WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 6.805
Volume 5, Issue 6, 661-681. Review Article ISSN 2277– 7105

NANOCOMPOSITES: PROPERTIES AND NEW APPLICATION OPPORTUNITIES

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Article Received on
04 April 2016,
Revised on 24 April 2016,
Accepted on 15 May 2016
DOI: 10.20959/wjpr20166-6345

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ABSTRACT

Nanocomposites, a high performance material exhibit unusual property combinations and unique design possibilities. With an estimated annual growth rate of about 25% and fastest demand to be in engineering plastics and elastomers, their potential is so striking that they are useful in several areas ranging from packaging to biomedical applications. In this unified overview the three types of matrix nanocomposites are presented underlining the need for these materials, their processing methods and some recent results on structure, properties and potential applications, perspectives including need for such materials in future space mission and other interesting applications together with market and safety aspects. Possible uses of natural materials such as clay based minerals, chrysotile and lignocellulosic fibers are highlighted. Being environmentally friendly, applications of nanocomposites offer new technology and business opportunities for several sectors of the aerospace, automotive, electronics and biotechnology industries.

KEYWORDS: composites, layered compounds, polymers, metals, ceramics.

1. INTRODUCTION

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometre range (1 nm = 10^{-9} m)[1]. Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached[2], even though the first inference on them was reported as early as 1992[3].

The number of published papers containing words such as nanoscience, nanotechnology, nanomaterials, etc., doubled in 1.6 years[4] in the late 1990s. Also, a literature survey made by the authors reveals that about 13.420 papers (of which 4028 contain the keywords nanocomposite and polymer in Web of Science-ISI: updated on 10 February 2009) have been published on nanocomposites in the last two decade (1988 2008). Similarly, patents with complete document on nanocomposites account for about 4663 during the same period as per Scirus www.scirus.com). Additionally, specific conferences and special issues of some journals have been devoted exclusively to the emerging science and technology of nanomaterials.

It has been reported that changes in particle properties can be observed when the particle size is less than a particular level, called 'the critical size' (Table 1)[5]. Additionally, as dimensions reach the nanometre level, interactions at phase interfaces become largely improved, and this is important to enhance materials properties. In this context, the surface area/volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure-property relationships. Further, discovery of carbon nanotubes (CNTs) in 1991[6] and their subsequent use to fabricate composites exhibiting some of the unique CNT related mechanical, thermal and electrical properties[7-9] added a new and interesting dimension to this area. The possibility of spinning CNTs into composite products and textiles[10] made further inroads for the processing and applications of CNT-containing nanomaterials. Nowadays, nanocomposites offer new technology and business opportunities for all sectors of industry, in addition to being environmentally friendly[11].

Table 1. Feature sizes for significant changes in properties reported in nanocomposite systems [reproduced from reference 5 with the kind permission of the author and the Japan Society of Powder and Powder Metallurgy].

Properties	Feature size (nm) at which changes might be expected
Catalytic activity	<5
Making hard magnetic materials soft	<20
Producing refractive index changes	<50
Producing super paramagnetism and others electromagnetic phenomena	<100
Producing strengthening and toughening	<100
Modifying hardness and plasticity	<100

As in the case of microcomposites, nanocomposite materials can be classified, according to their matrix materials, in three different categories as shown in Table 2.

Ceramic Matrix Nanocomposites (CMNC); Metal Matrix Nanocomposites (MMNC) and Polymer Matrix Nanocomposites (PMNC).

Table 2. Different types of nanocomposites.

Class	Examples
Metal	Fe-Cr/Al_2O_3, Ni/Al_2O_3, Co/Cr, Fe/MgO, Al/CNT, Mg/CNT
Ceramic	Al_2O_3/SiO_2, SiO_2/Ni, Al_2O_3/TiO_2, Al_2O_3/SiC, Al_2O_3/CNT
Polymer	Thermoplastic/thermoset polymer/layered silicates, polyester/TiO_2, polymer/CNT, polymer/layered double hydroxides.

Nanocomposite systems, including those reinforced with CNTs, have been extensively studied since the 1990s and, accordingly, there has been a steady and continuous increase in the number of publications on the subject, including reviews from time to time[2,12-35]. In spite of this growth, the majority of the reviews describe the current status of only one type of nanocomposite. Thus, there are only two reviews on CMNC[16,32] and three on CNT-reinforced nanocomposites[17,20,27] and a quite large number on PMNC[16,18,19,21,28-35]. In the case of PMNC, reviews deal with processing aspects, including those on layered silicates[18,26], conducting and biodegradable polymer-based systems[19,34,35], fibre reinforced[17,20] and structure/morphology/property aspects[16,35], as well as with applications and perspectives, including key opportunities and challenges in the development of structural and functional fibre nanocomposites[18,26,29].

Conducting polymer-based composites are novel materials with less than a decade of history. It is believed[19] that the total control of the whole conducting polymer-based composite system and the optimisation of their physical properties (such as electrical conductivity and colloidal stability) are yet to be achieved, while both their commercial availability in the near future and a big leap forward for materials science are expected with their appropriate utilization. In the case of biodegradable polymer-based nanocomposites, recent developments in preparation, characterization and properties, including crystallization behaviour and melt rheology, of both the matrix and the layered (montmorillonite) nanocomposites have been discussed[34,35]. Similarly, an emphasis on toughness and interfacial bonding between CNTs and polymer matrices is critically discussed[27] to underline the stress transfer from the matrix and the potential of these composites for possible macro scale CNT-polymer production. Here, problems encountered so far are considered, and hints given regarding a critical volume fraction of CNTs to get appropriate strengthening (as observed in microcomposites); possible failure mechanisms in such composites are also presented. Finally, to the best of our knowledge, and in view of the very limited work on metal-based nanocomposites including the ones with CNT reinforcements, no review is available to-date on this system.

Considering these facts and also the absence of a more general review comprising the three different kinds of nanocomposites (metal-, ceramic- and polymer-based), this paper gives an overview of them, including those with incorporation of CNTs. However, while doing so only a few relevant publications[2,4,7-9,11,14-308] are considered here. The main features, current status and recent developments in the area are provided, focussing on the preparation methods, structure, properties and applications of these systems to avoid repetition. Also, the potential uses of nanocomposites and the opportunities they provide, along with perspectives for the future and market and safety aspects are also presented. Nanocomposite coating is not covered, in order to keep the focus of the review.

1.1. Potentials and opportunities in nanocomposites

Before going into details regarding processing, structure, properties and applications of the three types of nanocomposites, let us look at the potentials of these systems and the general opportunities they provide. Ceramics have good wear resistance and high thermal and chemical stability. However, they are brittle. In this context, the low toughness of ceramics has remained a stumbling block for their wider use in industry. In order to overcome this limitation, ceramic-matrix nanocomposites have been receiving attention, primarily due to the significant enhancement on mechanical properties which can be achieved. For example, the incorporation of energy-dissipating components such as whiskers, fibres, platelets or particles in the ceramic matrix may lead to increased fracture toughness[309-311]. The reinforcements deflect the crack and/or provide bridging elements, hindering further opening of the crack. In addition, the incorporated phase undergoes phase transition in conjunction with the volume expansion initiated by the stress field of a propagating crack, contributing for the toughening and strengthening processes, even in nanocomposites[36].

The potential of ceramic matrix nanocomposites (CMNC), mainly the Al_2O_3/SiC system, was revealed by the pioneering work of Niihara[37,38]. Most studies reported so far have confirmed the noticeable strengthening of the Al_2O_3 matrix after addition of a low (i.e. ~10%) volume fraction of SiC particles of suitable size and hot pressing of the resulting mixture. Some studies have explained this toughening mechanism based on the crack-bridging role of the nanosized reinforcements[39]. Consequently, the incorporation of high strength nanofibres into ceramic matrices has allowed the preparation of advanced nanocomposites with high toughness and superior failure characteristics compared to the sudden failures of ceramic materials[40].

Metal matrix nanocomposites (MMNC) refer to materials consisting of a ductile metal or alloy matrix in which some nanosized reinforcement material is implanted. These materials combine metal and ceramic features, i.e., ductility and toughness with high strength and modulus. Thus, metal matrix nanocomposites are suitable for production of materials with high strength in shear/compression processes and high service temperature capabilities. They show an extraordinary potential for application in many areas, such as aerospace and automotive industries and development of structural materials[41]. Both MMNC and CMNC with CNT nanocomposites hold promise, but also pose challenges for real success.

Polymer materials are widely used in industry due to their ease of production, lightweight and often ductile nature. However, they have some disadvantages, such as low modulus and strength compared to metals and ceramics. In this context, a very effective approach to improve mechanical properties is to add fibres, whiskers, platelets or particles as reinforcements to the polymer matrix. For example, polymers have been filled with several inorganic compounds, either synthetic or natural, in order to increase heat and impact resistance, flame retardancy and mechanical strength, and to decrease electrical conductivity and gas permeability with respect to oxygen and water vapour[25]. Furthermore, metal and ceramic reinforcements offer striking routes to certain unique magnetic, electronic, optical or catalytic properties coming from inorganic nanoparticles, which add to other polymer properties such as processibility and film forming capability[42]. Using this approach, polymers can be improved while keeping their lightweight and ductile nature[31,43-47]. Another important aspect is that nanoscale reinforcements have an exceptional potential to generate new phenomena, which leads to special properties in these materials as will be seen later. It may be pointed out that the reinforcing efficiency of these composites, even at low volume fractions, is comparable to 40-50% for fibres in microcomposites[34].

Addition of reinforcements to a wide variety of polymer resins produces a dramatic improvement in their biodegradability. This underlines a good example of polymer matrix nanocomposites [PMNC] as promising systems[24] for ecofriendly applications. Besides, future space mission concepts involve large ultra lightweight spacecrafts termed "Gossamer"[48]. The materials required for such spacecrafts should possess and maintain a specific combination of properties for over a long period (10-30 years) in relatively harsh environments such as 173 to 373 K for satellites and cycling temperatures of 1273 K for re-entry vehicles, exposure to atomic O_2 and solar radiation. Some of the Gossamer spacecraft devices are movable mechanical parts such as gears and gyroscopes, and others include solar arrays/sails, antennae and drives, sunshields, rovers, radars, solar concentrators, and reflector arrays. It is reported[48] that these parts will have to be fabricated from flexible, appropriate materials, which can be folded or packaged into small volumes, similarly to those available in conventional launch vehicles, and should possess many of the common mission concepts. This is needed since the structure consisting of ultra lightweight parts would be deployed mechanically or by inflation into a large ultra-lightweight functioning spacecraft once it achieves the required orbit. It is imperative that the above mentioned characteristics should be available in one single material. Metal oxide-incorporated polymer nanocomposites seem to meet these requirements. It is expected that such spacecrafts offer a significant cost advantage compared to on-orbit construction, and the large size can enable some unique missions. Similarly, rocket propellants are prepared from a polymer-Al/Al_2O_3 nanocomposite to improve ballistic performance[306]. In addition, recent information on nanomaterials, nanoindustries and a host of possible A to Z applications of polymer nanocomposites have been reported[312].

On the other hand, even after a decade of research[27], CNTs have not fully realized their potentials as nanoscopic reinforcements[313-334] in polymer matrices. Thus great challenges and opportunities are still expected for the system. These are based on the following:

a) CNTs with small number of defects per unit length possess[27] 500 times more surface area per gram on the basis of equivalent volume fraction of a typical carbon fiber, high aspect ratio (~1000), very high tensile properties and electrical and thermal conductivities (more details are given in the next section).

b) Research on CNT-related areas has been most active, with publications doubling within six months[335]. Even the patenting activity in this area has been impressive, with about 3,000 applications filed from 2001 to June 2006 as per the literature survey.

c) Because of their hollow nature, CNTs can be opened and filled with a variety of materials including biological molecules[335], generating technological opportunities. Added to this, the challenges in obtaining homogeneous dispersions and strong interfacial interactions, which can be better done by surface grafting/functionalizations, make the use of CNTs in composites more intriguing[49].

d) Various applications of CNTs in composites have been reported extensively[30,33,313-334].

e) The possibility of spinning polymers to obtain textiles[10] certainly constitutes a great promise for their extended use in a variety of applications, particularly in the electronic and thermal management sectors.

f) Nanoreinforcements with biodegradable polymers have a high potential for the design of environmentally friendly 'green materials' for future applications.

On the whole, opportunities and rewards appear to be great with nanocomposites and hence there is a tremendous worldwide interest in these materials.

Properties

The structure of nanocomposites usually consists of the matrix material containing the nanosized reinforcement components in the form of particles, whiskers, fibres, nanotubes, etc.[93] Different investigators have employed various equipments and techniques for the characterization of nanocomposites, including atomic force microscopy (AFM), scanning tunnelling microscopy (STM), Fourier transformed infrared spectroscopy (FTIR), X ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), scanning and transmission electron microscopy (SEM/TEM), etc. For example, AFM is a powerful tool to study the surface even down to the nanometre scale, as evident from the work of Veith et al.[303,304]. Simultaneous small angle X ray scattering (SAXS) and X ray diffractometry (XRD) studies have been recently used for quantitative characterization of nanostructures and crystallite structures in some nanocomposites[34,307,308]. In addition, theoretical calculations/simulations have been worked out to predict strength properties, including stress/strain curves[41,52,166,169,207-212,290,291].

Before discussing structure and properties of nanocomposites, including those containing CNTs, a brief description of CNTs will be made here[313-334], because of their unique properties compared to other reinforcements. Briefly, the density of SWCNTs is less than one sixth of that of steel[335] while the density of MWCNT is one half of that of Al[30]. Tensile strengths of SWCNT and MWCNTs are reported[313 316,335] to be in a range much higher than of high strength steel, while Young's modulus values are comparable to those of diamond. They exhibit tremendous resilience, in that they can sustain bending to large angles and restraightening without damage, in which they differ from the plastic deformation of metals and the brittle fracture of carbon fibres. Similarly, theoretical thermal and electrical conductivities are comparable with that of diamond, with an almost negligible thermal expansion coefficient[30]. They also exhibit high thermal stability both in air and in vacuum, compared to the lower values obtained for metal wires in microchips, and high parallel and perpendicular magnetic susceptibilities. Theoretical surface area values of these materials are ca. 3,000 m^2/g[318-321], while the experimentally reported values vary depending on the gas used during the measurements. This information is summarized in Table 7.

Ceramic matrix nanocomposites

Ceramics are usually brittle and easily fractured as consequence of crack propagation. There have been attempts to make ceramics suitable for engineering applications through the incorporation of a ductile metal phase or another ceramic into the matrix. This leads to improved mechanical properties such as hardness and fracture toughness, which occur as a result of the relationship between the different phases, matrix and reinforcements, at the phase boundaries throughout the material. The surface area/volume ratio of the reinforcement materials is of fundamental importance in the understanding of the structure-property relationship in CMNCs. We shall therefore first discuss these improvements in some ceramic-based nanocomposites and relate them with the observed morphologies.

Ceramic matrix-discontinuous reinforcement nanocomposite systems

Table 8 shows examples of ceramic nanocomposites and of the observed improvements in their properties compared to the respective monolithic materials. Table 9 compares the mechanical properties of the Al_2O_3/SiC system and its microcomposite counterpart[39,103-105].

Table 8. Examples of ceramic matrix nanocomposites and their properties.

Matrix/Reinforcements	Properties	Reference
Si_3N_4/SiC	Improved strength and toughness	97
$MoSi_2/ZrO_2$	-	98
B_4C/TiB_2,	-	99
Al_2O_3/SiC	-	38
MgO/SiC	-	37
Mullite/SiC	-	100
Al_2O_3/ZrO_2	-	101
Al_2O_3/Mo, Al_2O_3/W	-	102
$Al_2O_3/NdAlO_3$	Improved photoluminescence	73

Table 9. Properties of Al_2O_3/SiC nano- and microcomposites[39, 103].

Properties/Material	Al_2O_3/SiCp composite	Al_2O_3/SiCp nanocomposite
Vickers Hardness [GPa]	-	22
Young's Modulus [GPa]	-	383
Fracture Strength [MPa]	106-283	549-646
Fracture Toughness [MPam$^{1/2}$]	2.4-6.0	4.6–5.5

It can be seen from these tables that there is a significant improvement in the strength of the nanocomposite compared with its micro counterpart. The fracture strength, as an example, is noticeably higher because of the higher interfacial interaction between the particles in nanocomposites. Besides, Al_2O_3-5 to 15% SiC systems exhibited[90] superficial grooves of plastic deformation compared to the intergranular fracture observed in monolithic materials. There was no time-dependant wear transition for these composites even at loads of 20-100 N, but pre-transition wear rates of 1-2 x 10^{-8} mm/Nm were observed for both the monolithic and composite materials. The specific wear rate decreased with sliding distance. This enhancement of properties observed in ceramic nanocomposites can also be illustrated by the Si_3N_4/SiC system (Table 10)[106,107].

Table 10. Fracture strength and fracture toughness for Si_3N_4/SiC nano- and microcomposites[106, 107].

Properties/Material	Si_3N_4/SiC composite	Si_3N_4/SiC nanocomposite
Fracture Strength [MPa]	700	1300
Fracture Toughness [MPam$^{1/2}$]	5.3	7

It can be seen that the nanocomposite presents significant improvements in fracture strength and toughness, high temperature strength and creep resistance compared with its micro counterpart and to the monolithic matrix component. For example, the Si_3N_4/30% SiC system has strength of 1080 MPa up to 1673 K, whereas the strength of the monolithic sample decreases considerably at high temperatures. Furthermore, at 1673 K and tension of 200 MPa, Si_3N_4 fails after 0.4 hours at 0.3% strain, whereas the Si_3N_4/10% SiC nanocomposite does not fail even after 1,000 hours at 1.5% strain.

Applications of Nanocomposites

From the foregoing, it becomes evident that nanocomposites may provide many benefits such as enhanced properties, reduction of solid wastes [lower gauge thickness films and lower reinforcement usage] and improved manufacturing capability, particularly for packaging applications. Tables 21 to 23 present potential applications of ceramic-, metal- and polymer-based nanocomposites, respectively. As it can be observed, the promising applications of nanocomposite systems are numerous, comprising both the generation of new materials and the performance enhancement of known devices such as fuel cells, sensors and coatings. Although the use of nanocomposites in industry is not yet large, their massive switching from research to industry has already started and is expected to be extensive in the next few years. For instance, the $(Al_{1-x}Ti_xN)/\alpha\text{-}Si_3N_4$ super hard nanocomposite, which has been developed by the Czech company SHM Ltd. as a tribological coating for tools, is suitable for hard and dry cutting operations such as drilling, turning and milling, and is reported to be now industrialized[337,339]. In this case, a novel method, which employs vacuum arc coating with a rotating cathode, is used for commercial production. This super hard $(Al_{1-x}Ti_x)N/\alpha\text{-}Si_3N_4$ possess high tensile strength, in the range of 10-110 GPa, and a lifetime 2-4 times higher than that of the materials currently employed as wear resistant coatings.

Similarly, one of the leading application areas is the automotive sector, with striking impact due to improved functionalities such as ecology, safety, comfort, etc. Details on the commercial usage of nanocomposites in automotives and future developments in this sector (including CNT-based nanocomposites) are now available[362]. For instance, there are reports on the current use of a number of nanocoatings in different parts of Audi, Evobus and Diamler Chrysler automobiles, as well as ongoing trials on fuel cells, porous filters (foams) and energy conversion components, which include nanoTiO_2-containing paints. Additionally, light weight bodies made of metal- or polymer-based nanocomposites with suitable reinforcements are reported to exhibit low density and very high strength (e.g. carbon Bucky fibers, with strength of 150 GPa and weight ≈ $1/5^{th}$ of steel). Also, two-phase heterogeneous nanodielectrics, generally termed dielectric nanocomposites, have wide applications in electric and electronic industries[338].

Metal and ceramic nanocomposites are expected to generate a great impact over a wide variety of industries, including the aerospace, electronic and military[305], while polymer nanocomposites major impacts will probably appear in battery cathodes[6,342], microelectronics[343], nonlinear optics[344], sensors[345], etc. Improved properties include significant enhancements in fracture strength (about 2 times) and toughness (about one half time); no time dependent wear transitions even at very low loads; higher high temperature strength and creep resistance; increased hardness with increasing heat treatment temperature;

hardness values higher than those of existing commercial steel and alloys; possibility of synthesis of inexpensive materials; and significant increase in Young's modulus [about 105%], shear modulus and fracture strength (almost 3 times compared to microcomposites). These are brought out mainly by the nanosize reinforcements used, which result in an appropriate morphology for the products. Tables 21 and 22 summarize the possible developments associated with these materials in catalysts, sensors, structural materials, electronic, optical, magnetic, mechanical and energy conversion devices suggested by researchers in the field.

Table 22. Potential applications of metal nanocomposite systems.

Nanocomposites	Applications
Fe/MgO	Catalysts, magnetic devices.
Ni/PZT	Wear resistant coatings and thermally graded coatings.
Ni/TiO_2	Photo-electrochemical applications.
Al/SiC	Aerospace, naval and automotive structures.
Cu/Al_2O_3	Electronic packaging.
Al/AlN	Microelectronic industry.
Ni/TiN, Ni/ZrN, Cu/ZrN	High speed machinery, tooling, optical and magnetic storage materials.
Nb/Cu	Structural materials for high temperature applications.
Fe/$Fe_{23}C6$/Fe_3B	Structural materials.
Fe/TiN	Catalysts.
Al/Al_2O_3	Microelectronic industry.
Au/Ag	Microelectronics, optical devices, light energy conversion.

CNT-ceramic composites, on their turn, are reported[340] to be potential candidates for aerospace and sports goods, composite mirrors and automotive spares requiring electrostatic painting. Such materials have also been reported[341] to be useful for flat panel displays, gas storage devices, toxic gas sensors, Li^+ batteries, robust but lightweight parts and conducting paints. One example is the Al_2O_3-CNT composite, which shows high contact damage resistance without a corresponding increase in toughness and hardness. It is reported[92] to be a candidate for engineering and biomedical applications.

Despite these possibilities, there are only limited examples of industrial use of nanocomposite, mainly due to the challenges in processing and the cost involved, particularly for non-structural applications. In fact, one recent review[371] deals with various methods for the preparation of super hard coatings with merits and demerits of each method. However, the intense research in both metal- and ceramic-based nanocomposites suggests that the days are not far off when they will be actually in use. The cost factor may be a particularly serious problem for general engineering applications, while this may not be the case for specialized applications in electronics, aerospace, biomedical and other sectors, since the advantages might far outweigh costs and concerns in these sectors.

On the other hand, polymer-based nanocomposites are in the forefront of applications due to their more advanced development status compared to metal and ceramic counterparts, in addition to their unique properties. These include 2-3 fold strength property increase, even with low reinforcement content (1-4 wt. (%)) [*e.g.* 102.7% in Young's modulus] with complete elimination of voids/holes; gas barrier properties (about 200,000 times over oriented PP and about 2000 times that of Nylon-6 with tenfold requirements of expensive organic modifiers)[372], biodegradation and reduced flammability [about 60% reduction of heat release rate], etc. In addition, a good possibility of enhancing the shelf life of the existing MRE packaging and trays used in the UGR-H&S polymeric materials has also been reported[350]. This is due to the limitations of existing MRE packings, which do not meet the US military standards such as minimum shelf life of 6 and 12 months at about 322 K (120 °F) and 299 K (80 °F) respectively. In this case, nanocomposites, which exhibit better gas barrier properties, can provide a longer shelf life. Such packaging, with different matrices and reinforcements, as well as different processing conditions, is being field tested by the US army since 2002 to arrive at an optimum combination. This is expected to reduce cost by 10-30% (nearly US$ 1-3 million) compared to the presently used materials, in addition to better performance.

Various types of polymer-based nanocomposites, containing insulating, semiconducting or metallic nanoparticles, have been developed to meet the requirements of specific applications. Recently, some PLS nanocomposites have become commercially available[18], being applied[237] as ablatives and as high performance biodegradable composites[265,267,280,343,346], as well as in electronic and food packaging industries[346,347]. These include Nylon-6 (e.g. Durethan LDPU60 by Bayer Food Packages)[18] and polypropylene for packaging and injection-molded articles, semi-crystalline nylon for ultra-high barrier containers and fuel systems, epoxy electrocoating primers and high voltage insulation, unsaturated polyester for watercraft lay-ups and outdoor advertising panels, and polyolefin fire-retardant cables, electrical enclosures and housings. some examples of commercially available polymer nanocomposites. As an example, Nylon-6/surface-modified montmorillonite 2 wt. (%) nanocomposites are currently available from two commercial sources, Honeywell Engineered Polymers & Solutions and Bayer AG. Some of the products made from nanocomposites are shown in Figure 42.

Figure 42. Nanocomposite-containing products [reproduced from references 347, 351, with the kind permission of US Army Natick Soldier Center, Plastics Technology, USA, AzoNano.com, PvtLtd., USA].

Technological contributions in the areas of gas barrier, reinforcement and flame retardancy have also been extensively exploited[355,356]. For example, heat-resistant polymer nanocomposites are used to make fire fighter protective clothing and lightweight components suitable to work in situations of high temperature and stress. This includes hoods of automobiles and skins of jet aircrafts, as opposed to heavier and costlier metal alloys. They can also replace corrosion-prone metals in the building of bridges and other large structures with potentially lighter and stronger capabilities[357, 358]. Also, unsaturated polyester (UPE) nanocomposites can be employed in fibre-reinforced products used in marine, transportation and construction industries[359-361]. Currently, UPE/fibreglass nanocomposites, whose formulations are available from Polymeric Supply, Inc., are being used in boat accessories that are stronger and less prone to colour fading[362].

Regarding the variety of applications of polymer nanocomposites, prominent impacts over the automotive industry can be highlighted, including their use in tyres, fuel systems, gas separation membranes in fuel cells and seat textiles, mirror housings on various vehicle types, door handles, engine covers, intake manifolds and timing belt covers[363,364], with some of these already being exploited. For example, a thermoplastic nanocomposite containing nanoflake reinforcements (trade name Basell TPO-Nano) is being employed for the development of stiff and light exterior parts, like the step-assists by GM[348]. Also, porous polymer nanocomposites can be employed for the development of pollution filters[365]. Other promising technological application in the horizon is in air bag sensors, where nano-optical platelets are kept inside the polymer outer layer for transmitting signals at speed of light gaining milliseconds to bring down the level of possible impact injuries[373]. Finally, polymer/inorganic nanocomposites with improved conductivity, permeability, water management and interfacial resistance at the electrode are natural candidates for the replacement of traditional Nafion PEM in fuel cells, and are currently under trial[349].

Improvements in the mechanical properties of polymer nanocomposites have also resulted in their many general/industrial applications. These include impellers and blades for vacuum cleaners, power tool housings, and mower hoods and covers for portable electronic equipment, such as mobile phones and pagers[366]. Another example is the use of polymer nanocomposites in glues for the manufacturing of pressure moulds in the ceramic industry.

The development of environmentally friendly, non-foil and better packaging materials can reduce the amount of solid waste, improve package manufacturing capabilities, and reduce the overall logistics burden to users. In this context, the incorporation of nanoclay particles into thermoplastic resins has shown to be highly effective to improve barrier properties and package survivability[351]. Such excellent barrier characteristics have resulted in considerable interest in clay nanocomposites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles[367]. The use of nanocomposite formulations would be expected to enhance considerably the shelf life of many types of food. Honeywell industries have also been active in developing a combined active/passive oxygen barrier system for polyamide-6 materials[368]. It is mentioned here that Triton Systems and the US Army are conducting further work on barrier performance in a joint investigation, as mentioned earlier. They are trying to develop a non-refrigerated packaging system capable of maintaining food freshness for three years. Polymer/clay nanocomposites are currently showing considerable promise for this application.

The reduction of solvent transmission is another interesting aspect of polymer/clay nanocomposites. A study conducted by the UBE Industries has revealed[347] significant reductions in fuel transmission through polyamide-6/66 polymers by incorporation of a nanoclay filler. As a result, these materials are very attractive for the development of improved fuel tanks and fuel line components for cars. In addition, the reduced fuel transmission means significant cost reductions. The presence of filler incorporation at nanolevels has also been shown to have significant effects on the transparency and haze characteristics of films[369] in comparison to conventionally filled polymers. The ability to minimize the extent to which water is absorbed can be a major advantage for polymer materials that are degraded in moist environments[370].

Finally, CNT-polymer composites are reported[28] to be potential candidates for data storage media, photovoltaic cells and photo diodes, optical limiting devices, drums for printers, etc.

Perspectives

Outstanding potentials of nanocomposites can be exemplified by the massive investments from many companies and governments throughout the world. As a result, nanocomposites are expected to generate a great impact in world economy and business. This is very much evident from the publications pouring in, particularly on a variety of properties suited for different applications[350]. According to a report from Principia Partners, which is illustrated in Table 25, a market size of over than U$ 1,834 billion (USD) is estimated by 2009, considering only the different applications of polymer/clay nanocomposites[350]. The estimative may not be exaggerated, since many of the application areas already use these composites, with some of them being commercialized by many leading industries. Packaging, coating and automotive sectors are in the forefront for the use of these new materials.

With increasing demand for high performance systems such as nanofillers and their composites and many sectors looking for them at low costs, optimistic estimates do not seem beyond reach[372]. A bright future is evident as many leading industrial laboratories, such as Argonne National Laboratory, are ready for commercialization of their nanoproducts [organoclays] and looking for industrial partners to develop and/or test them in a wide range of applications. Many of these are consumer products, and hence the envisaged market is expected to establish itself. For example, electroconductive polymers, nanosmart switches and sensors for automotives are already in use by GE and Cabot in USA, while since 2002 General Motors has successfully used nanocomposites containing clay and talc in their exterior structural components.

Further, as new power production and storage devices are attractive products, other nanotech revolutions expected to take place in the near future are reported[373] to be hydrogen storage, fuel cells, supercapacitors and batteries. In fact, it has been pointed out that the infrastructure cost of automotives would decrease by 10-100 times by the use of fuel cells alone, with other nanotechnologies having similar impact. Future areas of research, particularly for the automotive industry could be i) improved fire retardancy of nanocomposites, which can be used as interior parts, ii) improved weatherability for use as exterior parts, and iii) bipolarity, obtained by the use of nanocarbons, for the production of fuel cells. Similarly, the coating and internal structure of combustion engines may receive attention in the case of ceramic-based nanocomposites.

Nanoclays are expected to have 50% of the total nanomaterials market by 2020. Also, with the expected decrease in cost of CNTs, their nanocomposites are also expected to gain large share in the markets, thereby leading to the rapid commercialization of CNTs themselves[374]. It is also reported that two of the sectors, automotive and packaging, which will account for about 40% of demand by 2020, will be most important for the next decade or so. Then, the construction sector will probably dominate, while CNT-based nanocomposites will replace the presently used conducting materials in the electrical and electronic industries[375].

Considering the use of polymer-based nanocomposites during 2003 at 11,000 tons (11 million kg) at US$ 90.8 million, Business Communications Co. Inc., in its report on nanocomposites published in April 2004, has estimated this market to increase by nearly 3 times (35,960 tons) at US$ 211.1 during the current year (2008), with an annual growth rate (AAGR) of 18.4%[377]. Of this, thermoplastics, which were about 5.68 million kg at US$ 70.7 in 2003, would grow to 27.74 million kg with about 20.4% AAGR at US$ 178.9 million, while thermosets, with 5.45 million kg at US$ 20.1 million, would grow to 8.22 million kg with about 9.9 AAGR at US$ 32.2 million. Even if some difficulties are to be encountered for this, present applications of these materials are expected to grow higher than 20% of the total demand of polymer composites, with the fastest demand in engineered plastics and elastomers[374,376]. On the other hand, with thermoset-based nanocomposites being not so diverse compared to their thermoplastics counterparts, their market is expected to grow at the rate mentioned above based on the current uses of these composites in pre-finished wood flooring and other sectors.

There are other forecasts for US such as the ones from Freedonia Industry, which reports on the profiles of major industries in the area of nanocomposites in USA, market trends and indicators for these materials for every five years from 2010[375]. According to them, the demand for nanocomposites will be about 159 million kg by 2010 and about 3.2 billion kg, valued at US$ 15 billion, by 2020. The other estimate[376] for the global nanocomposite market rises to US$ 250 million with AAGR between 18-25% by 2008. It is also reported[374] that the packaging industry alone would use about 1.7 million kg of polymer nanocomposites in the beverage and food industries by 2009, and that this will grow to about 45 million kg. All the above mentioned projections, though varying marginally, may not be exaggerated in view of the research options made by some of the developed countries, with USA leading with 400 research centres and industries with investments to the tune of US$ 3.4 billion, Europe with 175 organizations/industries with about US$ 1.7 billion and Japan with 100 organizations[350].

Some of the challenges to be faced for the success of the above projections, which will also give future research directions, include: suitable reinforcements such as nanofibres with or without spinning, which will have higher strength properties, being lighter than their micro counterparts and hence appearing as superior structural components; use of nanofibres in different areas such as biomedical, electrical and optical, for various functional devices; conducting polymer-based nanomaterials for electrochemical applications; modification of the mechanical behaviour of nanocomposites to get higher performances; surface modification of polymer nanofibres for their use in polymer matrices to overcome the poor interfacial bonding; modelling and simulation of mechanical properties of nanofibre-containing composites, etc.[377].

Other issues, which are also expected to get due attention, include various processing parameters in the case of the three types of nanocomposites, without which their wide spread commercialization would not come through. These include problems with compatibility and de-agglomeration, which can be overcome through surface modification of reinforcements for homogeneous dispersion without agglomeration. The above, along with appropriate positioning of reinforcements [exfoliation and orientation] in the case of polymer-based composites are also issues to be solved.

Other promising area for future research on proper inexpensive reinforcements is the use of cheap and abundantly available polymeric (maybe recyclable) and reinforcing materials of natural origin for wide applications. If the latter can replace expensive carbon nanotubes, the cost of their nanocomposite products may be reduced to extend them to popular applications. Hence, concentrated efforts will be needed to find new formulations with materials from renewable resources (such as polymers derived from plasticized saccharides, polylactide (PLA), polyhydroxylalkanoates (PHAs), poly (ε -caprolactone), etc.), reinforced with easily available mineral/vegetal materials or synthetic reinforcements based on common elements like hydroxides, layered double hydroxides and layered hydroxide salts. The same procedure can also be used to improve the properties of synthetic biodegradable polymers. Research in these directions will be a certainty, keeping in view the increased attention on cleaner environment and ecology.

The study of nanocomposites is an interdisciplinary area, encompassing physics, chemistry, biology, materials science and engineering. Therefore, the knowledge arising from scientists with different backgrounds will undoubtedly create new science, and in particular new materials, with unforeseen technological possibilities such as creation of macroscopic engineered materials through nanoscale structures. It is therefore rightly pointed out that this calls for basic research on structure-property correlations in nanocomposites, leading to new challenges in the development of suitable fabrication techniques for dealing with nanoscale materials, for their characterization and mechanics, in order to understand interactions at such sizes[30]. Another exciting aspect is that nanocomposites will benefit many sectors of our society, including electronics and chemical, space and transportation industries, as well as medicine, health care and environmental protection. Because of this, nanocomposites are expected be of high impact in the improvement of our quality of life in the coming years.

As the properties of nanostructured composites are highly structure/size dependent, many research studies still have to be performed to provide a better understanding of the structure-property relationship in such systems. This is an essential requirement to allow the nanoscale design of multi-functional materials for engineering applications. In this regard, critical issues to be looked into include aspects of dispersion, alignment, volume and rate of fabrication and, finally, cost effectiveness. Some light has been thrown on these aspects[30]. Probably, processing-structure-properties maps similar to those developed for metals and alloys by Ashby[379] may further enhance the potentials of nanocomposites. This is because structure, which is dictated by the processing method, in turn dictates the properties of materials. Added to this is the engineering aspect of design.

For materials scientists, design could be one of the following[380]: i) design of materials having combinations of unique properties or ii) selection of materials having better characteristics for a specific purpose or iii) development of a new process for providing one of the above mentioned materials. Besides, in engineering a term called 'performance index' (P) is defined, which correlates the properties of materials for a given product, and helps in their selection for specific applications. The higher the value of P, the better will be the performance[380]. Further, another correlation generally used is between the relative cost and the performance index, whereby one can arrive at the economical material selection for a given product. The above concepts should also be applied in the case of nanocomposites, so that one could get the maximum benefit from them in any application.

Finally, as part of the social implications of this nascent and potential technology, there are some safety aspects to be considered while dealing with nanosized particles and their composites. For example, fabrics coated with nanoparticles are available, which can be configured to imbue the fabric with various attributes. Aerosolised chemical and biological agents are a clear threat that is likely to grow in the future. The release of nanoparticles into the environment is a major health and safety issue. Hence there is an increasing need for research into emission of nanocomposites and nanoparticles. Potentially harmful characteristics of nanotechnology products based on their large surface area, crystalline structure and reactivity may facilitate their easy transport into the environment or interaction with cell constituents, thus exacerbating many harmful effects related to their composition. One recent conference was devoted to the study of the safety and risks of nanoparticles[381], while the U.S. Environmental Protection Agency (EPA), as part of its Science to Achieve Results (STAR) program, is seeking applications that evaluate the potential impacts of manufactured nanomaterials on human health and the environment. This is important as new nanomaterials are constantly being manufactured; there is always a possibility of human and environmental exposure to waste streams, or other pathways entering the environment[382].

CONCLUSIONS

In conclusion, new technologies require materials showing novel properties and/or improved performance compared to conventionally processed components. In this context, nanocomposites are suitable materials to meet the emerging demands arising from scientific and technologic advances. Processing methods for different types of nanocomposites (CMNC, MMNC and PMNC) are available, but some of these pose challenges thus giving opportunities for researchers to overcome the problems being encluntered with nanosize materials. They offer improved performance over monolithic and microcomposite counterparts and are consequently suitable candidates to overcome the limitations of many currently existing materials and devices. A number of applications already exists, while many potentials are possible for these materials, which open new vistas for the future. In view of their unique properties such as very high mechanical properties even at low loading of reinforcements, gas barrier and flame related properties, many potential applications and hence the market for these materials have been projected in various sectors. Thus all the three types of nanocomposites provide opportunities and rewards creating new world wide interest in these new materials.

ACKNOWLEDGEMENTS

We are grateful to all authors of the papers, publishers of the journals from where tables and figures have been reproduced [The American Chemical Society, American Institute of Chemical Engineers, American Institute of Physics, Elsevier, Institute of Physics, Japan Society of Powder, Powder Metallurgy, John Wiley & Sons, Materials Research Society, Plastics Technology Magazine, Springer-Verlag, Wiley-VCH Verlag Gmbh & Co, web sites], for their courtesy and kind permission. The authors sincerely express their gratitude to Professor Jaisa F. Soares of Department of Chemistry, UFPR for her reading of the full manuscript, editing both technical and language aspects as well for her critical suggestions. We also acknowledge Mr. Gregorio Guadalupe Carbajal Arizaga, Department of Chemistry, UFPR, Mahesh Kestur Satya, USA, for their reading of the paper and useful suggestions.

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