Flexible heat-conductive polyimide composite materials

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In the paper results of development and study of thermally conductive polyimide composite materials based on binders from solution of aromatic polyamic acid Pyre ML RC 5069 and dispersed fillers from powders of aluminium nitride particles of micron and nano sizes are described. Technological schemes of manufacturing were chosen, structural modelling and calculating effective thermal conductivity of polyimide composites using COMSOL MULTIPHYSICS software package were carried out. Methods of manufacturing thin thermally conductive micro- and nano-structured PI composite polyimide coatings and layers and single-sided composite aluminium-polyimine varnish-foil dielectrics with thermal conductivity in the range of 1.0-2.0 W/(m·K) have been developed. Main chemical, mechanical, electrical and thermal properties of experimental samples of single-sided thermally conductive aluminium-polyimide varnish-foil dielectrics were investigated.

Keywords: thermally conductive polyimide composite materials; structural 3D models; thermally conductive aluminium-polyimide foil dielectrics; test quality structures.

Гнучкі теплопровідні поліімідні композиційні матеріали. *В. Борщов, О. Лістратенко, М. Сліпченко, М. Проценко, І. Тимчук, О. Кравченко, І. Борщов.*

У роботі проведено проектування та дослідження теплопровідних ПІ композиційних матеріалів на основі сполучних із розчинів поліамідної кислоти Pyre ML RC 5069 і дисперсних наповнювачів із порошків часток нітриду алюмінію мікронних і нано розмірів. Обрано технологічні схеми виготовлення, проведено структурне моделювання та розрахунок ефективної теплопровідності ПІ композитів за допомогою програмного комплексу COMSOL MULTIPHYSICS. Відпрацьовано способи виготовлення тонких теплопровідних композиційних ПІ покрить і шарів та односторонніх композиційних алюміній-поліімінних лакофольгових діелектриків з теплопровідністю у діапазоні 1,0 - 2,0 Вт/(м·К). Досліджено основні хімічні, механічні, електричні та теплові властивості експериментальних зразків односторонніх теплопровідних алюміній-поліімідних лакофольгових діелектриків.

1. Introduction

In recent years, heat-conducting polymer materials have become an alternative to use of metals and their alloys as heat-dissipating elements. However, the main obstacle is the low thermal conductivity of high-molecular weight materials. For main part of polymeric materials produced by the chemical industry, the thermal conductivity is in range of (0.1-0.3) W/(m·K). That is, traditional polymeric materials are heat-insulating materials that are unable to conduct heat. Increasing the thermal conductivity and thermal conductivity of polymeric

materials is possible by modifying the properties of the base polymers by introducing powder fillers with particles of micron, submicron, and nano sizes with high thermal conductivity. Using fillers in form of various powders of nitrides, carbides or metal oxides, such as AlN, SiC, ZnO, SiO_2, etc., provides good dielectric properties of polymeric materials along with high thermal conductivity [1, 2].

Development of advanced technologies for creating polymer-inorganic composite materials is one of the most dynamically developing area of modern materials science. Replacement of traditional polymeric materials by composites based on same polymers but filled with various fillers makes it possible to achieve a significant increasing level of material properties, such as increased mechanical strength and stiffness, heat resistance, thermal conductivity and some other properties. Composite materials are usually obtaining by mechanical or ultrasonic mixing of a polymer and a filler that has been pretreated with organomodifying compounds to give it organophilic properties.

Among polymeric composite materials, polyimide (PI) materials, despite their relatively high price, occupy one of leading positions due to their heat resistance and high strength properties, so it can be expected that development of new composite materials based on PI binders will always be of great scientific and industrial interest. As of today, PI materials have a wide range of possible applications as materials that operating for a long time in units of machines and devices and as insulating coatings. PI materials can be used at temperatures of (+250 − +500)°C (depending on time and environment), at cryogenic temperatures, under the influence of penetrating radiation with absorbed doses of 10^4 Mrad and more, under high mechanical loads and under combination of these conditions. They are effectively used in electrical engineering and radio electronics, aviation, rocket-space and other industries, as they can significantly reduce weight and dimensions of products, increase their reliability, power density and operating temperature. Continuously growing requirements to PI materials lead to necessity to enlarge a range and to create new composite polyimide systems with special properties, in particular, with high electrical insulation and, at the same time, thermal conductivity [3, 4, 5].

Currently, DuPont (USA), as well as the Chinese companies Suzhou Kying Industrial Materials Co.Ltd and SOLVER POLYIMIDE, maintain the world leadership in the creation of new PI materials and the expansion of their application areas on an industrial scale. They are professionally engaged in the research, development and serial production of a wide range of PI films, special heat-conducting PI films and films with heat-sealing coatings for electronic products, motors, transformers, electrical equipment and other devices. However, at the same time, only rather expensive heat-conducting PI films are freely available on the market, such as DuPont™ Kapton® MT with a thermal conductivity of 0.46 W/m·K, DuPont™ Kapton® MT+ with a thermal conductivity of 0.75 W/m·K, and KYPI-MT heat-conducting polyimide film from Suzhou Kying with a thermal conductivity of about 0.36 W/m·K. Such a not very large selection of thermally conductive PI films and low values of their thermal conductivity are related to both technological and commercial reasons [6, 7, 8].

Thus, the purpose of this work was to perform structural modeling and calculation of effective thermal conductivity of new domestic thermally conductive PI composites and to develop methods and technological schemes for their production. Creation of experimental samples of thermally conductive PI composite materials and single-sided thermally conductive aluminum-polyimide lacquer-film dielectrics with increased thermal conductivity of 1.0 - 2.0 W/(m·K). Experimental confirmation of their high chemical, mechanical, electrical and thermophysical properties, which would be competitive in comparison with modern foreign industrial analogues.

2 Subject and methods of study

2.1 Thermal conductive PI composites

2.1.1. Development of thermal conductive PI composite systems

Structure of composite materials and, in particular, dispersed-filled composite systems is describing in volume units and does not depend on specific density of dispersed-fillers and polymer matrix, which makes it possible to compare results for filled systems with various fillers. Thus, developing different variants of components of dispersed-filled thermal conductive PI composite materials with a set of specified properties should be carried out only in volume units (volume fractions, vol. fr., or volume percentage vol. %). Content and amount
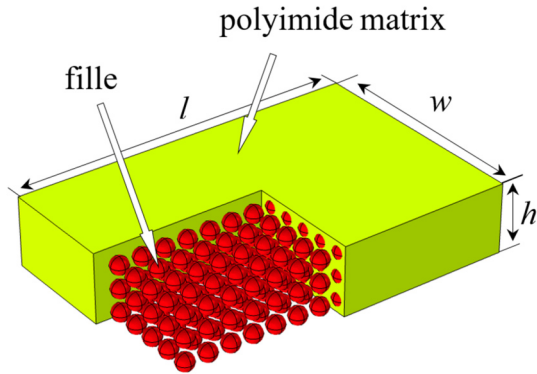
Fig. 1 - Structural schema of a thermally conductive PI composite

of dispersed filler during development is selecting according to classification of dispersed systems by structural principle (amount of filler and amount of PI matrix material (binder) are determining by volume percentage in the composite structure). After that, the content of dispersed filler and binder is converting from volume units in the composite to mass units of PI binder (PI varnish) and filler for accurately determining required basic amount of powder filler and PI varnish during the preparation of materials before manufacturing PI composites with a given structure.

At development of single-component thermally conductive PI composites with required geometric dimensions (thickness *h,* width *w,* length *l*), their structure and composition are selecting, as well as number and types of components (filler, binder) are specifying in volume units in accordance with calculated specified effective thermal conductivity of PI composite materials (Fig. 1).

A solution of aromatic polyamic acid Pyre ML RC 5069 from DuPont company (USA) was chosen as a binder material for designing thermal conductive PI composite systems. Pyre ML RC 5069 solution of aromatic polyamic acid (polyimide varnish) is the basic material for production of polyimide films DuPont™ Kapton® HN (USA). Kapton® HN thermosetting

films have high thermal stability and standard thermal conductivity (~ 0.12 W/(m·K)) [9, 10].

Dielectric powders of white aluminum nitride (AlN) from SIGMA-ALDRICH Chemie GmbH (Germany) were chosen as fillers, which belong to the group of powders with micron and nanosized particles. This choice is due to necessity to maintain acceptable thermophysical and mechanical properties of various types of developed thermal conductive PI composites with concentration of fillers in PI matrix in range of 50 vol. % up to 70 vol. %.

Using AlN as a filler for electrically insulating PI films or layers is due to the unique combination of its physical and electrical characteristics at a relatively low cost: good electrical insulation characteristics, moderate coefficient of thermal expansion, high fire resistance and chemical resistance, as well as a sufficiently high thermal conductivity of AlN particles in powders [11, 12].

In Table 1 thermophysical properties of materials for designing and structural modeling of single-component (with one type of filler material) thermally conductive PI composite systems are given.

Calculation of volume of the dispersed filler and volume of the PI matrix in the composite after imidization is carried out using expressions (1) and (2).

$$V_f = \frac{(w \times l \times h) \times \varphi_{vol.f}}{100\%} \quad (1),$$

$$V_{PI} = \frac{(w \times l \times h) \times \varphi_{vol.PI}}{100\%} \quad (2),$$

where: $\varphi_{vol.f}$ – volume of dispersed filler in composite system, vol. %;

$\varphi_{vol.PI}$ – volume of the *PI* matrix in composite system, vol. %;

l – length of composite, cm;

w – width of composite, cm;

h – thickness of composite, cm;

V_f – volume of dispersed filler in composite, cm^3;

V_{PI} – volume of polyimide matrix in composite, cm^3.

Table 1 – Thermophysical properties of materials for developing and structural modeling single-component thermal conductive composite PI systems.

№	Material	ω, % mass	ρ, g/cm^3	C, J/kg·K	λ, W/m·K
1	PI varnish Pyre ML RC 5069 [9].	12,3-13,3	1,05	-	-
2	AlN (white powder) [11, 12]	-	3,26	740	55
3	PI film after imidization [10]	-	1,42	1090	0,12

At manufacturing single-component thermal conductive composite PI coatings or layers, dry and imidization process is accompanied by simultaneous release of imidization water, forming imide cycles and removing solvent. This makes it possible to achieve 95-100% imidization rate of PI binder after heating at temperature ~300 °C during 30 minutes. Since a number of non-volatile substances in Pyre ML RC 5069 solution of aromatic polyamic acid is 12.3% - 13.3% by weight, calculation of required initial amount of polyamide varnish mixed with the filler to obtain the calculated volume of the PI matrix and the thickness of the composite PI coating or layer to be produced should be carried out in mass units using expression (3).

$$m_{P\square\text{varnish}} = \frac{V_{P\square} \times \rho_{P\square}}{\omega} \times 100\% \qquad (3),$$

where: $m_{PI\ varnish}$ − mass of polyimide varnish in mixed composition, g;

ω − content of non-volatile substances in polyimide varnish, mass %;

ρ_{PI} − specific weight of polyimide matrix in PI composite, g/cm^3;

V_{PI} − volume of polyimide matrix in PI composite, cm^3.

Recalculation of content of the dispersed filler from volume units to mass units for obtaining estimated amount of the polyimide composite at manufacturing process is carrying out using expression (4):

$$m_f = V_f \times \rho_f \qquad (4),$$

where: m_f − mass of dispersed filler in PI composite and in mixed composition, g;

ρ_f − specific weight of dispersed filler, g/cm^3;

V_f - volume of dispersed filler in PI composite, cm^3.

2.1.2. Technological scheme for manufacturing thermal conductive composite PI coatings or layers

Developed technological schema for manufacturing thermal conductive composite PI coatings or layers is shown on Fig.2.

2.1.3 Structural modeling thermal conductive PI composites and calculating their effective coefficients of thermal conductivity

At development of new thermal conductive PI composites, structural modeling and calculating their effective thermal conductivity coefficients were performed using method of direct modeling thermal conductivity of environment

1. Selecting structure and composition of PI composite coatings or layers to be developed

2. Preparing raw materials, equipment and devices.

3. Modifying surface of particles of dispersed powders of AlN fillers with organomodifying compounds to give them organophilic properties.

4. Mixing particles of dispersed AlN powders in solution of dimethylformamide and in Pyre ML RC 5069 solution of aromatic polyamic acid

5. Applying the mixed composition in solution of Pyre ML RC 5069 on technological surfaces for creating thermal conductive PI composite coatings or layers

6. Imidization of thermal conductive PI composite coatings or layers.

7. Studying characteristics of thermal conductive composite PI coatings or layers.
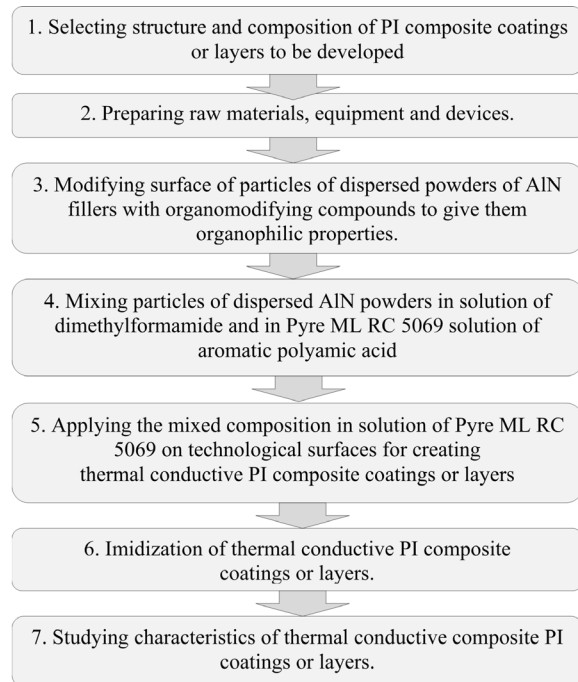
Fig. 2 - Technological scheme of manufacturing heat-conducting composite PI coatings or layers

with complex structure, which allows calculating the effective thermal conductivity for different arrangements of particles of thermally conductive filler powders in polyimide binders described in [13]. In this work was shown that calculating using COMSOL MULTIPHYSICS software package in accordance with this model make it possible to change concentration of the filler powder particles in the PI matrix, as well as to vary the particle sizes in a wide range, which makes it possible to take into account influence of structure and boundary layers on expected thermal properties of the composites being developed. With this approach the PI composite system (PI composite material), the thermal conductivity of which need to be calculated, is modeling as cube divided into elementary cells. In referred work also is showed that for improving thermal conductivity it is possible to inject into the polyimide matrix various dielectric fillers with micron-sized and smaller particles that have high thermal and physical characteristics, such as filler powders from SiO_2, SiC, Al_2O_3, and AlN. According to the results of theoretical modeling in [13], combined PI composite systems using mixtures of thermally conductive white AlN powders with particle sizes of 8 μm and 0.4 μm as fillers with a thermal conductivity of particles in powders of ∼ 55 W/(m·K) [12] showed quite

high estimated results of the effective thermal conductivity of PI composites. At total volume of fillers in highly filled PI matrix of about 80 vol. %, maximal effective thermal conductivity was about 4.46 W/(m·K). Presented results make it possible to predict possibility of industrial production of thermal conductive PI composite films with AlN fillers with an expected thermal conductivity of about 5.0 W/(m·K) and even more.

As is known [3, 4, 13], increasing thermal conductivity in highly filled polymer composite films is achieving when content of filler particles in a composite is at least 55 vol. % and increasing with further increasing content of the filler. In turn, increasing content of the filler more than 50 vol. % leads to a deterioration of deformation-strength properties of composites (strength and plasticity characteristics deteriorate). Maximal possible thermal conductivity is observing for variants of composite materials in which a mixture of micro-, sub-micro- or nanoparticle powders of fillers with a predominant content of micron-sized particles is used as a filler.

At the same time, the price of filler powders (1-10 microns) can be several times higher than that of powders with large sizes (tens of microns), and the price of nanopowders is almost two orders of magnitude higher than that of micron powders with large sizes. If amount of the filler in the composite is more than 50 vol. % then the cost of the new composite material being developed will be largely determined by the cost of the fillers. At the same time, the overall cost of the material can increase significantly, thus negating one of the main possible advantages of the new composite materials being developed over their counterparts – lower cost. Therefore, creating a polyimide composite that combines good mechanical and heat-conducting properties is quite difficult task. The main idea of effective management of thermophysical characteristics of the composite material at high degree of filling is maximization of heat-conducting paths along with minimizing ultimate thermal resistance filler-filler and filler-matrix [3, 4, 13]. Thus, when developing new highly filled thermally conductive PI composites with increased values of thermal conductivity in the range of 1.0 - 2.0 W/(m·K), authors of this work proceeded from necessity to create such structures of PI composite coatings and layers or films (25-30 µm) and methods of their manufacturing, which provide sig-

nificantly higher thermal conductivity (almost two times) at competitive costs of the films being developed, compared to modern industrial analogues, as well as their high chemical, mechanical, electrical and thermophysical properties have been experimentally confirmed.

At structural modeling of new PI composites, a solution of Pyre ML RC 5069 polyamide acid was chosen as a precursor of the PI matrix, and white aluminum nitride powders with particle sizes in the powders of at least 10 µm were chosen as a matrix filler to improve heat transfer through larger micron particles.

At creating the model, volume of the composite matrix can be imagined as an array of elementary cells, each of which contains one particle of the filler. Using the COMSOL MULTIPHYSICS® software package and formulas (5) and (6) [14], calculations of average heat fluxes were performed and estimated values of effective thermal conductivity coefficients of experimental PI composite films or layers, which are designed, were obtained, depending on the volume of the filler.

Structural 3D models of thermal conductive composite polyimide systems and results of calculating their effective thermal conductivity at different volume concentrations of the fillers are shown on Fig. 3.

For simplifying the calculation model of composite systems, some basic assumptions were adopted:

1. Tasks are considering stationary, since temperature equalization in the heat-conducting volume occurs much faster than change in external conditions.

2. Materials, which are components of the composite, are considered as isotropic. At the same time, their thermal conductivity does not depend on temperature.

3. Sizes of the filler particles are considered to be the same. Elementary cubic cells are filled with one particle of micron-sized spherical filler. The cubic elementary cells are uniformly distributed throughout the volume of the composite system. Fractional composition of particles is not taken into account.

4. Thermal contact between the particles and the polymer is assumed to be ideal (this assumption leads to an increase in the thermal conductivity of the composite due to zero thermal resistance at the boundary between environments polymer -particle).

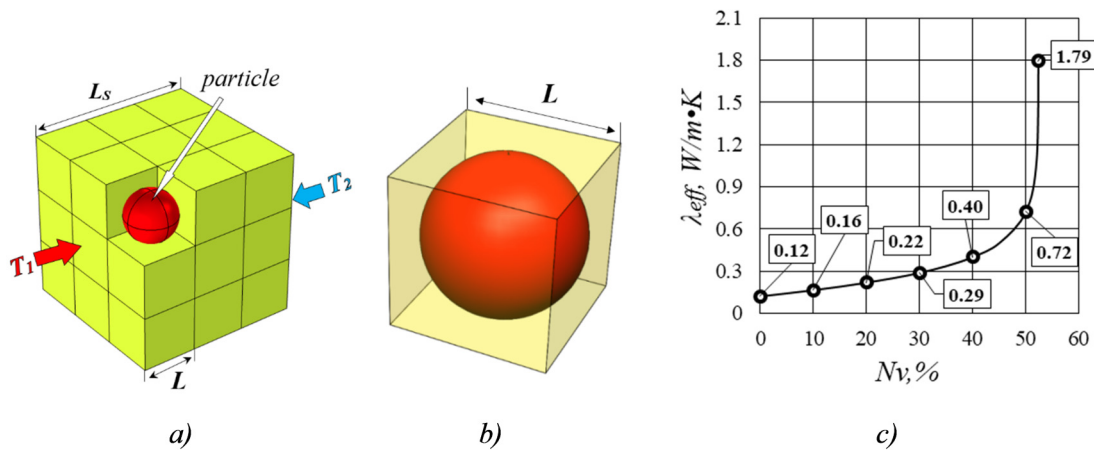5. Presence of microdefects is not taken into account.

Fig. 3 – Structural 3D models of composite systems and results of calculating their effective thermal conductivity: a) model of the composite system in form of a cubic lattice with edge length Ls, which is divided into elementary cubic cells with one spherical particle with diameter of 10 µm; b) model of an elementary cubic cell with an edge length L with one spherical particle with a diameter of 10 µm; c) effective thermal conductivity of PI composite systems with a filler with the size of aluminum nitride particles of 10 microns.

According to the model, relationship between length L of the edge of the cube of the unit cell (it determines size of calculation area and size of the particle) and volume of the particle V_f is given by the expression:

$$L = \left(\frac{V_f}{N_v}\right)^{\frac{1}{3}},\qquad (5)$$

where: N_v – volume concentration of particles;

V_f – volume of the particle.

Effective thermal conductivity λ_{eff} of the PI composite material was calculated using following expression:

$$\lambda_{eff} = q_m \frac{L}{|T_1 - T_2|},\qquad (6)$$

where: λ_{eff} – effective thermal conductivity of the composite material;

q_m – average heat flow;

L – length of edge of the cubic unit cell;

$T_1 - T_2$ – temperature difference of opposite faces.

On the opposite side faces of the composite system in form of a cubic lattice, which is divided into elementary cubic cells with one spherical particle with diameter of 10 µm (Fig. 3a) and, therefore, on the opposite side faces of an elementary cubic cell with one spherical particle with diameter of 10 µm of the composite different temperatures T_1 and T_2 are setting for the system. As a result, temperature gradient along one of direction is creating. There is no heat flow through other faces of the cube. Temperature T_2 corresponds to ambient temperature $T_a = 25$ °C. Temperature T_1 is $T_j = 80$ °C and cor-

responds to recommended maximal operating temperature, for example, in region of p-n junction of semiconductor heat sources. Thermal contact between the particles and the PI matrix is assumed to be ideal. This assumption allows for an increase in thermal conductivity of the composite due to zero thermal resistance at the polyimide-particle interface. If an elementary cubic cell c with an edge length L is filled with only one micron-sized spherical particle with diameter Ø equal to length of edge of the cube (Ø = L), the maximal volume concentration of the material of the spherical filler particle in such an elementary cubic cell of the composite system is no more than 52,4 vol. % and does not depend on size of the particle in the cubic cell (Fig. 3b).

On fig. 3c results of calculating the effective thermal conductivity of the PI composite at different volume concentrations of the fillers with aluminum nitride particle sizes of 10 µm are given.

From the analysis of the graph in Fig. 3 c, it follows that for the model of a PI composite with a filler consisting only of white AlN particles of spherical shape with a diameter of 10 µm at a concentration of PI matrix particles of 52.4 vol. %, the maximum calculated effective thermal conductivity is no more than 1.79 W/(m·K). Thus, simulation results theoretically confirmed possibility of manufacturing new highly filled microcomposite PI coatings and layers with thermal conductivity up to almost 2.0 W/(m·K) at concentration of AlN fillers about 50 vol. %.

In work [15] reporting about experimental studies of thermal conductivity of microcomposite PI films filled with AlN powders with particle sizes of about 4 µm. At concentration of AlN particles ~ 50 vol. % in the PI matrix, the thermal conductivity of the studied microcomposite films was 1.76 W/(m·K). Experimental results obtained in [15], when compared with the theoretically constructed graph (Fig. 3 c), practically coincide with the results of modeling PI composites with a white AlN filler with a particle size of about 10 µm at a concentration in the PI matrix of 52.4 vol. %, in which the maximum effective thermal conductivity was about 1.79 W/(m·K), which objectively confirms the sufficient practical accuracy of the application of the structural model developed by the authors and the method for calculating effective thermal conductivities in the design of various types of new highly filled polyimide composite materials.

Work [12] reports new experimental results on the thermal conductivity of microcomposite powders of thermally conductive functional materials on polymeric siloxane binders, in which, at a particle concentration of 40 vol. %, the maximum effective thermal conductivity was ~ 2.2 W/(m·K).

Work [16] informs on composites based on epoxy binders and Al_2O_3, BN, AlN micro- or nano-particles. For microcomposites with a filler content of about 60 vol. % coefficient of thermal conductivity reaches values of 5-11 W/(m·K) and for nanocomposites with smaller fillings the thermal conductivity is reduced down to 3 W/m·K.

Thus, the practical results of measuring the thermal conductivity of the studied samples of highly filled thermally conductive composite materials based on micro-AlN particles for different polymer binders obtained by different researchers experimentally confirm the values of their thermal conductivity in the range of 1.76-2.2 - 11 W/(m·K) at the concentration of AlN fillers in binders from 40-50 vol. % to 60 vol. %, respectively.

3 Experimental

Manufacturing many types of polymer composite materials (PCM) is traditionally based on mixing process. However, this method can be successfully applied only in cases where the degree of polymer filling does not exceed 50 vol. %. At higher range of filling (50-80 vol. %), heterogeneity and uneven distribution of the reinforcing additive in the polymer matrix inevitably appear. In this case, as a rule, no substance is dispersed during mixing to form particles of the same size, since powders consisting of monodisperse particles are aggregated, and presence of aggregates in the mixture leads to a wide distribution of particle sizes in composites. Achieving a good wetting of the surface of the particles with a binder is one of the necessary conditions for creating composite polyimide materials with a uniform distribution of filler particles and, accordingly, with necessary properties, in particular, strength characteristics. For increasing interfacial interaction for polymer-inorganic filler systems and improving physical and mechanical properties of polymer composite materials in composite polyimide materials, the most common processing is washing and drying filler powders, as well as applying finishing coatings to the surface of the filler particles to create a transitional layer between them and the polymer matrix. Applying organic substances with surface-active properties also makes it possible to obtain surfaces of filler particles isolated from each other and stable over time in composites. Even a small amount of aprette or substances with surface-active properties, about 0.1-0.5 %, applied on surface of a filler particles, significantly improves technological properties of the composite materials. Stable and homogeneous compositions can be obtained using isopropyl alcohol, polyvinyl alcohol, xylene or other organic substances as a protective environment for particles. In addition, many aprettes, such as organosilicon modifiers, are effective for many polymer matrices. However, it should be borne in mind that degree of improvement in properties of composites varies greatly depending on the type of binder. So, for example, surface functionalization of filler particles for the PI matrix is carried out by treating them in water-ethanol solution of modifier tetraethylorthosilicate $Si(OC_2H_5)_4$ or aminopropyltrimethoxysilane $NH_2(CH_2)_3Si(OCH_3)_3$. Such methods of surface modification either increase number of reactive functional groups, or increase the surface roughness of filler particles, which strengthens their physical connection with the PI matrix. Maximal concentration of the filler that can be created in thermally conductive PI composite materials without losing the positive effect of the PI matrix depends on how successfully this task is solved.

3.1. Production of thermally conductive composite PI coatings or layers

Manufacturing experimental samples of thermal conductive composite PI coatings or layers with fillers based on AlN particles was performed according to schema of manufacture process shown on Fig. 2.

At the first stage selection and preparation of raw materials, equipment and measuring devices was carried out. At the second stage, workplaces were prepared for manufacturing experimental samples of thermal conductive PI composites, including: workplace for mixing particles of dispersed AlN powders in solution of dimethylformamide and in solution of aromatic polyamic acid Pyre ML RC 5069; workplace for applying mixed composition of AlN particles in solution of aromatic polyamic acid Pyre ML RC 5069 on technological surfaces and for forming thermal conductive PI coatings or layers; workplace for manufacturing varnish-foil aluminum - polyimide dielectrics, in particular for forming layers of mixed composition of AlN particles in solution of aromatic polyamic acid Pyre ML RC 5069 on aluminum foil; workplace for drying and imidizing thermal conductiev PI coatings or layers.

Thickness of manufactured experimental samples of thermal conductive PI composites (at chosen width and length about 6-7 cm) is chosen in range of 25-30 μm (after imidization). Thus, at chosen overall dimensions calculated volume of PI composites is about $V = w \times l \times h = 0.123$ cm^3. At the same time, different variants of highly filled thermally conductive PI composite materials with concentration of filler particles of 50, 60 and 70 vol. % were chosen. Including fillers consisting only of aluminum nitride particles with a size of 10 microns. As well as PI composite materials with powdered AlN fillers with particle sizes in the mixture of 10 microns (98%) and 100 nm (2%).

Using equations (3) and (4) outgoing amount of solution of Pyre ML RC 5069 and AlN fillers was calculated for defining required amount of components of the PI composite system in mass units.

Before injection of powder AlN fillers into the solution of Pyre ML RC 5069, surface modification of AlN particles has been carried out. Modification of AlN particles surface was carried out in two ways: by modifying AlN particles surface using isopropyl alcohol and by modifying AlN particles surface using Si(OC$_2$H$_5$) tetraethylorthosilicate siloxane finish.

At manufacturing thermal conductive PI composite coatings or layers following sequence of operations have been performed:

1. To obtain a mixed composition in a solution of Pyre ML RC 5069, calculated amounts with fillers consisting only of AlN particles with a size of 10 μm, or calculated amounts with powder AlN fillers with particle sizes in a mixture of 10 μm (98%) and 100 nm (2 %) with a modified surface are mixed with N, N-dimethylformamide using an ultrasonic disperser (frequency 44 kHz, power of the ultrasonic generator - 2 kW/m^2, duration of dispersion - 60 minutes). After that obtained dispersion is injecting into the calculated amount of Pyre ML RC 5069 solution with further homogenization of the solution using a top-drive mechanical stirrer.

2. Then on technological surface from the obtained solution Pyre ML RC 5069 coating or layer is forming composite solution using AU-1 applicator with well-controlled gap, which makes it possible to obtain thickness of manufactured PI composite equal to 25-30 μm after imidization.

3. Next step is drying formed PI composite under hood in electric oven with gradual temperature rise at rate of 2.5-5.0 °C per minute from room temperature up to 100 °C and held at this temperature for 20-30 minutes with further dehydrocyclization of the PI matrix at gradual temperature rise at rate of 2.5-5.0 °C per minute up to 300 °C and held at this temperature for 30-40 minutes. After that the varnish foil aluminum - polyimide dielectric is removing from the electric oven and cooled to room temperature.

3.2. Manufacturing single-sided composite varnish-foil aluminum-polyimide dielectrics

At manufacturing single-sided composite thermal conductive adhesiveless aluminium-polyimide varnish-foil dielectrics following sequence of operations has been performed:

1. At the first stage, a sheet of aluminum alloy A5 foil with a thickness of 30 μm is prepared and etched in a 10% NaOH solution for 30 seconds at a temperature of 50 ºC to activate the surface of the foil, followed by washing in distilled water and drying in an oven at 100 ºC for 1 hour.

2. For creating mixed composition in solution of Pyre ML RC 5069, calculated amounts with highly dispersed fillers consisting only of AlN particles with a size of 10 μm, or cal-

culated amounts with powder AlN fillers with particle sizes in the mixture of 10 µm (98%) and 100 nm (2%) with modified surface, are mixed with N,N-dimethylformamide using an ultrasonic disperser (frequency 44 kHz, power of ultrasonic generator - 2 kW/m^2, duration of dispersion - 60 minutes). After that obtained dispersion is injecting into calculated amount of Pyre ML RC 5069 solution with further homogenization of the solution using a top-drive mechanical stirrer.

3. Then the composite layer is forming from the obtained composite solution of Pyre ML RC 5069 on aluminum foil using applicator AU-1 type with well-controlled gap, which makes it possible to obtain thickness of manufactured composite PI layer on aluminum foil equal to 25-30 µm after imidization.

4. Next step is drying formed PI composite under hood in electric oven with gradual temperature rise at rate of 2.5-5.0 °C per minute from room temperature up to 100 °C and held at this temperature for 20-30 minutes with further dehydrocyclization of the PI matrix at gradual temperature rise at rate of 2.5-5.0 °C per minute up to 300 °C and held at this temperature for 30-40 minutes. After that the varnish foil aluminum - polyimide dielectric is removing from the electric oven and cooled to room temperature.

3.3. Study of samples of thermal conductive composite PI coatings

Studying experimental composite thermal conductive PI materials have been carried out in normal climatic conditions. Visual inspection of the samples has been performed using optical devices (magnifying glass, microscope) with magnification level not less than 4 and 56, respectively.

For studying the thermal conductive PI composite coatings following samples with different options for filling PI matrices were manufactured:

- PI coating 25-30 µm thick with AlN particles (50 vol %) 10 µm size, which passed modification of particle surface using isopropyl alcohol and coating with AlN particles (50 vol %) 10 µm size which passed modification of particle surface using tetraethylorthosilicate $Si(OC_2H_5)_4$;

- PI coating 25-30 µm thick with AlN particles (60-70 vol. %) 10 µm size which passed modification of particle surface by isopropyl alcohol;

- PI coating 25-30 µm thick with mixture of AlN particles (50-70 vol. %) 10 µm size (98 %)

and 100 nm size (2 %) which passed particle surface modification using isopropyl alcohol.

At the first stage samples of PI coatings with AlN particles (50 vol. %) 10 µm size which passed particle surface modification with isopropyl alcohol and PI coatings with AlN particles (50 vol. %) 10 µm size which passed modification of particle surface using tetraethylorthosilicate $Si(OC_2H_5)_4$ were investigated. After manufacturing the experimental thermally conductive PI composite coatings with these structures, they had high mechanical strength, smooth, plastic, and flat surfaces regardless of the method of modifying the particle surface. Therefore for further study of other experimental samples of composite thermal conductive PI materials, based on necessity to create them in way which provides higher thermal conductivity and lower competitive cost compared to modern industrial analogues, it was decided to abandon using particle surface modification processes based on tetraethylorthosilicate $Si(OC_2H_5)_4$ which is more labor-intensive and more complicated as well as more expensive compared to processes of particle surface modification using isopropyl alcohol.

Need to be noted that after manufacturing and investigating experimental composite thermal conductive PI coatings with AlN particles (60-70 vol. %) 10 µm size which passed particle surface modification with isopropyl alcohol also had a smooth, plastic and even surface, which confirms aggregative stability of dispersion system "AlN - isopropyl alcohol" under conditions of uniform dispersion of micron-sized AlN particles in the PI matrix.

3.4. Investigations of samples of single-sided thermal conductive composite varnish-foil aluminum-polyimide dielectrics.

Following experimental samples of composite PI materials were manufactured for investigations of single-sided thermal conductive varnish-foil aluminum-polyimide dielectrics, namely:

-single-sided varnish- foil aluminum-polyimide dielectrics with PI layer 25-30 µm thick with AlN particles (50 vol. %) 10 µm size which passed particle surface modification with isopropyl alcohol and aluminum - polyimide dielectrics with PI AlN particles (50 vol. %) 10 µm size which passed particle surface modification with tetraethylorthosilicate $Si(OC_2H_5)_4$;

-single-sided varnish-foil aluminum - polyimide dielectrics with a PI layer 25-30 µm thick with mixture of AlN particles (50-70 vol. %)
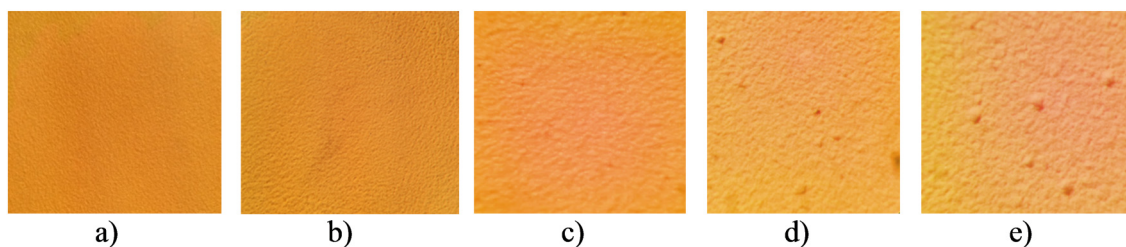
Fig. 4 - Appearances of surface of thermal conductive composite PI layers up to 30 µm thick: a) with AlN particles (50 vol %) 10 µm size which passed modification of particle surface using isopropyl alcohol; b) with AlN particles (50 vol. %) 10 µm size which passed modification of particle surface using tetraethylorthosilicate $Si(OC_2H_5)_4$; c) with mixture of AlN particles (50 vol. %) 10 µm size (98 %) and 100 nm size (2 %) which passed particle surface modification using isopropyl alcohol; d) with mixture of AlN particles (60 vol. %) 10 µm size (98 %) and 100 nm size (2 %) which passed particle surface modification using isopropyl alcohol; e) with mixture of AlN particles (70 vol. %) 10 µm (98 %) size and 100 nm (2 %) size which passed particle surface modification using isopropyl alcohol.

10 µm (98 %) size and 100 nm (2 %) size which passed particle surface modification with isopropyl alcohol.

After manufacture and investigations of experimental composite thermal conductive single-sided varnish-foil aluminum-polyimide dielectrics with PI layer 25-30 µm thick with AlN particles (50 vol. %) 10 µm size which passed particle surface modification with isopropyl alcohol and aluminum-polyimide dielectrics with PI AlN particles (50 vol. %) 10 µm size which passed particle surface modification with using tetraethylorthosilicate $Si(OC_2H_5)_4$, have had a smooth, plastic and even surface, what confirms aggregative stability of dispersion systems "AlN - isopropyl alcohol" and "AlN - tetraethylorthosilicate" under conditions of uniform dispersion of micron-sized AlN particles in the PI matrix (Fig. 4 a, b).

As it was already mentioned before, increasing content of the filler by more than 50 vol. % can leads to deterioration of deformation-strength properties of polymer composites, therefore, for confirming possibility to ensuring requirements for highly filled thermal conductive composite PI materials, experimental single-sided varnish-foil aluminum-polyimide dielectrics with PI layer 25-30 µm thick with mixture of AlN particles (50-70 vol.%) 10 µm size (98%) and 100 nm size (2%) which passed particle surface modification with isopropyl alcohol were manufactured and investigated. Nanosized particles of fillers were introduced into the composition of highly filled composite heat-conducting PI materials to improve their deformation-strength properties. Strengthening effect of nanoparticles in the composite is relating to effect of nanofiller on structure of the separation surfaces of the composite components due to appearance of nanoadhesion effect. The introduction of nanosized additives makes it possible to align the physical and mechanical properties of the main components of micro- and nanostructured composite PI materials and to some extent increase or create new consumer qualities and properties of the final product.

However, at manufacturing experimental samples of composite PI coatings and layers with fillers from 50 to 70 vol. %, after injections up to 2 % of AlN nanoparticles of ~ 100 nm size into the filler mixture, forming small number of agglomerates with sizes larger than 20 µm was observed in them (Fig. 4 c, d, e), even though AlN nanoparticles had previously passed surface functionalisation. Although the high specific surface area of AlN nanoparticles improves their interaction with the molecules of the polyimide matrix, at the same time, even with 2% of nanoparticles with sizes of ~ 100 nm in the mixture of AlN fillers, the aggregative stability of the dispersion system "AlN - isopropyl alcohol" decreases under the conditions of uneven dispersion of nanoparticles in the PI matrix.

Appearances of surface of the PI layers of manufactured experimental samples of highly filled single-sided varnish-foil aluminum-polyimide dielectrics which were chosen for investigations of their chemical, mechanical and electrical properties, as well as evaluating the quality of their manufacturing methods, are shown on Fig.4.

4. Results and discussion

Created test structures of quality (TSQ) of thermal conductive single-sided varnish-foil aluminum-polyimide dielectrics for checking their chemical, mechanical and electrical properties, as well as assessing the quality of their manufacturing methods, are shown on Fig.5.
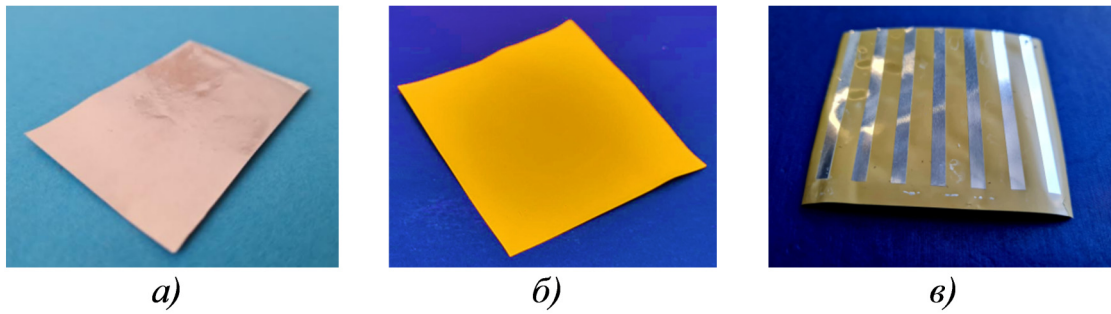
Fig. 5 - Test structures of quality for checking the main properties of experimental samples of thermal conductive single-sided varnish-foil aluminum-polyimide dielectrics: a), b) for electrical strength checking; c) for checking pull strength of aluminum foil.

In order to confirm compatibility with the main technological processes adopted in production of printed circuit boards the experimental samples of flexible single-sided thermal conductive varnish-foil aluminum-polyimide dielectrics were tested for compatibility with processes of coating photoresist on aluminum foil and thermal conductive composite PI layers, with processes of forming photoresist masks, chemical wet etching aluminum foil and composite PI layers, as well as photoresist removal and final cleaning of experimental samples.

Pull strength tests of aluminum foil have been performed according to harmonized IPC-TM-650 standard, test method 2.4.9. Pull strength of aluminum foil was tested on five samples 3 mm width and 60 mm length, which were created using photolithography, by the method of pulling at 180° angle. Before the test, one end of each strip of aluminum foil was manually separated from varnish PI layer and fixed in clamp of measuring device. On each strip minimal stable value of load, which leads to separating the foil strip for length at least 30 mm was defined. Adhesion strength of the foil was defined as an average arithmetic value of the load at the minimal and maximal delamination of the strips. Average arithmetic value of the loads of three parallel measurements of the foil was taken as a positive result.

Tests of electrical strength of the composite PI layers of single-sided vanish-foil aluminum-polyimide dielectrics have been carried out according to harmonized IPC-TM-650 standard, test method 2.5.6.3 "Dielectric breakdown voltage and dielectric strength" using AIM-90 breakdown voltage meter.

During those tests of test structures of quality following results were obtained:

- average values of the pull strength of aluminum foil from PI dielectrics were at least 1.75 N/cm);

- average values of the breakdown voltage of the dielectric thermal conductive PI film 25-30 μm thick ranged from 4.0 kV/mil (160 V/μm) up to 5.0 kV/mil (200 V/μm).

Studied experimental samples of heat-conducting PI composite materials confirmed the correctness of the selected structural and technological solutions and the technological scheme for the manufacture of heat-conducting composite PI layers of heat-conducting varnish-foil aluminum-polyimide dielectrics with specified design characteristics based on the mixed compositions of the Pyre ML RC 5069 solution with fillers from white AlN powders with micron particles and nano-sized, allowing to manufacture new PI composite materials with higher values of thermal conductivity in the range from 1.0 W/(m·K) to 2.0 W/(m·K).

5. Conclusions

In this work development and study of thermal conductive PI composite materials based on binders from solution of aromatic polyamic acid Pyre ML RC 5069 type and dispersed fillers from powders of micron and nano size AlN particles were carried out.

Technological schemas of manufacturing were selected, structural modeling and calculations of effective thermal conductivity of PI composites were carried out using COMSOL MULTIPHYSICS software.

Methods of manufacturing thin thermally conductive micro- and nanostructured composite PI coatings and layers, as well as single-sided micro- and nanostructured composite aluminium-polyimide varnish-foil dielectrics with thermal conductivity of PI layers in range from 1.0 up to 2.0 W/(m·K) which is almost twice higher then thermal conductivity of modern industrial analogues of PI composites.

Main chemical, mechanical, electrical and thermal properties of experimental samples

of single-sided thermal conductive aluminum-polyimide varnish-foil dielectrics were studied.

Innovative one-sided thermally conductive micro- and nanostructured composite varnish-foil aluminum-polyimide dielectrics have been developed, which are intended for use in radiation instrumentation, in particular for electronic modules with increased power for aviation and space applications, for individual dosimetry, matrix introscopy, as well as medical and industrial tomography.

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