	C1	C2	C3	C4
E_b , kV/mm	70.4 ± 2.8	71.1 ± 3.0	68.5 ± 2.1	67.8 ± 2.6

Micrographs of sub-molecular structure for composites C1–C4 are shown in Fig. 6.

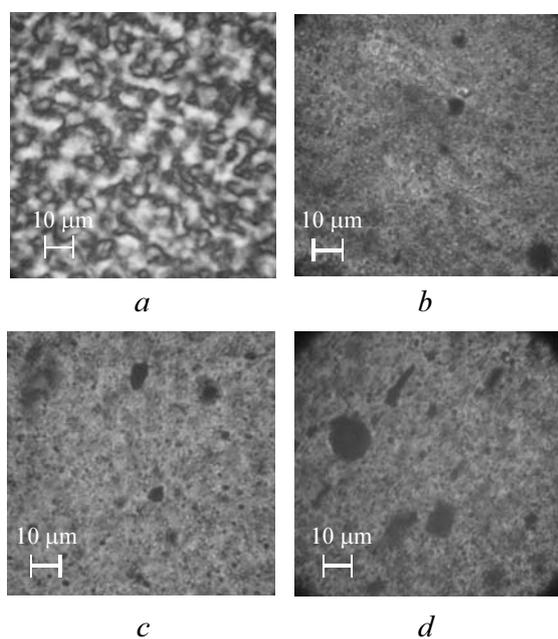


Fig. 6. Micrographs of sub-molecular structure for modified PVDF: a – C1; b – C2; c – C3; d – C4

It can be seen that the filling of PVDF by nanoparticles of Ni results in the essential modification of sub-molecular structure of composites. Large-size spherulite structure of PVDF is transformed into a small-size spherulite structure. Sub-molecular structure of modified PVDF becomes more inhomogeneous with increasing Ni content due to the increase in the

size of agglomerates of Ni-particles. The average size of Ni-agglomerates is 2 and 12.5 μm for C2 and C4 respectively.

Analysis of the results shows that anomalous high values of $\tan\delta$ for PCMs on the basis of PVDF modified by Ni are observed in the low-frequency range due to a non-linear increase in ϵ' . The value of $\tan\delta > 1$ is usually observed in ferroelectrics for which the complex permittivity dispersion in the low-frequency range relates with the orientation of electric moments inside domains [8]. Because PVDF is a partially crystalline polymer, then essential contribution into the increase of $\tan\delta$ at $T \geq 60...70^\circ\text{C}$ may give the increase of its conductivity due to dissociation of molecules inside amorphous regions of a polymer [8]. The shift of $\tan\delta$ peak towards the low-frequency range for C2 compared to PVDF (C1) may be caused by the change both of crystallinity and energy of cohesion interaction of matrix and filler. Besides, the increase of Ni content in PVDF-matrix may change the glass transition temperature of PCM. For that case the decrease in T_g is connected with both the decrease of packing density of molecules in a composite and formation of mechanical strain inside the PCM. On the other hand, the increase in T_g is conditioned by the limitation of mobility of the composite chains due to the filler [9]. Deviation of the glass transition temperature being found in this study may be connected with a joint effect of both factors mentioned above.

Typical results for PCMs on the basis of PVDF filled with PZT are listed in Table 4. It can be seen that the permittivity (ϵ') of PCMs is decreased not more than by 15% with temperature increase from 30 to 70 °C in the frequency range from 1 kHz to 1 MHz.

The permittivity at $F = 1\text{ MHz}$ and $T = 30^\circ\text{C}$ for nano-compositions C5...C7 is increased by 10...185% and $\tan\delta$ is decreased by 10% compared to those for PVDF-matrix. It is an evidence of good compatibility of PVDF-matrix and particles of PZT-filler.

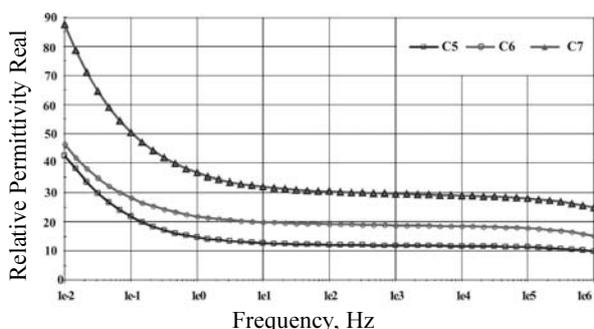
Figure 7 shows a non-linear increase in ϵ' for all PCMs in the low-frequency range. On the other hand, the permittivity of all PVDF/Ni/PZT composites is slowly changed over the frequency range from 10 Hz up to 1 MHz.

Since mechanical properties of PCMs with 65...70 wt. % of PZT are not so good as for PVDF, then the maximum filler content for PCMs on the basis of PVDF should be not more than 55–60 wt. %. The results of study of compositions C5...C7 at $F = 10^{-4}\text{ Hz}$ were shown in Table 2. It is obvious that the maximum increase in ρ_v is observed for C5...C7 over the temperature range from 20 up to 100 °C.

In this case, the activation energy of the conductivity process is decreased with increase in the filler content. It can be connected with the increase in the volume fraction of an amorphous phase in PVDF-matrix for composites C5...C7.

Table 4. The relationships ϵ' and $\tan\delta = f(T)$ for PCMs on the basis of PVDF

$T, ^\circ\text{C}$	F, kHz	C5		C6		C7	
		ϵ'	$\tan\delta, 10^{-2}$	ϵ'	$\tan\delta, 10^{-2}$	ϵ'	$\tan\delta, 10^{-2}$
30	1	11.95	1.46	18.93	1.53	28.59	1.85
	10	11.75	1.53	18.57	1.68	28.03	2.00
	100	11.45	3.93	18.08	4.06	27.09	4.29
	1000	10.41	14.2	16.40	14.52	24.77	12.94
50	1	12.29	2.95	19.41	2.61	29.27	3.00
	10	12.00	1.69	18.91	1.77	28.41	2.05
	100	11.67	2.77	18.50	2.32	27.60	2.86
	1000	11.29	7.94	17.83	7.21	26.23	7.80
70	1	12.66	7.08	19.61	4.42	29.72	5.23
	10	12.10	2.61	18.90	2.20	28.45	2.61
	100	11.80	2.04	18.46	1.95	27.59	2.46
	1000	11.54	4.58	18.05	4.61	26.65	6.98


 Fig. 7. Dependencies $\epsilon' = f(F)$ for PCMs with different PZT content at $T = 25^\circ\text{C}$

4. Conclusions

1. Modification of PVDF by < 0.5 wt % Ni results in the essential change of sub-molecular structure of PCMs. Large-size spherulite structure of PVDF is transformed into small-size spherulite structure.

2. The shift of $\tan\delta$ peak towards the low-frequency range for PVDF modified by Ni compared to PVDF may be caused by the change both of crystallinity and energy of cohesion interaction of matrix and filler.

3. The glass transition temperature of PCMs is very much influenced by the Ni content in PVDF-matrix.

4. The permittivity of PVDF/Ni/PZT composites is slowly changed over frequency range from 10 Hz to

1 MHz. Maximum PZT content in PCMs on the basis of PVDF should not be more than 60 wt %.

5. It is possible to design a novel composition with high specific storage energy more than 10^5 J/m^3 on the basis of PVDF-matrix filled with PZT nano-particles.

References

- [1] T.J. Lewis, in *Proc. Int. Conf. Solid Diel.*, 2004, Vol. 2, pp. 792–795.
- [2] T. Tanaka, *IEEE Trans. Diel. Elect. Ins.* **12**, 914 (2005).
- [3] H.L. Chan, Y.W. Chen, and C.L. Choy, *IEEE Trans. Diel. Elect. Ins.* **3**, 800 (1996).
- [4] O.S. Gefle, S.V. Lebedev, and Y.P. Pokholkov, *The barrier effect in dielectrics*, Tomsk: TML-Press, 2007, p. 172.
- [5] O.S. Gefle, S.V. Lebedev, Y.P. Pokholkov et al., *IEE Proc. Sci. Meas. Techn.* **148**, 125 (2001).
- [6] <http://www.solartronanalytical.com>. Solartron Analytical. Impedance/Gain-Phase Analyzer 1260 and Dielectric Interface 1296, Operating manual (2001).
- [7] M.V. Volkenshtein, *Physics of dielectrics*, Moscow, Foreign Literature, 1960.
- [8] D. Sinha, C. Muralidhar, and P.K.C. Pillai, in *Proc. Int. Conf. Diel.*, 1986, pp. 227–231.
- [9] V.P. Solomko, *Filled crystalline polymers*, Kiev, Naukova Dumka, 1980.