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## COMPLEX PERMITTIVITY FREQUENCY SPECTRA OF COMPOSITE DIELECTRICS ON THE BASIS OF POLYVINYLCHLORIDE

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*Complex permittivity frequency spectra of polymeric composite materials on the basis of plasticized polyvinylchloride filled with powders of ferroelectric ceramics PZT and titanium dioxide were studied in this work. It has been shown that it is possible to design a new composite material with high stored energy on the basis of polyvinylchloride matrix.*

### 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/m<sup>3</sup>) for high voltage impulse equipment. Such materials can find their application as an insulation of capacity storage devices operating under the impulse voltage. Depending on the purpose and area of application of high voltage impulse devices the front duration of voltage impulses can change in the range from nanoseconds to tens of milliseconds. Therefore, PCMs for capacity storage devices should have stable electrical and mechanical characteristics over the frequency range of external electric field. The problem consists in the fact that sufficient increase in the PCM permittivity is possible under the condition of high degree of polarity and compatibility of its components. The increase in polarity of organic component results in the frequency dispersion of the complex permittivity that causes instability of polymeric matrix characteristics itself. 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 [1–5]. It results in both the features of temporal distribution of the local field in some regions of polymeric system and frequency dispersion of the efficient complex permittivity of PCM. In this connection, to design PCM it is necessary to possess information about frequency spectrum of the complex permittivity of polymeric matrix itself and main regularities of change of the dielectric relaxation spectrum parameters when introducing inorganic filler particles into the polymeric matrix.

In [6, 7] it has been shown that application of plasticized polyvinylchloride (PVC) as a polymeric matrix allows us to design PCM with sufficiently high specific stored energy (up to  $10^5$  J/m<sup>3</sup>) in millisecond range of the front duration of voltage impulses ( $\tau_p=5\text{...}10$  ms). The aim of this work is to study the complex permittivity of the polymeric matrix and PCMs on the basis of plasticized PVC in the frequency range from  $10^{-2}$  to  $10^6$  Hz.

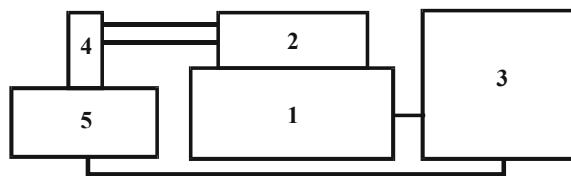
### Experimental technique and samples

Plasticized polyvinylchloride (PVC) was chosen as a basic material (matrix) for design of dielectrics with high specific stored energy. To increase the permittivity of PCM, PVC matrix was filled with powder materials

with high permittivity such as ferroelectric ceramics lead zirconate titanate (PZT) or titanium dioxide (TiO<sub>2</sub>) with an average particle size  $\sim 1$   $\mu$ m.

Powder fillers had been specially treated to improve both the contact between a polymeric matrix and filler and to destroy agglomerates. To dress the powder particle surface, the solution of stearic acid in gasoline was used. Portions of powder filler were immersed into a stearic acid solution in gasoline. Evaporation of the solvent excess was carried out at temperature 23 °C in the vacuum hood. The dried powder was weighted and its mass did not have to increase the sum of powder mass before dressing and stearic acid. Otherwise, the procedure was repeated to dry the powder mass completely. The dressed powder was mixed with the matrix.

Filling the matrix with PZT or TiO<sub>2</sub> powders was carried out by the method of hot rolling. The filler was gradually introduced into the matrix up to the required volume content. The volume content of filler in the matrix (C) was changed from 25 to 43 vol. %. The produced PCM plates were granulated. The granulated composite was used as a material for sample preparation. The special moulds filled with composite pellets were placed in the vacuum oven previously heated up to 160 °C for 2 h. The samples were produced by hot pressing in the hydraulic press with heated plates at pressure 10 MPa with time exposure 20 min at  $T=160$  °C and slow cooling under pressure. The samples were made as disks 75 mm in diameter and the thickness of  $650\pm 50$   $\mu$ m. On both work sample surfaces the silver potential and measuring electrodes were applied by the vacuum evaporation method. All samples were chosen by the random sampling method.



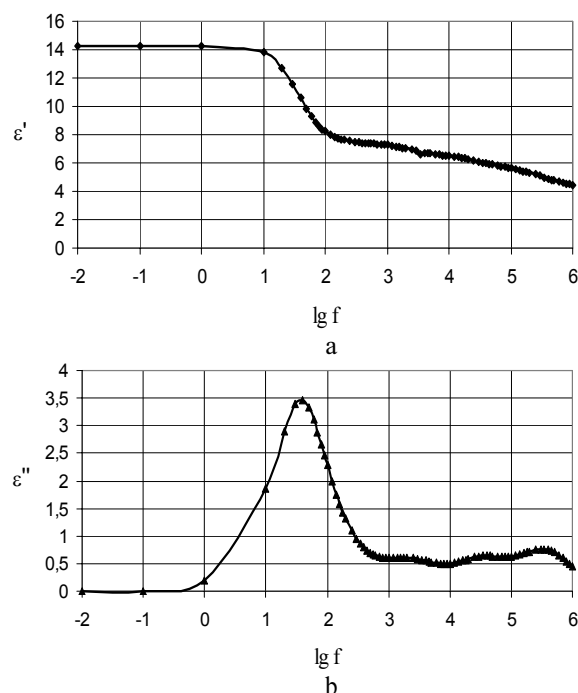
**Fig. 1.** Experimental setup: 1) Frequency response analyzer Solartron 1260 with built-in wideband generator and Fourier-transducer; 2) dielectric interface Solartron 1296; 3) PC with built-in GPIB-card; 4) test cell with sample; 5) temperature controller

Measurements of the real  $\epsilon'$  and imaginary  $\epsilon''$  components of the complex permittivity were performed under AC voltage by means of measuring instrument So-

lartron Analytical. Structure scheme of experimental setup is shown in fig. 1. Measurements were carried out in the frequency range from  $10^{-2}$  to  $10^6$  Hz. In this frequency range from 2 to 20 readings per decade were performed. The relative measuring error of the real and imaginary parts of the complex permittivity was not more than 2 and 3 %, respectively. Under each experimental condition not less than 5 samples were tested.

### Experimental results and discussion

The results of study of the real  $\varepsilon'$  and imaginary  $\varepsilon''$  parts of the complex permittivity of the PVC matrix are presented in fig. 2.



**Fig. 2.** Frequency dependences of  $\varepsilon'$  (a) and  $\varepsilon''$  (b) for the PVC matrix at 23 °C

It can be seen that the real part of the complex permittivity decreases approximately 3 times and the main maximum of the imaginary part of the complex permittivity is observed at frequency  $f=37$  Hz with increasing frequency from  $10^{-2}$  to  $10^6$  Hz. In the range from  $10^{-2}$  to  $10^6$  Hz  $\varepsilon'$  and  $\varepsilon''$  depend slightly on the frequency of external electric field but the broad frequency spectrum of  $\varepsilon''$  at  $f > 1$  kHz demonstrates the presence of components determining different contribution of the dipolar orientational polarization into the total dispersion of the complex permittivity [8, 9]. Their different contribution into the total dispersion of the complex permittivity is conditioned by the fact that polymer studied contains polar radicals in the main chain  $-C-Cl$  as well as polar groups of plasticizer molecules  $CH_3C_6H_4O_3PO$  (tricresyl phosphate) and  $C_4H_8OOC(CH_2)_8COOC_4H_8$  (dioctyl sebacate) [10] intrinsic dipole moment of which is  $(1...7) \cdot 10^{-30}$  C·m [9]. Besides, introduction of plasticizers into the matrix results in decrease of a polymer viscosity due to decrease of intermolecular interaction energy and change in the relaxation time of the di-

polar orientational polarization processes of polar groups and radicals. For example, introduction of 40 vol. % tricresyl phosphate causes the shift in maximum of dipolar elastic losses from 260 to 1000 Hz at temperature 30 °C [11] or decrease in the relaxation time of polarization 4 times.

It means that even insignificant content of polar plasticizers of different chemical composition in the polymer volume results in appearance of set of relaxation times of the dipolar orientational polarization over the frequency range of the external electric field.

To check this assumption the applicability of different function considered in [8] was estimated to describe the frequency dispersion of the real and imaginary components of the complex permittivity of plasticized PVC. It was found that frequency dependence of  $\varepsilon'$  and  $\varepsilon''$  at  $T=23$  °C is more adequately described by the superposition of the Debye functions which can be presented for the case of linear frequency  $f$  as

$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon \sum_{i=1}^4 \frac{g_i}{1 + (f/f_{oi})^2}, \quad (1)$$

$$\varepsilon'' = \Delta\varepsilon \sum_{i=1}^4 \frac{(f/f_{oi})g_i}{1 + (f/f_{oi})^2}, \quad (2)$$

where  $\varepsilon_\infty$  is the permittivity at  $f \gg 1/\tau_0$  (at  $f \rightarrow \infty$   $\varepsilon_\infty$  tends to square of the refractive index);  $\Delta\varepsilon = (\varepsilon_s - \varepsilon_\infty)$  is a parameter describing the total width of the dispersion for  $i$ -th set of relaxation times;  $\varepsilon_s$  is the permittivity at  $f \ll 1/\tau_0$  (at  $f \rightarrow 0$   $\varepsilon_s$  gains the meaning of the static permittivity);  $\tau_0$  is the relaxation time of  $i$ -th polarization process;  $f_{oi}$  is the relaxation frequency of  $i$ -th polarization process;  $g_i$  is the weighting coefficient describing the contribution of  $i$ -th polarization process into the total dispersion. The weighting coefficient in (1) and (2) should satisfy to the condition:  $g_1 + g_2 + \dots + g_N = 1$ .

The calculation results showed that in the frequency range from  $10^{-2}$  to  $10^6$  Hz the frequency dependences of  $\varepsilon'$  and  $\varepsilon''$  with the error not more than 1 % (for  $\varepsilon'$ ) and 2 % (for  $\varepsilon''$ ) were described by set of four components of the dielectric relaxation spectrum with the following parameters:  $\varepsilon_\infty=4,289$ ;  $\varepsilon_s=14,289$ ;  $\Delta\varepsilon=10,0$ ;  $f_{o1}=37$  Hz;  $g_1=0,69$ ;  $f_{o2}=2,285 \cdot 10^3$  Hz;  $g_2=0,085$ ;  $f_{o3}=3,198 \cdot 10^4$  Hz;  $g_3=0,09$ ;  $f_{o4}=3,628 \cdot 10^5$  Hz and  $g_4=0,135$ .

Taking into account the mass content of components in the PVC matrix, where per 140 wt. % of mixture there is 100 wt. % of PVC, the main contribution of  $g_i$  into the total dispersion of the complex permittivity is conditioned by the dipolar group polarization of PVC molecules. Other spectrum components are connected with orientation of dipolar molecules of plasticizers.

In figs. 3 and 4 the results of study of the frequency dependencies of  $\varepsilon'$  and  $\varepsilon''$  for PCM on the basis of plasticized PVC matrix with different volume content of PZT are presented. It is obvious that the real part of the complex permittivity at the frequency  $10^{-2}$  Hz is 2.6 and 4.4 times more compared with the polymeric matrix with increasing the filler content from 25 to 43 vol. %. In this case the maximum of the imaginary part of the complex permittivity in the range of infralow frequenci-

es is observed at the frequencies 20 and 9 Hz, respectively. The frequency dependencies of the complex permittivity (with a measuring error not more than 2 %) for PCM are described by the superposition of the Debye functions just like for the PVC matrix.

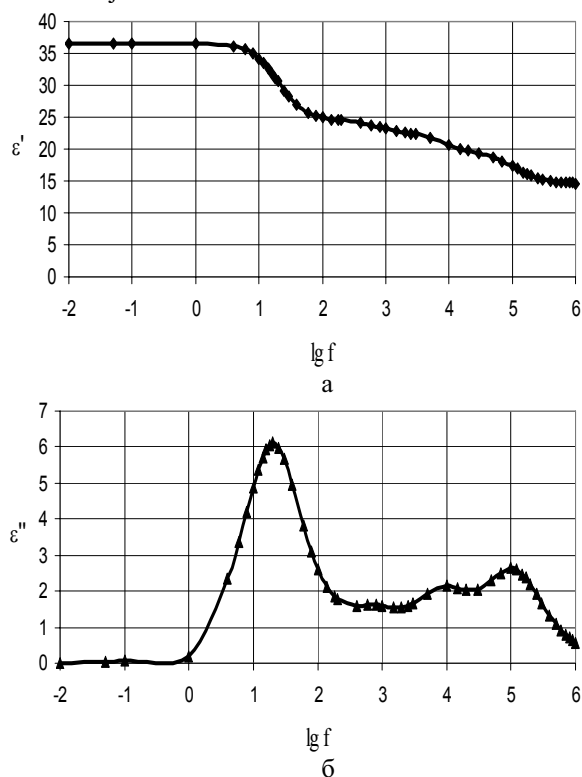


Fig. 3. Frequency dependences of  $\varepsilon'$  (a) and  $\varepsilon''$  (b) for PCM at  $C=25$  vol. % PZT and  $23^\circ\text{C}$

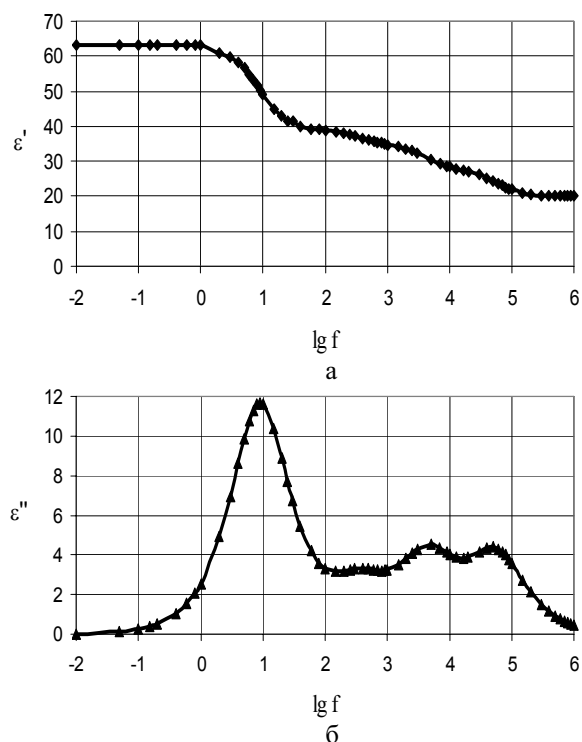


Fig. 4. Frequency dependences of  $\varepsilon'$  (a) and  $\varepsilon''$  (b) for PCM at  $C=43$  vol. % PZT and  $23^\circ\text{C}$

Parameters of the dielectric relaxation spectra for PVC matrix and PCMs with different content of PZT are listed in table. It can be seen from table that the increase of the filler content results in the relaxation frequency shift toward to the lower frequencies for all spectrum components, the increase in depth or the total width of the complex permittivity dispersion  $\Delta\varepsilon$  in approximate accordance with the filler content  $C$ , and in change of contribution of separate spectrum components  $g_i$  into the dispersion of the complex permittivity.

Table. Parameters of the dielectric relaxation spectra for PVC matrix and PCMs

Spectrum parameters	C, vol. % PZT		
	0	25	43
$\varepsilon_\infty$	4,289	14,6	20,0
$\varepsilon_c$	14,289	36,6	63,0
$\Delta\varepsilon$	10	22,0	42,0
$f_{01}, \text{Hz} / g_1$	37 / 0,69	20 / 0,55	9 / 0,55
$f_{02}, \text{Hz} / g_2$	2285 / 0,085	750 / 0,09	358 / 0,10
$f_{03}, \text{Hz} / g_3$	31980 / 0,09	8600 / 0,145	4300 / 0,17
$f_{04}, \text{Hz} / g_4$	362800 / 0,135	115000 / 0,215	57500 / 0,18

It should be noted that change of  $g_i$  for PCMs compared with the PVC matrix correlate well to the change of volume fraction of plasticizers. Such correlation proves the assumption on the fact that spectrum components with the relaxation frequency  $f_{02}..f_{04}$  characterise the contribution into the polarization of plasticizer molecules, increase in the content of which is necessary for keeping technological properties of PCMs (e.g. plasticity and melt flow rate).

In turn, the shift of  $f_{0i}$  toward to the lower frequencies of external electric field can be conditioned by increase in the activation energy of polarization processes due to the interaction of polar groups and radicals with PZT particles possessing high polarizability. The high polarizability of PZT is caused by the fact that simultaneously with the ionic relaxational polarization and the electronic polarization in this material the domain polarization is observed.

In spite of the fact that application of PVC matrix allows us to obtain sufficiently high values of the permittivity for PCMs at relatively low content of PZT, the availability of the complex permittivity dispersion results in the instability of PCM properties over the frequency range from  $10^{-2}$  to  $10^6$  Hz. Thus, at  $C=25$  vol. % PZT the permittivity of PCM decreases approximately 2.5 times and at  $C=43$  vol. % of PZT – 3.2 times. It shows irrationality of increasing the filler content in the PVC matrix more than 30...35 vol. % and necessity of searching for other ways of stabilization of PCM's electrical and mechanical characteristics.

Fig. 5 shows the frequency dependencies of  $\varepsilon'$  and  $\varepsilon''$  for PCM on the basis of PVC matrix filled with  $C=25$  vol. %  $\text{TiO}_2$ . It can be seen that the value of  $\varepsilon'$  decreases approximately by a factor of 2.3 with changing frequency of external electric field from  $10^{-2}$  to  $10^6$  Hz. The main maximum of dielectric losses is observed at the frequency  $f_{01} \approx 36$  Hz just like for the polymeric matrix ( $f_{01}=37$  Hz). This indicates a weak interaction between polar radicals - C-Cl and  $\text{TiO}_2$  particles in contrast to PZT which is explained by sufficiently low value of the permittivity of  $\text{TiO}_2$  because of the absence of the domain polarization.

Frequency dependencies of  $\varepsilon'$  and  $\varepsilon''$  with a measuring error less than 1 % (for  $\varepsilon'$ ) and 2 % (for  $\varepsilon''$ ) for PVC filled with  $\text{TiO}_2$ , just like for PVC filled with PZT are well described by the superposition of the Debye functions of four components of the dielectric relaxation spectrum with the following parameters:  $\varepsilon_\infty=9,7$ ;  $\varepsilon_c=22,4$ ;  $\Delta\varepsilon=12,7$ ;  $f_{01}=35,767$  Hz;  $g_1=0,4$ ;  $f_{02}=400$  Hz;  $g_2=0,21$ ;  $f_{03}=15000$  Hz;  $g_3=0,21$ ;  $f_{04}=120033$  Hz and  $g_4=0,18$ .

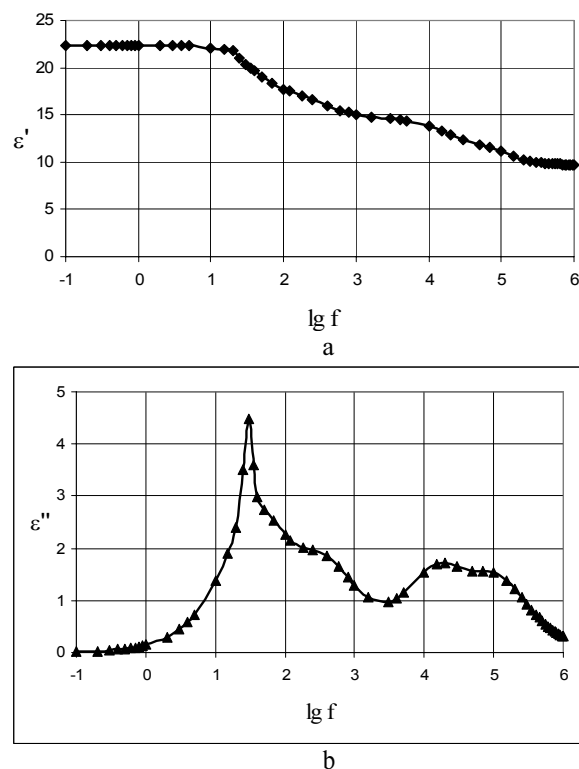


Fig. 5. Frequency dependences of  $\varepsilon'$  (a) and  $\varepsilon''$  (b) for PCM at  $C=25$  vol. %  $\text{TiO}_2$  at 23 °C

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Comparison of these parameters with table shows that application of  $\text{TiO}_2$  as a filler is more preferable from the viewpoint of decreasing the total dispersion of the complex permittivity. Thus, the value of  $\Delta\varepsilon$  for PCMs filled with  $\text{TiO}_2$  and PZT increases by a factor of 1.27 and 2.2 compared to the PVC matrix, respectively, i.e. increment  $\Delta\varepsilon$  is decreased by a factor of 1.7 at the same filler content. The disadvantage of  $\text{TiO}_2$  consists in the fact that the permittivity of PCM filled with  $\text{TiO}_2$  increases in less degree compared to that for PCM filled with PZT. Besides, application of  $\text{TiO}_2$  as a filler requires more volume fraction of plasticizers in PCM that is reflected in increasing contribution of the spectrum components  $g_2\dots g_4$  into the total dispersion of the permittivity. To solve this problem one needs to optimize PCM composition from the viewpoint of  $\text{TiO}_2$  compatibility with polar plasticizers of different types. At the same time, preliminary investigation shows that at the directional control of composition and properties of PCM on the basis of the PVC matrix it is possible to design insulating materials with high values of the permittivity and the specific stored energy over the frequency range from  $10^{-2}$  to  $10^6$  Hz.

## Conclusion

It was shown that it is possible to design PCM on the basis of the polar PVC matrix with the high specific stored energy. To obtain stable electrical and mechanical characteristics it is necessary to optimize PCM composition and type of fillers. The method of dielectric spectroscopy in frequency domain gives complete information on not only the behaviour of the complex permittivity but also on PCM structure. This is very important for the directional control of composition and properties of composite dielectrics.

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