Specific features of the synthesis and the physicochemical properties of nanocomposite polymer electrolytes based on poly(ethylene glycol) diacrylate with the introduction of SiO$_2$

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The specific features of the synthesis and the physicochemical properties of new nanocomposite polymer electrolytes (NPE) based on poly(ethylene glycol) diacrylate, a liquid electrolyte, and silicon dioxide were studied. The kinetics of polymerization of the system in question were studied by isothermal calorimetry and the optimal conditions for the hardening of the NPE were selected. The dependence of the conductivity of the electrolyte samples on the amount of SiO$_2$ nanopowder introduced, the presence of preliminary ultrasonic treatment of the nanocomposite mixture before the synthesis, and the storage duration of the samples was studied using the electrochemical impedance method. The maximum conductivity ($4.3 \cdot 10^{-3}$ S cm^{-1} at 20 °C) was observed for samples without preliminary treatment with the introduction of 6 wt.% of SiO$_2$ and for the samples after ultrasonic treatment with 8 wt.% of SiO$_2$. The electrolyte films with the optimal SiO$_2$ content of 4 wt.% maintained their properties for 24 months.

Key words: nanocomposite electrolytes, poly(ethylene glycol) diacrylate, LiBF$_4$, SiO$_2$ nanoparticles, kinetics of polymerization, ionic conductivity.

At the present time there is an increased interest toward the possibility of using nanocomposite polymer electrolytes (NPE) for the development of lithium power sources. Taking into account the specific features of the synthesis and the properties, they can be separated into two classes. The first class contains the NPE obtained by casting from a solution or by hot pressing a mixture polymer (predominantly poly(ethylene oxide))—lithium salt—nanopowder (Al$_2$O$_3$, TiO$_2$, SiO$_2$ CeO$_2$, *et al.*).[1—4] The second class is composed of gel-electrolytes based on nanocomposite polymer membranes,[5—8] the preparation process of which consists of two steps. First, a porous nanocomposite membrane based predominantly on a co-polymer of vinylidene fluoride with hexafluoropropylene and nanoparticles of inorganic oxides listed above is obtained, then it is soaked in a liquid aprotic electrolyte.

It should be noted that the introduction of nanoparticles considerably improves the conduction properties of electrolytes, as well as increases the mechanical durability of thin film materials from NPE, which is confirmed by multiple studies (see reviews[9—11]). This area is being actively researched, and, apparently, soon NPE will supplant ordinary polymer electrolytes in lithium-polymer batteries, as well as in other electrochemical devices.

Nanocomposite cross-linked polymer electrolytes[12—16] obtained by radical polymerization cannot be assigned to the NPE classes listed above. The formation of a three-dimensional polymeric network occurs in a liquid organic electrolyte (or without it) in the presence of inorganic nanoparticles by the radical mechanism. Benzoyl peroxide is used as the initiator. This class of NPE is still insufficiently studied. The goal of this work is to study the specific features of the synthesis of cross-linked NPE and its physicochemical properties.

Experimental

Poly(ethylene glycol) diacrylate (PEG-DAc) (Aldrich), M$_n$ = 700, T_{melt} = 12—17 °C, d = 1.12 g cm^{-3} was used in this work.
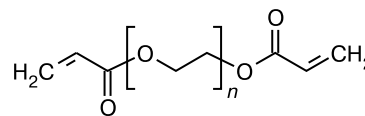
PEG-DAc

Benzoyl peroxide (BP) (Aldrich) was purified by recrystallization from chloroform and dried at ~20 °C first in air, then *in vacuo*. We used Aerosil 380 SiO$_2$ nanoparticles (surface 380 m^2 g^{-1}, an average particle size 7 nm); liquid electrolyte LiBF$_4$ (1 *M*) in γ-butyrolactone (GBL) (Ekotekh Ltd., Russia) with water content 0.008 wt.%.

The kinetics of radical polymerization of PEG-DAc in the presence of the liquid electrolyte, SiO_2 nanopowder, and benzoyl peroxide as an initiator was studied by isothermal calorimetry on a DAK-1-1 differential automatic calorimeter at 60 and 80 °C. The molar heat of polymerization of butyl acrylate ($Q = 77.87$ kJ mol^{-1}) ,[17] which does not changed in the homologous series CH_2=CHOCOR$_2$, was used to calculate the polymerization rate. The ampoules for the calorimetry measurements filled with the reaction mixture were evacuated (the pressure not higher than 10^{-4} Torr) and sealed. Apart from that, the measurements were also carried out in the presence of air oxygen.

Synthesis of polymer electrolyte samples. Weighted portions of the oligomer PEG-DAc, the liquid electrolyte, and benzoyl peroxide were stirred using a magnetic stirrer over 30—60 min at 40 °C to complete dissolution of BP crystals. Then SiO_2 nanopowder was added. Two methods were used for the preparation of nanocomposite mixtures for the synthesis: 1) by stirring on a magnetic stirrer at ~20 °C; 2) by treatment with ultrasound using a BANDELIN SONOPLUS ultrasonic homogenizer (100 W) for 20 s to achieve a homogeneous distribution of SiO_2 nanoparticles in the system. Partial polymerization of the mixture was observed due to its heating when the time of treatment with ultrasonic radiation was increased. The samples of the prepared nanocomposite mixture were placed between two 90×115-mm glasses, which were treated with an antiadhesive solution. The procedure for the preparation of the glass reactor for the synthesis of the polymer electrolyte is described in the work.[18] The hardening of the mixture was carried out according to the regime chosen in the present work. Transparent films with a thickness of ~0.25 mm and a size of 80×105 mm were obtained. The size and the thickness of the films were predetermined by the glass reactor size and the teflon spacer thickness. A microphotograph of the NPE sample with 12 wt.% of SiO_2 without ultrasonic treatment is given in Fig. 1, *b*.

Symmetrical cells with stainless steel blocking electrodes with an area equal to 0.2 cm^2 were used to measure the conductivity of NPE films by electrochemical impedance. The impedance of the cells was measured at 20 °C using an Electrochemical Instruments—Elins (Russia) Z-2000 impedance meter (frequency range $10 - 1 \cdot 10^5$ Hz) with a signal amplitude of 10 mV.

In order to characterize the mechanical properties of the NPE samples, the elastic modulus of the polymer gels was determined for the uniaxial compression of a column with a height of 1 cm and a diameter of 0.9 cm according to the procedure described earlier.[19] For this purpose, an installation composed of scales and a micrometer fixed on a bracket was assembled. A polymer electrolyte sample, which had a cylindrical shape and a height of 10 mm, was placed on a substrate on the weighing platform. The pressure was applied to the sample with the working surface of the micrometer tip. The micrometer was used to determine the deformation, the scales were used to determine the applied pressure. For each sample, more than 20 values were obtained in order to plot the dependence of the pressure (N m^{-2}) on the relative elongation. The measurements were repeated several times. The tangent of the slope was used to determine the elastic modulus E, which, in turn, is related to the polymer electrolyte microstructure by the following expression:

$$E = \nu RT,$$

where ν is the density of elastically active chains in the sample, R is the universal gas constant, T is the temperature.

Results and Discussion

Using isothermal microcalorimetry at 60 and 80 °C in the absence and in the presence of air oxygen, we studied the kinetics of radical three-dimensional polymerization of poly(ethylene glycol) diacrylate in a liquid electrolyte for different filler (silicon dioxide) contents (Fig. 2).

Figure 2 shows that the reduced polymerization rate w/[M] ([M] is the current oligomer concentration) is weakly dependent on the method of sample preparation, therefore subsequently we chose to cease the evacuation of the electrolyte mixture.

For the samples with 2 and 10 wt.% of SiO_2 added without evacuation, a 100% degree of conversion of PEG-DAc double bonds at 60 °C was achieved after 24 and 40 h, respectively. At 80 °C the polymerization proceeds only to 35—50 wt.% conversion. Clearly, at this temperature the initiator decomposes before the PEG-DAc conversion reaches the maximum value, because the BP half-life under these conditions is 3.7 h, while at 60 °C it is 48 h.

Based on the analysis of the kinetics of three-dimensional polymerization results (see Fig. 2, *a*, *b*), we used
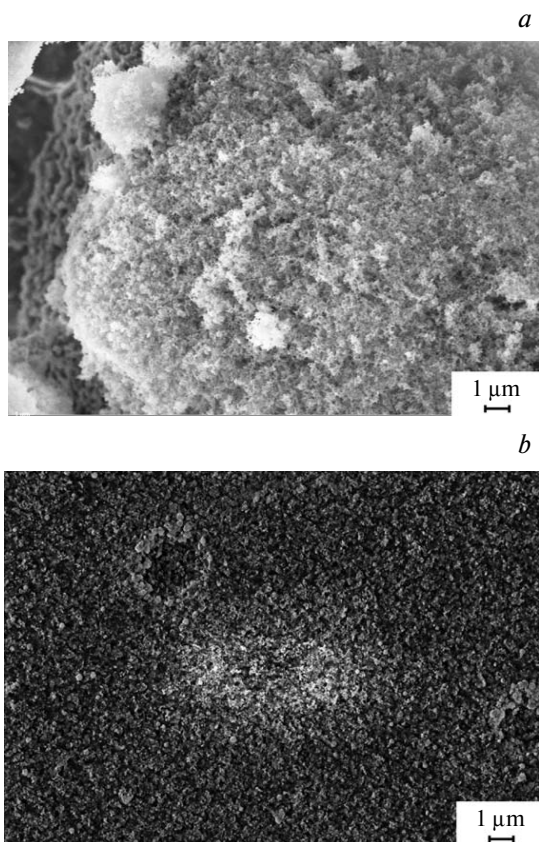

Fig. 1. Microphotographs of SiO_2 nanopowder (*a*) and NPE surface with the addition of 12 wt.% of SiO_2 (*b*).
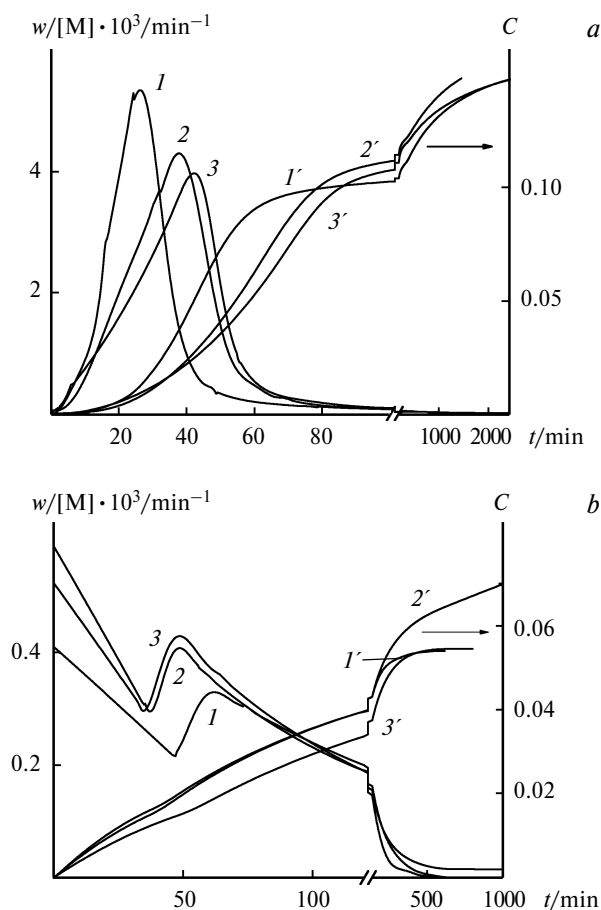
Fig. 2. Dependence of the reduced polymerization rate (*w*/[M]) of the NPE samples and the conversion (*C*) on time in the absence (*1, 1´*) and in the presence of air oxygen (*2, 2´, 3, 3´*). *T* = 60 (*a*), 80 °C (*b*). The starting composition of the samples, wt.%: PEG-DAc (15), BP (1), (1 *M* LiBF$_4$ in GBL) (82), SiO$_2$ (2) (curves *1, 1´, 2, 2´*); PEG-DAc (15), BP (1), (1 *M* LiBF$_4$ in GBL) (74), SiO$_2$ (10) (curves *3, 3´*).

the curing mode of hardening in order to obtain NPE with the maximum conversion (~100%): 3 h at 60 °C, 1 h at 70 °C, 1 h at 80 °C, 1 h at 120 °C. This synthesis regime was used to obtain 16 NPE samples with from 0 to 14 wt.% SiO$_2$ nanopowder content both with and without ultrasonic treatment of the starting mixture were obtained. The compositions of the samples are given in Table 1. All of the obtained electrolyte films (both with and without added SiO$_2$) were optically transparent (Fig. 3).

We measured the conductivity of all the obtained NPE samples. Four measurements were carried out for each sample. The experimental error was less than 1—2%. The impedance hodograph was a straight line with a slope of 70—80 deg. The results of the conductivity measurements are shown in Fig. 4.

Figure 4 shows that when SiO$_2$ nanopowder was introduced, the NPE conductivity first increased slightly, reaching 4.3·10^{-3} S cm^{-1} at 25 °C, and then decreased

Table 1. Composition of the NPE samples obtained without preliminary treatment and with ultrasonic (US) treatment of the starting mixture before synthesis

NPE	NPE with US	[SiO$_2$]	[1 *M* LiBF$_4$ in GBL]
		(wt.%)	
1	1*	0	84
2	2*	2	82
3	3*	4	80
4	4*	6	78
5	5*	8	76
6	6*	10	74
7	7*	12	72
8	8*	14	70

* The composition of the starting mixture for all the samples included PEG-DAc (15 wt.%) and BP (1 wt.%).

sharply. This tendency was observed for the NPE samples without preliminary treatment at 6 wt.% SiO$_2$ content and higher and for the samples after ultrasonic treatment at 8 wt.% SiO$_2$ content and higher. The dependence of conductivity on the nanoparticle content always has an extreme character. This is explained by the fact that initially the increase of nanoparticle content leads to the
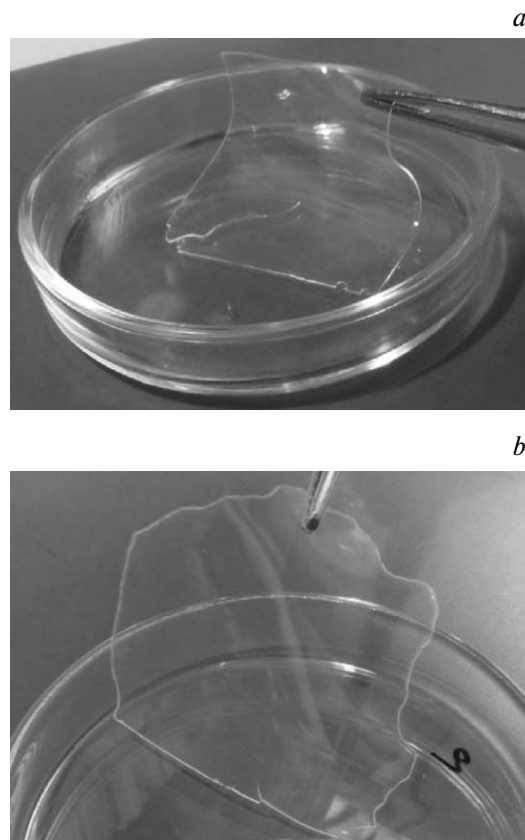

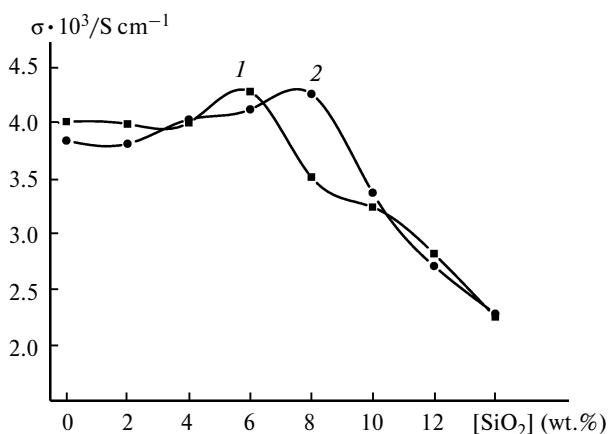**Fig. 3.** Photograph of NPE films without SiO$_2$ (*a*) and with the addition of 10 wt.% of SiO$_2$ (*b*).

Fig. 4. Dependence of the conductivity (σ) of the NPE samples on SiO_2 content: *1* is the sample without preliminary treatment, *2* is the sample after ultrasonic treatment.

Fig. 5. Dependence of the elastic modulus (E) of the NPE samples on SiO_2 content: *1* is the sample without preliminary treatment, *2* is the sample after ultrasonic treatment.

appearance of additional ion transport pathways; and when the number of particles becomes too high, they block these pathways. The difference in the types of dependences of conductivity on nanoparticle content (see Fig. 4) is clearly caused by a more uniform distribution of SiO_2 nanoparticles within the bulk of the NPE samples which have undergone ultrasonic treatment.

In contrast to electrolytes with the composition polymer—salt, for which the conductivity of the electrolyte was considerably increased due to ultrasonic treatment,[20] in our case the conductivity peak values for treated and untreated samples (see Fig. 4, curves *1* and *2*) were the same. Clearly, this is related to the fact that in gel-electrolytes with high aprotic electrolyte content (70—80 wt.%) conductivity is carried out predominantly by the liquid phase and nanoparticles play an insignificant role in the ion transport. In general, nanoparticles are introduced in order to improve the mechanical properties of gels.

The elastic modulus for the obtianed NPE samples was determined for uniaxial compression (Fig. 5) (see Table 1).

Figure 5 shows that the introduction of SiO_2 nanopowder into the polymerization system increased the elastic modulus for compression deformation. Ultrasonic treatment improves the quality of the polymer composite, achieving a more uniform distribution of SiO_2 particles in the sample bulk. The dependence of the elastic modulus on the nanoparticle content for the samples that had undergone ultrasonic treatment has two regions of ascent (the ranges from 0 to 2 wt.% and from 10 to 14 wt.% of SiO_2). Between these regions there is a plateau within which the elastic modulus is practically the same. The second ascent is possibly related to the restructuring of the sample, the appearance of anisometric structures as a result of the aggregation of nanoparticles.[21] In the samples without ultrasonic treatment, an increase of the
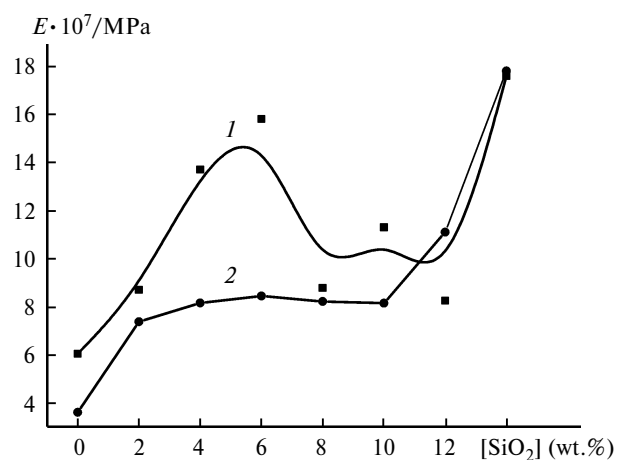
elastic modulus is also observed with increasing SiO_2 content, however due to the disorder of the NPE structure, the G values are scattered.

The preservation of properties of all the NPE samples was monitored on storage over 24 months at 25 °C in a desiccator over P_2O_5. After 24 months of storage, the films preliminarily treated with ultrasound remained transparent (Fig. 6, *a*), while the samples that had not undergone ultrasonic treatment became opaque (Fig. 6, *b*). The films that had a nanofiller content of less than 4 wt.% became brittle, and cracks appeared in the samples with 6 wt.% SiO_2 content and higher, indicating a poor retention of the solvent in such cross-linked structures (Fig. 6, *d*, *e*, *f*). Only for the samples with 4 wt.% of SiO_2, the NPE films retained integrity and elasticity (Fig. 6, *b*, *c*, *d*), making it possible to study their electrochemical properties (Table 2).

During the storage, the resistance of the samples NPE-3 and NPE-3* increased by 4.5% and 0.7%, respectively. This indicates a very high degree of preservation of conduction properties of the samples in question, especially those synthesized with ultrasonic treatment.

In conclusion, using isothermal calorimetry we studied the specific features of the formation of cross-linked polymer matrix of gel-electrolyte based on poly(ethylene glycol) diacrylate in 1 M $LiBF_4$ in γ-butyrolactone with

Table 2. Dependence of conductivity on the duration of storage of the NPE-3 and NPE-3* samples

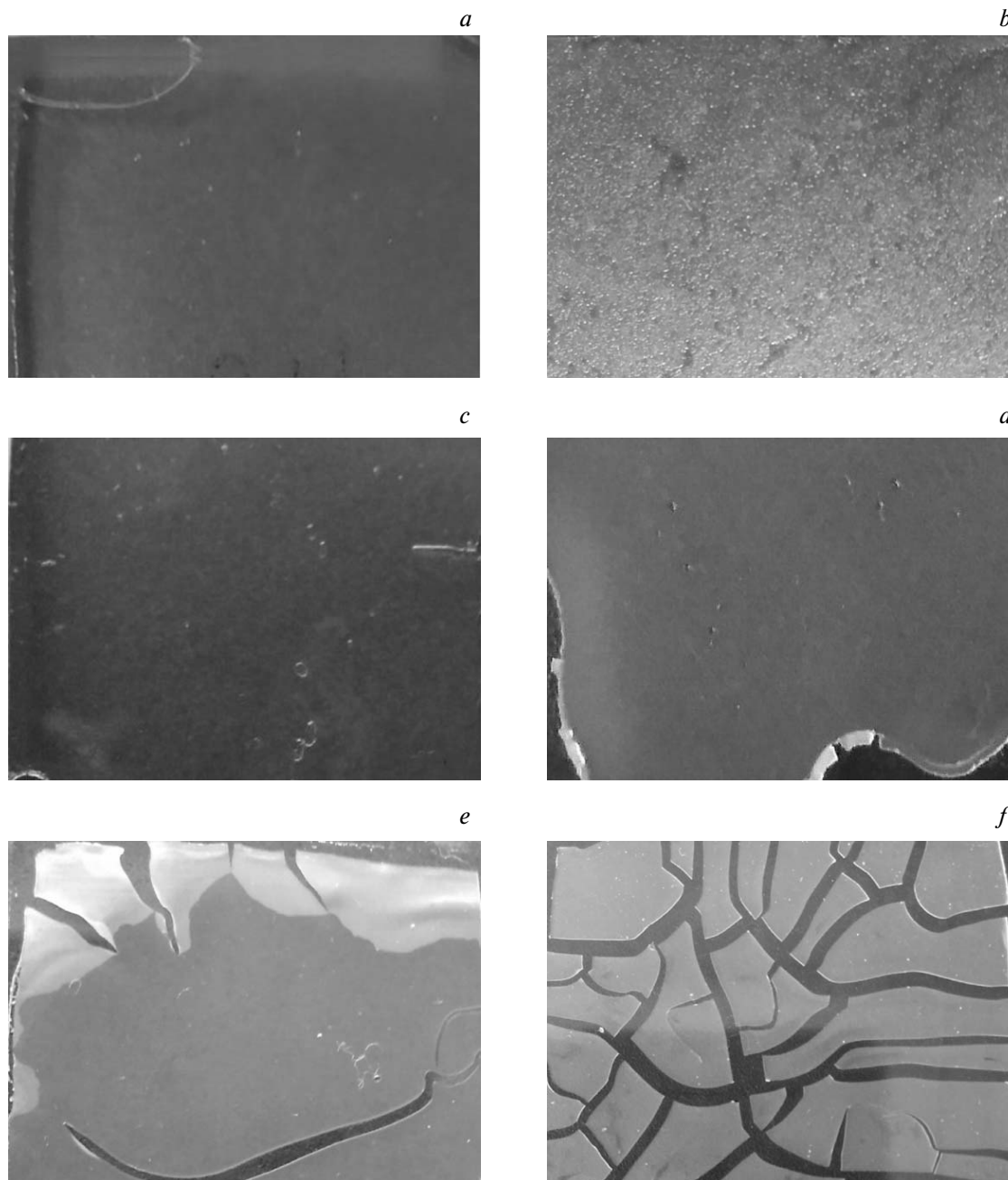| Sample	Electrolyte conductivity/mS cm^{-1}	
	$\tau = 0$	$\tau = 24$ months
NPE-3	4.00±0.03	3.30±0.01
NPE-3*	4.03±0.03	3.83±0.01

Fig. 6. Photographs of NPE films after storage over a period of 24 months for the compositions (see Table 1): 2* (*a*); 2 (*b*); 3* (*c*); 3 (*d*); 4* (*e*); 8 (*f*).

the introduction of 2 and 10 wt.% of SiO_2 nanopowder. The polymerization process proceeds to the complete conversion of the C=C bonds only at 60 °C.

Using the electrochemical impedance method, we studied the dependence of the conductivity of NPE samples on the amount of SiO_2 nanopowder introduced and the presence of ultrasonic treatment of the nanocomposite mixture before the synthesis. It was found that the maximum conductivity was reached for the NPE sample without ultrasonic treatment at a SiO_2 content of 6% and for the NPE sample with ultrasonic treatment, at 8 wt.%. Ultrasonic treatment was also found to have a positive influence on the mechanical properties of the NPE. Transparent films with a uniform distribution of SiO_2 nanoparticles were obtained. The NPE films with 4 wt.% SiO_2 content demonstrated a high preservation of mechanical and electrochemical properties over a period of 24 months.

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