NANOCOMPOSITES

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Summary

Nowadays, the industry of nanotechnology develops torrentially. One of the most perspective directions in introduction of nanotechnology into industry is manufacture of composite materials. Nanocomposites are nanomaterials consisting of two or more phases in which at least one phase is presented by nanoscale particles.

The world market of nanocomposites comprises three basic segments, namely, ceramic-, metal-, and polymer-matrix nanocomposites. Most often, polymers act as matrix. Metals and ceramics are used much less often. Nanostructure-based composites have unique properties: high durability and plasticity, high catalytic and magnetic characteristics, selective absorbing ability, tribotechnical properties, thermal fastness and chemical resistance. Such characteristics determine demand for nanocomposites in various industries: shipbuilding, aircraft engineering, chemistry, power engineering, medicine, biology, etc. It is demand for nanocomposites in many industries what promotes further growth of the sector.

It is known that creation of composites is complicated by essential difference of properties between matrix and filler that does not allow using the characteristics of stronger component to the full extent. Since the advent of nanosized fillers, there emerged a possibility of matching physical mechanical properties of the basic composite components – a matrix and a reinforcing filler. Strengthening action of nanoparticles in polymers is related rather with the influence of nanofiller on the structure of adjacent matrix layers: more dense packing of polymer molecules, crystallization and texturing of polymers, formation of other crystal modifications, than with additivity (addition) of mechanical properties of a matrix and a filler under the Hall-Petch law. Specific surface increase of a filler (decrease of diameter of fullerenes

or nanotubes) improves both its interaction with a matrix and properties of a composite as a whole. In this regard, homogeneous distribution of nanoparticles in a matrix is of much importance. Such distribution could be achieved only at very low concentration of nanoparticles (usually not more than 0,5 % by weight). This became possible due to very high specific area of the nanofiller surface which sometimes exceeds 1000 m^2/g depending on nanoparticle type.

The analysis of available information on nanocomposites leads to a conclusion that this research trend has huge prospects. The problems that were considered insoluble recently, now are on the agenda. For example, artificial heart valves are under development from analogy with natural model. Such valves combining advantages of mechanical and biological artificial limbs will have almost unlimited lifetime. These structures will be weaved from a nanofiber (a yarn of long nanotubes) by means of the newest technologies of microknitting manufacture.

With the advent of long carbon nanotubes, creation of heavy-duty ropes which can be used, in particular, in construction of a space elevator that will replace modern power-consuming, not ecofriendly and rather dangerous way of payload delivery into orbit also is predicted.

1. Introduction

1.1. The General Concepts of Composites

Composite materials (composites) are the multicomponent materials consisting, as a rule, of a plastic basis (matrix), reinforced (strengthened) by the fillers of high durability, rigidity etc. Combining of diverse substances leads to creation of a new material with properties qualitatively different from properties of individual components. By means of changing the structure of matrix and filler, their ratio and filler orientation, one receive a wide spectrum of materials with required set of characters. Many composites surpass traditional materials and alloys in respect of mechanical properties; at the same time, they are lighter. Use of composites usually allows both reducing weight of a construction and retaining or improving its mechanical characteristics.

Ability of minor fiber additives to increase considerably durability and viscosity of fragile materials was known since the most ancient times. The Old Testament (the Outcome, Chapter 5) narrates that Ancient Egyptians added straw as filler into bricks in order to increase their durability and to prevent cracking at drying in the hot sun. Many nations had similar technologies. The Incas used plant fibers in ceramics manufacturing, and English builders added a few hair in plaster until recently.

Covers for the Egyptian mummies made of pieces of fabric or papyrus impregnated with resin or glue are another example of Ancient Egyptian composite structures. This material (papier-mache) has been rediscovered only in 18th century (paper pieces were used instead of papyrus) and was popular to the middle of 20th century. Papier-mache was used for manufacturing of toys, advertising dummies, and sometimes even furniture. During the Second World War, this method was used for manufacturing of fuel tanks of planes. Painters sized canvas by special formulations before working, so canvas got quite different properties.

The ability of composites to adapt to the service conditions promotes their rapid development (Figure 1). Modern representatives of composite materials are fiberglasses, carbon fiber reinforced plastics (CFRP), organoplastics, metal composites, carbon-carbon materials and many others.

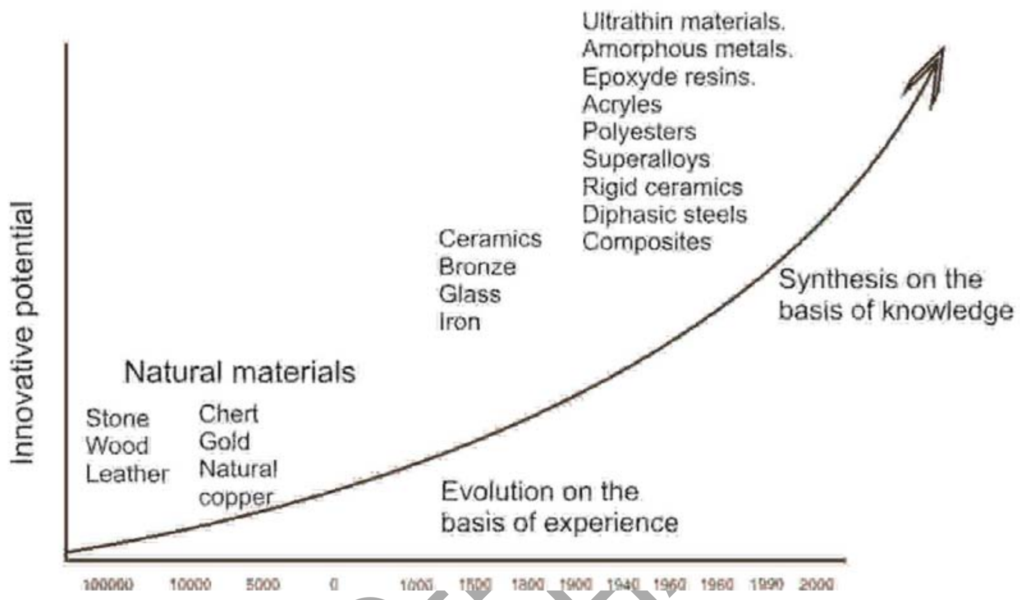

Figure 1. Historical trend of new materials development

1.1.1. Polymeric Composite Materials (PCM)

Composites that comprise polymeric material as a matrix (binder) are one of the most numerous and diverse kinds of materials. Their application in various fields gives considerable economic benefit. For example, use of PCM in manufacturing of space and aviation machinery allows saving the flying machine weight up to 30 %. Accordingly, weight reduction of an artificial satellite in the earth orbit by 1 kg saves more than 1,000 dollars. Air bus A-380 could not be created without the use of CFRP at all.

A number of various substances are used as filler in PCM. The basic groups of PCM are as follows.

(a) *Fiberglasses*: the polymeric composite materials reinforced by glass fibers molded from smelted inorganic glass. Most commonly, a matrix is thermosetting synthetic resins (phenolic, epoxide, polyester, etc.), and thermoplastic polymers (polyamides, polyethylene, polystyrene, etc.). These materials have enough high durability, low heat conductivity, high electro-insulating properties; moreover, they are transparent for radio waves.

(b) *CFRP*: these polymeric composites contain carbon fibers as a filler. Carbon fibers are derived from synthetic and natural fibers on the basis of cellulose, copolymers of acrylonitrile, oil and coal pitches and so on. The fibers are thermally processed, as a rule, in three stages (oxidation – 220 °C, carbonization – 1000–1500 °C, and graphitization – 1800–3000 °C); this leads to the formation of fibers with high carbon content (up to 99,5 % w/w). The carbon fibers obtained have different structure depending on processing mode and raw materials. More often, the same matrixes are used for manufacturing of CFRP and fiberglasses, namely, thermosetting and thermoplastic polymers. The basic advantages of CFRP in comparison with fiberglasses are their low density and higher module of elasticity; CFRP are very light-weighted and, at the same time, strong materials. Carbon fibers and CFPR have almost zero factor of linear expansion. All CFPR are black in color, carry electrical current well, what limits area of their application a little. CFPR are used in aircraft, rocket production, mechanical engineering, space-system engineering, biomedical engineering, prosthetic devices, at manufacturing of light bicycles, ski and other sports equipment.

(c) *Boron fiber reinforced polymers* (BFRP): the composite materials containing boron fibers as a filler; the fibers are introduced in a thermoset polymeric matrix and are presented both in the form of monothreads and in the form of the plaits braided by an auxiliary glass thread or tapes in which boron threads are bound with other threads. Because of the high rigidity of the threads, the resulting material possesses high mechanical properties (boron fibers have the greatest compression strength in comparison with fibers of other materials) and high fastness to aggressive conditions, but its high brittleness complicates processing and imposes restrictions in respect of the form of products made of BFRP. Moreover, the cost of boron fibers is very high in connection with peculiarities of production technology (boron precipitates from chloride on the tungsten support which cost can reach up to 30 % of the fiber cost). Thermal properties of BFRP are determined by thermal stability of a matrix, therefore working temperatures, as a rule, are low.

(d) *Organoplastics*: composites comprising organic synthetic fibers or occasionally natural and artificial fibers in the form of plaits or threads, fabrics, paper, etc., as a filler. In thermosetting organoplastics, epoxide, polyester and phenolic resins, as well as polyimides serve as a matrix, as a rule. The material contains 40–70 % of a filler. The filler content in organoplastics based on thermoplastic polymers, i. e. polyethylene, PVC, polyurethane, etc., varies in wider range – from 2 to 70 %. Organoplastics have low density, they are lighter than fiberglasses and CFRP; relatively high tensile strength; high shock and dynamic resistance, but, at the same time, low compression strength and bending resistance. The orientation of filler macromolecules plays an important role in improvement of mechanical characteristics of the organoplastics. Macromolecules of rigid-chain polymers such as polyparaphenylene terephthalamide (kevlar) are oriented mainly along the cloth axis thus possessing high tensile strength along fibers. The materials reinforced by kevlar are used in production of ballistic armor vests.

(e) *The polymers filled with powders*. More than 10,000 brands of filled polymers are known. The role of fillers consists both in cost reduction and in obtaining materials with special properties. For the first time, manufacture of filled polymer was started by Dr. Baekeland (Leo H. Baekeland, USA) who discovered a way of synthesis of phenol formaldehyde (bakelite) resin in the early 20th century. The first production sample on the basis of this technology was made in 1916; it was the transmission switch knob in *Rolls-Royce*. The filled thermosetting polymers are widely used up to now.

(f) *Textolites:* layered plastics reinforced by fabrics of various fibers. The manufacturing technology of textolites has been developed in 1920th on the basis of phenol formaldehyde resin. In order to obtain textolite plates, fabric cloths were impregnated with resin and further pressed at elevated temperatures. It is difficult to overestimate the role of an early application of textolites – coating for kitchen tables. Main principles of production of textolites remained the same, but now they are formed not only as plates, but also as shaped products. Of course, the range of initial materials had been extended. In textolites, binding agents are represented by wide range of thermoset and thermoplastic polymers; sometimes inorganic binders based on silicates and phosphates are used as well. Fabrics of various fibers – cotton, synthetic, glass, carbon, asbestos, basalt fibers, etc. – are used as fillers. Properties and application of textolites are accordingly diverse.

1.1.2. Metal-matrix Composite Materials

Aluminum, magnesium, nickel, copper, etc., are used as matrix in metal-based composites. A filler is represented by either high-strength fibers or high-melting-point particles of various degree of dispersion that are not dissoluble in the matrix metal.

Properties of dispersion-strengthened metal composites are isotropic, i. e., identical in all directions. Addition of 5-10 % of reinforcing filler (refractory oxides, nitrides, borides, carbides) leads to increase of resistibility of a matrix to loadings. The effect of increase in durability is rather insignificant; however, the increase in thermal stability of a composite in comparison with an initial matrix is valuable. So, introduction of fine powder of thorium oxide or zirconium oxide into heat-resisting chrome-nickel alloy allows increasing temperature at which goods made of this alloy are capable to work long from 1000 °C to 1200 °C. Dispersion-strengthened metal composites are produced by means of introduction of the filler powder into fused metal, or by the methods of powder metallurgy.

Reinforcing of metals by fibers, filamentary crystals, wires considerably raises both durability and heat resistance of a metal. For example, the alloys of Aluminum reinforced by boron fibers can be used at the temperatures up to 450–500 °C instead of 250–300 °C. Oxide, boride, carbide, nitride metal fillers and carbon fibers are used. Because of fragility, ceramic and oxide fibers do not allow plastic deformation of a material that makes considerable technological difficulties at manufacturing of products whereas use of more plastic metal fillers allows reforming. Such composites are produced by means of infiltration of bunches of fibers by metal melts, electrodeposition, blending with metal powder with subsequent baking and so on.

In 1970th, first materials reinforced by filamentary monocrystals ("whiskers") appeared. Filamentary crystals are produced by means of drawing alloy through the dies. "Whiskers" of Aluminum oxide, beryllium oxide, carbides of boron and silicon, Aluminum and silicon nitrides, etc., $0.3–15\times10^{-3}$ m in length and $1–30\times10^{-6}$ m in diameter are used. Reinforcing by "whiskers" allows increasing durability and heat resistance of a material significantly. For example, flow limit of a composite composed of silver containing 24% of "whiskers" of Aluminum oxide is 30 times higher than flow limit of silver and twice as large as flow limit of other composite silver-based materials.

Reinforcing of materials based on tungsten and molybdenum by "whiskers" of Aluminum oxide doubled their durability at a temperature of 1650 °C that allows using these materials for manufacturing of rocket nozzles.

1.1.3. Ceramic-matrix Composite Materials

Reinforcing of ceramic materials by fibers or metal and ceramic disperse particles allows obtaining high-strength composites, however, the assortment of fibers suitable for ceramics reinforcing is limited by properties of an initial material. Metal fibers are used often. Extension strength grows slightly, but thermal-shock resistance increases significantly: the material cracks less at heating, but, in some cases, durability of the material falls. It depends on the balance of coefficients of thermal expansion of a matrix and a filler.

Reinforcing ceramics by disperse metal particles leads to new materials (cermets) with increased stability, tolerance to thermal shock, enhanced heat conductivity. High-temperature cermets are used for production of details for gas turbines, armature of electric furnaces, rocketry details. Solid wear-resisting cermets are used for manufacturing of cutting tools and details. Besides, cermets are used in special technologies such as fuel elements of nuclear reactors on the basis of uranium oxide, friction materials for brake mechanisms and so on.

Ceramic composite materials are produced by hot pressing methods (tableting with subsequent compression sintering) or slip casting method (fibers are encapsulated into matrix suspension which is also exposed to baking after drying).

1.1.4. Hybrid Composite Materials

Other class of nanocomposites is represented by organo-inorganic “hybrid materials” where organic and inorganic components interpenetrate each other at nanometer level. Among them, composite hybrid materials are distinguished consisting of molecules of organic compounds (oligomers or polymers of low molecular weight) placed in inorganic matrix and bound with it by weak Van der Waals forces. The reversed situation when nanoparticles of an inorganic material are situated in a polymeric matrix is possible, too. For example, metal polymer nanocomposites containing great amount of ferromagnetic nanoparticles about 5×10^{-9} m in size located at distance of the order of 5×10^{-9} m may be used for production of quasiperiodic superficial structures with highest data density.

At creation of composite materials, the main problem is discrepancy of physical mechanical properties of matrix (binding) and reinforcing filling. In practice, usually, strength characteristics of reinforcing filler considerably surpass properties of matrix, or it possesses pronounced antiadhesive properties that do not allow proper using of its characteristics. Since the advent of nanodispersed additives, possibility of strengthening the weaker component and adjusting its strength characteristics to the necessary level arises. In turn, this considerably improves properties of the composite and allows applying, for example, other more technological polymers which were not used earlier because of the inadequate characteristics. Besides, researches have led to discovery of new properties of nanocomposites that change essentially initial materials properties. Works on modification of reinforcing materials by fastening of various nanoparticles on their surface that leads to essential change of their properties are in progress. There is a possibility of using new reinforcing materials which were not used earlier, for example, because of antiadhesive properties (high molecular weight polyethylene).

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Biographical Sketch

Nikolay Stepanishchev was born on June 26, 1951, in Lipetsk, Russia. Graduated from the Moscow Institute of Steel and Alloys in 1974, specialty: processing of metals by pressure.
Following graduating, he did his military service in missile arm. He worked at the State Institute for Metallurgical Plant Engineering (GIPROMEZ), at military aviation factories, including abroad. He has a degree of master of sports in model aeroplane flying. Participated in programs on designing of pilotless flying units. He has created and supervised over the enterprise for manufacturing of composite products on the basis of polyester resins. Now he works at the Bauman Moscow State Technical University (BMSTU) as the senior lecturer at the Faculty of Special Machinery. He is the author of *Manufacturing of Composites* (2006, Centre Polyester, Moscow) and a chapter of the manual *Nanosized Structures: Classification, Formation and Research*, (2008, BINOM Publishing House, Moscow). He presented the reports *Composite materials with nanosized additives for perspective space vehicles* and *Design decisions of easy reusable space vehicles of a tourist class* on XXXIII Academic Readings on Astronautics

(Moscow, Russia, January 2009). The main area of his researches is nanostructured composite materials on polymeric matrixes. For a long time (more than 30 years), he studied properties and production technologies of composite polymeric materials and products.