



## Current status and trends in the physicochemical properties of nanomaterials and nanotechnology researches

A V Umarov

Tashkent State Transport University, Tashkent, Uzbekistan

E-mail: abdulalom@inbox.ru

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### Abstract

According to the estimates of many authors, in 10-15 years, the world market for nanotechnology products will amount to about 1 trillion \$. The share of nanomaterials, in this case, is very large (about 340 billion). Therefore, research on nanomaterials properties becomes one of the most important tasks of the science of nanostructured materials. In this regard, it will be essential to expand research on the influence of size and thermal stability; as two common problems for almost all types of nanomaterials. This review article will discuss the most popular topics on nanomaterials, nanostructures, their history, characteristics and classification as well as status of their scientific articles published in recent years. This study focuses on a range of topics related to the development, research and manufacturing applications of nanomaterials and nanotechnology. There are many problems and challenges that scientists are investigating on them. For example: what are the main differences between the properties of interfaces of nanomaterials (including hybrid ones) from the characteristics of ordinary bulk states? How widely can the self-assembly technique of nanoscale devices elements be developed, considering possible installation errors?

**Keywords:** nanomaterials, nanotechnology, particle size, filler, composition, structure, classification.

### 1. Introduction

Today, one of the most rapidly developing areas in materials science is the study of objects with small particles - nanoparticles and nanomaterials. The main problems in this area are the production and research of nanoparticles and composite materials (functional materials). Several methods (physical, chemical, physicochemical and biological) have been developed to produce and study nanoparticles and nanotechnology methods, including laser ones.

The main scientific and practical interest in nanoparticles and nanomaterials is due to the fact that many of their physical, chemical and thermodynamic properties differ significantly from the properties of their constituent atoms or molecules and the properties of a macroscopic substance. Naturally, these properties open up great opportunities for obtaining new materials and creating new technologies based on them. It is expected that nanoparticles and nanomaterials will soon play an important role in technology and all areas of our lives.

To date, only a small part of the types of nanomaterials have been practically realized -

nanostructured nickel foil, soft magnetic alloy "Finmet", multilayer semiconductor heterostructures, superhard nitride films, etc. (see, for example, [1-6]). These are mainly the results of the manifestation of size effects, and the ideas [7-10] are still awaiting their full practical implementation.

Consider some of the scientific publications.

The article [11] discusses the current research on topical unresolved issues about the nature, kinetics and limiting values of hydrogen sorption by carbon nanostructures. These questions are among the key ones in the problem of creating a hydrogen car. The thermodynamic and diffusion characteristics and mechanisms of the chemical and physical sorption processes of hydrogen by graphite and related carbon nanomaterials are described, and methodological aspects of the study and optimization of such hydrogen sorbents. Experimental and theoretical prerequisites and prospects for the creation of a superabsorbent ( $\geq 10$  wt%) for accumulating hydrogen "on board a car" are discussed.

An example from another area of studying nanostructures in [12, 13] presents the current state of

the experimental study of the properties of hydrogen nanostructures. The behaviour of hydrogen in nanocrystalline materials is based on metals, alloys, intermetals, silicon, germanium and other semiconductors, and fullerenes, graphite and other nanotubes considered. Information on the methods of obtaining nanostructures based on these objects is briefly presented. The features of structure and defects, solubility of diffusion mobility, thermodynamic and physical properties are analyzed. Attention is drawn to many insufficiently studied aspects.

The authors [14, 15] discuss various approaches to forming nanocomposite coatings with high and ultrahigh hardness ranges from  $\leq 30$  to 100-120 GPa. The main attention is to analyze the mechanisms of increasing the hardness in thin ( $\leq 10 \mu\text{m}$ ) coatings. Several options for obtaining nanocomposite multicomponent coatings by magnetron sputtering, ion-stimulated and vacuum-arc deposition are considered. Classification of hard and superhard coatings with high thermal stability is given. Possible applications of nanostructured coatings and some prospects for further development of this direction are shown.

The review by R.A. Andrievski and A.M. Glezer [16] presents the current state of research on strength, superplasticity and other vital parameters that determine the mechanical properties of nanomaterials, alloys, intermetals, semiconductors and refractory compounds. Various theoretical approaches are described, the role of size effects and interfaces and other structural factors in the formation of strength and plasticity of nanostructured materials is analyzed. Structural models of plastic deformation and fracture and methods for measuring the mechanical properties of nanomaterials are critically analyzed. The article [17] presents the current state of research in the field of metallic nano- and micro glasses - the peculiarities of methods of production, structure and physical and mechanical properties. Various methods of certification of these objects are described, the role of size effects, temperature changes and ion irradiation in increasing the plasticity of metal glasses are characterized. Attention is drawn to insufficiently studied aspects. There are also several studies [18-21] devoted to the strength and superplasticity of nanostructures.

A significant difference between the fundamental properties of nanoparticles and nanomaterials from the properties of individual constituent atoms or molecules and the properties of a macroscopic substance is due to the enormous scientific and practical interest in nanoparticle assemblies (functional materials) based on them. In the last 20 years or so, there has been a rapid development of research with nanoparticles. Significant advances in nanoparticle science and nanotechnology have been achieved through the use of lasers.

The work [22-24] provides an overview of the directions and results of research in laser nanotechnology. Parameters, properties, applications, and physical and chemical methods for preparing and studying nanoparticles are discussed. The preparation of nanoparticles and nanostructures by laser ablation and

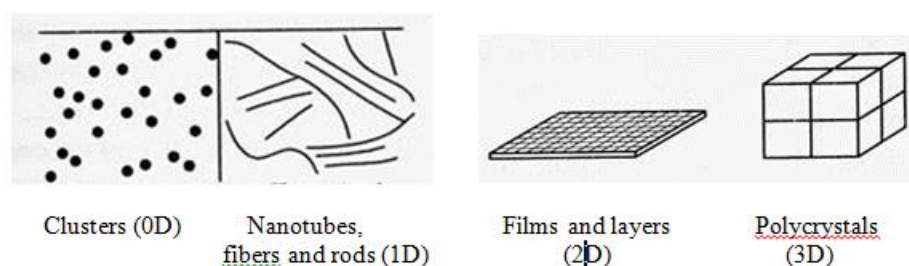
laser nanolithography and the physical foundations and principles of these methods are considered in detail. It is shown that with the help of laser radiation, it is possible to obtain, melt and evaporate nanoparticles, change their shape, structure, size and size distribution, study their dynamics, create periodic arrays, and various structures and assemblies of nanoparticles. The history of research development with nanoparticles and nanomaterials and laser nanotechnology methods in various fields are briefly considered.

The article [25-28] investigates some specific features of the structure and properties of dispersed-filled polymer nanocomposites. Such new effects for these materials as nano adhesion, amplification mechanisms, and others are described. Structural analysis was performed using fractal analysis and a cluster model of the structure of the amorphous state of polymers. The prospects for applying this class of nanomaterials are considered compared with those for other types of polymer nanocomposites.

The articles [29-31] provide an overview of the current state of research on the sorption properties of carbon nanotubes (CNTs). The structural features of CNTs, which determine their sorption properties and the mechanisms of sorption of gaseous and condensed substances by such structures, are considered. Special attention is paid to the problem of using CNTs for storing gaseous hydrogen and other gaseous substances. Methods of filling CNTs with liquid substances based on capillary phenomena and wetting the graphite surface of CNTs with liquids of different nature are analyzed. The properties of "pods" formed from filling single-walled CNTs with fullerene molecules are considered. The prospects for using the sorption properties of a nanotube in electrochemical and fuel cells, systems for storing materials, and obtaining subminiature metal conductors are discussed.

The review [32] is devoted to the problem of the influence of grain boundaries and crystal surfaces on the deformation properties of nanocrystalline and nanoscale materials, mainly metallic. The main experimental facts concerning the mechanical behaviour of nanocrystalline materials are presented; theoretical analysis of the found regularities is made based on the equations of dislocation kinetics, taking into account the properties of grain boundaries as sources, sinks and barriers for dislocations. Within the framework of a similar approach, the dimensional effects during plastic deformation of individual micro- and nanocrystals are discussed, taking into account the crystal surface as a predominant source and sink for dislocations. The paper [33] introduces extended boundary conditions for the gradient extended plasticity of crystals to represent realistic conditions on external surfaces, interphase boundaries or grain boundaries. They relate the magnitude of plastic slip to the density of surface defects and slip directions relative to the normal to surface. The characteristic features are highlighted, including the effect of surface compliance and surface hardening, depending on the size.

The structure and energy of grain boundaries (GBs)



**Figure 1.** Types of nanocrystalline materials (from [35]).

are important for predicting the properties of polycrystalline materials. In this paper [34], the authors used a high-throughput density functional theory workflow to create the Grain Boundary Database (GBDB), the largest database of DFT-derived grain boundary properties to date. In particular, they demonstrate a new large-scale template approach for calculating HT GB, which reduces the computational costs of converging GB structures by  $\sim 3-6$  times. The grain boundary energies and separation work have been rigorously verified against previous experimental and calculated data. Using this large GB dataset, the authors developed an improved GB energy prediction model for various elements based on cohesion energy and shear modulus. The open GBDB represents a significant step forward in the availability of GB's core properties, which they believe will help guide the future design of polycrystalline materials.

## 2. General characteristics and a brief history

The distinctive properties of nanomaterials are determined by their structure at the atomic level, particularly by the structure of interfaces and surfaces. In many cases, the role of nanoparticle size and structure is comparable to the role of the chemical composition of the particles. This adds another controllable parameter for developing new materials (nanomaterials) and the control of functional properties. Nanomaterials hold promise for promising technological applications, including nanoelectronics, nanophotonics, biomedicine, transportation, information storage, communications, the environment and space exploration, in the production of many vital objects.

This development of research on nanoparticles and nanomaterials is due to the fact that, first of all, the developed methods of nanotechnology make it possible to synthesize nanoparticles of practically arbitrary shape and composition. Secondly, modern diagnostic methods make it possible to study in detail the properties of nanoparticles and nanostructures. Third, the development of science makes it possible to predict and optimize the properties of nanoparticles and devices based on them. Today, it is possible to obtain and study nanoparticles and nanostructures based on metals, semiconductors, ceramics, polymers and other materials in various ways. The rapid development of experimental and theoretical methods has led to an understanding of many of the properties of nanoparticles and nanomaterials.

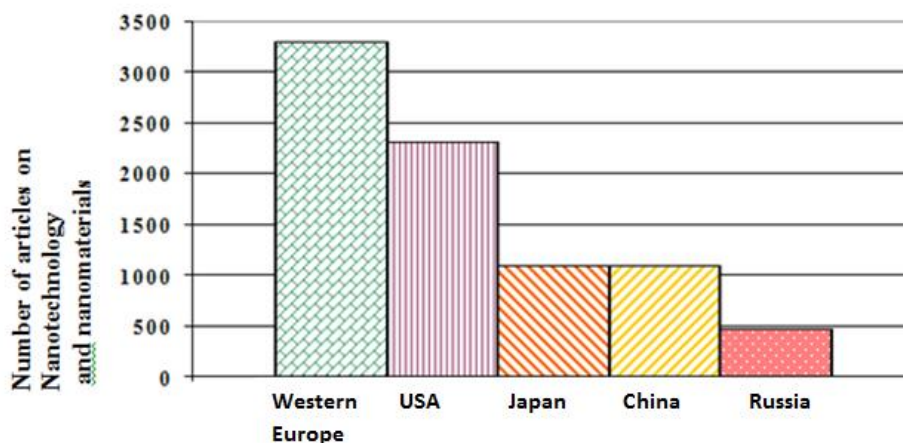
Typically, nanoparticles are small aggregates or

particles ranging from about 1 to 100 nm (or 10 to 1000 Å) in size. In general, nanoparticles contain clusters or large molecules of at least 50 to 100 atoms and about 1 nm in size. Nanoparticles also include particles consisting of tens or hundreds of thousands of atoms (or even more) and having a diameter of several tens to several hundred nanometers. For many years, such particles have been called colloids, often referring to this concept as suspending metal particles in an aqueous medium.

Distinguish between nanoparticles and nanomaterials three-, two-, one- and zero-dimensional (3D, 2D, 1D and 0D, respectively). Two-, one- and zero-dimensional nanoparticles and nanostructures are called quantum wells, quantum wires, and quantum dots. In 2D and 1D structures, the free motion of charge carriers is two- and one-dimensional, respectively. In quantum dots, the energy spectrum of electrons is "quantized" in three dimensions and, as in the case of a collection of single atoms, is a set of discrete levels separated by bands of forbidden states. The sizes of quantum dots usually range from 3 to 20 nm, depending on the interval between the electronic levels and the effective mass of the electron. Thus, in the case of non-spherical particles, nanomaterials include materials, the smallest structural elements of which at least in one dimension has a size in the range of 1 - 100 nm (figure 1) [35].

Nanomaterials are divided [35] into several main types: consolidated nanomaterials, nanowires, nanopolymers, nanobiomaterials, fullerenes and tubular nanostructures, catalysts, nanoporous materials, and supramolecular structures. Nanomaterials also include nanocrystals and the recently discovered material graphene (obtained in 2004) - an allotropic form of carbon with a hexagonal crystal lattice resembling a honeycomb, one atomic layer thick. Graphene represents a new class of unique nanomaterials. In 2010, A. Geim and K. Novoselov were awarded the Nobel Prize in Physics for "innovative experiments on the study of two-dimensional graphene material".

The types of nanomaterials considered above differ significantly both in manufacturing technology and in functional characteristics. They are united only by the characteristic small size of particles, grains, tubes, pores, which determine the structure and properties of the material. The minimum size of structural elements is 0.1 - 1 nm, i.e. corresponds to the size of individual atoms and molecules; the maximum size of 100 nm is accepted conventionally.



**Figure 2.** Number of articles dealing with the issues of nanomaterials and nanotechnology in 1999-2000. according to the Science Citation Index (USA) [38].

The term "nanotechnology" was first proposed by the Japanese N. Taniguchi in 1974 [36,37]. The possibility of creating materials with grain sizes less than 100 nm, which should have many interesting and useful additional properties in comparison with traditional microstructural materials, was pointed out by the German scientist G. Glater in 1981 [38-41]. He, and independently of him, the Russian scientist I.D. Morokhov introduced the concept of nanocrystals into the scientific literature [40-42]. Later, G. Glater also introduced the terms nanocrystalline materials, nanostructured, nanophase, nanocomposite, etc., into scientific use [43-44].

At present, interest in new classes of materials in the fields fundamental and applied science, industry, and business is constantly increasing [40-42,45]. This is due to reasons such as:

- striving for miniaturization of products,
- unique properties of materials in a nanostructured state,
- the need to develop and introduce new materials with qualitatively and quantitatively new properties,
- development of new technological techniques and methods based on the principles of self-assembly and self-organization,
- practical implementation of modern devices for research and control of nanomaterials (probe microscopy, retrogenic methods, nanohardness)
- development and implementation of new technologies (ion-plasma technologies for surface treatment and the creation of thin layers and films, LIGA (*Lithographie, Galvanoformung, Abformung*) technologies, which are a sequence of lithography, electroplating and molding processes, technologies for the production and molding of nanopowders, etc.).

In the coming years, the development of fundamental and applied concepts of nanomaterials and nanotechnology can lead to dramatic changes in many areas of human activity: in materials science, energy, electronics, computer science, mechanical engineering, medicine, agriculture, ecology. Along with computer information technology and biotechnology, nanotechnology is the foundation of the scientific and technological revolution in the 21st century [7,45,46].

A rather indicative fact is that a considerable proportion of scientific publications fall on publications dealing with the problems of nanomaterials and nanotechnologies. It is rather difficult to fully determine this share since, according to various sources, only 15-25 thousand articles on this topic have been published in the last few years. However, some ideas can be given by data on the so-called Science Citation Index for 1999-2000. (figure 2) [38].

A study of the Scopus database for 2016-2019 showed [<https://www.scopus.com/sources.uri>] that articles published on the topic Nanomaterials, Nanotechnology in 30 sources included in the Scopus database (such as Nature Nanotechnology, Nanotechnology, Science and Applications, Nanomedicine: Nanotechnology, Biology, and Medicine, Cancer Nanotechnology, Journal of Biomedical Nanotechnology, Nanotechnology, Environmental Nanotechnology, Monitoring and Management, Advances in Natural Sciences: Nanoscience and Nanotechnology, Nanotechnology Reviews, IEEE Transactions on Nanotechnology, etc.) 16954 articles were published in 4 years, cited 110591 times, and in 2019 alone, the number of citations in the Scopus database was 89420, or 80.86% of the total number of citations for four years (2016-2019). Studies show how the relevance of research in this area has increased in recent years (figure 3).

### 3. Terminology and classification of nanoparticles

The terminology for nanomaterials and nanotechnology is currently only being established. There are several approaches to how to define what nanomaterials are (figure 4).

Recently, several works [47-52] have been devoted to nanoparticles, production technology, and studies of their properties. The simplest approach is associated with the geometric dimensions of the structure of such materials. According to this approach, materials with a characteristic microstructure size from 1 to 100 nm are called nanostructures (or otherwise nanophase, nanocrystalline, supramolecular) [39-42].



Figure 3. A study of the Scopus database for 2016-2019.

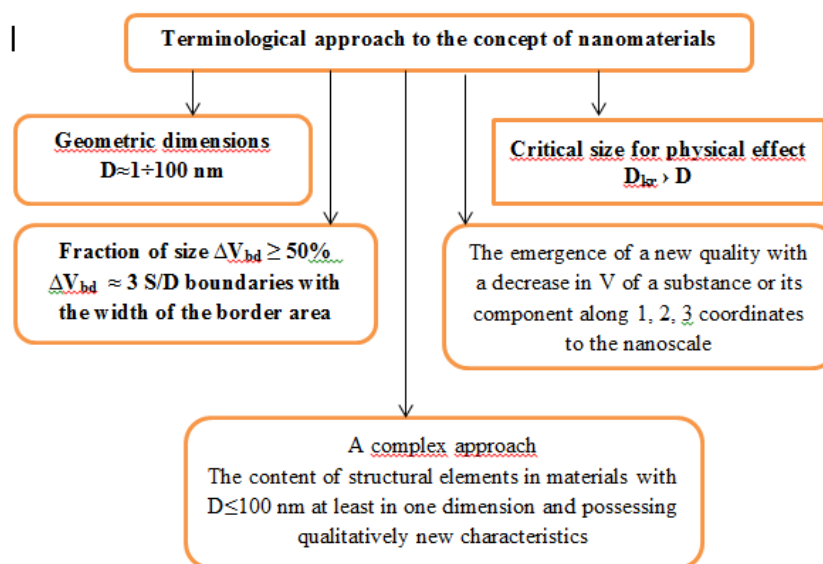


Figure 4. Terminological approaches to the concept of nanomaterials.

The choice of this size range is not accidental but is determined by a number of size effects and the coincidence of the crystallite sizes with the characteristic sizes for various physical phenomena. The lower limit is related to the lower limit of symmetry of the nanocrystalline material [53-55]. The point is that as the size of the crystal, which is characterized by a strict set of symmetry elements, decreases, a moment comes when some symmetry elements will be lost.

According to [54,55], for the most widespread crystals with a bcc and fcc lattice, this critical size equals three coordination spheres, which for iron is about 0.5 nm, and for nickel, it is about 0.6 nm. The value of the upper limit is due to the fact that noticeable and interesting from a technical point of view, changes in the physical and mechanical properties of materials (strength, hardness, coercive force, etc.) begin when the grain size decreases exactly below 100 nm [36,37,44].

The second approach [39,44,56] is associated with the considerable role of numerous interfaces in nanomaterials in forming their properties. Accordingly, the grain size

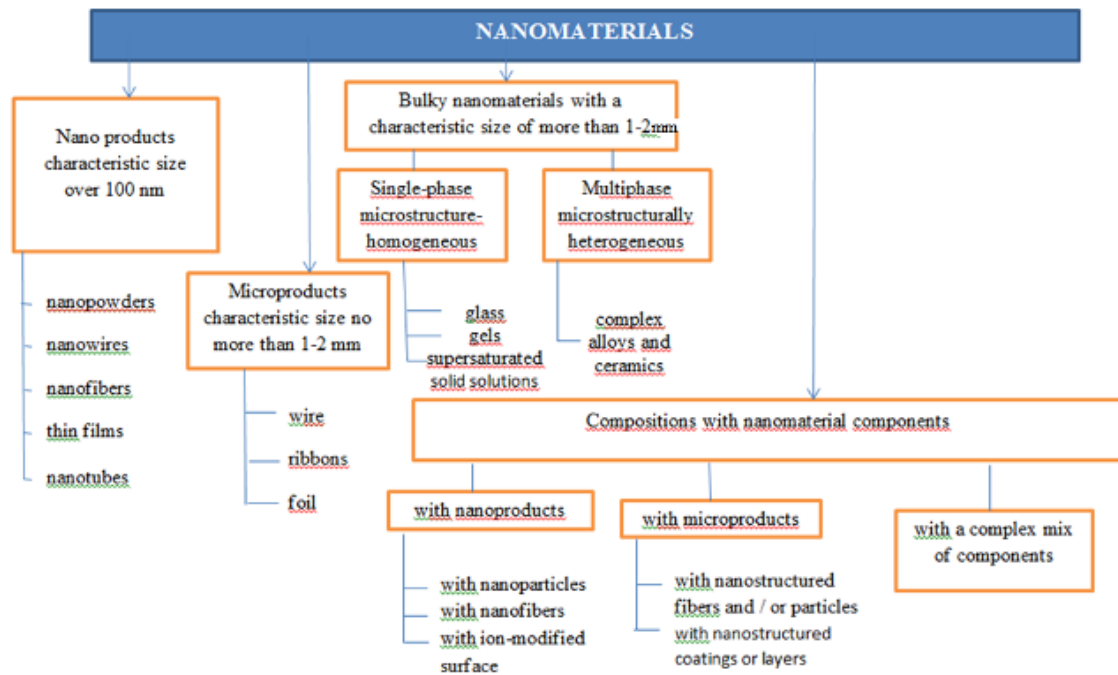
(D) in nanomaterials was determined in the range of several nanometers, i.e. in the interval when the volume fraction of interfaces in the total volume of the material is approximately  $\Delta V \approx 50\%$  or more. This share is roughly estimated from the ratio  $\Delta V \approx 3s / D$ , where  $s$  is the width of the border area. With a reasonable  $s$  value of about 1 nm, a 50% fraction of interfaces is achieved at  $D = 6$  nm.

There is also an approach [41], according to which for nanomaterials, the largest size of one of the structural elements should be equal to or less than the size characteristic of a certain physical phenomenon. So for strength properties: it will be the size of a defect-free crystal; for magnetic properties: the size of a single-domain crystal; for electrical conductivity: the mean free path of electrons. Having considered a number of works on nanoparticles [57-63], it can be concluded that significant disadvantages of this approach are [41, 57], firstly, the discrepancy between the sizes of structural elements for different properties and materials and, secondly, the difference in characteristic sizes for different states of the same material (for example,



**Table 1.** Calculated sizes (nm) of particles and grains that do not contain dislocation loops [41].

Material	Cu	Al	Ni	$\alpha$ -Fe
individual powder particles	250	60	140	23
grains in polycrystal	38	18	16	3

**Figure 5.** Classification of nanomaterials.

individual particles of a nanopowder and grains in a polycrystal - see table 1).

Some scientists [45] believe that if a new quality arises when the volume of a substance decreases along with one, two, or three coordinates to a nanometer scale, or this quality arises in a composition of such objects, then these formations should be attributed to nanomaterials and technologies for their production and further work with them; to nanotechnology.

In our opinion, the complete terminology at the moment is proposed in [46,53], where the following terms are used:

**nanotechnology** - a set of methods and techniques that provide the ability to create and modify objects in a controlled manner, including components with dimensions less than 100 nm, having fundamentally new qualities and allowing their integration into fully functioning systems of a large scale;

**nanomaterials** - materials containing structural elements, the geometrical dimensions of which is at least one dimension does not exceed 100 nm, and possessing qualitatively new properties, functional and operational characteristics;

**nanosystem technology** - fully or partially, functionally complete systems and devices based on nanomaterials and nanotechnologies, whose characteristics are fundamentally different from those of systems and devices of a similar purpose, created using traditional technologies.

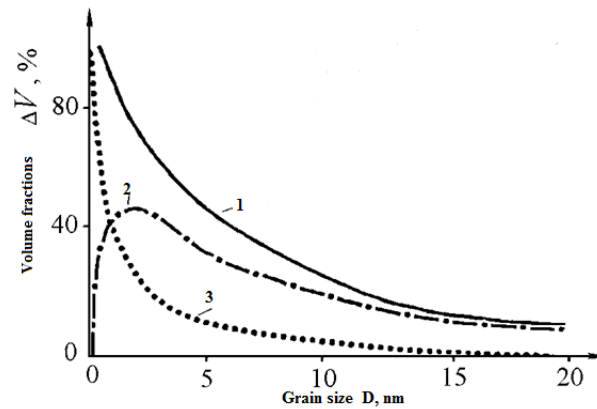
Following the above terminology, nanomaterials can be divided into four main categories (figure 5).

The first category includes materials in the form of solids, the dimensions of which in one, two or three spatial coordinates that they do not exceed 100 nm in size. Such materials include nanosized particles (nanopowders), nanowires and nanofibers., Very thin films (less than 100 nm thick), nanotubes, etc. Such materials can contain one structural element or crystallite (for powder particles) to several layers (for the film). In this regard, the first category can be classified as nanomaterials with a small number of structural elements or nanomaterials in the form of nanoproducts.

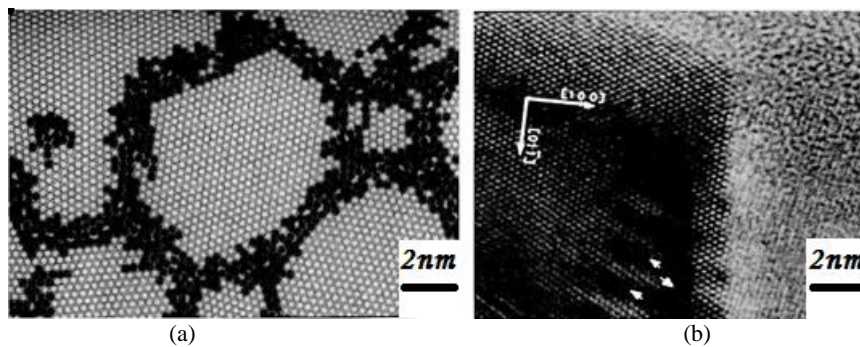
The second category includes materials in the form of small-sized products with a characteristic size in the approximate range of 1 micron to 1 mm. Usually, these are wires, tapes, foils. Such materials already contain a significant number of structural elements, and they can be classified as nanomaterials with a large number of structural elements (crystallites) or nanomaterials in the form of micro products.

The third category is massive (or otherwise bulky) nanomaterials with product sizes in the macro range (more than a few mm). Such materials consist of many nanoscale elements (crystallites) and are polycrystalline materials with a grain size of 1 nm to 100 nm. In turn, the third category of nanomaterials can be divided into two classes.

The first category includes single-phase materials (under the terminology [41], microstructurally homogeneous materials), the structure and/or chemical composition of which changes over the volume of the material only at the atomic level. Their structure, as a



**Figure 6.** Dependence of the volume fractions of interfaces, grain boundaries and triple joints [41] 1- section boundaries; 2- grain boundaries; 3- triple sticks.



**Figure 7.** a) - Atomic model of nanostructured material (atoms of the grain-boundary region in which the displacement exceeds 10% of the interatomic distances are shown in black) [64] and b) - Grain boundaries in nanostructured copper (transmission electron microscopy, the symbols indicate the introduced grain boundary dislocations) [65].

rule, is in a state far from equilibrium. Such materials include, for example, glasses, gels, and supersaturated solid solutions. The second class includes microstructurally heterogeneous materials that consist of nanosized elements (crystallites, blocks) with different structures and/or compositions. These are multiphase materials, for example, based on complex metal alloys.

The second and third categories of nanomaterials fall under the narrower definitions of nanocrystalline or nanophase materials [39-42].

The fourth category includes composite materials containing components from nanomaterials. In this case, the components can be nanomaterials classified in the first category (composites with nanoparticles and/or nanofibers, products with modified ion implantation of the surface layer or thin-film) and the second category (for example, composites reinforced with fibers and/or particles with nanostructure, materials with a modified nanostructured surface layer or coating). Composite materials with the complex use of nanocomponents can also be distinguished.

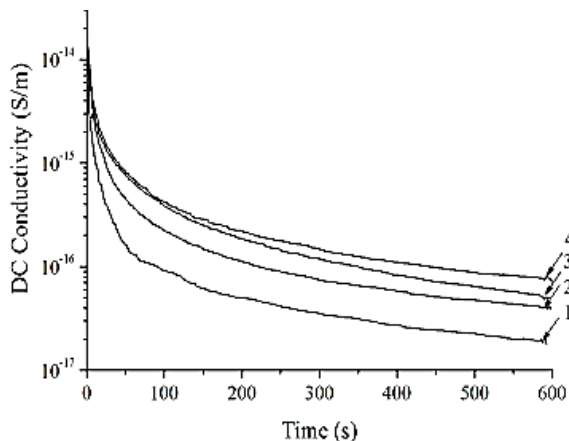
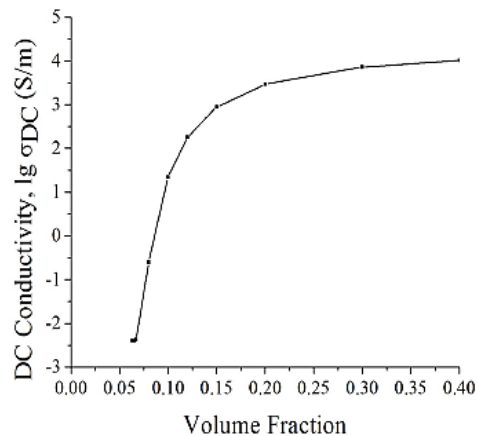
One of the reasons for the specific properties of nanomaterials is an increase in the volume fraction of interfaces with a decrease in the size of grains or crystallites in nanomaterials. In this case, the volume fraction of the following components can be distinguished: interfaces, grain boundaries and triple joints [40, 41]. The volume fraction of interfaces can be estimated by the formula:

$\Delta V_{TP} = 1 - [(D-s)/D]^3$ , where  $s$  is the thickness of the interfaces (on the order of 1 nm), and  $D$  is the characteristic grain or crystallite size. The volume fraction of grain boundaries - according to the formula:  $\Delta V_{T3} = [3s(D-s)^2]/D^3$ , and the volume fraction of triple joints as the difference:  $\Delta V_{TC} = \Delta V_{TP} - \Delta V_{T3}$ .

In figure 6, the dependences of the indicated volume fractions are calculated by these formulas [40,41]. It can be seen that with a decrease in the grain size from 1  $\mu\text{m}$  to 2 nm, the volume fraction of the intergranular component (interfaces) increases from 0.3 to 87.5%. The volume fractions of the intergranular and intragranular components reach the same value (50% each) at a grain size of about 5 nm. After the grain size decreases below 10 nm, the fraction of triple joints begins to increase enormously. This is attributed to the anomalous drop in hardness in this range of grain sizes [64]. Comprehensive experimental studies have shown that grain boundaries are of a nonequilibrium nature due to the presence of grain-boundary defects with a high density (figure 7) [42,65]. This nonequilibrium is characterized by excess energy of grain boundaries and the presence of long-range elastic stresses; the grain boundaries have a crystallographically ordered structure, and the sources of elastic fields are grain boundary dislocations and their complexes [42,66]. Review [66] provides a detailed overview of the synthesis, properties, and applications. Nanoparticles (NPs) exist in different forms. NPs are tiny materials ranging from 1 to 100 nm.

**Table 2.** Values of the DC conductivity were experimentally determined (AT 600 S) and calculated.

Sample	Mass concentration $c_{mi}$ (%)	Volume concentration $c_{vi}$ (%)	Experimental conductivity (S/m)	Calculated conductivity (S/m)
E0	0	0	$2.8 \times 10^{-17}$	$2.85 \times 10^{-17}$
E1	5	0.688	$3.92 \times 10^{-17}$	$3.93 \times 10^{-17}$
E2	10	1.377	$5.02 \times 10^{-17}$	$5.10 \times 10^{-17}$
E3	15	2.064	$7.13 \times 10^{-17}$	$6.88 \times 10^{-17}$

**Figure 8.** Variation with time of DC conductivity for E0 (1), E1 (2), E2 (3) and E3 (4) samples ( $T = 25^\circ\text{C}$ ).**Figure 9.** Variation of DC conductivity with filler volume fraction (values computed with the relation (1)).

#### 4. Investigation of the physicochemical properties of polymer nanocomposite materials

There are many works [67-103] on the study of nanocomposites, including the fundamental relationship structure/ properties, production technology and application of polymer nanocomposite materials.

In addition to presenting the scientific underpinnings of advances in polymer nanocomposite research, review [67] focuses on scientific principles and mechanisms concerning processing and fabrication methods, discussing commercial applications and health/safety concerns (a critical issue for manufacturing and scaling).

The Authors in Ref [68] investigated (figure 8) the time variation of the DC conductivity, determined by measuring the absorption/resorption currents at  $U_0 = 500$  V and  $T = 25^\circ\text{C}$ . The measurements were carried out on samples without (curve 1) and with different filler content (curves 2, 3 and 4). It turns out that an increase in the filler content entails an increase in the DC conductivity. However, this increase is not impressive (see table 2). These results indicate that the filler volume content ( $c_{vi}$ ) is not close to the percolation concentration ( $c_{vp}$ ). At this moment, the conductivity increases significantly (closer to the value of electromagnetic shielding ( $\sigma_c = 10^{-2}$  S/m, [68])). The percolation concentration was calculated from the conductivity values experimentally determined on samples E1, E2, and E3 (600 s after switching on the voltage).

Conductive Polymers (CP) are a group of polymeric materials that have received considerable attention due to their unique electronic, chemical and biochemical properties. This is reflected in their use in a wide range of potential applications, including light-emitting diodes, antistatic coatings, electrochromic materials, solar cells, chemical sensors, biosensors and drug release systems. Electrochemical DNA sensors based on CP can be used

in many areas related to human health. The review [69] summarizes recent progress in developing and using CP-based electrochemical DNA hybridization sensors. The various properties of CPs with regard to their use for immobilizing a DNA probe on the surface of electrodes are discussed, and the immobilization methods used to develop sensors for DNA hybridization together with various transduction methods are described. In the final part of the review [69], some problems are presented when using sensors for DNA hybridization based on CP and prospects for the future.

It was considered  $F = 0.64$ , and the exponent  $k$  was calculated as a function of  $c_v$ . Variation of DC conductivity with the filler content, for  $c_v > c_{vp}$ , is presented in figure 9. These results are similar to the ones obtained by Clingerman [70], Psarras [71], Mamunya [72] and Hui [73].

The article [74] investigates the effect of the filler content on the electrical conductivity of composites based on low density polyethylene (LDPE) -neodymium (Nd). Flat samples with dimensions  $100 \cdot 100 \cdot 0.5$  mm<sup>3</sup> were made from low density polyethylene (LDPE) as a polymer matrix and spherical neodymium particles (99% purity) as a filler by melt mixing using a compatible agent. The distribution of particles in the polymer matrix was analyzed using optical microscope microscopy and scanning electron microscopy (SEM). Variations in DC and AC conductivity with temperature, frequency and filler content have been studied. A symmetric hopping model for disordered structures was used to explain the results. Finally, the use of these materials in electrical engineering is analyzed.

Nanotechnology offers fundamentally new possibilities for creating a wide range of new materials, composites and structures at the molecular level.



**Table 3.** Mechanical properties of organoclay and polyamide in six nanocomposites with respect to extruders/screw configurations. (Reproduced from [138].)

Extruder type	Tensile modulus (GPa)	Tensile yield strength (MPa)
Single screw 7	3.3	77
Twin screw co-rotating intermeshing	3.7	81
Twin screw counter-rotating intermeshing	3.6	75
Twin screw counter-rotating non-intermeshing	4.0	85

It has the potential to redefine the methods used to design lighter, stronger, higher performing structures and processes with unique and unconventional properties. The review [75] summarizes various classes of nanocarbon materials: polymer composites and their applications.

In article [76], electrical conductivity, thermal conductivity and mechanical properties, namely elongation at break and stress at break, were investigated for composites based on high density polyethylene/graphite. A percolation concentration of about 11% by volume of filler was found for both filled polyethylenes. The degree of crystallinity of the polyethylene matrix did not significantly affect either the percolation concentration or the electrical conductivity of the composites. Measurement at direct current showed that the filler does not significantly affect the change in the degree of crystallinity of polyethylene matrices. The addition of inorganic spherical nanoparticles to polymers allows changing the physical properties of polymers as well as introducing new features into the polymer matrix. A review article [77] discusses the features of inorganic nanoparticles, the most important methods for synthesizing ceramic nanoparticles and nanocomposites, surface modification of nanoparticles and composite formation, including disadvantages.

Technologies based, such as selective laser sintering, electron beam melting, and selective laser melting, use laser or electron beams to selectively fuse polymer, metal, ceramic, or composite powders layer by layer into desired products according to their computer-aided design models. With unique mechanical, thermal, electrical, biocompatible, and fire-resistant properties, polymer composites for AM powder are attracting intense research interest due to their potential for a wide range of functional applications in aerospace, automotive, marine and marine, medical. Article [78] is a comprehensive review of recent advances in polymer composites, the preparation of their powders for AM, and the functionality and application of their printed matter.

Historically, composite materials have been developed empirically rather than based on the relationship between the macroscopic characteristics of mechanical characteristics associated with construction and the constituent material's internal atomic or molecular structure. Using computational techniques in a "virtual laboratory" would facilitate faster development cycles and increase the number of requests for candidate materials. The method discussed in [79] is hierarchical rather than parallel multiscale modeling and is based on a continuum analysis concept called "onset theory" to provide macroscopic guidance for chemical modeling.

Most of the works are devoted to studies of optical [80-83], electrical [84, 85], acoustic [86] properties, studies of morphology, structure and synthesis [87-94], thermal [95-99], paramagnetic [100-112] properties of composite materials filled with nanoparticles. Nanocomposites [Biron (2004), Gloaguen & Lefevre (2007)] represent a new generation of biphasic materials that bond the base matrix to nanofillers inserted between polymer chains. Nanofillers can significantly improve or modify the various properties of the materials in which they are incorporated, such as optical, electrical, mechanical, thermal, or flame retardant properties, sometimes in combination with conventional fillers. The properties of composite materials can be significantly affected by the ratio of the mixture of the organic matrix and nanofillers.

A number of authors focused on the manufacture of thin films of various metal oxides and phosphate compounds using stable metal complexes [113-131]. This is the molecular precursor method (MPM), one of the chemical processes used to make thin films. By the method of high-speed thermal decomposition of metal-containing compounds and organic acid salts in a polymer solution-melt, samples were obtained (in the form of powders) based on high-pressure polyethylene (LDPE) containing fillers in the form of CdS nanoparticles or copper-containing nanoparticles in a matrix [129-131].

Fiber-reinforced nanocomposites are manufactured through affordable RTM and VARTM processes described in different kinds of literature [132-135]. Hussain et al. [133] achieved about (by dispersing only 1% by weight nanosilicates) 18 and 24% improvement in flexural strength and fracture toughness, respectively in S2 glass/vinylester-clay nanocomposites compared to conventional composites [133]. Roy and Hussain [136,137] manufactured E-glass/PP clay nanocomposites using prepreg tapes with extruder and pultrusion machine. They achieved improvements in compressive strength and modulus using this technique. Fielding et al. [132] achieved uniform dispersion of the nanoclay of carbon fiber reinforced epoxy nanocomposites using RFI in the autoclave. Nanocomposites formed by melt blending have been described in different kinds of literature (figure 10) [138-141]. Dennis et al. [138] described how the type of extruder and screw design affects the degree of dispersion of nanoclay in a polyamide matrix (table 3).

Innovations in semiconductor materials and their processing have led to extreme miniaturization, thus resulting in very small, high performance Integrated Circuits (ICs). This innovation has been the cornerstone of the all-pervasiveness of electronics in every walk of life of humankind today and has revolutionized the way



**Figure 10.** TPO nanocomposites: application for automotive parts [139]: (a) M-Van step Assist: first commercial launch and (b) impala: second nanocomposite application. Through the courtesy of M. Verbrugge, General Motors.

**Table 4.** Initiatives for Pressure Sensor Technologies under NPMASS [142].

1	MOS integrated piezoresistive pressure sensors, based on Silicon On Insulator (SOI) substrates	IIT-Madras
2	Anisotropically etched capacitive high sensitivity pressure sensor	CEERI, Pilani
3	Development of Silicon MOEMS based pressure sensor	IISc, Bangalore
4	Pressure Sensor dies for strategic applications through DRIE, electronics with EMI/EMC compatibility	IISc, Bangalore
5	Packaging for absolute, differential and gauge modes	IISc, Bangalore and BEL, Bangalore
6	Pressure sensors for automotive applications	SCL, Chandigarh and M/s PRICOL, Coimbatore

we live today. For example, article [142] discusses various initiatives to develop MEMS technologies for pressure transducers shown in table 4. A variety of pressure sensor designs that have been undertaken include a piezoresistive sensor, capacitive sounding and optical sounding.

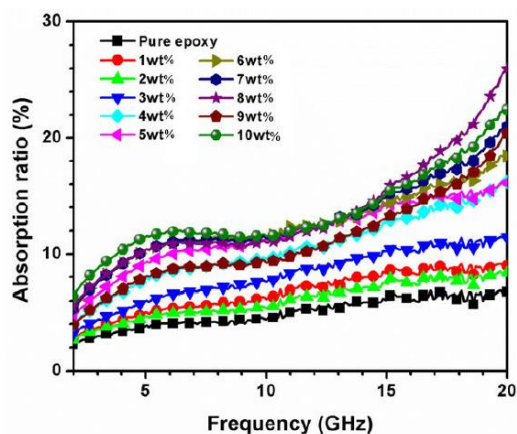
Nanocomposites as microwave absorbers are receiving much attention, synthesize of polypyrrole nanocomposites containing iron oxides, tin oxide, tungsten oxide, and titanium dioxide have been investigated. Pyrrole containing a dispersion of nanoparticle metal oxides was polymerized in situ, and the magnetic properties were reported. The electrical conductivity and dielectric losses can be tuned by varying the concentration and orientation of the nanotubes additions. It has been awarded a patent in this thermosetting matrices containing oriented nanotubes. Only a few weight per cent nanotubes need to be added to the polymer to achieve valuable properties.

Reports have been made to utilize carbon nanotubes CNTs to develop economical microwave (in the range of 8 GHz to 24 GHz) absorbers. These materials have wide applications in electrical energy storage (condensers) integrated into load-carrying structures, high strength CNTs polymer Vbers for energy absorption, electromagnetism shielding, etc (figure 11) [142].

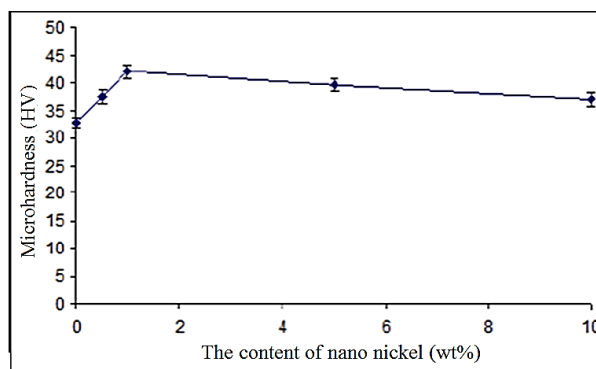
Nanosized metal particles filled polymer composites are finding numerous tribological applications in recent years. In the present work, the matrix properties were

investigated by introducing nickel (Ni) nanoparticles (60-100 nm, weight fractions of 0.5-10 %) into a bismaleimide (BMI) resin. The influence of these particles on the microhardness, friction and dry sliding wear behavior was measured using a microhardness tester, pin-on-disc wear set up. The experimental results indicated that BMI resin's coefficient of friction and the specific wear rate (SWR) could be reduced at Ni particles' relatively low weight fraction. The lowest value of neat BMI) was observed for the nanocomposite with a Ni weight fraction of 1%. The incorporation of Ni particles leads to an increased hardness of BMI, and the wear performance of the composites shows a good correlation with the hardness. The results have been supplemented with scanning electron micrographs to help understand the possible wear mechanisms (figure 12 and 13) [142].

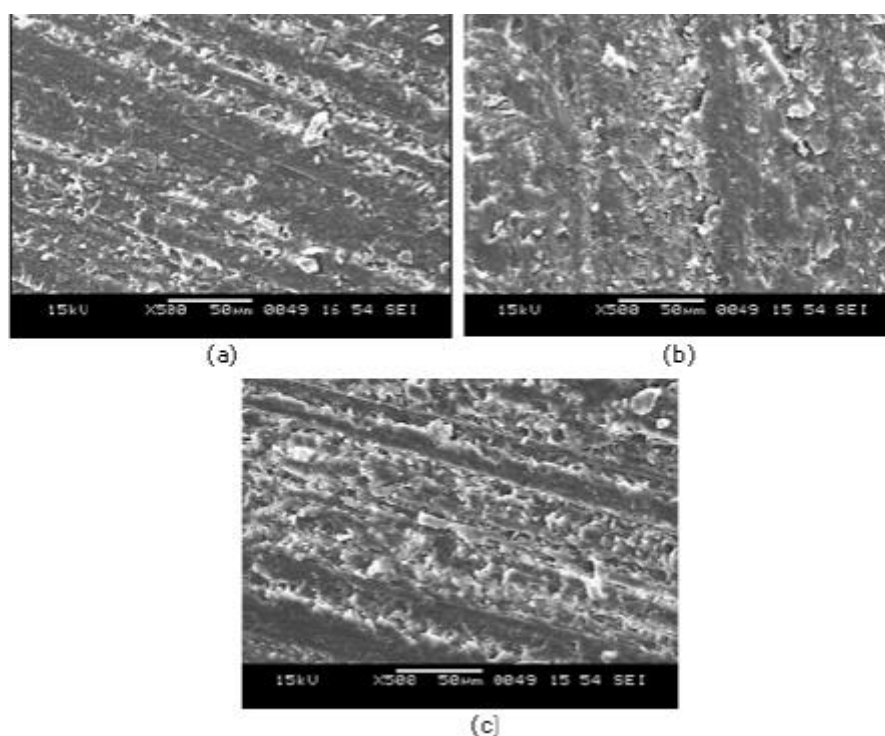
Polymers have poor fire resistance. If ignited, most polymers will burn quickly, releasing large quantities of heat, toxic gases, and soot. Polymers containing a few weight per cent of nanoparticle clays have greatly improved Vre resistance. The thermal properties of the polymer nanocomposite PNC are improved, melting and dripping are delayed, and the rate of burning is significantly reduced (by more than half). The presence of Wake-like clay nanoparticles reduces the dimension of polymer decomposition volatiles (the fuel) to the burning surface and reduces diUusion of air into the polymer.



**Figure 11.** Absorption ratio of the MWCNTs-epoxy composite samples in the microwave frequency range from 2-20 GHz [142].



**Figure 12.** Microhardness of Ni filled BMI nanocomposites [142].



**Figure 13.** Scanning electron micrographs of the worn surface of (a) neat BMI, (b) BMI with Ni weight fraction of 1 % and (c) BMI with Ni weight fraction of 5 % [142].

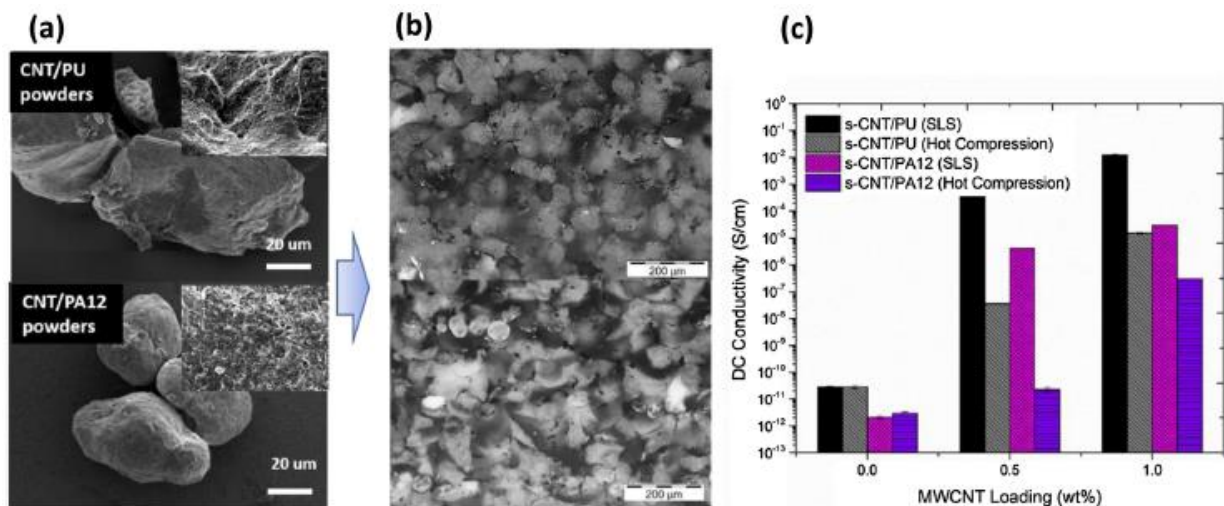
Further, the addition of clay nanoparticles improves mechanical properties significantly. Similar improvements were noted in polypropylene/CNTs nanocomposites. The high thermal conductivity of CNTs might increase heat input into the polymer and enhance the burning rate. However, contradict this observation in CNTs. Examples of applications include reducing fire risk in enclosed spaces in vehicles, submarines, aeroplanes, and ships [142]. The fire retardant behavior of polymers is a significant challenge for extending their use to most applications. Nanocomposites are very attractive since the small amount of nanostructure can improve the fire-resistant property of nanocomposites.

Nanocomposites are an emerging class of polymeric materials exhibiting excellent mechanical properties, enhanced modulus and dimensional stability, flame retardancy, improved scratch and more resistance,

superior thermal and processing properties, reduced warpage of components and enhanced impact resistance, making them suitable to replace metals in automotive and other applications. The key drivers for polymer nanocomposite-enabled parts in the automotive industry are reduction in vehicle weight, improved engine efficiency (fuel saving), reduction in CO<sub>2</sub> emissions, and superior Performance (greater safety, increased comfort and better driveability). The commercialization of polymer nanocomposites started in 1991 when Toyota Motor Co. first introduced nylon-6/clay nanocomposites to produce timing belt covers as a part of the engine for their Toyota Camry cars. In 2002, General Motors launched a step-assist automotive component made of polyolefin reinforced with three percent nanoclays. The automotive industry can benefit from polymer nanocomposites in several applications such as engines



**Figure 14.** Parts of a car (automotive) that nanocomposites are used in it [143].



**Figure 15.** (a) PA12 and PU powders coated with CNTs, (b) microstructures of SLS-printed CNT/PA12 composites, (c) electrical conductivities of CNT/PA12 and CNT/PU composites manufactured by SLS and hot compression [144]. Copyright 2018. Adapted with permission from Elsevier Inc.

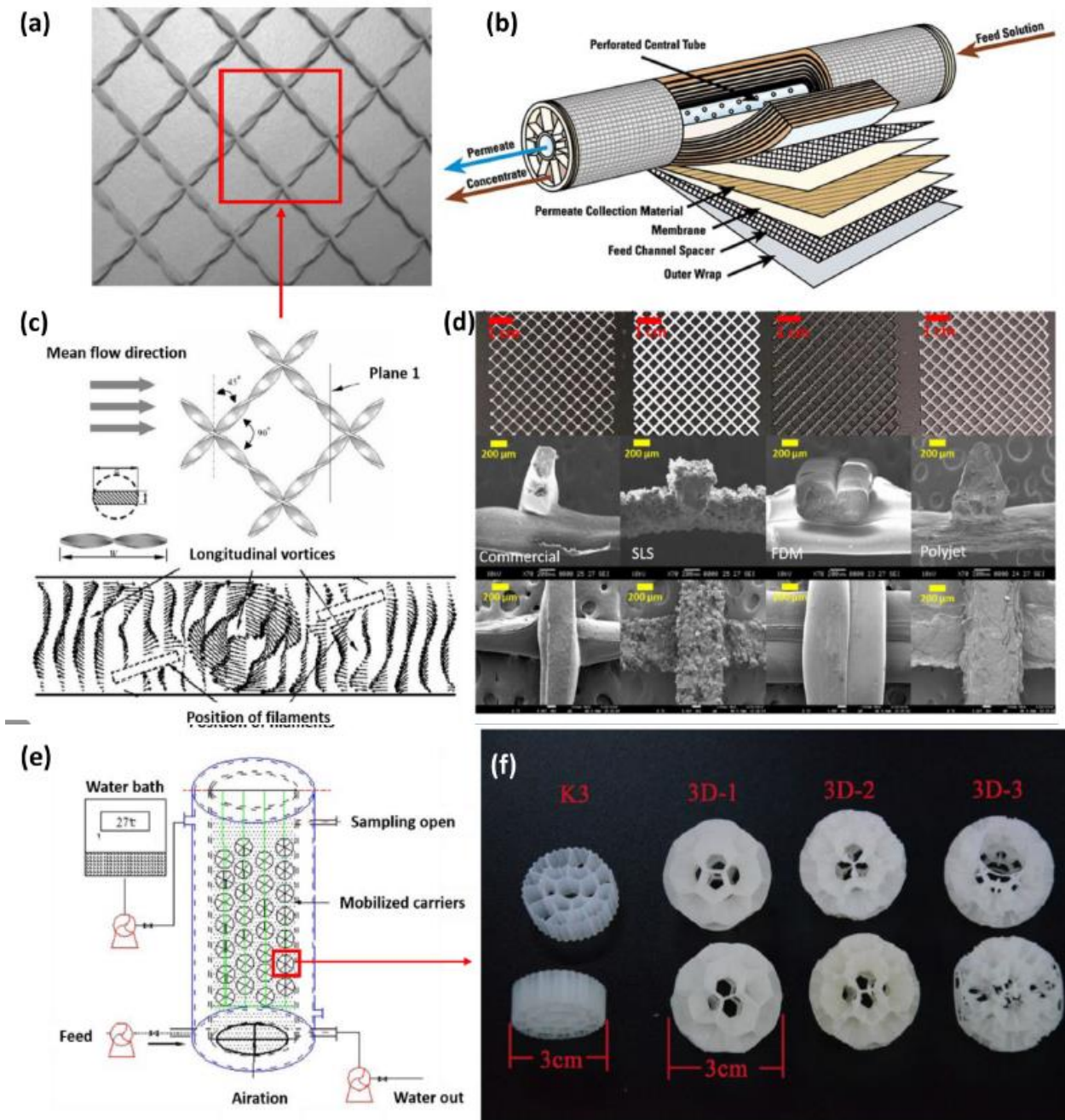
and power trains, suspension and braking systems, exhaust systems and catalytic converters, frames and body parts, paints and coatings, lubrication, tires, and electric and electronic equipment. Since then, extensive research in nanocomposites Veld has been carried out worldwide (figure 14)[143].

Further, Yuan et al. [144] demonstrated 3D auxetic metamaterials via CNT/PA12 with great potential for impact protection and cushion applications. Purification 3D structures can serve as a platform for all kinds of emerging environmental applications, particularly in the biofilm reactor [145] and membrane module components for removal or separation of pollutants and contaminants from liquid and gaseous environments such as spacers

and filtration membranes[146–148]. In the membrane separation system, free channel spacers within a module are critical for facilitating recirculation of the bulk fluid and the fluid close to the membrane surface. As shown in figure 15c, printed novel spacers can effectively increase the local shear rate and fluid velocity, thereby minimizing the concentrated polarization effect by enhancing the mass transfer [149,150].

Biofilm reactors with moving beds are typical devices used in wastewater treatment, and bio-carriers are essential components for enriching microorganisms and improving the amount of biomass in the reactor (figure 16e).





**Figure 16.** (a) Novel spacer design fabricated by SLS, (b) integrated membrane modules of water treatment with laminated structures, (c) longitudinal vortices in a flat channel filled with spacers and the vector plot of velocities in Plane 1 [150], (d) Photos and SEM images of spacers fabricated by the conventional process, SLS, FDM and Polyjet [147];(e) schematic of the sequencing biofilm batch reactor containing different types of bio-carriers and (f) 3D fullerene-type biocarriers used in the bioreactor [151-154]. Copyright 2005 Reproduced with permission from Elsevier Inc. Copyright 2017 Adapted with permission from Elsevier Inc. Copyright 2016 Reproduced with permission from Nature group.

**5. Conclusions**

Despite a large number of studies and publications, there are still gaps and ambiguities in research. There are problems that scientists are working on; for example: in the introduction to the collection, some of the questions facing researchers in nanotechnology were formulated.

1. What new unexpected quantum properties could nanostructures have, especially at room temperatures?
2. What are the main differences in the properties of

interfaces between nanomaterials (including hybrid types) from the characteristics of ordinary bulk states?

3. How widely can the self-assembly technique be developed for elements of nanoscale devices, taking into account possible errors during installation?

4. What technological processes can be economically viable for nanomaterials with adjustable and specified shape, composition, structure, and properties parameters?



Unfortunately, the level of our understanding of the main phenomena and characteristic of the nanostructural state is still clearly insufficient for deep understanding the

issue. Therefore, the readers are faced with the question of solving these problems.

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