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# EPOXY-SILICA NANOCOMPOSITES BASED ON ETHOXYSILANES AND DIGLYCIDYL ETHER OF DICYCLOHEXYLOLPROPANE

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**Abstract.** Sol-gel method was used to obtain epoxy-silica nanocomposites cured with dicarboxylic acid anhydride. Incorporation of filler into the system leads to plastisization of organic matrix: glass transition temperature decreases and sol-faction yield increases with filler content. At $w(SiO_2) = 0.5–3$ mas % effect of low additions is observed: molecular weight of chain between junctions decreases and thermostability of hybrid materials rises.

**Keywords:** epoxy-silica nanocomposites, anhydride curing, sol-gel method.

## 1. Introduction

At present development of the polymer science is directed to creation of new materials or improvement of the properties of already existing systems. An example of the approach that allows getting new materials is synthesis of organic-inorganic composites by synergistic combination of organic and inorganic phases [1, 2]. In such systems combining of useful properties of organic polymers (durability, flexibility, and simplicity of treatment) with properties of inorganic materials (thermal stability, high mechanical, electric, and optical characteristics) occurs. However, the properties of hybrid systems are not just simple averaging of the properties of their constituents. An important role is played by the components ratio, their size, shape, and uniformity of distribution. Usually inorganic particles which are formed in hybrid materials have sizes of less than 100 nm, that is why the systems remain transparent, and such hybrids obtained the name nanocomposites. One of the ways for receiving organic-inorganic nanocomposites is sol-gel method [3-5]. The precursors which are usually used for formation of inorganic phase within the organic polymeric matrix are alkoxides, in particular alkoxysilanes. On the first stage of

sol-gel process hydrolysis of silicon alkoxide takes place resulting in formation of silanol groups, on the second stage condensation of hydrolysis products with formation of inorganic net composed of –Si–O–Si– fragments occurs.

Widely used hybrids are epoxy-silica nanocomposites [6-10]. For the formation of organic matrix different epoxide oligomers are utilized. Varying of the conditions of obtaining and the composition of hybrids during sol-gel synthesis allows changing structure and properties of hybrid materials considerably. Nowadays there is an insufficient number of investigations of composites synthesized using dicarboxylic acids anhydrides as epoxy constituent hardeners. In work [11] triepoxide of 1,1-dimethylol-3-cyclohexene and *iso*-methyltetrahydrophtalic anhydride were used for organic matrix formation of hybrids. The resulting composites possessed high heat and thermal stability at low filler concentrations. The goals of this investigation were obtaining of epoxy-silica composites cured with acid anhydride based on diglycidyl ether of dicyclohexylolpropane using sol-gel method and different ways of silica particles sol formation, and studying the influence of filler content at characteristics of received hybrid materials.

## 2. Experimental

Unmodified polymeric samples were obtained by mixing diglycidyl ether of dicyclohexylolpropane (EPO-NEX™ RESIN 1510), *iso*-methyltetrahydrophtalic anhydride (*iso*-MTHPA, EPIKURE 3601, HEXION) and curing reaction accelerator 2,4,6-tris-(*N,N*-dimethylaminomethyl) phenol (UkrderzhNDIplastmas, UP-606/2).

Sol of silica particles was obtained by hydrolysis of mixture of tetraethoxysilane (TEOS, «Kremnijpolimer») with 3-glycidoxypropyltriethoxysilane (ES-1, «Altajhim-prom») at molar ratio of 2:1 (aqueous $HNO_3$ was used as

ethoxysilane precursors hydrolysis catalyst) in presence and absence of epoxy resin EPONEX 1510. The total $SiO_2$ content in the system was varied from 0.5 to 6 mas %. Acetone was used as a solvent in the sol-gel process (acetone/ethoxysilanes ratio 35/65, v/v). 24 hours after the start of the process the sols were evacuated at 293 K for 24 h to remove volatile components from the system (residual pressure 0.5 kPa). After that a stoichiometric amount of the curing agent (*iso*-MTHPA) and a curing reaction accelerator (UP-606/2, 0.3 wt % based on the total amount of anhydride and epoxy resin) was added. In the model reactions Aerosil A-300 (Kalush experimental-research factory of Chuiko Institute of Surface Chemistry NAS of Ukraine) was used.

The samples were prepared between glass plates with antiadhesive coating as 200±10 µm thick films. Block samples of composites were cylinders of the diameter and height of approximately ~10 mm obtained in the steel forms coated with isobutylene caoutchouc film. The curing was performed under the following conditions: 393 K, 1 h; 433 K, 2 h; and 453 K, 2 h.

The epoxy number (e.*n.*) was determined by titration with HBr solution in glacial acetic acid according to GOST (State Standard) 12497-78. Acid groups concentration (*a.n.*) was determined by acid-base titration with aqueous NaOH with thymol blue as indicator [12].

The light transmission coefficient of 200 µm thick film samples was determined with a KFK-3 photo-colorimeter (at a wavelength of 540 nm). The glass transition point of the polymers was determined by thermomechanical method with a laboratory installation consisting of a TK-500 thermocryochamber, a BTP-78 programmable temperature regulator, an M-217 electronic measuring system and an *XY* recording potentiometer. The measurements were performed on cylindrical block samples at a tensile stress of 0.75 MPa. A heating rate was 4 deg·min⁻¹. Molecular weight of chain between junctions was determined using thermomechanical data according to the formula: $M_c = 3\rho RT/E_\infty$, where $\rho$ – density of samples, $R$ – gas constant, $T$ – temperature, $E_\infty$ – the equilibrium rubbery modulus.

Sol-fraction yield ($W_{sol}$) of the polymers and composites was determined from the change in the weight of the polymer films after extraction of low-molecular-weight products with methanol at 323 K for 3 days. The oxidation rate of film samples with weight of 150–200 mg was determined by gas volumetry at 473 K and pressure of 0.1 MPa. Thermogravimetric studies were performed using derivatograph Q-1500D of Paulik – Paulik – Erdei system (MOM, Hungary) in the dynamic mode in the temperature range 293–1123 K, at the heating rate of 10 deg·min⁻¹. Aluminum oxide was used as a reference. The measurements were performed in air. Microscopic studies and elemental analysis were performed using the scanning electron microscope JSM-6390LV (JEOL Ltd., Japan) on carbon coated fractured surfaces of composites block samples.

# 3. Results and Discussion

The system used for obtaining of composite materials *via* the sol-gel technology is a multi-component one, with different groups that can both react with each other when $SiO_2$ particles are synthesized and cause negative processes resulting in unproductive loss of initial compounds. In work [13] it was shown that ethanol (as ethoxysilane precursors hydrolysis product) led to cleavage of anhydride cycle, and *iso*-MTHPA should be incorporated to the system directly before curing of composition. Authors [14, 15] noted that the presence of acidic catalyst of hydrolysis of ethoxysilane precursors in the sol-gel systems had insufficient influence on oxirane ring opening. In the studied systems change of epoxy number of EPONEX 1510 in the presence of 0.1 M nitric acid solution was investigated. Model mixtures with the same amount of components as used for sol formation but without ethoxysilanes were prepared: per 3 and 6 mas % $SiO_2$. Since there is an epoxy group in the structure of ES-1, change in epoxy number of compatibilizer in the presence of $HNO_3$ was examined too. It was determined that after ageing for 24 h epoxy number decreased, sufficiently in the systems with larger ratio of nitric acid to epoxy resin (Table 1). Longer sol components ageing caused further lowering of epoxy resin and compatibilizer epoxy numbers. Thus, the presence of acid in sols may result in decrease of EPONEX 1510 epoxy number, especially at high silica particles content in the composition, leading to disorder of epoxy resin – hardener stoichiometry, which can negatively affect the properties of hybrid materials. That is why one of the ways to avoid epoxy groups cleavage by nitric acid is carrying out ethoxysilanes' hydrolysis and silanol groups' condensation in the absence of epoxy resin. Under such conditions sol formation in the absence of epoxy resin can affect only ES-1 epoxy number values.

*Table 1*

**Relative decrease of EPONEX 1510 and ES-1 epoxy numbers in the presence of $HNO_3$**

| $t$, days | $\Delta e.n.$, % | | |
|---|---|---|---|
|  | I | II | III |
| 1 | 0.9 | 1.3 | 2.4 |
| 2 | 1.2 | 1.7 | 3.3 |
| 3 | 1.4 | 1.7 | 3.6 |

Notes: I – molar ratio HNO₃/EPONEX 1510 = 1·10⁻⁶; II – molar ratio HNO₃/EPONEX 1510 = 2.5·10⁻⁶; III – molar ratio HNO₃/ES-1 = 1.2·10⁻⁵

Influence of hydroxyl groups in the structure of silica particles on cleavage of epoxy groups in resin and anhydride cycle of hardener during the curing process was additionally studied. Model systems «EPONEX-1510/Aerosil», «EPONEX-1510/Aerosil/UP-606/2», «*iso*-MTHPA/Aerosil», and «*iso*-MTHPA/Aerosil/UP-606/2» were used for this purpose. It was determined that after system ageing for 1 h at 393 K (modeling of the first stage of curing process) decrease of relative values of *e.n.* and *a.n.* is observed, considerably in the presence of curing reaction accelerator UP-606/2 (Table 2). Thus, during the curing process opening of epoxy groups of the resin and anhydride cycle of the hardener may occur in the reaction with OH-groups of silica particles.

*Table 2*

**Relative decrease of EPONEX 1510 epoxy number and *iso*-MTHPA acid number in the presence of Aerosil**

| $\Delta$, % | Model system composition (mas %) | 1 h at 393 K |
|---|---|---|
| *e.n.* | EPONEX-1510/Aerosil/UP-606/2 (90.5/9.0/0.5) | 5.5 |
| | EPONEX-1510/Aerosil (91/9) | 3.9 |
| | EPONEX-1510 | 0.9 |
| *a.n.* | *iso*-MTPHA/Aerosil/UP-606/2 (93/6/1) | 3.0 |
| | *iso*-MTPHA/Aerosil (94/6) | 0.6 |

Taking into account the above data, synthesis scheme with two paths of epoxy-silica composites formation was proposed (Fig. 1). The obtained hybrids are homogeneous (especially for systems with silica particles sol formation in the absence of epoxy resin), which is evidenced by high values of light transmission coefficient. The higher the silica content in the composite the lower $T_{540}$ for both investigated systems (from 99.5 for unmodified polymer to 96 % for composites with silica content 6 mas %), which is explained by light scattering by aggregated filler particles. Both ways of composites formation provide for uniform sols: rapid homogenization occurs, especially with increase of ethoxysilanes and solvent amount.

It should be noted that when silica particles sols formation occurs in the presence of epoxy resin loss of homogeneity of the systems during curing takes place. At $w(SiO_2) = 3$, 4.5, and 6 mas %: phase separation begins (especially at maximum filler content), resulting in impossibility to obtain uniform films and block composite samples. It can be explained by thermodynamic incompatibility of sol and epoxy resin. Sol formation in the absence of organic constituent provides for more complete hydrolysis process passing, resulting in the presence of large amount of ethanol in the system (the product of ethoxysilane precursors hydrolysis), which may be

considered as an additional solvent together with acetone present in the system from the very beginning.

From the micrographs of fractured surface of composite block sample one can see silicon enriched areas – small light spots which have very ill-defined boundaries (Fig. 2a). Only raised silicon concentration in this areas allow labeling them as silica particles (dots 1–3); in dot 4 Si content does not exceed 0.7 %. Absence of clear boundary between silica particles surface and organic phase indicates the defectiveness of the structure of synthesized nanoparticles. This may be due to slow accumulation of three- and tetrafunctional siloxane fragments when acid catalysis of hydrolytic polycondensation of ethoxysilane precursors is used [16]. The presence of glycidyl groups in the structure of silica particles also hinders regular network of Si–O–Si fragments generation [17]. All these factors result in the formation of irregular silica particles structure and appearance of transitional layer between particles and epoxy matrix of the composite that can significantly affect the properties of hybrid materials. The size of particles in the investigated sample is on average 60–90 nm (Fig. 2b).
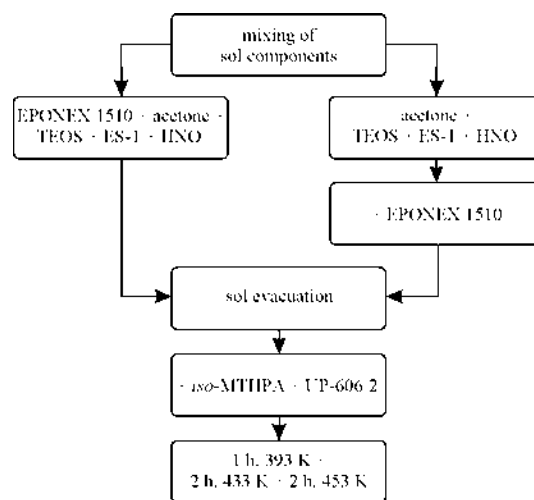


**Fig. 1.** Sol-gel synthesis of epoxy-silica composites with different ways of sol formation

Similar micrographs were received for composites with $w(SiO_2)$ 3 mas % when sol formation occurs in the presence of EPONEX-1510 (particles size 60–90 nm), and at filler content 1 and 3 mas % at sol formation in the absence of epoxy resin (~40 and 110–130 nm correspondingly). Increase of nanoparticles size in the composite with 3 mas % filler content when sol-gel synthesis is carried out in the absence of EPONEX-1510 may be explained by hydrolysis and condensation intensification due to diffusion processes acceleration in the system.

Investigation of the influence of ethoxysilanes incorporated into the system on thermomechanical properties of the composites shows decrease of glass transition point of hybrid materials with silica content

increase (Table 3), to a greater extent for the systems with sol formation in the presence of epoxy resin; broadening of $\alpha$-relaxation transition interval $\Delta T$ is also observed. This can be explained by existence of transitional layer between silica particles and organic matrix in the composites, resulting in formation of interpenetrating polymer networks and effect of mutual plasticization, leading to distortion of topological structure in hybrid materials. Plastisization effect usually leads to decrease of crosslink density and increase of low-molecular-weight compounds (sol-fraction) in the system, which is observed in this case. It was established that with ethoxysilanes content increase $W_{sol}$ values in the system raised, to a lesser extent for the systems with silica particles sol formation in the absence of epoxy resin.

Molecular weight of chain between junctions was determined using thermomechanical analysis data (Table 3). At silica content of 1 mas % decrease in $M_c$ values is observed. The further rise of silica particles concentration leads to gradual increase of molecular weight of chain between junctions. Extreme shape of concentration dependence $M_c$ may be due to possible formation of continuous cluster of polysiloxane particles in the region of low silica concentrations [18], resulting in composites' structure reinforcement and change of their properties. Significant increase of $M_c$ values at high siloxane constituent concentration may be explained by the fact that cluster is not formed, formation of large aggregates of silica particles is observed, and reinforcing effect is not displayed.
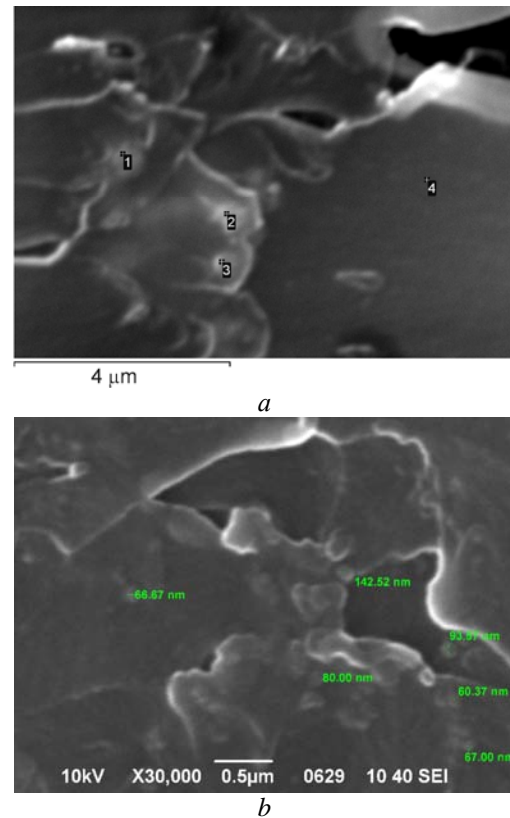


**Fig. 2.** SEM micrographs of the composite with $SiO_2$ content 1 mas % (silica particles sol formation in the presence of epoxy resin): elemental analysis (a) (Si, %: 4.5 (1); 7.3 (2); 5.8 (3) and 0.7 (4)) and particles size analysis (b)

*Table 3*

**Influence of silica content and way of sol formation
on thermomechanical properties and sol-fraction yield of the composites**

| $w(SiO_2)$, mas % | In the presence of resin | | | | In the absence of resin | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_g$, K | $\Delta T$, K | $W_{sol}$, % | $M_c$, g/mol | $T_g$, K | $\Delta T$, K | $W_{sol}$, % | $M_c$, g/mol |
| 0 | 401 | 10 | 1.1 | 804 | 401 | 10 | 1.1 | 804 |
| 0.5 | 396 | 10 | 2.6 | 1050 | 396 | 11 | 1.0 | 861 |
| 1.0 | 389 | 10 | 3.2 | 828 | 391 | 11 | 1.5 | 675 |
| 1.5 | 380 | 11 | 3.5 | 936 | 386 | 12 | 2.1 | 935 |
| 3.0 | 373 | 12 | 4.6 | 856 | 379 | 12 | 2.7 | 992 |
| 4.5 | 354 | 12 | 6.9 | 1202 | 364 | 15 | 4.2 | 1181 |
| 6.0 | 347 | 12 | 10.3 | 1562 | 349 | 12 | 6.4 | 1383 |

To determine the effect of changes in topological structure on thermal stability, influence of composition and hybrid materials formation conditions on high-temperature oxidation of film samples with molecular oxygen was investigated. The kinetic curves of oxygen uptake at 473 K for the unmodified polymer and composites are shown in Fig. 3. One can see that increase of silica particles content leads to rise of oxygen uptake as a result of topological defects and low-molecular-weight compounds content increase in the system. At low filler content in the composites oxidation rate in the beginning of the process is almost the same (curves 2 and 3).

The higher the silica content in the composites the higher maximal oxidation rate (Fig. 4). Composites obtained with silica particles sol formation in the absence of epoxy resin possessed higher thermal-oxidative destruction

resistance compared to parallel series. In the filler concentration range of 1.5–3 mas % oxidation rate for both series of samples is almost changeless, which may be associated with decrease in $M_c$ of the composites and, correspondingly, slowing down of the diffusion processes in the systems. Further increase of silica content leads to topological structure distortion, lowering of network density and rise of low-molecular-weight compounds content in the system.

*Table 4*

**Derivatographic analysis results for epoxy-silica composites, obtained with different ways of silica particles sols formation**

| $w(SiO_2)$, mas % | In the presence of resin | | In the absence of resin | |
|---|---|---|---|---|
| | $T_{10}$, K | $T_{max}$, K | $T_{10}$, K | $T_{max}$, K |
| 0 | 543 | 603 | 543 | 603 |
| 0.5 | 558 | 618 | 553 | 608 |
| 1.0 | 553 | 618 | 558 | 613 |
| 3.0 | 543 | 608 | 548 | 618 |
| 6.0 | 553 | 603 | 543 | 608 |
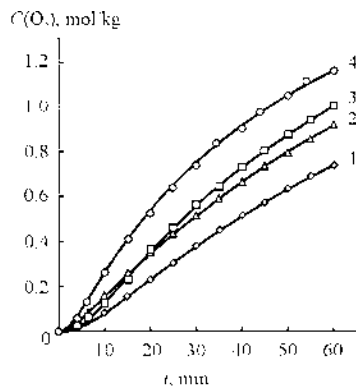


**Fig. 3.** Kinetic curves of oxygen uptake by film samples of composites, obtained by silica particles sol formation in the absence of epoxy resin. $SiO_2$ content, mas %: 0 (1), 1.5 (2), 3 (3) and 6 (4)
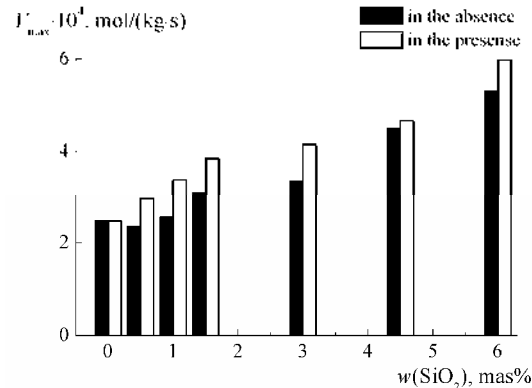


**Fig. 4.** Maximal oxidation rate $V_{max}$ as a function of silica content and different ways of silica particles sol formation
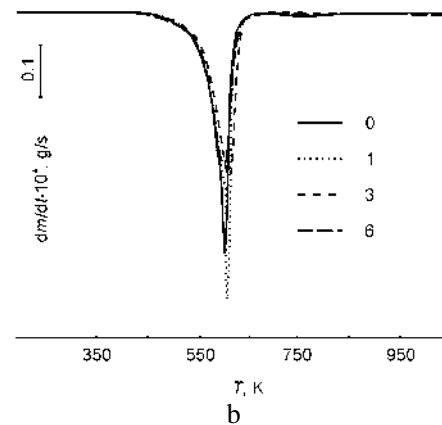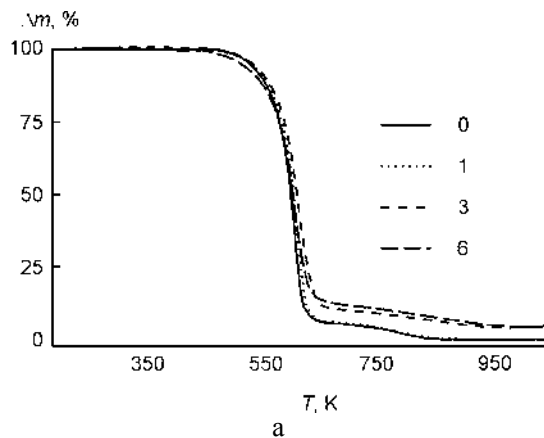


**Fig. 5.** *TG* (a) and *DTG* (b) curves of the composites, obtained at silica particles sol formation in the absence of epoxy resin. Silica content: 0, 1, 3, and 6 mas %

Influence of silica content on the resistance to thermal-oxidative degradation of the composites was investigated. Fig. 5 shows derivatographic curves of weight loss and rate of weight loss (*TG* and *DTG* correspondingly) for the composites obtained when silica particles sols were formed in the absence of epoxy resin. One can see that with the increase of filler content in the system (3 and 6 mas %) rate of weight loss decrease, the end of thermal destruction shifts to higher temperatures region. For composites with $w(SiO_2)$ 1 and 3 mas % *DTG* maxima shift to higher temperatures compared to the neat epoxy polymer. Derivatographic data analysis display that incorporation of filler into the system for both ways of silica particles sol formation leads to the rise of thermal stability of the composites, which is evidenced by temperatures of 10 % weight loss ($T_{10}$) and maximal rate of weight loss ($T_{max}$) (Table 4). Increase of composites thermal stability may be explained by formation of silica particles grafted to epoxy matrix and increase of crosslink density in the hybrids compared to unmodified polymer.

## 4. Conclusions

1. Sol-gel method was used to synthesize homogeneous epoxy-silica nanocomposites cured with acid anhydride with silica particles sol formation in the presence and in the absence of epoxy resin EPONEX-1510.

2. In the filler concentration range of 0.5–3 mas % the effect of low additions is observed. Effective molecular weight of chain between junctions decreases and thermal stability of the composites increases.

3. At silica content higher than 3 mas % increase of topological defects of epoxide network occurs resulting in lowering of glass transition point, increase of sol-fraction yield, and increase of oxygen uptake in the process of high-temperature oxidation of hybrid materials.

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**ЕПОКСИДНО-СИЛОКСАНОВІ НАНОКОМПОЗИТИ НА ОСНОВІ ЕТОКСИСИЛАНІВ І ДИГЛІЦИДИЛОВОГО ЕТЕРУ ДИЦИКЛОГЕКСИЛОЛПРОПАНУ**

*Анотація. Золь-гель методом одержано епоксидно-силоксанові нанокомпозити ангідридного тверднення. Встановлено, що при введенні в систему наповнювача відбувається пластифікація органічної матриці: знижується температура склування, збільшується вихід золь-фракції. При концентрації SiO₂ 0.5–3 мас % проявляється ефект малих добавок: спостерігається зниження молекулярної маси міжвузлових ланцюгів і підвищення термостабільності гібридних матеріалів.*

*Ключові слова: епоксидно-силоксанові нанокомпозити, ангідридне тверднення, золь-гель метод.*