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New approaches to creating promising heat-conductive electrical insulating polyimide nanocomposite materials

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This review is intended to analysis of works in field of creating electrically insulating heat-conductive polyimide composite films based on powders of micro- and nanoparticles with high dielectric and heat-conductive properties for use as effective thermal interface materials in various electronic devices in instrument engineering. Particular attention is paid to studies on the effect of size of nano- and microparticles of inorganic fillers on heat-conducting, dielectric, and physic-mechanical properties of nanocomposite polyimide materials. Carried-out analysis of results of works on studying dependence of thermal conductivity on ratio of micro- and nano-sized particles in mixtures and their amount in polyimides and on conditions of their polymerization for confirming possibility to increase values of thermal conductivity of promising polyimide materials from 0.12 W/m·K up to 5–10 W/m·K.

Keywords: electrical insulating heat-conductive polyimide composite films, micro- and nanoparticles, inorganic fillers.

Нові підходи до створення перспективних теплопровідних електроізоляційних поліімідних нанокомпозитних матеріалів. *В.М.Борщов, О.М.Лістратенко, М.А.Проценко, І.Т.Тимчук, О.В.Кравченко, О.В.Сіддія, М.І.Сліпченко, Б.М.Чічков*

Огляд присвячено аналізу робіт в області створення електроізоляційних теплопровідних поліімідних композиційних плівок на основі порошків мікро і наночастинок, що володіють високими діелектричними і теплопровідними властивостями для застосування в якості ефективних термоінтерфейсних матеріалів в різних електронних пристроях в приладобудуванні. Особливу увагу приділено роботам з дослідження впливу розмірів нано і мікрочастинок неорганічних наповнювачів на теплопровідні, діелектричні і фізико-механічні властивості нанокомпозиційних поліімідних матеріалів. Проведено аналіз результатів робіт з дослідження залежності теплопровідності від співвідношень мікронних і нанорозмірних частинок в сумішах і їх кількості в поліімідах і від умов їх полімеризації для підтвердження можливості збільшення значень теплопровідності перспективних поліімідних матеріалів від 0,12 Вт/м·К до 5·10 Вт/м·К.

1. Introduction

Problem of rejecting heat which is generating during operating semiconductor devices (for example, integrated circuits, computer components, LED light sources, etc.) has become dominant in recent years [1, 2]. Released heat must be rejected to surrounding space, otherwise, the semiconductor devices overheating, which significantly reducing reliability of their operating. Traditionally this problem was solved through using materials with high coefficient of thermal conductivity (mainly metals, their alloys, oxides, and nitrides).

In recent years, thermal conductive polymer materials (TCPM) have become an alternative to the use of metals and their alloys as heat-removing elements. However, the main obstacle, in this case, is low thermal conductivity of high molecularmaterials. For most polymeric materials produced by chemical industry coefficient of thermal conductivity is (0.1–0.3) W/(m·K). Therefore, traditional polymeric materials are heat-insulating materials and are incapable for heat conducting.Increasing coefficient of thermal conductivity (λ) and coefficient of thermal diffusivity (α) of polymeric materials is possible by modifying properties of basic polymers by injecting micro- , submicro- or nanosized fillers with high thermal conductivity. Powders of metals (Ag, Al, Cu, Fe, etc.), graphite, nitrides, and metal oxides are currently using as such fillers [3, 4]. Using TCPM makes it possible to abandon using metals at manufacturing heat-dissipative structural elements. Replacing expensive metals with heat-conducting polymer compositions can significantly reduce cost of semiconductor devices and units, as well as significantly reduce their weight [5]. Depending on field of application, TPCM with high thermal conductivity must have either good electrical insulating properties or high electrical conductivity. For example, electrical insulating TPCM are using as elements of heat-conductive substrates and printed circuit boards under voltage, and electrically conductive TPCM are using as elements of devices and unitsneed to be grounded during operating [6]. Using fillers in form of various carbon-containing materials (graphite, carbon black, carbon nanotubes) makes it possible to obtain TPCM with high thermal and electrical conductivities [7]. On the other hand, filling polymer matrices with powders of nitrides, carbides or metal oxides with high coefficient of thermal conductivity (AlN, SiC, ZnO, and SiO_2) ensure good dielectric properties of TPCM along with high thermal conductivity [8, 9].

Development of promising technologies for creating polymer-inorganic nanocomposite materials is one of the most dynamically developing area of modern materials science. Replacing of traditional polymer materials with composites based on the same polymers filled with various nanoparticles makes it possible to achieve a significant increase in the level of material properties — to increase the mechanical strength and rigidity of the material, heat resistance, and improve many other properties. Heat-conducting polymer composite materials containing inorganic fillers are widely using in electrical and heat techniques, electronics. Composite materials, as a rule, are obtaining by mechanical or ultrasonic mixing of a polymer and a filler that has been pretreated with organic modifying compounds for impart organophilic properties to it.

Among polymer composite materials, polyimide materials, despite the relatively high cost, occupy one of leading place due to thermal stability and high strength characteristics, therefore, it can be expected that development of new composite materials based on polyimide binders will always arouse tangible scientific and industrial interests. Presently polyimide materials have wide range of possible applications as materials that work for a long time in the parts of machines and devices, as well as insulating coatings. Polyimide materials can be used at temperatures (+250–+500)°C (depending on time and on environment), at cryogenic temperatures, at radiation load with absorbed doses of 10^4 Mrad and more, at high mechanical loads and in combination of these conditions. They are effectively using in electrical engineering and radioelectronics, aviation, rocket and space and other industries because they can significantly reduce weight and dimensions of products, increase their reliability, power density, and operating temperature. Analysis of scientific and technical data and practical works on development of heat-resistant polymer materials, in particular, polyimides, showed promising using thermoplastic polyamic acids (PAA) and varnishes, on basis of which free polyimide (PI) films are obtaining using monomers of various chemical structures. However, the ever-growing requirements to materials lead to necessity to increase standard range of available films and creating new types of polyimide systems with special properties, including with high electrical insulating and, at the same time, heat-conducting characteristics [10].

Thus, purpose of this work (review) was searching and analyzing data and results of theoretical and experimental studies, dissertation materials, literature sources, and patents in field of polyimide nanocomposite materials, summarizing obtained data and recommendations for development of promising heat-conductive electrical insulating polyimide nanocomposite materials. Especially practically proven recommendations for creating composite polyimide films with significantly increased thermal conductivity from typical values of 0.12 W/m·K up to 5–10 W/m·K, allowing their using as thermal interfaces in flexible varnished foil laminates for commutation boards and cables in various electronic devices,including detectors of electromagnetic radiation, in LED light sources and in space and terrestrial solar batteries for ensuring optimal thermal conditions.

2. *Subject and methods of research*

2.1 Thermally conductive polymer-based composites

If ability of solids states to conduct heat is related to their structure, composition and mainly characterizing by coefficient of thermal conductivity λ (W/m·K), then heat dissipation occurs at air-solid phase boundary. Laws of heat transfer in so-called natural convection mode are such that there is a certain specific limit on the amount of heat that can be absorbed from unit of heat-transfer surface by the surrounding air. This amount of heat is independent of the thermal conductivity of the heat-releasing material (wood, metal, plastic or paper). For cooling in general, this means that increasing coefficient of thermal conductivity makes sense only until moment when amount of heat transported through the body reaches a value that can be maximally accepted (dissipated) by air at last, limiting stage. According to calculations, the "effective" operating value of coefficient of thermal conductivity λ_{eff} is in range of 5–10 W/m·K. Further increasing is already excessive and does not leads to increasing in heat rejection as a whole. This conclusion is also confirmed by a series of experiments carried out by the American company Cool Polymers, in which point heat source with constant power (5 W) was fixed on same size plates made of materials with different thermal conductivity (Fig. 1).

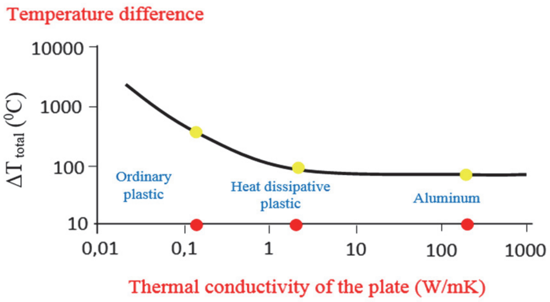

Fig. 1. Influence of thermal conductivity of the plate material on the unevenness of its temperature field.

Thus, it was confirmed that heat-conducting potential of copper, aluminum and other high thermal-conducting materials is using in free cooling mode, at best, only to one-tenth of its capabilities, and their use is technically redundant. This is especially actual for modern smartphones, computers, lamps, and other consumer devices and microelectronic devices that are being manufactured in millions.

Namely plastic frames, circuit boards and other numerous parts made of polymers are essentially unifying, integrating environment for interacting heat-generating radio-electronic and other functional elements. Mass part of polymers in such products is steadily increasing and, in some cases, reachingup to 90–95 %. Therefore, desire of developers to try to use polymers for cooling electronic devices is understandable. However, taking into account that polymeric materials, including polyimides, are typical heat insulators, with coefficients of thermal conductivity less then 0.2–0.3 W/m·K, this is the reason why difference by almost two orders between the real and requiredthermal conductivity for the manufacture of cooling devices did not allow developers to exploit generally recognized economic potential of polymers in mass production until relatively recently.

Low thermal conductivity of polymers, as a rule, is explaining by combination of extremely low ordering of their molecular structure and weakness of intermolecular interactions between elements of such structure. Unlike of low-molecular compounds, most of which in solid-state form crystal lattices, in polymers ordered elements —

crystallites — exist simultaneously with amorphous regions. Because of this, average free path of thermal phonons (quasiparticles — carriers of thermal energy, path length of which depends on the degree of ordering of the material) is 3–5 Å, which is comparable to interatomic distances. This leads to low-effective heat transfer in polymers. Proportion of ordered regions in whole supramolecular structure of a polymer is called as degree of crystallinity. For the same polymer, degree of crystallinity can vary depending on conditions of its production (mechanism of polymerization, temperature, pressure, the presence and structure of the catalyst), and as a result of physical or chemical effects which changing structure of already synthesized polymers — the so-called post-synthetic modifications. Increasing degree of crystallinity should elongate path of thermal phonons and thereby increase thermal conductivity of a polymer. It is also quite logical to solve problem of increasing thermal conductivity of polymers by filling them with heat-conductive materials [2, 11].

High-filled (degree of filling more than 50 % of volumeconcentration) polymer composites are functional materials which, depending on type of fillers used, can combine high thermal and electrical conductivity, magnetic properties, stiffness, low shrinkage and dimensional stability. At the same time, they can outperform metallic materials in terms of advanced production technology, ease of processing and finishing, lower weight, corrosion resistance, etc. These qualities can make it possible to use high-filled composites in practical applications where metal alloys are traditionally using (LED devices, reflectors, printed circuit boards, heat exchangers, radiators, frames, bearings, etc.).

Schematic representation of dependence of thermal conductivity of polymer composites on filler content is shown in Fig. 2. Unfilled polymers in their natural state are heat insulators, the thermal conductivity of which, as mentioned earlier, is 0.1–0.3 W/m·K. Low and medium filled polymers have the thermal conductivity of 0.3–2 W/m·K, which is insufficient for effective heat dissipation required for many technical applications.

Main difference between low-, medium-, and high-filled systems is heat transfer mechanism. In low- and medium-filled systems, micron-sized fillers do not provide continuous heat flow paths, so heat transfer in such composites is primarily determined by polymer matrix. In high-filled systems, particles are bonded to each other, creating continuous mesh through which heat transfer is carrying-out.

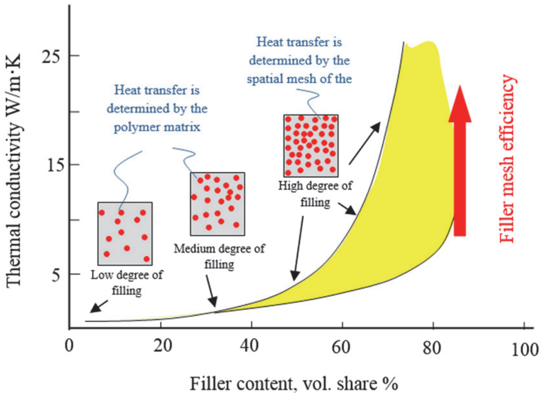

Fig. 2. Schematic dependence of thermal conductivity of polymer composites on content of filler.

Main idea of effective control of thermophysical characteristics of composite material at high degrees of filling is to maximize heat-conducting paths along with minimizing boundary thermal resistance "filler-filler" and "filler-matrix". High-filled (>50 % volume concentration) polymer composites can have thermal conductivity up to 32 W/m·K, and, therefore, from practical point of view,can be effective heat-conductive materials [2, 12].

2.2 Nanocomposites based on a polymer matrix and methods of obtaining them

As it was noted above, depth of influence of filler on properties of material is increasing with increasing in concentration of particles in the matrix. However, in practice, these concentrations of nanoparticles can be varied within fairly narrow ranges: usually concentrations of nanoparticles injecting into the polymer is few percent. Due to high surface activity of nanoparticles, they are characterized by pronounced tendency to aggregation and agglomeration with forming clusters, stacks (nanolayers), and bundles (cylindrical particles) of individual nanoparticles. Creating such aggregates leads to heterogenization of material structure and to significant decreasing in effectiveness of effect of nanofiller on its properties. Accordingly, the most important stage of any technology for preparing nanocomposite materials is process of injectingnanoparticles of filler into volume of matrix polymer and their mixing. Task that must be solved when organizing this process is to ensure uniform distribution of the injected nanoparticles in volume of matrix. Maximal concentration of the nanofiller, which can be created in the nanocomposite material without losing the positive effect, depends on how successfully this problem is solved.

There are two main mixing mechanisms: simple and dispersive. Simple mixing is understood as a process resulting in statistically random distribution of particles of initial components in volume of mixture without changing their initial sizes. Dispersive mixing is a mixing process that is accompanied by a changing (decreasing) initial particle size of components associated with their fragmentation, destruction of aggregates, deformation and decomposition of dispersed phase, etc.

Main task of dispersive mixing is to destroy aggregates of solid particles and distribute them in volume of liquid polymer.

At creating polymer nanocomposites with ready-made nanofiller following three main methods are using:

— mixing in solution (for polymers soluble in organic solvents);

— melt mixing (for thermoplastic polymers);

— in-situpolymerization.

It is well known that it is very difficult sufficiently effectively to disperse nanoparticles (NPs) in a solvent by simple mixing. Treatment with high-power ultrasound is quite effective at forming of dispersion of NPs. Ultrasonic processing is widely using in dispersing, emulsifying, crushing, and activation of particles. With help of ultrasonic processing, aggregates and coils of NPs can be effectively destroyed. Studies on various dispersions of nanoparticle agglomerates with different solids content have demonstrated significant advantages of ultrasonic processing over other technologies such as rotary mixers, piston homogenizers, ball mills, and colloid mills. For mixing in solution, polymer matrix must be soluble in at least one solvent. It is problematic for many polymers.

Melt mixing is generally applicable and enough simple method, especially in case of thermoplastic polymers. During melt molding process, NPs are mechanically dispersed in polymer matrix using a mixer with a high shear force at high temperatures. This approach is simple and compatible with existing industrial technologies. Shear forces destroy NP aggregates and prevent their formation.

Disadvantage of this method is that this method gives dispersion of NPs in polymer matrix, which is much worse than dispersion that can be achieved by mixing in a solution. In addition, NPs should be smaller because of high viscosity of composites with higher content of NPs.

At using the in-situ polymerization method, NPs are dispersed in monomer with subsequent polymerization. Moreover, higher percentage of fillers can be easily dispersed, and they form a strong interaction with matrix polymer. This method is used to prepare composites with polymers that cannot be processed by mixing in solution or mixing in melt, for example, insoluble and thermally unstable polymers [13].

2.3 Materials of micro- and nanoparticle powders for creating electrically insulating thermally conductive polymer composite materials

For increasing thermal conductivity of polymer materials while maintaining their necessary properties, including high electrical insulation characteristics, most often at creating polymer composites and nanocomposites, powders of micro and nanoparticles of following widely known and used in industrial production of dielectric heat-conducting materials are used,such as BN, AlN, TiO_2, and Al_2O_3, etc. (Table 1).

The practical possibility of significant increasing thermal conductivity of electrical insulating polymer composite materials, including polyimides, during injecting of dielectric heat-conducting materials into their volume as fillers, is confirmed by the examples below:

— injection of boron nitride (BN) particles. In [14] thermal conductivity of polymer nanocomposites containing hexagonal BN (HBN) was studied by theoretical and experimental methods. With disordered arrangement of 6.3 vol. % HBN increasing in thermal conductivity was 300 %. In this case he orientation, functionalization or coating of these particles with polyimide (PHBN) contributes to an even greater increasing in thermal conductivity. PCM containing 60 % of PHBN particles have thermal conductivity of 3.3 W/m·K, while without coating 2.6 W/m·K;

— injection of aluminum nitride particles. In [15] it was reported that the thermal conductivity of epoxy composite material containing 50 vol.% untreated aluminum nitride (AlN) was 1.25 W/m·K.

— injection of Al_2O_3 and BN particles. In [16] results of studies ofinfluence of parti-

Table 1. Thermal conductivity of fillers

№	Filler type	Coefficient of thermal conductivity, W/m*cdotБ*%%*ApB*K
1	Boron nitride	180
2	Aluminium nitride	285
3	Aluminium oxide	20

cle size and geometry of mixed fillers of different compositions on thermal and mechanical properties of hybrid composite systems are presented. Influence of system consisting of polygonal Al_2O_3 particles and BN plates on thermal conductivity of polymer composites has been studied. PCM containing 30 % hybrid filler Al_2O_3 + BN (1 μm) had significantly higher thermal conductivity (0.57 W/m·K) than unfilled one.

— injection of TiO_2 and BN particles. In [17] thermophysical properties of polyimide-based on tricyclodecentetracarboxylic acid dianhydride and 4,4′-diaminodiphenyl ether and its film compositions, including those with particles of boron nitride and titanium dioxide, were studied. Values of thermal conductivity for polyimide films with filler of boron nitride particles and TiO_2 particles with particle size of up to 10 μm have been determined. Thermal conductivity of the PI + boron nitride films (40 wt%) was 1.24 W/m·K, and thermal conductivity of the PI + TiO_2 films was about 1.12 W/m·K.

2.4 Polyimide composite materials and methods for injecting micro and nanoparticles into a polyimide matrix

Among polymer composite materials, polyimide materials occupy one of the leading places due to thermal stability and high strength indicators. Presently polyimide materials have a wide range of possible applications as materials that work for long time in the units of machines and devices, as well as insulating coatings at temperatures of 300°C and above. Composite materials obtained on their basis have following characteristics: maximal temperature of use of such materials is comparable to the analogous characteristics of titanium and aluminum, they have very high specific strength (significantly higher than those of titanium and steel). It is also of industrial interest that products of complex configuration can be obtained by pressing in mold, as result of which costs of machining the resulting products are significantly reduced. Composite materials based on polyimides can be used to obtain wide range of products, for example, such as: components of internal combustion engines using in aircraft, ship and automotive industries, blades, self-lubricating bearings used at high temperatures, heat and sound insulating panels, fire protection barriers, etc.

However, ever-growing requirements for materials lead to necessity to enlarge standard range of manufactured polyimide composite materials and create new types of polyimide systems with special properties, including those with high electrical insulating and heat-conducting properties for electronic modules and high-power devices. Therefore, it can be expected that the development of new composite materials based on polyimide binders will always arouse significant industrial interest [12].

Till presence based on aromatic polyimides, various research groups have developed several insulating heat-conducting polyimide composite films with thermophysical characteristics that are several times superior of initial polyimides, including development of effective technologies for their creating using micro- and nanoparticles of various dielectrics with high thermal conductivity as fillers.

In [17] polyimide composite films based on dianhydridetricyclodecentetracarboxylic acid and 4,4′-diaminodiphenyl ether, including those with boron nitride and titanium dioxide, were prepared.

Mixed compositions with boron nitride and titanium dioxide (particle size up to 10 μm) were obtained by homogenizing modifying additives in an amount of 1–40 wt. % at room temperature for an hour in solutions of polyimide in N,N′-dimethylacetamide with a concentration of 20 wt. %. Then, the solutions were cast into films with thickness of 55–65 μm on glass substrates.

In [18] inorganic fillers TiO_2 (rutile, particle size 30–40 nm) and Al_2O_3 (corundum, particle size 40–80 nm) were used to create film composites based on AD-9103 varnish. Polyimide film composites were manufactured in three stages:

1) Preparation of compositions with different weight ratios of polymer/filler by mixing solution of polypyromellitic acid in dimethylformamide.

2) Ultrasonic treatment of mixed compositions on the UZD-3.5 generator for 20 minutes.

3) applying of mixed compositions on glass substrates and curing according to chosen temperature regime.

Regimes of curing of mixed compositions for obtaining film composites were chosen in accordance with the data for formation of polyimide films based on AD-9103 varnish:

— 80°C — 1 h., 100°C — 1 h., 150°C — 1 h., 200°C — 1 h., 250°C — 1 h., heatingupto 320°C;

— heating rate to chosen temperatures, 5°C/min;

— content of inorganic fillers was 3 and 10 % of the mass.

In [19] objects of study were films based on rigid-chain polyimides. Polyimide based on commercially available varnish brand AD-9103 IC. The filler was a diamond charge (DC) obtained by detonation synthesis from a mixture of explosives.

For obtaining polyimide composite films, AD-9103 IC varnish was mixed with DC in amount of 5 and 10 wt. %. Dispersion of the mixed compositions was carried out on a laboratory ultrasonic generator "LUZD-1.5/1P" for 25 min. Previous experiments have shown that minimal optimal dispersion time for mixed compositions with DC is 25 min since a shorter processing time leads to formation of film with defects formed by aggregated particles of high-dispersed filler. Such defects lead to decreasing strength properties of film samples, and further increasing dispersion time does not significantly affect on quality of obtained films.

For obtaining polyimide composite films prepared mixtures were applied with an applicator on glass substrate and then curing with gradual heating to 300°C at rate of 5°C/min. Thereafter PI films were thermostated at 200°C for 1 hour.

In [20] methods of obtaining nanocomposite materials based on polyimide matrixes and nanoscale fillers are described. As noted earlier, all methods for preparing nanocomposites are ultimately aimed at increasing uniformity of distribution of nanoparticles in volume of polymer and, as a result, at obtaining high-quality nanocomposites with enlarged range of nanoparticle concentrations that can be injected into the polymer before the onset of intense aggregation processes.

However, in reality for each type of nanofiller, there is a certain limit of such concentration, exceeding which does not lead to further increasing level of material properties. Main disadvantage of such methods is fact that they make it possible to prevent processes of aggregation of nanoparticles only in rather narrow range of their concentrations in nanocomposite material and, as a consequence, allow achieving very limited increasing level of material characteristics. When the upper limit of this range is exceeded, intensive aggregation processes develop, and, as a consequence, there is significant slowdown and cessation of growth of required characteristics of material, and in some cases even their decreasing.

In this work is proposed solution aimed at further enlarging this range of concentrations of nanoparticles, injecting of which into polymer matrices does not lead to development of aggregation processes. Technical task and positive result of the proposed method is possibility of increasing limiting concentration of nanoparticles injected into polymer matrix, namely, into the volume of polymers belonging to class of aromatic polyimides, before development of their agglomeration processes and, accordingly, ensuring an increased level of characteristics of nanocomposite materials. Specified technical result is achieving in proposed method for producing nanocomposite materials based on polyimide matrices and nanosized fillers — nanoparticles of at least two types: nanoparticles of layer geometry, nanofibers, nanotubes, and nanocones/disks, due to joint or sequential injection of certain amounts of these nanoparticles into the volume of matrix polymer. In this case concentration of nanoparticles of each type remains enough low so that they remain uniformly distributed in volume of polymer and do not form aggregates. And total concentration of nanoparticles is enough high to provide significant gain in properties of resulting nanocomposite. In this case, high technical result is ensuring by injecting two or more different types of nanoparticles into matrix polymer. For preparing homogeneous dispersions of nanoparticles in solvent before their injecting into polymer solution, ultrasonic dispersion methods are used. Mixtures of polymer solution and dispersion of nanoparticles are homogenized using mechanical paddle-type agitators for 24 hours at speed of 1000 rpm. Obtained nanocomposite solution, containing polymer and several nanoparticles homogeneously distributed in it, is usingfor manufacturing films with improved characteristics. For this, films cast from nanocomposite solutions onto flat substrates using dies with adjustable gap are cured for 2 hours at 80 or 90°C, followed by heat treatment in heating regime up to 250°C at a rate of 3°C/min or up to 360°C at a rate of 5°C/min, followed by holding at this temperature for 30 or 20 minutes, respectively. In this case, nanoparticles of at least one of types used can be injected into polymer matrix at stage of its synthesis (*in situ* polymerization). Various types of nanoparticles can be used for preparing nanocomposite material. Various polyimides can be used as polymer matrices at preparation of nanocomposites by described method, in particular thermoplastic aromatic polyimides containing four or more aromatic rings in an elementary unit.

As a result of implementation of described above technical solutions it is possible to inject nanoparticles into polymer in total concentrations exceeding maximal concentrations of nanoparticles of one type, which can be dispersed in polymer before their intensive aggregation begins. Due to this, more significant increasing values of required characteristics of material is achieving than that realized at injection of same type nanoparticles in concentration equal to the sum of concentrations of various nanoparticles injected in accordance with proposed method.

It is known that practically all attempts to explain flowing of heat flux in polymer matrix containing heat-conducting particles are leading to theory of percolation (flow), according to which the thermal conductivity depends on volume fraction of the heat-conducting filler. Analysis of literature data on heat-conducting composites showed that the most promising is using high-filled PCM (more than 40–50 %) with high level of thermal conductivity. Main task in creating heat-conducting polymer composition is to ensure continuous chain structure of heat-conducting filler in polymer matrix, which makes it possible to obtain CM with thermal conductivity varying in wide range — from values typical for dielectrics to values that allow them to be used as heat-conducting materials. Creating heat-conducting paths in two-phase system depends on ability of particles of heat-conducting phase to create good thermal contact when they come into contact or approach. Main disadvantage of such system is that heat-conducting particles are isolated from each other and, thus, do not make the necessary contribution to through thermal conductivity of composite, unless, of course, their concentration is very high. At high concentration of heat-conducting particles (high percolation threshold), mechanical properties of the composite deteriorate significantly, and the material becomes hard and brittle. Therefore, creating composite that combines good mechanical and heat-conducting properties is very difficult task [21].

In turn, in [22] it is reported that decreasing size of filler particles in composite material down to nanoscale does not lead to a significant change in thermal conductivity compared to prototype materials using micron filler particles (at close values of the amount of filler). Decrease size of nanoparticles less than 20 nm leads to significant decreasing in value of coefficient of thermal conductivity. In particular, it is reported that when studying mixture of micron and nanosized filler particles as filler, thermal conductivity of composites increases. At the same time, size of micro- and nanoparticles of fillersusing in mixture does not effecton properties of composite as noticeably as their mass ratio in the mixture. It was found that ratio of size of microparticles to size of nanoparticles should not exceed 1000, but also should not be less than 100, since under these conditions optimal distribution of nanoparticles between microparticles is achieved and sufficient number of heat-conducting paths are formed; as a result, the thermal conductivity of the material decreasing.

Varying amount of filler in the material made it possible to establish that high heat-conducting and dielectric properties are achieved when content of filler particles in composite is at least 55 wt. % and increasing with further increasing filler content. Increasing content of the filler more than 90 wt. % leads to deterioration in deformation and strength properties (characteristics of strength and plasticity deteriorate). Mixtures of micro and nanopowders such as aluminum oxide, aluminum nitride, boron nitride, etc., or their mixtures were used as dispersed fillers for polymer matrices. Maximal thermal conductivity at order of 10–12 W/m·K has been observed for version of composite material, in which mixture of micro- and nanoparticles of filler powders with a predominant content of microparticles was used as a filler. Optimal variant of total filling polymer matrix powder mixtures was 78–80 %.

At 80 % composition of powder mixtures with average particle size up to 10 μm and 20 % with an average particle size up to 100 nm, materials had thermal conductivity up to 5.3 W/m·K, and with composition of powder mixtures of 20 % with average particle size up to 10 μm and 80 % with average particle sizes up to 100 nm, composite materials (CM) had thermal conductivity up to 4.3 W/m·K. At 70 % composition of powder mixtures with average particle size up to 10 μm and 30 % with average particle size up to 20 nm, CM had thermal conductivity up to 8.5 W/m·K, and with 30 % mixture of powders with average particle size up to 10 μm and 70 % with average particle sizes up to 20 nm CM had thermal conductivity up to 4.1 W/m·K. All obtained CM samples were good dielectrics with electrical conductivity exceeding 10^{-9}–10^{-7} Ohm^{-1}·cm^{-1}. Heat-conducting nanocomposites were prepared by mixing polymer and filler powders with using pretreatment of fillers with organic modifying compounds to impart organophilic properties to them. This approach makes it possible to maximize the range of concentrations of nanoparticles, injecting which into polymer matrices does not lead to development of aggregation processes.

4. Conclusions

At searching and analyzing scientific and technical information, various methods of increasing thermal conductivity of polymeric materials, including composite polyimide films, were considered. However, even though main idea of effective control of thermophysical characteristics of polymer materials at high degrees of filling of micro- and nanoparticles is to maximize heat-conducting paths along with minimizing boundary thermal resistance "filler-filler" and "filler-matrix", to solve this problem in practice turned out to be quite difficult. This is due, first of all, to fact that there are not so many filler materials that have both high thermal conductivity and high electrical insulating properties. In addition, cost of micro- and nanodispersed heat-conductive powders is also quite high, and methods of their injecting into polymer matrix, and especially into polyimide matrix, are rather complicated and laborious.

Influence of filler on properties of material increasing as concentration of particles in matrix increasing. However, in practice, these concentrations can be varied within rather narrow limits due to significant decreasing quality of manufactured composite films. This is especially relating to nanoparticles. Accordingly, the most important stage of any technology for preparing heat-conducting composite materials is process of injecting micro- and nanoparticles of filler into volume of matrix polymer and mixing them. Main task that must be solved when organizing this process is to ensure uniform distribution of the injected particles in the volume of the matrix. Maximal concentration of the filler, which can be created in the composite material without losing positive effect, depends on how successfully this problem is solved.

Analysis of available experimental data from various sources confirms that significant practical results have already been achieved in improving heat-conducting properties of composite polyimide films. Coefficients of thermal conductivity of such films are in the range from 1.12 to 10–12 W/m·K.

However, at the same time, industrially produced heat-conductive electrical insulating polyimide films, for example, the heat-conductive film of KYPI-MT type from Chinese company Suzhou Kying industrial materials Co.ltd., which is supplying to world market in large amount, has thermal conductivity only 0.43 W/m·K at cost of 260 US dollars per 1 kg [23]. Consequently, task of creating commercially available low-cost, but high-quality, heat-conductive polyimide composite materials with sufficiently high thermal conductivity (5–10 W/m·K) and without deteriorating strength and plasticity characteristics is currently relevant and technically in demand, which is engaged by a large number of research teams around the world.

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