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MATERIALS SCIENCE AND CORROSION PROTECTION

PREPARATION OF NANO-MODIFIED REACTOPLAST POLYMER COMPOSITES. PART 1. FEATURES OF USED NANOTECHNOLOGIES AND POTENTIAL APPLICATION AREAS OF NANOCOMPOSITES (A REVIEW)

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The prospects for development and practical application of nanotechnology, including for production of nano-modified polymer composites, were analyzed in terms of the achievements of modern science and technology. Characteristic features of nanofillers and possible future applications of carbon nanotubes were studied. The directions in which polymer nanocomposite production technology is developing, including economic aspects of implementing their formation nanotechnologies, were described.
Keywords: *reactoplast, polymer, technology, nanofiller, carbon, composite, construction, modification.*

The present series of five review articles focuses on various aspects of the preparation, use, and functional properties of nano-modified (NM) reactoplast polymer composites (PC) that are used in many areas of science and technology.

Part 1 analyzes the prospects for development and practical implementation of nanotechnologies, including the production of NMPC. *Part 2* reviews patents on effective technical means for forming nanocomposites with an accent on ultrasound (US) processing methods. *Part 3* analyzes methods for dispersing carbon nanotubes (CNT) in organic solvents and liquid polymeric media. *Part 4* analyzes the efficiency of modifying epoxide oligomer CNT. *Part 5* analyzes the advantages of using NM construction carboplasts over traditional carboplasts.

The global community is interested in nanotechnologies for at least three reasons.

1. The use of nanotechnology methods can produce fundamentally new devices and materials with characteristics significantly superior to the current level for analogous devices and materials.

2. Nanotechnology is a global interdisciplinary thrust that unites specialists from various science areas, e.g., physics, chemistry, biology, basic medicine, materials science, mechanical engineering, etc.

3. Several gaps in fundamental and applied knowledge were identified during the solution of actual nanotechnology science problems. This allowed the attention of the science and engineering community to be concentrated on this area.

Methods for synthesizing and controlling nanotechnology items for various applications, including the production technology for NM thermoreactive (reactoplast) PC, i.e., NMPC, are constantly being revised and improved. Therefore, a promising direction in modern science and technology is the production of PC based on polymers filled with carbon nanomaterials (CNM) such as CNT, fibrils, nanosheets, nanowires, etc. [1–4].

Characteristic Features of Nanofillers. According to commonly accepted definitions, nano-sized objects include nanoparticles (1–100 nm), clusters (1 nm), molecules (0.5 nm), colloidal particles (3–100 nm), and viruses (100 nm) [1].

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TABLE 1

Material	Young's modulus E, TPa	Tensile strength σ_t, GPa	Fracture elongation ε_f, %
UCNT	~ 1 (1–5)	13–53	16
Chair-type UCNT	0.94	126.2	23.1
Zigzag-type UCNT	0.94	94.5	15–17
Chiral UCNT	0.92	–	–
MCNT	0.8–0.9	150	–
Corrosion-resistant steel	~0.2	~0.65–1	15–50
Kevlar (fibrous polyamide material)	~0.15	~3.5	~2

According to numerous research results [1–8], particles less than 100 nm in size impart to materials formed from them new properties that are not typical of analogous traditional micro- and macromaterials.

Nano-sized objects exhibit new physical and chemical properties as a result of so-called size effects. The properties of nanoparticles and nanostructures are determined not by classical laws of Newtonian physics but by quantum-mechanical statistical laws of the nanocosm. Nanostructured materials (compared with microstructured materials) exhibit new properties and unusual characteristics because a so-called characteristic (or critical) length of the nanomaterial structural unit is associated with each property.

CNT are broadly applied nanoparticles. A CNT particle consists of one or several layers, each of which is a hexagonal graphite network based on hexagons of C atoms situated at the vertices. The upper ends of CNT are coated with hemispheres (structures similar to halves of fullerene molecules). CNT can be unilamellar (UCNT) and multilamellar (MCNT), straight and spiral. The properties of CNT depend directly on their geometry [1–4].

Three varieties of UCNT differ in the positioning of the hexagon side surface relative to the nanotube longitudinal axis, i.e., the achiral chair type, the achiral zigzag type, and the chiral (spiral) nanotubes. UCNT with the chair, zigzag, and spiral (chiral) structures are the most common.

The tube structure affects its chemical, electronic, and mechanical properties. In particular, whether or not a CNT is a conductor or semiconductor depends on its twist angle. UCNT contain fewer defects than other types of nanotubes. Table 1 presents the physicomechanical properties of UCNT and other materials (for comparison) [1].

The Young's modulus E of UCNT is greater than ~1 TPa. The tensile strength of CNT is approximately two orders of magnitude greater than the corresponding value of all known materials (metals). Furthermore, UCNT with high chemical stability and exceedingly high mechanical strength and hardness also retain the high thermophysical characteristics of carbon (thermal conductivity).

Table 2 presents the characteristics of CNM brand Taunit-MD [5].

Possible Applications of CNT. *Mechanical (chemical):* new fullerene technologies for synthesizing diamonds and diamond-like ultra-high hardness compounds (ultrastrong threads), NMPC (new classes of polymers with given mechanical, optical, electrical, and magnetic properties including for data recording and storage), nanobalances, new classes of antifriction coatings and lubricants including those based on fluorine-containing fullerene compounds, and new types of fuels and fuel additives (fuel cells).

Generators and engines: threads of paraffin and CNT can absorb thermal and light energy and convert it into mechanical energy, support greater than a million twist/untwist cycles at a rate of 12500 rpm or 1200 compression/decompression cycles per minute without visible signs of wear, and be used to produce energy from solar radiation [1–3].

Microelectronics: new classes of superconductors, semiconductors, magnets, ferroelectrics (transistors, nanowires, transparent conducting surfaces), the computer industry (microprocessors containing up to a billion transistors, memory chips of capacity up to 10 Gb).

Neurocomputer developments: formation of connections between biological neurons and electronic devices.

TABLE 2

Parameter	Taunit-MD
Outer diameter, nm	8–15
Inner diameter, nm	4–8
Length, μm	2 and greater
Total additive volume, % (after purification)	up to 5 (up to 1)
Bulk density, g/cm^3	0.03–0.05
Specific geometric surface area, m^2/g	300–320 and greater
Thermal stability, °C	up to 600

Capillary applications: capsules for active molecules, storage of metals and gases, nanopipettes.

Optical applications: new classes of nonlinear optical materials, ultrafine displays, LEDs.

Medicine (under active development): new classes of compounds for pharmacology and medicine including antiviral and neurotropic drugs, sorbents for hemosorption, drug delivery to strictly determined *in vivo* targets, creation of artificial musculature.

Ecology: decontamination of water from heavy metals.

Environmental monitoring: UCNT (individual, in large assemblies or networks), miniature sensors with ultrahigh sensitivity for detection of gaseous or dissolved molecules (new types of catalysts and sensors for determining the composition of liquid and gaseous media, capsules for safe storage of radioactive wastes).

Furthermore, sheets of CNT can be used as flat transparent speakers.

Features of Polymer Nanocomposite Production Technology. Traditional PC contain micron-sized reinforcing fillers (e.g., the diameters of mineral and carbon fibers are 7–15 μm). NMPC contain filler particles of sizes <100 nm.

Compositions with nano-sized components of various chemical natures, i.e., carbon, inorganic (metallic, ceramic), and organic, were developed and are being used. The principal material for doping NMPC is still carbon, despite the broad spectrum of utilized nano-sized components. Therefore, higher-order carbon nanostructures are used as nano-sized fillers for NMPC.

The NMPC production technology depends on the type of nanoparticles incorporated into the polymer. The specific properties of the nanoparticles cause definite complications upon ensconcing them in the polymer matrix. The high surface energy of CNT causes them to aggregate (coalesce). CNT can lose their unique properties if they react chemically with other substances (the polymer matrix).

NMPC are difficult to prepare using traditional technologies for filling polymers. Therefore, NMPC are produced in practice by incorporating nano-sized fillers with thermoplast or thermoreactive binders that act as a matrix in the NMPC. The degraded rheological properties of such composites (increased viscosity of a solution or melt) are fully compensated by the improved functional properties with a much lower bulk content in the composite of nanosized filler (compared with traditional PC).

Conditioning polymers with nano-sized fillers (with contents in the composite up to 1–5 vol.%) can increase the elastic and strength properties, the deformation thermal stability, and the friction stability and can stabilize the item dimensions. Materials with the required electrical, magnetic, and optical properties and with controlled diffusion rates of gases and liquids can be fabricated. Fillers are used to develop thixotropic lacs, enamels, glues, and polymeric films and coatings with high hardness, wear resistance, electrical conductivity, optical transparency, and band-gap properties and with the capability for self-cleaning (nanostructured hydrophobic coatings based on dendrimers with a lotus-effect). NMPC are used to prepare polyelectrolyte membranes with reduced swelling, NM hydrophilic and hydrophobic coatings (including protective coatings for electronics and sensors) and are promising for developing a new generation of construction and specialty materials.

A technical feature of NMPC production must be emphasized. A nanosuspension for subsequent preparation of a nanocomposite based on it is produced by adding CNT to a polymeric binder. The optimum concentration and even distribution of the CNT in the binder determine how effective the final strengthening of the NMPC is. De-aggregation and further dispersion of nanoparticles in liquid polymeric media are some of the main technical problems in preparing NMPC because of the specifics of the used nanoparticles (tendency to aggregate).

Thus, NMPC production technology depends on the type of particle incorporated into the polymer. NMPC are difficult to prepare by the traditional methods used for composites. Various solutions and surfactants including in combination with high-frequency ultrasound treatment are used to disperse fullerites (CNT aggregates).

Possible Applications of Nanotechnologies in Chemical and Oil-Gas Equipment. NMPC based on CNT are considered more and more often as promising alternatives to traditional plastics, the physicochemical properties and technical production aspects of which have been studied in detail [7, 8]. Hydrophobic nanocoatings on surfaces of buildings and equipment, e.g., antistatic coatings on fuel pipelines and surface coatings on metal items to make them chemically resistant and water-repellant and to give them anti-friction properties during prolonged operating times, are promising for increasing the efficiency of chemical and oil-gas facilities.

Yet another application of nanotechnologies is the preparation of PC, glues, and sealants to strengthen areas where stresses are concentrated (openings, penetrations, moldings, bevels, etc.) in various supporting constructs; the curing of defects, microcracks, and other imperfections arising during the fabrication of supporting constructs and their operation; the elimination and sealing of gaps in apertures and bolted and riveted connections, etc.

For example, the tensile strength of glues containing CNT (~1%) is 25% greater than that of the initial composition [5, 6]. Carbon nanoparticles in addition to nanodispersed mineral and metal fillers (nanoclays, nanopowders of tungsten, molybdenum, and aluminum) are used in thermo- and reactoplasts to produce NMPC for construction and special applications.

Polymers filled with CNT (1–5 vol.% in the composition) can show qualitative and quantitative advantages for NMPC based on them [5, 6] over the starting materials. These are elastic and strength properties increased by 20–25%, deformation thermal stability, cracking resistance, and stabilized sizes. Incorporation of carbon nanoparticles into epoxide carboplasts increases the shear stress (up to 60%) and tensile strength (up to 190%) because CNT prevent the propagation of microcracks.

Also, nanotechnologies are promising for improving the preparation of various high-strength and corrosion-resistant structural and construction components based on reinforced reactoplast PC, in particular, epoxide carboplasts.

Economic Aspects of Nanotechnology Implementation. The volume of nanocomposites utilized in automobiles, machinery, chemistry, fuel, packing materials, nanoelectronics, etc., is increasing by 18–25% per year according to various estimates. Nanotechnologies are used in various sectors such as biotechnology (9%), data storage devices (15%), semiconductors (18%), optics (2%), electrochemistry (3%), new materials (30%), and NM polymers and nanocomposites (8%) [5, 6].

Because the production of fulleroid-type nanomaterials entails high intrinsic costs, those applications of fulleroids in which industrially meaningful macroeffects can be achieved by using, in the words of A. N. Ponomarev, General Director of the Applied Nanotechnology Science and Technology Center (St. Petersburg, Russia), "homeopathic" doses of nanomaterials are especially interesting [5].

Another approach to reducing the intrinsic cost of forming nanocomposites is to use natural mineral fillers as the nano-sized phase [SiO_2, Al_2O_3, $Al(OH)_3$, silicic acid, $BaSO_4$, etc.]. PC filled up to 10% (usually 2–5 vol.%) with such particles exhibit high elastic and strength properties, deformation thermal stability, and thermal stability and low shrinkage, water absorption, and gas permeability in addition to high fire-resistance [5, 6].

If the problem of applying the results from research on the fundamental properties of CNT could be solved, a broad spectrum of methods for producing cheap CNT in large quantities could be invented. Unfortunately, the broad application of CNT is still impossible. However, properties of CNT such as ultraminiature sizes, high strength and electrical conductivity, high emission characteristics, high chemical stability and porosity, and the ability to bind various chemical radicals provides hope that CNT will be applied effectively and broadly in metrology, electronics and nanoelectronics, chemical engineering, etc. [9–11].

New nanotechnologies developed through research will find broad applications in the production of construction and functional NMPC. The reduction of the mass of such items due to the improvement of their physical and mechanical properties is a crucial direction in industrial resource and energy conservation.

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