1 Introduction to Nanotechnology

1.1 Definition of Nanotechnology

The Subcommittee on Nanoscale Science, Engineering, and Technology (NSET), Committee on Technology (CoT), National Science and Technology Council (NSTC) defines nanotechnology as [1]:

> Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.
>
> A nanometer is one-billionth of a meter. A sheet of paper is about 100,000 nanometers thick; a single gold atom is about a third of a nanometer in diameter. Dimensions between approximately 1 and 100 nanometers are known as the nanoscale. Unusual physical, chemical, and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules.

Mauro Ferrari, Professor of Molecular Medicine at the University of Texas Health and Science Center, of experimental therapeutics at the M.D. Anderson Cancer Center, and of Bioengineering at Rice University, provides the following definition [2]:

> At the nanoscale there is no difference between chemistry and physics, engineering, mathematics, biology or any subset thereof. An operational definition of nanotechnology involves three ingredients: (1) nanoscale sizes in the device or its crucial components, (2) the man-made nature, and (3) having properties that only arise because of the nanoscopic dimensions.

Professor Ferrari points out how the line between disciplines becomes blurred at such a small scale. This is why nanotechnology is characterized in such broad terms – it bridges the competencies of all the sciences.

Professor Robert Langer, one of thirteen institute professors at Massachusetts Institute of Technology, defines nanotechnology in simpler terms [2]:

> Nanotechnology is concerned with work at the atomic, molecular, and supramolecular levels in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure.

The common thread among these definitions is the mention of the molecular scale, or nanoscale. The importance of this molecular scale will be explored in this chapter.

The extent of U.S. government activity alone can be gauged from the fact that currently twenty federal agencies and departments participate in the National Nanotechnology Initiative (NNI website: http://www.nano.gov) in fiscal year (FY) 2016. The NNI, established in FY 2001, is a U.S. government research and development (R&D) initiative involving twenty federal departments, independent agencies, and commissions working together toward the shared and challenging vision of "a future in which the ability to understand and control matter at the nanoscale leads to a revolution in technology and industry that benefit society" [3]. The NNI is managed within the framework of the National Science and Technology Council (NSTC). The Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the NSTC Committee on Technology (CoT) coordinates planning, budgeting, program implementation, and review of the progress for the initiative. The National Nanotechnology Coordination Office (NNCO) acts as the primary point of contact for information on the NNI. The NNI website provides public outreach on behalf of the NNI and promotes access to and early application of the technologies, innovations, and expertise derived from NNI activities.

In 2014, federal agencies invested a total of $1.57 billion in nanotechnology-related activities. The 2016 federal budget provides more than $1.5 billion for NNI, affirming the administration's continuing commitment to a robust U.S. nanotechnology effort. Nearly half (43%) of this budget request is focused on applied R&D and support for the Nanotechnology Signature Initiatives (NSIs), reflecting an increased emphasis within the NNI on commercialization and technology transfer. The cumulative NNI investment since FY 2001, including 2016 request, now total more than $22 billion. It has been more than one and a half decades of major investment and progress in nanoscience and nanotechnology, which was summarized by a "Special Report to the President and Congress on the Fourth Assessment of the National Nanotechnology Initiative" [4] and "The National Nanotechnology Initiative – Supplement to the President's Budget for Fiscal Year 2016" [1].

1.2 Brief History of Nanotechnology

Japanese scientist Norio Taniguchi first coined the term "nanotechnology" in 1974 in reference to small-scale semiconductor interactions, but unknowing uses of the technology and predictions of the concept came earlier [5]. One example of the early use of nanotechnology, however unknowingly, was by medieval artists making stained glass between 500 and 1450 AD. Little did they know that the metallic additives to molten glass used for coloration acted as nanoparticles, scattering light in different ways to produce different colors [5].

The idea of nanotechnology was first introduced to the public in 1959 by Richard Feynman in his esteemed lecture series entitled "There's Plenty of Room at the

Figure 1.1. Richard Feynman at work (Courtesy of Caltech).

Bottom" [4–8]. In this talk Feynman describes a future where scientists control matter with atomic precision (Figure 1.1) [6]. He anticipates, in a seemingly prophetic fashion, the creation of microscopes that could resolve individual molecules, densely packed computer chips, and miniature robots that could aid in surgery and drug delivery [5, 6].

Part of Feynman's dream became realized in 1981 with the development of the Scanning Tunneling Microscope (STM) capable of observations with 0.1 nm resolution [7]. The STM enabled scientists to directly observe manipulations at the molecular scale and thereby served as a key fundamental tool for nanotechnology research.

Advances in microscopy have led to a number of other high-resolution visualization and characterization techniques, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS) [9]. These instruments will be described in Chapter 6.

Feynman's vision of nanoscale microchips came true in 2001 when IBM constructed the first logic gate using carbon nanotubes [7]. This sort of miniaturization in the realm of computing enabled by nanotechnology is what has given birth to smartphones, tablets, and ultrabooks we enjoy today. Other discoveries and applications anticipated by Feynman include the use of nanoscale devices in medicine. Readers should refer to the NNI website, www.nano.gov, under "Nanotechnology 101/Nanotechnology Timeline," which traces the development of nanotechnology from the first concept to the latest development.

1.3 What Is the Significance of *"Nanoscale Materials"*?

Nanoscale (nanoscopic scale) materials, which can be either stand-alone solids or subcomponents in other materials, are less than 100 nm in one or more dimensions. To put this dimension in perspective, a nanometer (nm) is one-billionth of a meter and one millionth of a millimeter, about four times the diameter of an atom. Truly grasping the scale of the nanometer is difficult for our macro-oriented brains, but real-world comparisons can help give us a sense. For example, the blink of an eye is to a year is what a nanometer is to a meter stick [6]. Figures 1.2 [7] and 1.3 show some interesting examples. Figure 1.2 shows some examples: a single-walled carbon nanotube is about 1 nm in diameter; DNA is about 2.5 nm in diameter; a nanoparticle is about 4 nm in diameter; a bacterium is about 2.5 μm in length; a single strand of hair is about 100 μm in diameter; a large raindrop is about 2.5 mm in diameter; an ant is about 4 mm long; an average house is about 10 m wide; and the Indianapolis Motor Speedway is 4 km per lap. Additional interesting materials for comparison are a human red blood cells (10,000 nm), a cell of bacteria *E. colis* (1,000 nm), a viral cell (100 nm), a polymer coil (40 nm), quantum rods (Q-rods) (30 nm in length) with an aspect ratio of 10:1, and a quantum dot (QD) (7 nm in diameter), all shown in Figure 1.3.

To illustrate the inherent value of manipulating matter on such a scale, Daniel Ratner, Professor of Bioengineering at the University of Washington, proposes a helpful thought experiment [7]. Suppose we have a 3 x 3 x 3 foot cube of pure gold. If we were to bisect this cube in each dimension, we would have eight smaller cubes. These new cubes would exhibit the same intrinsic properties as the original – each would still be heavy, shiny, and yellow, with the same chemical and structural properties. If we were to continue bisecting until we have cubes sized on the order of microns (10^{-6} of a meter), the inherent bulk properties of the material would still remain constant. And this is not specific to gold; the same holds true for steel, plastic, ice, or any pure solid. However, if we were to reach the nanoscale, quantum effects would begin to dominate, and the gold's properties, including its color, melting point, and intermolecular chemistry, would change. These quantum effects had been "averaged out of existence" in the bulk material [8]. At the nanoscale, the force of gravity gives way to van der Waal's forces, surface tension, and other quantum forces [10].

1.4 Why Is This *"Nanoscale"* So Special and Unique?

Nanomaterials are also known as *nanoscale structures, nanoscale materials, nanophase, or nanoparticles* in the literature. To distinguish nanomaterials from bulk, it is crucial to demonstrate the unique properties of nanomaterials and their prospective impacts in science and technology. Nanomaterials can be classified as one-dimensional nanoscale structures (platelet-type), two-dimensional nanoscale structures (fiber-type), and three-dimensional nanoscale structures (particulate-type). These three most important nanomaterials are illustrated schematically in Figure 1.4 and are described in detail in Chapter 2. Nanoscale structures have very

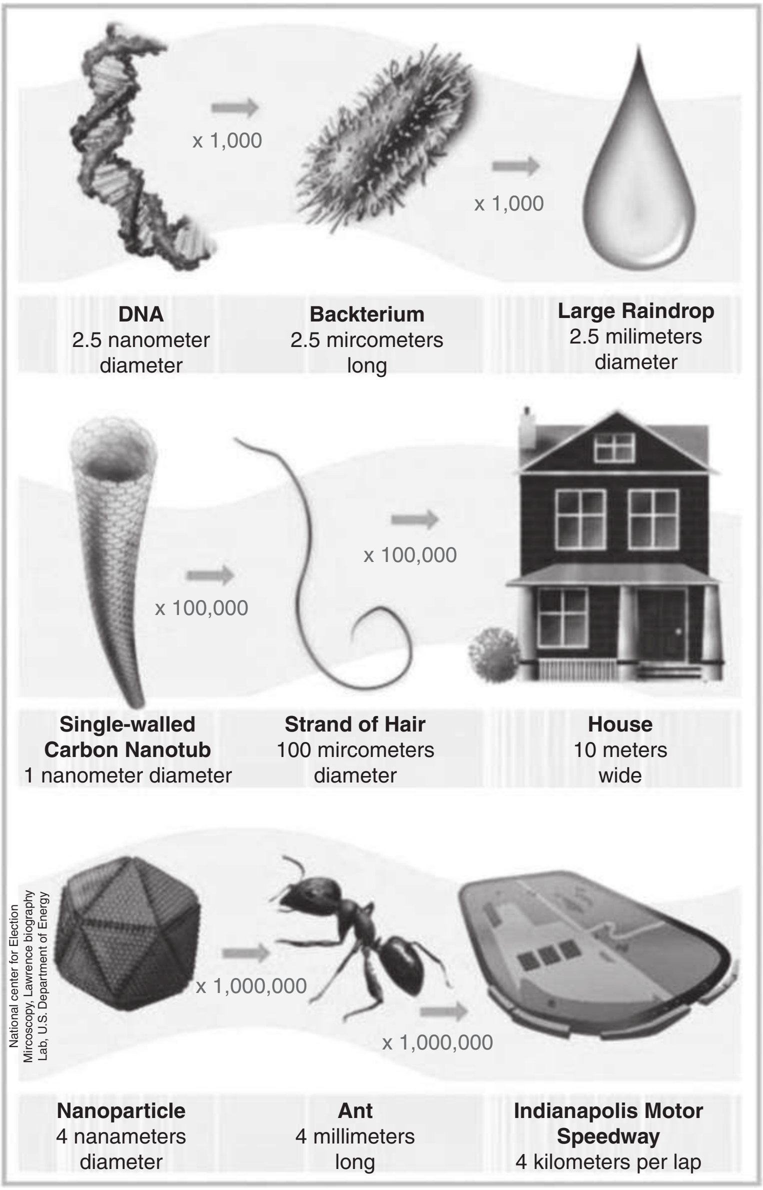

Figure 1.2. Visual examples of the size and scale of nanotechnology [5].
Source: www.nano.gov.

high surface-to-volume and aspect ratios, making them ideal for use in polymer nanocomposites.

Wave-like properties of electrons inside matter and atomic interactions are influenced by materials' variations in nanoscale length. By creating nanoscale structures it is possible to control the fundamental properties of materials, such as their melting temperature, magnetic properties, charge capacity, and even their color, without changing the nanoscale structures' chemical composition. This will lead to

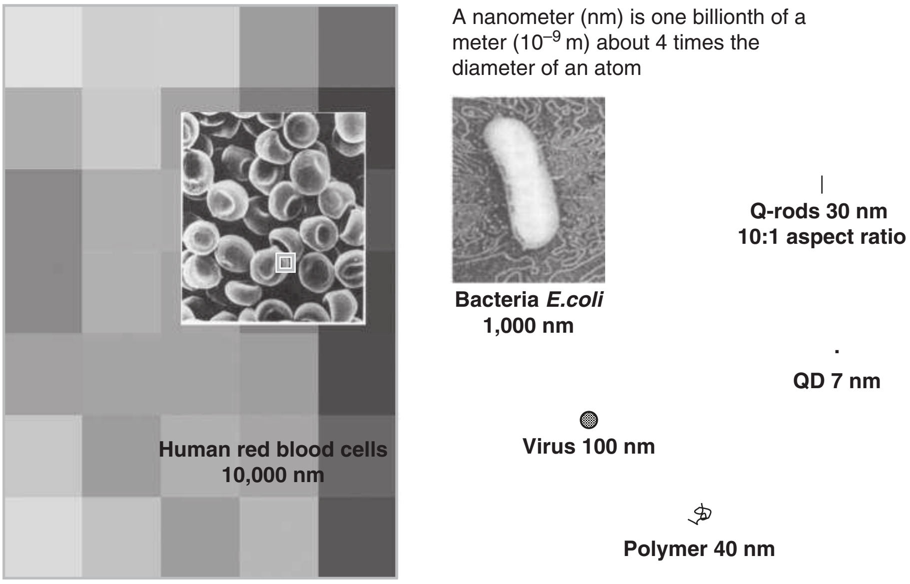

Figure 1.3. What "nano" really means? (Courtesy of R. Vaia).

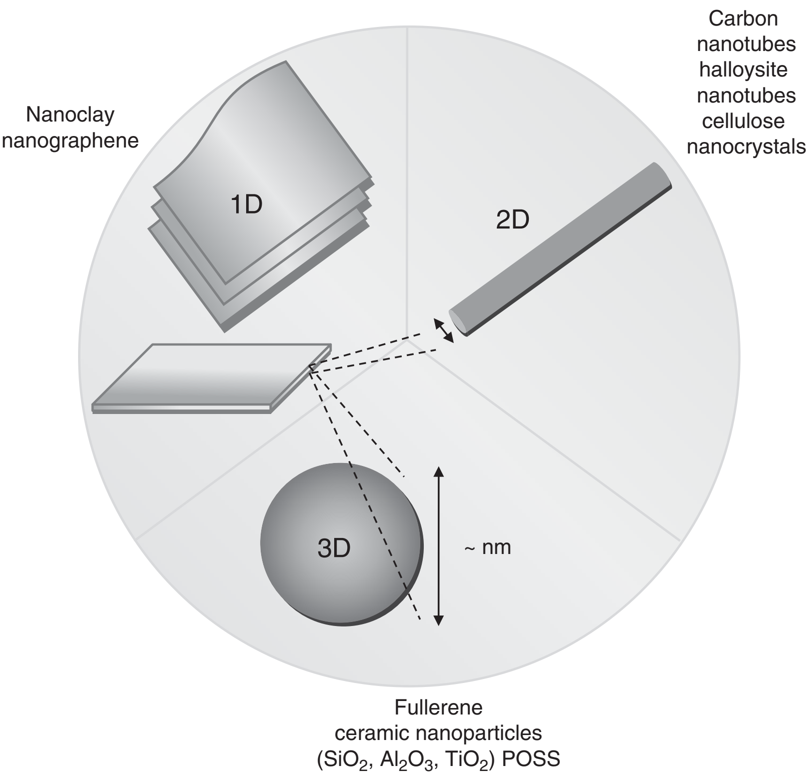

Figure 1.4. Schematic showing 1D, 2D, and 3D nanoscaled dimensions.

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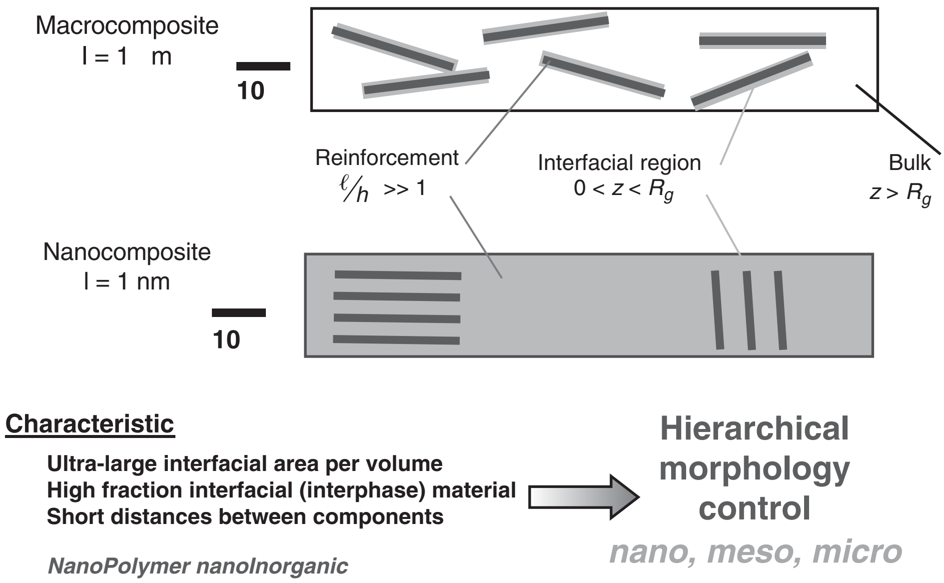

Figure 1.5. Nanoscale materials uniqueness (Courtesy of R. Vaia).

new, high-performance polymers and nanotechnologies that were impossible previously. Nanoscale structures, such as nanoparticles, have very high surface-to-volume and aspect ratios, making them ideal for use in polymer nanocomposites.

For the past five decades, we have been working with macrocomposites, such as filled polymers or fiber-reinforced polymer matrix composites, where the length scale of the polymer fillers or the fiber diameters is in micrometers, as shown in Figure 1.5. The reinforcement length scale is in micrometers, and the interface of fillers is close to the bulk polymer matrix. For the past two decades, we have been discovering nanocomposites, where the length scale of the reinforcement (nanoparticles) is on the nanometer scale (Figure 1.5). These nanocomposites have *ultra-large interfacial area per volume*, and the distances between the polymer and filler components are extremely short. Polymer coils and chains are 40 nm in diameter, and the nanomaterials are on the same order of magnitude as the polymer. As a result, molecular interaction between the polymer coils/chains and the nanomaterials will give polymer nanocomposites very unusual material properties that conventional polymers do not possess.

Before discussing the properties of nanomaterials, it may be advantageous to describe an example demonstrating the elementary consequences of the small size of nanoparticles [9]. The first and most important consequence of a small particle size is its huge surface area, and in order to obtain an impression of the importance of this geometric variable, the surface-over-volume ratio should be addressed. Assuming a particle is spherical, the surface a of one particle with diameter D is $a = \pi D^2$, and the corresponding volume v is $v = \pi D^3/6$. Therefore, the surface/volume ratio is

$$R = a/v = 6/D \tag{1.1}$$

This ratio is inversely proportional to the particle size, and as a consequence, the surface increases with decreasing particle size. The same is valid for the surface per mol A, a quantity that is extremely important in thermodynamic considerations.

$$A = na = M/(\rho\pi D^3/6)\ \pi D^2 = 6M/\rho D \tag{1.2}$$

In Equation (1.2), n is the number of particles per mol, M is the molecular weight, and ρ is the density of the material. Similar to the surface-over-volume ratio, the area per mol increases inversely in proportion to the particle diameter. Hence, huge values of surface area are achieved for particles that are only a few nanometers in diameter.

The unique properties and improved performance of nanomaterials are determined by their sizes, surface structures, and interparticle interactions. The role played by particle size is comparable to the role of the particle's chemical composition, adding another parameter for designing and controlling particle behavior. To fully understand the impacts of nanomaterials in nanoscale science and technology, one needs to learn why nanomaterials are so special!

The excitement surrounding nanoscale science and technology provides unique opportunities to develop revolutionary materials. Nanoscale science and technology is a relatively young field that encompasses nearly every discipline of science and engineering. Nanoscale structures are a new branch of materials research attracting a great deal of attention because of its potential applications in chemical catalysis, computing, imaging, material synthesis, medicine, printing, and many other fields.

1.5 How Polymer Nanocomposite Works?

The advent of academic, government, and industrial nanotechnology research has spurred significant growth opportunities for nanocomposites for the consumer, defense, aerospace, and health industries [12–15]. This is evident from the number of journal papers reporting on nanotechnology scientific research, and the number of patents issued by the U.S. Patent and Trademark Office (PTO) grew significantly in the past thirty years. It has been reported that from 2005 to 2006, the U.S. PTO issued 4,081 nano patents involving 9,491 inventors representing 34 countries [13]. This is a good indicator of how widespread the nanotechnology research activities have been across several disciplines. This book mainly focuses on a branch of nanotechnology research involving only the polymers, specifically polymer nanocomposites (PNCs).

The major objective of PNC research is to explore the different methods to achieve significant enhancement of properties over those of the traditional matrix polymers using only a small fraction of nanomaterials. The nanomaterials are defined as having at least one dimension measuring less than 50 nm [15]. These nanomaterials are expected to create new physical and chemical properties beyond what traditional filled polymeric material possess. It is well known from decades-long PNC research that some nanomaterials improve only one type of property, such as mechanical, thermal, flammability, or electrical, while a selected few nanomaterials can contribute to improving multifunctional properties.

The uniqueness of these novel PNCs will enable the circumvention of classic polymer performance by accessing new properties and exploiting synergies between PNCs that only occur when the nanoscale morphology and the fundamental physics associated with a property coincide. They represent a radical alternative to traditional filled polymers. In contract to traditional polymer systems where reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers. Polymer nanocomposites consist of improved mechanical, thermal, ablation, flammability, electrical, optical, permeability, charge dissipation, chemical resistance, magnetic, catalytic, and other properties (as discussed in detail in later chapters of this book). Polymer nanocomposite can differ completely from those of its component materials, thereby opening up unprecedented technologies. A common example of currently available PNCs are carbon nanotubes, which can help enhance electrical and thermal conductivities, increase stiffness, and enhance crack deflection and toughness. Other common nanomaterials used in polymer nanocomposites are TiO_2 and ZnO for optical properties, nitrides and carbides for hardness and wear resistance, nanoclay for flammability, and nanometals for color.

The challenges in the field of PNC research are threefold. First, the identification of the proper nanomaterial-polymer pairs is essential and critical. Otherwise, the desired properties cannot be realized. Second, the nanomaterials must be nano-dispersed in the matrix polymers. Otherwise, anticipated properties cannot be achieved. Third, not all true polymer nanocomposites are cost-effective. The cost constraint largely governs the scope of current PNCs research and commercialization in industrial laboratories. Some novel, innovative academic PNC research will never be commercialized due to the prohibitive cost of nanomaterials, time-consuming processing and fabrication steps, and sometimes the lack of proper market. Of the three challenges presented in this paragraph, the first two challenges relate to academic research and the third challenge relates to industrial research concerning PNC preparation and commercialization.

In physical form, these nanomaterials (nanoparticles) are usually available as agglomerates. In the case of a platelet-type nanocomposite (see Chapter 2 for more detailed descriptions), a large number of individual platelets are held together as microscopic agglomerates by attractive forces originating in electrostatic, ionic, and van der Waals forces. The state of agglomeration of nanomaterials is usually dictated by the manufacturing methods, and the particle agglomerates serve as the starting material in the preparation of PNCs. The agglomerates, when combined with the matrix polymer in a solution or a melted state, are subjected to several dispersion forces, including shear, ultrasonic, and centrifugal, to disperse individual particles to the nanoscale in the matrix polymer (see Chapter 5 for detailed discussions). The transformation from initial microscopic particle agglomerates to individual nanoparticles by dispersion forces is among the challenges engineers and scientists have been confronting for the past two decades.

Uniform and individual dispersion of these nanoparticle agglomerates produces *ultra-large interfacial area per volume* between the nanoparticle and the matrix polymer. Polymer nanocomposites fundamentally differentiate from traditional filled polymers due to the immense internal interfacial area and the nanoscopic nature of the nanomaterials. As a result, the overall performance of PNCs cannot be understood by simple scaling rules that apply to traditional polymeric composites. New combinations of properties derived from the nanoscale structures of PNCs provide opportunities to circumvent traditional performance associated with conventional reinforced polymers, thus epitomizing the promise of PNCs.

Numerous examples can be found in the literature demonstrating substantial improvements in multifunctional properties of PNCs. Its value comes from providing value-added properties not present in the neat resin, without sacrificing the inherent processability and mechanical properties of the neat resin. The preparation of a blend or composite with multifunctionality requires a trade-off between desired performance, mechanical properties, cost, and processability. The term "nanocomposite," when used to describe properties comparisons, is intended to relate to traditional unfilled and filled polymers and not fiber-reinforced polymer matrix composites (PMCs). Polymer nanocomposites may provide matrix resins with "multifunctionality," but they should not be considered in the near and intermediate term as a potential replacement for current state-of-the-art carbon fiber–reinforced PMCs.

1.6 Strengths and Weaknesses of Nanoparticles

This is a relatively young field that has huge growth potential. In the last twenty to thirty years, extensive research has been conducted in understanding how nanoparticles affect the chemical nature of compounds and their overall effect on a material's properties. The most dramatic effect noticed is that when working on this level, the surface area of the nanoparticle is tremendous for its size. In a study conducted by the University of Rostock and the Fritz Haber Institute of the MPG in Germany [16], the surface area and diameter of gold catalyst nanoparticles were measured. Six samples of nanoparticles were synthesized, varying in shape: icosahedral, cuboctahedral, decahedral, truncated octahedron, and spherical. Given this small size and these various shapes, these nanoparticles have very large surface areas. The surface area is inversely proportional to the diameter of the nanoparticle. In this study, the smallest particles averaging 1.6 nm in diameter had a surface area of 173 m^2/g. If a hefty spoonful – about 2.5 grams – of this nanoparticle were flattened out, it could cover an entire basketball court. With a large surface area per volume, a nanoparticle is able to make numerous bonds with the surrounding molecules, far more than a particle on the micron scale. The ability to form so many bonds leads the nanoparticles to create an extremely solid molecular structure that, in turn, increases the mechanical properties of materials. Due to having a large surface area-to-volume ratio, fewer nanoparticles can be incorporated in materials that are able to outperform the same materials made by conventional mean using the micron scale.

Although nanoparticles have many strengths, there are some drawbacks. Although the cost of creating nanoparticles has declined within the last few years, it is still high. Mass-producing nanoparticles is a difficult task. Taking the production