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Nanocomposite Polyimide Materials

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Abstract

The transition to nanosized fillers allows to significantly improve the characteristics of composites while reducing their degree of filling, and in some cases to achieve new properties unattainable with the use of traditional fillers and modifiers. Polymeric nanocomposites have unique barrier properties, electrical conductivity, thermal conductivity, increased strength, heat resistance, and thermal stability, as well as reduced flammability. It is known that the addition of nanodispersed layered silicates and various forms of carbon nanofillers to polymeric matrices can significantly affect the mechanisms of thermal and thermooxidative destruction and burning of nanocomposites. In this chapter, we compare the properties of composite materials based on nanostructured silicon carbide and carbon nanotubes with modified and unmodified surfaces obtained on three types of polyimide matrices (matrix No. 1 based on pyromellitic dianhydride and 4,4'-oxydianiline, matrix No. 2 based on 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and p-phenylenediamine, and matrix No. 3 based on pyromellitic dianhydride and 4-[4-(4-aminophenoxy) phenoxy] phenylamine). The dynamic viscosity of polyamide acid, the physicomechanical characteristics of film polymer composite materials, the determination of thermal stability, and thermooxidative destruction mechanism of composites were determined.

Keywords: polyimides, polyimide matrix, nanocomposites, composite materials, carbon nanotubes, silicon carbide, fillers

1. Introduction

The wide introduction of polymer materials in various fields of production is due to their special mechanical and physicochemical characteristics, such as elasticity, low brittleness,

directional changes in structure and properties under physicochemical effects. To reduce the cost of material and give it special properties, various fillers are actively used.

Most of the composite materials are developed for the aerospace industry, which has always been and still is the most high-tech branch of modern production. At the same time, these materials and technologies for their production are also innovative drivers in many other sectors, such as construction, engineering, energy, instrumentation, medicine.

To produce materials with increased rigidity, impact, and tribological properties, during the last decade a lot of research has been devoted to the modification of polymers by nanoparticles. These composites exhibit unique properties that combine the advantages of inorganic fillers, such as stiffness, high thermal stability, and mechanical properties with processability, flexibility, and plasticity of organic polymers. Due to the influence of nanosized fillers on the bulk properties of polymer nanocomposites, it is possible to achieve such unique properties by adding small amounts of nanofillers to the polymer matrix.

Polymeric nanocomposites representing a new class of materials have unique barrier properties, electrical conductivity, thermal conductivity, increased strength, heat resistance, and thermal stability, as well as reduced combustibility. It is known that the addition of nanodispersed layered silicates and various forms of carbon nanofillers to polymeric matrices can significantly affect the mechanisms of thermal and thermooxidative destruction and burning of nanocomposites.

One of the most important issues facing nanotechnology is how to get molecules to group themselves in a certain way, to organize themselves, in order to eventually obtain new materials or devices capable of long-term preservation of their performance properties under the action of high and very low temperatures, chemical agents, increased radiation, and other factors. One of the main ways to solve this problem is the creation of composite materials based on a polyimide (PI) matrix. Adding different amounts of nanoparticles at different stages of polymerization of the matrix, increasing the number of available monomers (dianhydrides acid), and reversibility of the imidization reaction (the second stage of the synthesis reaction) will allow to vary the molecular and molecular mass characteristics and, as a consequence, their thermal resistance and solubility to processing, deformation-strength, and other properties of future composites.

In the world literature, examples of nanocomposite materials based on polyimide matrix filled with carbon nanotubes (CNTs), carbon fibers, and nanostructured silicon carbide (SiC) are known, and their thermal and deformation strength and other properties have been measured. Expanding the diversity of polyimide matrices and varying the content of nanostructured materials allow us to obtain a huge variety of composite materials.

Thus, creation of new composite materials with high performance characteristics and technology for their production is a very urgent and important task.

During the last decade, a lot of research has been devoted to the combination of polymers with nanoparticles to produce materials with increased rigidity, impact, and tribological properties [1]. The growing demand for nanomaterials is due to the fact that new chemical and physical properties are achievable with the addition of nanosized fillers to the polymer matrix, even if the same material without a nanofiller does not have such advantages. This is due to the influence of the unique nature of the nanosized filler on the bulk properties of nanocomposites on

a polymer basis [2, 3]. Polymer nanocomposites are extensively studied for a potentially wide range of applications due to their ease of processing, low production costs, good adhesion to the substrate, and unique physicochemical properties. Dispersing of inorganic materials in a polyimide matrix is a complex task and a key factor affecting the final properties of hybrid materials. The addition of a cross-linking agent is a solution to overcome the difficulties associated with dispersing. By adding a cross-linking agent, organic and inorganic materials can be covalently bonded and compatibility between these two phases can be improved [4, 5].

The transition to nanofillers has significantly improved the performance of composites and achieved new properties unattainable with the use of traditional fillers and modifiers.

With the development of industries, an increase in the operating temperature range occurs, as a result of which the requirements for materials increase.

2. Polyimides: the structure of polyimide matrices

Polyimides are one of the most interesting polymers, which have increased heat resistance and are widely used in the manufacture of high-temperature plastics, adhesives, dielectrics, and other materials.

Currently, polyimide resins are used as matrices to create reinforced composites based on lightweight carbon fibers, as a replacement for metal parts in the aerospace industry and airframe, due to their outstanding thermal and mechanical resistance, as well as resistance to the action of ionizing radiation. Polyimide resins are widely used in such areas as microelectronics, aerospace, gas separation, and the production of fuel cells. They are used in the cable industry for the production of electrical insulating varnishes and enamels, which have high heat resistance, elasticity, and good dielectric properties.

As is known, polyimides (PI) can be aliphatic, alicyclic, or aromatic, depending on the chemical structure. Depending on the structure of the chain, polyimides can be linear or three-dimensional [6]. There are polyimides with aliphatic links in the main chain of the macromolecule and purely aromatic polyimides. The first are solid, readily crystallizable substances of white or yellow color. Polypyromellitimides based on aliphatic diamines containing less than seven carbon atoms in the molecule have high melting points that are higher than the temperatures of their onset of decomposition (above 350°C) and do not dissolve in known organic solvents. Polypyromellitimides based on aliphatic diamines containing, in the chain, more than seven carbon atoms or having a branched hydrocarbon chain (at least seven carbon atoms), as well as polyimides of other aromatic tetracarboxylic acids and various aliphatic diamines, soften at temperatures of 300°C.

Aromatic polyimides are characterized by high heat resistance, and the most heat-resistant polyimides based on pyromellitic acid (**Figure 1**) and 1,4,5,8-naphthalenetetracarboxylic (**Figure 2**) acids, practically not softening before the onset of thermal decomposition, have a glass transition temperature of 500°C.

The heat resistance of other polyimides is well regulated by varying the nature of the monomers and is usually 300–430°C [7]. Most aromatic polyimides, especially high-heat-resistant,

Figure 1. Structural formula of pyromellitic acid.

Figure 2. Structural formula of 1,4,5,8-naphthalenetetracarboxylic acid.

are insoluble in known organic solvents and are inert to the action of oils, and also hardly change under the action of dilute acids.

With the introduction of various substituents into the side chain, especially card groups (phthalide, phthalimidine, fluorene, anthrone), the solubility of polyimides is substantially improved. Thus, polypyromellitimide aniline phthalate is soluble in dimethylformamide (DMF), m-cresol, sym-tetrachloroethane, and hexafluoro-2-propanol. Polyimides based on 3,3',4,4'-benzophenone tetracarboxylic acid or 3,3',4,4'-diphenyloxide tetracarboxylic acid and anilinflurene polyimides are also dissolved in methylene chloride and chloroform [8]. Under the influence of alkalis and superheated steam, aromatic polyimides hydrolyze. However, the propensity for hydrolysis depends significantly on their nature. Thus, polyimides with five-membered imide cycles are much less hydrolytically stable than analogous polyimides with six-membered rings.

Aromatic polyimides are distinguished by high radiation resistance [9]. Thus, poly(4,4'-diphenylene oxide pyromellitimide) films retain good mechanical and electrical characteristics after irradiation with high-energy electrons at a dose of 102 MJ/kg (films of polystyrene and polyethylene terephthalate become brittle after irradiation with a dose of 5 MJ/kg). Polyimides are resistant to the action of ozone, i.e., retain 50% strength after exposure to 3700 hours in air with an admixture of 2% ozone; they are also resistant to UV radiation. An important feature of aromatic polyimides is their high thermal stability.

The most heat-resistant are polyimides containing only imide rings and aromatic rings. In a vacuum and an inert atmosphere, aromatic polypyromellitimides are resistant to 500°C, and a significant reduction in mass (up to ~65% of the initial one) occurs above this temperature, after

which the mass of the residue remains practically unchanged up to 3000°C. Aromatic polyimides are also stable under conditions of prolonged isothermal heating; there is a decrease in the mass of poly-4,4'-diphenylene oxide-pyromellitimide after heating in an inert atmosphere for 15 hours at 400, 450, and 500°C by 1.5, 3.0, and 7.0%, respectively. Significantly more intensive polyimides decompose during thermal oxidation. The main products of destruction of aromatic polyimides are CO and CO₂.

To date, a wide range of polymers have been obtained by changing the chemical structure of the dianhydride (Q) and diamine (R) fragments of macromolecules (**Figure 3**), differing in structure and properties.

By chemical structure and physical properties (softened and melted), they are divided into four groups.

- Group A: polyimides consist only of aromatic groups and imide cycles. These polyimides are non-softening, $T_m > T_d$, hard, brittle with maximum heat resistance (**Figure 4**).
- Group B are the PI with hinges (connections around which a chain turn is possible) in the dianhydride fragment. These are non-softening, rigid polymers, with some elasticity (**Figure 5**).
- Group C are the PI with hinges in the diamine fragment. These are rigid, strong, and elastic polymers that do not have a clearly defined range of softening temperatures (**Figure 6**).
- Group D are the PI with hinges in the diamine and in the dianhydride fragment. These polymers are elastic and have a clear region of softening and melting (**Figure 7**).

So, all the cyclic structures can be divided into several types, the thermostability of which will decrease in the following order: conjugated carbocycles (carbon) $\geq$ ladder structures > condensed heterocycles > isolated heterocycles > non-conjugated carbocycles [6].

As noted above, the stability of polyimides at high temperatures is naturally determined primarily by their chemical structure. The data on the dependence of thermal stability on the chemical structure are of great importance both in determining the ways of further synthesis of thermostable polyimides and in selecting among them the most practically promising ones.

A huge number of polyimides obtained on the basis of a large number of dianhydrides of tetracarboxylic acids have been synthesized and characterized. The main practical application

Figure 3. General structural formula of polyimide.

Figure 4. Benzidine polypyromellitimide (Group A).

Figure 5. 3,3',3,4'-Benzophenone tetracarboxylic acid dianhydride and p-phenylenediamine polyimide (Group B).

Figure 6. Polyimide based on pyromellitic dianhydride (Group C).

Figure 7. Polyimide based on 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (Group D).

was found for polyimides made of pyromellitic acid dianhydrides; 3,3',4,4'-diphenyloxide tetracarboxylic acid; and 3,3',4,4'-benzophenone tetracarboxylic acid.

3. Composite materials containing nanosized filler

The introduction of small amounts of modern fillers, such as carbon nanotubes, carbon fibers, and nanostructured silicon carbide, increases the thermal stability, which makes it possible to obtain a composite material with high performance properties.

Recently, carbon nanotubes (CNTs) have attracted attention, since nanocomposites based on them will have improved mechanical properties. In addition, they can provide a certain type of electrical conductivity. It is expected that the combination of CNTs and polyimides will play an important role in the development of new, highly effective nanocomposites [10].

There are two general methods for obtaining composites. One is the mixing of CNTs with a polymer matrix in a molten form to produce a composite. The other is the dispersion of CNTs in the polymer solution, curing the resulting solution and removing the solvent.

Park et al. have reported on a method of effective dispersion of single-walled carbon nanotubes (SWNTs) in a polyimide matrix [11]. The obtained SWNT polyimide films are electrically conductive and optically transparent. A jump in the conductivity was observed between 0.02 and 0.1 vol.% SWNT; during this process the nanocomposite was converted from a capacitor to a conductor. Appending 0.1 vol.% SWNT increased the conductivity by 10 orders of magnitude, which exceeds the antistatic criterion for thin films for space applications ($1 \times 10^{-8} \text{ S cm}^{-1}$). A polyimide film containing 1.0 vol.% SWNT still passed 32% of visible light at 500 nm, while the film obtained by direct mixing passed less than 1%. A dynamic mechanical test showed that elastic modulus increases by 60% by addition of 1.0 vol.% SWNT; also the thermal stability of polyimide improves in the presence of SWNT.

Connel et al. [12] have reported on a synthesis of alkoxysilane polyamide acid (PAA), with SWNTs added to the previously prepared polyamide acid solution. When the loading was 0.05 wt.% SWNT, the percolation barrier was reached, which is evident from the sharp drop in the surface resistance of the material. Surface resistance and bulk resistance indicate that the SWNT polyimide composite is conductive. However, the presence of SWNT in polyimide has very small influence on T_g and the tensile strength of the polymer [12]. Increase in ionic strength of the polyimide matrix by adding an inorganic salt (CuSO_4) led to the formation of an SWNT network sufficient for conductivity. The addition of 0.014 wt.% CuSO_4 into a composite containing 0.03 wt.% SWNT led to films, reduced by four orders of magnitude of the surface and bulk resistance [13, 14]. There is an increased electrical conductivity of nanocomposite films; however, electric percolation occurs at larger loads than those that are commonly used in SWNT polyimide nanocomposites. The parameters of the film modulus slightly increase with growth of SWNT content. Electrospun fibers were obtained from the same SWNT polyimide suspensions used for the preparation of films. Images obtained by high-resolution scanning electron microscopy showed that SWNT are inside fibers and can have an orientation parallel to the fiber axis [15].

Sun and coworkers [16] have reported on the production of functionalized CNT by using polyimides with side hydroxyl groups. It was found that the obtained polyimide functionalized CNT are soluble in the same solvents as the original polyimide. A significant advantage of this method is that these functionalized nanotubes can be used directly to produce polyimide-CNT composites with relatively high content of nanotubes.

Electrically conductive polyimide composites are made from corresponding polyimides and electrically conductive fillers, such as carbon nanotubes, graphite, and acetylene black. The polyimide precursor (polyamide acid) was synthesized from 3,4,3',4'-biphenyl tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether by means of intensive mechanical stirring at -5°C . The results of the experiments showed that the electrically conductive composites based on carbon nanotubes and polyimide possess better electrical, mechanical, and adhesive properties than the other two composites [17].

In addition to carbon nanotubes, one of the promising fillers is nanostructured silicon carbide (SiC). SiC nanoparticles are chosen because of their unique physical properties, such as

excellent chemical stability, heat resistance, high electron mobility, excellent thermal conductivity, outstanding mechanical properties. They are used to produce high-performance composites and are used in electronics [18, 19]. These properties make SiC nanoparticles a suitable material for the production of polymer nanocomposites with a reinforced structure [20].

There are reports of the nanocomposite films' properties, which were obtained by two simple methods from a new polyimide and nanoparticles of silicon carbide, SiC. In the first method, the SiC nanoparticles were initially functionalized with epoxy end groups using 3-glycidypropyltrimethoxysilane (mSiC); then, this solution was mixed with polytriazoles. A homogeneous solution for preparation of the film based on polytriazoles and mSiC was heated in vacuo. In the second method, a new diamine containing the 1,2,4-triazole ring, and the commercially available dianhydride (4,4'-(hexafluoroisopropylidene) diphthalic dianhydride) reacted in situ in the presence of SiC nanoparticles to form a homogeneous mixture of polyamide acid and silicon carbide (PAA/SiC). Next, after a high-temperature process in a vacuum, the mixture turned into a film based on polytriazoles and SiC. The research results showed that a strong chemical bond between the SiC nanoparticles and the polymer matrix leads to an increase in the glass transition temperature T_g from 300°C to higher than 350°C, the tensile strength from 108 MPa to 165 MPa, and the temperature of 5% weight loss ($T_{d5\%}$) from 380 to 500°C. The intensity of photoluminescence also increased, and moreover, with an increase of the SiC content, a shift in the blue region of the spectrum can be observed [21].

A highly effective composite material based on silicon carbide (SiC) and bismaleinimide, modified with allylic novolak for abrasive tools and wear-resistant elements, was developed and characterized. The research results showed that the residual strength at 440°C (1 hour) decreased to 64%, and the thermooxidative stabilities, compared to SiC/polyimide composites, which were made in a similar way, were also better. The ratio of polymer in the composite affects the mechanical properties—its flexural strength increases with the increase of bismaleinimide ratio. However, the excess content of bismaleinimide results in the formation of bubbles in the composite structure. The best composite with a flexural strength of 82.4 MPa was obtained by using 13 wt.% bismaleinimide. After treatment at 280°C for 1 hour, the flexural strength increased by 34% because of the further polymer cross-linking at a higher temperature [22].

It is expected that the combination of polyimides and other organic/inorganic compounds will play an important role in the development of innovative high-performance nanocomposites for various applications.

One of the main problems in obtaining nanocomposites is the prevention of aggregation of particles. It is quite difficult to obtain a monodisperse distribution of nanoparticles in a polymer matrix. This problem can be solved by modifying the nanoparticle surface, which allows improving the interaction of the inorganic modifier and the polymer. There are two main versions of modification. The first is carried out by adsorption or reaction of the surface layer with small molecules (for example, with silanizing agents). The second option is based on grafting polymer molecules through covalent bonds to hydroxyl groups existing on the surface of nanoparticles. The second method has the advantage that it allows one to obtain particles with necessary and predictable properties, due to the possibility of fine selection of the type of particles, grafted monomer, and process conditions.

4. Preparation of composite materials based on a polyimide matrix modified by inorganic nanofillers

There are two basic mixing mechanisms: simple and dispersive.

Simple mixing is the process in which a random distribution of the particles of the initial components in the volume of the mixture occurs without changing their initial dimensions.

Dispersive mixing is a process of mixing, which is accompanied by a change (decrease) in the initial particle sizes of the components, due to their fragmentation, aggregate destruction, deformation, and disintegration of the dispersed phase, etc. The main task of dispersive mixing is to destroy aggregates of solid particles and distribute them in the volume of a liquid polymer [23].

When creating polymer nanocomposites with an already prepared nanofiller, three main methods are used:

- Mixing in solution (for solubles in organic solvents of polymers)
- Melt mixing (for thermoplastic polymers)
- In-situ polymerization

Since the polyimide matrixes used are insoluble in organic solvents and their softening temperature exceeds 300°C, it is advisable to use in-situ polymerization.

4.1. Methods for producing composite materials based on a polyimide matrix modified with carbon nanotubes and silicon carbide

Carbon nanotubes have excellent mechanical, electrical, and magnetic properties, as well as a nanometer scale with a high length-to-diameter ratio, which makes them an ideal reinforcing agent for high-strength polymer composites. However, CNTs usually form bundles stabilized by van der Waals forces, which are extremely difficult to disperse in the polymer matrix. The biggest problem in the production of reinforced CNT composites is the efficiency of the dispersion of CNTs in the polymer matrix. There are several methods for dispersing nanotubes in a polymer matrix, such as mixing in solution, melt mixing, electroforming, in-situ polymerization, and chemical functionalization of carbon nanotubes.

4.1.1. *Mixing in solution*

With this approach, the dispersion of carbon nanotubes in a suitable solvent and the polymer are mixed in solution. The CNT/polymer composite is formed by precipitation or by evaporation of the solvent. It is well known that it is very difficult to efficiently disperse nanotubes in a solvent by simple mixing. Processing with high-power ultrasound is more effective in the formation of the dispersion of CNTs. Ultrasonic treatment is widely used for dispersing, emulsifying, crushing, and activating particles. With the help of ultrasound, it is possible to effectively destroy aggregates and coils of carbon nanotubes.

The chemical effects of ultrasonic dispersion are associated with a rapid (on a scale of microseconds) intensive collapse of cavitation bubbles created during the passage of ultrasonic waves through a liquid medium [24]. Sonochemical theory and related studies have shown that ultrasonic cavitation can generate high local temperature and pressure [25].

Nanomaterials tend to agglomerate with stirring in a liquid, while the creation of nanocomposites requires efficient dispersion and a uniform distribution of nanoparticles in the liquid.

To overcome the strength of the bonds after wetting the powder, effective ways of deagglomeration and dispersion are needed. The ultrasonic disintegration of agglomerates in suspensions allows full use of the potential of nanomaterials. Studies on various dispersions of agglomerates of nanoparticles with different solids content have demonstrated significant advantages of ultrasound compared to other technologies, such as rotary agitators, piston homogenizers, ball mills, and colloidal mills.

4.1.2. Melt mixing

For mixing in solution, the polymer matrix must be soluble in at least one solvent. This is problematic for many polymers. Melt mixing is generally applicable and fairly simple, especially when used in the case of thermoplastic polymers. In the melt spinning process, carbon nanotubes are mechanically dispersed in the polymer matrix using a high-shear mixer at high temperature [26]. This approach is simple and compatible with existing industrial technologies. Shear forces destroy CNT aggregates and prevent their formation.

The disadvantage of this method is that this method produces a dispersion of carbon nanotubes in the polymer matrix, which is significantly worse than the dispersion that can be achieved by mixing in solution. In addition, carbon nanotubes should be smaller because of the high viscosity of the composites with a higher content of carbon nanotubes.

4.1.3. In-situ polymerization

Using this method, carbon nanotube or nanostructured silicon carbide is dispersed in the monomer followed by polymerization. Moreover, a higher percentage of fillers can be easily dispersed, and they form a strong interaction with the polymer of the matrix. This method is used for the preparation of composites with polymers that cannot be processed by mixing in solution or melt mixing, for example insoluble and thermally unstable polymers.

In the case of using a polyimide matrix, which is obtained by polycondensation, it is expedient to use the in-situ polymerization method.

4.2. Modification of the nanofiller surface

4.2.1. Modification of the surface of carbon nanotubes

To date, there are no generally accepted standards describing the characteristics and properties of manufactured nanotubes. Their properties are individual for each manufacturer. Nanotubes can initially differ in diameter (and number of layers), average length, content of

impurities (primarily amorphous carbon, metal catalyst residues and adsorbates), degree of aggregation, and other less important parameters.

In order to effectively use carbon nanotubes as a component of polymer composites, it is considered advisable to modify their surface to increase the strength of the nanotube and polymer matrix interaction, as well as to improve the dispersibility of nanotubes. To solve this problem, a functionalization method has been chosen that allows the creation of carboxyl functional groups on the surface of nanotubes, since this allows binding of the filler with covalent bonds to the polymer molecule; this is achieved by oxidation of the initial nanotubes with a mixture of nitric and sulfuric acids. Such functionalization of nanotubes is accompanied by the opening of their ends and, in some cases, by “cutting” nanotubes during oxidation. Also, oxygen-containing groups create a negative electrostatic charge on the surface, which contributes to less aggregation and better dispersibility. Oxidative functionalization also reduces the amount of residual amorphous carbon.

The presence of the $-\text{C}(\text{O})\text{OH}$ group is judged by the presence in the IR spectrum of the characteristic bands $\nu_{\text{C=O}} = 1614\text{--}1620\text{ cm}^{-1}$ ($-\text{COO}^-$) and $\nu_{\text{C=O}} = 1710\text{--}1735\text{ cm}^{-1}$ ($-\text{COOH}$), and also bands at $1585\text{--}1590$, $1200\text{--}1205$ and 1800 cm^{-1} .

4.2.2. *Modification of the surface of nanostructured silicon carbide*

As a modifying agent capable of forming strong contacts with inorganic particles, organosilicon compounds containing alkoxysilyl groups are most often used. The interaction of organosilicon compounds with silicon oxide, which is present on the surface of nanostructured silicon carbide, chemically binds the organosilicon fragment and the surface hydroxyl groups of the particle. This leads to the hydrophobization of the surface of the filler particle, which makes it possible to form a strong contact with the polymer. In addition, a reactive amino group appears on the surface of the particles, allowing additional covalent binding to be achieved.

In this case (3-aminopropyl) triethoxysilane (trade name: Silane coupling agent KN-550) was used as the modifying agent, which has a wide field of application in the field of composites production. This cross-linking agent is very sensitive to moisture; therefore, it is necessary to use dried solvents to modify the filler surface with it.

To evaluate the effectiveness of surface modification of nanostructured silicon carbide, infrared spectroscopy and the CHNS method were used (the nitrogen content of the final compound was estimated).

4.3. **Preparation of composite materials based on silicon carbide and carbon nanotubes**

The main process for obtaining dispersion-filled plastic masses (for the preparation of composites based on polyimide and CNT or nanostructured silicon carbide) is mixing. These are complex physicomachanical and physicochemical processes associated with the action of force fields, the displacement of the original components of the mixture in the reactor volume along complex trajectories, with the formation of a system characterized by a randomly distributed distribution of components.

As noted earlier, the polyimide matrices used are insoluble in organic solvents, and their softening temperature exceeds 300°C, which means that it is expedient to use the in-situ polymerization method as a basis.

The technologies of obtaining a composite material in the form of a powder and in the form of films were studied.

The process of obtaining a powder of composite material was divided into four stages:

- Modification of the surface of nanostructured silicon carbide or carbon nanotubes
- Dispersion of inorganic filler in a solution of high-boiling solvent and diamine
- Carrying out the polymerization and imidization reaction
- Isolation of the resulting composite in the form of a powder

The process of obtaining a film composite material was divided into five stages:

- Modification of the surface of nanostructured silicon carbide or carbon nanotubes
- Dispersion of inorganic filler in a solution of high-boiling solvent and diamine
- Carrying out the polymerization reaction to obtain a precursor solution (polyamide acid)
- Application of the resulting polyamide acid solution to the substrate
- Drying of the solvent followed by stepwise imidization in a vacuum drying cabinet

Experiments were carried out to produce composites based on nanostructured silicon carbide with a modified and unmodified surface, and also based on carbon nanotubes with a modified and unmodified surface. These experiments were conducted to study the effect of different contents of inorganic fillers with varying degrees of surface modification on the properties of the resulting composite materials (**Table 1**).

All the composites obtained were characterized by the methods of elemental analysis, IR spectrometry. Thermal and thermooxidative destruction was evaluated, and the glass transition temperature of the resulting materials was determined.

As initial polymer matrices, polyimide matrices with different degrees of structural rigidity were chosen.

1. matrix No. 1 was obtained by the interaction of pyromellitic dianhydride and 4,4'-oxydianiline (PMDA/ODA) (**Figure 8**);
2. matrix No. 2 was obtained by the interaction of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and p-phenylenediamine (BTDA/pPDA) (**Figure 9**);
3. matrix No. 3 was obtained by the interaction of pyromellitic dianhydride and 4-[4-(4-aminophenoxy)phenoxy] phenylamine (PMDA/AFFA) (**Figure 10**).

No.	Type of inorganic filler	Surface state of inorganic filler	Inorganic filler content, wt. %
1	Matrix No. 1 (pyromellitic dianhydride and 4,4'-oxydianiline (PMDA/ODA))		
	Nanostructured SiC	Unmodified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Nanostructured SiC	Modified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Single-walled carbon nanotubes	Unmodified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%
	Single-walled carbon nanotubes	Modified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%
2	Matrix No. 2 (3,3', 4,4'-benzophenone tetracarboxylic acid dianhydride and p-phenylenediamine (BTDA/pPDA))		
	Nanostructured SiC	Unmodified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Nanostructured SiC	Modified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Single-walled carbon nanotubes	Unmodified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%
	Single-walled carbon nanotubes	Modified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%
3	Matrix No. 3 (pyromellitic dianhydride and 4-[4-(4-aminophenoxy)phenoxy] phenylamine (PMDA/AFFA))		
	Nanostructured SiC	Unmodified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Nanostructured SiC	Modified	0.05%, 0.1%, 0.25%, 0.5%, 1%, 2%
	Single-walled carbon nanotubes	Unmodified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%
	Single-walled carbon nanotubes	Modified	0.1%, 0.25%, 0.5%, 0.75%, 1%, 2%

Table 1. Experiments of producing powders of composite materials based on nanostructured SiC and CNT.

4.4. Properties of the resulting composite materials

4.4.1. Effect of nanosized filler on the viscosity of the precursor for the production of film composite materials

Solutions of polyamide acids (PAAs) are precursors in the preparation of polyimide films and composites based on them, and the degree of viscosity of this solution is an important parameter for the success of this experiment.

The effect of different contents of nanosized silicon carbide and carbon nanotubes on the viscosity of a precursor in the preparation of film composite materials was studied.

Figure 8. Structural formula of matrix No. 1.

Figure 9. Structural formula of matrix No. 2.

Figure 10. Structural formula of matrix No. 3.

To assess the effect of different inorganic filler contents on the viscosity of the precursor solution, the filler, dianhydride, diamine, and solvent were mixed in such proportions during the experiment so that a 20 wt.% polyamide acid solution was obtained. Precursors were obtained for two kinds of matrices (matrix No. 1 and matrix No. 2).

As can be seen from the data presented in **Figures 11** and **12**, for each filler with different types of modification on different matrices, there are areas of extremum in which, apparently, the percolation limit value for a given filler in a given polymer is found. The filler with the modified surface binds to the matrix with “hard” covalent bonds, and the filler with the unmodified surface is bound to the matrix by the intermolecular Van der Waals interaction, so the maximum value of the viscosity for the latter is much lower.

It can be seen from these graphs that in some cases there are two extrema (matrix No. 1 filler carbon nanotubes and matrix No. 2 filler nanostructured SiC and CNT). Probably, this is due to the fact that the filler content that lies between these peaks somehow inhibits the growth of the polymer chain, which has a very negative effect on the viscosity of the PAA solution.

The increase in the viscosity of PAA when CNT is introduced (more than 0.75 wt.%) is associated with the large surface area of carbon nanotubes, which “swell” in the solvent, and this increases the viscosity of the solution. It negatively affected the physico-mechanical properties of the composites.

4.4.2. Influence of nanosized filler on physicomachanical characteristics of film composite materials

The effect of different contents of nanostructured silicon carbide and carbon nanotubes on the physicomachanical characteristics of the resulting film composite materials was studied.

Figure 11. Dependence of the dynamic viscosity of a precursor for a matrix based on polyimide PMDA/ODA on the content of inorganic fillers.

Figure 12. Dependence of the dynamic viscosity of a precursor for a matrix based on polyimide BTDA/pPDA on the content of inorganic fillers.

From the precursor solutions, the films were cast and subjected to stepwise imidization in a vacuum oven at 80°C for 6 hours, then at 150, 200, 250, and 300°C for 1 hour at each temperature and then at 350°C for 15 min.

Film composite materials were also produced on two types of matrices (matrix No. 1 and matrix No. 2).

To assess the effect of nanostructured filler (degree of filling) on strength characteristics, polymer films were tested in terms of basic physicomechanical properties (elongation, tensile strength).

It is established that the strength characteristics of the material are significantly influenced by the introduction of a filler into the polymer system. The effective action of the filler is determined by such factors as the shape and size of the particles, the interaction of the filler particles with the polymer, the interaction between the filler particles in the polymer medium, and the amount of filler.

Based on the data obtained, it can be seen that when the content of the active filler increases to the optimum value, an increase in strength occurs. After achieving the optimum filling, the strength is reduced, and the indicator is subsequently saved at the achieved level. An increase

in the content of filler (more than 1%) promotes the agglomeration of particles, causing significant difficulties in obtaining a homogeneous system; this leads to a deterioration in the physicomechanical parameters.

As can be seen from **Figures 13** and **14**, the type of filler has a significant effect on the nature of the intermolecular interaction. Fillers with a modified surface make it possible to increase the intermolecular interaction, increase the number of intermolecular bonds that carry a mechanical load upon deformation, and also reduce the probability of thermofluctuation rupture of macromolecules in defective areas. From the data obtained, it can be seen that the tensile strength increases significantly in samples containing modified fillers, which is explained by an increase in the dispersibility of the filler particles when the surface is modified. The increase in strength indexes with the use of modified fillers is also associated with an increase in the degree of dispersion of the filler and an increase in the degree of homogeneity of the polyamide acid.

Thus, it was found that the optimal content of nanostructured SiC in the samples PMDA + ODA, BTDA + pPDA is 0.1 wt.%, which provides the maximum increase in tensile strength and elongation at break due to the alignment of internal stresses in the films. For composites with carbon nanotubes based on matrix No. 1, it is 0.25 wt.%, and for matrix No. 2, it is 0.1 wt.%. A different optimum of filling of polymer matrices is associated with different sizes of SiC and CNT particles.

Figure 13. Dependence of physicomechanical properties of the composite based on the PMDA/ODA matrix on the content of the filler.

Figure 14. Dependence of physicomechanical properties of the composite based on the BTDA/pPDA matrix on the content of the filler.

4.4.3. Influence of nanosized filler on thermal stability and thermooxidative stability of the resulting composites

The influence of the content of inorganic fillers with modified and unmodified surfaces on the thermal stability in an inert gas atmosphere (argon) and thermooxidative stability in air was studied. Composite materials were obtained in two ways (two-stage method—in the form of films and one-step method—in the form of powders).

Powders of composite materials on three types of matrices were obtained by a one-stage synthesis method (matrix No. 1, matrix No. 2, matrix No. 3).

Due to the low activity of 4-[4-(4-aminophenoxy) phenoxy] phenylamine, it is not possible to obtain a composite based on it by a two-step synthesis.

Two-stage synthesis composites on two kinds of matrices were obtained (matrix No. 1 and matrix No. 2).

To evaluate the effect of nanostructured fillers on thermal stability and thermooxidation stability, differentiation of thermogravimetric curves of the resulting composite materials was carried out, which are registered in an inert and oxidizing atmosphere.

The dependence of thermooxidative stability and thermal destruction of the composite on the content of the filler is shown below in **Figures 15–17**.

Figure 15. Dependence of thermooxidative stability (left) and thermal destruction (right) of the composite based on the PMDA/ODA matrix on the content of the filler.

The dependence of the effect of carbon nanotubes on thermal stability and thermal oxidation stability of composite materials based on matrix No. 1 is similar to the effect of the introduction of nanostructured silicon carbide. However, in view of the different particle sizes of these fillers, the percolation threshold for carbon nanotubes is higher and the maximum point is 0.75 wt.%. Also, in the case of introducing carbon nanotubes, a decrease in the thermal properties at 0.5 wt.% is observed in all samples with different degrees of surface modification. This is probably due to the fact that with this filler content, it is not possible to obtain a high-molecular weight polymer.

When studying the effect of nanostructured silicon carbide on the properties of thermal stability of composite materials based on No. 2 (BTDA/pPDA) matrix, it was shown that the introduction of this filler into the polymer in a one-step synthesis does not significantly affect the thermooxidative stability of the resulting composite materials, which cannot be said about a two-stage method of production where a maximum is observed with a modified filler content of 0.5 wt.%, and an increase of more than 60°C. The effect of nanostructured silicon carbide on thermal degradation turned out to be completely opposite (**Figure 16**).

Due to the high thermal and oxidative stability of matrix No. 2, the introduction of carbon nanotubes affects negatively this parameter, and it decreases with increasing filler content. At the same time, the influence of the content of CNTs with different degrees of surface modification on the thermal destruction of a composite based on the BTDA/pPDA matrix can be

Figure 16. Dependence of thermooxidative stability (left) and thermal destruction (right) of the composite based on the BTDA/pPDA matrix on the content of nanostructured silicon carbide.

described as follows. The graph has a maximum at 0.75 wt.%, which corresponds to the percolation threshold of carbon nanotubes in this matrix; this does not depend on the degree of modification of the filler nor on the method of its preparation (**Figure 17**).

To confirm the revealed regularities, the effect of nanostructured silicon carbide and carbon nanotubes on a polyimide matrix with a more “flexible” structure, which is matrix No. 3 (PMDA/AFFA), was studied.

It was shown that the percolation threshold with the introduction of nanoSiC is in the range of 0.05 wt.% and there is a significant increase in thermooxidative stability and resistance to thermal destruction of powders of composites obtained by a single-step process. The addition of carbon nanotubes to matrix No. 3 also increases these material properties up to 0.75 wt.%, with a decrease in these parameters at 0.5 wt.%, which was also observed in other experiments.

As can be seen from the presented data, the effect of nanostructured silicon carbide and carbon nanotubes on different matrices is very different, but practically does not depend on the method of obtaining the composite material. The difference exists only in the numerical value

Figure 17. Dependence of thermooxidative stability (left) and thermal destruction (right) of the composite based on the BTDA/pPDA matrix on the content of nanostructured carbon nanotubes.

of the parameter being determined, but not in the character of the curve and the extremum points.

Thus, it was found that to increase thermal and oxidative stability and resistance to thermal degradation:

- for matrix No. 1, the optimal content of nanostructured silicon carbide is 0.1 wt.%, and for carbon nanotubes, it is 0.25 wt.%;
- for matrix No. 2, the extremum content of nanostructured silicon carbide is 0.05 and 0.5 wt.%, and for carbon nanotubes, it is 0.25 and 0.75 wt.%;
- for matrix No. 3, the optimal content of nanostructured silicon carbide is 0.05 wt.%, and for carbon nanotubes, it is 0.25 and 0.75 wt.%.

5. Conclusion

In this chapter, we compared the properties of composite materials based on nanostructured silicon carbide and carbon nanotubes with modified and unmodified surfaces obtained on three types of polyimide matrices (matrix No. 1 based on pyromellitic dianhydride and 4,4'-oxydianiline; matrix No. 2 based on 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and p-phenylenediamine; and matrix No. 3 based on pyromellitic dianhydride and 4-[4-(4-aminophenoxy) phenoxy] phenylamine).

The influence of different amounts of nanostructured silicon carbide and carbon nanotubes on the viscosity of the intermediate precursor (polyamide acid solution), as well as the thermal stability and mechanical properties of final composites based on the polyimide binder, was obtained and tested on three types of polyimide matrices.

It was found that for composites based on nanostructured silicon carbide and carbon nanotubes, the optimal content of inorganic filler is the interval for silicon carbide from 0.05 to 0.1 wt.%, for single-walled carbon nanotubes from 0.1 to 0.75 wt.%.

It was found that the effect of inorganic fillers on the properties obtained by thermal imidization in a high-temperature solvent of powders of composite materials depends to a large extent on the chemical nature of the polyimide matrix. The influence of the inorganic filler on the properties of the film composite material obtained by the stepwise high-temperature imidization in a vacuum medium is the same and practically independent of the structure of the matrix.

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