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## Effect of Highly Disperse Silicon Dioxide on Properties of Polymeric Composites Polychlorotrifluoroethylene – Silver Iodide

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An experimental research has been made into properties of polymeric composite materials (PCM) whose polymeric ingredient is polychlorotrifluoroethylene (PCTFE). Subjects of inquiry included lowdimensional systems PCTFE – AgI and PCTFE – AgI-SiO<sub>2</sub>, with the content of silver iodide and silicon dioxide being equal to 0-100 vol % and 0-0.5 vol %, respectively. The characteristics under investigation were electrophysical properties in a superfrequency range and thermophysical properties (thermal capacity, linear thermal expansion coefficient). It has been found that incorporation of doping admixtures of nanodimensional SiO<sub>2</sub> into such a system leads to significant changes in the supermolecular structure of its polymeric constituent.

**Key words:** nanodimensional silicon, superionic conduction, phase transition, complex permittivity, thermal capacity.

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### Introduction

Designing of new functional materials is considered to be one of the promising directions of researches. Such materials may be created on the basis of disperse systems with extended surface and strong physicochemical interactions among their components. There are sufficient grounds to believe that such substances will be distinguished for their novel unique properties associated with shifts of parameters of phase transitions in active constituents, with changes of conformational composition of macromolecules, with regular patterns of variation of matrix components, etc.

Such materials can be created on the basis of superionic conductors that are noted for their specific physico-chemical properties. Of significance are objects with constituents that contain nanodimensional particles. Both from scientific and practical points of view it is of significance to pursue comprehensive researches into effect of interactions among components at interfaces on electrophysical and thermophysical characteristics of multicomponent systems.

The authors of Ref. [1,2] have presented some results of their researches into such polymeric composite materials (PCM) as polychlorotrifluoroethylene–silver iodide (PCTFE – AgI) and polychlorotrifluoroethylene–silver iodide–silicon dioxide (PCTFE – AgI-SiO<sub>2</sub>), with the major attention being focused on processes which proceed at temperatures

close to that of transition of AgI to its superionic state (T = 420 K). It has been found that the supermolecular structure (SMS) of the polymer exerts an effect on electrophysical and thermophysical characteristics of these composites. In order to substantiate structuration processes in the polymeric matrix it is expedient to investigate properties of PCTFE in the temperature interval from 293 K to the phase transition temperature of the filler.

This paper was intended to study influence of highly disperse silicon dioxide on electro- and thermophysical properties of polymeric composites PCTFE – AgI.

### I. Results and discussion

The composite samples necessary for the studies were prepared using

nanodimensional silicon dioxide (aerosil A-300, S<sub>sp</sub> = 300 m<sup>2</sup>g<sup>-1</sup>) which was preliminarily calcined for 2 h at T = 873 K;

chemically pure silver iodide with its particle size from 2 to 6 μm, with the geometry of a particle being similar to that of rectangular parallelepiped with a side ratio of 1:1:3;

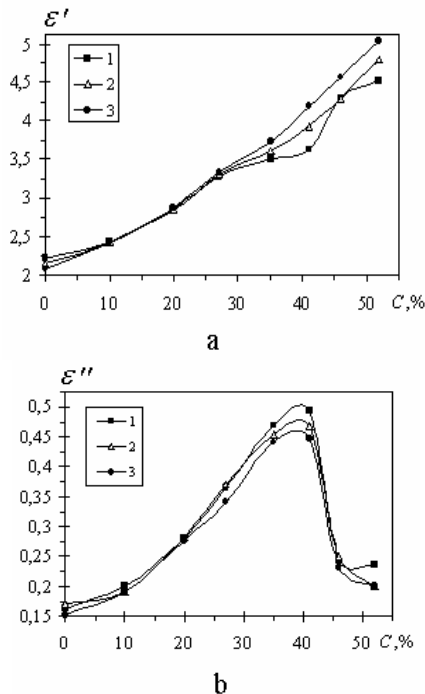
PCTFE of grade II, TBM-240, with spherical particles with a size of ≈ 200 nm.

With a view to prepare such samples a physical mixture of AgI, SiO<sub>2</sub>, and PCTFE was homogenized. The

first step of the homogenization was addition of SiO<sub>2</sub> (0.4 vol %) to AgI. Our microscopic studies showed that after mixing of the ingredients the majority of silicon dioxide particles were situated on the AgI surface, which weakened their ability to aggregate. Addition of powdery PCTFE to the mixture was also accompanied by allocation of its particles on the AgI surface. Then the mixture was compacted at the temperature equal to the melting point of the polymer ( $T_{\text{comp}} = 523 \text{ K}$ ) at a pressure of 200 MPa. The cooling rate was equal to  $2 \text{ K min}^{-1}$ .

The above-said studies of electrophysical properties of systems PCTFE – AgI and PCTFE – AgI-SiO<sub>2</sub> were performed with the help of a superfrequency interferometer [3] at the frequency range from 8 to 12 GHz and the temperature interval from 293 to 393 K.

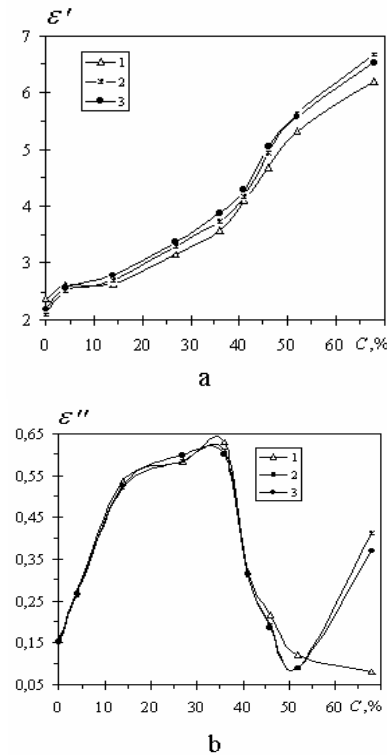
One of the subjects of inquiry were components of complex permittivity of the systems under investigation. The dependences of  $\epsilon'$  and  $\epsilon''$  on content (C) of AgI for system PCTFE – AgI at various temperatures are displayed in Fig. 1. It is seen that  $\epsilon'$  is linearly (additively) dependent on the filler content and with increasing temperature becomes higher. On the concentration dependence of  $\epsilon''$  one can observe a maximum of values at a content of C of about 40 vol %. Another peculiarity of the behaviour of  $\epsilon''$  consists in the fact that with increasing temperature the  $\epsilon''$  values decrease.



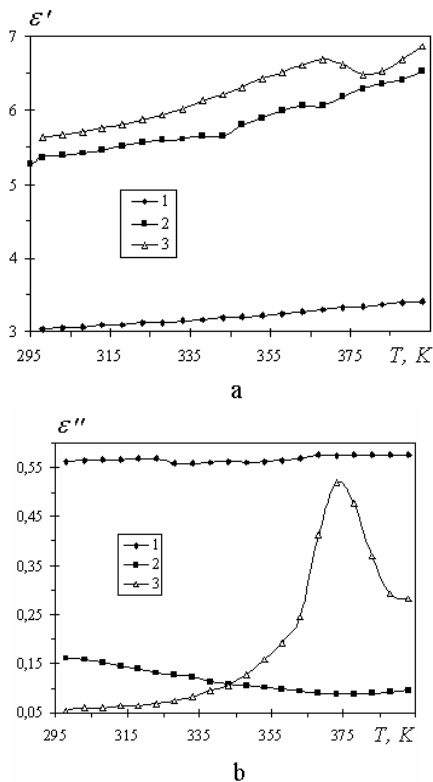
**Fig. 1.** Dependences of real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) components of complex permittivity on content (C in vol %) of AgI for system PCTFE – AgI at various temperatures. 1 – 303 K; 2 – 353 K; 3 – 383 K.

The corresponding dependences observed for system PCTFE – AgI-SiO<sub>2</sub> are shown in Fig. 2. It is seen that  $\epsilon'$

is practically linearly dependent on content of AgI. For the composites with a filler content of  $C < 46 \text{ vol } \%$



**Fig. 2.** Dependences of real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) components of complex permittivity on content (C in vol %) of AgI for system PCTFE – AgI-SiO<sub>2</sub> at various temperatures. 1 – 303 K; 2 – 353 K; 3 – 383 K.



**Fig. 3.** Temperature dependences of real  $\epsilon'$  (a) and imaginary  $\epsilon''$  (b) components of complex permittivity for system PCTFE – AgI-SiO<sub>2</sub> at various contents of AgI (in vol %). 1 – 27; 2 – 53; 3 – 68.

heating of samples leads to an insignificant change in their  $\varepsilon'$  values. In the case of highly filled samples elevation of temperature results in a more substantial increase in the real component of complex permittivity. At the concentration interval  $14 \leq C \leq 36$  vol % the dependence  $\varepsilon'' = f(C)$  exhibits a substantial increase in the  $\varepsilon''$  values. It should be noted that for samples with a content of  $C \geq 68$  vol % heating of composites PCTFE – AgI-SiO<sub>2</sub> manifests itself in especially sharp changes in the  $\varepsilon''$  values.

The major processes that determine values of  $\varepsilon'$  and  $\varepsilon''$  for crystalline polymers are processes of molecular relaxation in amorphous or defective regions [4]. Significant dielectric losses in PCTFE are due to asymmetry of its main (monomeric) link of the macromolecule. In addition, any change in SMS exerts a substantial effect on electrophysical properties of PCTFE. For example, it is known that a reduction in the degree of crystallinity of 10-50 % brings about an increase in the specific electroconductivity by a factor of 10–1000 [4].

Our analysis of the experimental results displayed in Figs. 1 and 2 gives us grounds to believe that addition of SiO<sub>2</sub> to system PCTFE – AgI leads to a change, in the first place, in the polymeric constituent, which manifests itself by a shift of the  $\varepsilon''$  maximum into a region with a somewhat lower content of AgI in comparison to the bicomponent system. The character of the observed concentration dependences provides evidence for the fact that in the case of an AgI concentration up to 40 vol % the polymer structure varies its properties towards a decrease in the crystallinity even on addition of a small amount of SiO<sub>2</sub>.

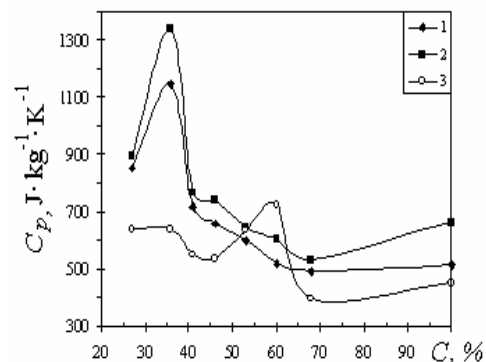
The substantial increase in the dielectric losses  $\varepsilon''$  with the maximum at  $C = 40$  vol % and its shift into the region of lower contents of AgI upon introduction of nanodimensional SiO<sub>2</sub> (0.4 vol %) (Fig. 2) can be attributed to an increase in the amount of the amorphous phase of PCTFE in the boundary layers of the polymer around particles of the disperse fillers. The inference is corroborated by the results of our thermophysical researches (Fig. 4).

The experimental data gathered for a sample of PCM with an AgI content of 68 vol % are different from the above-discussed (Fig. 3). It is evident that the  $\varepsilon''$  values are substantially dependent on temperature, with their temperature dependence having a maximum at  $T = 368$  K. This fact indicates that the polymer in the sample has a special state which is distinguished from that in other samples of PCM by the presence of high-frequency relaxation processes in the polymer.

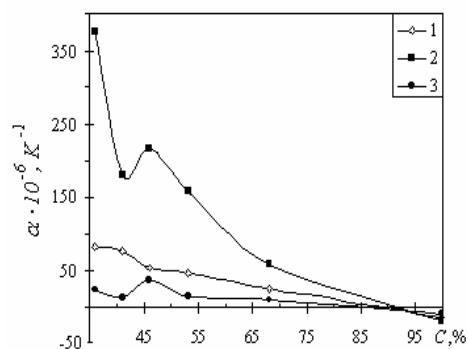
It has been found that with increasing temperature the  $\varepsilon''$  values for the sample with an AgI content of 68 vol % increase and have a maximum at 368 K, which gives evidence for the fact that the polymer is in a special state with a higher degree of amorphism. This polymer portion is situated in a layer that is parietal to the filler surface and differs from other layers by superhigh-frequency relaxation processes in the polymer. In the case of the samples exhibiting a decrease in the  $\varepsilon''$  values

with increasing temperature the manifestation of relaxation processes can be observed at temperatures lower than 293 K [4].

It has also been shown that introduction of nanodimensional SiO<sub>2</sub> into the binary system leads to a substantial changes in the thermophysical properties of PCTFE and AgI, which is displayed by the corresponding concentration dependences (Figs. 4, 5).



**Fig. 4.** Dependence of the specific heat capacity ( $C_p$ ) for system PCTFE – AgI-SiO<sub>2</sub> (1,2) and for system PCTFE – AgI (3) on filler content ( $C$ ) at various temperatures. 1 – 343 K; 2 – 413 K; 3 – 458 K.



**Fig. 5.** Dependence of  $\alpha$  for samples of PCTFE – AgI-SiO<sub>2</sub> (1, 2) and PCTFE – AgI (3) on the filler content at various temperatures. 1, 3 – 353 K; 2 – 413 K.

These changes consist in a considerable increase in the heat capacity ( $C_p$ ) (Fig. 4) and in the temperature coefficient of linear expansion ( $\alpha$ ) at a lower content of AgI (Fig. 5). In the situation with the PCTFE – AgI the dependence  $C_p = f(C_f)$  exhibit a maximum at a filler content of about 60 vol %. For the system containing SiO<sub>2</sub> the maximum is more pronounced and is shifted into a region with a lower content of AgI (namely, 36 vol %). The above-mentioned changes correspond with the behaviour of the dependence  $\alpha = f(C_f)$  (Fig. 5).

## Conclusions

Thus, introduction of such dopants as nanodimensional silicon dioxide exerts an effect on the SMS of the PCTFE – AgI. Silicon dioxide is also able to

make an influence on disperse AgI, which manifests itself in a marked enhancement of domination of transverse acoustic vibrations of its frequency spectrum [6] and in a change in its physico-mechanical properties [7].

It has been found that at temperatures up to the temperature of the phase transition of AgI to the conducting state the values of real components  $\epsilon'$  of complex permittivity for the both systems under investigation increase linearly with its content, while values of  $\epsilon''$  have maximums at about 40 vol % of AgI for system PCTFE – AgI and at 30 vol % for system PCTFE – AgI-SiO<sub>2</sub>.

By the thermophysical techniques it has been shown that introduction of a nanodimensional SiO<sub>2</sub> as a dopant into the systems under study leads to substantial changes in the SMS of their polymeric components. The shift of the maximum of the imaginary component  $\epsilon''$  of complex

permittivity into a region with lower contents of AgI as well as the behaviour of the temperature dependence of  $\epsilon'$  for the polymeric composite material PCTFE – AgI-SiO<sub>2</sub> whose AgI content is equal to 68 vol % are related to structural variations that take place in PCTFE under the influence of the filler.

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- [1] O.M. Garkusha, P.P. Gorbyk, V.V. Levandovs'kyi, L.K. Yanchevs'kyi, M.V. Bakuntseva. Physico-mechanical and Thermophysical Properties of the System Disperse Silver Iodide-Polychlorotrifluoroethylene // *Metallofizika i Noveishiyе Tekhnologii*, **23**(6), pp. 797-609 (2001).
- [2] P.P. Gorbyk, R.V. Mazurenko, V.V. Levandovs'kyi, C.M. Makhno, O.O. Chuiko. Effect of Silicon Dioxide on Electrophysical Properties of the System Polychlorotrifluoro-ethylene–Silver Iodide // *Dopovidi NAN Ukraine*, **5**, pp. 133-137 (2005).
- [3] L.M. Ganyuk, V.D. Ignatkov, C.M. Makhno, P.M. Soroka. Study of Dielectric Properties of a Fibrous Material // *Ukr. Fiz. Zh.*, **40**(6), pp. 627-629 (1995).
- [4] G.P. Mikhailov, B.I. Sazhin, V.S. Presnyakov. Influence of Density of Polychlorotri-fluoroethylene on Dielectric Losses // *Kolloidn. Zh.*, **20**(4), pp. 461-464 (1958).
- [5] M.V. Bakuntseva, O.M. Garkusha, P.P. Gorbyk, V.V. Levandovs'kyi, L.K. Yanchevs'kyi. Peculiarities of the Behaviour of the Temperature Coefficient of Linear Expansion of the System Polychlorotrifluoroethylene–Silver Iodide // *Dopovidi NAN Ukraine*, **9**, pp. 95-99 (2002).
- [6] S.I. Novikova. *Thermal Expansion of Solids*, Nauka: Moscow, p. 292 (1974).
- [7] P.P. Gorbyk, V.V. Levandovs'kyi, R.V. Mazurenko, C.M. Makhno, M.O. Rokyt's'kyi, Effect of Disperse Silver Iodide and Silicon Dioxide on Properties of Nanostructural Composite Materials // *Abstracts of Papers, Nanostructural Systems. Electronic and Atomic Structure and Properties (NANSYS'2004)*, Akadempriodika: Kyiv, p. 187 (2004).

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## Вплив високодисперсного діоксиду кремнію на властивості полімерних композитів системи поліхлортрифторетилен – йодид срібла

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Проведено експериментальні дослідження властивостей полімерних композиційних матеріалів низькорозмірних систем ПХТФЕ – AgI та ПХТФЕ – AgI-SiO<sub>2</sub> з вмістом 0-100% AgI і SiO<sub>2</sub> до 0,5 %: електрофізичних в надвисокочастотному діапазоні; теплофізичних (теплоємність, температурний коефіцієнт лінійного розширення). Показано, що внесення в систему лежучих домішок нанорозмірного SiO<sub>2</sub> веде до значних змін надмолекулярної структури полімера.