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PHYSICOCHEMICAL AND STRUCTURAL CHARACTERISTICS OF HYBRID NANOCOMPOSITES BASED ON BRANCHED POLYIMIDE WITH A LOW CONTENT OF INORGANIC COMPONENT

The series of organic-inorganic hybrid nanocomposites based on branched polyimide matrix and with different amounts of tetraethoxysilane (TEOS) (5, 20, and 50 wt.% of the initial polyamic acid mass) were synthesized and studied using nitroxyl paramagnetic probe, measuring dielectric permittivity, X-ray structural analysis and optical microscopy. It was shown that in some cases the introduction of inorganic component is accompanied by a decrease in the segmental mobility of polyimide matrix as a result of the partial immobilization of organic macrochains during the formation of inorganic microregions. In the presence of inorganic component, a weak dependence of the polymer permeability on the content of the organic component in the system is observed, also the specific density changes little with an increase in TEOS content. Extreme changes in the segmental mobility and dielectric permittivity of the branched matrix formed in the presence of 5 wt% TEOS were found compared to systems of other compositions. This can be caused to a large extent by structural changes in the system. At a low content of TEOS occurs significant «loosening» of organic matrix, a sharp decrease in the dielectric constant and a significant increase in the segmental mobility of the polyimide matrix. Small angle X-ray scattering diffractograms demonstrate drastic changes in polyimide composite heterogeneity in the presence of 5 wt.% TEOS content. According to the optical microscopy data, the introduction of TEOS into polyimide is accompanied by the formation of microaggregates of inorganic nanoparticles in the system, the number and average size of which depend on the SiO_2 content and looks most homogeneous at a low TEOS content.

***Keywords:** branched polyimide, hybrid nanocomposite, paramagnetic probe, dynamic characteristics, permeability.*

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ФІЗИКО-ХІМІЧНІ І СТРУКТУРНІ ХАРАКТЕРИСТИКИ ГІБРИДНИХ НАНОКОМПОЗИТІВ НА ОСНОВІ РОЗГАЛУЖЕНОГО ПОЛІІМІДУ ЗА НИЗЬКОГО ВМІСТУ НЕОРГАНІЧНОЇ КОМПОНЕНТИ

Синтезовано та досліджено серію органо-неорганічних гібридних нанокомпозитів на основі розгалуженої поліі\мідної матриці та тетраетоксисилану (ТЕОС) за різного вмісту ТЕОС (5, 20 і 50 мас. % від вихідної маси поліамідокислоти) з використанням нітроксильного парамагнітного зонда, вимірювання діелектричної проникності, рентгеноструктурного аналізу та оптичної мікроскопії. Показано, що в деяких випадках введення неорганічного компонента супроводжується зниженням сегментальної рухливості полііімідної матриці

внаслідок часткової іммобілізації органічних макроланцюгів при формуванні неорганічних мікрообластей. Спостерігається слабка залежність проникності полімеру від вмісту неорганічної складової в системі, пито-ма густина також мало змінюється зі збільшенням вмісту ТЕОС. Виявлено екстремальну зміну діелектрич-ної проникності та сегментальної рухливості розгалуженої матриці, сформованої за наявності 5 мас.% ТЕОС, порівняно з системами іншого складу. Це значною мірою може бути викликано структурними змінами в системі. За низького вмісту ТЕОС відбувається значне «розпушення» органічної матриці, різке зниження діелектричної проникності та значне збільшення сегментальної рухливості поліімідної матриці. Дифрактограми малокутового рентгенівського розсіювання демонструють різкі зміни гетерогенності поліімідного композиту за 5 мас. % вмісту TEOS. Згідно з даними оптичної мікроскопії, введення ТЕОС у поліімід супроводжується утворенням у системі мікроагрегатів неорганічних наночастинок, кількість і середній розмір яких залежить від вмісту SiO_2 і є найбільш однорідним за низького вмісту ТЕОС.

Ключові слова: розгалужений поліімід, гібридний нанокомпозит, парамагнітний зонд, динамічні характеристи-ки, проникність.

Introduction

Organic-inorganic composite can combine the advantages of inorganic filler and organic polymer matrix. Polyimide (PI) matrix have such valuable properties as heat resistance, strength, low coefficient of thermal expansion and dielectric constant whereas the presence of inorganic particles allows obtaining advanced materials with valuable physicochemical properties: thermo-mechanical, dielectric and barrier properties [1-5].

Among the widely applied physical methods information on structurally heterogeneous nanocomposites based on PI can be obtained by analyzing the dynamics of paramagnetic nitroxyl probes in a size scale close to the size of the molecule of such a probe [6-9].

This article examines organic-inorganic polyimide nanocomposites based on a branched PI matrix and tetraethoxysilane (TEOS) in particular with introduced in 5 wt.% content, which were studied by EPR method using the stable nitroxyl radical 2,2,6,6,-tetramethylpiperidine-1-oxy (TEMPO) as a paramagnetic probe (PMP). The data obtained using these methods were compared with the results of measuring the composite specific density, dielectric constant, as well as with the data of X-ray structural analysis and optical microscopy.

Experimental section

Materials. Dimethylacetamide was dried over P_2O_5 for a day and then distilled at 438K. Pyromellitic dianhydride (99%; Acros), 3-aminopropyltriethoxysilane (99.9%; Merck), 4,4'-diaminodiphenyl ether (99.9%; Merck), 3,5-diaminobenzoic acid (99.9%; Merck) and tetraethoxysilane (TEOS) (99.9%; Merck) were used without further purification.

Synthesis of hybrid nanocomposite

To obtain nanocomposites based on PI and TEOS, a two-stage polyimide synthesis method was used. In the first stage, polyamic acid (PAK) with ethoxysilane end-groups was synthesized on the basis of pyromellitic dianhydride with mixture of diamines: diaminodiphenyl ether and 3,5-diaminobenzoic acid in the mole ratio of components 9:1, 7:3, 1:1, and TEOS in the presence of 3-aminopropyltriethoxysilane. Precursors of polyimide nanocomposites were obtained by adding various amounts of TEOS (5, 20, and 50 wt.% of the original PAK mass) to the polyamic acid solution. After carrying out the hydrolysis and thermal imidization reactions, the corresponding nanocomposites with different contents of inorganic component (4.70, 9.34, 17.16 wt.% by the weight of composite (theoretically calculated values based on chemical equations)) were obtained. In detail, the method of obtaining nanocomposites based on PI and TEOS using sol-gel technology was previously described in [10].

Schematically, the chemical structure of the obtained nanocomposites can be depicted as follows:
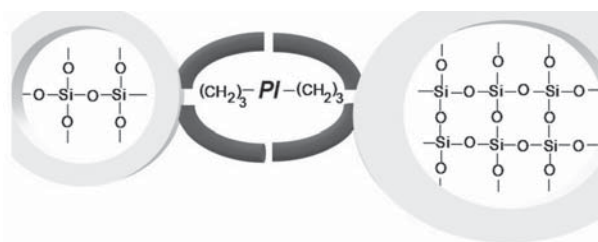
where the PI block has the following structure:
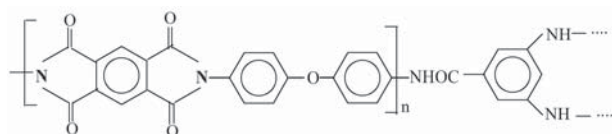
The presence of diaminobenzoic acid in the reaction mixture can cause to side reactions in the system leading to polyimide chain branching. 4,4,-Diaminodiphenyl ether, which did not react with pyromellitic dianhydride, can react with the carboxyl groups of 3,5-diaminobenzoic acid, as described in detail earlier [11]. By changing the ratio of diaminodiphenyl ether and diaminobenzoic acid, the degree of branching of the polyimide chain can be adjusted.

EPR spectra were recorded in the temperature controlled resonator of a 3-cm radio spectrometer RE-1306 at a temperature of 293K. The calibration samples were diphenylpicrylhydrazyl (DPPH) with g=2.0036 and Mn^{2+} ions in the MgO matrix with g=2.0015 and certified value of the splitting of the ultrafine structure components. Spectra were recorded using an ADC (Insoftus) at a sampling rate of 5 points per second. The introduction of PMP into the studied samples was carried out by diffusion from a solution of TEMPO in dichloromethane. The films were exposed in a PMP solution with a concentration of C = 0.02 M for a day at 293K, followed by vacuuming the samples at the same temperature to remove solvent residues from the polymer bulk. The correlation time τ and width of the nitroxyl spectrum , were determined from the TEMPO spectrum parameters according to [8, 9]. The value of integral intensity of the probe EPR spectrum was determined as double integral of the TEMPO spectrum contour in the polymer system, divided by the weight of the sample.

The specific density of the samples was measured by hydrostatic weighing in isooctane according to [12].

Studies of dielectric permittivity ε' were carried out in the temperature range from 293 K to 393 K and the frequency interval from 10^2 to 10^5 Hz using a dielectric spectrometer implemented on the basis of an alternating current bridge P5083.

Small angle X-ray scattering (SAXS) was applied to analyze the micro heterogeneous structure of the PI composite using a low-angle X-ray diffractometer (the X-ray source was a BSV-22 with a copper anode) with Kratky collimation
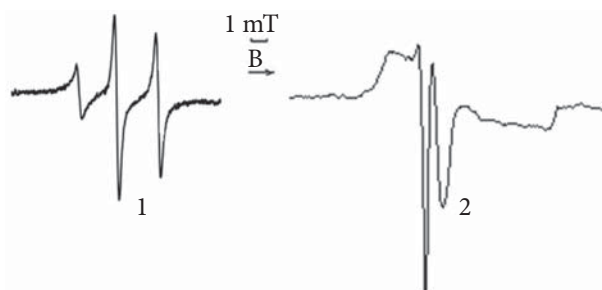

Fig. 1. EPR spectra of the nitroxyl probe: nitroxyl spectrum in toluene (*1*); superposition of signals from PMP located in the regions with different mobility in PI composite containing 5 wt.% TEOS (*2*)

of the primary beam. The samples studied were 15-5 mm strips with a thickness of 1.5-3.0 mm. Low-angle diffraction patterns were obtained for angles from 2.36 to 4.0 with a spacing of 1.18. Correction of the intensity profile to the collimation point was carried out by Vonk's method [13].

Optical microscopy images of films "on transmittance" were obtained using a microscope XY-B2, equipped with a digital video eyepiece ICM 532 and an image processing system AMCAP/VIDCAP (Microsoft).

Result and discussion

The time of reorientation of a nitroxyl PMP in a magnetic field (correlation time τ) allows the estimation of the segmental mobility of macrochains. The mobility of PMP is also characterized by the spectrum width (spectral parameter). Both τ and are the smaller the greater is the mobility of the probe. Integral intensity of the PMP spectrum is proportional to the number of paramagnetic centers, penetrated into the sample and characterizes the polymer permeability [6, 8, 9].

The shape of the EPR spectra of PMP TEMPO in the investigated composites at room temperature has a complex asymmetric structure. It essentially differs from the EPR spectrum of TEMPO in a homogeneous medium (Fig. 1a). This type of spectra corresponds to the superposition of "fast" and "slow" PMP signals with different values of the correlation time (Fig. 1b) due to the PI composite structural heterogeneity [13-16].

Table. **Characteristics of PI nanocomposites**

TEOS content, wt.%	τ, ns	$2A_{zz}$, mT	$I^{(1)}$	$\varepsilon^{(2)}$	ρ, g/cm³	Inorganic component content, wt.%
0	54,2	5,9	1,00	4,50	1,42	0
5	38,2	6,1	1,87	3,83	1,42	4,70
20	95,9	6,0	0,76	4,53	1,43	9,34
50	30,1	6,0	0,18	4,44	1,44	17,16

[1] pure PI was chosen as a reference matrix;

[2] Values of dielectric constant ε, determined as a real part of complex dielectric permittivity at 20 °C and a frequency of 1 kHz.

The value of the correlation time τ calculated according to [8, 9, 11] corresponds to the "fast" ($10^{-11} < \tau < 10^{-9}$ s) fraction of PMP in a heterogeneous system and can be considered as an effective value characterizing the more mobile part of the composite.

Table shows values of PMP correlation time (**τ**), relative PMP spectra integral intensity (**I**), dielectric constant (**ε**) and specific density values (**ρ**).

As can be seen from Table, the values of the integral intensity of the PMP spectra in nanocomposites with different TEOS content correlate with changes in their segmental mobility, except for the system with 50 wt.% TEOS content. On the other hand for the PI investigated systems, there is no correlation between the mobility changes in nanocomposites and the TEOS content. Measurement of the specific density of branched polyimide and nanocomposites shows that it changes little with the TEOS content.

From the values given in Table, it can be seen that the width of the signal is characteristic of the region of fast PMP movements for all the considered systems. However, the obtained correlation time values do not always correspond to the region

of fast rotational diffusion of PMP, indicating the contribution of "slow probes" to the correlation time distribution due to the structural heterogeneity of the PI composite.

In accordance with this assumption small angle X-ray scattering (SAXS) diffractogramms show the formation of heterogeneous structure of nanocomposites based on the branched polyimide matrix.

According to the SAXS data, the microheterogeneity of PI composites changes compared to pure PI. In the presence of 5 wt.% TEOS generation of organosilicon nanophase is accompanied by disappearance of the interference maximum characteristic for the diffractogram of the initial polyimide. The curve acquires a diffuse character and a very low level of small-angle scattering. With increasing of TEOS content to 20 wt.% the periodicity characteristic of pure PI is restored and we can see significant increase of intensity of scattering in a region from 0,1 up to 0,5 nm (Fig.2).

Recently much attention has been drawn to research in the field of materials based on polymers with reduced dielectric constant [17-19]. Therefore, the data are of interest which show a signifi-
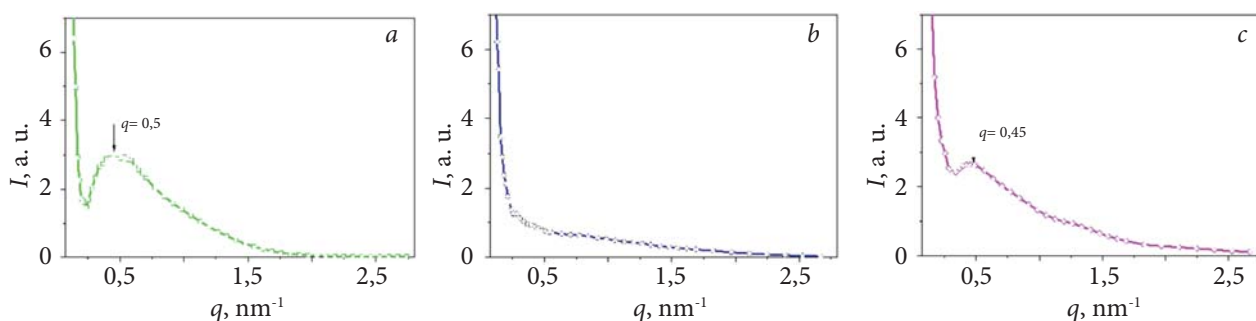

Fig. 2. SAXS diffractograms of polyimide (*a*) and composites with 5 wt.% (*b*) and 20 wt.% (*c*) TEOS
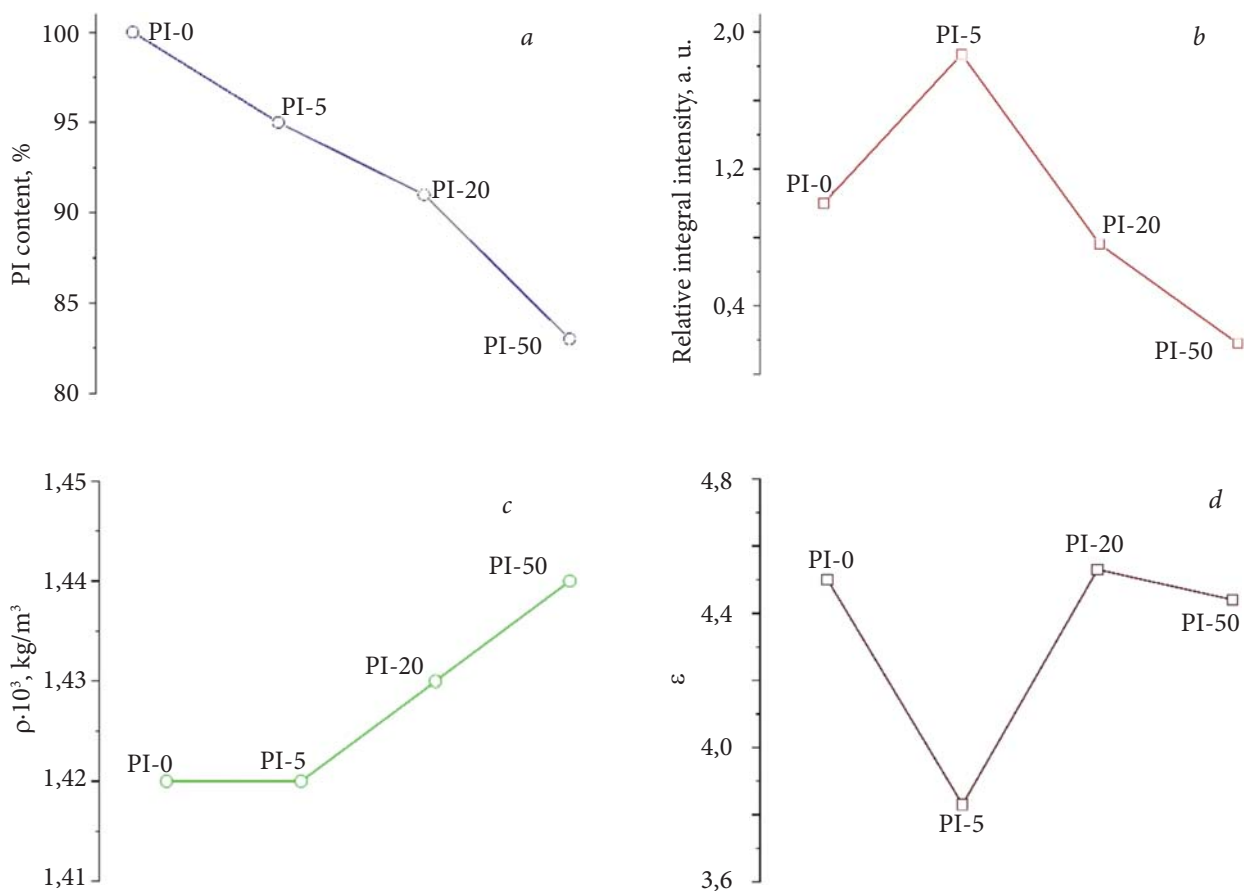
Fig. 3. The polyimide component content in the composite (*a*), the relative integral intensity of the TEMPO spectra (*b*), specific density (*c*) and dielectric constant (*d*) for composites

Fig. 4. Microimages of samples of branched PI composites based on mixture of diamines with the component ratio of 1:1 and different TEOS content: 0 (*a*); 5 (*b*); 20 (*c*) and 50 wt.% (*d*)

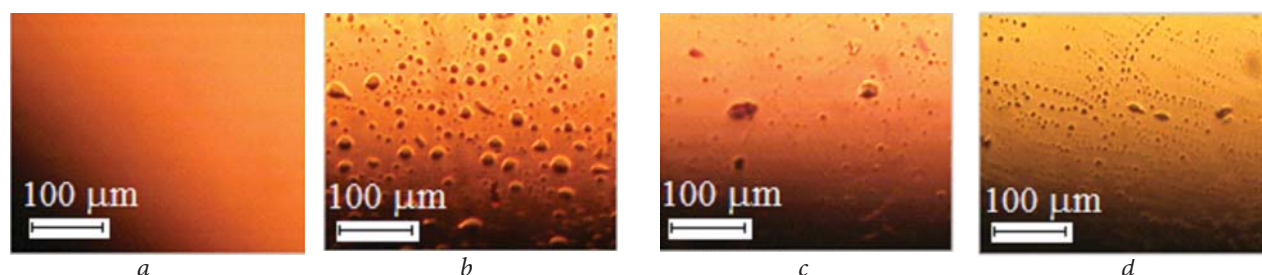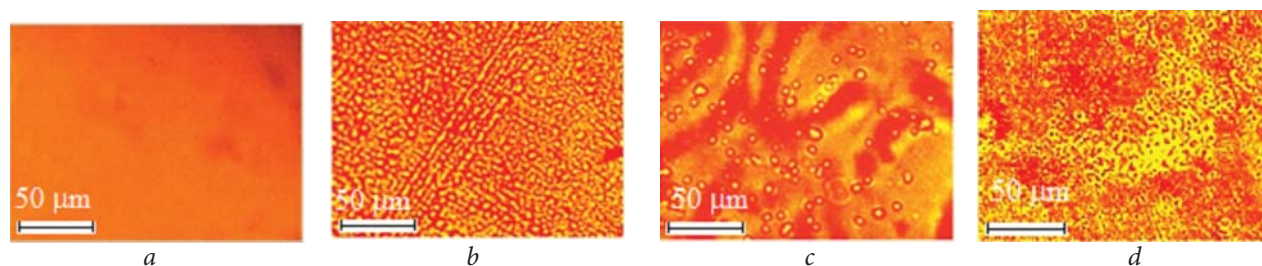**Fig. 5.** Microimages of samples of branched PI composites based on mixture of diamines with component ratio of 7:3 and different TEOS content: 0 (*a*); 5 (*b*); 20 (*c*) and 50 wt.% (*d*)

cant increase in the integral intensity of the probe spectrum of the sample with 5 wt.% TEOS as compared to the original matrix. This indicates a significant increase of paramagnetic centers number in the volume of this sample. With the same weight of samples and the same conditions of introduction of PMP easier diffusion of TEMPO molecules into this sample allows us pointing on significant "loosening" of the branched matrix formed in the presence of 5% TEOS. Loosening of the PI matrix of composites with a different structure and composition was also observed in [18].

It should be noted that due to the steric constraints PMP can penetrate only into the organic matrix of the hybrid nanocomposites.
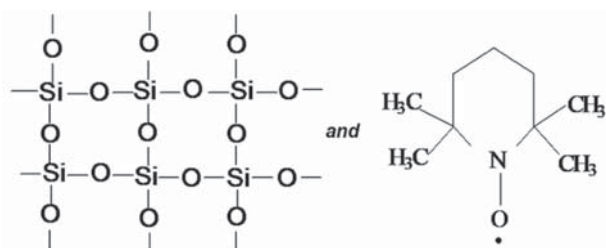
Therefore, in general case, as when the content of PI organic component in the composite decreases, the number of paramagnetic centers in the samples should also decrease. However, the diffusion of PMP into the branched PI does not correlate with the changes in the weight fraction of PI in the composites (Fig. 3). These results and the significant increase in probe diffusion in the sample with 5 wt.% TEOS can be largely attributed to structural changes in the system. The mechanism of occurrence of such structural changes during the formation of PI composite with a low content of inorganic phase requires further study.

Optical microscopy reveals the different character of the formation of aggregates of inorganic nanoparticles when various TEOS content is introduced into PI [20, 21].

Fig 4 and 5 demonstrate microimages of composites based on branched PI with different branching degree and different TEOS content.

According to the optical microscopy data, the introduction of TEOS into polyimide is accompanied by the formation of microaggregates of inorganic nanoparticles in the system, the number and average size of which depends on the content of inorganic component and looks most homogeneous for the composites with 5 wt.% TEOS.

The mutual influence of organic and inorganic components in the formation of hybrid sol-gel nanocomposites must be taken into account, since in such systems, on the one hand, the inorganic phase affects the structure and dynamic characteristics of the organic phase and, on the other hand, the peculiarities of polymer matrix influence the final morphology and properties of inorganic nanophase [22, 23].

Conclusion

EPR analysis of organic-inorganic hybrid nanocomposites based on branched polyimide matrix and different amounts of TEOS (5, 20, and 50 wt.% of the initial polyamic acid weight) showed that the introduction of inorganic component in some cases is accompanied by a decrease in the segmental mobility of polyimide matrix as a result of the partial immobilization of organic macrochains during the formation of inorganic microregions.

For the investigated systems, there is no correlation of mobility changes in nanocomposites with inorganic component content. In the presence of inorganic component, a weak dependence of the polymer permeability on the content of the polyimide component in the system is observed. The specific density changes little with an increase in TEOS content.

The obtained correlation time values, PMP spectrum shape and width indicate the contribution both "fast probes" and "slow probes" to the correlation time distribution due to the PI composite structural heterogeneity.

It was found that the branched matrix formed in the presence of 5 wt.% TEOS exhibited extreme changes in the segmental mobility and dielectric permittivity compared to systems of other compositions. This can be caused to a large extent by structural changes in the system. At low TEOS content, there is a significant "loosening" of the organic matrix, a sharp decrease in the dielectric constant and a significant increase in the segmental mobility of the polyimide matrix. Optical microscopy confirms that the number and average size of the formed inorganic inhomogeneities in the system depend on the SiO_2 content and indicates the peculiarities of their formation at a low TEOS content.

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