

REVIEW ARTICLE

Nano-composites and their applications: A review

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ABSTRACT

Nanocomposites are high performance materials which reveal rare properties. Nanocomposites have an estimated annual growth rate of 25% and fastest demand to be in engineering plastics and elastomers. Their prospective is so prominent that they are valuable in numerous areas ranging from packaging to biomedical applications. In this review, the various types of matrix nanocomposites are discussed highlighting the need for these materials, their processing approaches and some recent results on structure, properties and potential applications. Perspectives include need for such future materials and other interesting applications. Being environmentally friendly, applications of nanocomposites propose new technology and business opportunities for several sectors of the aerospace, automotive, electronics and biotechnology industries.

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1. Introduction

Nanocomposites are composites in which at least one of the phases demonstrates dimensions in the nanometre range^[1,2]. The word nanotechnology is novel but the existence of functional devices and structures of nanometer dimensions is primitive. In the fourth century, Roman glassmakers were formulating glasses encompassing nanosized metals. Nanocomposite materials have materialized as appropriate substitutes to incredulous restrictions of micro-composites. They are also testified to be the resources of 21st century in the view of having design rareness and property groupings that are not found in conventional composites^[3-5]. Nevertheless, they pose preparation challenges associated to the regulator of basic arrangement and stoichiometry in the nanocluster phase. Nanocomposites are high performance materials demonstrating rare property arrangements^[6-8]. Their potential is so conspicuous that they are beneficial in numerous areas ranging from packaging to biomedical applications. In this paper, the various types of matrix nanocomposites are presented underlining the need for these materials. Their processing methods, structure, properties and potential applications are discussed^[9,10].

Nanocomposites suggest rare properties that ascend from their small size, large surface area, and the relations of phases at their interfaces. They are striking for their prospective to develop performance of drugs, catalysts, biomaterials and other high value added materials. It has been reported that deviations in particle properties can be observed

when the particle size is less than a particular level, called 'the critical size'^[11,12]. As dimensions reach the nanometre level, interactions at phase interfaces become mostly enhanced. Additionally, unearthing of carbon nanotubes and their successive use to formulate composites demonstrating some of the unique carbon nanotubes related mechanical, thermal and electrical properties, added a new and fascinating dimension to this area. Currently, nanocomposites offer new technology and business opportunities for all zones of industry, in addition to being environmentally friendly^[13-15].

2. Prospects of nano-composites

Nanocomposites offer an exceptionally extensive range of prospective applications from electronics, optical communications and biological systems to new materials. Many possible applications have been explored and many devices and systems have been considered. More potential applications and new devices are being proposed. It is evidently impossible to recapitulate all the devices and applications that have been studied. It is interesting to note that the applications of nanocomposites in diverse fields have clearly different demands, and thus face different challenges, which necessitate different approaches^[16-18]. The reinforcements re-fract the crack and deliver connecting elements, deterring further opening of the crack. The integrated phase experiences and phase transition in conjunction with the volume increase introduced by the stress field of a propagating crack, contributing for the toughening and strengthening processes. The potential of ceramic matrix nanocomposites, chiefly the Al₂O₃/SiC system, was exposed by the revolutionary work of Niihara. The toughening mechanism was based on the crack-bridging role of the nanosized reinforcement. The merger of high strength nano-fibres into ceramic matrices has permitted the preparation of advanced nanocomposites with high toughness and superior failure characteristics compared to the sudden failures of ceramic materials^[19,20].

Space mission projects implicate ultra-lightweight space-crafts. These spacecraft devices are mobile mechanical parts such as gyroscopes, gears, solar arrays, antennae, drives, sunshields, rovers,

radars, solar concentrators, and reflector arrays. These parts will have to be manufactured from flexible, appropriate materials, which can be folded or packaged into small volumes. This is needed since the structure consisting of ultra-lightweight parts would be deployed mechanically into a large ultra-lightweight functioning. It is imperative that the above mentioned characteristics should be available in one single material. Similarly, rocket propellants are prepared from a polymer-Al/Al₂O₃ nanocomposite to improve ballistic performance^[21-23].

2.1 Processing of nanocomposites

Ceramic metallic nanocomposite matrix materials include Al₂O₃, SiC, SiN, etc., while metal matrices employed in metal matrix nanocomposites are mainly Al, Mg, Pb, Sn, W and Fe, and a whole range of polymers, e.g. vinyl polymers, condensation polymers, polyolefins, and speciality polymers are used in polymer matrix nanocomposites. Both synthetic and natural crystalline reinforcements have been used, such as Fe and other metal powders, clays, silica, TiO₂ and other metal oxides. Similarly, carbon nanotubes are prepared mostly by chemical/vapour deposition methods. In the case of carbon nanotubes, use of surfactants, oxidation or chemical functionalization of surfaces is some of the techniques employed. Physical blending and in-situ polymerization are used for improving dispersion in the case of carbon nanotube-reinforced polymer composites, while alignment of carbon nanotubes could be achieved by techniques such as ex-situ techniques^[24,25].

2.2 Structure and properties of nanocomposites

The structure of nanocomposites consists of the matrix materials, containing the nanosized reinforcement components in the form of particles, whiskers, fibres, nanotubes, etc. Various techniques have been employed to characterize the 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 calorim-

etry (DSC), scanning and transmission electron microscopy (SEM/TEM), etc. 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^[26-28].

Briefly, the density of single walled carbon nanotubes is less than one sixth of that of steel while the density of multi walled carbon nanotubes is one half of that of Al. Tensile strengths of single walled carbon nanotube and multi walled carbon nanotubes are reported 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. 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^[29-30].

2.3 Ceramic matrix nanocomposites (CMNC)

The most common methodologies for preparation of CMNC, are conventional powder method, polymer precursor route, spray pyrolysis, vapour techniques and chemical methods, which include the sol-gel process, colloidal and precipitation approaches and the template synthesis. Ceramics are usually brittle and easily fractured as consequence of crack propagation. Ceramics are made 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^[31,32].

3. Ceramic matrix-discontinuous reinforcement nanocomposite systems

tems

There is a significant improvement in the strength of the nanocomposite compared with its micro-counterpart. The fracture strength is noticeably higher because of the higher interfacial interaction between the particles in nanocomposites. Besides, Al₂O₃-5 to 15% SiC systems exhibited superficial grooves of plastic deformation compared to the intergranular fracture observed in monolithic materials. Furthermore, at 1673 K and tension of 200 MPa, Si₃N₄ fails after 0.4 hours at 0.3% strain, whereas the Si₃N₄/10% SiC nanocomposite does not fail even after 1,000 hours at 1.5% strain. Coming to morphological studies, microstructures of some ceramic matrix nanocomposites of Al₂O₃ and Fe₂O₃ contain a good distribution of Co and Ni nano-particles^[33,34].

3.1 Ceramic matrix-carbon nanotube systems

When the volume content of carbon nanotubes is lower than 5 vol. %, both bending strength and fracture toughness increase with increasing volume of carbon nanotubes. However, loadings higher than 5% cause decrease in these two properties. At 5 vol. %, the increment in strength and fracture toughness, compared with that of monolithic SiO₂, is up to 65 and 100%, respectively. This increase in mechanical properties is due to the large aspect ratio and excellent mechanical properties of carbon nanotubes, according to the theory of short fibre-reinforced composites^[35-37]. The decrease in bending strength at high loading is due to the limitation caused by carbon nanotubes during densification, as they express a higher probability for agglomeration. Also, the higher the loading of carbon nanotubes, the higher is their pull out from the matrix during stress transfer. Unusual behaviours such as high contact-damage resistance without a corresponding enhancement in toughness have also been reported in Al₂O₃/nanotube composites. The micro-hardness of these systems increases as the carbon nano-tube content is increased up to 4 wt. (%). This is probably due to grain size effects and the reinforcement role of carbon nanotubes. As the carbon nanotube content increased above 10 wt. (%), wear losses also notably increased^[38-40].

Preparation of SiC/carbon nanotubes showed a 10% upgradation in the strength and fracture toughness as compared to the monolithic ceramics. These results were attributed to nanotube/matrix debonding and crack deflection. As a consequence, many attempts have been made to improve mechanical properties through the incorporation of carbon nanotubes in ceramic matrices. However, the detected improvements were not as intense as expected. Single walled carbon nanotubes applied in the reinforcement of ceramic composites through spark-plasma sintering, resulted in a 194% increase in fracture toughness over pure alumina. A 24% increase in fracture toughness over the matrix was observed in nanograined Al_2O_3 composite containing 10 vol. % multi walled carbon nanotubes, which was attributed to the oxidation of carbon nanotubes before dispersion. In this case, the material was produced in three conditions, viz., mixed, hot pressed (1573 K) and sintered to near theoretical density^[41-43].

3.2 Metal Matrix Nanocomposites (MMNC)

The discovery of new alloys has been escorted by major developments. The bronze was initiated by the discovery that intimate mixing of copper and tin, yielded a much stronger metal than copper. Regardless of methods of synthesis, most nanocrystalline based metal-metal nanocomposites exhibit a remarkable resistance to grain growth. Thermal stability and the mechanisms involved in nanocrystalline materials are not only related to the microstructural and compositional parameters but also associated to porosity, impurity, grain size distribution, texture and microstrain resulted during the processing of nanocrystalline materials. The simple mixing of two different metal nanocomposites will transpire with new properties. Nanocomposite systems such as carbon nanotubes, have been extensively studied. There has been a continuous increase in the number of publications on the subject, including reviews from time to time. In the case of PMNC, reviews deal with processing aspects, including those on layered silicates, conducting and biodegradable polymer-based systems, fibre reinforced structure, morphology and property as-

pects as well as with applications and perspectives, including key opportunities and challenges in the development of structural and functional fibre nanocomposites^[44-46].

The techniques used for the processing of metal matrix-nanocomposites are spray pyrolysis, liquid metal infiltration, rapid solidification, vapour techniques, electrodeposition and chemical methods, which include colloidal and sol-gel processes. Fe-based nanocomposites are prepared by solidification techniques. Branagan stresses on “devitrified nanocomposite steel”. The formation of nano-phases was explained by the high nucleation frequency within the limited time for growth of grains before impingement. Use of ultrasound helped to improve the wettability between the matrix and the particles^[47-48].

3.3 Metal-discontinuous reinforcement systems

The $\alpha\text{-Fe/Fe}_{23}\text{C}_6/\text{Fe}_3\text{B}$ system provides a good example of how unique properties may arise from metal nanocomposites. Vickers hardness values of these two forms of the alloy produced by Branagan and Tang were found to be 10.3 and 11 GPa in the asolidified condition. The ribbon variety showed increased hardness with increasing heat treatment temperature, showing a maximum of 16.2 GPa at 973 K and there after decreasing to 10.5 GPa at 1123 K. This can be compared to the decreasing trend of the ingot type (8 and 6.6 GPa at 873 and 973 K respectively). The Al/SiC system also illustrates the advantages of metal nano-composites compared to their micro counterparts. There is a linear increase in hardness with increasing volume fraction of the harder phase (SiC) until the maximum value of 2.6 GPa for the sample that contains 10 vol. % of SiC. The values of Young’s and shear modulus increase significantly with increasing SiC content, suggesting the formation of a nanocomposite material containing a brittle phase (SiC) embedded in the ductile Al matrix. Al/SiC nanocomposite exhibits notably higher Young’s modulus and hardness than its micro counterpart. For example, the nanocomposite shows 12.6% increase in hardness and 105.1% in Young’s modulus. Also, Al/Pb nanocomposites exhibit improved frictional fea-

tures^[49-51].

4. Metal matrix-carbon nanotube composites

Electrical properties of an Al/carbon nanotube system measured between 4.2 K and room temperature revealed an increase from 4.9 to 6.6 $\mu\Omega$ cm at room temperature for 1 and 4 wt. (%) carbon nanotubes, but a decrease to 5.5 $\mu\Omega$ cm for 10 wt. (%) carbon nanotube), compared to the value of 3.4 $\mu\Omega$ cm for the Al matrix. At lower temperatures, resistivity of all composites decreased linearly, as in the case of metals, with an abrupt drop of about 90%. On the other hand, compression testing of these Al-carbon nanotube composites exhibited identical stress strain curves for both the composite without the precursor and pure Al, except for large elastic strain, while those with the precursor, though similar in shape, exhibited increased compression stresses. At a higher multi walled carbon nanotube loading (1.6 vol. %), proof stress increased seven fold, in contrast to a not so significant enhancement in polymer-carbon nanotube composites. The enhanced mechanical property has been attributed to the confinement of the Al matrix by the multi walled carbon nanotubes on nanoscale^[52-55].

4.1 Strengthening mechanisms in metal matrix-composites

Upon cooling, dislocations form at the reinforcement/matrix interface due to the thermal mismatch. The thermally induced dislocation punching results in indirect strengthening of the matrix. In age-hardenable matrix-materials, the thermally induced dislocations serve as heterogeneous nucleation sites for precipitate formation during the aging treatment^[56,57].

4.2 Polymer matrix-discontinuous reinforcement (non-layered) nanocomposites

The reinforcing materials engaged in the fabrication of polymer nanocomposites can be categorized according to their dimensions. Examples comprise spherical silica, metal particles and semiconductor nanoclusters. The second kind of reinforcement is formed by nanotubes or whiskers, which contain two dimensions in the nanometre

scale and one larger, forming an extended structure. Carbon nanotubes and cellulose whiskers, broadly studied as reinforcing nanofillers, can be included in this second category^[58-60]. The third type of reinforcement is characterized by only one dimension in the nanometre range. In this group, the filler contains sheets one to a few nanometres thick and hundreds to thousands nanometres long. This family is called polymer-layered nano-composites. Many synthetic and natural crystalline hosts that are able, under specific conditions, to intercalate a polymer have been described. Examples include graphite, metal chalcogenides, clays, layered silicate and layered double hydroxides. Nanocomposites based on clay and layered silicates have been usually explored due to the handiness of clay starting materials and their eminent intercalation chemistry^[61-63].

4.3 Polymer nanocomposites with layered reinforcements

Although the chemistry of polymers towards layered silicates has long been known, the field of polymer layered silicate nanocomposites has gained inspiring attention. Firstly, the results obtained on Nylon-6 (N6)/montmorillonite nanocomposites, which showed that a small concentration of layered silicate lead to notable changes in thermal and mechanical properties. Secondly, the observation by Vaia *et al.* is possible to melt-mix polymers with layered silicates, without the use of organic solvents. The incorporation of montmorillonite into a Nylon-6 matrix has led to a noteworthy enhancement in its mechanical properties. The Young's modulus (or tensile modulus), for example, of pure Nylon-6 (1.11 GPa) was strongly upgraded when the nanocomposite was formed. The Nylon-6/MMT with a filler content of 4.1 wt. (%) gave a value of 2.25 GPa, which corresponds to an increase of 102.7%. Also, regarding Nylon-6 nanocomposites, a strong interaction between matrix and silicate layers occurs via formation of hydrogen bonds. This behaviour can also be supported by propene-modified maleic anhydride (PP-MA)/LS nanocomposites^[64-66].

Exfoliated Nylon-6 and intercalated PMMA nanocomposites exhibited a prodigious increase in

the stress at break. This can be due to the polar (PMMA) and ionic interactions (Nylon-6 grafted onto the layers) between the matrix and the silicate layers. This increase is larger in Nylon-6 nanocomposites. On the other hand, propylene-based nanocomposites displayed only a small enhancement in tensile stress, which can be explained by the lack of interfacial adhesion between non-polar PP and polar-layered silicates. However, addition of maleic anhydride-modified polypropylene to the polypropylene matrix has confirmed to be effective in the intercalation of the PP chains and the maintenance of the ultimate stress at a satisfactory level. This finding is attributed to the weak interactions at the polystyrene-clay interface. It is imperative to note that in previous compositions in which polar interactions were developed, strengthening at the filler matrix interface was observed. Usually, when LS are dispersed in thermoplastics such as PMMA, PS or PP, the elongation at break is reduced^[67-70]. The reported decrease in elongation is from 150% in pure PP matrix, to 105% for a 6.9 wt. (%) non-intercalated clay micro-composite. On the other hand, in a nanocomposite filled with 5 wt. (%) silicate layers, the more noticeable drop was 7.5%. Conversely, this loss in eventual elongation did not occur in elastomeric epoxy or polyol polyurethane matrices. In these cases, introduction of the nanoclay in cross-linked matrices causes a rise of the elongation at break. While a drop in the elongation at break can be perceived for the conventional composite, a minor improvement in this property can be observed for the intercalated nanocomposite^[71-73].

Finally, exfoliated nanocomposites exhibit a large increase in the elongation at break. This is probably due to the plasticizing effect of the galleries, their contribution to the formation of dangling chains and conformational effects at the clay-matrix interface. The combination of improved stiffness (Young's modulus), toughness (stress at break) and elasticity (strain at break) makes elastomeric nanocomposites suitable candidates for the generation of a new family of high performance materials. Polyimide is another example of a polymer matrix material showing an increase in both stress and elongation at break. For example, when filled with mont-

morillonite exchanged with hexadecylammonium, these properties increase with the filler loading at least up to 5 wt. (%). At higher filler contents, both properties drop towards values lower than those described for the filler-free matrix due to the formation of non-exfoliated aggregates which make these composites more brittle^[74,75].

Another nanocomposite system studied in great detail is Nylon-6 protonated aminododecanoic acid, which has been studied for its impact resistance properties. The nanocomposite synthesized by in-situ intercalative polymerization had its Izod impact strength reduced from 20.6 to 18.1 J/m compared with the pure matrix when 4.7 wt. (%) of nanoclay was incorporated. Charpy impact testing displayed a similar reduction from 6.21 kJ/m² to 6.06 kJ/m² for the 4.7 wt. (%) nanocomposite. There is good resistance to impact, high Young's modulus, good flexural modulus and a notable enhancement in the heat distortion temperature, going from 338 K for pure Nylon-6 to more than 423 K for the nanocomposite, have allowed this material to replace glass fibre-reinforced nylon or polypropylene in the production of timing belt covers of automotive engines^[76-78].

5. Conclusions

Innovative technologies necessitate materials exhibiting unique properties and upgraded performance. Therefore, nanocomposites are appropriate materials to meet the developing demands arising from scientific and technologic advances. Processing methods for different types of nanocomposites pose challenges, thus giving opportunities for researchers to overcome the problems faced with nanosized materials. They propose better performance over counterpart materials and are subsequently appropriate materials to overcome the restrictions of many presently prevailing materials and devices. Many applications previously exist. These materials have much potential in engineering field. Due to high mechanical properties, gas barrier, flame related properties, and the market for these materials have been projected in various sectors. Thus, all types of nanocomposites offer opportunities and rewards, creating new world wide interest in these new materials.

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