MODERN FILLERS OF METAL AND POLYMER MATRICES

The review article describes modern fillers of metal and polymer matrices, their properties and applications. We discuss the main parameters of fillers, their advantages and disadvantages, the results of investigations and experiments, which may be useful for scientists and engineers working in the fields of chemistry and mater-


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1. Introduction

Nanomaterials are interesting objects of research, as they are widely used both in industrial and household purposes. The use of nanofillers (NF) and the possibility of compounding nanomaterials (NM) with each other have allowed the creation of nanocomposites [1–7], which open up fundamentally new classes of materials and significantly expand the areas of application of nanomaterials.

Due to the potentially growing demand for lightweight materials as components of the structure of vehicles and building structures (fire-resistant insulating layer, lightweight solar panels, thermal, water barriers, etc.), nanocomposites have become substitutes for traditional heavy components such as metals and ceramics, although they are also used to develop modern nanocomposites [3–7]. At the same time, nanocomposite materials are also characterized by increased tribological (friction, wear, and lubrication), mechanical, and thermal properties [1, 3, 7], which is important for rocket science, aerospace, and heavy industry.

An analysis of the state and development trends of nanoindustry objects allows us to conclude that when considering promising composite materials based on a metal matrix, the main attention is paid to the nature and chemistry of its filler, and when creating composites based on a polymer matrix, the main emphasis is on the nature and chemistry of the carrier itself and filler.

For filling composites with a metal carrier matrix, as a rule, carbon nanostructures are chosen, which make it possible to increase the strength properties of the material. As regards the main emphasis of polymer composites, the analysis of literature data indicates that preference is given to a carrier matrix based on epoxy and polyester resins. Urea-formaldehyde resins are somewhat inferior to them due to increased toxicity.
To create products from such composites, as a rule, the principle of casting is used. There is a wide variety of fillers, both natural and obtained by different methods of synthesis [8–17], which today need some generalization and their systematization.

The main advantages in creating composites based on a metal matrix are as follows:

• fillers allow you to control the structural state of the melt and help form additional crystallization centres;

• composite fillers are able to increase the strength characteristics of the material, when compared with the pure material of the carrier matrix;

• carbon nanofillers can be the strongest graphitizer, which is important for the iron industry.

The main advantages of creating modern composites based on polymers are:

• the possibility of using both solid and liquid polymers, which allows you to make an easy choice of the density of the working material;

• polymers are both electrically conductive properties (polyphenylenevinylene, polyacetylene, polythiophene, polypyrrole, polyaniline and polyphenylene sulphide) and electrically insulating, which allows you to create electrical equipment without metals;

• high soundproofing properties and low thermal conductivity of polymers also allow their use in construction and industry;

• polymers can have chemical, radiation, water and atmospheric resistance, which makes it possible to create products with a wide range of their applications;

• most polymers have a high resistance to interaction with bio- and microorganisms;

• a wide range of polymers allows you to choose the most approximate necessary physical and chemical operating parameters of the future product (strength, density, which allows you to change the weight of the product);

• easy creation of products of various shapes, and additive technologies allow the production of complex working 3D products, which can consist of different moving elements with different chemical composition;

• polymers are able to change their state of aggregation (liquid/solid) with temperature changes (e.g., polylactic acid melting point: 160–190 °C; ABS: 210–240 °C) and pressure, which makes it easy to create composites based on such polymers the method of mixing the polymer with the filler to a homogeneous state, where the polymer becomes a carrier matrix, and the fillers are usually bulk materials;

• the possibility of simple recycling of the composite, which allows you to create a closed cycle of production of products with their subsequent disposal as a worn or waste product.
Silicon dioxide (SiO₂) [2] and nanostructures of the [1] type: fullerenes [9, 10, 16, 18–22], fullerites [23–24], endofullerenes [25–27, 10], nanotubes and nanofibres [19, 20, 23, 28–30], graphenes and graphene-like structures (boron nitride, silicene, phosphorene, disulfides, diselenides, ditellurides, dinitrides, antimonene (Sb) and others) can be used to manufacture modern nanocomposite materials based on a metal and polymer matrix.

However, for composites based on polymer matrices as nanofillers, there is a famous wider spec kite, where nanosize particles of metals or their alloys are most often used, of which oxides of ferromagnetic metal nanoparticles (Fe₃O₄, Co₃O₄, NiO, and NiFe₂O₄ [31–33]) of various oxides (WO₃, TiO₂, Nb₂O₅, V₂O₅, MoO₃, BaTiO₃) are of particular interest.

Fullerene-type carbon nanostructures can be considered as promising materials for hydrogen sorption [34–40] similar to sorbents based on metals [41–49] and various alloys [50–66]. Such materials can be considered as carrier matrix fillers for creating new generation composites.

Today, work is already underway on the use of nanostructures as fillers in 3D printing technologies, which makes it possible to create materials with increased strength and electrical conductivity [4–7].

The advantages of using nanosize fillers in carrier matrices are that, due to their ultrafine size, high specific surface area of nanoparticles, and their specific morphology (e.g., 2D graphene-type filler and 3D fullerene, nanotube-type filler, nanopowders of metals and their alloys).

The introduction of even a small amount of nanofiller can significantly change the physicochemical and functional characteristics of the matrix itself, as well as impart new properties to the created composite materials [1, 4–7]. Due to nanodispersed fillers, it is possible to improve electrical and thermal conductivity, mechanical properties, while the use of traditional micron-size fillers can lead to a significant deterioration in the technological characteristics of the matrix, such as strength, elasticity, heat resistance, etc. [4–7, 67–70].

Nanoreinforced materials show a higher level of mechanical strength than their counterparts with microfillers in a carrier matrix [1, 71].

The following factors affect the nanocomposites’ properties:

- the carrier matrix characteristics;
- the nanoparticles, which, as filler, are introduced into the carrier matrix (the structure of the nanomaterial).
- the interfacial interaction between the surface of the nanofiller and the matrix.
- the dispersion of the filler (micro- or nanoparticles).
- the uniform distribution of the filler in the matrix phase (homogeneity of the composite) [72].
- the technology of creating a high-quality nanocomposite (e.g., elimination of porosity or interaction product when introducing filler).
To create a composite with enhanced mechanical characteristics (e.g., bending strength, elongation, rupture, etc.), as a rule, reinforcing fillers (nanofibres, nanotubes, etc.) are chosen, capable of forming a reinforcing phase in the polymer carrier matrix composite.

2. Methods for Obtaining Nanocomposites

To obtain nanocomposites, as a rule, the polymer matrix is first dissolved in an appropriate solvent, and then, a nanofiller is added to the dissolved polymer under vigorous stirring [1, 68].

The filler is treated for its better adhesion, and for polymer composites, the \textit{in situ} polymerization method is used, where, in the presence of nanoparticles, the following occurs: usually, the surface of a nanofiller is pre-treated or modified, then oxidizing agents, monomers /or hardeners/ or a doping agent are added with stirring [69]. This method of forming a nanocomposite promotes better interaction between the carrier matrix and the nanofiller, and also makes it possible to create a high-quality composite, where the widespread nanofiller is uniform in the matrix, which significantly improves the properties of the resulting composite [70].

In addition, the principles of nanotechnology require the separation of filler particles in terms of shape, molecular structure, and size. According to studies [1, 73–75], in order to achieve the maximum programmed effect in the composite, the size of the filler should be of 1–100 nm for nanofillers and of 100–500 nm for microfillers. To meet these requirements, different equipment is used, in particular, high-pressure homogenizers, dispersers, etc. [1, 73–75].

3. Properties and Application of Composite Materials

The authors of the article [1] consider the possibility of modifying cast iron by adding nanomaterials with carbon nanostructures. The article also discusses new ideas on the structure of the cast iron melt, which can be used to control the process of formation of additional crystallization centres. As a result of high-quality nanomodification, products of high quality and strength can be obtained. From the article [1], the following nanomaterials can be distinguished that can be used to modify cast iron: graphene, carbon nanotubes, fullerenes, fullerene black and soot. These nanomaterials can be added to cast iron melt to control the structural state and form additional crystallization centres. While in nanomodification, the main thing is to control the structural state of the melt to control the process of formation of additional crystallization centres. Thus, the selective effect on fullerene complexes and carbon nanoparticles contained in the iron–carbon melt makes it possible to carry out the nanomodification of cast iron with the addition of carbon...
nanostructures. The use of carbon nanostructures (CNS) in metal–CNS composites is because carbon is the strongest graphitizer. That is, the nano-modification of cast iron can lead to the formation of a structure of a mixed graphite form, which explains the high complex of mechanical properties after modification with nanoadditives. In addition, the use of carbon nanostructures makes it possible to obtain high-quality cast iron castings with a favourable structure of graphite and a metal matrix.

The mechanical and physical properties of nanocomposites depend on the type of nanofiller, the degree of dispersion, and its quantitative content. It is stated in [75] that the characteristics of the filler surface demonstrate a significant effect on the mechanical properties of nanocomposites.

In Ref. [76] polymer–carbon nanotube nanocomposites with controlled morphology and increased thermal conductivity were developed. Polymer–graphene and polymer–graphite based nanocomposites have demonstrated excellent water resistance properties [77] used in food, pharmaceutical, and anticorrosion coatings in the packaging industry. The use of carbon nanotubes with a diameter of 40–50 nm and 200–300 nm as a filler significantly improves the performance of the material [78].

The research paper [2] studied AlSi_{10}Mg alloy (Table 1) containing silicon (Si), where (as a result of the study) it was found that the laser power and the material processing speed had a significant effect on the porosity volume, while the laser beam diameter and the particle melting rate were not high. In the work, the level of porosity (Table 2) was established mathematically during the laser selective melting (SLM) processing of AlSi_{10}Mg alloys. In addition, to predict the correlation, the following methods were used in the work: response surface methodology (RSM), artificial neural network (ANN), fuzzy logic (FL), and adaptive-network-based fuzzy inference system (ANFIS). This research is important for the development of future 3D printing (SLM) technology.

Silica (SiO_{2}) nanoparticles modified with aminobutyric acid (C_{4}H_{9}NO_{2}) increase the strength of the nylon-based composite by improving interfacial adhesion between the filler and the polymer matrix. The maxi-

Table 1. AlSi_{10}Mg alloy chemical composition (wt.%) [2]

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<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Sn</th>
<th>Ti</th>
<th>Al</th>
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<tr>
<td></td>
<td>9.92</td>
<td>0.137</td>
<td>0.004</td>
<td>0.291</td>
<td>0.04</td>
<td>0.01</td>
<td>0.004</td>
<td>0.003</td>
<td>0.006</td>
<td>Bal</td>
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Table 2. AlSi_{10}Mg alloy porosity calculations for SLM processing [2]

<table>
<thead>
<tr>
<th>Run</th>
<th>Laser power, W</th>
<th>Scan speed, mm/s</th>
<th>Hatch spacing, a_1</th>
<th>Island size, mm</th>
<th>Porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>175</td>
<td>1025</td>
<td>0.65</td>
<td>6.5</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>173</td>
<td>1025</td>
<td>0.65</td>
<td>6.5</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Modern Fillers of Metal and Polymer Matrices

The maximum increase in the strength of the composite is observed when adding 5 wt.% filler [79]. The physical value ‘Young’s modulus’ (modulus of normal elasticity) indicates a linear increase in resistance to stretching, compression during elastic deformation with an increase in the silica content (up to 40 wt.%), and also demonstrates a weak dependence on the particle size of the composite filler, namely, 200–450 nm and 1–2 µm [80].

It was found that the antimicrobial activity of nanoparticles prevents the growth of pathogenic microorganisms on the surface of composites [81]. High efficiency has been shown, when using the process of automated and modern food packaging using 3D technology [82, 83]. Authors of Ref. [84] developed a nanocomposite based on nanofibre containing silver (Ag) coated with epoxy resin and silicon dioxide (SiO₂) for packaging foodstuffs and electronics.

As follows from the last works, the size (micro-, nanofiller or their mixture) and the type of filler (chemical composition and structure of the filler) for the carrier matrix will depend on the functional purpose of the composite. The purpose of such composites can be a wide range of composites with improved mechanical, thermal, non-combustible, dielectric, heat-conducting, antimicrobial properties. To increase the quality and extend the safe storage time of food products, it is promising and expedient to use nanostructured fillers that can prevent the penetration of microorganisms and bacteria into composite packaging.

A wide choice of nanofillers with a huge variety of structures/properties opens up even more prospects for the use of leading nanocomposites [85]. When considering fillers as oxides of transition metals WO₃, TiO₂, Nb₂O₅, V₂O₅, MoO₃, one can observe the electrochromic effect in the polymer composites, that is, there is a reaction of the material to electric current or light with a change in optical permeability (the degree of transparency of the material changes). Where tungsten oxide (WO₃) is most effective and in the polymer matrix, it gives flexibility to products and facilitates their manufacture, it can change the colour of glass for windows, sunglasses, etc. [86, 87].

The leading polymers include polyaniline (PANI), polypyrrole (PPy), polyacetylene (PAc), polythiophene (PTh), and their derivatives (Fig. 1).

At the same time, there is a fundamentally different type of polymer nanocomposites, which become electrically conductive when a poly-

Fig. 1. Structural formulas of polyaniline (a), polypyrrole (b), polyacetylene (c), and polythiophene (d) [89]
mer (carrier matrix), *i.e.*, a conductor or dielectric, is combined with a nanofiller, *i.e.*, a conductor or dielectric. Such nanocomposites are widely used due to the synergistic effects arising from the combination of the carrier matrix and filler [88].

There are works (see, *e.g.*, Ref. [90]), where leading polymers were converted into nanostructures that became nanofillers, based on which the insulating materials were created. This approach to the source materials allows you to create new composites, and allows you to change the properties and purpose of the source materials. This made it possible to form a separate group of leading nanocomposites [90]. At the same time, dielectric or semiconductor nanostructures can be coated with electrically conductive polymers to fabricate leading hybrid composites [91]. Also in Ref. [91], there are studies where hybrid composites have been used to fabricate more complex polymer nanocomposites, with already improved compatibility between the matrix and nanofiller.

The use of metals with ferromagnetic properties, namely the transition elements Fe, Co, and Ni (3D metals) and the rare earth metals Gd, Tb, Dy, Ho, and Er, make it possible to impart magnetization to the composite without an external magnetic field. In addition, this effect remains when oxides of such metals are used, since ferrum oxide (Fe₂O₃) upon introduction increased the magnetic and catalytic properties of traditional adsorbents, after which their recycling becomes possible and they are more effective nanoadsorbents of a new generation [91].

Biobased nanocomposites were developed from epoxidized soybean oil, bisphenol diglycidyl ether A-(DGEBA), and organically modified montmorillonite (MMT) [92–93]. When soy-based epoxy resin (30/70 wt.%) was mixed with different organophilic fillers with different content of montmorillonite clay (bentonite): 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.%, where the tensile strength of such composites increased by 2%, 7%, 12.6% and 23%, 3%, respectively. The maximum increase in the mechanical properties of bionanocomposites was recorded at a filler content of 25%. The authors attribute the improvement in both strength and impact strength of the studied materials to the plasticizing effect of long aliphatic chains in the soy-based epoxy–polymer matrix and the strengthening effect of the clay nanolayer in the composite.

Today it is known [94–98] that the mechanical properties of polymer composites filled with nanocellulose are improved by the action of cellulose nanomaterials due to the high specific surface area and interfacial interaction with the polymer matrix, but at a low filler content and with its uniform distribution in the matrices. To improve the mechanical properties of nanocomposites, it is necessary to choose the optimal ratio of phases, their content, and the required dispersion. In addition, it is necessary to ensure the minimum agglomeration of cellulose, since this causes a huge amount of entanglement in the structure.
of the nanocomposite and contributes to local stress concentration as a result of mechanical loading, which can subsequently cause destruction of the composites. The improvement of the mechanical properties of composites with nanocellulose filler occurs due to strong internal and intermolecular hydrogen bonds with the polymer matrix, which occurs due to the high values of the surface area and the aspect ratio of nanocellulose. Chitosan and nanocellulose composites made using lactic acid (C₃H₆O₃) have almost 50% better mechanical properties than nanocomposites obtained using acetic acid (CH₃COOH) [99]. The nanocomposite made from a mixture of a suspension of latex and nanocellulose shows a significant improvement in the mechanical properties of the content of 6% nanocellulose due to hydrogen bonding.

The works [100–102] studied composites based on polylactic acid (PLA, (C₃H₄O₂)ₙ), which is biocompatible with the human body. Studies have found that nanocomposites have enhanced mechanical, thermal and impact properties.

Authors of Ref. [103] studied composites based on polylactic acid filled with cellulose fibre, where the content was as follow: 5 wt.%, 10 wt.% and 20 wt.%, which were treated with an anionic surfactant to improve the dispersion of cellulose in the matrix. The results of the experiments showed that increasing the surfactant in the city led to an improvement in the dispersion of the filler, but worsened the properties of the PLA. The results of mechanical tests demonstrated the maximum modulus of elasticity for a composite of 5 wt.% of cellulose fibres, and with increasing surfactant content, the elongation tensile strength of the tested nanocomposites was higher than that of their non-reinforced counterparts. The authors explain the change in the mechanical properties of the composite by the poor interaction of cellulose fibres with the matrix, which is directly related to the nature of the fibre and the type of mechanical and chemical treatment.

Synthetic polymers derived from petrochemical resources due to their exceptional properties of gas and water barriers and economic efficiency are widely used for packaging a variety of products. The authors of Refs. [104–107] point to the use of polyamide, epoxy resin, polyethylene, and other polymers as polymer matrices for the manufacture of packaging composites.

In addition, highly efficient packaging materials were obtained based on synthetic and biodegradable polymers using the following fillers: carbon nanotubes [108, 109], graphene [110, 111], graphene oxide [112], nanoclay [113], and nonorganic nanostructures. Silver (Ag) [116], gold (Au), titanium oxide (TiO₂), and zinc oxide (ZnO) [117, 118], as well as calcium carbonate (CaCO₃) [119] nanoparticles made it possible to significantly increase the mechanical, thermal, electrical, and other characteristics of nanocomposites Modified nanofillers are used to im-
part desired functional properties to packaging materials [120–122]. Thus, polymer nanocomposites have improved characteristics necessary for their use as packaging materials: impermeability to oxygen (O₂) and moisture (H₂O), solvent resistance, thermal stability, biological and antimicrobial properties, incombustibility, and mechanical strength.

A promising use of nanocomposites in photovoltaic devices is in organic solar cells (or organic photovoltaic (OPV) devices), namely, devices, which convert solar energy, such as visible light and ultraviolet, into electrical energy using the photovoltaic effect. In such devices, organic photoactive materials [123] generate photocurrents. On the other hand, inorganic photovoltaic cells, in contrast to silicon solar cells, are lighter, more flexible, and thinner, may have a larger area, may have a low cost, and a high optical absorption coefficient. There are various types of organic photoactive materials: the polymers-based solar cells are among them [124–126].

Based on the polymer–cellulose nanocomposite material, a humidity and temperature sensor was developed and created [127]. To produce such a nanocomposite material, cellulose was obtained from cotton pulp using a solution of lithium chloride (LiCl) and N,N-dimethylacetamide. Nanosize polypyrrole was used as the second component of the nanocomposite. Nanosize polypyrrole was deposited on the surface of cellulose, and its effect on the cellulose membrane was studied using atomic force microscopy. Nanosize polypyrrole was deposited on the surface of cellulose, and its effect on the cellulose membrane was studied using atomic force microscopy. The authors mainly focused on the sensitivity of the material to moisture rather than on the structural integrity of the nanocomposite material. However, the analysis showed that the nanolayer of polypyrrole was successfully deposited on the surface of the cellulose. Since the material was not structurally analysed, it was not possible to find out what served as the reinforcement of the nanocomposite: cellulose or polypyrrole itself.

4. Prospects for the Use of Different Fillers for Composites

Analysing the research of scientists in the field of composite materials over the past three decades, one can single out the main thing that an important role is played by the modifying effect and content of various nanofillers on the mechanical and physical properties of nanocomposites. If we try to isolate the main types of nanofillers, then, they can be divided into 2D and 3D fillers, where three-dimensional fillers will be divided into crystalline and reinforcing structures (Table 3).

Two-dimensional fillers include graphene and graphene-like structures, as well as all sheet structures of the phyllosilicate type. Graphene (Fig. 2) [128] is currently the strongest and super material even known
in the world of materials science. A large surface area, excellent thermal conductivity, high electron mobility and electron transport properties, high Young’s modulus, and light transmission dependent on the number of layers (Fig. 2, b) as well as type and spatial configurations of possible point (impurities, vacancies) and line (grain boundaries, atomic terraces and steps, nanoripples or wrinkles) defects [129–166] characterize the graphene sheets. In the work [167], the authors reviewed polymer composites based on graphene and graphene-like nanofillers, which described their properties (mechanical, thermal, electrical, and medical) and their prospects for application, and also considered further developments in the field of polymer composites based on graphene with a description of their properties, synthesis and processing.

Sheet nanofillers in polymer nanocomposites are more often found in the form of layered silicates belonging to the structural class of phyllosilicates. The layered silicates montmorillonite, hectorittasaponite, etc. are commonly used [168–170]. The structure of such materials is shown in Fig. 3.

Authors of Ref. [171] showed that various layered compounds, such as BN, WS₂, MoS₂, MoSe₂, TaSe₂, NbSe₂, MoTe₂, NiTe₂, and Bi₂Te₃, can be easily dispersed in common solvents. From which films-nanoplates

<table>
<thead>
<tr>
<th>Table 3. Modern types of nanofillers for composites</th>
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<tr>
<td>Types of nanofillers for composites</td>
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<tr>
<td>Two-dimensional fillers</td>
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<tr>
<td>• Philosilicates</td>
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<tr>
<td>• Graphene and graphene layers (graphite, C)</td>
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<tr>
<td>• Boron nitride (BN)</td>
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<td>• Silicene (Si)</td>
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<tr>
<td>• Phosphorene (P)</td>
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<tr>
<td>• Disulfides (WS₂, MoS₂, TiS₂, VS₂, CrS₂, ZrS₂, NbS₂, PdS₂, HfS₂, TaS₂, PtS₂)</td>
</tr>
<tr>
<td>• Diselenides (MoSe₂, TaSe₂, NbSe₂, TiSe₂, VSe₂, CrSe₂, ZrSe₂, PdSe₂, HfSe₂, WSe₂, PtSe₂)</td>
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<tr>
<td>• Ditellurides (MoTe₂, NiTe₂, VTe₂, CrTe₂, ZrTe₂, NbTe₂, PdTe₂, HfTe₂, TaTe₂, WTe₂, PtTe₂, Bi₂Te₃)</td>
</tr>
<tr>
<td>• Dinitrides (YN₂, ZrN₂, MoN₂, TcN₂)</td>
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<tr>
<td>• Antimonene (antimony (Sb))</td>
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<tr>
<td>Three-dimensional fillers</td>
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<tr>
<td>Crystal structures</td>
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<tr>
<td>• Metal nanopowers or their alloys</td>
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<td>• Oxydimetals</td>
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<td>• Nanoclays</td>
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<td>• Silica nanoparticles (SiO₂)</td>
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<td>Reinforcing structures</td>
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<tr>
<td>• Nanofibres</td>
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<td>• Nanotubes</td>
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<td>• Cellulose</td>
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</table>
can be created, and by mixing them with polymer solutions, polymer nanocomposites are obtained that have improved physical and chemical characteristics compared to a pure polymer. The results of analyses carried out on transmission electron microscopy (TEM) confirm the layered structure of the compounds (Fig. 4).

Carbon nanotubes (CNTs) are one of the most widely used fillers. CNT is a graphene sheet rolled into a tube, where the edges of the graphene sheet are interconnected. CNTs are divided into single-walled
carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). SWCNT has a single-walled structure, while in MWCNT the number of shells is ≥2, where tubular structures are located in each other [171–173], such nanotubes can have open or closed ends (sides) as shown in Fig. 5. CNTs have a hollow structure, where the carbon atoms are linked by a covalent bond. CNTs have fairly unique mechanical and physical properties controlled by their geometry and dimensions. They are characterized by very high values of the elastic modulus and very high strength [172, 173].

The papers [174–177] describe the properties of polymeric hydrophilic and hydrophobic matrices filled with nanocellulose, which are used in biomedical, packaging, electronic, environmental, and other industries. This biomaterial has broad prospects for applications in advanced self-replenishing materials. Nanocellulose is the general name for cellulosic nanomaterials such as bacterial nanocellulose produced by certain bacterial strains, cellulose nanofibres and nanocrystalline cellulose.
lose extracted from lignocellulosic biomass. As noted by the authors [176–178], nanocellulose differs from inorganic fillers in its easy accessibility, biocompatibility, low cost, physical and chemical properties of the surface. Cellulose nanofillers can be considered as environmentally friendly and self-replenishing materials. To achieve significant results, the surface modification of nanomaterials plays an important role, especially when nanocellulose is added to a nonpolar polymer matrix, and the presence of a large number of hydroxyl groups on the surface of such filler opens up many possibilities for its modification.

Espino-Perez et al. [179] used modified hydrophobic nanocrystalline cellulose prepared by solvent-free esterification using carboxylic and phenylacetic acids (\(\text{C}_8\text{H}_8\text{O}_2\)) and hydrocinnamic acid molecules. Carboxyl groups in a carboxylic acid react with hydroxyl groups to form an ester functional. The hydrophobicity of nanocellulose can be improved by the presence of phenolic groups attached by phenylacetic acid to the surfaces of the nanofiller. Authors of Ref. [180] modified the nanocellulose using a long hydrophobic alkyl chain through bimolecular nucleophilic substitution to improve the dispersion of nanofillers in the polymer carrier matrix.

The authors of Ref. [181] note that the use of composites with biofillers, the so-called ‘green’ nanocomposites, has recently attracted increased interest. Polymers are ‘green’, if they can be obtained from natural sources (starch, lignin, cellulose acetate, polylactic acid, polyhydroxyaconoates, polyhydroxy butyrate, etc.) and some synthetic sources (aliphatic and aromatic polyesters, polyvinyl alcohol, modified polyolefins, etc.). Such materials are classified as biopolymers with a wide range of uses [181–184].

They are used in the automotive industry, construction, to create packaging and medical materials. ‘Green’ nanocomposites, created by a combination of natural self-replenishing fillers and organic polymers, have unique properties. Plant fibres are suitable as fillers in polymers due to
their relatively high strength, stiffness, low cost, and low CO₂ emissions into the environment during their processing or disposal. In addition, unlike other reinforcing materials, they are renewable annually and can be recycled or biodegradable without harming the environment [181–183].

Authors of Ref. [185] developed nanocomposites based on polylactic acid (PLA) with a compatibilizer and cellulose fibres uniformly dispersed in an organic solvent. Polyethylene glycol (PEG) was added to the matrix as a component to improve the interfacial bond/adhesion between the matrix and fibres (filler). Composites were obtained by mixing the components using N,N-dimethylacetamide. The created composite based on cellulose nanofibres made it possible to increase the tensile strength and relative elongation by 28.2% and 25%, respectively, compared to pure PLA. The authors of the work focus on the poor interfacial bond between cellulose nanofibres and the PLA carrier matrix and argue that PEG coats the surface of cellulose nanofibres and acts not only as a PLA plasticizer to increase its relative elongation, but also as a compatibilizer between hydrophobic PLA and hydrophilic nanofibre cellulose. It was also shown in Ref. [185] that PEG prevents the aggregation of nanofibres, due to which cellulose nanofibres are uniformly dispersed in the PLA matrix, forming an ordered structure. The results of the FT-IR analysis suggest that PEG improved intermolecular interaction based on the existence of intermolecular hydrogen bonding between the nanofibres and PLA. In this work, the studies were carried out using the atomic force microscope (AFM), where microphotographs of cellulose nanofibrils were obtained, and scanned electron microscope (SEM), where we can see the fracture surfaces of PLA/cellulose and PLA/cellulose/PEG nanofibrils (Fig. 6).

A biodegradable epoxy nanocomposite can be made by adding nanocellulose to an epoxy matrix [186]. Such high nanocellulose content composite may be more environmentally friendly than a commercially available biopolymer such as pure polylactide. As a rule, the biodegradation of an epoxy nanocomposite begins with the matrix filler (nanocellulose). When microorganisms interact with cellulose, holes can appear in composites of this class, which subsequently increase the specific surface area of the material and accelerate the biodegradation and destruction of the rest of the composite. Each unit of cellulose has three hydroxyl groups (if they are not occupied by hydrogen bonds), which are potential entry points for microorganisms.

As evidenced in Ref. [186], nanocrystalline cellulose containing a hydrogel decomposes somewhat faster. This is due to the presence of micropores formed by the hydrogel, which did not interact with the nanocrystal. The swelling coefficient of a nanocomposite hydrogel decreases with an increase in the size of the nanocrystal due to the stronger interaction of the nanocrystal through hydrogen bonding in gels.
Acrylic nanocellulose in nanocomposite films retains good transparency when prepared in situ miniemulsion polymerization technology using a binder that improves dispersion and prevents nanocellulose aggregation during the polymerization process.

5. Combined or Hybrid Nanocomposites

Carbon nanofillers, such as carbon nanotubes, graphene, and their hybrid graphene-carbon nanotubes (GCNTs), due to their properties, play an important role in a wide range of applications [187, 188]. The properties of graphene and CNTs were not fully realized in nanocomposites due to CNTs agglomeration and graphene sticking during processing,
which led to deterioration in the final properties of nanocomposites. To avoid such drawbacks, graphene as two-dimensional (2D) fillers and carbon nanotubes as three-dimensional (3D) fillers have been used to make hybrid nanofillers. GCNTs are excellent combined nanofiller, which has three-dimensional interconnected hierarchical structures, where the physicochemical properties of the composite based on them have significantly improved characteristics over analogues. The nanofiller GCNTs has opened up new ways of researching the production of advanced materials of a new generation.

Epoxy resin (ER) composites with graphene have a significantly higher thermal conductivity ($q$) and are used as components of electronic devices, since they effectively dissipate heat. However, the presence of thermal resistance at the matrix–filler interface, which limits a further increase in the $q$ value. The authors of Refs. [188, 190] reported on a framework made of graphene cross-linked with siloxane and exfoliation of a graphene oxide film followed by self-polymerization of silanol inside graphene. The siloxane molecular structure not only cross-links adjacent graphene sheets, but also forms chemical bonds with the epoxy matrix, resulting in a significant reduction in interball and interfacial thermal resistance. Composite ER/siloxane containing 20.2 wt.% graphene exhibits a $q$-factor of $54.2 \text{ W m}^{-1}\cdot\text{K}^{-1}$, which is about two times higher than that of an epoxy-graphene resin composite without the addition of siloxane, and 270 times higher than that of an unfilled epoxy resin.

The 2D layered black phosphorus has shown great potential in electronics and optoelectronics due to its adjustable band gap and high carrier mobility. However, the usefulness of the unique 2D structure and reactivity of black phosphorus remains underestimated in the field of energy materials. In Ref. [179], using the sol-gel process, where a sol is obtained with its subsequent transformation into a gel, black phosphorus nanosheets coated with graphene oxide aerogel were obtained (Fig. 7), which makes it possible to predict the possibility of using black phosphorus (or its quasi-2D analogue, i.e., phosphorene [191–193]) in catalytic decomposition mineral.

The heat transfer process in silicone composites with graphene fillers (including lateral ones [194–196]) of different dimensions was studied in Refs. [189, 190, 194] without the use of a hardener. Graphene fillers consist of multilayer graphene flakes with sizes from 400 nm to 1200 nm and the number of layers from one to $\approx 100$. As found, in the studied range of transverse filler sizes, the thermal conductivity of composites increases with an increase in the size of graphene sheets. The difference in thermal properties may be related to the phonon mean free path in graphene, which is estimated to be around 800 nm at room temperature. The thermal resistance of composites with graphene fillers with transverse dimensions above 1200 nm is also lower than that of
composites with graphene fillers with transverse dimensions of 400 nm. The effect of filler content and size on the thermal conductivity of composites was explained in terms of the Kanari model [197]. The results obtained are important for selecting the optimal parameters of layered graphene-like or sheet structures in the form of composite fillers intended for use in various materials for heat removal from electronics.

Interfacial mechanical properties between graphene and matrix play a key role in the properties of nanocomposites. In a polymer matrix, attaching polymer molecular chains to graphene can improve the dispersion of graphene in the polymer matrix and change the mechanical interfacial properties between graphene and the polymer matrix. Using molecular dynamics simulations, the interfacial mechanical properties between graphene, functional polymer molecular chains, and a polyethylene matrix were studied in Refs. [198, 199]. The influence of the number of fixed chains and their length between the phase mechanical properties is analysed. The results of modelling studies have shown that anchoring short polyethylene molecular chains to graphene can significantly improve the interfacial shear strength and fracture toughness in functionalized nanocomposites.

**Biodegradable composites.** Given the rapid growth of the world’s population, the disposal of municipal solid waste is increasing and affecting the ecological situation of the planet as a whole. One of the main problems with most synthetic polymers derived from petroleum-based products is their inability to biodegrade, resulting in their accumulation over time. Biodegradable plastic can be a good alternative for industrial and public use. It is less harmful to the environment, therefore, does not contribute to the accumulation of solid plastic waste during disposal. The idea is that enzymes will degrade biodegradable plastics released into the environment, and non-enzymatic processes such as hydrolysis [200] can break down their long polymer chains. The biodegradability of plastics depends on the feedstock and chemical composition, the basic structure of polymeric materials, and the environment in which they are planned to be disposed. A non-degradable polymer can (to a certain extent) be decomposed by fillers such as cellulose nanoparticles.

The development of composites based on biodegradable polymer matrices and fillers is today one of the hot topics in the field of creating new materials that do not harm the planet and do not pollute the environment.

### 6. Summary and Conclusions

The paper describes the main achievements of the 20th century in the field of creating nanocomposites, where metals and polymers are the carrier matrix for nanofillers. The properties and applications of materials with
modern micro- and nanofillers have a wide range of applications, which are partially described in the proposed work. Such nanocomposites will stimulate further research in the field of nanotechnology, namely, the development of syntheses of new nanomaterials and the creation of new nanocomposites based on them for their promising applications.

Summarising the obtained results, we can underline the findings following below:

- the main types of nanofillers have been identified;
- the main advantages of creating modern composites are given;
- characteristics of the dependence of the parameters of nanocomposites are given;
- it has been established that fillers make it possible to control the structural state of the melt and help form additional crystallization centres;
- it has been established that the characteristics of the filler surface have a significant effect on the mechanical properties of nanocomposites;
- it has been established that carbon fillers can be the strongest graphitizer, which is important for the iron industry;
- it has been established that the mechanical and physical properties of nanocomposites depend on the type of nanofiller, the degree of dispersion, and its quantitative content;
- it has been established that nanostructured fillers are promising for use in composites;
- in view of this, it can be concluded that in order to improve the mechanical properties of composites, the following acts are needed:
  - select the optimal phase ratio;
  - to choose dispersion for nano- (1–100 nm) and microfiller (100–500 nm);
  - uniform distribution of the filler in the matrix;
  - eliminate or minimize the agglomeration of the filler when creating a composite;
  - before using fillers in composites, take into account the porosity of the system;
  - take into account the modifying effect of the filler on the matrix;
  - modification of fillers to improve adhesive properties;
  - in case of using a combined filler (several fillers), take into account their compatibility in the composite.

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Ол. Д. Золотаренко¹,², Н.В. Сігарьова¹, М.І. Терець¹,
Н.А. Швачко²,³, Н.А. Гаврилюк¹, Д.Л. Старокадомський¹,
С.В. Шульга¹, О.В. Хора¹, Ан.Д. Золотаренко¹,², Д.В. Щур²,⁴,
М.Т. Габдуллин⁵, Д.В. Ісмаїлов⁶,⁷, О.П. Рудакова¹,², І.В. Загорулько⁸
¹ Інститут хімії поверхні ім. О.О. Чуйка НАН України,
вул. Генерала Наумова, 17, 03164 Київ, Україна
² Інститут проблем матеріалознавства ім. І.М. Францевича НАН України,
вул. Омелина Пріцаєка, 3, 03142 Київ, Україна
³ Київський національний університет будівництва і архітектури,
просп. Повітрофлотський, 31, 03037 Київ, Україна
⁴ Інститут прикладної фізики НАН України,
вул. Петровавлівська, 58, 40000 Суми, Україна
⁵ Казахстансько-британський технічний університет,
вул. Толе бі, 59, 050040 Алмати, Казахстан
⁶ Казахський національний університет ім. Аль-Фарабі,
просп. Аль-Фарабі, 71, 050040 Алмати, Казахстан
⁷ НАТ «Казахський національний дослідницький технічний університет імені К.І. Сатбаєва»,
вул. Сатбаяева, 22, 050013 Алмати, Казахстан
⁸ Інститут металофізики ім. Г.В. Курдюмова НАН України,
бульв. Академіка Вернадського, 36, 03142 Київ, Україна

СУЧАСНІ НАПОВНЮВАЧІ МЕТАЛЕВИХ І ПОЛІМЕРНИХ МАТРИЦЬ
Описано сучасні наповнювачі металевих і полімерних матриць, їхні властивості
та галузі застосування. Обговорюються основні параметри наповнювачів, їхні
переваги та недоліки, результати досліджень та експериментів, що може бути
корисним для вчених та інженерів, які працюють у хемічних і матеріалознавчих
галузях, займаючись розробкою нових перспективних матеріалів. Оглянуто різ­
ні матеріали, які використовуються в якості наповнювачів металевих і полімер­
них матриць. Для створення композитів нового покоління з поліпшеними влас­
tивостями використовуються наноструктурні матеріали, такі як графен, фулле­
рени, нанотрубки, нанопорошки металів та їхніх стопів. Вуглецеві наповнювачі
можуть бути найсильнішим графітізатором, що важливо для чорної металургії.
Нанонаповнювачі мають ультрадисперсні розміри та високі значення питомої
поверхні, що уможливлює значне змінення фізико-хемічних і функціональних
характеристик матриці. Зазначається, що використання наповнювачів уможливив­
лює контроль структурного складу розтопу та сприяє формуванню додаткових
центрів кристалізації. Це, в свою чергу, може значно впливати на властивості
матеріалу, такі як механічна міцність, термостійкість та інші.

Ключові слова: несуча матриця, нанокомпозити, двовимірні (2D) та тривимірні
(3D) наповнювачі, метали, оксиди металів, наноструктури, кристалічні структури.