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Polyfunctional Nanostructured Composite Materials for LED Technology

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***Abstract* – New alumosilicate filled with aluminum oxyhydroxide (AlO(OH)) is offered as a dielectric substrate (DS) for LED devices. Obtained from these substances the DS have high thermal conductivity up to λ = 133.61 W/m×K, whose value depends on the amount of AlO(OH) in the DS. High thermal conductivity is achieved by homogeneous distribution of a large number of AlO(OH) nanosize particles in the crowns of the dendrimer alumosilicate ensembles. The size of the AlO(OH) particles is comparable to that of the voids between the branches in the alumosilicate crowns. As a conductive adhesive for fixing of LED chips on the DS the copolymer of vinyl chloride-maleic anhydride, nano- and microparticles of silver (70 wt. %) composite is offered, the volume resistivity of the wirings being up to $3.1 \cdot 10^{-8}$ Ohm×m. Adhesive strength of the filled alumosilicate (80% of AlO(OH)) applied under shear on the aluminum plate (its roughness to be 11.3 mkm) is 47 N/mm^2.**

***Index Terms* – Composite materials, nanostructures, intermolecular interactions, supramolecular structures, sol-gel products, macromolecular conformations, dielectric composition, conductive polymer composition, LED bar.**

I. INTRODUCTION

Undoubted advantage of LED devices over other sources of light is their unique opportunity of usage in information technology, different types of lighting and in advertising design. The basic requirement for the modern market of LEDs and LED technology is increasing of the light flux and life, heat dissipation, as well as reducing of energy consumption. Achieving these characteristics is possible only by using new composite materials and modern technologies. Primarily, this requirement concerns dielectric substrates (**DS**) of the LED bars.

Market analysis suggests that the most available conductive composition now is the EPO-TEK H20E-175 of the EPOXY technology company with electrical resistivity of $4 \cdot 10^{-6}$ Ohm×m. Namics and Ferro companies offer silver-pastes of high thermal conductivity and of low electrical resistivity. Dielectric adhesives having thermal conductivity up to 2.4 W/m×K and adhesion strength of 25 N/mm^2 are available from Namics and Dow Corning.

The main disadvantages of the said compositions are as follows: high cost, limited selection of support bases (**SB**) for LED devices whose surface can be applied on by the dielectric compositions (**DiC**), high sintering temperatures, as well as the use of costly equipment for production. Manufacturers of LED devices constantly require more new functional composite materials (**CM**). The need for new highly resistant to the mechanical stress and aggressive environments, to various types of radiation and high vacuum or high pressure, resistant to high or low temperatures functional **CM** encouraged the scientists to look for new approaches to the synthesis of the polymers and creation of special composites that meet these requirements. Traditional synthetic methods for obtaining the **CM** do not always allow achieving the required performance. This, in particular, applies to those cases where the structuring of the materials is carried out by nanoparticles.

The first goal is to develop a controllable chemical synthesis directly during formation and modification of the **CM** properties, as soon as the phase, nanostructural and other features that define physical, mechanical, chemical and service properties of the products are being programmed at the very stage of the synthesis. It is not always possible to obtain nanostructured **CM** of desired stoichiometry, homogeneity, high purity and those of specific microstructure using classical methods of the synthesis. It is true especially in those cases when polyfunctional materials with special consumer properties are required [1-3].

The second goal requires a special approach to the formation and producing of both the conductive and dielectric components of LED devices. The FILAMENT COB LED lamps e.g., have LED bars of new ceramic-based generation. The LED crystals are pasted on the LED bars with sequential ultrasound splicing. At the end the contacts are to be withdrawn and the device to be embedded into proper luminophore. Such LED bars have an advantage over the polymer bars, which melt at the sealing of the glass bulb. However, the ceramic bars are not without drawbacks as well, because made of Al oxide by means of high temperature sintering, the ceramic base has insufficient heat conductivity (24 ÷ 30 W/m×K).

The aim of the work is to develop new approaches to manufacture of LED bars with high thermal characteristics, differing by the structure of composite materials of the dielectric substrate and by structure of the new mixtures of substances to paste crystals on them.

II. MATERIALS AND EXPERIMENTAL PROCEDURES

Aluminum was chosen as a high thermal conductivity material for the **SB** of LED bars**.** The **DiC** applied on Al surface of the **SB**, represents alumosilicate filled with Al

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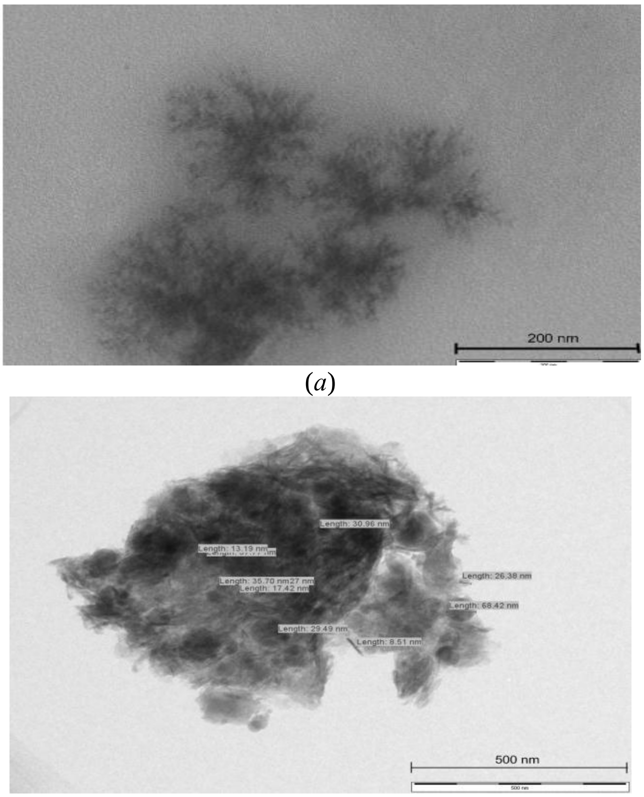
oxyhydroxide, which improves heat transfer to the **SB** extending the life of the LED light source in general.

III. FILLED ALUMOSILICATE AS DIELECTRIC SUBSTRATE

It was mentioned, that alumosilicate filled with aluminum oxyhydroxide was investigated and offered as the **DS**. Its sol-gel synthesis was carried out from preliminarily prepared oligomeric alumosilicates [4, 5]. Conformational analysis of the latter by quantum-chemical method allowed us to find synthetic approaches to obtain alumosilicates with desired dendritic micro structure (dendrimer supramolecular structure) (Fig. 1) at the very stage of **DS** formation [6].

Dendrimer alumosilicate has a highly branched supramolecular structure which consists of a large number of interlacing short alumosilicate ‘twigs’ resembling a tree crown (Fig. 1*a*). Such supramolecular structure allows one to place an enormous number of nano- and microparticles of aluminum oxyhydroxide (**AlO(OH)**) in the voids between the twigs (Fig. 1*b*).



(*a*)

(*b*)

Figure 1. Electron microphotographs of highly branched dendrimeric sol-gel alumosilicate (*a*) and of **AlO(OH)** (*b*) to be placed in between the crowns of the dendrimer ensembles.

The distribution of the **AlO(OH)** microparticles in the crowns of alumosilicate dendrimers was performed by means of mechanochemical mixing followed by ultrasonic treatment [7].

The volume sizes of **AlO(OH)** are comparable with voids sizes between the branches (twigs) of alumosilicate crowns (Fig. 1*b*), which allows one to distribute the filler particles in between the twigs and the crowns. Formed from these systems, the **DS** have high thermal conductivity, whose value was determined by the laser flash (the Parker’s method). It is based on homogeneous pulsed heating of the sample, the pulse tending to zero pulse duration, so that all the light energy is absorbed instantly. Thermal conductivity λ (W/m×K) was calculated by the formula

$$\lambda(T) = a(T) \cdot \rho(T) \cdot C_p(T),$$

where: T – temperature; a, cm^2/s - thermal diffusivity; ρ, g/cm^3- bulk (true) density; C_p, J/kg×K - specific thermal capacity. The thermal diffusivity a is determined by the Parker’s method and heat capacity C_p - by the LFA 467 device of NETZSCH company relative to the reference sample. Experimental samples of alumosilicate filled with different **AlO(OH)** content were prepared in the form of cylinders with a diameter of 12.7 and a height of 2 mm.

Mathematical analysis of thermal diffusivity was carried out by a special program that uses a set of differential mathematical models for different applications. The thermal diffusivity a was calculated under adiabatic conditions by the equation

$$a = 0.1388 \cdot \frac{l^2}{t_{50}}$$

where a, m^2/s - thermal diffusivity; l, m - sample thickness; t_{50}, s - time corresponding the temperature increase by 50%, relative to the temperature of the rear wall of the sample. Special program allows one to control the process of measuring and to evaluate the results, both in manual and fully automatic regime. Parameter t_{50} of the sample ***1*** is 11 s; of the sample ***2*** – 5 s, and of the sample ***3*** – 0.95 s (the height of all samples is the same: $l = 0.002$ m).

The volume (true) density was determined by gravimetric method using a pycnometer; it was calculated by the formula

$$\rho = \frac{m \cdot \rho_f}{m + m_1 + m_2}$$

where m, g – weight of the sample; ρ_f ,g/cm^3– density of the liquid; m_1,g – weight of the volume meter with the material; m_2, g – weight of the volume meter with the liquid and the material.

Table 1. Heat conductivity parameters of the alumosilicate samples with different filler contents (60, 70 and 80 wt.%) measured by the Parker’s method

Parameters	Sample number (fraction of the filler, wt.%)			AlN sintered at high temperature is the Reference Sample
	1 (60)	*2* (70)	*3* (80)	
p (kg/m^3)	3171	3197	3220	3280
a (m^2/s)	$5.05 \cdot 10^{-6}$	$11.1 \cdot 10^{-6}$	$58.44 \cdot 10^{-6}$	$74.2 \cdot 10^{-6}$
C_p (J/kg×K)	683	695	710	740
λ (W/m×K)	10.93	24.67	133.61	180

The maximal thermal conductivity (λ = 133.61 W/m×K) corresponds to sample ***3*** with aluminum oxyhydroxide in the amount of 80 wt.% which is optimal, if one takes into account all other qualifying standards for the **DiC**.

Comparison of the properties of the sample ***3*** with the properties of AlN leaves no doubt about the possibility of commissioning such LED bars. It is interesting to note, that commercial **DiC** Prolimatech PK-3 has the highest thermal conductivity (11.2 W/m×K), which is nearly 12 times less than that of sample ***3*** (Table 1). The commonly used **DiC** is Namics XS8472, whose thermal conductivity (λ = 2.4 W/m×K) is almost 56 times less than that of sample ***3*** (Table 1).

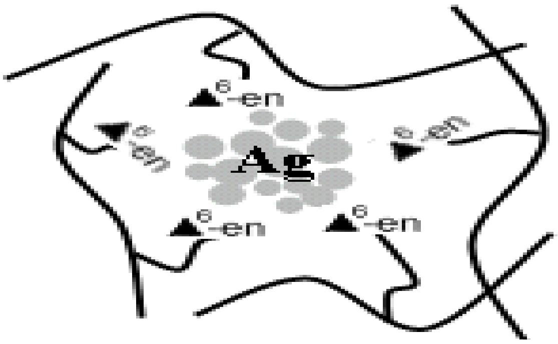
IV. CONDUCTIVE POLYMER COMPOSITION AS AN ADHESIVE FOR FIXING LED CHIPS ON DIELECTRIC SUBSTRATES

Compositions based on conductive fillers and synthetic polymer matrices are widely used as adhesives in almost all LED devices. It is glued joints (interfaces) are in major causes become the cause of these devices failures. In the first place this happens in the power switches operating under frequent cyclic on-load operation. The failure probability of the LED module increases exponentially with temperature increase. Reliability of the LED devices operation depends directly on heat dissipation from the chips. In other words, the composition linking the crystals with the **DS** must have low electric resistivity and good thermomechanical properties.

In order to place crystals on the **DS** with silver containing composites low-temperature sintering technology (LTST) is used. It allows one to improve the reliability of LED modules under high temperature cyclic effects. Nano- and micro powders of aluminum, nickel, copper, silver, gold and platinum are used as the conductive components in the adhesive compositions. The desire to reduce the cost of conductive pastes and adhesives leads to numerous attempts to replace expensive metals. Sometimes, in order to reduce the cost of adhesive composites they use silver-plated copper or silver-plated nickel which does not always leads to the desired results. In order to compare the effectiveness of nano- and micro silver powders obtained by two different methods, i.e. by electroexplosion and by electrical discharge of silver granules in chemically different solvents. Comparison was carried out with aluminum and copper powders [7].

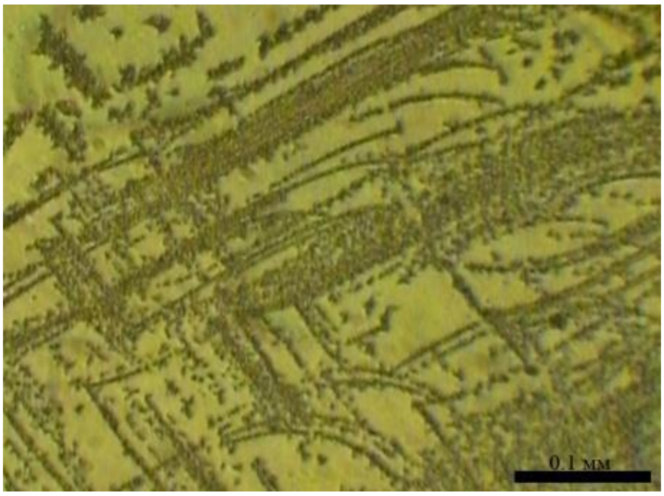
The results of thermogravimetric, dilatometric and thermal measurements of the powders mentioned allowed to find a method for producing a powder with the lowest sintering temperature. Such powders are obtained by electroerosion treatment of silver grains in water, and they may be used in the LTST up to the degradation temperature of the polymer matrix [6].

The vinyl chloride-maleic anhydride copolymer (VC-MA) possessing good film forming properties and high adhesion to metals, as the polymer matrix for the conductive polymer compositions (**CPC**), was used. Amphiphilic macromolecules of the **VC-MA** copolymer are flexible enough in such solvents as dioxane, tetrahydrofuran, acetone, dimethylformamide, alcohols, water and others. Their flexibility changes considerably in their midst. By varying the flexibility of macromolecules in solution one can control the morphology of the **CPC**, i.e. can change the size and volume geometry of the interdomain voids acting as accumulators of the electro conductive metal particles. Moreover, the unique property of **VC-MA** macromolecules is their ability to increase its affinity for the surface of silver or aluminum nanoparticles due to spontaneous formation of Δ^6-*en* structural units in the specific sections lengthwise the macromolecules [8]:

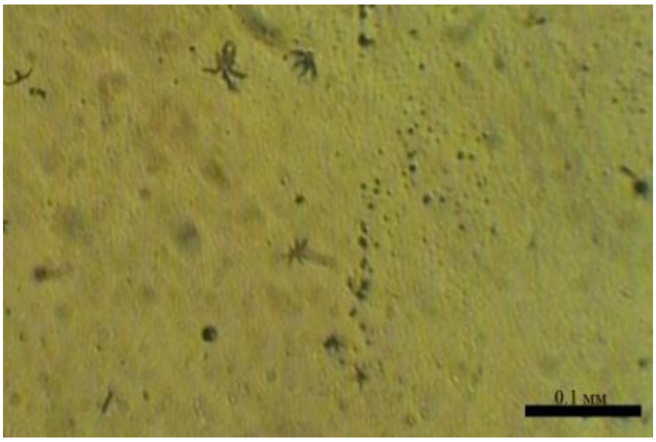


Polar Δ^6-*en* units increase adhesion of Ag agglomerates towards the [~Δ^6-en ~] structural units located on the interface of the microparticles of Ag agglomerates and the domains formed from macromolecules of **VC-MA** copolymer. In other words, presence of polar Δ^6-*en* units impedes to "exude" the microparticles out from the wirings and promote their permanent residency in the microvoids by means of strong intermolecular interactions. It is possible to select conditions to control the morphology of the CPC using the package GAUSSIAN98 and results of hydrodynamic experiments. One of the examples is described in detail in paper [8].

Visual evaluation of the microvoids geometry, as accumulators for the electro conductive microparticles of Ag, is represented illustratively in Figure 2, which clearly shows that extended microvoids are formed in the **VC-MA** films cast from tetrahydrofuran (Fig. 2*a*), while in the films cast from ethyl acetate (Fig. 2*b*) such structures are not formed at all, other things being equal. In other words, the most spacious microvoids for settlement of the silver particles are formed in those solvents where the macromolecules are uncoiled maximally. Tetrahydrofuran is such a solvent for **VC-MA** copolymers and microparticles of Ag.



(*a*)



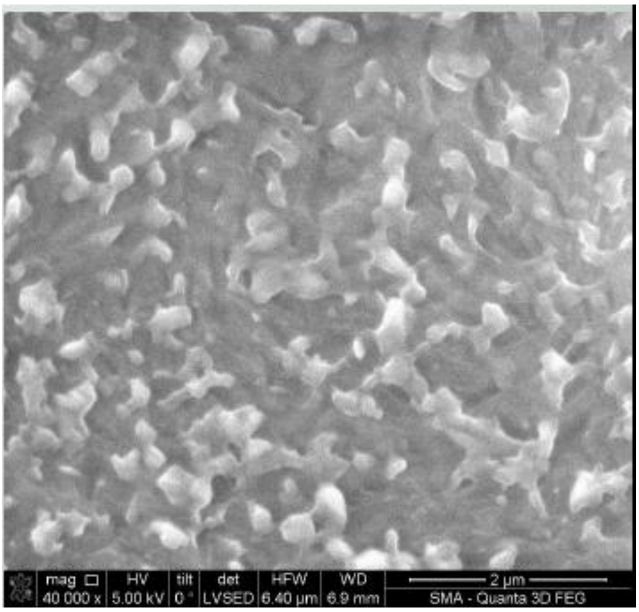
(*b*)

Figure 2. Microphotographs of pure **VC-MA** films cast from tetrahydrofuran (*a*) and from ethyl acetate (*b*). Magnification 480.

Further to evaluate the continuity of the wirings in the **CPC** we have investigated the surface topology of the **CPC** (Fig. 3) by high resolution electron microscopy with secondary double-beam electron field emission on the scanning electron-ion SMAQuanta 3D FEG microscope; the accelerating voltage and the scale are shown in the pictures. Comparison of the size of structures on the surface of the **CPC** in Fig. 3 *a* and *b* suggests formation of continuous topology of conductive silver tracks or wirings. However, a definite answer to the question of the continuity of the conductive wirings can only give the experimental value of electrical resistivity. We measured the electrical resistivity of about 20 samples of different conductive topologies containing from 50 to 70 wt.% of Ag by the four-probe method (Table. 2) and calculated the values of volume resistivity by the formula

$$\rho = \frac{R \cdot S}{l},$$

where *R*, Ohm – resistance; *l*, m – length between contacts; *S*, m^2 is the cross-sectional area calculated by $S = b \cdot d$, where *b*, m – the track width; *d*, m – track height.



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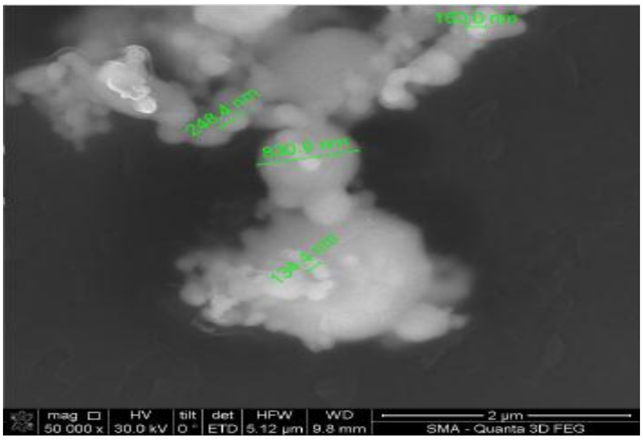

(*b*)

Figure 3. Electron microphotographs of the surface of the **CPC**, containing **VC-MA** copolymer as a polymeric matrix (*a*) and nano- and microparticles of silver dispersed therein (*b*)

It is interesting to note that the specific electrical volume resistance of the wirings with 70 wt% of Ag is $3.1 \cdot 10^{-8}$ Ohm×m, being close to that of pure silver, whose electrical resistance measured under the same conditions is $1.6 \cdot 10^{-8}$ Ohm×m. Obviously, the wirings formed under conditions described in [6] have continuous morphology. Microvoids of the polymer matrix display interconnected hollow channels populated by nano- and microparticles of silver, forming continuous dense conductive wirings. It is interesting to note that the geometry and dimensions both of the domains and of the interdomain voids can be diverse and even intricate [9, 10].

The **CPC** from EPO-TEK H20E-175 EPOXY technology firm has electrical resistivity of $4 \cdot 10^{-6}$ Ohm×m, which is two orders higher than that of the **CPC** with 70% of silver we have obtained ($3.10 \cdot 10^{-8}$ Ohm×m).

Table. 2. Electrical resistance of the **CPC** with different content of nano- and microparticles of silver

Sample № (fraction of nano-, micro-particles of silver in the **CPC**, wt.%)	*R*, Ом	ρ* **·10⁸**, Ом×м
1 (40)	2.15	34000
2 (40)	2.06	
3 (40)	2.07	
4 (50)	0.0199	322
5 (50)	0.0204	
6 (50)	0.0192	
7 (60)	0.00175	28.8
8 (60)	0.00181	
9 (60)	0.00177	
10 (70)	0.000168	3.1
11 (70)	0.000201	
12 (70)	0.000202	

* ρ, Ohm×m – volume resistivity of the wirings formed in the **CPC**, the average of three measurements; *R*, Ohm – resistance of the wiring; *d* = 0.00065 m – the height (thickness) of the wiring; *b* = 0,005 cm – width of the wiring; *l* = 0.02 m – the length between the contacts. The height (thickness) of the wirings formed in the **CPC** was determined on the eddy current thickness meter **«QuaNix 1500»**

It should be added that the most important performance characteristics of the **DiC** and the **CPC** include not only the electrical resistance and thermal conductivity, but the adhesion strength as well. Thus, the adhesion strength of one of the most common dielectric compositions ***Namics XS8472*** is equal to 25 N/mm^2, which is not sufficient for reliable performance of the devices in many cases.

In order to determine the adhesion strength under shear on the interface of the **DiC**, obtained from alumosilicate with **AlO(OH)** as a filler, and the aluminum **SB** we have carried out preliminary studies with varying roughness of many aluminum **SB**. Adhesive strength of 80% filled alumosilicate applied on the aluminum plate with 3.11 microns degree of roughness is equal to 47 N/mm^2 [11]. For comparison, adhesion strength of the alumosilicate applied on a smooth surface (0.05 microns roughness) is equal to 19 N/mm^2.

Adhesion strength of a series of **SB**, both of different degrees of roughness and of different nature of their surfaces are under study.

V. CONCLUSION

1. Dielectric composite material based on aluminum silicate filled with aluminum oxyhydroxide having high thermal conductivity up to 133.61 W/m×K and large adhesion strength is obtained. It can be used for manufacturing of light-emitting diode matrices.

2. A new conductive polymer composition, based on mixture of vinyl chloride-maleic anhydride copolymer with silver nano- and microparticles, can be used as adhesive for placing LED crystals on dielectric substrates. The conductive adhesive material has a low electrical resistivity up to $3.1 \cdot 10^{-8}$ Ohm×m, which approaches to the resistance of pure silver ($1.6 \cdot 10^{-8}$ Ohm×m).

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