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AN OVERVIEW ON ZnO REINFORCED COMPOSITES

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ABSTRACT

Zinc oxide reinforced composites are a promising class of materials with a wide range of potential applications. By combining ZnO with other materials, scientists and engineers can achieve advanced functionalities that go beyond the properties of the individual components. The article offers to researchers and specialists an organized and thoughtful overview on outlining the impacts of composites, emphasis on ZnO nanoparticles reinforced composites.

KEYWORDS: ZnO, composites, reinforced, bonds in composites, ZnO reinforced composites

1. Introduction

Composites are combinations of two (or more) materials in which one of them, called the reinforcement phase, is in the form of fibres, plates, or particles, and included in other materials called the matrix phase. Reinforcement and matrix materials can be metals, ceramics, or polymers. Particles used for reinforcement include ceramics and glasses such as small mineral particles, metallic particles, or metallic oxides such as alumina and amorphous materials including polymers and carbon. Composite materials can be reinforced by dispersion with nano and microparticles particles or large particles preferentially or randomly oriented. Nanoparticles have an atomic profile that can be utilized to control the physical and chemical properties of advanced composite materials.

The era of advanced composite materials is noteworthy for tending to the issues of standard composites totally different applications.

The dispersed phase is, as a rule, a stable oxide of aluminium oxide (Al_2O_3), thorium oxide (ThO_2), zirconium oxide (ZrO_2), beryllium oxide (BeO), magnesium oxide (MgO) or zinc oxide (ZnO). The dispersed phase must have certain dimensions, shape, quantity, and distribution to obtain the best properties for the composite material. At the same time, it must have low solubility in the matrix material and no chemical reaction between the particles and the matrix.

Researchers have made approaches to refit the properties of typical fiber-reinforced composites by treating the fiber with zinc oxide nanoparticles (ZnO NP).

This review looks at the potential advantage of treating typical strands with ZnO nanoparticles to modify the surface geography of features to move forward the properties of common fiber reinforced composites. The article also depicts the utilize of ZnO NPs to obtain different levelled fibres that can help update the properties of fiber composites and highlight avenues for future investigation in this area.

To endorse the researchers' interest in developing, characterizing, and investigating the properties of composites reinforced with ZnO particles, the types of publications were analysed: article, proceeding paper, review article, early access, book chapters, meeting abstract, letter, editorial materials the search was performed in the Web of Science database [1], as presented in Fig. 1.

The according bibliometric study was conducted to the following keywords: ZnO nanoparticles, reinforced composites, ZnO reinforced composites, ZnO reinforced fiber composites, for the period 2016-2023. The refinement of the articles was done later considering the authors from Romania. Fig. 2 shows interest in disseminating results for the study of ZnO nanoparticles and reinforced composites. There is a continuous increase in the experimentation of these research topics.

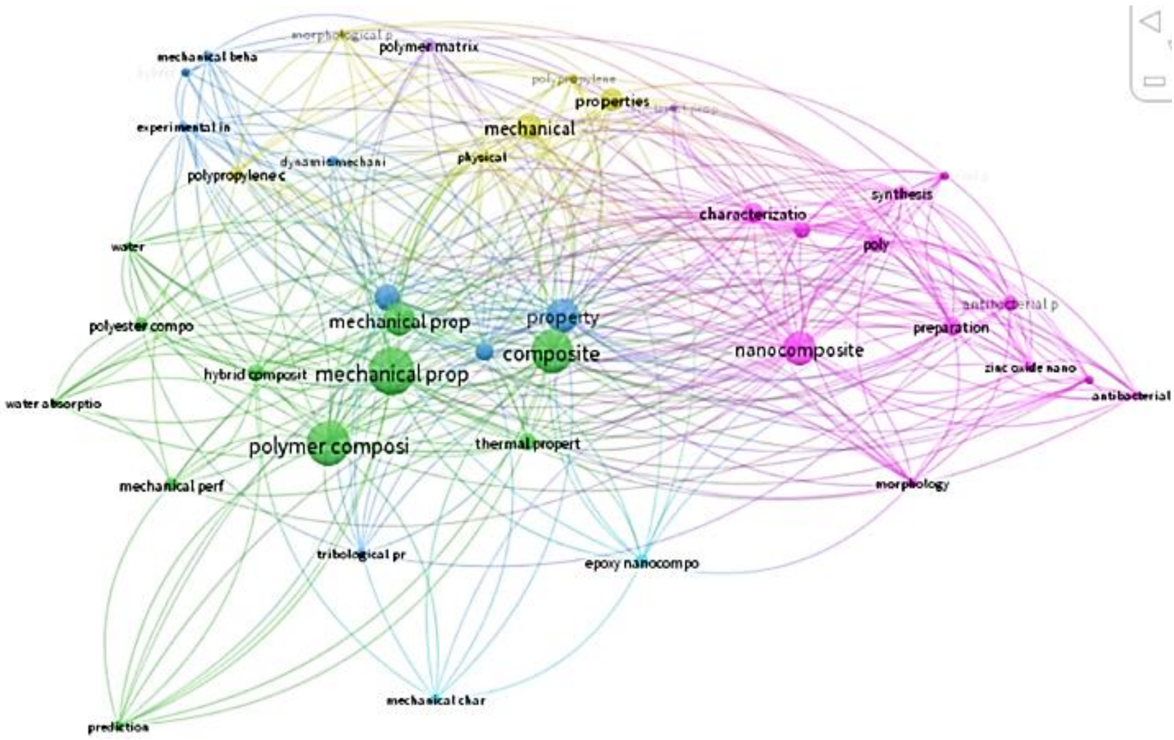

Fig. 1. *Occurrence of keywords composites-ZnO nanoparticles-reinforced particles, top cited papers published in Web of Science*

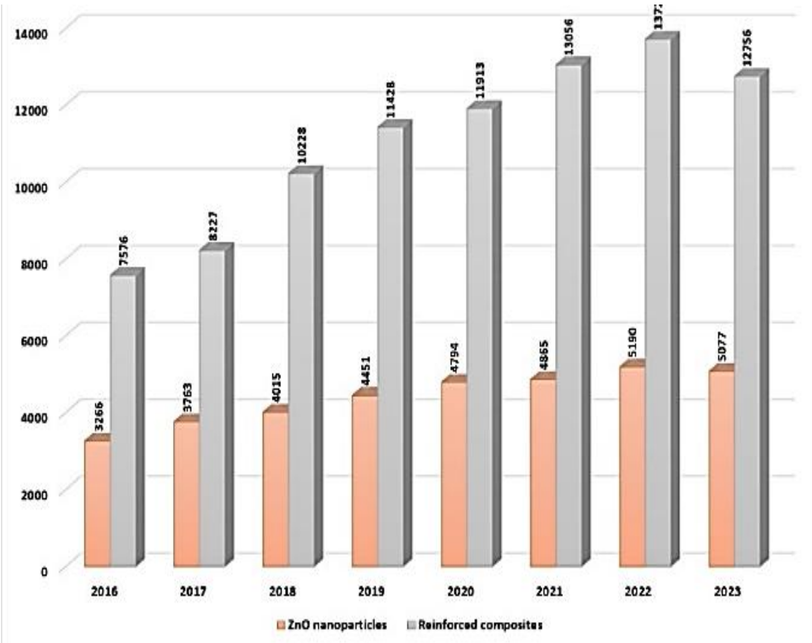

Fig. 2. *Publication' evolution regarding the topics: ZnO nanoparticles and Reinforced composites*

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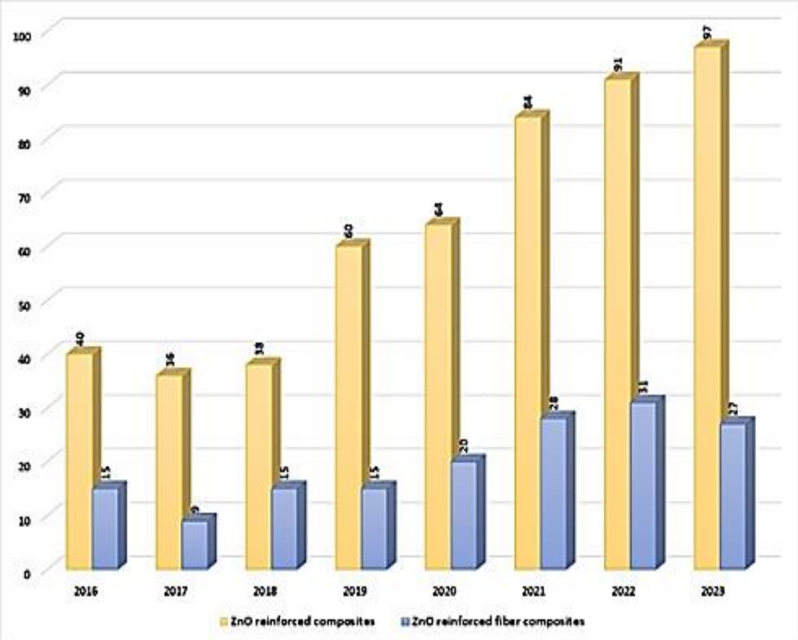

Fig. 3. *Publication' evolution in WOS regarding the topics: ZnO nanoparticles and Reinforced fiber composites*

By refining the results by introducing the key terms ZnO reinforced composites and ZnO reinforced fiber composites, the small number of research results is highlighted at international level in Fig. 3. The number of publications varies between 15 and 97, between 2016-2023. This leads us to the conclusion that there are unexplored areas and emerging themes. Regarding the scientific research of the Romanian authors on the above-mentioned topics, it is noted that the elaboration and characterization of ZnO nanoparticles and reinforced composite materials were studied separately, as presented in Fig. 4.

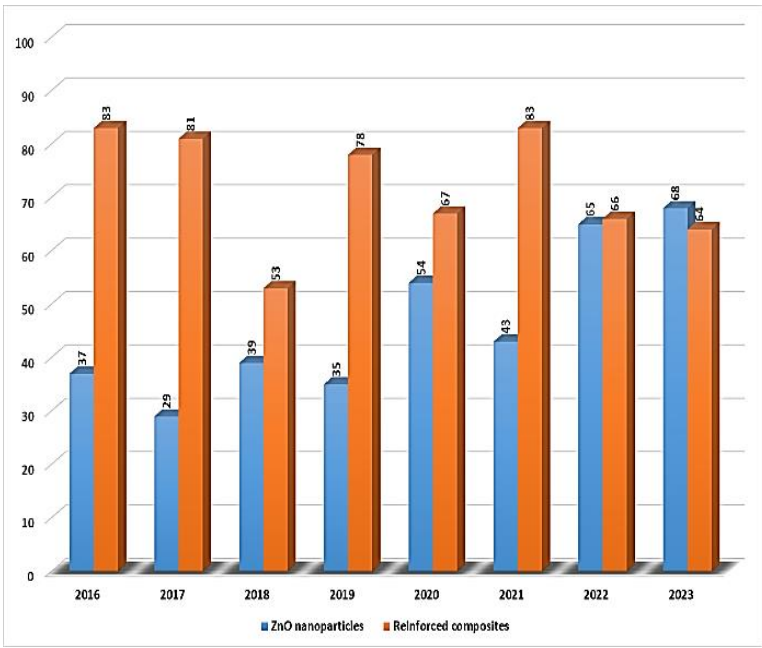

Fig. 4. *Publication' evolution, Romanian authors, in WOS database*

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2. Characteristics of composites

2.1. Characteristics of Matrix

The classic classification of- through intergranular segregation, composites is according to the matrix, in the order of the temperature of use. Composite materials with an organic matrix can only be used on a temperature scale that does not exceed from 200 to 300 °C, while other types of composites exceed 600 °C for a metal matrix and 1000 °C for a ceramic matrix. Thus, composite materials can be classified into:

a) polymer matrix composites are certainly the most developed from the point of view of commercial importance and due to the capacity of the manufacturing process. Polymer composites have revolutionized various industries due to their superior properties compared to neat polymers.

b) metal matrix composites - some of their manufacturing processes are inspired by the processes used in powder metallurgy. The reinforcements can be oxides, borons, carbides, nitrides. Metal-matrix composites, also called MMCs (metal-matrix composites), have developed thanks to the manufacturing processes and thanks to the low costs.

c) ceramic matrix composites for high temperature applications such as oxides, carbides, or nitrides. The use of ceramics is limited precisely because of their fracture toughness, resistance to fatigue and thermal shocks. To solve these problems, the incorporation of a second ductile phase in the ceramic matrix is a solution. This process can be done in two ways:

- through intergranular segregation;
- by intragranular dispersion.

2.2. Reinforced composites

Composites offer exceptional strength and stiffness while being significantly lighter than traditional materials like metals. This makes them ideal for applications demanding weight reduction, such as aerospace, construction, sport, medicine, biomedical engineering, and automotive industries. By varying the type, amount, and orientation of the reinforcement, it can be tailoring the composite's properties to meet specific needs. For instance, unidirectional fiber orientation offers high strength in that direction, while a woven structure provides more balanced properties.

Within the vast world of reinforced composites lies a sub-category known as particle-reinforced composites. These composites, unlike their fiber-reinforced counterparts, utilize particles – typically smaller and more dispersed – to enhance the properties of the matrix. A schema of reinforced composites is presented in Fig. 5. Large particles have diameters exceeding 1 micrometre and volume concentrations ranging from 25-50%.

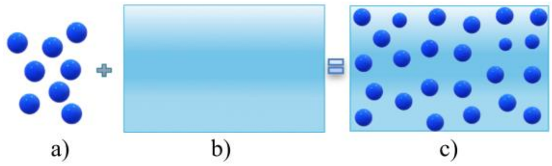

Fig. 5. *Schema of particle reinforcement: a) particles; b) matrix; c) reinforced composites*

Ceramic particles (oxides, nitrides, borures) are dispersed in a metal matrix, used for cutting tools due to their hardness and wear resistance.

2.3. Benefits of ZnO Armatures Particles

2.3.1. ZnO properties

ZnO is a common compound, and it's generally considered safe for human use. ZnO is a versatile and interesting material with a wide range of potential applications. ZnO can be an insulator, a semiconductor (3.37 eV, band gap), or even transparent conductor. This makes it useful in a variety of applications, from sunscreens and gels to solar cells and transistors. Also, ZnO to convert pressure into electricity, making it potentially useful for energy harvesting.

ZnO is sensitive to various gases, making it useful in gas sensors for detecting harmful gases in industrial and environmental monitoring applications.

Depending on the type of polymer matrix and the processing techniques, ZnO/polymer composites can exhibit enhanced electrical conductivity compared to the neat polymer. This opens doors for applications in antistatic materials, electromagnetic interference (EMI) shielding, and even transparent conductive films.

ZnO can absorb ultraviolet radiation, which is why it's found in many sunscreens. ZnO nanoparticles have been shown to exhibit antibacterial properties, which can be utilized in medical applications such as wound dressings, antibacterial coatings for medical devices, and textile treatments. When dispersed in a polymer matrix, they can create UV-protective films for various applications, such as coatings for sunscreens, textiles, and building materials.

ZnO nanoparticles can exibit catalytic activity, which finds applications in environmental remediation, such as water purification and air pollution control.

Among the wide range of nanostructured metal oxides, ZnO nanoparticles can be synthesized by all synthesis methods: mechanical, chemical, physical [2, 3].

2.3.2. Methods to ZnO NP synthesis

Mechanical methods are a type of bottom-up approach for synthesizing nanoparticles. They involve applying physical forces to break down bulk materials into nanoparticles. The zinc salt or zinc oxide microparticles break down into nanoparticles, using high energy ball milling.

Hydrolysis and hydrothermal are the most common methods which use a combination of hydrolysis and condensation reactions. A soluble zinc salt, like zinc nitrate ($Zn(NO_3)_2$) or zinc acetate ($Zn(CH_3COO)_2$), is dissolved in water. This solution acts as the precursor for ZnO formation. Hydrolysis agent (like NaOH) is added to the solution, which increases the pH and initiates the hydrolysis reaction. The zinc ions (Zn^{2+}) from the precursor react with OH^- ions from hidroxide to form zinc hydroxide ($Zn(OH)_2$). $Zn(OH)_2$ further undergoes condensation reactions, where water molecules are eliminated, leading to the formation of ZnO nanoparticles. The reaction mixture is then placed in an autoclave and heated to a specific temperature (typically between 100-200 °C). The high-pressure and high-temperature conditions (in the case of hydrothermal process) promote the growth and crystallization of ZnO nanoparticles with desired size and morphology [4].

The physical methods used a focused fascicle beam on a zinc precursor target. The high energy of the beam ablates(vaporate) the target. The vapours are condensed on cooled substrate in form of films or can be collected in form of powders. Compared with already presented methods these one offers the advantage of achieving pure ZnO nanoparticles without impurities from elaboration process [3, 5].

2.4. ZnO reinforced polymer composites

2.4.1. ZnO reinforced polymer composites

ZnO reinforced polymer composites are formed by incorporating zinc oxide particles into a polymer matrix. ZnO nanoparticles can be readily incorporated into various polymer matrices using conventional processing techniques like solution casting and melt blending. ZnO nanoparticles are particularly attractive for this purpose due to their high aspect ratio and large surface area, which can lead to significant improvements in the properties of the composite material. ZnO can improve the strength, stiffness, and toughness of polymers. This is because the ZnO particles act as stress concentrators, which transfer the applied load from the polymer matrix to the particles themselves. ZnO is a semiconductor material, which means that it can conduct electricity. This makes ZnO-reinforced polymer composites useful for a variety of electrical applications, such as electrostatic discharge (ESD) protection and electromagnetic interference (EMI) shielding. ZnO has excellent UV absorption properties, which can be beneficial for polymers that are susceptible to degradation from UV light exposure. ZnO-reinforced polymer composites can therefore be used for applications such as outdoor furniture and automotive parts.

2.4.2. Types of bonding in ZnO reinforced nanocomposites

ZnO reinforced nanocomposites are materials that combine the unique properties of zinc oxide (ZnO) nanoparticles with a polymer matrix. The incorporation of ZnO nanoparticles can significantly enhance the mechanical, electrical, and thermal properties of the composite material.

Ionic bonding occurs between positively charged ions (cations) from the ZnO nanoparticles and negatively charged ions (anions) from the polymer matrix, as presented in Fig. 6. The electrostatic attraction between these oppositely charged ions creates a strong bond at the interface between the nanoparticle and the polymer.

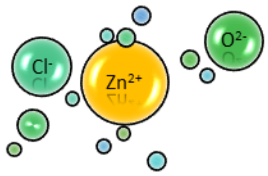

***Fig. 6.** Ionic bond in ZnO reinforced composites*

Covalent bonding involves the sharing of electrons between atoms from the ZnO nanoparticles and the polymer matrix, as shown in Fig. 7. Covalent bonding can create very strong and directional bonds, which can improve the mechanical properties of the composite.

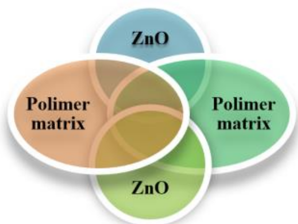

***Fig. 7.** Scheme of covalent bonding*

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Hydrogen bonding occurs between a hydrogen atom bonded to an electronegative atom (such as oxygen or nitrogen) in the polymer matrix and a lone pair of electrons on an oxygen atom from the ZnO nanoparticle, as shown in Fig. 8. Hydrogen bonding can create a weaker interaction than ionic or covalent bonding, but it can still play a role in improving the interfacial adhesion between the nanoparticle and the polymer.

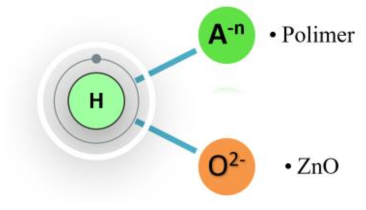

Fig. 8. *Scheme of hydrogen bonding*

Van der Waals forces are weak, temporary attractive forces that arise between neutral atoms or molecules. Van der Waals forces can exist between the ZnO nanoparticles and the polymer matrix, and they can contribute to the overall interfacial adhesion, as presented in Fig. 9.

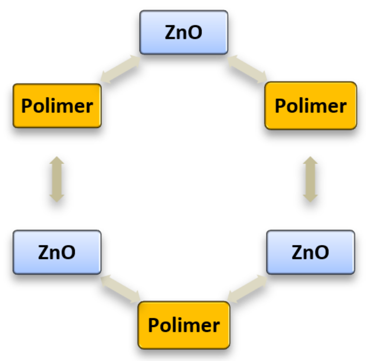

Fig. 9. *Scheme of Van der Waals bonds in polymer composites*

In some polymer-based composites, especially those with non-polar polymers, van der Waals forces may contribute to interactions between individual polymer chains within the matrix. This can influence the overall mechanical properties like stiffness and creep resistance of the composite. In many composites, the primary load transfer mechanism relies on stronger chemical bonds or mechanical interlocking between the fiber and matrix.

3. Multifunctional approach

Recent advancements in ZnO reinforced polymer composites focus on their enhanced mechanical, barrier, antimicrobial, and functional properties. The synergistic effects of ZnO incorporation on the performance of various polymer matrices are explored [1, 6] This involves controlling the arrangement of ZnO particles within the composite material. Introducing nanostructures like nanorods, wires, and tubes can significantly enhance mechanical properties and electrical conductivity. Additionally, controlling the size and distribution of ZnO grains can optimize the composite's strength and toughness [7].

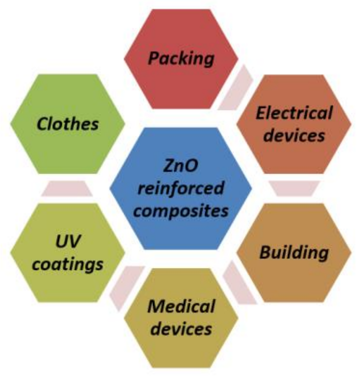

Fig. 10. *Multifunctional approach of ZnO reinforced composites*

Doping involves introducing foreign elements into the ZnO crystal lattice. Elements like aluminum (Al) and gallium (Ga) can create point defects that modify electrical properties, such as conductivity and carrier concentration. Alloying ZnO with other metal oxides, like magnesium oxide (MgO), can improve its stability and introduce new functionalities [3].

ZnO nanoparticles act as effective reinforcing agents, improving the tensile strength, flexural modulus, and impact strength of polymer composites. This is attributed to strong interfacial adhesion between the nanoparticles and the polymer matrix, leading to efficient stress transfer [7]. Modifying the surface of ZnO particles can enhance their compatibility with other materials in the composite or introduce entirely new functionalities. Coating ZnO with polymers or functional molecules can improve compatibility and promote specific interactions at the interface. Creating surface roughness or hierarchical structures can improve adhesion between ZnO and other phases or enhance tribological properties like wear resistance [8].

ZnO nanoparticles create an indirect path for gas molecules, significantly enhancing the gas barrier properties of polymer composites. This is particularly beneficial for food packaging applications, where it helps to maintain product freshness and extend shelf life [9]. These composites offer superior gas barrier properties, improved mechanical strength, and inherent antimicrobial activity.

ZnO nanoparticles exhibit inherent antimicrobial activity, making the composites effective against various bacteria and fungi. This property finds applications in food packaging, medical devices, and hygiene products [6]. ZnO nanoparticles can impart various functionalities to the composites depending on their size, shape, and dispersion. For example, ZnO can enhance electrical conductivity, UV-shielding ability, and flame retardancy, opening doors for applications in electronics, sunscreens, and fire-resistant materials [10]. ZnO reinforced composites can be used in building materials to enhance their mechanical strength, UV resistance [11], and self-cleaning properties [4]. The electrical conductivity and semiconducting behavior of ZnO nanoparticles make these composites suitable for applications in sensors, solar cells, and electronic [12].

The biocompatibility and antimicrobial properties of ZnO make these composites promising candidates for drug delivery systems, implants, and wound dressings [13, 14].

4. Conclusions

Combining ZnO with other materials like polymers or ceramics allows researchers to create composites with synergistic properties. This means that the combined properties of the composite are greater than the sum of the individual components.

Perspective research in nanomaterials delves beyond the current state of the field, analysing trends and identifying future directions. It often focuses on the broader implications of nanomaterials and raises critical questions that need to be addressed for responsible development. Some perspective research in nanomaterials can be:

- Perspective research can explore ways to assess these risks, develop safer nanomaterials by design, and implement regulations for responsible use.
- Future research can identify areas for improvement, such as reducing energy use in synthesis or developing methods for safe and sustainable recycling of nanomaterials.
- Ethical regulations about their potential impact on society can focus on issues like the democratization of nanotechnology (who has access and control?), the potential for misuse in military applications, and the need for public education and engagement.
- Developing frameworks for regulation that balance innovation with risk qualification can help the standardized methods for characterizing and testing nanomaterials.

By carefully designing the composite structure and choosing the appropriate reinforcing phases, scientists can achieve tailored electrical, mechanical, and chemical functionalities for specific applications.

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