

Electrophysical properties of polymer composites penton-silver iodide system in 8–12 GHz frequency region

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The heat field influence on electrophysical properties of polymer composites of the penton — dispersed silver iodide (AgI) system at volume filling from 0 to 100 % have been studied in 8–12 GHz frequency range. It has been shown that both real (ϵ') and imaginary (ϵ'') complex dielectric permittivity components below the temperature of AgI dielectric-ionic phase transition ($T_c = 420$ K) depend on the content of the system components, and the imaginary component depends also on the polymer supermolecular structure. After AgI transition into ionic state, a percolation transition is observed in concentration dependences at critical percolation threshold about 30 vol.% filler content and extreme maxima about $C = 50\%$. The ϵ' and ϵ'' values exceed almost in twice the corresponding AgI characteristics. The results are discussed within the frame structure model.

Исследовано влияние тепловых полей на электрофизические свойства полимерных композитов системы пентапласт-дисперсный иодид серебра (AgI) с содержанием 0–100 % в диапазоне частот 8–12 ГГц. Показано, что значения действительной (ϵ') и мнимой (ϵ'') составляющих комплексной диэлектрической проницаемости до температуры фазового перехода AgI ($T_c = 420$ К) диэлектрик-суперионник зависит от содержания компонентов, а значение мнимой составляющей — также и от надмолекулярной структуры полимера. После перехода AgI в суперионное состояние на концентрационных зависимостях наблюдается перколяционный переход с критическим порогом перколяции около 30 % (об.) содержания наполнителя и экстремальными максимумами в области значений $C = 50$ %. Значения ϵ' и ϵ'' при этом почти в 2 раза превышают соответствующие характеристики для AgI. Результаты обсуждаются в рамках каркасной структурной модели.

The development of new functional materials with pre-specified and controlled characteristics is an actual problem. Those can be obtained basing on disperse systems with developed surface and active physicochemical interaction of components. Such materials may show new properties connected with interphase layer formation and changes of phase transition parameters in active components, and also polymer supermolecular structure (SMS) changes depending on the filler dispersity.

Among others, of interest are the materials based on ionic conductors, especially with nanodimensional components. The complex research of the phase interaction between components influence on the material electrophysical, thermophysical and physico-mechanical properties is actual both from scientific and practical points of view. Thus, basing on the research of poly(chlorotrifluoroethylene)-silver iodide and poly(chlorotrifluoroethylene)-silver iodide-silicon dioxide filled systems, an essential

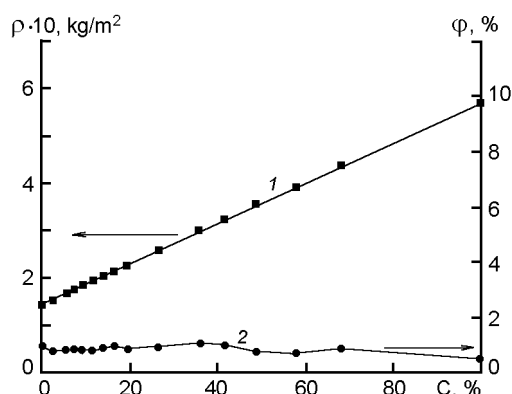


Fig. 1. Dependences of density (1) and porosity (2) on AgI content in a penton-dispersed silver iodide PCM.

influence of components interaction on the interface thereof on electrophysical and thermophysical characteristics, as well as new and unique properties of composites have been shown [1–4].

This paper is aimed at study of influence of heat fields and filler content changes on electrophysical properties of penton — AgI systems polymer composites in SF-region.

For composites preparing the following components were used: silver iodide "pure" grade, particle size 1 to 6 μm ; penton [3,3-bis(chloromethyl)oxacyclobutane], particle size about 45 μm , the particle geometry being similar to cubic. To prepare the samples, a mixture of AgI and penton was homogenized carefully. Then the mixture was compacted at the temperature equal to the polymer melting point ($T_{comp} = 483 \text{ K}$) under identical pressure conditions (20 MPa). The cooling rate was $0.5 \text{ K}\cdot\text{min}^{-1}$. The electrophysical characteristics of penton — AgI systems were determined using a superhigh frequency interferometer [4] within 8 to 12 GHz frequency range and 293 to 433 K temperature interval. Density and porosity were measured using hydrostatic weighting.

The experimental data on density and porosity of polymeric composite materials (PCM) depending on AgI content are shown in Fig. 1. The density values agree with calculated ones within the experimental accuracy. The porosity of all PCM samples does not exceed 1 %, that fact enables to consider the system as a two-component one. Temperature dependences of complex permittivity for composites with AgI content from 0 to 100 vol.% at 293–453 K tem-

perature range are shown in Fig. 2. The ϵ' (a) and ϵ'' (b) values for PCM system are seen to do not change considerably during heating up to the AgI phase transition temperature ($T_c = 420 \text{ K}$). An exception makes the temperature dependence $\epsilon''(T)$ for $C \sim 69 \%$ AgI content. The ϵ'' values for that sample increase considerably under heating and attain a relaxation maximum at $T \approx 318 \text{ K}$. Since the filler becomes ionic conductor as the temperature T_c is reached, the temperature dependences $\epsilon'(T)$ and $\epsilon''(T)$ increase sharply to certain extreme values above AgI phase transition temperature. In particular, for PCM containing 50 % of filler, ϵ'' value increases by a factor of 1.7.

Basing on the data obtained, concentration dependences of real ϵ' and imaginary ϵ'' components of complex dielectric permittivity at temperatures below and above the AgI phase transition have been plotted. In concentration dependences below the filler phase transition temperature (Fig. 3a), $\epsilon'(C)$ values rise from 2.5 to 6.5 in proportion with increasing AgI content. However, $\epsilon''(C)$ dependences exhibit maxima in the filler concentration region $C \approx 16 \%$ and minima at $C \approx 50 \%$ (Fig. 3b). In concentration dependences above the phase transition temperature, in particular at $T = 426 \text{ K}$, ϵ' and ϵ'' values exceed significantly those for corresponding PCM at $T < T_c$ (Fig. 3). As is seen in Fig. 3 (c, d), the ϵ' and ϵ'' changes at the filler content increase up to 30 % are relatively small as compared to ϵ' and ϵ'' values at temperatures below the AgI phase transition temperature. Then their values increase sharply and attain a maximum at $C \approx 50 \%$.

The low porosity of compacted AgI and samples with maximal filler content (Fig. 1) is connected with plastic straining of disperse filler particle shape under thermal compaction. At the same time, the presence of insignificant porosity in all samples evidences a need to optimize the PCM performance characteristics. The porosity can be lowered by increasing pressure during thermal compaction. Elimination of macropores allows to improve PCM functional characteristics (electro- and thermophysical characteristics, linear expansion, etc.), performance (physico-mechanical characteristics, wear resistance) and to protect filler against environmental factors.

The basic processes defining the ϵ' and ϵ'' values in semi-crystalline polymers, in-

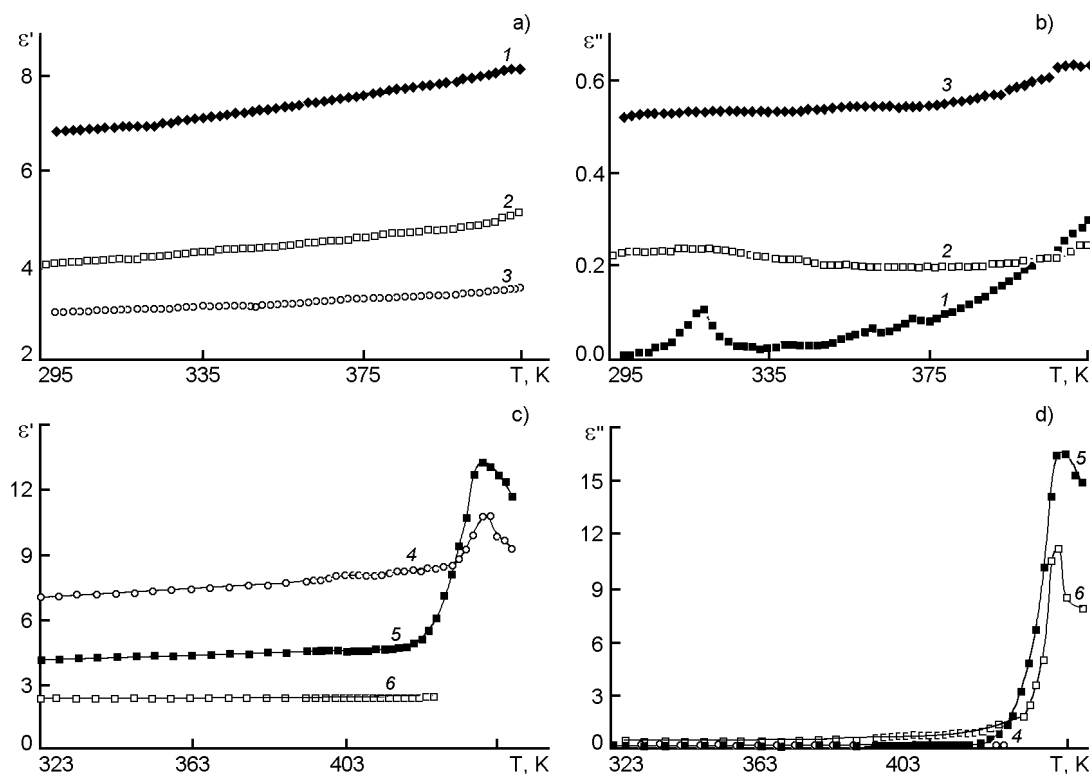


Fig. 2. Temperature dependences of real (a, c) and imaginary (b, d) complex dielectric permittivity components for penton-AgI PCM at AgI content (per cent): 69 (1), 46 (2), 14 (3), 0 (4), 50 (5) and 100 (6).

cluding penton, are molecular relaxation processes in amorphous and imperfect regions [5]. The considerable dielectric losses in the polymer are conditioned by the dissymmetry of his primary (monomeric) unit. Variations in the polymer supermolecular structure influences appreciably its electrophysical properties. The penton electric conductivity is known to vary significantly depending on the crystallinity level. Under crystallization, its specific resistance changes by a factor of 10 to 1000 [6]. The polychlorotrifluoroethylene (PCTFE) crystallinity level decrease by 10–50 % causes increase of its electric conductivity by 1–3 orders of magnitude [5].

The results obtained can be discussed within the frame structure model of cubic lattice [7, 8], based on two-phase model of polymer-filler, four-component structure model (filler, polymer with structure of boundary layer near the filler particles and with particular properties, polymer in transitional boundary layers, and bulk polymer with structure and properties without filler particles); model concepts of percolation and cluster theory. The model provides active interaction of components, variations in the polymer and filler properties in PCM of dif-

ferent compositions, selection possibility of optimum pressure, temperature and time PCM processing conditions taking into account the polymer matrix and dispersed filler (physico-mechanical properties, shape and dimensions, particle size distribution, etc.).

Considering the experimental results presented in Fig. 2 and Fig. 3, it can be stated that below the filler phase transition temperature ($T_c = 420$ K), values of real (ϵ') and imaginary (ϵ'') components of the PCM complex permittivity can be influenced by variations in polymer SMS caused by the dispersed filler (Fig. 2 and Fig. 3) and changes in the filler content (Fig. 3). According to the four-component structure model [7, 8], the filler content increase results in a gradually reducing number of polymeric PCM components: at first, the bulk polymer disappears, then the polymer in boundary (transitional) layers. In high-filled PCM, the polymer component is presented only by the layer neighboring to the filler surface. As it is obvious from Fig. 2 and Fig. 3, the imaginary component ϵ'' of the system complex permittivity is more sensitive to the polymer SMS changes. As the AgI content increases, changes in the polymer component occur, that is reflected

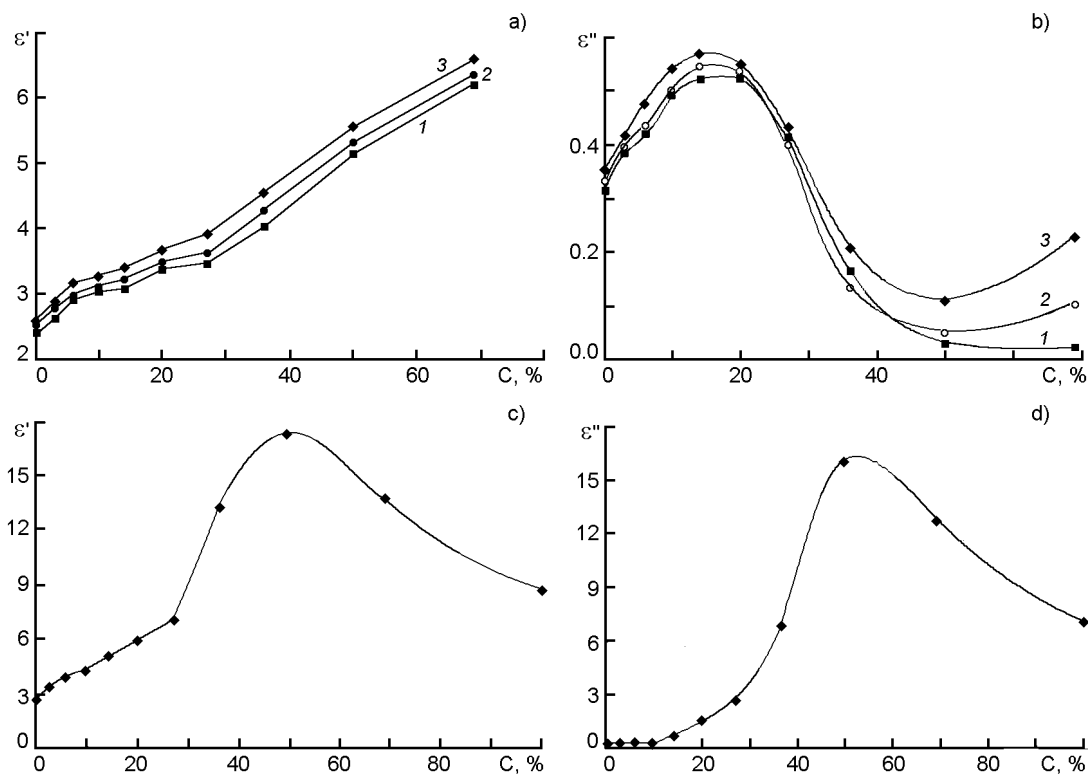


Fig. 3. Dependences of real (a, c) and imaginary (b, d) complex dielectric permittivity components at 10 GHz frequency on AgI content in penton-AgI PCM at temperatures (K): 299 (1), 373 (2), 407 (a, b) and 426 (c, d) (3).

as maximal ϵ'' values in the region of relatively low AgI content (about 16 %) and minimal values in region where the polymer component is mainly in transitional and filler-neighboring boundary layers [1].

The character of $\epsilon''(C)$ concentration dependences indicates that the polymer structure and its properties vary depending on the crystallinity level. For example, substantial increasing of dielectric losses (ϵ'') with maximum at 16 % AgI must be associated with increasing amount of amorphous phase. The minimum ϵ'' values at the filler content about 50 % stands for more "perfect" polymer structure in transition boundary layers [1]. Increasing ϵ'' values for specimen with AgI content of 69 % under heating and maxima at $T = 318$ K point to specific, relatively more amorphous polymer state with imperfect structure in crystalline regions in the layer neighboring to the filler surface. It differs from other ones by the presence of relaxation processes in polymer and relaxation maximum at $T = 318$ K connected with glass transition process in the polymer, which is registered in SHF range [6].

The drastic increase of PCM ϵ' and ϵ'' within the 420–440 K temperature range is connected with realization of β - α dielectric-ionic phase transition in AgI. A similar phenomenon was also observed in PCTFE-AgI PCM system [7–10]. The filler (AgI) transition into ionic state at $T > T_c$ promotes the active increase of his absorbing possibility of electromagnetic waves and thus specific electric conductivity [7]. A slight increase of ϵ' and ϵ'' in PCM systems, containing up to 30 % AgI, as compared to the corresponding samples at $T < T_c$ (Fig. 3) can be explained by the filler transition to ionic state at $T > T_c$ (for example, at 426 K). The more intense increase of ϵ' and ϵ'' at further increasing AgI content ($C > 30$ %) evidences the macrostructural transition from isolated clusters system to the infinite filler cluster with critical percolation threshold at $C = 30$ % and extreme maximum at about 50 % AgI (Fig. 3). In this case, the PCM system shows unique properties: real (ϵ') and imaginary (ϵ'') complex permittivity components exceed about twice the corresponding values for ionic conductor (AgI); perhaps this is caused by formation of an

interphase layer with special structure and properties due to active physico-chemical interaction of the components and increasing phase interface. Changing the extension of the components interface, the system electrophysical properties can be controlled within certain limits [10].

Thus, the experimental research has been revealed substantial variations in the PCM electrophysical properties depending on temperature, content of components, their structure, and formation of interphase layers with special structure and properties due to active interaction. For the polymer component, the variations are displayed as formation of the polymer transitional and boundary layers around the filler particles with structure and properties different from those of bulk polymer; as gradual change of SMS and properties at increasing filler content from three-, two- to single-component structure with maximal amorphization at 16 % AgI content; as changes in fractal geometry of heterogeneous disordered structures and structural percolation transition from continuous cluster to isolated ones at decreasing polymer content. For dispersed filler, the variations mentioned are displayed as changes of fractal geometry of heterogeneous structures and structural percolation transition from isolated clusters to continuous one at increasing filler content. The percolation transition for the penton — dispersed silver iodide

system is observed at 30 % AgI content. An extreme maximum at $C = 50$ % is connected with maximal boundary surface between components in ionic state of silver iodide.

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Електрофізичні властивості полімерних композитів системи пентапласт-йодид срібла у діапазоні частот 8–12 ГГц

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Досліджено вплив теплових полів на електрофізичні властивості полімерних композитів системи пентапласт-дисперсний йодид срібла (AgI) з вмістом 0–100 % у діапазоні частот 8–12 ГГц. Показано, що значення дійсної (ϵ') та уявної (ϵ'') складових комплексної діелектричної проникності до температури фазового переходу AgI ($T_c = 420$ K) діелектрик-суперіонік залежить від вмісту компонентів, а значення уявної складової — також від надмолекулярної структури полімера. Після переходу AgI у суперіонний стан на концентраційних залежностях спостерігається перколяційний перехід з критичним порогом перколяції близько 30 % (об) вмісту наповнювача та екстремальними максимумами в області значень $C = 50$ %. Значення ϵ' та ϵ'' при цьому майже в 2 рази перевищують відповідні характеристики для AgI. Результати обговорюються у рамках каркасної структурної моделі.